

**Kinetics of the
gas-phase reactions**

R. Atkinson

Kinetics of the gas-phase reactions of OH radicals with alkanes and cycloalkanes

R. Atkinson

Air Pollution Research Center, and Department of Environmental Sciences, and Department of Chemistry, University of California, Riverside, CA 92507, USA

Received: 27 February 2003 – Accepted: 2 June 2003 – Published: 29 July 2003

Correspondence to: R. Atkinson (ratkins@mail.ucr.edu)

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Abstract

The available database concerning rate constants for gas-phase reactions of the hydroxyl (OH) radical with alkanes through early 2003 is presented over the entire temperature range for which measurements have been made (~180–2000 K). Measurements made using relative rate methods are re-evaluated using recent rate data for the reference compound (generally recommendations from this review). In general, whenever more than one study has been carried out over an overlapping temperature range, recommended rate constants or temperature-dependent rate expressions are presented.

1. Introduction

Large quantities of volatile organic compounds (VOCs) are emitted into the atmosphere from anthropogenic and biogenic sources, and a large number of VOCs are present in ambient air (including those formed in situ from the atmospheric reactions of other VOCs). In the troposphere, VOCs can be transformed by photolysis (at wavelengths ≥ 290 nm), reaction with hydroxyl (OH) radicals (mainly during daylight hours), reaction with nitrate (NO_3) radicals (during evening and nighttime hours), and reaction with ozone (O_3) (Atkinson, 2000).

Alkanes are an important class of VOCs (Calvert et al., 2002) which in the atmosphere react with OH radicals and, to a lesser extent, with NO_3 radicals (Atkinson, 2000). Rate constants for the gas-phase reactions of OH radicals with alkanes have been periodically reviewed and evaluated (Atkinson, 1986, 1989, 1994, 1997), and the reactions of OH radicals with $\leq \text{C}_4$ alkanes are included in the ongoing NASA (2003) and IUPAC (2003) data evaluations (which are now only available on the World Wide Web, at the locations given in NASA (2003) and IUPAC, 2003). This review and evaluation continues the previous reviews and evaluations of Atkinson (1986, 1989, 1994, 1997), and employs the same general format.

For each alkane and cycloalkane for which experimental kinetic data are available in

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

the readily accessible literature, these rate constants are listed. In the table associated with each reaction, the experimental techniques used are denoted by the abbreviations listed in Table 1. For example, use of a flash photolysis system to generate OH radicals with resonance fluorescence monitoring of OH radicals is denoted by PF-RF. When relative rate methods (denoted in the “Technique” column by “RR”) were used, the rate constant for the reference compound from the most recent review and evaluation is used to re-evaluate the rate constant for the alkane in question (which therefore may be different from that cited in the original publication). For relative rate studies, the rate constant used for the reference reaction to place the measured rate constant ratio(s) on an absolute basis is noted, and is that recommended from this evaluation (including the rate constants derived in this review and evaluation for the reactions of OH radicals with H₂ and CO), unless noted otherwise.

For absolute rate studies, the temperature-dependent rate expressions are also given (if cited), either as the Arrhenius expression $k = Ae^{-B/T}$ (in which case no entry is given in the column labeled n) or as the three-parameter expression $k = AT^n e^{-B/T}$. When rate constants have been measured over a range of temperatures, Arrhenius plots of $\ln k$ vs $1/T$ often exhibit curvature (Atkinson, 1986, 1989, 1994, 1997), and hence the recommended temperature-dependent expressions are then given in terms of the three-parameter expression $k = CT^n e^{-D/T}$ rather than the Arrhenius expression $k = Ae^{-B/T}$. Generally a value of $n = 2$ is used (Atkinson, 1986, 1989, 1994, 1997), resulting in the expression $k = CT^2 e^{-D/T}$. At any given temperature T , an Arrhenius expression can be derived from the three-parameter expression $k = CT^n e^{-D/T}$, with $A = Ce^{nT}$ and $B = D + nT$. While an Arrhenius expression may be adequate over short temperature ranges, extrapolation outside of the temperature range for which the Arrhenius expression is valid is likely to result in significant errors in the predicted rate constant.

The available rate data, from both absolute and relative rate measurements, for the reactions of OH radicals with alkanes and cycloalkanes are reviewed and evaluated

**Kinetics of the
gas-phase reactions**

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

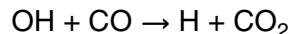
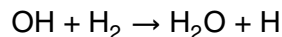
Full Screen / Esc

Print Version

Interactive Discussion

in the following sections. For the reactions of OH radicals with methane, ethane and propane (and for CH₃D and CD₄), the recommendations are based solely on absolute rate measurements. However, for the >C₃ alkanes and for the cycloalkanes, rate constants obtained from relative rate studies are an important part of the data-base (and in some cases are the only data available), and the recommendations then use a combination of absolute and relative rate data. As shown in Table 2, for a series of C₃–C₁₀ *n*-alkanes and cyclohexane at room temperature the relative rate studies of Atkinson et al. (1982a, b), Benhke et al. (1987, 1988), Nolting et al. (1988) and DeMore and Bayes (1999) are in generally excellent agreement, and these relative rate studies severely constrain room temperature rate constant recommendations for the ≥C₅ *n*-alkanes once rate constants for propane and *n*-butane are recommended from absolute (or mainly absolute) studies.

There are a number of alkanes for which the OH radical reaction rate constants have been measured relative to those for the reactions of OH radicals with H₂ or CO, often at elevated temperatures.



The available rate constants for these two reactions have been reviewed and evaluated to obtain temperature, and in the case of the CO reaction, pressure dependent rate expressions in order to place the measured rate constant ratios on an absolute basis. For the reaction of OH radicals with H₂, the absolute rate constants measured by Tully and Ravishankara (1980), Ravishankara et al. (1981), Bott and Cohen (1989), Oldenborg et al. (1992) and Talukdar et al. (1996) have been fitted to the three-parameter expression $k = AT^2e^{-B/T}$ to obtain

$$k(\text{H}_2) = 9.61 \times 10^{-18} T^2 e^{-1457/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 238–1548 K.

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

The rate constant for the reaction of OH radicals with CO is temperature and pressure dependent (and with the pressure dependence depending on the specific diluent gas used), with the effect of pressure decreasing as the temperature increases. The kinetics of this reaction have been investigated and evaluated by Golden et al. (1998), with the recommended rate constant being derived from the experimental data using an RRKM model. In this review and evaluation, a simpler (and somewhat more approximate) rate expression analogous to that used previously (Atkinson, 1989) has been derived from the recommended experimental rate constants tabulated by Golden et al. (1998), of

$$k(\text{CO}) = 9.1 \times 10^{-19} T^{1.77} e^{580/T} [1 + 2.4 \times 10^{-20} [M](T/298)^{-1}] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range ~290–3000 K and for the pressures encountered in this review article, where [M] is the concentration of M = air, O₂ or N₂ in molecule cm⁻³. Because of the greater uncertainties in the rate constant for this reaction (as a function of temperature, pressure and diluent gas), rate constants obtained from experimental studies using the reaction of OH radicals with CO as the reference reaction are given relatively low weight in the evaluations, or are not used if other rate data are available.

The estimated uncertainties in the recommended 298 K rate constants are subjective and are in the range ±20–30%. However, it is considered unlikely that future new rate data will change many of the room temperature rate constants by more than 10%; this is approximately the change that has occurred in recommended rate constants for alkanes since the Atkinson (1986) review, with recommended rate constants for most alkanes decreasing by ~10% since 1986.

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

2. Rate data for alkanes and cycloalkanes

2.1. OH + methane

The available rate data are listed in Table 3. The recent studies of Bott and Cohen (1989), Vaghjiani and Ravishankara (1991), Finlayson-Pitts et al. (1992), Lancar et al. (1992), Dunlop and Tully (1993), Mellouki et al. (1994), Gierczak et al. (1997) and Bonard et al. (2002) are in good agreement, as shown by the Arrhenius plot in Fig. 1. However, over the temperature range ~250–420 K the rate constants measured in these studies are significantly lower than most of the earlier absolute measurements (Atkinson, 1994). Gierczak et al. (1997) fit their data and the earlier data of Vaghjiani and Ravishankara (1991) from the same laboratory to a three-parameter expression, and obtained the rate expression $k(\text{methane}) = 1.85 \times 10^{-20} T^{2.82} e^{-987/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This rate expression is plotted as the solid line in the Arrhenius plot (Fig. 1), and provides an excellent fit to the data of Bott and Cohen (1989), Vaghjiani and Ravishankara (1991), Finlayson-Pitts et al. (1992), Lancar et al. (1992), Dunlop and Tully (1993), Mellouki et al. (1994), Gierczak et al. (1997) and Bonard et al. (2002), agreeing with the 1234 K rate constant of Bott and Cohen (1989) to within 1% and with the 800 K rate constant of Dunlop and Tully (1993) and the 295–668 K rate constants of Bonard et al. (2002) to within 10%. Accordingly, the rate expression of Gierczak et al. (1997) is recommended, with

$$k(\text{methane}) = 1.85 \times 10^{-20} T^{2.82} e^{-987/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 190–1240 K, and with

$$k(\text{methane}) = 6.40 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

The overall uncertainty in the rate constant at 298 K is estimated to be $\pm 20\%$.

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

2.2. OH + methane-d₁

The available rate data are listed in Table 4, and Fig. 2 shows an Arrhenius plot of the rate constants of Gordon and Mulac (1975), DeMore (1993a), Gierczak et al. (1997) and Saueressig et al. (2001). The relative rate constants of DeMore (1993a) are slightly higher than those of Gierczak et al. (1997), by up to ~20% at 360 K. The rate constants of DeMore (1993a), Gierczak et al. (1997) and Saueressig et al. (2001) have been fitted to the three parameter expression $k = AT^2e^{-B/T}$, leading to the recommendation of

$$k(\text{methane-d}_1) = 5.19 \times 10^{-18} T^2 e^{-(1332 \pm 54)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 240–430 K, where the indicated error in B is two least-squares standard deviations, and with

$$k(\text{methane-d}_1) = 5.28 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

The overall uncertainty in the rate constant at 298 K is estimated to be $\pm 20\%$. The recommended rate expression is shown as the solid line in Fig. 2.

2.3. OH + methane-d₂

As shown in Table 5, rate constants are available only from the studies of Gordon and Mulac (1975) and Gierczak et al. (1997), with only one temperature-dependent study (Gierczak et al., 1997). The rate constant of Gordon and Mulac (1975) at 416 K is ~40% higher than predicted from extrapolation of the Arrhenius expression of Gierczak et al. (1997). In the absence of further studies, the Arrhenius expression of Gierczak et al. (1997) should be used (but only over the temperature range 270–360 K).

2.4. OH + methane-d₃

As shown in Table 6, rate constants are available only from the studies of Gordon and Mulac (1975) and Gierczak et al. (1997), with only one temperature-dependent study

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

(Gierczak et al., 1997). The rate constant of Gordon and Mulac (1975) at 416 K is in reasonable agreement with that predicted from extrapolation of the Arrhenius expression of Gierczak et al. (1997). In the absence of further studies, the Arrhenius expression of Gierczak et al. (1997) should be used (but only in the temperature range 270–360 K).

2.5. OH + methane-d₄

The available rate data are listed in Table 7. Figure 3 shows an Arrhenius plot of the absolute rate constants measured by Gordon and Mulac (1975), Dunlop and Tully (1993) and Gierczak et al. (1997). The rate constant of Gordon and Mulac (1975) at 416 K is a factor of 2 lower than those of Dunlop and Tully (1993) and Gierczak et al. (1997), which are in excellent agreement over the temperature range common to both studies (293–413 K). The rate constants of Dunlop and Tully (1993) and Gierczak et al. (1997) have been fitted to the three parameter expression $k = AT^2e^{-B/T}$, leading to the recommendation of

$$k(\text{methane-d}_4) = 5.70 \times 10^{-18} T^2 e^{-(1882 \pm 32)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 240–800 K, where the indicated error in B is two least-squares standard deviations, and with

$$k(\text{methane-d}_4) = 9.16 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

The overall uncertainty in the rate constant at 298 K is estimated to be $\pm 20\%$. As seen from the Arrhenius plot in Fig. 3, the recommendation underpredicts the rate constants at the two lowest temperatures (244 and 250 K) employed by Gierczak et al. (1997) by 20–25%. Use of a T^3 dependence in the pre-exponential factor makes little difference, with $k(\text{methane-d}_4) = 4.91 \times 10^{-21} T^3 e^{-(1478 \pm 24)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k(\text{methane-d}_4) = 9.11 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, and the predicted rate constant at 244 K is 14% lower than the measured value of Gierczak et al. (1997).

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

2.6. OH + ethane

The available rate data are listed in Table 8. Over the temperature range ~200–800 K the absolute rate constants of Overend et al. (1975), Howard and Evenson (1976b), Leu (1979), Lee and Tang (1982), Margitan and Watson (1982), Tully et al. (1983, 1986a), Smith et al. (1984), Devolder et al. (1984), Schmidt et al. (1985), Baulch et al. (1985), Stachnik et al. (1986), Bourmada et al. (1987), Wallington et al. (1987), Lafage et al. (1987), Zabarnick et al. (1988), Abbatt et al. (1990), Schiffman et al. (1991), Dóbé et al. (1991, 1992), Sharkey and Smith (1993), Talukdar et al. (1994), Crowley et al. (1996), Donahue et al. (1996, 1998) and Clarke et al. (1998) are in good agreement. Because several of these studies involved measurement of the rate constant for the reaction of OH radicals with ethane at one temperature (generally room temperature) as a check on the experimental technique used (Leu, 1979; Lee and Tang, 1982; Margitan and Watson, 1982; Devolder et al., 1984; Bourmada et al., 1987; Lafage et al., 1987; Zabarnick et al., 1988; Dóbé et al., 1991, 1992), the rate constants from the more extensive absolute studies of Tully et al. (1983, 1986a), Smith et al. (1984), Stachnik et al. (1986), Wallington et al. (1987), Abbatt et al. (1990), Talukdar et al. (1994), Donahue et al. (1996, 1998) and Clarke et al. (1998), together with the elevated temperature rate constants of Bott and Cohen (1991a) and Koffend and Cohen (1996), are shown in the Arrhenius plot in Fig. 4. The agreement is seen to be generally excellent, and a least-squares analysis of the rate data of Smith et al. (1984), Tully et al. (1986a) (which is taken to supersede the earlier study of Tully et al., 1983), Stachnik et al. (1986), Wallington et al. (1987), Abbatt et al. (1990), Bott and Cohen (1991a), Talukdar et al. (1994), Koffend and Cohen (1996), Donahue et al. (1996, 1998) and Clarke et al. (1998), using the expression $k = AT^2e^{-B/T}$, leads to the recommendation of

$$k(\text{ethane}) = 1.49 \times 10^{-17} T^2 e^{-(499 \pm 14)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

over the temperature range 180–1230 K, where the indicated error in B is two least-squares standard deviations, and

$$k(\text{ethane}) = 2.48 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}.$$

The overall uncertainty in the rate constant at 298 K is estimated to be $\pm 20\%$. The recommended rate expression is shown as the solid line in the Arrhenius plot in Fig. 4. The rate constants measured by Crowley et al. (1996) at 247, 294 and 303 K to check for systematic errors in a newly constructed apparatus are in good agreement with the recommended rate expression, being within 4% of the recommendation at 294 and 303 K and within 12% of the recommendation at 247 K.

The elevated temperature rate constants derived from the relative rate studies of Baldwin et al. (1970b) (as re-evaluated by Baldwin and Walker, 1979) and Hucknall et al. (1975) are in reasonable agreement with the recommendation, to within 7% and 15%, respectively, thereby suggesting that the rate data from these two relative rate studies can be used with some confidence in the evaluations of rate data for other alkanes (see also the discussion of the rate constant for the propane reaction).

2.7. OH + ethane- d_3 and ethane- d_6

The available rate data are listed in Tables 9 (ethane- d_3) and 10 (ethane- d_6). The only study of these reactions to date is that of Tully et al. (1986a). The data of Tully et al. (1986a) for ethane, ethane- d_3 and ethane- d_6 show that the CH_3 and CD_3 groups can be treated independent of whether the neighboring group is a CH_3 or CD_3 group. Thus, to a good approximation the rate constant for CH_3CD_3 is given by $0.5[k(\text{ethane}) + k(\text{ethane-}\text{d}_6)]$, with a deuterium isotope effect of

$$k_H/k_D [= k(\text{ethane})/k(\text{ethane-}\text{d}_6)] = (1.01 \pm 0.06)e^{(456 \pm 27)/T}$$

over the temperature range 293–705 K, and with $k_H/k_D = 4.61 \pm 0.56$ at 293 K (Tully et al. (1986a).

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

2.8. OH + propane

The available rate data are listed in Table 11. The absolute rate constants measured over the temperature range 190–800 K by Tully et al. (1983), Droege and Tully (1986a) (which is viewed as superseding the earlier study of Tully et al., 1983), Nielsen et al. (1988), Abbatt et al. (1990), Mac Leod et al. (1990), Schiffman et al. (1991), Talukdar et al. (1994), Mellouki et al. (1994), Donahue et al. (1998), Clarke et al. (1998), Carl and Crowley (2001) and Kozlov et al. (2003) are in generally good agreement. The data from the more extensive studies of Droege and Tully (1986a), Abbatt et al. (1990), Mac Leod et al. (1990), Talukdar et al. (1994), Mellouki et al. (1994), Donahue et al. (1998), Clarke et al. (1998) and Kozlov et al. (2003) and the higher temperature data of Bott and Cohen (1984) and Smith et al. (1985) are shown in the Arrhenius plot in Fig. 5. A least-squares analysis of the data of Bott and Cohen (1984), Smith et al. (1985), Droege and Tully (1986a), Abbatt et al. (1990), Mac Leod et al. (1990), Talukdar et al. (1994), Mellouki et al. (1994), Donahue et al. (1998) and Clarke et al. (1998), using the expression $k = AT^2e^{-B/T}$, leads to the recommendation of

$$k(\text{propane}) = 1.65 \times 10^{-17} T^2 e^{-(87 \pm 18)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 190–1220 K, where the indicated error in the value of B is two least-squares standard deviations, and

$$k(\text{propane}) = 1.09 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}.$$

The overall uncertainty in the rate constant at 298 K is estimated to be $\pm 20\%$. The recommended rate constant expression is shown in the Arrhenius plot as the solid line (Fig. 5). The rate constants measured recently by Kozlov et al. (2003) agree with the recommendation to within 5% over the entire temperature range studied (210–480 K).

The rate constants derived from the relative rate studies of Baker et al. (1970) (as re-evaluated by Baldwin and Walker, 1979), Hucknall et al. (1975), Atkinson et al. (1982b), Edney et al. (1986), Behnke et al. (1987), Finlayson-Pitts et al. (1993) and DeMore

and Bayes (1999) are in generally excellent agreement with the recommendation, to within 7%, 5%, 2%, 3%, 15%, 4% and 8%, respectively. The rate constants derived from the relative rate measurements of DeMore and Bayes (1999) trend from being 2% higher than the recommendation at 428 K to being 7% lower than the recommendation at 227 K. This good agreement of the relative rate data of Baldwin and Walker (1979) (a re-evaluation of the earlier study of Baker et al., 1970), Hucknall et al. (1975), Atkinson et al. (1982b), Edney et al. (1986), Behnke et al. (1987) and DeMore and Bayes (1999) with absolute rate constant data means that these relative rate studies can be used with some confidence in the evaluations of rate data for $\geq C_4$ alkanes for which fewer absolute rate studies have been carried out.

An Arrhenius plot of the absolute and relative rate data of Talukdar et al. (1994), Mellouki et al. (1994), Clarke et al. (1998), DeMore and Bayes (1999) and Kozlov et al. (2003) for temperatures < 300 K is shown in Fig. 6. The agreement is excellent, with the largest disagreement with the recommended expression (shown by the solid line) being 7% and with, for reference, the lowest temperature measurement by Clarke et al. (1998) at 190 K being 4% higher than the recommendation (and well within the stated 7% measurement uncertainty cited by Clarke et al., 1998).

2.9. OH + propane- d_2 , propane- d_3 , propane- d_5 , propane- d_6 and propane- d_8

The available rate data are listed in Tables 12 (propane- d_2), 13 (propane- d_3), 14 (propane- d_5), 15 (propane- d_6) and 16 (propane- d_8). To date, the only study of these reactions is that of Droege and Tully (1986a). The data obtained for propane, propane- d_2 , propane- d_3 , propane- d_5 , propane- d_6 and propane- d_8 show that the CH_3 , CH_2 , CD_3 and CD_2 groups can be treated as having rate constants which are independent of the isotopic nature of the neighboring group(s) (Droege and Tully, 1986a). Using the k_H/k_D ratio for CH_3/CD_3 groups obtained from the rate data for ethane, ethane- d_3 and ethane- d_6 (Tully et al., 1986a; see reactions above), Droege and Tully (1986a) derived rate constants for H-atom abstraction from the primary C–H bonds of the two CH_3

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

groups ($2k_{\text{primary}}$) and from the secondary C–H bonds in the CH_2 groups ($k_{\text{secondary}}$), of

$$2k_{\text{primary}} = 1.75 \times 10^{-14} T^{0.97} e^{-798/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$2k_{\text{primary}} = 3.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

and

$$k_{\text{secondary}} = 7.76 \times 10^{-17} T^{1.61} e^{18/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{\text{secondary}} = 7.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Droege and Tully (1986a) also derived the deuterium isotope effect for H-/D-atom abstraction from secondary CH_2 or CD_2 groups, of

$$k_{\text{H}}/k_{\text{D}}(\text{CH}_2/\text{CD}_2 \text{ groups}) = (1.13 \pm 0.19) e^{(262 \pm 78)/T}$$

over the temperature range 295–854 K, with

$$k_{\text{H}}/k_{\text{D}}(\text{CH}_2/\text{CD}_2 \text{ groups}) = 2.62 \pm 0.49 \text{ at } 295 \text{ K.}$$

2.10. OH + *n*-butane

The available rate data are listed in Table 17. The absolute rate constant measurements carried out over the temperature range 231–509 K by Schmidt et al. (1985), Droege and Tully (1986b), Abbatt et al. (1990), Schiffman et al. (1991), Talukdar et al. (1994), Donahue et al. (1998) and Chuong and Stevens (2002) are in good agreement, with earlier absolute rate measurements of Greiner (1970), Perry et al. (1976) and Paraskevopoulos and Nip (1980) at room temperature being ~10–15% higher than these more recent studies. Figure 7 shows an Arrhenius plot of the absolute rate constants of Droege and Tully (1986b), Abbatt et al. (1990), Talukdar et al. (1994) and Donahue et al. (1998) together with the relative rate data of Baker et al. (1970) (as re-evaluated by Baldwin and Walker, 1979), Hucknall et al. (1975) and DeMore and Bayes

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

(1999). A least-squares fit of these data (Hucknall et al., 1975; Baldwin and Walker, 1979; Droege and Tully, 1986b; Abbatt et al., 1990; Talukdar et al., 1994; Donahue et al., 1998; DeMore and Bayes, 1999), using the expression $k = AT^2e^{-B/T}$, results in the recommendation of

5 $k(n\text{-butane}) = 1.81 \times 10^{-17} T^2 e^{(114 \pm 22)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

over the temperature range 230–760 K, where the indicated error in the value of B is two least-squares standard deviations, and

$$k(n\text{-butane}) = 2.36 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

The overall uncertainty in the rate constant is estimated to be $\pm 20\%$ at 298 K. The recommended rate constant expression is shown as the solid line in the Arrhenius plot (Fig. 7).

While the rate constants derived from relative rate studies of Atkinson et al. (1981) and Atkinson and Aschmann (1984) agree with the recommendation within the experimental uncertainties, these rate constants (Atkinson et al., 1981; Atkinson and Aschmann, 1984) for the n -butane reaction were measured relative to that for reaction of the OH radical with propene, with the rate constant ratio of ~ 10 being outside of the range (~ 0.2 – 5) of highest accuracy.

2.11. OH + n -butane- d_{10}

The available rate data are listed in Table 18. The room temperature rate constant of Paraskevopoulos and Nip (1980) is 20–25% lower than those of Droege and Tully (1986b), which is the only temperature-dependent study to date. Combining their rate constants for n -butane and n -butane- d_{10} with the deuterium isotope ratio k_H/k_D obtained for the ethane reaction (Tully et al., 1986a), and using the fraction of the overall OH radical reaction proceeding by H-atom abstraction from the secondary CH_2 groups in n -butane estimated by Atkinson (1986), Droege and Tully (1986b) derived rate con-

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

starts for H-atom abstraction from the primary C–H bonds of the two CH₃ groups ($2k_{\text{primary}}$) and from the secondary C–H bonds in the two CH₂ groups ($2k_{\text{secondary}}$), of

$$2k_{\text{primary}} = 6.86 \times 10^{-17} T^{1.73} e^{-379/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$2k_{\text{primary}} = 3.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

5 and

$$2k_{\text{secondary}} = 1.20 \times 10^{-16} T^{1.64} e^{124/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$2k_{\text{secondary}} = 2.08 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}.$$

Droege and Tully (1986b) also derived the deuterium isotope effect for H-/D-atom abstraction from secondary CH₂ or CD₂ groups, of

10 $k_H/k_D(\text{CH}_2/\text{CD}_2 \text{ groups}) = (1.31 \pm 0.12) e^{(196 \pm 33)/T}$

over the temperature range 294–509 K, with

$$k_H/k_D(\text{CH}_2/\text{CD}_2 \text{ groups}) = 2.52 \pm 0.17 \text{ at } 294 \text{ K}.$$

This deuterium isotope ratio of $k_H/k_D(\text{CH}_2/\text{CD}_2 \text{ groups})$ obtained from the *n*-butane and *n*-butane-d₁₀ reactions is essentially identical to the ratio of 2.62 ± 0.49 at 295 K
15 obtained from the propane, propane-d₂, propane-d₃, propane-d₅, propane-d₆ and propane-d₈ reactions (Droege and Tully, 1986a).

2.12. OH + 2-methylpropane

The available rate data are listed in Table 19. The absolute rate constants measured over the temperature range 213–864 K by Tully et al. (1986b), Schiffman et al. (1991),
20 Talukdar et al. (1994) and Donahue et al. (1998) are in good agreement. Figure 8 shows an Arrhenius plot of the absolute rate constants of Tully et al. (1986b), Bott

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

and Cohen (1989), Talukdar et al. (1994) and Donahue et al. (1998) (no precise temperature was specified in the Schiffman et al., 1991 study) together with the relative rate data of Baker et al. (1970) (as re-evaluated by Baldwin and Walker, 1979), Hucknall et al. (1975) and Atkinson et al. (1984). The agreement is good and a least-squares analysis of these data (Hucknall et al., 1975; Baldwin and Walker, 1979; Atkinson et al., 1984; Tully et al., 1986b; Bott and Cohen, 1989; Talukdar et al., 1994; Donahue et al., 1998), using the expression $k = AT^2e^{-B/T}$, leads to the recommendation of

$$k(2\text{-methylpropane}) = 1.17 \times 10^{-17} T^2 e^{(213 \pm 24)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 210–1150 K, where the indicated error in the value of B is two least-squares standard deviations, and

$$k(2\text{-methylpropane}) = 2.12 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}.$$

The overall uncertainty in the rate constant is estimated to be $\pm 20\%$ at 298 K. The recommended rate constant expression is also shown as the solid line in the Arrhenius plot (Fig. 8).

2.13. OH + 2-methylpropane- d_1 , 2-methylpropane- d_9 and 2-methylpropane- d_{10}

The available rate data are listed in Tables 20 (2-methylpropane- d_1), 21 (2-methylpropane- d_9) and 22 (2-methylpropane- d_{10}). To date, the only study of these reactions is that of Tully et al. (1986b). Combining their rate constants for 2-methylpropane, 2-methylpropane- d_1 , 2-methylpropane- d_9 and 2-methylpropane- d_{10} with the deuterium isotope ratio $k_H/k_D(\text{CH}_3/\text{CD}_3 \text{ groups})$ obtained from the 2,2-dimethylpropane (neopentane) reaction (Tully et al., 1985, 1986a), Tully et al. (1986b) derived rate constants for H-atom abstraction from the primary C–H bonds of the three CH_3 groups ($3k_{\text{primary}}$) and from the tertiary C–H bond in the CH group (k_{tertiary}), of

$$3k_{\text{primary}} = 3.81 \times 10^{-16} T^{1.53} e^{-391/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

$$3k_{\text{primary}} = 6.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

and

$$k_{\text{tertiary}} = 9.52 \times 10^{-14} T^{0.51} e^{-32/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{\text{tertiary}} = 1.56 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}.$$

- 5 Tully et al. (1986b) also derived the deuterium isotope effect for H-/D-atom abstraction from the tertiary CH or CD group, of $k_H/k_D(\text{CH/CD group}) = 1.91$ at 294 K.

2.14. OH + *n*-pentane

The available rate data are listed in Table 23. The absolute rate studies of Abbatt et al. (1990), Talukdar et al. (1994) and Donahue et al. (1998) are in good agreement at
 10 room temperature, and those of Talukdar et al. (1994) and Donahue et al. (1998) agree well over the temperature range common to both studies (300-370 K). However, rate constants derived from the relative rate studies of Atkinson et al. (1982b), Behnke et al. (1987, 1988), Harris and Kerr (1988), Donaghy et al. (1993) and DeMore and Bayes (1999) are consistently ~10% lower than the absolute rate constants. Figure 9 shows
 15 an Arrhenius plot of the absolute rate constants of Abbatt et al. (1990), Talukdar et al. (1994) and Donahue et al. (1998) together with the relative rate data of Baldwin and Walker (1979), Atkinson et al. (1982b), Harris and Kerr (1988) and DeMore and Bayes (1999). An appreciable amount of scatter in the data is apparent, both between and within the various studies. A least-squares analysis of the rate constants from these
 20 studies (Baldwin and Walker, 1979; Atkinson et al., 1982b; Harris and Kerr, 1988; Abbatt et al., 1990; Talukdar et al., 1994; Donahue et al., 1998; DeMore and Bayes, 1999), using the expression $k = AT^2 e^{-B/T}$, leads to the recommendation of

$$k(n\text{-pentane}) = 2.52 \times 10^{-17} T^2 e^{(158 \pm 40)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

over the temperature range 220–760 K, where the indicated error in the value of B is two least-squares standard deviations, and

$$k(n\text{-pentane}) = 3.80 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}.$$

The overall uncertainty in the rate constant at 298 K is estimated to be $\pm 25\%$. The recommended rate constant expression is shown as the solid line in the Arrhenius plot (Fig. 9). In the temperature range 224–390 K, the absolute rate constants are generally slightly higher than the recommendation, while the relative rate constants of Harris and Kerr (1988) and DeMore and Bayes (1999) are slightly lower than the recommendation. Obviously, additional data are needed over the entire temperature range of $\sim 200\text{--}1000$ K.

2.15. OH + 2-methylbutane

The available rate data are listed in Table 24. Rate constants have only been measured at room temperature using relative rate studies (Lloyd et al., 1976; Darnall et al., 1978; Cox et al., 1980; Atkinson et al., 1984), and exhibit a significant amount of scatter. The most recent and extensive study of Atkinson et al. (1984) is used to recommend that

$$k(2\text{-methylbutane}) = 3.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty of $\pm 30\%$.

2.16. OH + 2,2-dimethylpropane

The available rate data are listed in Table 25, and the data-base is relatively small. Figure 10 shows an Arrhenius plot of the data of Greiner (1970), Baker et al. (1976) (as re-evaluated by Baldwin and Walker, 1979), Paraskevopoulos and Nip (1980), Atkinson et al. (1982a), Tully et al. (1986a) and Nielsen et al. (1991b). Clearly, at room temperature the measured rate constants show an appreciable amount of scatter, ranging from $7.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to $9.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In particular,

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

there is a discrepancy between the 299 K rate constant derived from the relative rate study of Atkinson et al. (1982a) (the data of which are in excellent agreement with absolute and relative rate studies for other alkanes) and the absolute rate constant at 287 K measured by Tully et al. (1986a).

- 5 A least-squares analysis of the relative rate constants of Baker et al. (1976) (as reevaluated by Baldwin and Walker, 1979) and Atkinson et al. (1982a) and the absolute rate constants of Tully et al. (1986a), using the expression $k = AT^2e^{-B/T}$, results in the recommendation of

$$k(2,2\text{-dimethylpropane}) = 1.86 \times 10^{-17} T^2 e^{-(207 \pm 56)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

- 10 over the temperature range 280–910 K, where the indicated uncertainty in the value of B is two least-squares standard deviations, and

$$k(2,2\text{-dimethylpropane}) = 8.25 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated uncertainty at 298 K of $\pm 20\%$. This recommended expression is shown in the Arrhenius plot by the solid line (Fig. 10).

- 15 2.17. OH + 2,2-dimethylpropane- d_{12}

As shown in Table 26, the only study of this reaction to date is that of Tully et al. (1985, 1986a). From their rate constants for 2,2-dimethylpropane and 2,2,-dimethylpropane- d_{12} , Tully et al. (1986a) obtained the deuterium isotope ratio for H- (or D-) atom abstraction from CH_3 and CD_3 groups of

- 20 $k_H/k_D(\text{CH}_3/\text{CD}_3 \text{ groups}) = (0.94 \pm 0.09)e^{(472 \pm 47)/T}$

over the temperature range 287–903 K. At 298 K, $k_H/k_D(\text{CH}_3/\text{CD}_3 \text{ groups}) = 4.6$, identical to the value $(4.61 \pm 0.56 \text{ at } 293 \text{ K})$ derived from the ethane, ethane- d_3 and ethane- d_6 reactions (Tully et al., 1986a).

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

2.18. OH + *n*-hexane

The available rate data are listed in Table 27, and to date only two absolute rate studies have been carried out, that of Koffend and Cohen (1996) at 962 K and that of Donahue et al. (1998) over the temperature range 300–390 K. Furthermore, the only temperature-dependent studies are the absolute rate study of Donahue et al. (1998) (300–390 K) and the relative rate study of DeMore and Bayes (1999) (292–397 K), with no rate constants having been measured below 290 K.

Figure 11 shows an Arrhenius plot of the absolute rate constants of Koffend and Cohen (1996) and Donahue et al. (1998) together with the relative rate data of Atkinson et al. (1982a), Klein et al. (1984) and DeMore and Bayes (1999). In the temperature range 292–390 K the agreement between the absolute and relative rate studies is good. The room temperature relative rate data of Atkinson et al. (1983a), Atkinson and Aschmann (1984), Behnke et al. (1987, 1988) and McLoughlin et al. (1993), which are not shown in the Arrhenius plot in Fig. 11, are also in good agreement with these data of Atkinson et al. (1982a), Klein et al. (1984), Donahue et al. (1998) and DeMore and Bayes (1999). However, as shown by the dashed line in the Arrhenius plot (Fig. 11), a least-squares analysis of the rate constants from the studies of Atkinson et al. (1982a), Klein et al. (1984), Koffend and Cohen (1996), Donahue et al. (1998) and DeMore and Bayes (1999) using the expression $k = AT^2e^{-B/T}$ leads to a rate constant expression of $k(n\text{-hexane}) = 1.82 \times 10^{-17} T^2 e^{361/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 290–970 K, which does not fit the data particularly well.

A least-squares analysis of the rate constants in the temperature range 292–390 K of Atkinson et al. (1982a), Klein et al. (1984), Donahue et al. (1998) and DeMore and Bayes (1999) using the Arrhenius expression $k = Ae^{-B/T}$ leads to

$$k(n\text{-hexane}) = 2.29 \times 10^{-11} e^{-(442 \pm 52)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

where the indicated error in the value of *B* is two least-squares standard deviations,

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

and

$$k(n\text{-hexane}) = 5.20 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

A least-squares analysis of the rate constants of Atkinson et al. (1982a), Klein et al. (1984), Koffend and Cohen (1996), Donahue et al. (1998) and DeMore and Bayes (1999) using the expression $k = AT e^{-B/T}$ leads to

$$k(n\text{-hexane}) = 2.54 \times 10^{-14} T e^{-(112 \pm 28)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 290–970 K, where the indicated error in the value of B is two least-squares standard deviations, and

$$k(n\text{-hexane}) = 5.20 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 20\%$. This expression is shown as the solid line in Fig. 11. The Arrhenius expression $k(n\text{-hexane}) = 2.29 \times 10^{-11} e^{-442/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and the expression $k(n\text{-hexane}) = 2.54 \times 10^{-14} T e^{-112/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ lead to rate constants which agree to within 1% over the temperature range 280–390 K; the use of either expression outside of this temperature range 280–390 K may be unreliable.

Provisionally, the rate expression

$$k(n\text{-hexane}) = 2.54 \times 10^{-14} T e^{-112/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

is recommended for the temperature range 290–970 K, although additional data at temperatures $> 400 \text{ K}$ are needed. In particular, it is necessary to confirm the 962 K rate constant of Koffend and Cohen (1996), which appears low by comparison with the recommendation for n -pentane.

2.19. OH + 2-methylpentane

As shown in Table 28, rate constants for 2-methylpentane are available only at room temperature from relative rate studies. The rate constants derived from the studies of

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Lloyd et al. (1976), Cox et al. (1980) and Atkinson et al. (1984) are in agreement within their stated uncertainties. The most recent and extensive study of Atkinson et al. (1984) is used to recommend that

$$k(2\text{-methylpentane}) = 5.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

5 at 298 K, with an estimated uncertainty of $\pm 25\%$.

2.20. OH + 3-methylpentane

As shown in Table 29, rate constants for 3-methylpentane are available only at room temperature from relative rate studies. The rate constants derived from the studies of Lloyd et al. (1976) and Atkinson et al. (1984) are in agreement within their stated
10 uncertainties. The most recent and extensive study of Atkinson et al. (1984) is used to recommend that

$$k(3\text{-methylpentane}) = 5.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated uncertainty of $\pm 25\%$.

2.21. OH + 2,2-dimethylbutane

15 As shown in Table 30, rate constants are available only from the relative rate studies of Atkinson et al. (1984) and Harris and Kerr (1988). At room temperature the rate constants from these two studies (Atkinson et al., 1984; Harris and Kerr, 1988) are in agreement within their stated uncertainties. Figure 12 shows an Arrhenius plot of the rate constants of Atkinson et al. (1984) and Harris and Kerr (1988). Within the scatter
20 of the data, the plot is a good straight line, and a least-squares analysis of the data of Atkinson et al. (1984) and Harris and Kerr (1988) leads to the Arrhenius expression of

$$k(2,2\text{-dimethylbutane}) = 3.37 \times 10^{-11} e^{-(809 \pm 84)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

over the temperature range 240–330 K, where the indicated uncertainty in the value of B is two least-squares standard deviations, and

$$k(2, 2\text{-dimethylbutane}) = 2.23 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated uncertainty at 298 K of $\pm 25\%$. This recommended Arrhenius expression, which should not be used outside of the temperature range 240–330 K, is shown as the solid line in the Arrhenius plot (Fig. 12). As noted previously (Atkinson, 1989), the temperature dependence of this rate constant ($B = 809 \text{ K}$) is higher than the estimated value ($B = 445 \text{ K}$ for the temperature range 245–328 K, Kwok and Atkinson, 1995), and needs to be confirmed.

2.22. OH + 2,3-dimethylbutane

As shown in Table 31, few kinetic studies are available for this reaction, and the available rate constants show significant scatter. Figure 13 shows an Arrhenius plot of the absolute rate constants of Greiner (1970) and Bott and Cohen (1991b) together with the rate constants derived from the relative rate studies of Atkinson et al. (1982a) and Harris and Kerr (1988). The absolute room temperature rate constant of Greiner (1970) is $\sim 25\text{--}30\%$ higher than the relative rate data of Atkinson et al. (1982a) and Harris and Kerr (1988), and the temperature dependence obtained by Greiner (1970) is negative. The rate constants derived from the relative rate study of Harris and Kerr (1988) exhibit a fair amount of scatter and many also have significant stated uncertainties (two standard deviations of up to $\pm 20\%$). Accordingly, the absolute 1220 K rate constant of Bott and Cohen (1991b) and the 299 K relative rate constant of Atkinson et al. (1982a) have been used with the expression $k = AT^2 e^{-B/T}$ to obtain the recommendation of

$$k(2, 3\text{-dimethylbutane}) = 1.66 \times 10^{-17} T^2 e^{407/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with

$$k(2, 3\text{-dimethylbutane}) = 5.78 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

and with an estimated overall uncertainty at 298 K of $\pm 25\%$. This expression is shown in the Arrhenius plot as the solid line (Fig. 13), and fits the Harris and Kerr (1988) data reasonably well (although the Harris and Kerr (1988) rate data are consistent with a zero temperature dependence over the range 247–327 K), being $\sim 10\%$ higher than the Harris and Kerr (1988) rate constants at 325–327 K.

2.23. OH + *n*-heptane

As shown in Table 32, the database for this reaction is small, with the only absolute rate study being that Koffend and Cohen (1996) at 1086 K (note that, assuming that the experimental data listed in their Table III is correct, then the temperature is incorrectly stated in both the abstract and Table VII of Koffend and Cohen (1996) as 1186 K). The room temperature rate constants are all from relative rate studies (Atkinson et al., 1982b; Klöpffer et al., 1986; Behnke et al., 1987, 1988; Ferrari et al., 1996). A least-squares analysis of the rate constants from the studies of Atkinson et al. (1982b), Behnke et al. (1987, 1988), Koffend and Cohen (1996) and Ferrari et al. (1996), using the expression $k = AT^2e^{-B/T}$, leads to the recommendation of

$$k(n\text{-heptane}) = 1.95 \times 10^{-17} T^2 e^{406/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 290–1090 K, and

$$k(n\text{-heptane}) = 6.76 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 20\%$.

2.24. OH + 2,4-dimethylpentane

As shown in Table 33, the only study of this reaction to date is that of Atkinson et al. (1984).

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

2.25. OH + 2,2,3-trimethylbutane

The available rate data are listed in Table 34. The only absolute rate study of this reaction is that of Greiner (1970), with the rate constants being quite scattered and that at room temperature being ~25% higher than the relative rate data of Darnall et al. (1976), Atkinson et al. (1984) and Harris and Kerr (1988). The rate constants derived from the relative rate study of Harris and Kerr (1988) with 2,2-dimethylbutane as the reference compound are subject to large uncertainties (~20–30%) and are also highly variable (as are those using *n*-pentane as the reference compound, though to a lesser extent).

Figure 14 shows an Arrhenius plot of the rate constants of Greiner (1970), Baldwin et al. (1981), Atkinson et al. (1984) and Harris and Kerr (1988). Using the relative rate constants of Baldwin et al. (1981) and Atkinson et al. (1984) and the rate expression $k = AT^2e^{-B/T}$ leads to the recommendation of

$$k(2,2,3\text{-trimethylbutane}) = 9.20 \times 10^{-18} T^2 e^{459/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 290–760 K, and

$$k(2,2,3\text{-trimethylbutane}) = 3.81 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of ±25%. This recommended rate constant is shown as the solid line in the Arrhenius plot (Fig. 14). While the rate constants of Harris and Kerr (1988) obtained relative to those for *n*-pentane and 2,2-dimethylbutane are highly scattered, the rate constants of Harris and Kerr (1988) relative to those for *n*-hexane are in excellent agreement (to within 5% and within their stated uncertainties) with the recommended expression over the temperature range 243–324 K (Fig. 14).

2.26. OH + *n*-octane

The available rate data are listed in Table 35, with only two absolute rate studies (Greiner, 1970; Koffend and Cohen, 1996) and three room temperature relative rate

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

**Kinetics of the
gas-phase reactions**

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

measurements (Atkinson et al., 1982b; Behnke et al., 1987; Nolting et al., 1988) having been carried out. Figure 15 shows an Arrhenius plot of the absolute rate constants of Greiner (1970) and Koffend and Cohen (1996) together with the relative rate data of Atkinson et al. (1982b), Behnke et al. (1987) and Nolting et al. (1988). The three relative rate measurements (Atkinson et al., 1982b; Behnke et al., 1987; Nolting et al., 1988) are in excellent agreement, and a least-squares analysis of the rate constants from the studies of Atkinson et al. (1982b), Behnke et al. (1987) and Koffend and Cohen (1996) (the study of Nolting et al., 1988 was not used in the evaluation because the *n*-octane rate constant is used to derive the *n*-heptane rate constant which was the reference compound in the Nolting et al., 1988 study), using the expression $k = AT^2e^{-B/T}$, leads to the recommendation of

$$k(n\text{-octane}) = 2.72 \times 10^{-17} T^2 e^{361/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 290–1080 K, and

$$k(n\text{-octane}) = 8.11 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 29 K of $\pm 20\%$. This rate expression is shown as the solid line in the Arrhenius plot (Fig. 15). The rate constant obtained relative to *n*-heptane by Nolting et al. (1988) at 312 K is in excellent agreement with the recommendation.

2.27. OH + 2,2,4-trimethylpentane

As shown in Table 36, few studies of the kinetics of this reaction have been carried out. Figure 16 shows an Arrhenius plot of the rate constants of Greiner (1970), Atkinson et al. (1984) and Bott and Cohen (1991b). At room temperature the agreement between the studies of Greiner (1970) and Atkinson et al. (1984) is good. Using the relative rate constant of Atkinson et al. (1984) and the 1186 K absolute rate constant of Bott and Cohen (1991b) and the rate expression $k = AT^2e^{-B/T}$ leads to the recommendation of

$$k(2, 2, 4\text{-trimethylpentane}) = 2.35 \times 10^{-17} T^2 e^{140/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 290–1190 K, and

$$k(2,2,4\text{-trimethylpentane})=3.34 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated overall uncertainty at 298 K of $\pm 20\%$. This recommended rate constant is shown as the solid line in the Arrhenius plot (Fig. 16). The absolute rate constants of Greiner (1970) are in generally good agreement with this recommendation, and a least-squares analysis of the rate constants of Greiner (1970), Atkinson et al. (1984) and Bott and Cohen (1991b) leads to the rate constant $k(2,2,4\text{-trimethylpentane})=2.10 \times 10^{-17} T^2 e^{190/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the same temperature range of 290–1190 K, with $k(2,2,4\text{-trimethylpentane})=3.53 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

2.28. OH + 2,3,4-trimethylpentane

As shown in Table 37, the only study of this reaction to date is that of Harris and Kerr (1988).

2.29. OH + 2,2,3,3-tetramethylbutane

As shown in Table 38, few studies of the kinetics of this reaction have been carried out. Figure 17 shows an Arrhenius plot of the rate constants of Greiner (1970), Baldwin et al. (1979), Atkinson et al. (1984), Tully et al. (1985) and Bott and Cohen (1991b). The agreement at room temperature between the studies of Greiner (1970), Atkinson et al. (1984) and Tully et al. (1985) is good. A least-squares analysis of the relative rate constants of Baldwin et al. (1979) (these data also being given in Baldwin and Walker, 1979) and Atkinson et al. (1984) and the absolute rate constants of Tully et al. (1985) and Bott and Cohen (1991b), using the rate expression $k = AT^2 e^{-B/T}$, leads to the recommendation of

$$k(2,2,3,3\text{-tetramethylbutane})=1.99 \times 10^{-17} T^2 e^{-(178 \pm 123)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

over the temperature range 290–1180 K, where the indicated uncertainty in the value of B is two least-squares standard deviations, and

$$k(2, 2, 3, 3\text{-tetramethylbutane}) = 9.72 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated overall uncertainty at 298 K of $\pm 20\%$. This recommended rate constant is shown as the solid line in the Arrhenius plot (Fig. 17). The absolute rate constants of Greiner (1970) are in generally good agreement with this recommendation.

2.30. OH + n -nonane

The available rate data are listed in Table 39. The room temperature rate constants for n -nonane are all from relative rate studies (Atkinson et al., 1982b; Behnke et al., 1987, 1988; Nolting et al., 1988; Ferrari et al., 1996; Kramp and Paulson, 1998), and are in good agreement. A least-squares analysis of the rate constants of Atkinson et al. (1982b), Behnke et al. (1987, 1988), Nolting et al. (1988), Koffend and Cohen (1996), Ferrari et al. (1996) and Kramp and Paulson (1998), using the expression $k = AT^2e^{-B/T}$, leads to the recommendation of

$$k(n\text{-nonane}) = 2.53 \times 10^{-17} T^2 e^{(436 \pm 34)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 290–1100 K, where the indicated uncertainty in the value of B is two least-squares standard deviations, and

$$k(n\text{-nonane}) = 9.70 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated overall uncertainty at 298 K of $\pm 20\%$. The relative rate constant of Coeur et al. (1998, 1999) is in agreement, within the apparently sizeable error limits, with the recommendation.

2.31. OH + 3,3-diethylpentane

As shown in Table 40, the only study of this reaction to date is that of Nielsen et al. (1991b). The absolute and relative rate measurements of Nielsen et al. (1991b) agree

within their stated experimental uncertainties. A rate constant of $k(3,3\text{-diethylpentane})=4.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K is recommended, with an estimated overall uncertainty of $\pm 25\%$.

2.32. OH + *n*-decane

5 As shown in Table 41, the available room temperature rate constants for *n*-decane are all from relative rate studies (Atkinson et al., 1982b; Nolting et al., 1988; Behnke et al., 1988; Aschmann et al., 2001), and are in good agreement. A least-squares analysis of the rate constants of Atkinson et al. (1982b), Nolting et al. (1988), Behnke et al. (1988), Koffend and Cohen (1996) and Aschmann et al. (2001), using the expression
10 $k = AT^2 e^{-B/T}$, leads to the recommendation of

$$k(n\text{-decane})=3.17 \times 10^{-17} T^2 e^{(406 \pm 56)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 290–1110 K, where the indicated uncertainty in the value of *B* is two least-squares standard deviations, and

$$k(n\text{-decane})=1.10 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

15 with an estimated overall uncertainty at 298 K of $\pm 20\%$.

2.33. OH + 3,4-diethylhexane

As shown in Table 42, the only study of this reaction to date is that of Aschmann et al. (2001).

2.34. OH + *n*-undecane

20 As evident from Table 43, the room temperature rate constants derived from the relative rate studies of Nolting et al. (1988) and Behnke et al. (1988) are in good agreement.

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

An average of these two rate constants (Nolting et al., 1988; Behnke et al., 1988) leads to the recommendation of

$k(n\text{-undecane}) = 1.23 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K,

by extrapolating the 312 K and 300 K rate constants to 298 K using a reasonable value of B (425 K) and with an estimated overall uncertainty at 298 K of $\pm 20\%$.

2.35. OH + n -dodecane

As evident from Table 44, the room temperature rate constants derived from the relative rate studies of Nolting et al. (1988) and Behnke et al. (1988) are in good agreement. An average of these two rate constants leads to the recommendation of

$k(n\text{-dodecane}) = 1.32 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K,

by extrapolating the 312 K and 300 K rate constants to 298 K using a reasonable value of B (425 K) and with an estimated overall uncertainty at 298 K of $\pm 20\%$.

2.36. OH + n -tridecane

As shown in Table 45, the room temperature rate constants derived from the relative rate studies of Nolting et al. (1988) and Behnke et al. (1988) are in good agreement. An average of these two rate constants leads to the recommendation of

$k(n\text{-tridecane}) = 1.51 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K,

by extrapolating the 312 K and 300 K rate constants to 298 K using a reasonable value of B (425 K) and with an estimated overall uncertainty at 298 K of $\pm 25\%$.

2.37. OH + n -tetradecane, n -pentadecane and n -hexadecane

As shown in Tables 46 (n -tetradecane), 47 (n -pentadecane) and 48 (n -hexadecane), the only study of these reactions to date is that of Nolting et al. (1988).

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

2.38. OH + cyclopropane

The available rate data are listed in Table 49. Rate constants are available from the absolute rate studies of Jolly et al. (1985), Dóbé et al. (1991, 1992) and Clarke et al. (1998) and from the relative rate studies of DeMore and Bayes (1999) and Wilson et al. (2001). Figure 18 shows an Arrhenius plot of the data from these studies (for the study of Wilson et al. (2001) only the data obtained relative to the rate constant for ethane are plotted). The absolute rate constants of Dóbé et al. (1991, 1992) are significantly higher than the other data, more so at room temperature, with the discrepancy decreasing as the temperature increases (Fig. 18). Accordingly, the data of Dóbé et al. (1991, 1992) are not used in the evaluation of the rate constant for this reaction. While this discrepancy could be due to the presence of reactive impurities in the cyclopropane sample used by Dóbé et al. (1991, 1992), Dóbé et al. (1991, 1992) stated that the cyclopropane sample was $\geq 99.99\%$ pure with 0.01% propene impurity (Dóbé et al., 1992) (which would result in a $\sim 4\%$ increase in the measured rate constant at 298 K). The room temperature rate constants of Jolly et al. (1985), Clarke et al. (1998), DeMore and Bayes (1999) and Wilson et al. (2001) are in good agreement. However, as evident from the Arrhenius plot (Fig. 18), the absolute rate constants of Clarke et al. (1998) over the temperature range 200–360 K exhibit a lower temperature dependence than do the relative rate data of DeMore and Bayes (1999) and Wilson et al. (2001) over the temperature range 276–463 K.

A least-squares analysis of the rate constant data of Jolly et al. (1985), Clarke et al. (1998), DeMore and Bayes (1999) and Wilson et al. (2001) (relative to ethane; while the rate constants obtained by Wilson et al. (2001) relative to ethane agree with those obtained relative to CH_3CHF_2 (to within $\sim \pm 10\%$), due to the larger uncertainty in the rate constant for the reaction of OH radicals with CH_3CHF_2 only the rate constants relative to ethane are used in the evaluation), using the expression $k = AT^2e^{-B/T}$, leads to the recommendation of

$$k(\text{cyclopropane}) = 4.21 \times 10^{-18} T^2 e^{-(454 \pm 87)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

over the temperature range 200–460 K, where the indicated uncertainty in the value of B is two least-squares standard deviations, and

$k(\text{cyclopropane}) = 8.15 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K,

with an estimated uncertainty at 298 K of +10%, –30%. This recommended expression is shown in the Arrhenius plot as the solid line (Fig. 18). Obviously, further data are needed at temperatures <290 K to better assess the temperature dependence of the rate constant in the range 200–300 K. The significantly different temperature dependencies obtained by Clarke et al. (1998) and by DeMore and Bayes (1999) and Wilson et al. (2001) lead to the recommended rate expression giving an ~10% higher calculated 298 K rate constant than measured by Jolly et al. (1985), Clarke et al. (1998), DeMore and Bayes (1999) and Wilson et al. (2001).

2.39. OH + isopropylcyclopropane

As evident from Table 50, the only study of this reaction to date is that of Atkinson and Aschmann (1988).

2.40. OH + cyclobutane

As shown in Table 51, rate constants are available from the absolute rate studies of Dóbé et al. (1991, 1992) and from the relative rate studies of Gorse and Volman (1974) and DeMore and Bayes (1999). Figure 19 shows an Arrhenius plot of the data from these studies. The room temperature rate constant of Gorse and Volman (1974) obtained relative to that for the reaction of OH radicals with CO is significantly lower than the rate constants of Dóbé et al. (1991, 1992) and DeMore and Bayes (1999), and is not used in the evaluation of the rate constant for this reaction. While the temperature dependencies obtained by Dóbé et al. (1991, 1992) and DeMore and Bayes (1999) are similar, the rate constants of DeMore and Bayes (1999) are uniformly ~15% higher than those of Dóbé et al. (1991, 1992) (Fig. 19). Because of the good agreement of the relative rate data of DeMore and Bayes (1999) with absolute and relative rate constants for

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

other alkanes and cycloalkanes, the data of DeMore and Bayes (1999) are preferred, despite their rate constants being the highest. Accordingly, a least-squares analysis of the rate constants of DeMore and Bayes (1999), using the expression $k = AT^2e^{-B/T}$, results in the recommendation of

5 $k(\text{cyclobutane}) = 2.10 \times 10^{-17} T^2 e^{(25 \pm 81)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

over the temperature range 270–370 K, where the indicated uncertainty in the value of B is two least-squares standard deviations, and

$$k(\text{cyclobutane}) = 2.03 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

10 with an estimated uncertainty at 298 K of $\pm 30\%$. This recommended expression is shown in the Arrhenius plot as the solid line (Fig. 19). Obviously, further data are needed.

2.41. OH + cyclopentane

The available rate data are listed in Table 52. Rate constants are available from the absolute rate studies of Jolly et al. (1985), Droege and Tully (1987), Bott and Cohen
15 (1989) and Donahue et al. (1998) and from the relative rate studies of Volman (1975), Darnall et al. (1978), Atkinson et al. (1982a), Kramp and Paulson (1998) and DeMore and Bayes (1999). The study of Atkinson et al. (1982a) is judged to supersede the earlier study of Darnall et al. (1978), and Fig. 20 shows an Arrhenius plot of the data of Atkinson et al. (1982a), Jolly et al. (1985), Droege and Tully (1987), Bott and Cohen
20 (1989), Kramp and Paulson (1998), Donahue et al. (1998) and DeMore and Bayes (1999). There is an appreciable amount of scatter in the measured room temperature rate constants, with the rate constant of Kramp and Paulson (1998) relative to 1,3-butadiene being lower than the other rate data, and the absolute rate constants of Donahue et al. (1998) are both quite scattered and generally higher than the rate
25 constants of Atkinson et al. (1982a), Jolly et al. (1985), Droege and Tully (1987),

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kramp and Paulson (1998) (including those relative to *n*-nonane, propene and *trans*-2-butene), and DeMore and Bayes (1999). A least-squares analysis of the rate constants of Atkinson et al. (1982a), Jolly et al. (1985), Droege and Tully (1987), Bott and Cohen (1989), Kramp and Paulson (1998), Donahue et al. (1998) and DeMore and Bayes (1999), using the expression $k = AT^2e^{-B/T}$, leads to the recommendation of

$$k(\text{cyclopentane}) = 2.73 \times 10^{-17} T^2 e^{(214 \pm 45)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 270–1200 K, where the indicated uncertainty in the value of *B* is two least-squares standard deviations, and

$$k(\text{cyclopentane}) = 4.97 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated uncertainty at 298 K of $\pm 25\%$. This recommended expression is shown in the Arrhenius plot as the solid line (Fig. 20).

A least-squares analysis of the rate constants of Atkinson et al. (1982a), Jolly et al. (1985), Droege and Tully (1987), Bott and Cohen (1989), Kramp and Paulson (1998) (only the rate constants relative to *n*-nonane, propene and *trans*-2-butene, because of the possibility that 1,3-butadiene reacted significantly with NO₂ and/or O(³P) atoms, Kramp and Paulson, 1998) and DeMore and Bayes (1999), using the expression $k = AT^2e^{-B/T}$, leads to $k(\text{cyclopentane}) = 2.64 \times 10^{-17} T^2 e^{(219 \pm 21)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270–1200 K, where the indicated uncertainty in the value of *B* is two least-squares standard deviations, and $k(\text{cyclopentane}) = 4.89 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (i.e. within 3% of the recommended expression over the temperature range 270–1200 K).

2.42. OH + cyclopentane-d₁₀

As shown in Table 53, rate constants for cyclopentane-d₁₀ are available only from the absolute rate study of Droege and Tully (1987). Combining their absolute rate constants for cyclopentane-h₁₀ (*k_H*) and cyclopentane-d₁₀ (*k_D*) results in a rate constant

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

ratio of

$$k_H/k_D(\text{CH}_2/\text{CD}_2 \text{ groups}) = (1.16 \pm 0.10)e^{(254 \pm 16)/T}$$

over the temperature range 295–491 K, with

$$k_H/k_D(\text{CH}_2/\text{CD}_2 \text{ groups}) = 2.74 \pm 0.17 \text{ at } 295 \text{ K.}$$

- 5 This temperature-dependent expression for k_H/k_D and the ratio at room temperature are similar to the deuterium isotope ratios $k_H/k_D(\text{CH}_2/\text{CD}_2 \text{ groups})$ obtained by Droege and Tully (1986a) for the propane reactions ($k_H/k_D(\text{CH}_2/\text{CD}_2 \text{ groups}) = (1.13 \pm 0.19)e^{(262 \pm 78)/T}$ over the temperature range 295–854 K, $k_H/k_D(\text{CH}_2/\text{CD}_2 \text{ groups}) = 2.62 \pm 0.49$ at 295 K), by Droege and Tully (1986b) for the *n*-butane reactions
- 10 ($k_H/k_D(\text{CH}_2/\text{CD}_2 \text{ groups}) = (1.31 \pm 0.12)e^{(196 \pm 33)/T}$ over the temperature range 294–509 K, $k_H/k_D(\text{CH}_2/\text{CD}_2 \text{ groups}) = 2.52 \pm 0.17$ at 294 K) and by Droege and Tully (1987) for the cyclohexane reactions ($k_H/k_D(\text{CH}_2/\text{CD}_2 \text{ groups}) = (1.16 \pm 0.06)e^{(237 \pm 10)/T}$ over the temperature range 292–491 K, $k_H/k_D(\text{CH}_2/\text{CD}_2 \text{ groups}) = 2.59 \pm 0.16$ at 292 K).

2.43. OH + cyclohexane

- 15 The available rate data are listed in Table 54. Rate constants are available from the absolute rate studies of Greiner (1970), Nielsen et al. (1986), Bourmada et al. (1987), Droege and Tully (1987), Saunders et al. (1994) and Donahue et al. (1996, 1998), and from a number of relative rate studies (Gorse and Volman, 1974; Wu et al., 1976; Atkinson et al., 1982a, 1983b; Tuazon et al., 1983; Edney et al., 1986; Japar et al., 1990; Atkinson and Aschmann, 1992; Sommerlade et al., 1993; DeMore and Bayes, 1999).
- 20 Most of these rate constants have been measured only at room temperature. There is an appreciable amount of scatter in the room temperature rate constants, which range from 5.2×10^{-12} to $8.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Figure 21 shows an Arrhenius plot of the absolute rate constants of Droege and Tully (1987) and Donahue et al. (1998)
- 25 together with the relative rate constants of Atkinson et al. (1982a, 1983b), Tuazon et

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

al. (1983), Atkinson and Aschmann (1992) and DeMore and Bayes (1999) (relative to *n*-butane and *n*-pentane; their data relative to propane (DeMore and Bayes, 1999) have not been used because of the relatively high rate constant ratios determined using this reference compound and hence potentially higher uncertainties). The absolute rate constants of Donahue et al. (1998) are seen to be quite scattered (as is also the case for the cyclopentane reaction), and are hence not used in the evaluation. A least-squares analysis of the rate constants of Droege and Tully (1987), Atkinson et al. (1982a, 1983b), Tuazon et al. (1983), Atkinson and Aschmann (1992) and DeMore and Bayes (1999), using the expression $k = AT^2e^{-B/T}$, leads to the recommendation of

$$k(\text{cyclohexane}) = 3.26 \times 10^{-17} T^2 e^{(262 \pm 33)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 290–500 K, where the indicated uncertainty in the value of *B* is two least-squares standard deviations, and

$$k(\text{cyclohexane}) = 6.97 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated uncertainty at 298 K of $\pm 20\%$. This recommended expression is shown in the Arrhenius plot as the solid line (Fig. 21).

The relative rate data of Japar et al. (1990), Sommerlade et al. (1993), Kramp and Paulson (1998) and those of DeMore and Bayes (1999) relative to propane (not used in the evaluation; see above) are in excellent agreement with the recommended rate constant, while that of Edney et al. (1986) is 20% lower.

2.44. OH + cyclohexane-*d*₁₂

As evident from Table 55, rate constants for cyclohexane-*d*₁₂ are available only from the absolute rate study of Droege and Tully (1987). Combining their absolute rate constants for cyclohexane-*h*₁₂ (*k_H*) and cyclohexane-*d*₁₂ (*k_D*) results in a rate constant ratio of

$$k_H/k_D = (1.16 \pm 0.06)e^{(237 \pm 10)/T}$$

over the temperature range 292–491 K, with

$$k_H/k_D = 2.59 \pm 0.16 \text{ at } 292 \text{ K.}$$

As noted for the cyclopentane-d₁₀ reaction, this temperature-dependent expression for k_H/k_D and the ratio at room temperature are similar to the deuterium isotope ratios k_H/k_D (CH₂/CD₂ groups) obtained by Droege and Tully (1986a) for the propane reactions (k_H/k_D (CH₂/CD₂ groups) = $(1.13 \pm 0.19)e^{(262 \pm 78)/T}$ over the temperature range 295–854 K, k_H/k_D (CH₂/CD₂ groups) = 2.62 ± 0.49 at 295 K), by Droege and Tully (1986b) for the *n*-butane reactions (k_H/k_D (CH₂/CD₂ groups) = $(1.31 \pm 0.12)e^{(196 \pm 33)/T}$ over the temperature range 294–509 K, k_H/k_D (CH₂/CD₂ groups) = 2.52 ± 0.17 at 294 K) and by Droege and Tully (1987) for the cyclopentane reactions (k_H/k_D (CH₂/CD₂ groups) = $(1.16 \pm 0.10)e^{(254 \pm 16)/T}$ over the temperature range 295–491 K, k_H/k_D (CH₂/CD₂ groups) = 2.74 ± 0.17 at 295 K).

2.45. OH + methylcyclohexane

As shown in Table 56, the only study of this reaction to date is that of Atkinson et al. (1984).

2.46. OH + *n*-butylcyclohexane

As shown in Table 57, the only study of this reaction to date is that of Aschmann et al. (2001).

2.47. OH + cycloheptane

As shown in Table 58, rate constants for cycloheptane are available only from the absolute rate studies of Jolly et al. (1985) and Donahue et al. (1998). As shown in the Arrhenius plot (Fig. 22), the room temperature rate constants from these two

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

studies (Jolly et al., 1985; Donahue et al., 1998) are in good agreement. A least-squares analysis of the rate constants from these two studies, using the expression $k = AT^2e^{-B/T}$, leads to the recommendation of

$$k(\text{cycloheptane}) = 3.99 \times 10^{-17} T^2 e^{(373 \pm 119)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

- 5 over the temperature range 290–390 K, where the indicated uncertainty in the value of B is two least-squares standard deviations, and

$$k(\text{cycloheptane}) = 1.24 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$$

with an estimated uncertainty at 298 K of $\pm 25\%$. This recommended expression is shown in the Arrhenius plot as the solid line (Fig. 22).

10 2.48. OH + cyclooctane

As evident from Table 59, the only study of this reaction to date is that of Donahue et al. (1998). A least-squares analysis of the rate constants of Donahue et al. (1998), using the expression $k = AT^2e^{-B/T}$, leads to $k(\text{cyclooctane}) = 5.91 \times 10^{-17} T^2 e^{(276 \pm 143)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 300–390 K, where
15 the indicated uncertainty in the value of B is two least-squares standard deviations, and with $k(\text{cyclooctane}) = 1.33 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

2.49. OH + bicyclo[2.2.1]heptane, bicyclo[2.2.2]octane and bicyclo[3.3.0]octane

As shown in Tables 60 (bicyclo[2.2.1]heptane), 61 (bicyclo[2.2.2]octane) and 62 (bicyclo[3.3.0]octane), the only study of these reactions to date is that of Atkinson et al.
20 (1983c).

2.50. OH + *cis*-bicyclo[4.3.0]nonane and *trans*-bicyclo[4.3.0]nonane

As shown in Tables 63 (*cis*-bicyclo[4.3.0]nonane) and 64 (*trans*-bicyclo[4.3.0]nonane), the only study of these reactions to date is that of Atkinson

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

et al. (1983c). The rate constant ratio $k(\text{cis-bicyclo}[4.3.0]\text{nonane})/k(\text{trans-bicyclo}[4.3.0]\text{nonane})$ was determined to be 0.966 ± 0.014 at 299 ± 2 K (Atkinson et al., 1983c).

2.51. OH + *cis*-bicyclo[4.4.0]decane and *trans*-bicyclo[4.4.0]decane

- 5 As shown in Tables 65 (*cis*-bicyclo[4.4.0]decane) and 66 (*trans*-bicyclo[4.3.0]decane), the only study of these reactions to date is that of Atkinson et al. (1983c). The rate constant ratio $k(\text{cis-bicyclo}[4.4.0]\text{decane})/k(\text{trans-bicyclo}[4.4.0]\text{decane})$ was determined to be 0.976 ± 0.021 at 299 ± 2 K (Atkinson et al., 1983c).

2.52. OH + tricyclo[5.2.1.0^{2,6}]decane and tricyclo[3.3.1.1^{3,7}]decane

- 10 As shown in Tables 67 (tricyclo[5.2.1.0^{2,6}]decane) and 68 (tricyclo[3.3.1.1^{3,7}]decane), the only published study of these reactions to date is that of Atkinson et al. (1983c).

2.53. OH + *trans*-pinane, tricyclene and quadricyclane

As shown in Tables 69 (*trans*-pinane), 70 (tricyclene) and 71 (quadricyclane), the only study of these reactions to date is that of Atkinson and Aschmann (1992).

- 15 **Acknowledgement.** The author gratefully thanks the US Department of Energy for support of this research through Contract No. DE-FG03-01ER63095. While this research has been funded by a Federal Agency, the results and content of this publication do not necessarily reflect the views and opinions of the Agency or the US Government.

References

- 20 Abbatt, J. P. D., Demerjian, K. L., and Anderson, J. G.: A new approach to free-radical kinetics: radially and axially resolved high-pressure discharge flow with results for OH + (C₂H₆, C₃H₈, *n*-C₄H₁₀, *n*-C₅H₁₂) → products at 297 K, J. Phys. Chem., 94, 4566–4575, 1990.

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

- Aschmann, S. M., Arey, J., and Atkinson, R.: Atmospheric chemistry of three C₁₀ alkanes, J. Phys. Chem. A, 105, 7598–7606, 2001.
- Atkinson, R.: Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions, Chem. Rev., 86, 69–201, 1986.
- 5 Atkinson, R.: Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds, J. Phys. Chem. Ref. Data, Monograph 1, 1–246, 1989.
- Atkinson, R.: Gas-phase tropospheric chemistry of organic compounds, J. Phys. Chem. Ref. Data, Monograph 2, 1–216, 1994.
- Atkinson, R.: Gas-phase tropospheric chemistry of volatile organic compounds: 1. Alkanes and alkenes, J. Phys. Chem. Ref. Data, 26, 215–290, 1997.
- 10 Atkinson, R.: Atmospheric chemistry of VOCs and NO_x, Atmos. Environ., 34, 2063–2101, 2000.
- Atkinson, R. and Aschmann, S. M.: Rate constants for the reaction of OH radicals with a series of alkenes and dialkenes at 295 ± 1 K, Int. J. Chem. Kinet., 16, 1175–1186, 1984.
- Atkinson, R. and Aschmann, S. M.: Rate constant for the reaction of OH radicals with isopropylcyclopropane at 298 ± 2 K: effects of ring strain on substituted cycloalkanes, Int. J. Chem. Kinet., 20, 339–342, 1988.
- 15 Atkinson, R. and Aschmann, S. M.: OH radical reaction rate constants for polycyclic alkanes: effects of ring strain and consequences for estimation methods, Int. J. Chem. Kinet., 24, 983–989, 1992.
- Atkinson, R., Carter, W. P. L., Winer, A. M., and Pitts, J. N., Jr.: An experimental protocol for the determination of OH radical rate constants with organics using methyl nitrite photolysis as an OH radical source, J. Air Pollut. Control Assoc., 31, 1090–1092, 1981.
- 20 Atkinson, R., Aschmann, S. M., Winer, A. M., and Pitts, J. N., Jr.: Rate constants for the reaction of OH radicals with a series of alkanes and alkenes at 299 ± 2 K, Int. J. Chem. Kinet., 14, 507–516, 1982a.
- 25 Atkinson, R., Aschmann, S. M., Carter, W. P. L., Winer, A. M., and Pitts, J. N., Jr.: Kinetics of the reactions of OH radicals with *n*-alkanes at 299 ± 2 K, Int. J. Chem. Kinet., 14, 781–788, 1982b.
- Atkinson, R., Aschmann, S. M., and Carter, W. P. L.: Kinetics of the reactions of O₃ and OH radicals with furan and thiophene at 298 ± 2 K, Int. J. Chem. Kinet., 15, 51–61, 1983a.
- 30 Atkinson, R., Aschmann, S. M., and Pitts, J. N., Jr.: Kinetics of the gas-phase reactions of OH radicals with a series of α , β -unsaturated carbonyls at 299 ± 2 K, Int. J. Chem. Kinet., 15, 75–81, 1983b.

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Atkinson, R., Aschmann, S. M., and Carter, W. P. L.: Rate constants for the gas-phase reactions of OH radicals with a series of bi- and tricycloalkanes at 299 ± 2 K: effects of ring strain, *Int. J. Chem. Kinet.*, 15, 37–50, 1983c.

Atkinson, R., Carter, W. P. L., Aschmann, S. M., Winer, A. M., and Pitts, J. N., Jr.: Kinetics of the reactions of OH radicals with a series of branched alkanes at 297 ± 2 K, *Int. J. Chem. Kinet.*, 16, 469–481, 1984.

Baker, R. R., Baldwin, R. R., and Walker, R. W.: Addition of C_3H_8 , n- and i- C_4H_{10} to slowly reacting mixtures of hydrogen and oxygen at $480^\circ C$, *Trans. Faraday Soc.*, 66, 2812–2826, 1970.

Baker, R. R., Baldwin, R. R., and Walker, R. W.: Addition of neopentane to slowly reacting mixtures of $H_2 + O_2$ at $480^\circ C$. Part II. The addition of the primary products from neopentane, and the rate constants for H and OH attack on neopentane, *Combust. Flame*, 27, 147–161, 1976.

Baldwin, R. R.: Inhibition of the hydrogen + oxygen reaction by propane, *Trans. Faraday Soc.*, 60, 527–538, 1964.

Baldwin, R. R. and Simmons, R. F.: The mechanism of the inhibition of the hydrogen + oxygen reaction by ethane, *Trans. Faraday Soc.*, 53, 964–971, 1957.

Baldwin, R. R. and Walker, R. W.: Inhibition of the hydrogen + oxygen reaction by n- and iso-butane, *Trans. Faraday Soc.*, 60, 1236–1246, 1964.

Baldwin, R. R. and Walker, R. W.: Rate constants for hydrogen + oxygen system, and for H atoms and OH radicals + alkanes, *J. Chem. Soc. Faraday Trans. 1*, 75, 140–154, 1979.

Baldwin, R. R., Norris, A. C., and Walker, R. W.: Reactions of methane in slowly reacting hydrogen-oxygen mixtures, 11th International Symposium on Combustion, 1966; The Combustion Institute, Pittsburgh, PA, 889–897, 1967.

Baldwin, R. R., Hopkins, D. E., Norris, A. C., and Walker, R. W.: The addition of methane to slowly reacting hydrogen-oxygen mixtures: reactions of methyl radicals, *Combust. Flame*, 15, 33–46, 1970a.

Baldwin, R. R., Hopkins, D. E., and Walker, R. W.: Addition of ethane to slowly reacting mixtures of hydrogen and oxygen at $500^\circ C$, *Trans. Faraday Soc.*, 66, 189–203, 1970b.

Baldwin, R. R., Walker, R. W., and Walker, R. W.: Addition of 2,2,3,3-tetramethylbutane to slowly reacting mixtures of hydrogen and oxygen, *J. Chem. Soc. Faraday Trans. 1*, 75, 1447–1457, 1979.

Baldwin, R. R., Walker, R. W., and Walker, R. W.: Addition of 2,2,3-trimethylbutane to slowly

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

reacting mixtures of hydrogen and oxygen at 480°C, J. Chem. Soc. Faraday Trans. 1, 77, 2157–2173, 1981.

Barnes, I., Bastian, V., Becker, K. H., Fink, E. H., and Zabel, F.: Reactivity studies of organic substances towards hydroxyl radicals under atmospheric conditions, Atmos. Environ., 16, 545–550, 1982.

Barnes, I., Bastian, V., Becker, K. H., Fink, E. H., and Nelsen, W.: Oxidation of sulphur compounds in the atmosphere: I. Rate constants of OH radical reactions with sulphur dioxide, hydrogen sulphide, aliphatic thiols and thiophenol, J. Atmos. Chem., 4, 445–466, 1986.

Baulch, D. L., Craven, R. J. B., Din, M., Drysdale, D. D., Grant, S., Richardson, D. J., Walker, A., and Watling, G.: Rates of hydroxyl radical reactions with methane, ethane and propane over the temperature range 403–696 K, J. Chem. Soc. Faraday Trans. 1, 79, 689–698, 1983.

Baulch, D. L., Campbell, I. M., and Saunders, S. M.: Rate constants for the reactions of hydroxyl radicals with propane and ethane, J. Chem. Soc. Faraday Trans. 1, 81, 259–263, 1985.

Behnke, W., Nolting, F., and Zetzsch, C.: A smog chamber study on the impact of aerosols on the photodegradation of chemicals in the environment, J. Aerosol Sci., 18, 65–71, 1987.

Behnke, W., Holländer, W., Koch, W., Nolting, F., and Zetzsch, C.: A smog chamber for studies of the photochemical degradation of chemicals in the presence of aerosols, Atmos. Environ., 22, 1113–1120, 1988.

Blundell, R. V., Cook, W. G. A., Hoare, D. E., and Milne, G. S.: Rates of radical reactions in methane oxidation, 10th International Symposium on Combustion, 1964; The Combustion Institute, Pittsburgh, PA, 445–452, 1965.

Böhland, T., Temps, F., and Wagner, H. Gg.: An LMR-spectrometer operating up to mm-wavelengths for kinetic investigations with discharge flow and flash photolysis systems, Z. Phys. Chem. Neue Folge., 142, 129–140, 1984.

Bonard, A., Daële, V., Delfau, J.-L., and Vovelle, C.: Kinetics of OH radical reactions with methane in the temperature range 295–660 K and with dimethyl ether and methyl-*tert*-butyl ether in the temperature range 295–618 K, J. Phys. Chem. A, 106, 4384–4389, 2002.

Bott, J. F. and Cohen, N.: A shock tube study of the reaction of hydroxyl radical with propane, Int. J. Chem. Kinet., 16, 1557–1566, 1984.

Bott, J. F. and Cohen, N.: Comment on Madronich, S. and Felder, W.: Direct measurements of the rate coefficients for the reaction $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$ over 300–1500 K, 20th International Symposium on Combustion, 1984; The Combustion Institute, Pittsburgh, PA, 711–712, 1985.

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

- Bott, J. F. and Cohen, N.: A shock tube study of the reaction of the hydroxyl radical with H_2 , CH_4 , $c\text{-C}_5\text{H}_{10}$, and $i\text{-C}_4\text{H}_{10}$, *Int. J. Chem. Kinet.*, 21, 485–498, 1989.
- Bott, J. F. and Cohen, N.: A shock tube study of the reaction of methyl radicals with hydroxyl radicals, *Int. J. Chem. Kinet.*, 23, 1017–1033, 1991a.
- 5 Bott, J. F. and Cohen, N.: A shock tube study of the reactions of the hydroxyl radical with several combustion species, *Int. J. Chem. Kinet.*, 23, 1075–1094, 1991b.
- Bourmada, N., Lafage, C., and Devolder, P.: Absolute rate constants of the reactions of OH with cyclohexane and ethane at 296 ± 2 K by the discharge flow method, *Chem. Phys. Lett.*, 136, 209–214, 1987.
- 10 Bradley, J. N., Hack, W., Hoyermann, K., and Wagner, H. Gg.: Kinetics of the reaction of hydroxyl radicals with ethylene and with C_3 hydrocarbons, *J. Chem. Soc. Faraday Trans. 1*, 69, 1889–1898, 1973.
- Bradley, J. N., Capey, W. D., Fair, R. W., and Pritchard, D. K.: A shock-tube study of the kinetics of reaction of hydroxyl radicals with H_2 , CO , CH_4 , CF_3H , C_2H_4 , and C_2H_6 , *Int. J. Chem. Kinet.*, 8, 549–561, 1976.
- 15 Calvert, J. G., Atkinson, R., Becker, K. H., Kamens, R. M., Seinfeld, J. H., Wallington, T. J., and Yarwood, G.: *The mechanisms of atmospheric oxidation of aromatic hydrocarbons*, Oxford University Press, New York, NY, 2002.
- Campbell, I. M., Handy, B. J., and Kirby, R. M.: Gas phase chain reaction of $\text{H}_2\text{O}_2 + \text{NO}_2 + \text{CO}$, *J. Chem. Soc. Faraday Trans. 1*, 71, 867–874, 1975.
- 20 Campbell, I. M., McLaughlin, D. F., and Handy, B. J.: Rate constants for reactions of hydroxyl radicals with alcohol vapours at 292 K, *Chem. Phys. Lett.*, 38, 362–364, 1976.
- Carl, S. A. and Crowley, J. N.: 298 K rate coefficients for the reactions of OH with $i\text{-C}_3\text{H}_7\text{I}$, $n\text{-C}_3\text{H}_7\text{I}$ and C_3H_8 , *Atmos. Chem. Phys.*, 1, 1–7, 2001.
- 25 Chuong, B. and Stevens, P. S.: Measurements of the kinetics of the OH-initiated oxidation of isoprene, *J. Geophys. Res.*, 107, D13, ACH 2-1 to ACH 2-12, 2002.
- Clarke, J. S., Kroll, J. H., Donahue, N. M., and Anderson, J. G.: Testing frontier orbital control: kinetics of OH with ethane, propane, and cyclopropane from 180 to 360 K, *J. Phys. Chem. A*, 102, 9847–9857, 1998.
- 30 Coeur, C., Jacob, V., Foster, P., and Baussand, P.: Rate constant for the gas-phase reaction of hydroxyl radical with the natural hydrocarbon bornyl acetate, *Int. J. Chem. Kinet.*, 30, 497–502, 1998.
- Coeur, C., Jacob, V., and Foster, P.: Gas-phase reaction of hydroxyl radical with the natural

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

- hydrocarbon bornyl acetate, *Phys. Chem. Earth (C)*, 24, 537–539, 1999.
- Cox, R. A., Derwent, R. G., and Holt, P. M.: Relative rate constants for the reactions of OH radicals with H₂, CH₄, CO, NO and HONO at atmospheric pressure and 296 K, *J. Chem. Soc. Faraday Trans. 1*, 72, 2031–2043, 1976.
- 5 Cox, R. A., Derwent, R. G., and Williams, M. R.: Atmospheric photooxidation reactions, reactivity, and mechanism for reaction of organic compounds with hydroxyl radicals, *Environ. Sci. Technol.*, 14, 57–61, 1980.
- Crowley, J. N., Campuzano-Jost, P., and Moortgat, G. K.: Temperature dependent rate constants for the gas-phase reaction between OH and CH₃OCl, *J. Phys. Chem.*, 100, 3601–
- 10 3606, 1996.
- Darnall, K. R., Winer, A. M., Lloyd, A. C., and Pitts, J. N., Jr.: Relative rate constants for the reaction of OH radicals with selected C₆ and C₇ alkanes and alkenes at 305 ± 2 K, *Chem. Phys. Lett.*, 44, 415–418, 1976.
- Darnall, K. R., Atkinson, R., and Pitts, J. N., Jr.: Rate constants for the reaction of the OH radical with selected alkanes at 300 K, *J. Phys. Chem.*, 82, 1581–1584, 1978.
- 15 Davis, D. D., Fischer, S., and Schiff, R.: Flash photolysis-resonance fluorescence kinetics study: temperature dependence of the reactions OH + CO → CO₂ + H and OH + CH₄ → H₂O + CH₃, *J. Chem. Phys.*, 61, 2213–2219, 1974.
- DeMore, W. B.: Rate constant ratio for the reaction of OH with CH₃D and CH₄, *J. Phys. Chem.*,
- 20 97, 8564–8566, 1993a.
- DeMore, W. B.: Rate constants for the reactions of OH with HFC-134a (CF₃CH₂F) and HFC-134 (CHF₂CHF₂), *Geophys. Res. Lett.*, 20, 1359–1362, 1993b.
- DeMore, W. B.: Rates of hydroxyl radical reactions with some HFCs, *Proc. SPIE, Int. Soc. Opt. Eng.*, 1715, 72–77, 1993c.
- 25 DeMore, W. B. and Bayes, K. D.: Rate constants for the reactions of hydroxyl radical with several alkanes, cycloalkanes, and dimethyl ether, *J. Phys. Chem. A*, 103, 2649–2654, 1999.
- Devolder, P., Carlier, M., Pauwels, J. F., and Sochet, L. R.: Rate constant for the reaction of OH with nitric acid: a new investigation by discharge flow resonance fluorescence, *Chem. Phys. Lett.*, 111, 94–99, 1984.
- 30 Dixon-Lewis, G. and Williams, A.: Some observations on the combustion of methane in premixed flames, 11th International Symposium on Combustion, 1966; The Combustion Institute, Pittsburgh, PA, 951–958, 1967.
- Dóbbé, S., Turányi, T., Bérces, T., and Márta, F.: The kinetics of hydroxyl radical reactions with

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

- cyclopropane and cyclobutane, Proc. Indian Acad. Sci. (Chem. Sci.), 103, 499–503, 1991.
- Dóbé, S., Turányi, T., Ilog, A. A., and Bérces, T.: Rate constants of the reactions of OH radicals with cyclopropane and cyclobutane, Int. J. Chem. Kinet., 24, 191–198, 1992.
- Donaghy, T., Shanahan, I., Hande, M., and Fitzpatrick, S.: Rate constants and atmospheric lifetimes for the reactions of OH radicals and Cl atoms with haloalkanes, Int. J. Chem. Kinet., 25, 273–284, 1993.
- Donahue, N. M., Clarke, J. S., Demerjian, K. L., and Anderson, J. G.: Free-radical kinetics at high pressure: a mathematical analysis of the flow reactor, J. Phys. Chem., 100, 5821–5838, 1996.
- Donahue, N. M., Anderson, J. G., and Demerjian, K. L.: New rate constants for ten OH alkane reactions from 300 to 400 K: an assessment of accuracy, J. Phys. Chem. A, 102, 3121–3126, 1998.
- Droege, A. T. and Tully, F. P.: Hydrogen-atom abstraction from alkanes by OH. 3. Propane, J. Phys. Chem., 90, 1949–1954, 1986a.
- Droege, A. T., and Tully, F. P.: Hydrogen-atom abstraction from alkanes by OH. 5. *n*-Butane, J. Phys. Chem., 90, 5937–5941, 1986b.
- Droege, A. T. and Tully, F. P.: Hydrogen-atom abstraction from alkanes by OH. 6. Cyclopentane and cyclohexane, J. Phys. Chem., 91, 1222–1225, 1987.
- Dunlop, J. R. and Tully, F. P.: A kinetic study of OH radical reactions with methane and perdeuterated methane, J. Phys. Chem., 97, 11148–11150, 1993.
- Edney, E. O., Kleindienst, T. E., and Corse, E. W.: Room temperature rate constants for the reaction of OH with selected chlorinated and oxygenated hydrocarbons, Int. J. Chem. Kinet., 18, 1355–1371, 1986.
- Ernst, J., Wagner, H. Gg., and Zellner, R.: A combined flash photolysis/shock-tube study of the absolute rate constants for reactions of the hydroxyl radical with CH₄ and CF₃H around 1300 K, Ber. Bunsenges. Phys. Chem., 82, 409–414, 1978.
- Fairchild, P. W., Smith, G. P., and Crosley, D. R.: A laser pyrolysis/laser fluorescence technique for combustion chemical kinetics, 19th International Symposium on Combustion, 1982; The Combustion Institute, Pittsburgh, PA, 107–115, 1982.
- Fenimore, C. P. and Jones, G. W.: Rate of reaction of methane with H atoms and OH radicals in flames, J. Phys. Chem., 65, 2200–2203, 1961.
- Fenimore, C. P. and Jones, G. W.: The decomposition of ethylene and ethane in premixed hydrocarbon-oxygen-hydrogen flames, 9th International Symposium on Combustion, 1963;

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Academic Press, New York, NY, 597–606, 1963.

Ferrari, C., Roche, A., Jacob, V., Foster, P., and Baussand, P.: Kinetics of the reactions of OH radicals with a series of esters under simulated conditions at 295 K, *Int. J. Chem. Kinet.*, 28, 609–614, 1996.

5 Finlayson-Pitts, B. J., Ezell, M. J., Jayaweera, T. M., Berko, H. N., and Lai, C. C.: Kinetics of the reactions of OH with methyl chloroform and methane: implications for global tropospheric OH and the methane budget, *Geophys. Res. Lett.*, 19, 1371–1374, 1992.

Finlayson-Pitts, B. J., Hernandez, S. K., and Berko, H. N.: A new dark source of the gaseous hydroxyl radical for relative rate measurements, *J. Phys. Chem.*, 97, 1172–1177, 1993.

10 Fristrom, R. M.: Radical concentrations and reactions in a methane-oxygen flame, 9th International Symposium on Combustion, 1963; Academic Press, New York, NY, 560-575, 1963.

Gierczak, T., Talukdar, R. K., Herndon, S. C., Vaghjiani, G. L., and Ravishankara, A. R.: Rate coefficients for the reactions of hydroxyl radicals with methane and deuterated methanes, *J. Phys. Chem. A*, 101, 3125–3134, 1997.

15 Golden, D. M., Smith, G. P., McEwen, A. B., Yu, C.-L., Eiteneer, B., Frenklach, M., Vaghjiani, G. L., Ravishankara, A. R., and Tully, F. P.: OH(OD) + CO: measurements and an optimized RRKM fit, *J. Phys. Chem. A*, 102, 8598–8606, 1998.

Gordon, S. and Mulac, W. A.: Reaction of the OH($X^2\pi$) radical produced by the pulse radiolysis of water vapor, *Int. J. Chem. Kinet.*, Symposium No. 1, 289–299, 1975.

20 Gorse, R. A. and Volman, D. H.: Photochemistry of the gaseous hydrogen peroxide-carbon monoxide system: rate constants for hydroxyl radical reactions with hydrogen peroxide and isobutane by competitive kinetics, *J. Photochem.*, 1, 1–10, 1972/73.

Gorse, R. A. and Volman, D. H.: Photochemistry of the gaseous hydrogen peroxide-carbon monoxide system. II: Rate constants for hydroxyl radical reactions with hydrocarbons and for hydrogen atom reactions with hydrogen peroxide, *J. Photochem.*, 3, 115–122, 1974.

25 Greiner, N. R.: Hydroxyl-radical kinetics by kinetic spectroscopy. I. Reactions with H₂, CO, and CH₄ at 300° K, *J. Chem. Phys.*, 46, 2795–2799, 1967a.

Greiner, N. R.: Hydroxyl-radical kinetics by kinetic spectroscopy. II. Reactions with C₂H₆, C₃H₈, and *iso*-C₄H₁₀ at 300° K, *J. Chem. Phys.*, 46, 3389–3392, 1967b.

30 Greiner, N. R.: Hydroxyl radical kinetics by kinetic spectroscopy. VI. Reactions with alkanes in the range 300–500° K, *J. Chem. Phys.*, 53, 1070–1076, 1970.

Harker, A. B. and Burton, C. S.: A study of the mechanism and kinetics of the reaction of O(³P) atoms with propane, *Int. J. Chem. Kinet.*, 7, 907–917, 1975.

ACPD

3, 4183–4358, 2003

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

- Harris, S. J. and Kerr, J. A.: Relative rate measurements of some reactions of hydroxyl radicals with alkanes studied under atmospheric conditions, *Int. J. Chem. Kinet.*, 20, 939–955, 1988.
- Hoare, D. E.: Reactions of gaseous hydroxyl radicals, *Nature*, 194, 283, 1962.
- Hoare, D. E.: Studies of the reactions of hydroxyl radicals. I, *Proc. Roy. Soc. (London)*, A291, 73–83, 1966.
- Hoare, D. E. and Patel, M.: Role of OH and HO₂ radicals in the slow combustion of mixtures of methane, ethane and ethylene, *Trans. Faraday Soc.*, 65, 1325–1333, 1969.
- Hoare, D. E. and Peacock, G. B.: Studies of the reactions of hydroxyl radicals. II, *Proc. Roy. Soc. (London)*, A291, 85–93, 1966.
- Horne, D. G. and Norrish, R. G. W.: Rate of H-abstraction by OH from hydrocarbons, *Nature*, 215, 1373–1374, 1967.
- Howard, C. J. and Evenson, K. M.: Rate constants for the reactions of OH with CH₄ and fluorine, chlorine, and bromine substituted methanes at 296 K, *J. Chem. Phys.*, 64, 197–202, 1976a.
- Howard, C. J. and Evenson, K. M.: Rate constants for the reactions of OH with ethane and some halogen substituted ethanes at 296 K, *J. Chem. Phys.*, 64, 4303–4306, 1976b.
- Hucknall, D. J., Booth, D., and Sampson, R. J.: Reactions of hydroxyl radicals with alkanes, *Int. J. Chem. Kinet.*, Symposium No. 1, 301–315, 1975.
- Huder, K., and DeMore, W. B.: Rate constants for the reaction of OH with CH₃CCl₂F (HCFC-141b) determined by relative rate measurements with CH₄ and CH₃CCl₃, *Geophys. Res. Lett.*, 20, 1575–1577, 1993.
- Husain, D., Plane, J. M. C., and Slater, N. K. H.: Kinetic investigation of the reactions of OH ($X^2\pi$) with the hydrogen halides, HCl, DCl, HBr and DBr by time-resolved resonance fluorescence ($A^2 \sum^+ - X^2\pi$), *J. Chem. Soc. Faraday Trans. 2*, 77, 1949–1962, 1981.
- IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry: Evaluated kinetic and photochemical data for atmospheric chemistry, <http://www.iupac-kinetic.ch.cam.ac.uk/>, 2003.
- Japar, S. M., Wallington, T. J., Andino, J. M., and Ball, J. C.: Atmospheric reactivity of gaseous dimethyl sulfate, *Environ. Sci. Technol.*, 24, 313–315, 1990.
- Jeong, K.-M. and Kaufman, F.: Kinetics of the reaction of hydroxyl radical with methane and nine Cl- and F-substituted methanes. 1. Experimental results, comparisons, and applications, *J. Phys. Chem.*, 86, 1808–1815, 1982.
- Jeong, K.-M., Hsu, K.-J., Jeffries, J. B., and Kaufman, F.: Kinetics of the reactions of OH with C₂H₆, CH₃CCl₃, CH₂ClCHCl₂, CH₂ClCClF₂, and CH₂FCF₃, *J. Phys. Chem.*, 88, 1222–1226,

**Kinetics of the
gas-phase reactions**

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

1984.

Jolly, G. S., Paraskevopoulos, G., and Singleton, D. L.: Rates of OH radical reactions. XII. The reactions of OH with $c\text{-C}_3\text{H}_6$, $c\text{-C}_5\text{H}_{10}$, and $c\text{-C}_7\text{H}_{14}$. Correlation of hydroxyl rate constants with bond dissociation energies, *Int. J. Chem. Kinet.*, 17, 1–10, 1985.

5 Jonah, C. D., Mulac, W. A., and Zeglinski, P.: Rate constants for the reaction of OH + CO, OD + CO, and OH + methane as a function of temperature, *J. Phys. Chem.*, 88, 4100–4104, 1984.

Klein, Th., Barnes, I., Becker, K. H., Fink, E. H., and Zabel, F.: Pressure dependence of the rate constants for the reactions of C_2H_4 and C_3H_6 with OH radicals at 295 K, *J. Phys. Chem.*, 10
88, 5020–5025, 1984.

Klöpffer, W., Frank, R., Kohl, E.-G., and Haag, F.: Quantitative Erfassung der photochemischen Transformationsprozesse in der Troposphäre, *Chemiker-Zeitung*, 110, 57–61, 1986.

Koffend, J. B. and Cohen, N.: Shock tube study of OH reactions with linear hydrocarbons near 1100 K, *Int. J. Chem. Kinet.*, 28, 79–87, 1996.

15 Kozlov, S. N., Orkin, V. L., Huie, R. E., and Kurylo, M. J.: OH reactivity and UV spectra of propane, *n*-propyl bromide, and isopropyl bromide, *J. Phys. Chem. A*, 107, 1333–1338, 2003.

Kramp, F. and Paulson, S. E.: On the uncertainties in the rate coefficients for OH reactions with hydrocarbons, and the rate coefficients of the 1,3,5-trimethylbenzene and *m*-xylene reactions with OH radicals in the gas phase, *J. Phys. Chem. A*, 102, 2685–2690, 1998.

20 Kwok, E. S. C. and Atkinson, R.: Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-reactivity relationship: an update, *Atmos. Environ.*, 29, 1685–1695, 1995.

Lafage, C., Pauwels, J.-F., Carlier, M., and Devolder, P.: Rate constant for the reaction OH + H_2S in the range 243–463 K by discharge-flow laser-induced fluorescence, *J. Chem. Soc. Faraday Trans. 2*, 83, 731–739, 1987.

25 Lancar, I. T., Le Bras, G., and Poulet, G.: Redétermination de la constante de vitesse de la réaction $\text{CH}_4 + \text{OH}$ et son implication atmosphérique, *C. R. Acad. Sci. Paris, Série II*, 315, 1487–1492, 1992.

Lee, J. H. and Tang, I. N.: Absolute rate constants for the hydroxyl radical reactions with ethane, furan, and thiophene at room temperature, *J. Chem. Phys.*, 77, 4459–4463, 1982.

30 Leu, M.-T.: Rate constant for the reaction $\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$, *J. Chem. Phys.*, 70, 1662–1666, 1979.

Lloyd, A. C., Darnall, K. R., Winer, A. M., and Pitts, J. N., Jr.: Relative rate constants for reaction

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

of the hydroxyl radical with a series of alkanes, alkenes, and aromatic hydrocarbons, J. Phys. Chem., 80, 789–794, 1976.

Mac Leod, H., Balestra, C., Jourdain, J. L., Laverdet, G., and Le Bras, G.: Kinetic study of the reaction $\text{OH} + \text{HI}$ by laser photolysis-resonance fluorescence, Int. J. Chem. Kinet., 22, 1167–1176, 1990.

Madronich, S. and Felder, W.: Direct measurements of the rate coefficient for the reaction $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$ over 300–1500 K, 20th International Symposium on Combustion, 1984; The Combustion Institute, Pittsburgh, PA, 703–713, 1985.

Margitan, J. J., Kaufman, F., and Anderson, J. G.: The reaction of OH with CH_4 , Geophys. Res. Lett., 1, 80–81, 1974.

Margitan, J. J. and Watson, R. T.: Kinetics of the reaction of hydroxyl radicals with nitric acid, J. Phys. Chem., 86, 3819–3824, 1982.

McLoughlin, P., Kane, R., and Shanahan, I.: A relative rate study of the reaction of chlorine atoms (Cl) and hydroxyl radicals (OH) with a series of ethers, Int. J. Chem. Kinet., 25, 137–149, 1993.

Mellouki, A., Téton, S., Laverdet, G., Quilgars, A., and Le Bras, G.: Kinetic studies of OH reactions with H_2O_2 , C_3H_8 and CH_4 using the pulsed laser photolysis – laser induced fluorescence method, J. Chim. Phys., 91, 473–487, 1994.

Morris, E. D., Jr. and Niki, H.: Reactivity of hydroxyl radicals with olefins, J. Phys. Chem., 75, 3640–3641, 1971.

Morris, E. D., Jr., Stedman, D. H., and Niki, H.: Mass spectrometric study of the reactions of the hydroxyl radical with ethylene, propylene, and acetaldehyde in a discharge-flow system, J. Am. Chem. Soc., 93, 3570–3572, 1971.

NASA Panel for Data Evaluation: Chemical kinetics and photochemical data for use in stratospheric modeling, <http://jpldataeval.jpl.nasa.gov/>, 2003.

Nielsen, O. J., Pagsberg, P., and Sillesen, A.: Kinetics of the reaction of OH with ethane and a series of Cl- and F-substituted methanes at 300–400 K, studied by pulse radiolysis combined with kinetic spectroscopy, Proc. 3rd European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants, D. Reidel Publishing Co., Dordrecht, Holland, 283–292, 1984.

Nielsen, O. J., Munk, J., Pagsberg, P., and Sillesen, A.: Absolute rate constants for the gas-phase reaction of OH radicals with cyclohexane and ethane at 295 K, Chem. Phys. Lett., 128, 168–171, 1986.

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

**Kinetics of the
gas-phase reactions**

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Nielsen, O. J., Sidebottom, H. W., O'Farrell, D. J., Donlon, M., and Treacy, J.: Absolute and relative rate constants for the gas-phase reaction of OH radicals with CH_3NO_2 , CD_3NO_2 and $\text{CH}_3\text{CH}_2\text{CH}_3$ at 295 K and 1 atm, Chem. Phys. Lett., 146, 197–203, 1988.

Nielsen, O. J., Sidebottom, H. W., Donlon, M., and Treacy, J.: Rate constants for the gas-phase reactions of OH radicals and Cl atoms with *n*-alkyl nitrites at atmospheric pressure and 298 K, Int. J. Chem. Kinet., 23, 1095–1109, 1991a.

Nielsen, O. J., O'Farrell, D. J., Treacy, J. J., and Sidebottom, H. W.: Rate constants for the gas-phase reactions of hydroxyl radicals with tetramethyllead and tetraethyllead, Environ. Sci. Technol., 25, 1098–1103, 1991b.

Nolting, F., Behnke, W., and Zetzsch, C.: A smog chamber for studies of the reactions of terpenes and alkanes with ozone and OH, J. Atmos. Chem., 6, 47–59, 1988.

Oldenborg, R. C., Loge, G. W., Harradine, D. M., and Winn, K. R.: Kinetic study of the $\text{OH} + \text{H}_2$ reaction from 800 to 1550 K, J. Phys. Chem., 96, 8426–8430, 1992.

Overend, R. P., Paraskevopoulos, G., and Cvetanović, R. J.: Rates of OH radical reactions. I. Reactions with H_2 , CH_4 , C_2H_6 , and C_3H_8 at 295 K, Can. J. Chem., 53, 3374–3382, 1975.

Paraskevopoulos, G. and Nip, W. S.: Rates of OH radical reactions. VII. Reactions of OH and OD radicals with *n*- C_4H_{10} , *n*- C_4D_{10} , H_2 and D_2 , and of OH with *neo*- C_5H_{12} at 297 K, Can. J. Chem., 58, 2146–2149, 1980.

Peeters, J. and Mahnen, G.: Reaction mechanisms and rate constants of elementary steps in methane-oxygen flames, 14th International Symposium on Combustion, 1972; The Combustion Institute, Pittsburgh, PA, 133–146, 1973.

Perry, R. A., Atkinson, R. and Pitts, J. N., Jr.: Rate constants for the reaction of OH radicals with *n*-butane over the temperature range 297–420° K, J. Chem. Phys., 64, 5314–5316, 1976.

Ravishankara, A. R., Nicovich, J. M., Thompson, R. L., and Tully, F. P.: Kinetic study of the reaction of OH with H_2 and D_2 from 250–1050 K, J. Phys. Chem., 85, 2498–2503, 1981.

Saueressig, G., Crowley, J. N., Bergamaschi, P., Brühl, C., Brenninkmeijer, C. A. M., and Fischer, H.: Carbon 13 and D kinetic isotope effects in the reactions of CH_4 with $\text{O}(^1\text{D})$ and OH: new laboratory measurements and their implications for the isotopic composition of stratospheric methane, J. Geophys. Res., 106, 23 127–23 138, 2001.

Saunders, S. M., Hughes, K. J., Pilling, M. J., Baulch, D. L., and Smurthwaite, P. I.: Reactions of hydroxyl radicals with selected hydrocarbons of importance in atmospheric chemistry, Proc. SPIE, Int. Soc. Opt. Eng., 1715, 88–99, 1993.

Saunders, S. M., Baulch, D. L., Cooke, K. M., Pilling, M. J., and Smurthwaite, P. I.: Kinetics

- and mechanisms of the reactions of OH with some oxygenated compounds of importance in tropospheric chemistry, *Int. J. Chem. Kinet.*, 26, 113–130, 1994.
- Schiffman, A., Nelson, D. D., Jr., Robinson, M. S., and Nesbitt, D. J.: High-resolution infrared flash kinetic spectroscopy of OH radicals, *J. Phys. Chem.*, 95, 2629–2636, 1991.
- 5 Schmidt, V., Zhu, G. Y., Becker, K. H., and Fink, E. H.: Study of OH reactions at high pressures by excimer laser photolysis-dye laser fluorescence, *Ber. Bunsenges. Phys. Chem.*, 89, 321–322, 1985.
- Sharkey, P., and Smith, I. W. M.: Kinetics of elementary reactions at low temperatures: rate constants for the reactions of OH with HCl ($298 \geq T/K \geq 138$), CH₄ ($298 \geq T/K \geq 178$) and
- 10 C₂H₆ ($298 \geq T/K \geq 138$), *J. Chem. Soc. Faraday Trans.*, 89, 631–638, 1993.
- Simonaitis, R., Heicklen, J., Maguire, M. M., and Bernheim, R. A.: The mercury-sensitized photodecomposition of nitrous oxide in the presence of mixtures of carbon monoxide and methane, *J. Phys. Chem.*, 75, 3205–3213, 1971.
- Smith, C. A., Molina, L. T., Lamb, J. J., and Molina, M. J.: Kinetics of the reaction of OH with
- 15 pernitric and nitric acids, *Int. J. Chem. Kinet.*, 16, 41–55, 1984.
- Smith, G. P., Fairchild, P. W., Jeffries, J. B., and Crosley, D. R.: Laser pyrolysis/laser fluorescence studies of high-temperature reaction rates: description of the method and results for OH + CH₄, C₃H₈, and C₃H₆, *J. Phys. Chem.*, 89, 1269–1278, 1985.
- Sommerlade, R., Parlar, H., Wrobel, D., and Kochs, P.: Product analysis and kinetics of the
- 20 gas-phase reactions of selected organosilicon compounds with OH radicals using a smog chamber-mass spectrometer system, *Environ. Sci. Technol.*, 27, 2435–2440, 1993.
- Stachnik, R. A., Molina, L. T., and Molina, M. J.: Pressure and temperature dependences of the reaction of OH with nitric acid, *J. Phys. Chem.*, 90, 2777–2780, 1986.
- Stuhl, F.: Rate constant for the reaction of OH with *n*-C₄H₁₀, *Z. Naturforsch.*, 28A, 1383–1384,
- 25 1973.
- Sworski, T. J., Hochanadel, C. J., and Ogren, P. J.: Flash photolysis of H₂O vapor in CH₄. H and OH yields and rate constants for CH₃ reactions with H and OH, *J. Phys. Chem.*, 84, 129–134, 1980.
- Talukdar, R. K., Mellouki, A., Gierczak, T., Barone, S., Chiang, S.-Y., and Ravishankara, A. R.: Kinetics of the reactions of OH with alkanes, *Int. J. Chem. Kinet.*, 26, 973–990, 1994.
- 30 Talukdar, R. K., Gierczak, T., Goldfarb, L., Rudich, Y., Madhava Rao, B. S., and Ravishankara, A. R.: Kinetics of hydroxyl radical reactions with isotopically labeled hydrogen, *J. Phys. Chem.*, 100, 3037–3043, 1996.

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

- Trevor, P. L., Black, G., and Barker, J. R.: Reaction rate constant for $\text{OH} + \text{HOONO}_2 \rightarrow \text{products}$ over the temperature range 246 to 324 K, *J. Phys. Chem.*, 86, 1661–1669, 1982.
- Tuazon, E. C., Carter, W. P. L., Atkinson, R., and Pitts, J. N., Jr.: The gas-phase reaction of hydrazine and ozone: a nonphotolytic source of OH radicals for measurement of relative OH radical rate constants, *Int. J. Chem. Kinet.*, 15, 619–629, 1983.
- Tully, F. P., and Ravishankara, A. R.: Flash photolysis-resonance fluorescence kinetic study of the reactions $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ and $\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$ from 298 to 1020 K, *J. Phys. Chem.*, 84, 3126–3130, 1980.
- Tully, F. P., Ravishankara, A. R., and Carr, K.: Kinetic study of the reactions of the hydroxyl radical with ethane and propane, *Int. J. Chem. Kinet.*, 15, 1111–1118, 1983.
- Tully, F. P., Koszykowski, M. L., and Binkley, J. S.: Hydrogen-atom abstraction from alkanes by OH. I. Neopentane and neooctane, 20th International Symposium on Combustion, 1984; The Combustion Institute, Pittsburgh, PA, 715–721, 1985.
- Tully, F. P., Droege, A. T., Koszykowski, M. L., and Melius, C. F.: Hydrogen-atom abstraction from alkanes by OH. 2. Ethane, *J. Phys. Chem.*, 90, 691–698, 1986a.
- Tully, F. P., Goldsmith, J. E. M., and Droege, A. T.: Hydrogen-atom abstraction from alkanes by OH. 4. Isobutane, *J. Phys. Chem.*, 90, 5932–5937, 1986b.
- Vaghjiani, G. L. and Ravishankara, A. R.: New measurement for the rate coefficient for the reaction of OH with methane, *Nature*, 350, 406–409, 1991.
- Volman, D. H.: Comment in “General Discussion Session III”, *Int. J. Chem. Kinet.*, Symposium No. 1, 358, 1975.
- Wallington, T. J., Neuman, D. M., and Kurylo, M. J.: Kinetics of the gas phase reaction of hydroxyl radicals with ethane, benzene, and a series of halogenated benzenes over the temperature range 234–438 K, *Int. J. Chem. Kinet.*, 19, 725–739, 1987.
- Westenberg, A. A. and Fristrom, R. M.: Methane-oxygen flame structure. IV. Chemical kinetic considerations, *J. Phys. Chem.*, 65, 591–601, 1961.
- Westenberg, A. A., and Fristrom, R. M.: H and O atom profiles measured by ESR in C_2 hydrocarbon- O_2 flames, 10th International Symposium on Combustion, 1964; The Combustion Institute, Pittsburgh, PA, 473–487, 1965.
- Wilson, W. E. and Westenberg, A. A.: Study of the reaction of hydroxyl radical with methane by quantitative ESR, 11th International Symposium on Combustion, 1966; The Combustion Institute, Pittsburgh, PA, 1143–1150, 1967.
- Wilson, W. E., Jr., O'Donovan, J. T., and Fristrom, R. M.: Flame inhibition by halogen com-

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

pounds, 12th International Symposium on Combustion, 1968; The Combustion Institute, Pittsburgh, PA, 929–942, 1969.

Wilson, E. W., Jr., Sawyer, A. A., and Sawyer, H. A.: Rates of reaction for cyclopropane and difluoromethoxydifluoromethane with hydroxyl radicals, J. Phys. Chem. A, 105, 1445–1448, 2001.

Wu, C. H., Japar, S. M., and Niki, H.: Relative reactivities of HO-hydrocarbon reactions from smog chamber studies, J. Environ. Sci. Health, A11, 191–200, 1976.

Zabarnick, S., Fleming, J. W., and Lin, M. C.: Kinetics of hydroxyl radical reactions with formaldehyde and 1,3,5-trioxane between 290 and 600 K, Int. J. Chem. Kinet., 20, 117–129, 1988.

Zellner, R. and Steinert, W.: A flash photolysis study of the rate of the reaction $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$ over an extended temperature range, Int. J. Chem. Kinet., 8, 397–409, 1976.

ACPD

3, 4183–4358, 2003

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

**Kinetics of the
gas-phase reactions**

R. Atkinson

Table 1. List of abbreviations used in tables of rate data, under “Technique” column

Abbreviation	Experimental Technique
FP	Flash photolysis
DF	Discharge flow
PLP	Pulsed laser photolysis
RR	Relative rate
PR	Pulse radiolysis
LH	Laser heating
SH	Shock heating (shock tube)
RA	Resonance absorption
RF	Resonance fluorescence
KS	Kinetic spectroscopy
MMS	Molecular modulation-spectroscopy
LIF	Laser induced fluorescence
MS	Mass spectrometry
EPR	Electron paramagnetic resonance
LMR	Laser magnetic resonance

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the gas-phase reactions

R. Atkinson

Table 2. Relative rate constants for a series of alkanes at room temperature

alkane	Atkinson et al. (1982a, b) (299±2 K)	Behnke et al. (1987) (300±3 K)	Nolting et al. (1988) (312 K)	Behnke et al. (1988) (300 K)	DeMore and Bayes (1999) (298 K)
propane	0.473±0.016	0.539			0.467
<i>n</i> -butane	1.00	1.00		1.00	1.00
<i>n</i> -pentane	1.60±0.04	1.62	(1.60) ^a	1.63±0.04	1.57
<i>n</i> -hexane	2.21±0.04	2.19	2.31±0.24	2.24±0.04	2.19
<i>n</i> -heptane	2.83±0.07	2.78	2.80±0.11	2.88±0.06	
<i>n</i> -octane	3.49±0.07	3.37	3.28±0.17	3.46±0.06	
<i>n</i> -nonane	4.13±0.13	4.07	3.80±0.19	4.06±0.11	
<i>n</i> -decane	4.42±0.22		4.36±0.23	4.88±0.11	
cyclohexane	2.91±0.10 2.93±0.02				2.86

^a Based on the data cited in the table from the studies of Atkinson et al. (1982b), Behnke et al. (1987, 1988) and DeMore and Bayes (1999).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Table 3. Rate constants and temperature-dependent parameters for the reaction of OH radicals with methane

$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	n	$B(\text{K})$	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at $T(\text{K})$	Technique	Reference	Temperature Range (K)
			21±10.5	1650–1840	RR [relative to $k(\text{CO})$ $= 9.1 \times 10^{-19} T^{1.77} e^{580/T}$]	Westenberg and Fristrom (1961)	1650–1840
			12.5	1445	RR[relative to $k(\text{CO})$ $= 9.1 \times 10^{-19} T^{1.77} e^{580/T}$]	Fenimore and Jones (1961)	1220–1800
			12.8	1560			
			11.1	1580			
			12.9	1690			
			16.8	1800			
			0.181	673	RR[relative to $k(\text{CO})$ $= 9.1 \times 10^{-19} T^{1.77} e^{580/T}$]	Hoare (1962)	673–923
			0.256	723			
			0.54	798			
			0.77	873			
			1.03	923			
			26	~1370–1680	RR[relative to $k(\text{CO})$ $= 9.1 \times 10^{-19} T^{1.77} e^{580/T}$]	Fristrom (1963)	~1370–1680
			0.45±0.23	773	RR [relative to $k(\text{CO})=2.49 \times 10^{-13}$]	Blundell et al. (1965)	773–823
			0.185	673	RR[relative to $k(\text{CO})$ $= 9.1 \times 10^{-19} T^{1.77} e^{580/T}$]	Hoare (1966)	673–923
			0.291	723			
			0.54	798			
			0.80	873			
			1.09	923			
			0.59	798	RR[relative to $k(\text{CO})=2.58 \times 10^{-13}$]	Hoare and Peacock (1966)	
			0.87±0.18	773	RR [relative to $k(\text{H}_2)$ $= 8.72 \times 10^{-13}$]	Baldwin et al. (1967)	
			5.0±1.7	1285	Flame-RA/MS	Dixon-Lewis and Williams (1967)	
			0.0108±0.0025	300	DF-EPR	Wilson and Westenberg (1967)	
			0.00880±0.00034	301±1	FP-KS	Greiner (1967a)	
83		2516	0.0179 ^a	298	FP-KS	Horne and Norrish (1967)	298–423
			18±4	1750–2000	RR [relative to $k(\text{CO})$ $= 9.1 \times 10^{-19} T^{1.77} e^{580/T}$]	Wilson et al. (1969)	1750–2000

**Kinetics of the
gas-phase reactions**

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Table 3. Continued

$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	n	$B(\text{K})$	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at $T(\text{K})$	Technique	Reference	Temperature Range (K)
5.5	1898±52		0.96±0.09	773	RR [relative to $k(\text{H}_2)$ = 8.72×10^{-13}]	Baldwin et al. (1970a)	295–498
			0.00849±0.00072	295	FP-KS	Greiner (1970)	
			0.00953±0.00029	295			
			0.0106±0.0003	296			
			0.0103±0.0006	296			
			0.00804±0.00020	301			
			0.00805±0.00042	301			
			0.00903±0.00088	302			
			0.0154±0.0006	333			
			0.0352±0.0007	370			
			0.0611±0.0024	424			
			0.121±0.004	492			
			0.120±0.004	493			
			0.121±0.003	493			
			0.113±0.003	497			
			0.122±0.003	498			
			0.185 ^{+0.185} _{-0.093}	548	[relative to $k(\text{CO})=1.85 \times 10^{-13}$]	Simonaitis et al. (1971)	
50	3020		6.7 ^a	1500	Flame-MS	Peeters and Mahnen (1973)	1100–1900
2.36	1711±88		0.00185±0.00010	240	FP-RF	Davis et al. (1974)	240–373
			0.00185±0.00017	240			
			0.00495±0.00025	276			
			0.00749±0.00010	298			
			0.0075±0.00075	298			
			0.0069±0.0008	298			
			0.0236	373			
			0.00715±0.00042	293	DF-RF	Margitan et al. (1974)	
			0.0212±0.0004	359			
			0.0306±0.0001	384			
3.83	1842±21		0.0422±0.0018	407			293–427
			0.0521±0.0016	427			
			0.0261±0.0027	381	PR-RA	Gordon and Mulac (1975)	
			0.0548±0.0017	416			
			0.00651±0.00027	295±2	FP-RA	Overend et al. (1975)	
			0.0095±0.0014	296±2	DF-LMR	Howard and Evenson (1976a)	

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Table 3. Continued

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
5.76×10^{-9}	3.08	1010	0.0088±0.0007	298	FP-RA	Zellner and Steinert (1976)	298–892
			0.0148	330			
			0.020	358			
			0.028	381			
			0.061	444			
			0.070	453			
			0.113	498			
			0.174	525			
			0.257	564			
			0.251±0.033	576			
			0.276±0.033	584			
			0.335	622			
			0.551	629			
			0.822	671			
			0.830	680			
			1.12	738			
			1.21	756			
			1.51	776			
			2.71	892			
			0.00638±0.00074	296±2	RR [relative to <i>k</i> (H ₂) = 6.13 × 10 ⁻¹⁵]	Cox et al. (1976)	
			9.0	1300			
			3.82	1140	SH/FP-RA	Ernst et al. (1978)	1140–1505
			3.82	1160			
			4.48	1165			
			3.49	1188			
			3.49	1192			
			4.82	1203			
			4.15	1220			
			3.82	1245			
			3.99	1260			
			4.15	1260			
			3.49	1265			
			4.48	1270			
			4.65	1270			
			3.82	1275			
			3.99	1275			
			3.99	1303			
			4.32	1313			
			5.65	1335			
			5.31	1404			
			5.15	1410			
			4.48	1415			
			5.65	1500			
			5.31	1505			

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Table 3. Continued

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	n	B (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference	Temperature Range (K)
1.32×10^{-5}	1.92	1355	0.0070±0.0007	296	FP-RA (of CH ₃) with computer modeling	Sworski et al. (1980)	298–1020
			0.00750±0.00060	298	FR-RF	Tully and Ravishankara (1980)	
			0.0473±0.0045	398			
			0.081±0.011	448			
			0.145±0.012	511			
			0.167±0.006	529			
			0.314±0.040	600			
			0.275±0.044	619			
			0.578±0.058	696			
			0.84±0.15	772			
			1.50±0.15	915			
			2.00±0.20	1020			
			0.00766±0.00064	300	FP-RF	Husain et al. (1981)	
			1.25±0.45	830±50	LH-LIF	Fairchild et al. (1982)	830–1400
			1.3±0.4	1030±50			
			4.3±1.0	1400±50			
1.28×10^{-12}	4.23	453±776	0.00557±0.00054	269	DF-RF	Jeong and Kaufman (1982); Jeong et al. (1984)	269–473
			0.00789±0.00049	297			
			0.0178±0.0012	339			
			0.0347±0.0023	389			
			0.0549±0.0035	419			
			0.102±0.007	473	RR [relative to $k(\text{CO})=9.1 \times 10^{-19}$ $T^{1.77} e^{580/T}$]	Baulch et al. (1983)	413–693
			0.0379±0.0032	413			
			0.0541±0.0064	417			
			0.0350±0.0032	422			
			0.0636±0.0066	443			
			0.0773±0.0068	471			
			0.0963±0.0070	505			
			0.103±0.018	517			
			0.0926±0.0178	521			
			0.112±0.006	546			
			0.166±0.004	553			
			0.275±0.016	603			
			0.366±0.022	663			
			0.627±0.065	693			

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Table 3. Continued

$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	n	$B(\text{K})$	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at $T(\text{K})$	Technique	Reference	Temperature Range (K)
			0.00650	298	PR-RA	Jonah et al. (1984)	298–1229
			0.00846	298			
			0.0189	348			
			0.0351	373			
			0.106	398			
			0.0938	415			
			0.175	424			
			0.124	450			
			0.209	483			
			0.174	483			
			0.336	543			
			0.584	571			
			0.545	613			
			0.760	667			
			0.893	709			
			0.991	712			
			1.04	769			
			1.52	858			
			2.48	873			
			2.27	974			
			2.01	974			
			4.50	1071	FP-RF	Madronich and Felder (1985)	298–1512
			3.22	1125			
			4.19	1125			
			4.93	1229			
			0.0085±0.0006	298±3			
			0.0228±0.0043	362±10			
			0.0463±0.0034	407±5			
			0.0629±0.009	410±14			
			0.154±0.014	510±10			
			0.177±0.017	525±10			
			0.202±0.010	546±5			
			0.439±0.038	626±16			
			0.478±0.07	698±22			
			1.48±0.08	900±12			
			212±0.23	967±35			
			2.16±0.11	1005±15			
			2.72±0.15	1103±17			
			3.34±0.20	1164±17			
			2.41±0.22	1174±22			
			3.18±0.17	1176±17			
			3.89±0.25	1196±17			
			4.26±0.39	1196±37			
			3.77±0.32	1238±18			
			3.68±0.23	1244±17			
			3.58±0.27	1261±23			
			3.80±0.37	1261±18			

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Table 3. Continued

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	n	$B(K)$	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference	Temperature Range (K)
2.57 × 10 ⁻⁵	1.83	1396±134	4.74±0.20	1300±18			
			4.20±0.21	1307±18			
			4.84±0.50	1314±23			
			5.32±0.31	1345±18			
			5.61±0.34	1365±19			
			6.44±0.53	1396±19			
			5.98±0.69	1455±20			
			6.52±1.15	1510±20			
			6.74±0.35	1512±20			
			3	1220	SH-RA	Bott and Cohen (1985)	830–1412
			1.25±0.6	830	LH-LIF	Smith et al. (1985)	
			2.25±1.0	870			
			1.55±0.7	930			
			2.0±1.0	966			
			2.1±1.2	975			
			1.33±0.5	1030			
			3.6±0.9	1120			
			1.7±0.7	1150			
			2.35±0.7	1176			
			3.3±1.0	1200			
			2.9±0.35	1240			
			4.4±0.8	1400			
			4.2±0.8	1412			
			4.3±0.9	1234±15			
			0.00093±0.00003	223	PLP-LIF	Vaghjiani and Ravishankara (1991)	
			0.00102±0.00002	223			
			0.00104±0.00002	223			
0.00097±0.00003	223						
0.00086±0.00002	223						
0.00089±0.00003	223						
0.00086±0.00004	223						
0.00089±0.00004	223						
0.00088±0.00004	223						
0.00103±0.00002	223						
0.00086±0.00002	223						
0.00125±0.00002	233						
0.00133±0.00002	233						
0.00125±0.00003	233						
0.00118±0.00002	233						
0.00118±0.00003	233						
0.00119±0.00001	233						
0.00121±0.00002	233						
0.00182±0.00002	250						
0.00204±0.00005	250						

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Table 3. Continued

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
			0.00198±0.00003	250			
			0.00350±0.00005	273			
			0.00352±0.00007	273			
			0.00338±0.00007	273			
			0.00371±0.00016	273			
			0.00375±0.00005	273			
			0.00367±0.00004	273			
			0.00364±0.00005	273			
			0.00592±0.00018	295			
			0.00647±0.00006	297			
			0.00636±0.00022	297			
			0.00630±0.00007	298			
			0.00620±0.00018	298			
			0.00684±0.00025	303			
			0.00713±0.00018	303			
			0.00674±0.00013	303			
			0.00674±0.00008	303			
			0.00715±0.00011	303			
			0.00712±0.00038	303			
			0.01026±0.00015	325			
			0.01598±0.00011	350			
			0.02617±0.00042	380			
			0.04287±0.00052	420			
			0.04253±0.00052	420			
			0.04244±0.00057	420			
			0.04336±0.00063	420			
			0.04366±0.00056	420			
			0.04184±0.00061	420			
1.59 × 10 ⁻⁸	2.84	978	0.04304±0.00047	420			
2.94		1815±30					
			0.00409±0.00026	278	DF-RF	Finlayson-Pitts et al. (1992)	278–378
			0.00560±0.00063	298			
			0.00575±0.00098	298			
			0.0106±0.0017	313			
			0.00792±0.00007	313			
			0.0105±0.0028	333			
			0.0109±0.0006	333			
			0.0150±0.0025	348			
			0.0143±0.0036	348			
			0.0205±0.0019	363			
4.0		1944±114	0.0236±0.0008	378			
			0.0262±0.0027	378	DF-EPR	Lancar et al. (1992)	378–422
			0.0427±0.0018	422			

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Table 3. Continued

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	n	B (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference	Temperature Range (K)
$9.45 \times 10^{-8}{}^b$	$2.58{}^b$	$1082{}^b$	<0.0003	178±2	PLP-LIF	Sharkey and Smith (1993)	178–298
			0.00165±0.0002	216±2			
			0.0076±0.0003	298±2			
			0.00562±0.00043	293	PLP-LIF	Dunlop and Tully (1993)	293–800
			0.0371±0.0022	409			
			0.0422±0.0023	420			
			0.101±0.004	498			
			0.152±0.010	547			
			0.237±0.014	602			
			0.367±0.022	654			
			0.474±0.026	704			
			0.576±0.032	745			
			0.756±0.042	800			
			0.0054±0.0002	292	PLP-LIF	Saunders et al. (1993)	233–343
			0.00132±0.00005	233	PLP-LIF	Mellouki et al. (1994)	
0.00208±0.00030	243						
0.00215±0.00030	252						
0.00370±0.00020	273						
0.00642±0.00060	295						
0.00634±0.00056	298						
0.0105±0.0006	323						
0.0168±0.0015	343						
2.56	1765 ± 146	0.00036±0.00002	195	FP-LIF	Gierczak et al. (1997)	195–296	
		0.00040±0.00002	200				
		0.00049±0.00003	206				
		0.00063±0.00006	213				
		0.00075±0.00007	218				
		0.00082±0.00042	223				
		0.00602±0.00010	295				
		0.00585±0.00022	295				
		0.00590±0.00016	295				
		0.00615±0.00026	295				
$1.85 \times 10^{-8}{}^c$	$2.82{}^c$	$987{}^c$	0.00620±0.00016	296			

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 3. Continued

$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	n	$B(\text{K})$	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at $T(\text{K})$	Technique	Reference	Temperature Range (K)
5.65×10^{-9}	3.01	959±36	0.00623±0.00020	295	PLP-LIF	Bonard et al. (2002)	295–668
			0.00916±0.00028	319			
			0.0219±0.0007	367			
			0.0426±0.0018	419			
			0.0763±0.0021	464			
			0.133±0.004	519			
			0.205±0.009	569			
			0.306±0.010	619			
			0.422±0.014	668			

^a Calculated from the cited Arrhenius expression.

^b Fit of combined data sets of Dunlop and Tully (1993) and Vaghjani and Ravishankara (1991) over the temperature range 223–800 K.

^c Fit of combined data sets of Gierczak et al. (1997) and Vaghjani and Ravishankara (1991) over the temperature range 195–420 K.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Table 4. Rate constants and temperature-dependent parameters for the reaction of OH radicals with methane-d₁

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
			0.0365±0.0017	416	PR-RA	Gordon and Mulac (1975)	
			0.00588	298	RR [relative to <i>k</i> (methane) = 1.85 × 10 ⁻²⁰ <i>T</i> ^{2.82} <i>e</i> ^{-987/<i>T</i>} from combination of <i>k</i> (CH ₃ D)/ <i>k</i> (CH ₃ CFCl ₂) and <i>k</i> (CH ₃ CFCl ₂)/ <i>k</i> (methane) ^d)	DeMore (1993a)	298–358
			0.00562	298			
			0.00546	298			
			0.00553	298			
			0.00721	308			
			0.00884	318			
			0.0129	338			
			0.0147	348			
			0.0184	358			
			0.0187	358			
			0.00504	293	RR[relative to <i>k</i> (methane) = 1.85 × 10 ⁻²⁰ <i>T</i> ^{2.82} <i>e</i> ^{-987/<i>T</i>} from combination of <i>k</i> (CH ₃ D)/ <i>k</i> (CF ₃ CH ₂ F) and <i>k</i> (CF ₃ CH ₂ F)/ <i>k</i> (methane) ^d)	DeMore (1993a)	293–361
			0.00550	299			
			0.00608	303			
			0.00720	311			
			0.00852	320			
			0.0104	331			
			0.0127	343			
			0.0143	348			
			0.0145	350			
			0.0181	361			
			0.00150±0.00005	249	FP-LIF	Gierczak et al. (1997)	249–422
			0.00160±0.00016	253			
			0.00183±0.00014	258			
			0.00216±0.00018	263			
			0.00259±0.00013	268			
			0.00284±0.00014	273			
			0.00328±0.00020	278			
			0.00382±0.00020	286			
			0.00448±0.00012	291			
			0.00506±0.00029	298			
			0.00506±0.00029	298			
			0.00505±0.00018	298			
			0.00615±0.00010	307			
			0.00734±0.00014	317			
			0.00935±0.00048	330			
			0.01143±0.00081	343			
			0.01357±0.00060	353			
			0.01564±0.00058	362			
			0.02021±0.00076	376			
			0.02389±0.00057	391			

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 4. Continued

$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	n	$B(\text{K})$	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at $T(\text{K})$	Technique	Reference	Temperature Range (K)
1.07×10^{-5}	1.87	1332 ± 20	0.0281 ± 0.0016	403	RR [relative to $k(\text{methane})$ $= 6.14 \times 10^{-15}$]	Saueressig et al. (2001)	
			0.0321 ± 0.0027	413			
			0.0374 ± 0.0012	422			
			0.00474 ± 0.00007	296			

^a From Huder and DeMore (1993).

^b From DeMore (1993b).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the gas-phase reactions

R. Atkinson

Table 5. Rate constants and temperature-dependent parameters for the reaction of OH radicals with methane-d₂

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
			0.0299±0.0017	416	PR-RA	Gordon and Mulac (1975)	
			0.00160±0.00030	270	PLP-LIF	Gierczak et al. (1997)	270–354
			0.00364±0.00044	297			
			0.00353±0.00034	297			
			0.00559±0.00032	324			
2.18		1926±250	0.00908±0.00054	354			

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 6. Rate constants and temperature-dependent parameters for the reaction of OH radicals with methane-d₃

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
			0.0111±0.0005	416	PR-RA	Gordon and and Mulac (1975)	
			0.00102±0.00004	270	FP/PLP-LIF	Gierczak et al. (1997)	270–354
			0.00171±0.00020	293			
			0.00177±0.00010	295			
			0.00197±0.00004	297			
			0.00328±0.00034	323			
1.46		1972±80	0.00564±0.00020	354			

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Table 7. Rate constants and temperature-dependent parameters for the reaction of OH radicals with methane-d₄

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
8.70×10^{-10}	3.23	1334	0.0050±0.0002	416	PR-RA	Gordon and and Mulac (1975)	
			0.00083±0.00008	293	PLP-LIF	Dunlop and Tully (1993)	293–800
			0.00215±0.00018	333			
			0.00422±0.00032	365			
			0.00910±0.00058	409			
			0.0191±0.0011	459			
			0.0306±0.0022	498			
			0.0530±0.0032	547			
			0.0900±0.0056	602			
			0.150±0.010	654			
			0.197±0.012	704			
			0.302±0.018	753			
			0.385±0.024	800			
			0.00019±0.00002	244	FP-LIF	Gierczak et al. (1997)	244–413
			0.00023±0.00003	250			
			0.00027±0.00002	259			
			0.00033±0.00002	265			
			0.00039±0.00002	269			
			0.00044±0.00002	276			
			0.00056±0.00006	282			
			0.00066±0.00004	289			
			0.00085±0.00002	296			
			0.00084±0.00004	296			
			0.00086±0.00005	299			
			0.00087±0.00002	300			
			0.00132±0.00005	310			
			0.00156±0.00018	320			
			0.00223±0.00005	333			
			0.00295±0.00008	346			
			0.00367±0.00012	357			
			0.00577±0.00022	380			
			0.00697±0.00018	391			
			0.0101±0.0001	413			
			0.00985±0.00040	413			
5.65×10^{-9}	3.01	1545±15	0.00979±0.00040	413			

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Table 8. Rate constants and temperature-dependent parameters for the reaction of OH radicals with ethane

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	n	B (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference	Temperature Range (K)	
209	1812±302	0.478 ^a	13.2	813	RR[relative to $k(\text{H}_2)$ = 1.06×10^{-12}]	Baldwin and Simmons (1957)	1420–1610	
			15.2	1420	RR[relative to	Fenimore and		
			17.3	1440	$k(\text{CO}) = 9.1 \times 10^{-19}$	Jones (1963)		
			21.0	1600	$T^{1.77} e^{580/T}$]			
			21.0	1600				
			24.9	1610				
			1.7	1300	RR[relative to	Westenberg and	1300–1550	
			12	1550	$k(\text{CO}) = 9.1 \times 10^{-19}$ $T^{1.77} e^{580/T}$]	and Fristrom (1965)		
18.6	1232±54	1.55±0.04	0.292±0.039	302±2	FP-KS	Griner (1967b)	298–423	
			≤ 1.0	300	DF-EPR	Wilson and Westenberg (1967)		
			6.0	734	RR[relative to	Hoare and		734–798
			7.2	773	$k(\text{methane}) = 1.85 \times$	Patel (1969)		
			9.8	798	$10^{-20} T^{2.82} e^{-987/T}$]			
			4.97	773	RR[relative to $k(\text{H}_2)$ = 8.72×10^{-13}]	Baldwin et al. (1970b); Baldwin and Walker (1979)	734–798	
			0.311±0.007	297	FP-KS	Greiner (1970)	297–493	
			0.340±0.010	298				
			0.239±0.014	299				
			0.282±0.007	299				
			0.304±0.035	300				
			0.224±0.042	301				
			0.457±0.010	335				
			0.751±0.050	369				
			0.937±0.059	424				
			1.55±0.04	493				
			0.664±0.034	381	PR-RA	Gordon and Mulac (1975)	381–416	
			0.797±0.050	416				

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Table 8. Continued

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
			3.40±0.39	653	RR[relative to <i>k</i> (methane) = 3.54 × 10 ⁻¹³]	Hucknall et al. (1975)	
			0.264±0.017	295±2	FP-RA	Overend et al. (1975)	
			0.290±0.060	296	DF-LMR	Howard and Evenson (1976b)	
			25.9	1300	RR[relative to <i>k</i> (H ₂) = 5.30 × 10 ⁻¹²]	Bradley et al. (1976)	
			0.26±0.04	298	DF-RF	Leu (1979)	
			0.231±0.040	295±1	DF-RF	Lee and Tang (1982)	
			0.080	238	FP-RF	Margitan and Watson (1982)	
			0.659±0.048	403	RR[relative to <i>k</i> (CO) = 9.1 × 10 ⁻¹⁹ <i>T</i> ^{1.77} e ^{580/<i>T</i>}]	Baulch et al. (1983)	403–683
			1.17±0.12	443			
			1.27±0.09	493			
			2.52±0.19	561			
			2.29±0.26	595			
			4.73±0.56	683			
			0.259±0.021	297	FP-RF	Tully et al. (1983)	297–800
			0.771±0.076	400			
			1.58±0.10	499			
			2.61±0.33	609			
			3.65±0.25	697			
1.43 × 10 ⁻²	1.05	911	5.07±0.34	800			
			0.196±0.013	248	DF-RF	Jeong et al. (1984)	248–472
			0.228±0.014	273			
			0.310±0.020	294			
			0.306±0.021	298			
			0.426±0.027	333			
			0.403±0.027	333			
			0.538±0.035	375			
			0.529±0.034	375			
			0.799±0.054	428			
			0.770±0.048	429			
			0.993±0.068	464			
3.87 × 10 ⁻⁹	3.09	-171 ± 343	1.03±0.067	472			
6.11		886±36					

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Table 8. Continued

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
16.1		1173	0.324	300	PR-RA	Nielsen et al. (1984)	300–400
			0.105±0.004	240	FP-RF	Smith et al. (1984)	240–295
			0.147±0.006	251			
			0.205±0.009	273			
18.0		1240±110	0.263±0.010	295			
			0.275	295	DF-RF	Devolder et al. (1984)	
			0.22±0.03	295	PLP-LIF	Schmidt et al. (1985)	
			0.267±0.040	295±2	DF-RF	Baulch et al. (1985)	
			0.239±0.010	292.5	PLP-LIF	Tully et al. (1986a)	292–705
			0.407±0.017	340			
			0.651±0.027	396			
			1.15±0.048	478			
			1.23±0.051	484			
			2.01±0.083	577			
			2.11±0.088	586			
8.51 × 10 ⁻⁶	2.06	430	3.48±0.144	705			
			0.298±0.021	295	PR-RA	Nielsen et al. (1986)	
			0.127±0.008	248	PLP-RA	Stachnik et al. (1986)	248–297
			0.129±0.009	248			
			0.251±0.006	297			
			0.250±0.006	297			
			0.31±0.06	295.9±1.2	RR(relative to <i>k</i> (propane)=1.08× 10 ⁻¹²)	Edney et al. (1986)	
			0.277±0.03	296±2	DF-RF	Bourmada et al. (1987)	
			0.088±0.013	226	FP-RF	Wallington et al. (1987)	226–363
			0.107±0.010	241			
			0.162±0.018	261			
			0.230±0.026	296			
8.4		1050±100	0.497±0.055	363			
			0.287	294	DF-RF	Lafage et al. (1987)	294–413
			1.12	413			
			0.253	294	DF-LIF	Lafage et al. (1987)	
			0.261±0.013	296	PLP-LIF	Zabarnick et al. (1988)	
			0.238±0.016	297±2	DF-LIF	Abbatt et al. (1990)	

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Table 8. Continued

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)	
1.53×10^{-5} 10.3	2	512±7 1108±40	0.243±0.012	~ 298 ^b	PLP-IR	Schiffman et al. (1991)	138–298	
			0.274±0.040	298	PLP-RF	Dóbé et al. (1991, 1992)		
			15.4±2.4	1225±16	SH-RA	Bott and Cohen (1991a)		298–373
			0.013±0.002	138	PLP-LIF	Sharkey and Smith (1993)		
			0.025±0.003	178				
			0.0785±0.004	216				
			0.295±0.014	298				
			0.276±0.007	298	RR[relative to <i>k</i> (propane) = 1.65 × 10 ⁻¹⁷ <i>T</i> ² <i>e</i> ^{-87/<i>T</i>}]	Finlayson-Pitts et al. (1993)		
			0.270±0.012	298				
			0.362±0.014	323				
			0.468±0.013	348				
			0.579±0.010	373	PLP-LIF	Talukdar et al. (1994)	231–377	
			0.0882±0.0024	231				
			0.1269±0.0069	252				
			0.1303±0.0015	253				
			0.1778±0.0043	273				
			0.2461±0.0032	299				
			0.3380±0.0037	327				
			0.4589±0.0050	355				
			0.5641±0.0082	377	SH-RA	Koffend and Cohen (1996)	247–303	
			8.37	974±16				
			0.108±0.002	247				
			0.228±0.004	294				
			0.267±0.003	303	DF-LIF	Donahue et al. (1996)	298–407	
			0.255±0.03	300				
			0.259±0.008	300	DF-LIF	Donahue et al. (1998)		
0.355±0.011	325							
0.390±0.012	340							
0.438±0.023	360							
0.561±0.017	375							
0.604±0.018	390							

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 8. Continued

$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	n	$B(\text{K})$	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at $T(\text{K})$	Technique	Reference	Temperature Range (K)
			0.0269±0.0027	180	DF-LIF	Clarke et al. (1998)	180–360
			0.0377±0.0004	190			
			0.0454±0.0025	200			
			0.0651±0.0007	213			
			0.0808±0.0012	225			
			0.0967±0.0018	238			
			0.1251±0.0014	250			
			0.1640±0.0018	265			
			0.2081±0.0016	280			
			0.2515±0.0021	295			
			0.2953±0.0050	310			
			0.3464±0.0037	325			
			0.3744±0.0038	340			
			0.4637±0.0164	360			

^a Calculated from the cited Arrhenius expression.

^b Room temperature; assumed to be ~298 K.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 9. Rate constants and temperature-dependent parameters for the reaction of OH radicals with ethane-d₃

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
			0.142±0.007	293	PLP-LIF	Tully et al. (1986a)	293–705
			0.250±0.011	338			
			0.419±0.018	396			
			0.794±0.033	478			
			1.52±0.063	586			
7.65 × 10 ⁻⁷	2.38	817	2.65±0.110	705			

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 10. Rate constants and temperature-dependent parameters for the reaction of OH radicals with ethane-d₆

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
			0.0523±0.0060	293	PLP-LIF	Tully et al. (1986a)	293–705
			0.105±0.007	339.5			
			0.199±0.010	396			
			0.435±0.020	478			
			0.965±0.041	586			
2.43×10^{-7}	2.56	1317	1.83±0.077	705			

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Table 11. Rate constants and temperature-dependent parameters for the reaction of OH radicals with propane

$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	n	$B(\text{K})$	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at $T(\text{K})$	Technique	Reference	Temperature Range (K)	
12.0	679 ± 39		26.0	793	RR[relative to $k(\text{H}_2)=9.62 \times 10^{-13}$]	Baldwin (1964)	296–497	
			1.36 ± 0.20	298 ± 1	FP-KS	Greiner (1967b)		
			7.79	753	RR[relative to $k(\text{H}_2)=7.87 \times 10^{-13}$]	Baker et al. (1970); Baldwin and Walker (1979)		
			1.21 ± 0.08	296	FP-KS	Greiner (1970)		
			1.26 ± 0.14	298				
			1.19 ± 0.05	298				
			1.01 ± 0.04	299				
			1.10 ± 0.05	299				
			1.31 ± 0.02	299				
			1.30 ± 0.14	299				
			1.44 ± 0.04	335				
			1.91 ± 0.05	375				
			2.19 ± 0.07	423				
			2.92 ± 0.12	497				
			3.19 ± 0.15	497				
			3.16 ± 0.07	497				
			2.97 ± 0.15	497				
			3.39 ± 0.15	497				
			0.83 ± 0.17	300	DF-EPR/MS	Bradley et al. (1973)		
			2.22 ± 0.55	298	RR[relative to $k(\text{CO})=1.55 \times 10^{-13}$]	Gorse and Volman (1974)		
			2.16 ± 0.10	381	PR-RA	Gordon and Mulac (1975)	381–416	
			1.91 ± 0.09	416				
			5.23 ± 0.75	613	RR[relative to $k(\text{ethane}) = 1.48 \times 10^{-17} T^2 e^{-499/T}$]	Hucknall et al. (1975)	613–653	
			6.45 ± 0.83	653				
			1.98 ± 0.09	329 ± 5	MMS	Harker and Burton (1975)		
			2.02 ± 0.11	295 ± 2	FP-RA	Overend et al. (1975)		

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Table 11. Continued

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)	
1.59 × 10 ⁻³	1.40	428	1.39 ± 0.20	300 ± 1	RR[relative to <i>k</i> (<i>n</i> -butane) = 2.38 × 10 ⁻¹²]	Darnall et al. (1978)	428–696	
			2.0	300	RR[relative to <i>k</i> (ethene) = 8.44 × 10 ⁻¹²] ^a	Cox et al. (1980)		
			1.12 ± 0.04	299 ± 1	RR[relative to <i>k</i> (<i>n</i> -butane) = 2.37 × 10 ⁻¹²]	Atkinson et al. (1982b)		
			1.86 ± 0.15	428	RR[relative to <i>k</i> (CO)=9.1 × 10 ⁻¹⁹ <i>T</i> ^{1.77} e ^{580/<i>T</i>}]	Baulch et al. (1983)		
			2.74 ± 0.24	489				
			2.82 ± 0.10	538				
			4.10 ± 0.22	589				
			4.95 ± 0.55	641				
			7.58 ± 0.72	696				
			1.05 ± 0.04	297	FP-RF	Tully et al. (1983)	297–690	
			1.48 ± 0.06	326				
			2.51 ± 0.20	378				
			3.37 ± 0.23	469				
			4.78 ± 0.34	554				
			8.78 ± 0.97	690				
			26.2 ± 6.6	1220 ± 15	SH-RA	Bott and Cohen (1984)		
			1.0 ± 0.2	295	PLP-LIF	Schmidt et al. (1985)		
			1.20 ± 0.19	295 ± 2	DF-RA	Baulch et al. (1985)		
			21.9 ± 6.0	1074	LH-LIF	Smith et al. (1985)		
			1.10 ± 0.04	293	PLP-LIF	Droege and Tully (1986a)	293–854	
			1.52 ± 0.06	342				
			1.61 ± 0.07	351.5				
			2.14 ± 0.09	401				
			2.49 ± 0.10	428				
			3.24 ± 0.13	491				
			3.36 ± 0.14	501.5				

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Table 11. Continued

$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	n	$B(\text{K})$	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at $T(\text{K})$	Technique	Reference	Temperature Range (K)
1.04×10^{-4}	1.72	145	3.34 ± 0.14	505			
			4.84 ± 0.20	602			
			4.84 ± 0.20	603			
			7.28 ± 0.30	732			
			9.31 ± 0.38	854			
			1.05 ± 0.14	296.0 ± 1.1	RR[relative to $k(n\text{-butane}) = 2.33 \times 10^{-12}$]	Edney et al. (1986)	
			1.28	300 ± 3	RR[relative to $k(n\text{-butane}) = 2.38 \times 10^{-12}$]	Behnke et al. (1987)	
			1.27 ± 0.11	295 ± 2	PR-RA	Nielsen et al. (1988)	
			1.21 ± 0.10	297 ± 2	DF-LIF	Abbatt et al. (1990)	
			1.22 ± 0.08	298	PLP-RF	Mac Leod et al. (1990)	
			1.02 ± 0.05	298 ^b	PLP-IR	Schiffman et al. (1991)	
			1.40 ± 0.30	298	PLP-RF	Dóbé et al. (1991)	
			0.996 ± 0.043	298 ± 2	RR[relative to $k(2\text{-methylpropane}) = 2.12 \times 10^{-12}$]	Nielsen et al. (1991a)	
			1.07 ± 0.06	298	RR[relative to $k(n\text{-butane}) = 2.36 \times 10^{-12}$]	Finlayson-Pitts et al. (1993)	
			1.07 ± 0.05	298			
			1.11 ± 0.04	298	RR[relative to $k(2\text{-methylpropane}) = 2.12 \times 10^{-12}$]	Finlayson-Pitts et al. (1993)	
			1.05 ± 0.06	298			
			0.942 ± 0.095	298 ± 2	RR[relative to $k(\text{ethane}) = 2.48 \times 10^{-13}$]	DeMore (1993c)	
			0.623 ± 0.016	233	PLP-LIF	Talukdar et al. (1994)	233–376
			0.741 ± 0.019	252			

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Table 11. Continued

$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	n	$B(\text{K})$	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at $T(\text{K})$	Technique	Reference	Temperature Range (K)
1.58×10^{-5} 10.1	2	74 ± 25 657 ± 46	0.862 ± 0.023	272	PLP-LIF	Mellouki et al. (1994)	233–363
			1.123 ± 0.040	299			
			1.342 ± 0.064	325			
			1.574 ± 0.052	351			
			1.816 ± 0.067	376			
9.81		650 ± 30	0.61 ± 0.04	233	PLP-LIF	Mellouki et al. (1994)	233–363
			0.75 ± 0.04	253			
			0.92 ± 0.04	273			
			1.05 ± 0.04	295			
			1.25 ± 0.04	318			
			1.51 ± 0.02	343	DF-LIF	Donahue et al. (1998)	299–394
			1.65 ± 0.07	363			
			1.09 ± 0.03	300			
			1.37 ± 0.04	325			
			1.46 ± 0.04	340			
			1.60 ± 0.09	360			
			1.85 ± 0.06	375	DF-LIF	Clarke et al. (1998)	190–360
			1.83 ± 0.10	390			
			0.3626 ± 0.0247	190			
			0.4136 ± 0.0127	200			
			0.4864 ± 0.0095	213			
			0.5602 ± 0.0063	225	RR[relative to $k(\text{ethane}) =$ 1.49×10^{-17} $T^2 e^{-499/T}]$	DeMore and Bayes (1999)	227–428
			0.6475 ± 0.0053	238			
			0.7532 ± 0.0051	250			
			0.8691 ± 0.0147	265			
			1.129 ± 0.0159	295			
			1.276 ± 0.0182	310			
			1.356 ± 0.0140	325			
			1.480 ± 0.0136	340			
			1.640 ± 0.0229	360			
			0.540	227			
			0.611	237			
			0.671	246			
			0.808	265			
			0.878	273			
			0.961	283			
			0.999	287			
			1.09	298			

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 11. Continued

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
			1.35	323			
			1.52	343			
			1.62	349			
			1.96	383			
			2.52	428			
			1.15 ± 0.1	298	PLP-RF	Carl and Crowley (2001)	
			1.17 ± 0.1	298			
			0.46 ± 0.02	210	FP-RF	Kozlov et al. (2003)	210–480
			0.539 ± 0.007	220			
			0.579 ± 0.009	230			
			0.732 ± 0.012	250			
			0.884 ± 0.016	272			
			1.13 ± 0.02	298			
			1.43 ± 0.03	330			
			1.86 ± 0.05	370			
			2.43 ± 0.04	420			
5.81 × 10 ⁻⁵	1.83	167	3.34 ± 0.07	480			

^a From Atkinson (1997).
^b Room temperature; assumed to be ~298 K.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 12. Rate constants and temperature-dependent parameters for the reaction of OH radicals with propane-d₂ [CH₃CD₂CH₃]

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
2.02×10^{-4}	1.63	383	0.610±0.028	295	PLP-LIF	Droege and Tully (1986a)	295–854
			0.802±0.034	328.5			
			1.20±0.05	376.5			
			1.72±0.07	437.2			
			2.47±0.10	503.5			
			3.79±0.16	603			
			5.92±0.24	732			
			7.86±0.32	854			

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Kinetics of the
gas-phase reactions

R. Atkinson

Table 13. Rate constants and temperature-dependent parameters for the reaction of OH radicals with propane-d₃ [CH₃CH₂CD₃]

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
2.26×10^{-5}	1.90	40	0.984±0.050	295	PLP-LIF	Droege and Tully (1986a)	295–854
			1.28±0.06	328.5			
			1.62±0.07	376.5			
			2.17±0.09	437.2			
			2.88±0.12	503.5			
			4.19±0.18	603			
			6.20±0.26	728			
			8.06±0.34	854			

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 14. Rate constants and temperature-dependent parameters for the reaction of OH radicals with propane-d₅ [CH₃CD₂CD₃]

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
2.59×10^{-5}	1.91	303	0.478±0.021	295	PLP-LIF	Droege and Tully (1986a)	295–840
			0.621±0.026	328.5			
			0.950±0.040	376.5			
			1.38±0.06	437.2			
			1.96±0.08	503.5			
			3.13±0.13	603			
			4.93±0.20	728			
			6.60±0.27	840			

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Kinetics of the
gas-phase reactions

R. Atkinson

Table 15. Rate constants and temperature-dependent parameters for the reaction of OH radicals with propane-d₆ [CD₃CH₂CD₃]

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
1.03×10^{-5}	2.00	23	0.826±0.040	295	PLP-LIF	Droege and Tully (1986a)	295–840
			0.999±0.045	328.5			
			1.37±0.06	376.5			
			1.79±0.08	437.2			
			2.46±0.10	503.5			
			3.55±0.15	603			
			5.31±0.22	732			
			6.78±0.28	840			

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 16. Rate constants and temperature-dependent parameters for the reaction of OH radicals with propane-d₈ [CD₃CD₂CD₃]

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
2.36×10^{-7}	2.53	15	0.408±0.045	295	PLP-LIF	Droege and Tully (1986a)	295–854
			0.527±0.043	328.5			
			0.746±0.047	376.5			
			1.09±0.06	437.2			
			1.50±0.07	503.5			
			2.55±0.11	603			
			4.25±0.18	728			
			5.88±0.25	854			

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Table 17. Rate constants and temperature-dependent parameters for the reaction of OH radicals with *n*-butane

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
14.1	524 ± 94		34.6	793	RR [relative to $k(\text{H}_2)=9.62 \times 10^{-13}$]	Baldwin and Walker (1964)	298–495
			10.4	753	RR [relative to $k(\text{H}_2)=7.87 \times 10^{-13}$]	Baker et al. (1970); Baldwin and Walker (1979)	
			2.56 ± 0.09	298	FP-KS	Greiner (1970)	
			2.59 ± 0.22	301			
			2.79 ± 0.32	336			
			2.96 ± 0.10	373			
			4.85 ± 0.19	425			
			4.12 ± 0.15	428			
			4.90 ± 0.17	495			
			4.1	298	RR [relative to $k(\text{propene}, 1 \text{ Torr He}) = 1.7 \times 10^{-11}]^a$	Morris and Niki (1971)	
			2.35 ± 0.35	298	FP-RF	Stuhl (1973)	
			3.01 ± 0.76	298	RR [relative to $k(\text{CO})=1.55 \times 10^{-13}$]	Gorse and Volman (1974)	
			4.22 ± 0.17	298	PR-RA	Gordon and Mulac (1975)	
			4.15 ± 0.17	381			
			4.98 ± 0.17	416			
17.6	559 ± 151		9.49 ± 0.80	653	RR [relative to $k(\text{propane}) = 6.16 \times 10^{-12}$]	Hucknall et al. (1975)	298–416
			2.46 ± 0.15	292 ± 2	RR [relative to $k(\text{CO})=1.66 \times 10^{-13}$]	Campbell et al. (1975)	
			2.72 ± 0.27	297.7	FP-RF	Perry et al. (1976)	
			3.54 ± 0.35	351.0			
			4.69 ± 0.47	419.6			

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Table 17. Continued

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
2.34 × 10 ⁻⁵	1.95	−134	2.67 ± 0.22	297 ± 2	FP-RA	Paraskevopoulos and Nip (1980)	294–509
			2.52 ± 0.25	299 ± 2	RR [relative to <i>k</i> (propene) = 2.62 × 10 ⁻¹¹] ^b	Atkinson et al. (1981)	
			2.71 ± 0.33	295 ± 1	RR [relative to <i>k</i> (propene) = 2.68 × 10 ⁻¹¹] ^b	Atkinson and Aschmann (1984)	
			2.3 ± 0.3	295	PLP-LIF	Schmidt et al. (1985)	
			2.42 ± 0.10	294	PLP-LIF	Droege and Tully (1986b)	
			2.95 ± 0.12	332			
			3.53 ± 0.15	377			
			4.56 ± 0.19	439			
			5.84 ± 0.25	509	RR [relative to <i>k</i> (ethene) = 8.44 × 10 ⁻¹²] ^b	Barnes et al. (1986)	
			2.70 ± 0.34	300			
			2.36 ± 0.04	300	RR [relative to <i>k</i> (<i>n</i> -octane) = 8.15 × 10 ⁻¹²]	Behnke et al. (1988)	
			2.25 ± 0.10	297 ± 2	DF-LIF	Abbatt et al. (1990)	
			2.32 ± 0.08	~298 ^c	PLP-IR	Schiffman et al. (1991)	
2.04 × 10 ⁻⁵ 11.8	2	−85 ± 8 470 ± 40 (231–298 K)	1.560 ± 0.015	231	PLP-LIF	Talukdar et al. (1994)	231–378
			1.788 ± 0.018	252			
			2.097 ± 0.024	273			
			2.459 ± 0.018	299			
			2.828 ± 0.060	328			
			3.196 ± 0.032	352			
			3.647 ± 0.022	378			

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 17. Continued

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
			2.43 ± 0.07	300	DF-LIF	Donahue et al. (1998)	299–386
			2.74 ± 0.08	325			
			2.87 ± 0.09	340			
			3.48 ± 0.10	375			
			3.54 ± 0.11	390			
			1.52	235	RR [relative to <i>k</i> (propane) = 1.65 × 10 ⁻¹⁷ T ² e ^{-87/T}]	DeMore and Bayes (1999)	235–361
			1.73	251			
			1.90	264			
			1.96	275			
			2.24	293			
			2.33	298			
			2.70	328			
			2.96	336			
			3.24	358			
			3.32	361			
			2.6 ± 0.5	300	DF-LIF	Chuong and Stevens (2002)	
			2.6 ± 0.2	300			

^a Measured under the same conditions by Morris et al. (1971).

^b From Atkinson (1997).

^c Room temperature; assumed to be ~298 K.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 18. Rate constants and temperature-dependent parameters for the reaction of OH radicals with *n*-butane-d₁₀

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
			0.697±0.0069	297±2	FP-RA	Paraskevopoulov and Nip (1980)	
			0.893±0.037	294	PLP-LIF	Droege and Tully (1986b)	294–599
			1.13±0.05	332			
			1.49±0.06	377			
			2.07±0.09	439			
			2.87±0.12	509			
2.92 × 10 ⁻⁶	2.20	–33	3.98±0.17	599			

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Table 19. Rate constants and temperature-dependent parameters for the reaction of OH radicals with 2-methylpropane

$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	n	$B(\text{K})$	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at $T(\text{K})$	Technique	Reference	Temperature Range (K)	
8.7	387 ± 63		19.2	793	RR [relative to $k(\text{H}_2)=9.62 \times 10^{-13}$]	Baldwin and Walker (1964)	297–498	
			2.13 ± 0.12	297 ± 1	FP-KS	Greiner (1967b)		
			9.92	753	RR [relative to $k(\text{H}_2)=7.87 \times 10^{-13}$]	Baker et al. (1970); Baldwin and Walker (1979)		
			2.14 ± 0.12	297	FP-KS	Greiner (1970)		
			2.23 ± 0.05	297				
			2.67 ± 0.17	298				
			2.56 ± 0.05	304				
			2.69 ± 0.15	305				
			3.01 ± 0.07	338				
			2.91 ± 0.07	371				
			3.04 ± 0.14	374				
			3.57 ± 0.15	425				
			4.25 ± 0.22	498				
			3.64 ± 0.91	298	RR [relative to $k(\text{CO})=1.55 \times 10^{-13}$]	Gorse and Volman (1972/73); Gorse and Volman (1974)		
			7.88 ± 0.44	653	RR [relative to $k(\text{propane}) = 6.16 \times 10^{-12}$]	Hucknall et al. (1975)		
			2.2	303	RR [relative to $k(\text{cis-2-butene}) = 5.49 \times 10^{-11}$] ^a	Wu et al. (1976)		
			2.20 ± 0.05	300 ± 1	RR [relative to $k(\text{n-butane}) = 2.38 \times 10^{-12}$]	Darnall et al. (1978)		
			2.70 ± 0.22	267 298 324	PLP-RF	Trevor et al. (1982)		
			3.6					
			3.62 ± 0.40					
			2.07 ± 0.05	297 ± 2	RR [relative to $k(\text{n-butane}) = 2.34 \times 10^{-12}$]	Atkinson et al. (1984)	267–324	

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Table 19. Continued

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	n	$B(K)$	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at $T(K)$	Technique	Reference	Temperature Range (K)	
4.31×10^{-5}	1.80	-175	1.83 ± 0.34	296	PLP-LMR	Böhland et al. (1984)	293–864	
			1.9 ± 0.3	295	PLP-LIF	Schmidt et al. (1985)		
			2.19 ± 0.11	293	PLP-LIF	Tully et al. (1986b)		
			2.59 ± 0.13	342				
			3.21 ± 0.16	403				
			3.49 ± 0.17	424				
			4.03 ± 0.20	470				
			4.58 ± 0.23	509.5				
			5.49 ± 0.27	574				
			7.40 ± 0.37	705				
			10.13 ± 0.51	864				
			2.18 ± 0.31	297.8 ± 0.4	RR [relative to $k(n\text{-butane}) = 2.35 \times 10^{-12}$]	Edney et al. (1986)		
			20.9 ± 4.2	1146 ± 15	SH-RA	Bott and Cohen (1989)		
			2.11 ± 0.09	~298 ^b	PLP-IR	Schiffman et al. (1991)		
			1.55 ± 0.18	213	PLP-LIF	Talukdar et al. (1994)	213–372	
			1.58 ± 0.09	224				
			1.69 ± 0.06	234				
			1.67 ± 0.06	243				
			1.745 ± 0.06	253				
			1.82 ± 0.11	272				
			2.13 ± 0.10	296				
			2.19 ± 0.04	297				
			1.96 ± 0.09	298				
			2.29 ± 0.07	323				
2.40 ± 0.10	343							
2.54 ± 0.03	357							
9.32×10^{-6} 5.72	2	-274 ± 16 293 ± 40 (213–298 K)	2.73 ± 0.06	372				

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 19. Continued

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
			2.09 ± 0.06	300	DF-LIF	Donahue et al. (1998)	298–388
			2.38 ± 0.07	325			
			2.47 ± 0.09	340			
			2.62 ± 0.08	375			
			2.72 ± 0.14	390			

^a From Atkinson (1997).

^b Room temperature; assumed to be ~298 K.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 20. Rate constants and temperature-dependent parameters for the reaction of OH radicals with 2-methylpropane-d₁ [(CH₃)₃CD]

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
1.20×10^{-4}	1.69	85	1.36±0.07	293.5	PLP-LIF	Tully et al. (1986b)	293–864
			1.81±0.09	344			
			2.44±0.12	403			
			3.35±0.17	473			
			4.84±0.24	574			
			7.12±0.36	705			
			9.90±0.49	864			

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 21. Rate constants and temperature-dependent parameters for the reaction of OH radicals with 2-methylpropane-d₉ [(CD₃)₃CH]

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
1.08×10^{-7}	2.57	-569	1.70±0.09	293.5	PLP-LIF	Tully et al. (1986b)	293–864
			1.91±0.10	343			
			2.27±0.11	403			
			2.81±0.14	471			
			3.64±0.18	574			
			5.28±0.26	705			
			7.61±0.38	864			

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 22. Rate constants and temperature-dependent parameters for the reaction of OH radicals with 2-methylpropane-d₁₀ [(CD₃)₃CD]

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
9.12×10^{-8}	2.63	-352	0.956±0.067	293.5	PLP-LIF	Tully et al. (1986b)	293–864
			1.21±0.08	340.5			
			1.58±0.09	403			
			2.10±0.12	473			
			3.09±0.15	574			
			4.92±0.25	705			
			7.30±0.37	864			

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Table 23. Rate constants and temperature-dependent parameters for the reaction of OH radicals with *n*-pentane

$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
			6.6	303	RR [relative to <i>k</i> (<i>cis</i> -2-butene) = 5.49×10^{-11}] ^a	Wu et al. (1976)	
			3.26 ± 0.12	300 ± 1	RR [relative to <i>k</i> (<i>n</i> -butane) = 2.38×10^{-12}]	Darnall et al. (1978)	
			14.2	753	RR [relative to <i>k</i> (H ₂)=7.87 × 10^{-13}]	Baldwin and Walker (1979)	
			5.3	300	RR [relative to <i>k</i> (ethene) = 8.44×10^{-12}] ^a	Cox et al. (1980)	
			4.1	300	RR [relative to <i>k</i> (ethene) = 8.44×10^{-12}] ^a	Barnes et al. (1982)	
			3.78 ± 0.05	299 ± 2	RR [relative to <i>k</i> (<i>n</i> -hexane) = 5.22×10^{-12}]	Atkinson et al. (1982b)	
			3.87	300 ± 3	RR [relative to <i>k</i> (<i>n</i> -butane) = 2.38×10^{-12}]	Behnke et al. (1987)	
			3.98 ± 0.15	312	RR [relative to <i>k</i> (<i>n</i> -heptane) = 6.97×10^{-12}]	Nolting et al. (1988)	
2.49 ± 0.32			243	243	RR [relative to	Harris and Kerr (1988)	243–325
2.60 ± 0.21			263	263	<i>k</i> (2-methylpropane)		
3.02 ± 0.29			273	273	= 1.17×10^{-17}		
3.67 ± 0.17			298	298	$T^2 e^{213/T}$]		
3.97 ± 0.37			314	314			
4.40 ± 0.20			325	325			

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Table 23. Continued

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
			3.15 ± 0.72	247	RR [relative to	Harris and Kerr (1988)	247–327
			2.78 ± 0.33	253	<i>k</i> (<i>n</i> -butane) =		
			2.91 ± 0.26	263	1.81×10^{-17}		
			3.05 ± 0.19	273	$7^2 e^{114/T}$]		
			3.27 ± 0.25	275			
			3.30 ± 0.20	282			
			3.94 ± 0.14	295			
			3.94 ± 0.35	305			
			3.78 ± 0.34	314			
			4.27 ± 0.11	325			
			4.19 ± 0.33	327			
			3.83 ± 0.05	300	RR [relative to	Behnke et al. (1988)	
					<i>k</i> (<i>n</i> -octane) =		
					8.15×10^{-12}]		
			4.21 ± 0.18	297 ± 2	DF-LIF	Abbatt et al. (1990)	
			3.87 ± 0.05	302	RR [relative to	Donaghy et al. (1993)	
					<i>k</i> (2-methylpropane) =		
					2.16×10^{-12}]		
			2.64 ± 0.06	224	PLP-LIF	Talukdar et al. (1994)	224–372
			2.67 ± 0.14	233			
			2.75 ± 0.10	233			
			2.85 ± 0.10	233			
			3.11 ± 0.09	253			
			3.54 ± 0.11	272			
			4.02 ± 0.20	296			
			4.01 ± 0.11	297			
			4.04 ± 0.10	297			
			4.50 ± 0.12	309			
			4.83 ± 0.08	323			
			5.06 ± 0.12	340			
			5.54 ± 0.26	358			
3.13 × 10 ⁻⁵	2	-116 ± 24	5.81 ± 0.16	372			
15.0		392 ± 40					
		(224–297 K)					

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 23. Continued

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
			3.98 ± 0.13	300	DF-LIF	Donahue et al. (1998)	299–407
			4.68 ± 0.33	325			
			4.59 ± 0.18	340			
			5.47 ± 0.16	360			
			5.83 ± 0.44	375			
			6.44 ± 0.37	390			
			3.76	308	RR [relative to <i>k</i> (propane) = 1.65 × 10 ⁻¹⁷ <i>T</i> ² <i>e</i> ^{-87/<i>T</i>}]}	DeMore and Bayes (1999)	308–345
			4.50	345			
			2.74	233	RR [relative to <i>k</i> (<i>n</i> -butane) = 1.81 × 10 ⁻¹⁷ <i>T</i> ² <i>e</i> ^{114/<i>T</i>}]}	DeMore and Bayes (1999)	233–364
			3.00	253			
			3.25	273			
			3.71	298			
			4.15	326			
			4.63	351			
			4.92	364			

^a From Atkinson (1997).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Kinetics of the
gas-phase reactions

R. Atkinson

Table 24. Rate constants for the reaction of OH radicals with 2-methylbutane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference
2.70±0.54	305±2	RR[relative to $k(n$ -butane) = 2.45×10^{-12}]	Lloyd et al. (1976)
3.30±0.07	300±1	RR[relative to $k(n$ -butane) = 2.38×10^{-12}]	Darnall et al. (1978)
3.7	300	RR[relative to $k(\text{ethene})$ = 8.44×10^{-12}] ^a	Cox et al. (1980)
3.60±0.10	297±2	RR[relative to $k(n$ -butane) = 2.34×10^{-12}]	Atkinson et al. (1984)

^a from Atkinson (1997).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Table 25. Rate constants and temperature-dependent parameters for the reaction of OH radicals with 2,2-dimethylpropane

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)		
14.1	844 ± 45		0.741 ± 0.020	292	FP-KS	Greiner (1970)	292–493		
			0.859 ± 0.039	292					
			0.875 ± 0.025	298					
			1.16 ± 0.08	335					
			1.41 ± 0.04	370					
			2.11 ± 0.10	424	RR [relative to <i>k</i> (H ₂) = 7.87 × 10 ⁻¹³]	Baker et al. (1970)			
			2.54 ± 0.09	493					
			13.1 ± 2.4	753					
			8.03	753				RR [relative to <i>k</i> (H ₂) = 7.87 × 10 ⁻¹³]	Baker et al. (1976); Baldwin and Walker (1979)
			0.91 ± 0.15	300 ± 1				RR [relative to <i>k</i> (<i>n</i> -butane) = 2.38 × 10 ⁻¹²]	Darnall et al. (1978)
8.60 × 10 ⁻⁹	3.05	-340	0.910 ± 0.10	297 ± 2	FP-RA	Paraskevopoulos and Nip (1980)	287–901		
			0.705 ± 0.037	299 ± 2	RR [relative to <i>k</i> (<i>n</i> -hexane) = 5.22 × 10 ⁻¹²]	Atkinson et al. (1982a)			
			0.909 ± 0.115	287	PLP-LIF	Tully et al. (1985, 1986a)			
			1.27 ± 0.14	350					
			2.08 ± 0.19	431					
			3.17 ± 0.25	518					
			4.46 ± 0.38	600					
			7.02 ± 0.67	705					
			10.1 ± 1.1	812					
			12.5 ± 1.5	901	PR-RA	Nielsen et al. (1991b)			
			0.79 ± 0.10	298 ± 2					
			0.78 ± 0.10	298 ± 2	RR [relative to <i>k</i> (<i>n</i> -butane) = 2.36 × 10 ⁻¹²]	Nielsen et al. (1991b)			

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 26. Rate constants and temperature-dependent parameters for the reaction of OH radicals with 2,2-dimethylpropane-d₁₂

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
1.08×10^{-7}	2.71	307	0.180 ± 0.012	290	PLP-LIF	Tully et al. (1985, 1986a)	290–903
			0.375 ± 0.025	352			
			0.728 ± 0.048	430			
			1.30 ± 0.09	508.5			
			2.19 ± 0.17	598			
			3.94 ± 0.34	705			
			5.62 ± 0.55	812			
			8.09 ± 0.89	903			

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Table 27. Rate constants for the reaction of OH radicals with *n*-hexane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
5.1±1.1	305±2	RR [relative to <i>k</i> (<i>n</i> -butane) = 2.45 × 10 ⁻¹²]	Lloyd et al. (1976)	
6.0	303	RR [relative to <i>k</i> (<i>cis</i> -2-butene) = 5.49 × 10 ⁻¹¹] ^a	Wu et al. (1976)	
5.6±0.8	292	RR [relative to <i>k</i> (<i>n</i> -butane) = 2.28 × 10 ⁻¹²]	Campbell et al. (1976)	
5.23±0.09	299±2	RR [relative to <i>k</i> (<i>n</i> -butane) = 2.37 × 10 ⁻¹²]	Atkinson et al. (1982a)	
5.55±0.20	298±2	RR [relative to <i>k</i> (propene) = 2.63 × 10 ⁻¹¹] ^a	Atkinson et al. (1983a)	
5.31±0.46	295±1	RR [relative to <i>k</i> (propene) = 2.68 × 10 ⁻¹¹] ^a	Atkinson and Aschmann (1984)	
5.17±0.52	295	RR [relative to <i>k</i> (<i>n</i> -butane) = 2.32 × 10 ⁻¹²]	Klein et al. (1984)	
6.2	300	RR [relative to <i>k</i> (toluene) = 5.58 × 10 ⁻¹²] ^b	Klöpffer et al. (1986)	
5.91±0.68	300±2	RR [relative to <i>k</i> (ethene) = 8.44 × 10 ⁻¹²] ^a	Barnes et al. (1986)	
5.20	300±3	RR [relative to <i>k</i> (<i>n</i> -butane) = 2.38 × 10 ⁻¹²]	Behnke et al. (1987)	
5.75±0.56	312	RR [relative to <i>k</i> (<i>n</i> -heptane) = 6.97 × 10 ⁻¹²]	Nolting et al. (1988)	
5.27±0.04	300	RR [relative to <i>k</i> (<i>n</i> -octane) = 8.15 × 10 ⁻¹²]	Behnke et al. (1988)	
5.37±0.20	301±2	RR [relative to <i>k</i> (<i>n</i> -pentane) = 3.86 × 10 ⁻¹²]	McLoughlin et al. (1993)	
21.8	962±16	SH-RA	Koffend and Cohen (1996)	
5.45±0.16	300	DF-LIF	Donahue et al. (1998)	298–393
6.11±0.18	325			
6.23±0.19	340			
6.43±0.45	360			
7.33±0.62	375			
7.29±0.22	390			

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 27. Continued

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Temperature Reference	Range (K)
5.07	292	RR [relative to $k(\text{propane}) = 1.65 \times 10^{-17} T^2 e^{-87/T}$]	DeMore and Bayes (1999)	292–366
5.12	298			
5.46	307			
5.73	315			
5.74	321			
6.22	337			
5.97	339			
6.84	353			
6.67	357	RR [relative to $k(n\text{-butane}) = 1.81 \times 10^{-17} T^2 e^{114/T}$]	DeMore and Bayes (1999)	294–367
7.37	366			
5.00	294			
5.31	310			
5.65	329			
6.33	354	RR [relative to $k(n\text{-pentane}) = 3.90 \times 10^{-12}$]	DeMore and Bayes (1999)	
6.62	367			
5.41	303			

^a From Atkinson (1997).

^b From Calvert et al. (2002).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Kinetics of the
gas-phase reactions

R. Atkinson

Table 28. Rate constants for the reaction of OH radicals with 2-methylpentane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference
4.34 ± 0.87	305 ± 2	RR[relative to $k(n\text{-butane}) = 2.45 \times 10^{-12}$]	Lloyd et al. (1976)
5.3	300	RR[relative to $k(\text{ethene}) = 8.44 \times 10^{-12}$] ^a	Cox et al. (1980)
5.15 ± 0.22	297 ± 2	RR[relative to $k(n\text{-butane}) = 2.34 \times 10^{-12}$]	Atkinson et al. (1984)

^a From Atkinson (1997).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 29. Rate constants for the reaction of OH radicals with 3-methylpentane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T(K)	Technique	Reference
5.9±1.2	305±2	RR[relative to $k(n\text{-butane}) = 2.45 \times 10^{-12}$]	Lloyd et al. (1976)
5.24±0.10	297±2	RR[relative to $k(n\text{-butane}) = 2.34 \times 10^{-12}$]	Atkinson et al. (1984)

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 30. Rate constants for the reaction of OH radicals with 2,2-dimethylbutane

$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference	Temperature Range (K)
2.41±0.08	297±2	RR[relative to $k(n\text{-butane}) = 2.34 \times 10^{-12}$]	Atkinson et al. (1984)	
1.18±0.24	245	RR[relative to $k(n\text{-pentane}) = 2.52 \times 10^{-17} T^2 e^{158/T}$]	Harris and Kerr (1988)	245–328
1.36±0.18	247			
1.33±0.25	253			
1.58±0.20	263			
1.82±0.34	273			
1.80±0.29	283			
2.14±0.35	299			
2.22±0.32	303			
2.37±0.24	303			
2.56±0.25	313			
2.91±0.44	326			
2.79±0.27	328			

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 31. Rate constants and temperature-dependent parameters for the reaction of OH radicals with 2,3-dimethylbutane

$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	n	$B(\text{K})$	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at $T(\text{K})$	Technique	Reference	Temperature Range (K)
4.79	-129±67		7.46±0.22	300	FP-KS	Greiner (1970)	300–498
			6.71±0.22	336			
			6.81±0.35	372			
			7.11±0.65	424			
			5.94±1.25	498			
			4.94±0.99	305±2	RR [relative to $k(2\text{-methylpropene}) = 4.94 \times 10^{-11} \text{ J}^2$]	Darnall et al. (1976)	
			4.94±0.26	300±1			
			4.0	300	RR [relative to $k(n\text{-butane}) = 2.38 \times 10^{-12}$]	Darnall et al. (1978)	
					RR [relative to $k(\text{ethene}) = 8.44 \times 10^{-12} \text{ J}_a$]	Cox et al. (1980)	
			5.79±0.03	299±2	RR [relative to $k(\text{cyclohexane}) = 7.00 \times 10^{-12}$]	Atkinson et al. (1982a)	

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 31. Continued

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
			6.11±1.05	247	RR [relative to <i>k</i> (<i>n</i> -butane) = 1.81 × 10 ⁻¹⁷ $T^2 e^{114/T}$]	Harris and Kerr (1988)	247–327
			5.02±1.08	253			
			5.40±0.62	263			
			5.19±0.87	273			
			5.22±1.06	275			
			5.29±0.33	282			
			5.48±0.21	295			
			5.56±0.40	305			
			4.65±0.72	314			
			5.68±0.11	325	RR [relative to <i>k</i> (<i>n</i> -pentane) = 2.52 × 10 ⁻¹⁷ $T^2 e^{158/T}$]	Harris and Kerr (1988)	247–327
			5.45±0.50	327			
			5.56±0.38	247			
			5.15±0.82	253			
			5.53±1.05	263			
			5.29±0.41	273			
			5.46±0.85	275			
			5.48±0.53	282			
			5.21±0.15	295			
			5.71±0.12	305			
			5.22±0.50	314			
			5.76±0.09	325			
			5.68±0.18	327			
			34.5±5.2	1220±16	SH-RA	Bott and Cohen (1991b)	

^a From Atkinson (1997).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 32. Rate constants for the reaction of OH radicals with *n*-heptane

$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at <i>T</i> (K)	Technique	Reference
6.68 ± 0.11	299 ± 2	RR [relative to $k(n\text{-hexane}) = 5.22 \times 10^{-12}$]	Atkinson et al. (1982b)
7.8	300	RR [relative to $k(\text{toluene}) = 5.58 \times 10^{-12}$] ^a	Klöppfer et al. (1986)
6.60	300 ± 3	RR [relative to $k(n\text{-butane}) = 2.38 \times 10^{-12}$]	Behnke et al. (1987)
6.78 ± 0.08	300	RR [relative to $k(n\text{-octane}) = 8.15 \times 10^{-12}$]	Behnke et al. (1988)
33.4	1086 ± 16	SH-RA	Koffend and Cohen (1996)
6.97 ± 0.29	295 ± 2	RR [relative to $k(n\text{-octane}) = 8.05 \times 10^{-12}$]	Ferrari et al. (1996)

^a From Calvert et al. (2002).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Table 33. Rate constants for the reaction of OH radicals with 2,4-dimethylpentane

$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at $T(\text{K})$	Technique	Reference
4.77 ± 0.10	297 ± 2	RR [relative to $k(n\text{-butane}) = 2.34 \times 10^{-10}$]	Atkinson et al. (1984)

Kinetics of the
gas-phase reactions

R. Atkinson

Table 34. Rate constants and temperature-dependent parameters for the reaction of OH radicals with 2,2,3-trimethylbutane

$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	n	$B(\text{K})$	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at $T(\text{K})$	Technique	Reference	Temperature Range (K)
7.95	115 ± 73		5.23 ± 0.12	296	FP-KS	Greiner (1970)	296–497
			4.87 ± 0.12	303			
			4.50 ± 0.34	371			
			4.60 ± 0.27	373			
			6.33 ± 0.19	497			
			3.66 ± 0.74	305 ± 2	RR [relative to $k(2\text{-methylpropene}) =$ $4.94 \times 10^{-11}]^a$	Darnall et al. (1976)	
			9.6 ± 1.2	753	RR [relative to $k(\text{H}_2)=7.87 \times$ $10^{-13}]$	Baldwin et al. (1981)	
			3.81 ± 0.08	297 ± 2	RR [relative to $k(n\text{-butane}) =$ $2.34 \times 10^{-12}]$	Atkinson et al. (1984)	
			3.02 ± 0.45	263	RR [relative to $k(n\text{-pentane}) =$ 2.52×10^{-17} $T^2 e^{158/T}]$	Harris and Kerr (1988)	263–303
			4.13 ± 0.39	283			
			4.06 ± 0.24	303			
	3.90 ± 0.55	303					
	2.97 ± 0.98	263	RR [relative to $k(2,2\text{-dimethylbutane})$ $= 3.37 \times$ $10^{-11} e^{-809/T}]$	Harris and Kerr (1988)	263–303		
	2.32 ± 1.16	283					
	4.60 ± 0.85	303					
	4.57 ± 1.02	303					

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 34. Continued

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
			3.73 ± 0.51	243	RR [relative to <i>k</i> (<i>n</i> -hexane) = 2.54 × 10 ⁻¹⁴ <i>T</i> e ^{-112/<i>T</i>}]}	Harris and Kerr (1988)	243–324
			3.55 ± 0.22	244			
			3.48 ± 0.34	253			
			3.81 ± 0.47	263			
			3.76 ± 0.68	273			
			3.86 ± 0.54	282			
			3.87 ± 0.18	295			
			3.85 ± 0.19	314			
			3.98 ± 0.49	324			
			3.84 ± 0.15	324			

^a From Atkinson (1997).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Kinetics of the
gas-phase reactions

R. Atkinson

Table 35. Rate constants and temperature-dependent parameters for the reaction of OH radicals with *n*-octane

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
29.5	364±61		8.42±1.25	296	FP-KS	Greiner (1970)	296–497
			12.0±0.7	371			
			10.8±0.5	371			
			14.3±0.4	497			
			8.25±0.11	299±2	RR [relative to <i>k</i> (<i>n</i> -hexane) = 5.22 × 10 ⁻¹²]	Atkinson et al. (1982b)	
			8.03	300±3	RR [relative to <i>k</i> (<i>n</i> -butane) = 2.38 × 10 ⁻¹²]	Behnke et al. (1987)	
			8.16±0.28	312	RR [relative to <i>k</i> (<i>n</i> -heptane) = 6.97 × 10 ⁻¹²]	Nolting et al. (1988)	
			44.2	1078±16	SH-RA	Koffend and Cohen (1996)	

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 36. Rate constants and temperature-dependent parameters for the reaction of OH radicals with 2,2,4-trimethylpentane

$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	n	$B(\text{K})$	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at $T(\text{K})$	Technique	Reference	Temperature Range (K)
15.5	426±64		3.90±0.15	298	FP-KS	Greiner (1970)	298–493
			3.55±0.12	305			
			4.37±0.24	339			
			5.25±0.15	373			
			5.43±0.14	423			
			6.63±0.42	493			
			3.32±0.15	297±2	RR [relative to $k(n\text{-butane}) = 2.34 \times 10^{-12}$]	Atkinson et al. (1984)	
			37.2±5.6	1186±16	SH-RA	Bott and Cohen (1991b)	

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 37. Rate constants for the reaction of OH radicals with 2,3,4-trimethylpentane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference	Temperature Range (K)
7.78±0.20	243	RR[relative to $k(n\text{-hexane}) = 2.54 \times 10^{-14} T e^{-112/T}$]	Harris and Kerr (1988)	243–313
7.85±0.83	253			
6.63±0.40	263			
6.95±0.37	273			
6.46±0.21	295			
6.49±0.11	303			
6.62±0.56	313			
7.23±0.17	313			

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the gas-phase reactions

R. Atkinson

Table 38. Rate constants and temperature-dependent parameters for the reaction of OH radicals with 2,2,3,3-tetramethylbutane

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	n	B (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference	Temperature Range (K)
16.2	802±63		1.08±0.02	294	FP-KS	Greiner (1970)	294-495
			1.16±0.11	301			
			1.42±0.04	335			
			2.04±0.09	370			
			2.21±0.07	424			
			3.52±0.12	495			
4.75 × 10 ⁻⁶	2.20	68	6.30±0.79	753	RR [relative to $k(\text{H}_2) = 7.87 \times 10^{-13}$]	Baldwin et al. (1979); Baldwin and Walker (1979)	290–738
			0.959±0.071	297±2	RR [relative to $k(n\text{-butane}) = 2.34 \times 10^{-12}$]	Atkinson et al. (1984)	
			0.948±0.020	290	PLP-LIF	Tully et al. (1985)	
			1.48±0.04	348.5			
			2.38±0.03	423.5			
			3.58±0.05	506			
			5.27±0.09	606			
			9.36±0.35	737.5			
			29.9±4.5	1180±16	SH-RA	Bott and Cohen (1991b)	

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 39. Rate constants for the reaction of OH radicals with *n*-nonane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference
9.76±0.27	299±2	RR [relative to <i>k</i> (<i>n</i> -hexane) = 5.22 × 10 ⁻¹²]	Atkinson et al. (1982b)
9.69	300±3	RR [relative to <i>k</i> (<i>n</i> -butane) = 2.38 × 10 ⁻¹²]	Behnke et al. (1987)
9.45±0.28	312	RR [relative to <i>k</i> (<i>n</i> -heptane) = 6.97 × 10 ⁻¹²]	Nolting et al. (1988)
9.55±0.19	300	RR [relative to <i>k</i> (<i>n</i> -octane) = 8.15 × 10 ⁻¹²]	Behnke et al. (1988)
45.5	1097±16	SH-RA	Koffend and Cohen (1996)
9.72±0.22	295±2	RR [relative to <i>k</i> (<i>n</i> -octane) = 8.05 × 10 ⁻¹²]	Ferrari et al. (1996)
10.3±0.3	296±2	RR [relative to <i>k</i> (propene) = 2.66 × 10 ⁻¹¹] ^a	Kramp and Paulson (1998)
9.16±1.2 ^b	295±2	RR [relative to <i>k</i> (<i>n</i> -octane) = 8.05 × 10 ⁻¹²]	Coeur et al. (1998, 1999)

^a From Atkinson (1997).

^b Two standard deviation uncertainty estimated from the data given (Coeur et al., 1998, 1999); could be larger, at ±2.1.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Kinetics of the
gas-phase reactions

R. Atkinson

Table 40. Rate constants for the reaction of OH radicals with 3,3-diethylpentane

$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
5.1 ± 0.8	298 ± 2	PR-RA	Nielsen et al. (1991b)
4.46 ± 0.28	298 ± 2	RR [relative to $k(\text{cyclohexane}) = 6.97 \times 10^{-12}$]	Nielsen et al. (1991b)

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 41. Rate constants for the reaction of OH radicals with *n*-decane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference
10.4±0.5	299±2	RR [relative to <i>k</i> (<i>n</i> -hexane) = 5.22 × 10 ⁻¹²]	Atkinson et al. (1982b)
10.8±0.4	312	RR [relative to <i>k</i> (<i>n</i> -heptane) = 6.97 × 10 ⁻¹²]	Nolting et al. (1988)
11.5±0.2	300	RR [relative to <i>k</i> (<i>n</i> -octane) = 8.15 × 10 ⁻¹²]	Behnke et al. (1988)
56.4	1109±16	SH-RA	Koffend and Cohen (1996)
11.6±0.4	296±2	RR [relative to <i>k</i> (<i>n</i> -octane) = 8.07 × 10 ⁻¹²]	Aschmann et al. (2001)

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Table 42. Rate constants for the reaction of OH radicals with 3,4-diethylhexane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference
6.92 ± 0.45	296 ± 2	RR [relative to <i>k</i> (<i>n</i> -octane) = 8.07 × 10 ⁻¹²]	Aschmann et al. (2001)

Kinetics of the
gas-phase reactions

R. Atkinson

Table 43. Rate constants for the reaction of OH radicals with *n*-undecane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference
12.7±0.3	312	RR [relative to <i>k</i> (<i>n</i> -heptane) = 6.97 × 10 ⁻¹²]	Nolting et al. (1988)
12.3 ± 0.2	300	RR [relative to <i>k</i> (<i>n</i> -octane) = 8.15 × 10 ⁻¹²]	Behnke et al. (1988)

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 44. Rate constants for the reaction of OH radicals with *n*-dodecane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference
14.0±0.5	312	RR [relative to <i>k</i> (<i>n</i> -heptane) = 6.97 × 10 ⁻¹²]	Nolting et al. (1988)
12.9±0.2	300	RR [relative to <i>k</i> (<i>n</i> -octane) = 8.15 × 10 ⁻¹²]	Behnke et al. (1988)

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Kinetics of the
gas-phase reactions

R. Atkinson

Table 45. Rate constants for the reaction of OH radicals with *n*-tridecane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference
16.2±0.6	312	RR [relative to <i>k</i> (<i>n</i> -heptane) = 6.97 × 10 ⁻¹²]	Nolting et al. (1988)
14.4±0.2	300	RR [relative to <i>k</i> (<i>n</i> -octane) = 8.15 × 10 ⁻¹²]	Behnke et al. (1988)

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Table 46. Rate constants for the reaction of OH radicals with *n*-tetradecane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference
17.9±0.7	312	RR [relative to <i>k</i> (<i>n</i> -heptane) = 6.97 × 10 ⁻¹²]	Nolting et al. (1988)

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Table 47. Rate constants for the reaction of OH radicals with *n*-pentadecane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference
20.7±1.0	312	RR [relative to <i>k</i> (<i>n</i> -heptane) = 6.97 × 10 ⁻¹²]	Nolting et al. (1988)

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Table 48. Rate constants for the reaction of OH radicals with *n*-hexadecane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference
23.2±1.3	312	RR [relative to <i>k</i> (<i>n</i> -heptane) = 6.97 × 10 ⁻¹²]	Nolting et al. (1988)

Table 49. Rate constants and temperature-dependent parameters for the reaction of OH radicals with cyclopropane

$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	n	$B(\text{K})$	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at $T(\text{K})$	Technique	Reference	Temperature Range (K)
3.9 1.17×10^{-4}	1.5	1107 ± 51 522 ± 44	0.0621 ± 0.0138	298 ± 2	FP-RA	Jolly et al. (1985)	298–492
			0.111 ± 0.024	298 ± 3	PLP-RF	Dóbé et al. (1991, 1992)	
			0.133 ± 0.008	325 ± 1			
			0.152 ± 0.022	337 ± 1			
			0.191 ± 0.042	362 ± 1			
			0.236 ± 0.016	388 ± 1			
			0.365 ± 0.058	467 ± 2			
			0.412 ± 0.034	476 ± 3			
			0.462 ± 0.062	492 ± 3			
			0.0212 ± 0.0043	200	DF-LIF	Clarke et al. (1998)	200–360
			0.0296 ± 0.0017	213			
			0.0347 ± 0.0004	225			
			0.0378 ± 0.0004	238			
			0.0426 ± 0.0004	250			
			0.0515 ± 0.0013	265			
			0.0591 ± 0.0007	280			
			0.0657 ± 0.0008	295			
			0.0752 ± 0.0012	310			
			0.0897 ± 0.0024	325			
			0.1009 ± 0.0002	340			
			0.1161 ± 0.0075	360			
			0.0538	276	RR [relative to $k(\text{ethane}) =$ 1.49×10^{-17} $T^2 e^{-499/T}]$	DeMore and Bayes (1999)	276–421
			0.0742	298			
			0.0765	300			
			0.0952	316			
			0.140	348			
			0.167	363			
			0.198	383			
			0.243	403			
			0.285	421			

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 49. Continued

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
			0.0751 ± 0.0025	298.3 ± 0.1	RR [relative to <i>k</i> (ethane) = 1.49×10^{-17} $T^2 e^{-499/T}$]	Wilson et al. (2001)	298–459
			0.0769 ± 0.0010	298.3 ± 0.1			
			0.108 ± 0.001	323.4 ± 0.2			
			0.189 ± 0.003	373.1 ± 0.3			
			0.260 ± 0.003	401.3 ± 2			
			0.300 ± 0.003	415.6 ± 2			
			0.381 ± 0.008	444.9 ± 2			
			0.427 ± 0.003	458.7 ± 2			
			0.0571 ± 0.0003	271.5 ± 0.3	RR [relative to <i>k</i> (CH ₃ CHF ₂) = 1.98×10^{-18} $T^2 e^{-460/T}$] ^a	Wilson et al. (2001)	271–463
			0.0634 ± 0.0030	278.3 ± 0.1			
			0.0797 ± 0.0008	298.2 ± 0.1			
			0.0885 ± 0.0009	304.3 ± 0.0			
			0.110 ± 0.004	324.5 ± 0.2			
			0.148 ± 0.004	348.7 ± 0.2			
			0.184 ± 0.003	372.7 ± 0.2			
			0.237 ± 0.005	399.3 ± 0.2			
			0.262 ± 0.011	408.2 ± 2			
			0.297 ± 0.009	424.7 ± 2			
			0.341 ± 0.015	446.6 ± 2			
			0.407 ± 0.016	463.4 ± 1.3			

^a From the IUPAC evaluation (IUPAC, 2003)

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 50. Rate constants for the reaction of OH radicals with isopropylcyclopropane

$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
2.61 ± 0.05	296 ± 2	RR [relative to $k(n\text{-butane}) = 2.33 \times 10^{-12}$]	Atkinson and Aschmann (1988)

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 51. Rate constants and temperature-dependent parameters for the reaction of OH radicals with cyclobutane

$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	n	$B(\text{K})$	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at $T(\text{K})$	Technique	Reference	Temperature Range (K)
5.06×10^{-4}	1.5	115±40	1.2±0.3	298	RR [relative to $k(\text{CO}) = 1.55 \times 10^{-13}$]	Gorse and Volman (1974)	298–469
			1.75±0.15	298	PLP-RF	Dóbbé et al. (1991)	
			1.75±0.12	298±3	PLP-RF	Dóbbé et al. (1992)	
			2.22±0.20	327±1			
			2.36±0.14	360±2			
			2.89±0.30	392±2			
			3.49±0.28	429±2			
			3.98±0.40	469±3			
			1.74	272	RR [relative to $k(\text{propane})$ $= 1.65 \times 10^{-17}$ $T^2 e^{-87/T}]$	DeMore and Bayes (1999)	272–366
			1.93	288			
			1.95	293			
			1.90	298			
			2.11	303			
			2.24	309			
			2.63	343			
			3.06	366			

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Table 52. Rate constants and temperature-dependent parameters for the reaction of OH radicals with cyclopentane

$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	n	$B(\text{K})$	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at $T(\text{K})$	Technique	Reference	Temperature Range (K)
6.04×10^{-4}	1.52	-111	6.3	298	RR [relative to $k(\text{CO}) = 1.55 \times 10^{-13}$]	Volman (1975)	295–491
			4.11±0.25	300±1	RR [relative to $k(n\text{-butane}) = 2.38 \times 10^{-12}$]	Darnall et al. (1978)	
			4.93±0.05	299±2	RR [relative to $k(\text{cyclohexane}) = 7.00 \times 10^{-12}$]	Atkinson et al. (1982a)	
			5.18±0.38	298±2	FP-RA	Jolly et al. (1985)	
			5.02±0.22	295	PLP-LIF	Droege and Tully (1987)	
			6.12±0.27	344			
			7.23±0.32	402.5			
			9.45±0.41	491			
			46.5±9.3	1194±15	SH-RA	Bott and Cohen (1989)	
			4.84±0.10	296±2	RR [relative to $k(n\text{-nonane}) = 9.67 \times 10^{-12}$]	Kramp and Paulson (1998)	
			4.85±0.09	296±2	RR [relative to $k(\text{propene}) = 2.66 \times 10^{-11}$] ^a	Kramp and Paulson (1998)	
			4.86±0.21	296±2	RR [relative to $k(\text{trans-2-butene}) = 6.48 \times 10^{-11}$] ^a	Kramp and Paulson (1998)	
			4.34±0.05	296±2	RR [relative to $k(1,3\text{-butadiene}) = 6.72 \times 10^{-11}$] ^a	Kramp and Paulson (1998)	

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 52. Continued

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
			5.89±0.26	300	DF-LIF	Donahue et al. (1998)	299–395
			6.35±0.59	325			
			6.18±0.19	340			
			7.64±0.23	360			
			7.25±0.38	375			
			7.53±0.45	390			
			4.34	273	RR [relative to	DeMore and Bayes (1999)	273–423
			4.68	292	<i>k</i> (<i>n</i> -butane) =		
			4.90	310	1.81×10^{-17}		
			5.23	326	$T^2 e^{114/T}$]		
			5.99	348			
			5.99	354			
			6.55	373			
			7.30	398			
			7.87	423			
			4.39	277	RR [relative to	DeMore and Bayes (1999)	277–360
			5.47	318	<i>k</i> (<i>n</i> -hexane) =		
			5.99	338	2.54×10^{-14}		
			6.41	360	$T e^{-112/T}$]		

^a From Atkinson (1997).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Kinetics of the
gas-phase reactions

R. Atkinson

Table 53. Rate constants and temperature-dependent parameters for the reaction of OH radicals with cyclopentane-d₁₀

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	n	$B(K)$	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at $T(K)$	Technique	Reference	Temperature Range (K)
4.50×10^{-3}	1.21	-257	1.83 ± 0.08	295	PLP-LIF	Droege and Tully (1987)	295–602
			2.46 ± 0.11	342			
			3.33 ± 0.15	401			
			4.81 ± 0.21	491			
			6.75 ± 0.29	602			

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Table 54. Rate constants and temperature-dependent parameters for the reaction of OH radicals with cyclohexane

$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	n	$B(\text{K})$	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at $T(\text{K})$	Technique	Reference	Temperature Range (K)
23.5	319 ± 73		7.95 ± 0.44	295	FP-KS	Greiner (1970)	295–497
			8.40 ± 0.55	338			
			7.71 ± 0.72	338			
			11.8 ± 0.6	370			
			9.93 ± 0.24	373			
			10.4 ± 0.6	425			
			10.1 ± 0.6	425			
			12.4 ± 0.4	497			
			6.9 ± 1.8	298	RR [relative to $k(\text{CO})=1.55 \times 10^{-13}$]	Gorse and Volman (1974)	
			6.6	303			
					RR [relative to $k(\text{cis-2-butene}) = 5.49 \times 10^{-11}$] ^a	Wu et al. (1976)	
			6.89 ± 0.21	299 ± 2	RR [relative to $k(n\text{-hexane}) = 5.22 \times 10^{-12}$]	Atkinson et al. (1982a)	
			6.95 ± 0.05	299 ± 2	RR [relative to $k(n\text{-butane}) = 2.37 \times 10^{-12}$]	Atkinson et al. (1982a)	
			7.07 ± 0.42	299 ± 2	RR [relative to $k(\text{propene}) = 2.62 \times 10^{-11}$] ^a	Atkinson et al. (1983b)	
			6.86 ± 0.10	300 ± 3	RR [relative to $k(n\text{-butane}) = 2.38 \times 10^{-12}$]	Tuazon et al. (1983)	
			5.24 ± 0.36	295	PR-RA	Nielsen et al. (1986)	
			5.78 ± 0.42	297.6 ± 0.4	RR [relative to $k(n\text{-butane}) = 2.35 \times 10^{-12}$]	Edney et al. (1986)	
			8.6 ± 0.8	296 ± 2	DF-RF	Bourmada et al. (1987)	

Kinetics of the gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Kinetics of the
gas-phase reactions

R. Atkinson

Table 54. Continued

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
1.09 × 10 ⁻³	1.47	-125	7.14 ± 0.31	292	PLP-LIF	Droege and Tully (1987)	292–491
			8.49 ± 0.37	342			
			10.1 ± 0.44	401			
			12.9 ± 0.56	491			
			7.07 ± 0.35	~298 ^b	RR [relative to <i>k</i> (ethene) = 8.52 × 10 ⁻¹²] ^a	Japar et al. (1990)	
			6.69 ± 0.40	296 ± 2	RR [relative to <i>k</i> (<i>n</i> -butane) = 2.33 × 10 ⁻¹²]	Atkinson and Aschmann (1992)	
			6.89	297 ± 2	RR [relative to <i>k</i> (<i>n</i> -hexane) = 5.17 × 10 ⁻¹²]	Sommerlade et al. (1993)	
			6.7 ± 0.9	298	DF-LIF	Saunders et al. (1994)	
			7.6 ± 0.8	300	DF-LIF	Donahue et al. (1996)	
			7.33 ± 0.10	296 ± 2	RR [relative to <i>k</i> (toluene) = 5.67 × 10 ⁻¹²] ^c	Kramp and Paulson (1998)	
			6.76 ± 0.07	296 ± 2	RR [relative to <i>k</i> (1,3-butadiene) = 10 ⁻¹¹] ^a × 6.72	Kramp and Paulson (1998)	
			7.16 ± 0.07	296 ± 2			

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 54. Continued

$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	n	$B(\text{K})$	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at $T(\text{K})$	Technique	Reference	Temperature Range (K)
			6.89 ± 0.21	296 ± 2	RR [relative to $k(\text{trans-2-butene}) =$ $6.48 \times 10^{-11}]^a$	Kramp and Paulson (1998)	
			7.66 ± 0.23	300	DF-LIF	Donahue et al. (1998)	299–394
			7.68 ± 0.23	325			
			7.84 ± 0.24	340			
			9.96 ± 0.34	360			
			9.06 ± 0.27	375			
			10.3 ± 0.6	390			
			6.66	301	RR [relative to $k(\text{propane}) =$ $1.12 \times 10^{-12}]$	DeMore and Bayes (1999)	
			6.59	301			
			6.75	298	RR [relative to $k(n\text{-butane}) =$ 1.81×10^{-17}	DeMore and Bayes (1999)	298–363
			7.77	326			
			8.49	350	$T^2 e^{114/T}]$		
			8.91	363			
			6.83	298	RR [relative to $k(n\text{-pentane}) =$ 2.52×10^{-17}	DeMore and Bayes (1999)	298–368
			7.39	312			
			8.20	338	$T^2 e^{158/T}]$		
			9.25	368			

^a From Atkinson (1997).
^b Room temperature; assumed to be ~298 K.
^c From Calvert et al. (2002).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 55. Rate constants and temperature-dependent parameters for the reaction of OH radicals with cyclohexane-d₁₂

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	<i>n</i>	<i>B</i> (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference	Temperature Range (K)
3.48×10^{-4}	1.62	-56	2.76 ± 0.12	292	PLP-LIF	Droege and Tully (1987)	292–603
			3.64 ± 0.16	342			
			4.83 ± 0.21	401			
			6.94 ± 0.30	491			
			9.78 ± 0.42	603			

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Table 56. Rate constants for the reaction of OH radicals with methylcyclohexane

$10^{12} \times A$ (cm ³ molecule ⁻¹ s ⁻¹)	at T(K)	Technique	Reference
9.64 ± 0.24	297 ± 2	RR [relative to $k(n\text{-butane}) = 2.34 \times 10^{-12}$]	Atkinson et al. (1984)

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Table 57. Rate constants for the reaction of OH radicals with *n*-butylcyclohexane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference
14.7 ± 0.5	296 ± 2	RR[relative to <i>k</i> (<i>n</i> -octane) = 8.07 × 10 ⁻¹²]	Aschmann et al. (2001)

Kinetics of the
gas-phase reactions

R. Atkinson

Table 58. Rate constants for the reaction of OH radicals with cycloheptane

$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at $T(\text{K})$	Technique	Reference	Temperature Range (K)
13.1 ± 2.1	298 ± 2	FP-RA	Jolly et al. (1985)	
12.0 ± 0.3	300	DF-LIF	Donahue et al. (1998)	298–388
13.4 ± 0.4	325			
13.3 ± 0.4	340			
14.9 ± 0.4	375			
16.4 ± 1.4	390			

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

**Kinetics of the
gas-phase reactions**

R. Atkinson

Table 59. Rate constants for the reaction of OH radicals with cyclooctane

$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference	Temperature Range (K)
13.4 ± 0.4	300	DF-LIF	Donahue et al. (1998)	298–387
15.0 ± 0.4	325			
14.9 ± 0.4	340			
16.6 ± 0.5	375			
19.1 ± 0.6	390			

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Table 60. Rate constants for the reaction of OH radicals with bicyclo[2.2.1]heptane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference
5.12 ± 0.13	299 ± 2	RR [relative to $k(\text{cyclohexane}) = 7.00 \times 10^{-12}$]	Atkinson et al. (1983c)

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Table 61. Rate constants for the reaction of OH radicals with bicyclo[2.2.2]octane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference
13.7 ± 1.0	299 ± 2	RR [relative to $k(\text{cyclohexane}) = 7.00 \times 10^{-12}$]	Atkinson et al. (1983c)

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Table 62. Rate constants for the reaction of OH radicals with bicyclo[3.3.0]octane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T(K)	Technique	Reference
10.3 ± 0.5	299 ± 2	RR [relative to $k(\text{cyclohexane}) = 7.00 \times 10^{-12}$]	Atkinson et al. (1983c)

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Table 63. Rate constants for the reaction of OH radicals with *cis*-bicyclo[4.3.0]nonane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference
16.0 ± 1.2	299 ± 2	RR [relative to <i>k</i> (cyclohexane) = 7.00 × 10 ⁻¹²]	Atkinson et al. (1983c)

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Table 64. Rate constants for the reaction of OH radicals with *trans*-bicyclo[4.3.0]nonane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference
16.5 ± 1.2	299 ± 2	RR [relative to <i>k</i> (cyclohexane) = 7.00 × 10 ⁻¹²]	Atkinson et al. (1983c)

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Table 65. Rate constants for the reaction of OH radicals with *cis*-bicyclo[4.4.0]decane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference
18.6 ± 1.3	299 ± 2	RR [relative to <i>k</i> (cyclohexane) = 7.00 × 10 ⁻¹²]	Atkinson et al. (1983c)

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Table 66. Rate constants for the reaction of OH radicals with *trans*-bicyclo[4.4.0]decane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference
19.0 ± 1.2	299 ± 2	RR [relative to <i>k</i> (cyclohexane) = 7.00 × 10 ⁻¹²]	Atkinson et al. (1983c)

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Table 67. Rate constants for the reaction of OH radicals with tricyclo[5.2.1.0^{2,6}]decane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference
10.6 ± 0.4	299 ± 2	RR [relative to <i>k</i> (cyclohexane) = 7.00 × 10 ⁻¹²]	Atkinson et al. (1983c)

Kinetics of the
gas-phase reactions

R. Atkinson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Table 68. Rate constants for the reaction of OH radicals with tricyclo[3.3.1.1^{3,7}]decane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference
21.5 ± 1.9	299 ± 2	RR [relative to <i>k</i> (cyclohexane) = 7.00 × 10 ⁻¹²]	Atkinson et al. (1983c)

Kinetics of the
gas-phase reactions

R. Atkinson

Table 69. Rate constants for the reaction of OH radicals with *trans*-pinane; (1R, 2R)-2,6,6-trimethylbicyclo[3.3.1]heptane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference
12.4 ± 1.0	296 ± 2	RR [relative to <i>k</i> (<i>n</i> -butane) = 2.33 × 10 ⁻¹²]	Atkinson and Aschmann (1992)

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

Kinetics of the
gas-phase reactions

R. Atkinson

Table 70. Rate constants for the reaction of OH radicals with tricyclene; 1,7,7-trimethyltricyclo[2.2.1.0^{2,6}]heptane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference
2.66 ± 0.21	296 ± 2	RR [relative to $k(n\text{-butane}) = 2.33 \times 10^{-12}$]	Atkinson and Aschmann (1992)

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Kinetics of the
gas-phase reactions

R. Atkinson

Table 71. Rate constants for the reaction of OH radicals with quadricyclane; quadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptane

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference
1.70 ± 0.16	296 ± 2	RR [relative to $k(n\text{-butane}) = 2.33 \times 10^{-12}$]	Atkinson and Aschmann (1992)

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

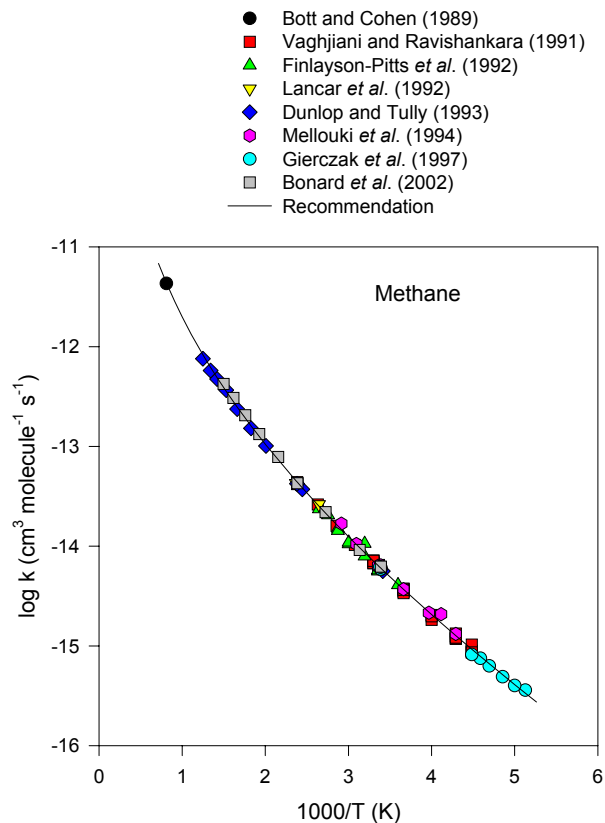
Full Screen / Esc

Print Version

Interactive Discussion

**Kinetics of the
gas-phase reactions**

R. Atkinson

**Fig. 1.** Arrhenius plot of selected rate data for the reaction of OH radicals with methane.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

© EGU 2003

Kinetics of the
gas-phase reactions

R. Atkinson

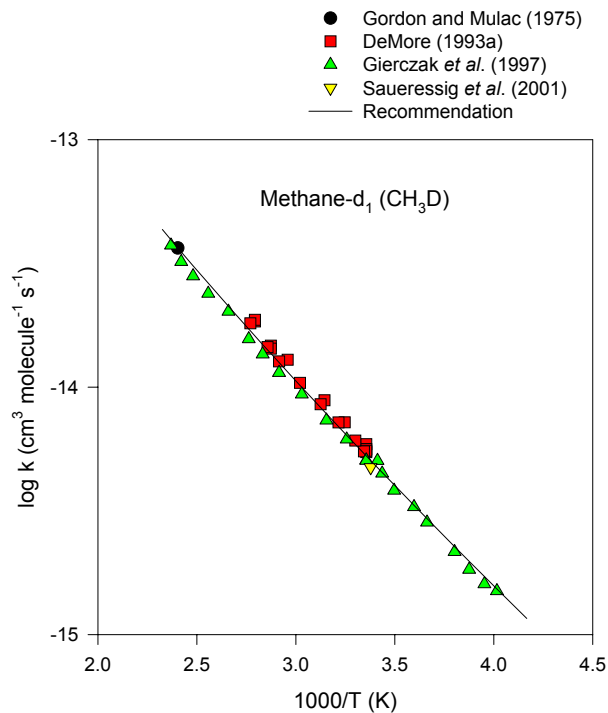


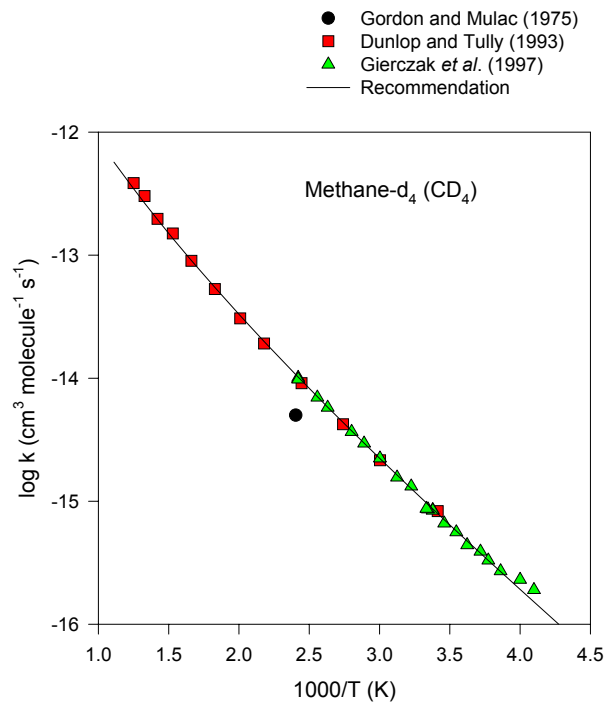
Fig. 2. Arrhenius plot of the rate data for the reaction of OH radicals with methane-d₁ (CH₃D).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

© EGU 2003

**Kinetics of the
gas-phase reactions**

R. Atkinson

**Fig. 3.** Arrhenius plot of the rate data for the reaction of OH radicals with methane-d₄ (CD₄).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

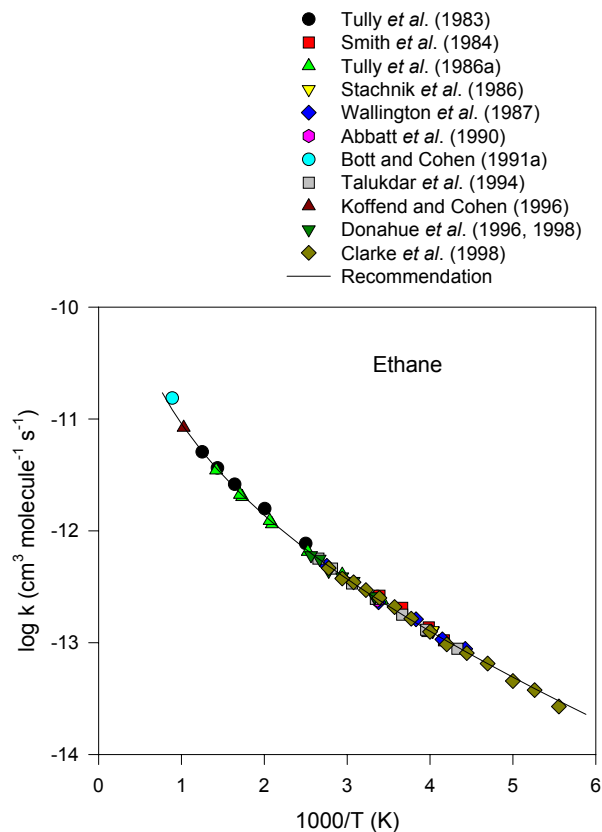
Print Version

Interactive Discussion

© EGU 2003

**Kinetics of the
gas-phase reactions**

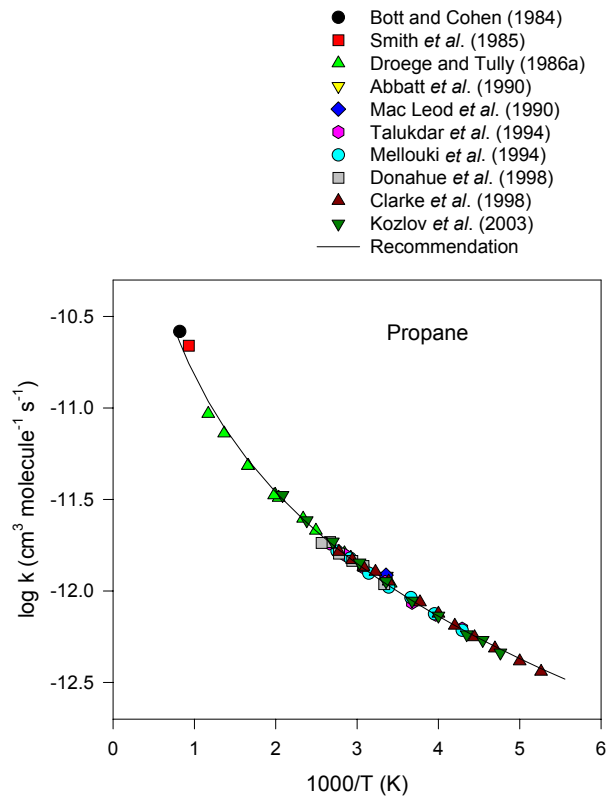
R. Atkinson

**Fig. 4.** Arrhenius plot of selected rate data for the reaction of OH radicals with ethane.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

© EGU 2003

**Kinetics of the
gas-phase reactions**

R. Atkinson

**Fig. 5.** Arrhenius plot of selected rate data for the reaction of OH radicals with propane.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

**Kinetics of the
gas-phase reactions**

R. Atkinson

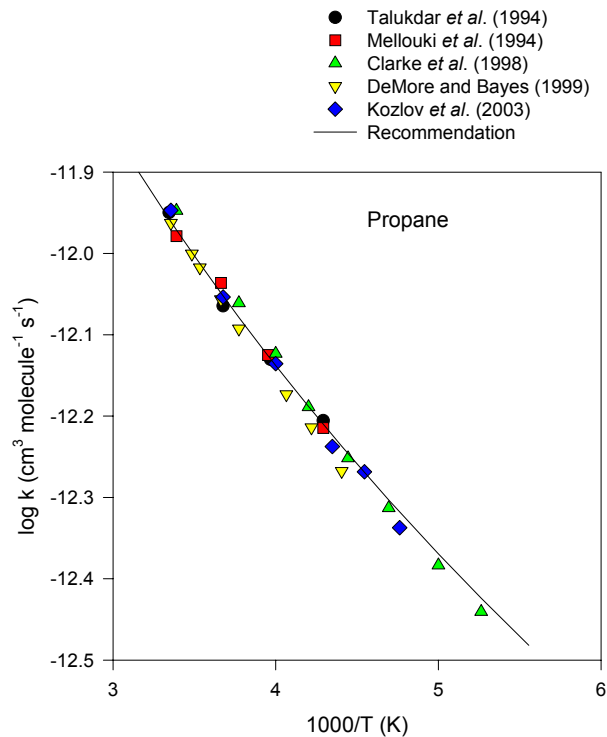


Fig. 6. Arrhenius plot of selected rate data for the reaction of OH radicals with propane at temperatures < 300 K.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

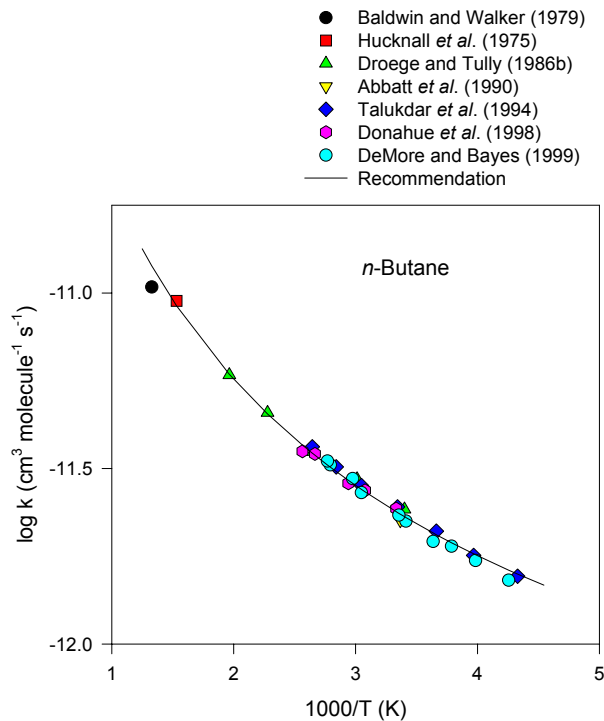
Print Version

Interactive Discussion

© EGU 2003

**Kinetics of the
gas-phase reactions**

R. Atkinson

**Fig. 7.** Arrhenius plot of selected rate data for the reaction of OH radicals with *n*-butane.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

**Kinetics of the
gas-phase reactions**

R. Atkinson

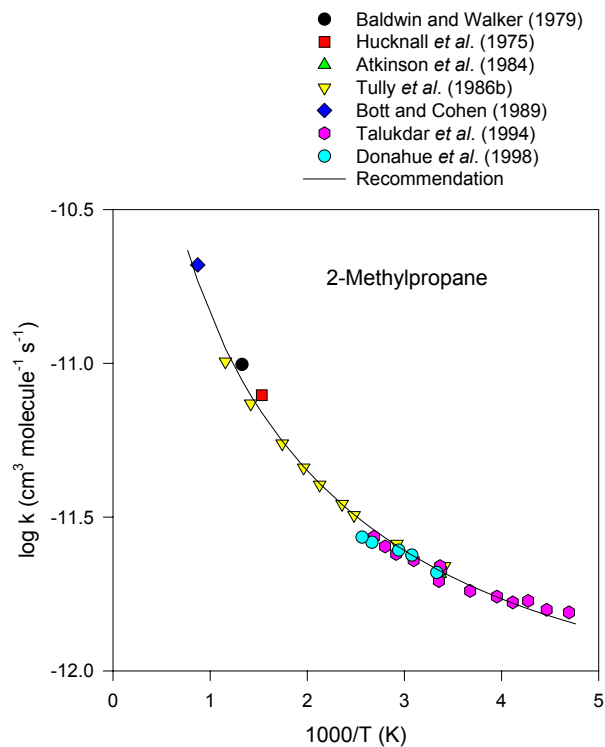


Fig. 8. Arrhenius plot of selected rate data for the reaction of OH radicals with 2-methylpropane.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

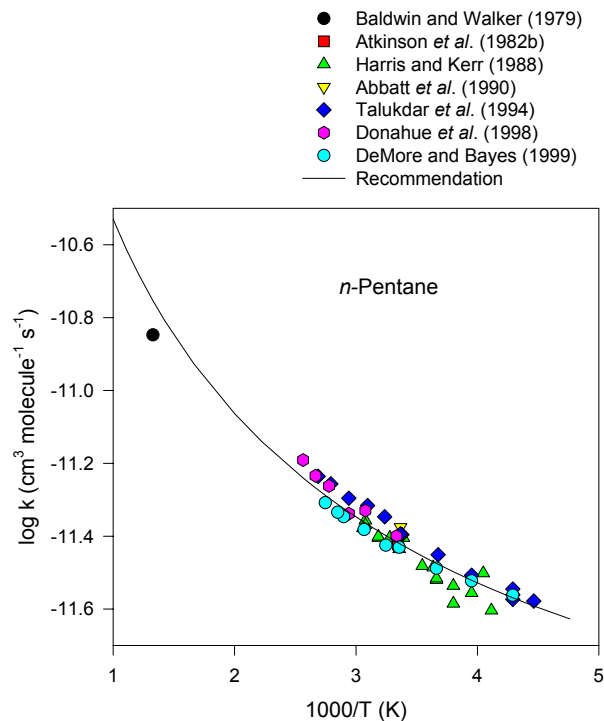
Print Version

Interactive Discussion

© EGU 2003

**Kinetics of the
gas-phase reactions**

R. Atkinson

**Fig. 9.** Arrhenius plot of selected rate data for the reaction of OH radicals with *n*-pentane.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

**Kinetics of the
gas-phase reactions**

R. Atkinson

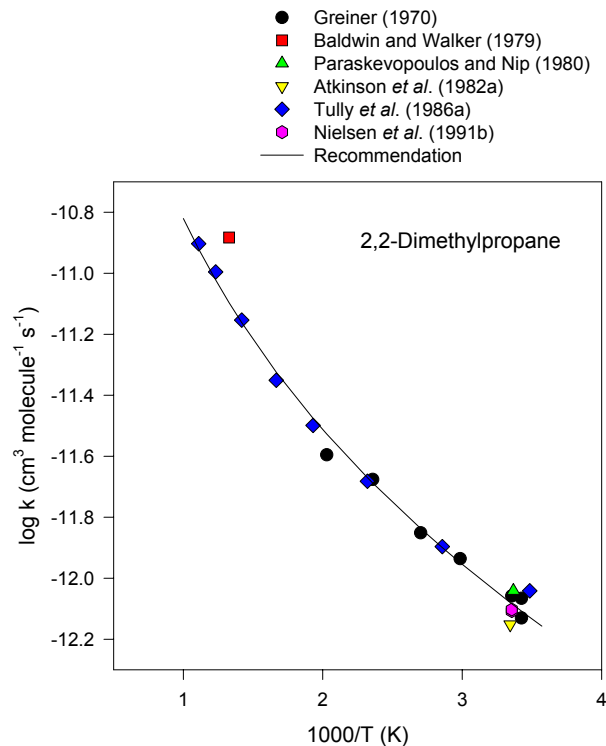


Fig. 10. Arrhenius plot of selected rate data for the reaction of OH radicals with 2,2-dimethylpropane.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

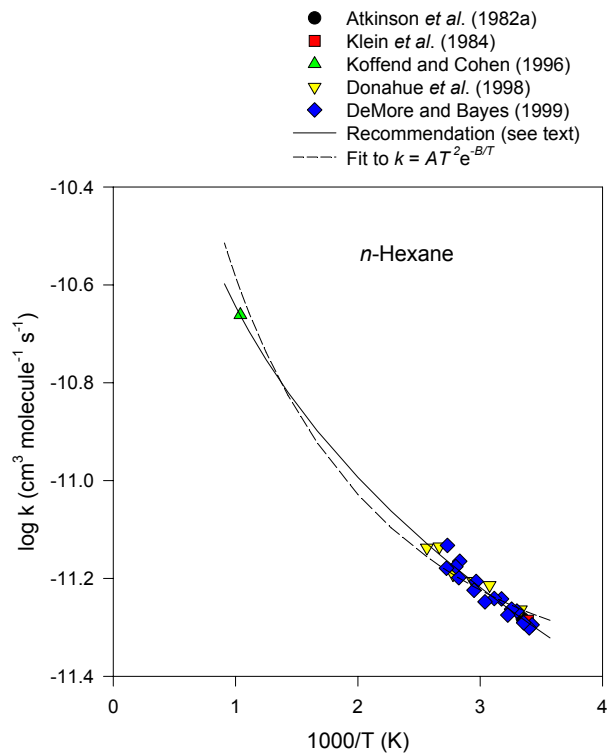
Print Version

Interactive Discussion

© EGU 2003

**Kinetics of the
gas-phase reactions**

R. Atkinson

**Fig. 11.** Arrhenius plot of selected rate data for the reaction of OH radicals with *n*-hexane.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

**Kinetics of the
gas-phase reactions**

R. Atkinson

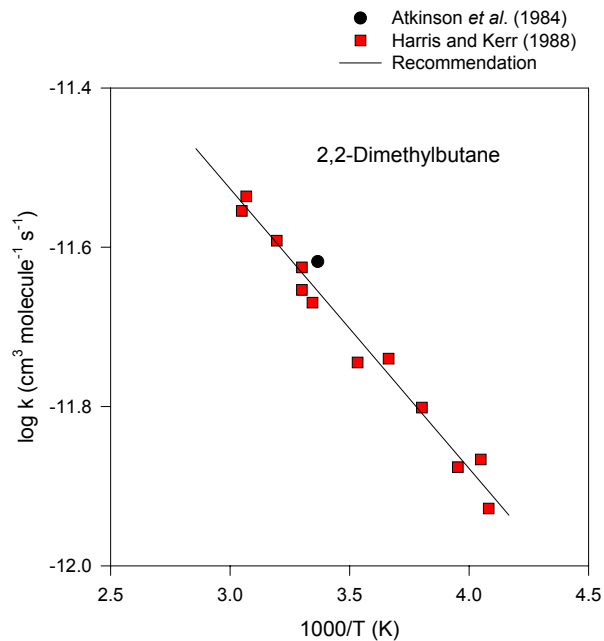


Fig. 12. Arrhenius plot of the rate data for the reaction of OH radicals with 2,2-dimethylbutane.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

© EGU 2003

**Kinetics of the
gas-phase reactions**

R. Atkinson

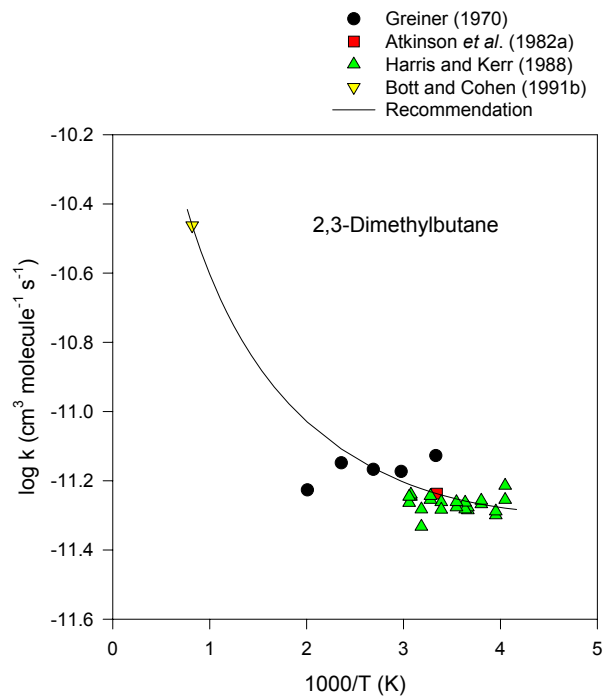


Fig. 13. Arrhenius plot of selected rate data for the reaction of OH radicals with 2,3-dimethylbutane.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

© EGU 2003

**Kinetics of the
gas-phase reactions**

R. Atkinson

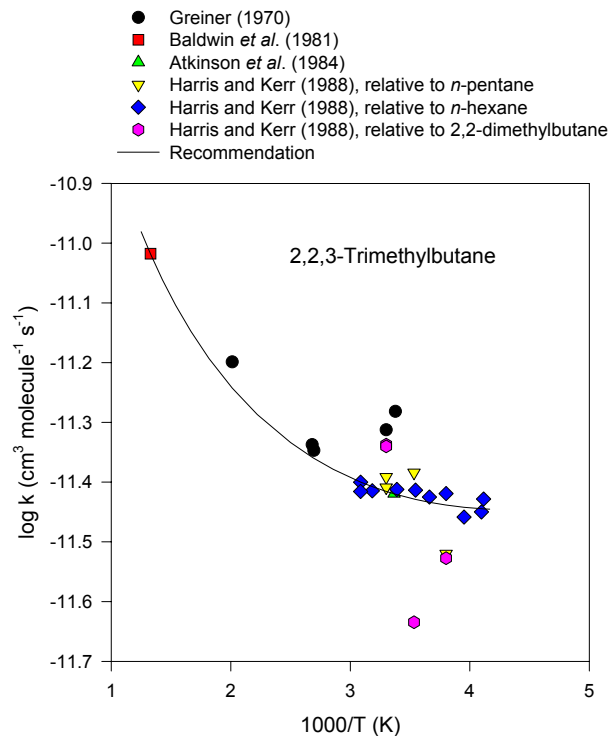


Fig. 14. Arrhenius plot of selected rate data for the reaction of OH radicals with 2,2,3-trimethylbutane.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

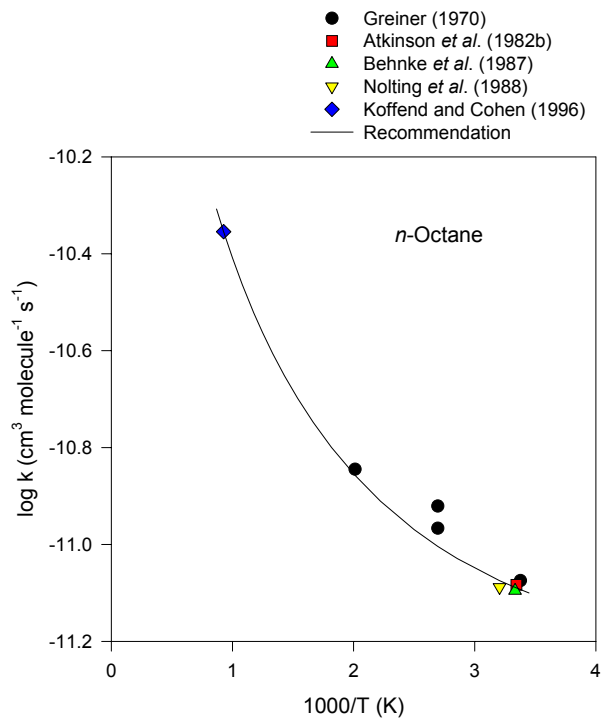
Print Version

Interactive Discussion

© EGU 2003

**Kinetics of the
gas-phase reactions**

R. Atkinson

**Fig. 15.** Arrhenius plot of the rate data for the reaction of OH radicals with *n*-octane.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

**Kinetics of the
gas-phase reactions**

R. Atkinson

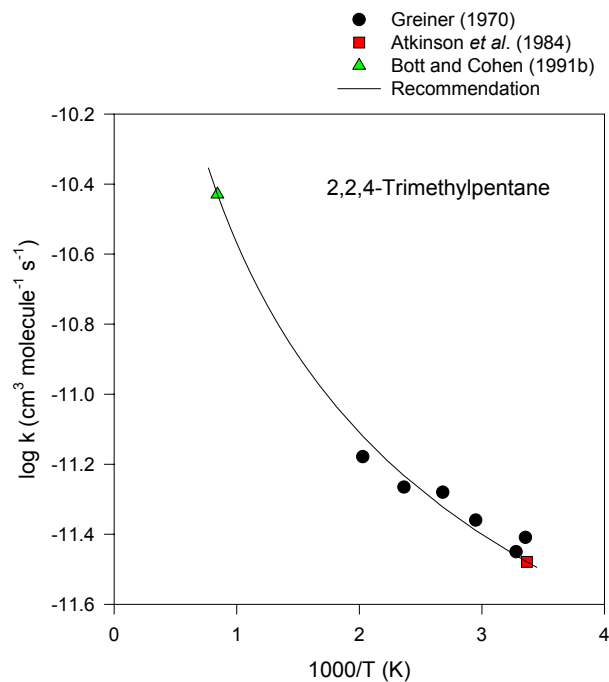


Fig. 16. Arrhenius plot of the rate data for the reaction of OH radicals with 2,2,4-trimethylpentane.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

**Kinetics of the
gas-phase reactions**

R. Atkinson

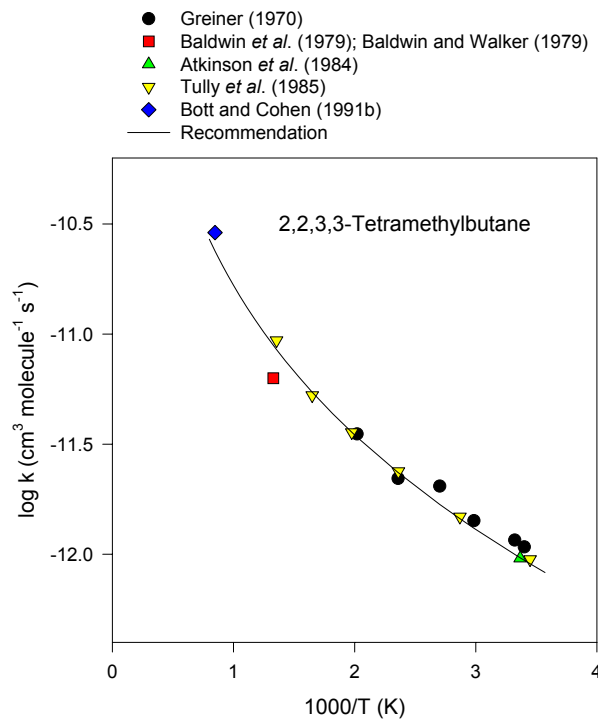


Fig. 17. Arrhenius plot of the rate data for the reaction of OH radicals with 2,2,3,3-tetramethylbutane.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003

**Kinetics of the
gas-phase reactions**

R. Atkinson

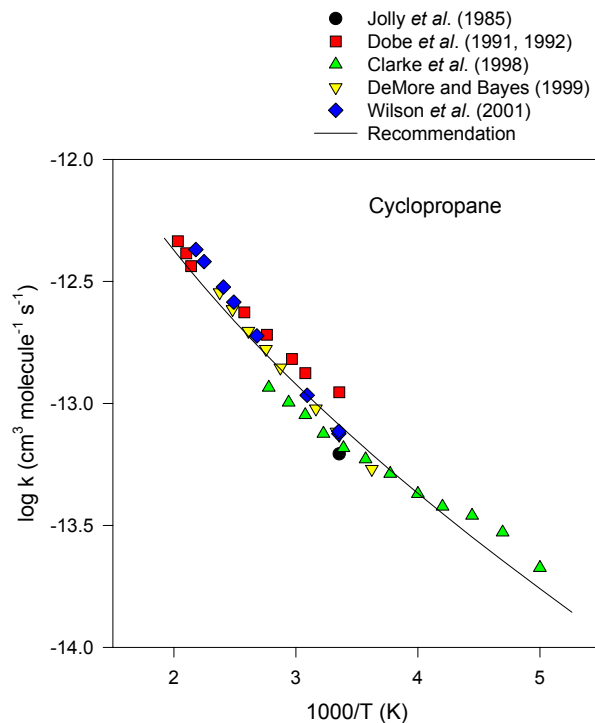


Fig. 18. Arrhenius plot of selected rate data for the reaction of OH radicals with cyclopropane.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

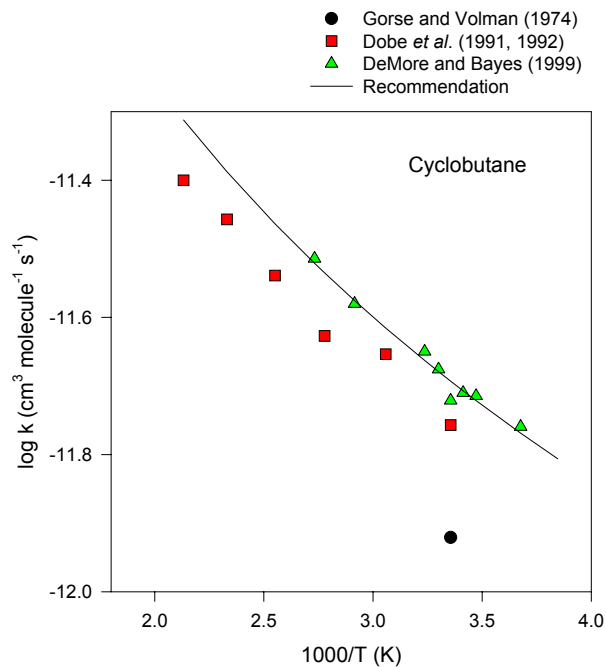
Print Version

Interactive Discussion

© EGU 2003

**Kinetics of the
gas-phase reactions**

R. Atkinson

**Fig. 19.** Arrhenius plot of the rate data for the reaction of OH radicals with cyclobutane.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

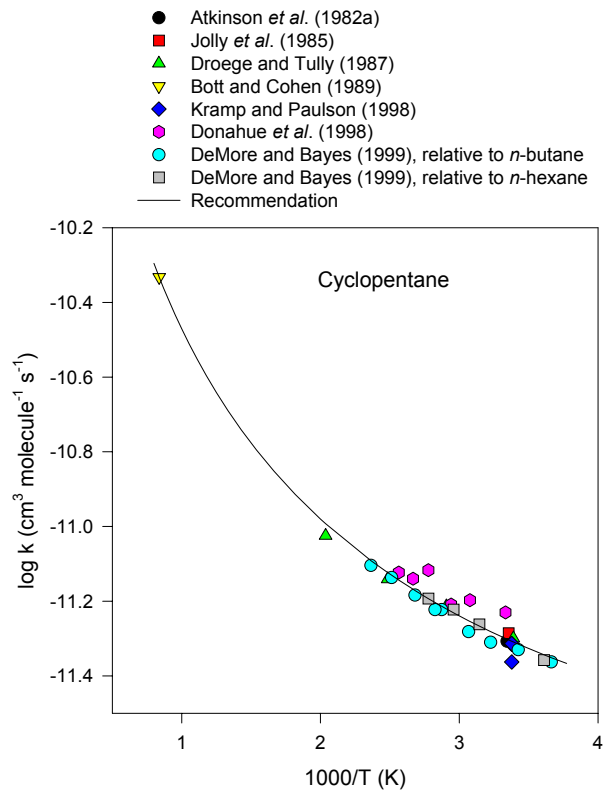
Print Version

Interactive Discussion

© EGU 2003

**Kinetics of the
gas-phase reactions**

R. Atkinson

**Fig. 20.** Arrhenius plot of selected rate data for the reaction of OH radicals with cyclopentane.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

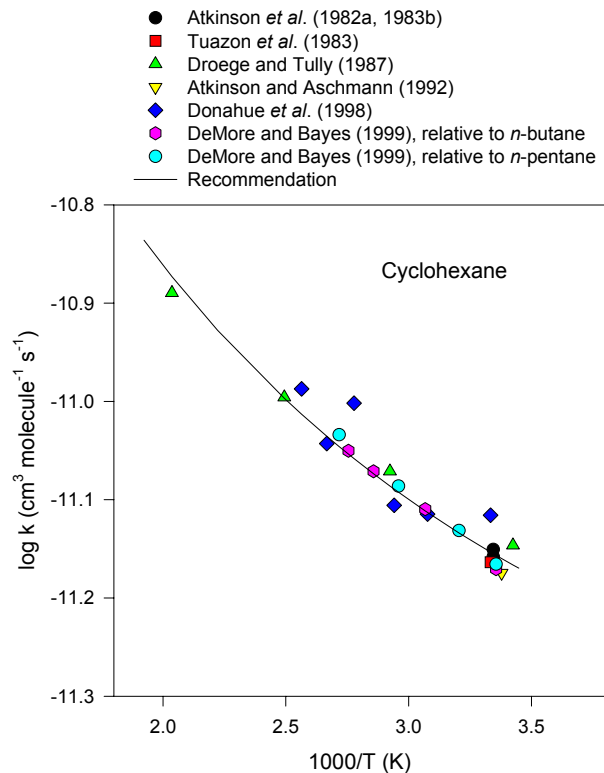
Print Version

Interactive Discussion

© EGU 2003

**Kinetics of the
gas-phase reactions**

R. Atkinson

**Fig. 21.** Arrhenius plot of selected rate data for the reaction of OH radicals with cyclohexane.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

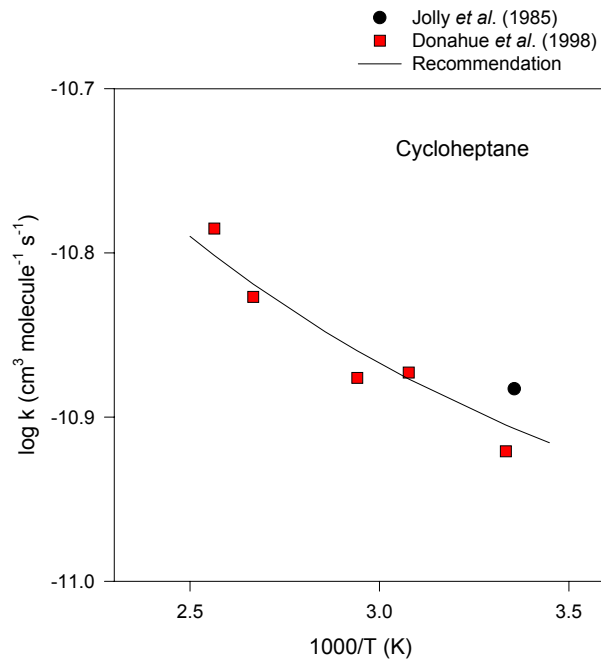
Print Version

Interactive Discussion

© EGU 2003

**Kinetics of the
gas-phase reactions**

R. Atkinson

**Fig. 22.** Arrhenius plot of the rate data for the reaction of OH radicals with cycloheptane.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2003