

**OH + propane and
iodopropanes**

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298 K rate coefficients for the reaction of OH with *i*-C₃H₇I, *n*-C₃H₇I and C₃H₈

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Abstract

The kinetics of the title reactions were investigated using the laser photolysis - resonance fluorescence method, employing the sequential two-photon dissociation of NO₂ in the presence of H₂ as the OH source. The 298 K rate constant for OH + C₃H₈ was found to be $(1.15 \pm 0.1) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, in excellent agreement with the literature recommendation, and with a separate determination using HNO₃ photolysis at 248 nm as the OH source. The 298 K rate constants for OH + *n*-C₃H₇I and *i*-C₃H₇I were measured for the first time and found to be (1.47 ± 0.08) and $(1.22 \pm 0.06) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, respectively. The errors include an assessment of systematic error due to concentration measurement, which, for the propyl-iodides was minimised by on-line UV-absorption spectroscopy. The implications of these results for the reactive iodine budget of the marine boundary layer are discussed.

1. Introduction

Iodine compounds play an important role in the chemistry of the marine boundary layer (MBL) (Chameides and Davis, 1980; Jenkin et al., 1985; Chatfield and Crutzen, 1990; Jenkin, 1993; Davis et al., 1996; Vogt et al., 1999; McFiggans et al., 2000). The major source of iodine are biogenic alkyl-iodides such as CH₃I, (Singh et al., 1983; Happell and Wallace, 1996) which is produced by metabolic processes in macroalgae and phytoplankton, and released from the ocean to the atmosphere. Recent measurements also indicate the presence of larger alkyl-iodides, with surprisingly high average concentrations of gas-phase *i*-C₃H₇I (up to 2 ppt) found in the Arctic troposphere and both *i*-C₃H₇I and *n*-C₃H₇I being detected in Arctic sea-water samples (Schall and Heumann, 1993; Vogt et al., 1999). In addition, multiply-substituted alkyl-iodides such as CH₂I₂ (Carpenter et al., 1999) have been observed, which indicates a stronger overall emission of inorganic iodine to the marine atmosphere than previously assumed. The generation of reactive inorganic iodine species from these organic compounds oc-

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curs mainly via photodissociation, with lifetimes varying from 200 s to 90 hrs (Roehl et al., 1997) to yield iodine atoms, I. The dominant fate of I in the atmosphere is reaction with ozone to form the iodine oxide radical, IO, which can take part in gas-phase, ozone destroying reaction cycles. Recent measurements of IO at a number of coastal locations (Alicke et al., 1999; Stutz et al., 1999; Allan et al., 2000) support the concept of an active iodine chemistry over large parts of the marine atmosphere. The OH radical is the primary initiator of oxidation in the troposphere and its concentration determines the lifetimes, and thus the abundance of most naturally and anthropogenically emitted chemical species (Crutzen, 1983) including CH₄ and also non-methane hydrocarbons. For multiply substituted alkyl-iodides, the absorption spectrum extends well into the actinic region, and the reaction with OH is not likely to contribute significantly to their degradation. In contrast, the mono-substituted alkyl-iodides have considerably longer photolytic lifetimes, and reaction with OH may compete with photolysis. The greatest potential for reaction with OH will be associated with those alkyl-iodides that possess a large number of relatively weak C-H bonds. Given the trend in OH rate constants with CH₄, C₂H₆ and C₃H₈, which varies from 6.2×10^{-15} (CH₄) to 2.5×10^{-13} (C₂H₆) and 1.1×10^{-12} cm³ s⁻¹ (C₃H₈) at 298 K, respectively (Atkinson et al., 1997), *n*-C₃H₇I and *i*-C₃H₇I would appear to be the best choice for investigation. At present, although the lifetimes of *n*-C₃H₇I and *i*-C₃H₇I with respect to photodissociation have been calculated, the rate constants for reaction with OH are unknown. The aims of the present study were therefore to make the first measurements of the rate constants for the reaction of OH with *n*-C₃H₇I (1) and *i*-C₃H₇I, (2) at room temperature. As a test of our experimental methodology, we have re-measured the rate constant of the well characterised reaction between OH and propane (3) at the same temperature.



2. Experimental

2.1. General

The laser photolysis / OH-resonance fluorescence experimental set-up has been described in detail in recent publications (Crowley et al., 1996; Carl and Crowley, 1998). Pulsed (5–6ns) radiation at 439.44 nm was provided by a Nd-YAG pumped dye-laser operating at 10 Hz with coumarin 120 dye. The laser emission was expanded to a collimated beam of about 5 mm diameter and passed through 3 irises of \approx 4 mm diameter before entering the photolysis cell through a quartz window at the Brewster angle. Pulse energies were monitored with a Joule meter placed behind the exit Brewster window of the cell. OH radicals were excited by a micro-wave powered discharge lamp and their fluorescence detected at right angles to both the axis of propagation of the laser beam and the micro-wave lamp by a photomultiplier operating in photon counting mode which was screened by a 309 ± 5 nm interference filter. Between 1000 and 5000 decay profiles were averaged at 10 Hz to improve signal-to-noise ratios.

The concentrations of *i*-C₃H₇I and *n*-C₃H₇I were determined by their absorption of UV light (D₂ lamp) in a separate cell of 174 cm optical path length, which was connected serially in flow prior to the photolysis cell and maintained at room temperature. The entire absorption region of *n*-C₃H₇I, and *i*-C₃H₇I between 220 and 380 nm was recorded by diode array spectroscopy, and concentrations determined by least-squares fitting to uv-absorption spectra measured in this laboratory (Roehl et al., 1997). For propane, which has no absorption spectrum in the UV, the concentration was determined by calculating a mixing ratio based on relative and total flows through calibrated mass flow controllers and the total pressure, determined by capacitance manometer. The concentration of NO₂ was also occasionally determined by its optical absorption around 400 nm, although this parameter is not necessary for the extraction of rate data in the kinetic experiments.

The Teflon-coated, stainless steel photolysis cell is equipped with a thermostatted glass gas inlet and is itself maintained at 298 K by flowing thermostatted liquid through

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a series of bore-holes. The temperature of the gas at the intersection of the microwave lamp and laser beam was determined with a constantin-alumel thermocouple and is known to an accuracy of better than 2 K.

2.2. Generation of OH

- 5 OH generation is initiated by the photolysis of NO₂ according to the following scheme (Carl and Crowley, 1998):



15 In all experiments the total pressure was 20 Torr (1 Torr = 1.333 mBar), the NO₂ concentration was held constant at $\approx 5 \times 10^{14} \text{ cm}^{-3}$ (occasionally determined optically), with the H₂ concentration at about $2 \times 10^{16} \text{ cm}^{-3}$. Under these conditions, OH generation, the rate of which is limited by reaction (8), is complete within about 10 μs after the laser pulse. As we discuss in a previous publication (Carl and Crowley, 1998), OH is formed in vibrationally excited states in both reactions (7) and (8). The control experiments with C₃H₈ provide confirmation that either OH ($v > 0$) is rapidly quenched by
20 NO₂ in our experiments (the rate constant for quenching of OH ($v = 1$) by NO₂ is $4.8 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (Smith and Williams, 1985)), or that vibrational excitation in OH has no significant influence on the rate constants measured.

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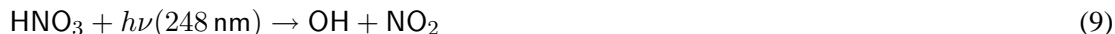
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Typically, laser fluences of $\approx 20\text{--}40 \text{ mJ cm}^{-2}$ were used to generate between $\approx 2 \times 10^{11}$ and $1 \times 10^{12} \text{ OH cm}^{-3}$. Experiments were also carried out in which the 248 nm photolysis of HNO_3 was used as OH source:



5 This source proved to be unsuitable for study of the reactions of OH with $\text{C}_3\text{H}_7\text{I}$ due to the extensive dissociation of the iodides by the 248 nm laser light (see below), but was used for OH + C_3H_8 . *n*- $\text{C}_3\text{H}_7\text{I}$ (Aldrich, 99%) and *i*- $\text{C}_3\text{H}_7\text{I}$ (Aldrich, 99%) were used after repeated degassing. The stated maximum 1% impurity in *n*- $\text{C}_3\text{H}_7\text{I}$ is thought to be *i*- $\text{C}_3\text{H}_7\text{I}$, and vice-versa. C_3H_8 (Linde, 99.95%), Ar (Linde, 99.999%), H_2 (Linde, 99.999%) and NO_2 (purchased as N_2O_4 , Merck, 99.5%) were used without further purification.

3. Results and discussion

All experiments were carried out under pseudo first-order conditions, with the alkyl iodide, RI, in large excess. i.e. $[\text{RI}] \gg [\text{OH}]$. The decay of OH is then described by:

$$15 \quad [\text{OH}]_t = [\text{OH}]_0 \exp - \{ (k_{\text{bi}}[\text{RI}] + k_{\text{NO}_2}[\text{NO}_2] + d)t \} \quad (\text{i})$$

where $[\text{OH}]_t$ is the OH concentration at time = t after the laser pulse, k_{bi} the bimolecular rate constant for the reaction with RI, k_{NO_2} the rate constant for reaction of OH with NO_2 and d the rate constant for diffusion out of the reaction zone. The first-order decay rate constant, k' was obtained by non-linear least-squares fitting of the OH decays and is related to the desired rate constant, k_{bi} as shown in equation (ii).

$$20 \quad k' = k_{\text{bi}}[\text{RI}] + k_{\text{NO}_2}[\text{NO}_2] + d \quad (\text{ii})$$

The decay rate of OH due to reaction with NO_2 appears as an intercept in the plot of k' versus $[\text{RI}]$. Efforts were therefore made to ensure that the concentration of NO_2 (which was maintained by flow controller) remained constant during the course of experiments

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in which the decay of OH in various excess amounts of organic were measured. The spectral deconvolution procedure showed that $[\text{NO}_2]$ was stable to $\approx 1\%$ over such a measurement, which converts to a variation in the pseudo-first order decay rate of only $\pm 60 \text{ s}^{-1}$ in a total decay rate of between 800 and 5000 s^{-1} , depending on the concentration (and identity) of the excess reactant. The observed small degree of scatter in the plots of k' versus $[\text{RI}]$ confirm this.

3.1. OH + C₃H₈

The primary objective in re-measuring the rate constant for OH + C₃H₈ was to test our experimental procedure, especially the use of two-photon dissociation of NO₂ in the presence of H₂ as the OH source, the reliability of which has not yet been completely assessed. For this reason a conventional OH source (248 nm photolysis of HNO₃) was also used to enable direct comparison. Figure 1 shows the decay of OH in the presence of varying excess amounts of C₃H₈ using NO₂ + 2 $h\nu$ (439.44 nm) as OH source. As anticipated, the decay of OH is strictly exponential, and as shown in Fig. 2, its rate varies linearly with [C₃H₈]. The rate constant derived via equation (ii) is $(1.15 \pm 0.03) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ (2 σ precision). The overall accuracy of the rate constant is determined by the accuracy of the concentration measurement of the propane, and is estimated as $\approx 10\%$. The final result is thus $(1.15 \pm 0.1) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. Data obtained using reaction (9) as the OH source are also displayed in Fig. 2 (solid circles) and yield a rate constant $(1.17 \pm 0.1) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. These results are clearly in excellent agreement with each other, and with the recommended literature value (Atkinson et al., 1997; DeMore et al., 1997) of $(1.1 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ providing validation of our experimental methods.

3.2. OH + *n*-C₃H₇I and OH + *i*-C₃H₇I

Experiments on OH + *i*-C₃H₇I were carried out using both HNO₃ photolysis at 248 nm and NO₂/H₂ photolysis at 439.44 nm, data for OH + *n*-C₃H₇I was obtained using

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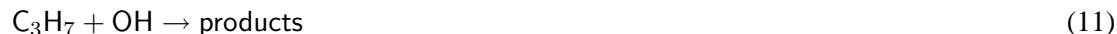
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the NO₂/H₂ photolysis source only. The concentrations of the iodo-propanes were determined by absorption spectroscopy (see above) and least squares fitting to known UV absorption spectra (Roehl et al., 1997). The quality of the fits was such that the estimated errors in concentration are less than 5%, including errors in the absorption cross-sections close to the maxima.

The first-order decay rates of OH were similar in quality to those shown for C₃H₈ and displayed the expected linear dependence on the concentration of the iodo-propane. For a given *i*-C₃H₇I concentration, the value of *k'* was found to be independent of laser fluence when varied by a factor of about 3, and thus initial [OH] by a factor ≈ 10 for those experiments carried out using NO₂/H₂ photolysis. However, when the photolysis of ≈ 1 × 10¹⁵ HNO₃ cm⁻³ at 248 nm was used as the OH source, the decay rate was found to be strongly dependent on laser fluence. As an example, increasing the 248 nm laser fluence from ≈ 2 mJ cm⁻² to ≈ 8 mJ cm⁻² resulted in an increase in the measured decay rate (for a fixed *i*-C₃H₇I) from 1060 ± 10 s⁻¹ to 1360 ± 10 s⁻¹. This is attributed to the efficient photo-fragmentation of *i*-C₃H₇I at 248 nm where it absorbs strongly (σ ≈ 1 × 10⁻¹⁸ cm²).



and a rapid reaction (Tsang, 1988) of OH with the radical product:



This problem was clearly not encountered when using 439.44 nm radiation to generate OH radicals as the *i*-C₃H₇I does not absorb at this wavelength, and highlights the advantages of using pulsed visible radiation instead of UV radiation, as only very few small molecules have absorption spectra that extend beyond 400 nm. The data obtained with HNO₃ + 248 nm photolysis therefore only define an upper limit to the rate constant for OH + *i*-C₃H₇I (see Table 1). Data obtained with NO₂/H₂ photolysis at 439.44 nm are summarised in Table 1, and the plot of *k'* versus concentration of iodo-propane is displayed in Fig. 3. The rate constants obtained are (1.47 ± 0.08) × 10⁻¹²

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$\text{cm}^3 \text{s}^{-1}$ and $(1.22 \pm 0.06) \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$ for OH with $n\text{-C}_3\text{H}_7\text{I}$ and $i\text{-C}_3\text{H}_7\text{I}$, respectively (errors are 2σ precision plus 5% estimated systematic error in concentration measurement). As $i\text{-C}_3\text{H}_7\text{I}$ and (by analogy) $n\text{-C}_3\text{H}_7\text{I}$ react rapidly with $\text{O}(^3\text{P})$ (Gilles et al., 1996), it is necessary to assess the potential impact of this on the reported rate constants. The products of the reaction of $\text{O}(^3\text{P})$ with the iodo-propanes are IO, HOI, C_3H_6 , and C_3H_7 (Klaasen et al., 1996).



OH is expected to react rapidly not only with propyl radicals (see above) but, by analogy with BrO and ClO, also with IO radicals (DeMore et al., 1997). The potential perturbation of the OH kinetics due to the formation of reactive products was investigated by varying the pulse energy at 439.44 nm and thus the initial OH and $\text{O}(^3\text{P})$ concentrations by a factor of 10. This had no effect on the resulting pseudo-first order decays, ruling out a significant secondary loss of OH. The potential enhancement in measured rate constants for both $n\text{-C}_3\text{H}_7\text{I}$ and $i\text{-C}_3\text{H}_7\text{I}$ due to the presence of I_2 impurity was also examined. The rate constant for reaction between OH and I_2 (14) is at $\approx 2 \times 10^{-10} \text{ cm}^3 \text{s}^{-1}$ very large, and I_2 impurity at the percent level would result in a factor of two overestimation of the true rate constant.



For this reason, the visible absorption by highly concentrated mixtures of the alkyl iodides in the region where I_2 absorbs strongly was examined for traces of I_2 . None were found, and we were able to set an upper limit to the fractional concentration of I_2 of 3×10^{-4} in $n\text{-C}_3\text{H}_7\text{I}$ and $i\text{-C}_3\text{H}_7\text{I}$. This implies an upper limit to the contribution to the overall OH decay (and thus to k_1 and k_2) of just 3%.

At $(1.47 \pm 0.08) \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$ the rate constant obtained for $n\text{-C}_3\text{H}_7\text{I}$ is ≈ 20 percent larger than that for $i\text{-C}_3\text{H}_7\text{I}$ ($(1.22 \pm 0.06) \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$). This trend is to be expected if one considers that the overall rate of H-abstraction from the CH_2 group

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in propane is a factor 4 faster than from the CH₃ groups (Talukdar et al. 1994) implying a 298 K rate constant of $3.7 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ per primary H-atom and $4.4 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ per secondary H-atom. Replacement of a primary H-atom with I (as for *n*-C₃H₇I) should not reduce the overall rate of abstraction as much as replacing one of the more reactive secondary H-atoms (as in *i*-C₃H₇I). The fact that both *n*-C₃H₇I and *i*-C₃H₇I react more rapidly with OH than calculated from the remaining number of primary and secondary H-atoms, suggests that the presence of the I-atom results in a weakening of the neighbouring C-H bonds as seen for the reactions of CH₃I with OH ($k_{298} = 7.2 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$) and CH₄ + OH ($k_{298} = 6.3 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$) (DeMore et al., 1997). An alternative explanation is that the reaction partially proceeds via a complex mechanism in which OH attack at the C-I bond can lead to products, in a similar fashion to reactions of O(³P) with alkyl-iodides (Gilles et al., 1996; Klaasen et al., 1996)(see above) and OH with CF₃I (Brown et al., 1990; Berry et al., 1998). There is also theoretical evidence supporting a complex mechanism for the reaction of OH with haloethanes (Sekušak and Sabljic, 1997).



However, the latest estimates for the heat of formation of HOI (Berry et al., 1998) suggest that reaction (1a) is endothermic by $> 20 \text{ kJmol}^{-1}$ for both *n*-C₃H₇I and *i*-C₃H₇I and therefore unlikely to be significant in the present experiments at 298 K, or in the atmosphere. As the present study gives no indications to the contrary, we assume that the reaction proceeds via H-atom abstraction to give H₂O and an iodine containing alkyl radical as products.



4. Conclusions and atmospheric implications

The overall rate constant for the reaction of OH with propane was measured using both 248 nm photolysis of HNO₃ and two-photon (439.44 nm) dissociation of NO₂ in the presence of H₂ as OH sources. Within experimental scatter both methods give the same result ($k = (1.15 \pm 0.06) \times 10^{-12}$ and $(1.17 \pm 0.06) \times 10^{-12}$ cm³ s⁻¹, respectively), and are in excellent agreement with the literature recommendation. The 298 K rate constants obtained for *n*-C₃H₇I and *i*-C₃H₇I are (1.47 ± 0.08) and $(1.22 \pm 0.06) \times 10^{-12}$ cm³ s⁻¹ respectively. These rate constants can be used to assess the relative importance of OH reaction and photolysis as destruction pathways for *n*-C₃H₇I and *i*-C₃H₇I in the atmosphere. The J-values for *n*-C₃H₇I and *i*-C₃H₇I, calculated for a 40° solar zenith angle are reported as $\approx 8 \times 10^{-6}$ s⁻¹ and 2×10^{-5} s⁻¹ respectively (Roehl et al., 1997). Using the rate constants above, and assuming a OH concentration of 5×10^6 cm⁻³, we calculate a loss rate of about 7×10^{-6} s⁻¹ and 6×10^{-6} s⁻¹ for *n*-C₃H₇I and *i*-C₃H₇I, respectively due to reaction with OH. For both *n*-C₃H₇I and *i*-C₃H₇I the loss rate due to reaction with OH is therefore of similar magnitude to that by photolysis and should be incorporated into estimates of the source strength of reactive iodine in the marine boundary layer. The 298 K rate constant for reaction of *n*-C₃H₇I and *i*-C₃H₇I with Cl have recently been measured (Cotter et al., 2001) and found to be 6.6×10^{-11} and 4.6×10^{-11} cm³ s⁻¹, respectively. The Cl/OH rate constant ratios for *n*-C₃H₇I and *i*-C₃H₇I are thus 45 and 38, respectively. Estimations of the relative, average OH/Cl-atom concentrations in the marine boundary layer vary between low values (Pszenny et al., 1993; Singh et al., 1996; Wingenter et al., 1996) of ≈ 10 –100 to high values (Singh et al., 1996; Rudolph et al., 1997) of > 1000 . Thus, in air masses where the activation of chlorine from sea-salt is possible, the reaction of Cl atoms with *n*-C₃H₇I and *i*-C₃H₇I may, during part of the day, compete with the OH reactions and photolysis. Daily averaged OH concentrations over the MBL are however likely to exceed those of Cl so that OH reactions will generally represent the main (non-photolytic) reactive sink.

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The products of the OH reactions and photolysis of C₃H₇I are different. Whereas the photolysis of the alkyl iodide yields a I-atom, the reaction with OH probably results in formation of an iodine containing alkyl radical (see above) that can react with O₂ to form a peroxy radical, the nature of which will depend on the position of the I-atom in the alkyl iodide, and on the position of OH attack. The fate of the peroxy radicals will be reaction with NO in marine air masses influenced by pollution to form carbonyl compounds and, through a series of secondary reactions, will generally lead to the release of the I-atom to the gas phase. In air masses where NO is low, the reaction of the peroxy radical with HO₂ will dominate to form peroxides, which may eventually also release I-atoms via their photochemical oxidation, or which may be lost to the ocean by deposition. Experimental studies of product formation in the reactions of OH with *n*-C₃H₇I and *i*-C₃H₇I are required to elucidate the fate and impact of these molecules on the iodine chemistry of the marine boundary layer.

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Table 1. 298 K kinetic data for OH + propanes. Notes: An * means:- bimolecular rate constants for each temperature obtained by weighted least squares fitting to k' versus concentration of C_3H_8 , $n-C_3H_7I$ or $i-C_3H_7I$. The estimated total errors in the rate constant are $\approx 5\%$ for $n-C_3H_7I$ and $i-C_3H_7I$ and 10% for C_3H_8 .

Reactant	OH source	$k_{bi} \pm 2\sigma^*$ $10^{-12} \text{ cm}^3 \text{ s}^{-1}$
$n-C_3H_7I$	NO_2 (439.44 nm)	1.47 ± 0.02
$i-C_3H_7I$	NO_2 (439.44 nm)	1.22 ± 0.01
$i-C_3H_7I$	HNO_3 (248 nm)	< 1.48
C_3H_8	HNO_3 (248 nm)	1.17 ± 0.01
C_3H_8	NO_2 (439.44 nm)	1.15 ± 0.03

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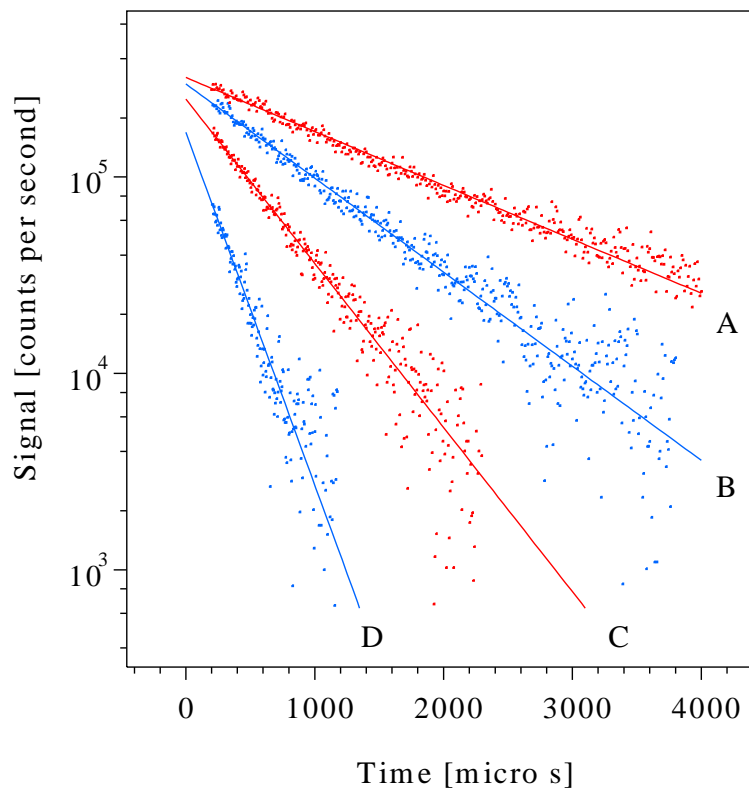
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Fig. 1. Exponential decays of OH in the presence of various excess concentrations of C_3H_8 . The concentrations of C_3H_8 (in cm^{-3}) were: A = 0; B = 4.10×10^{14} , C = 1.12×10^{15} , D = 3.12×10^{15} .

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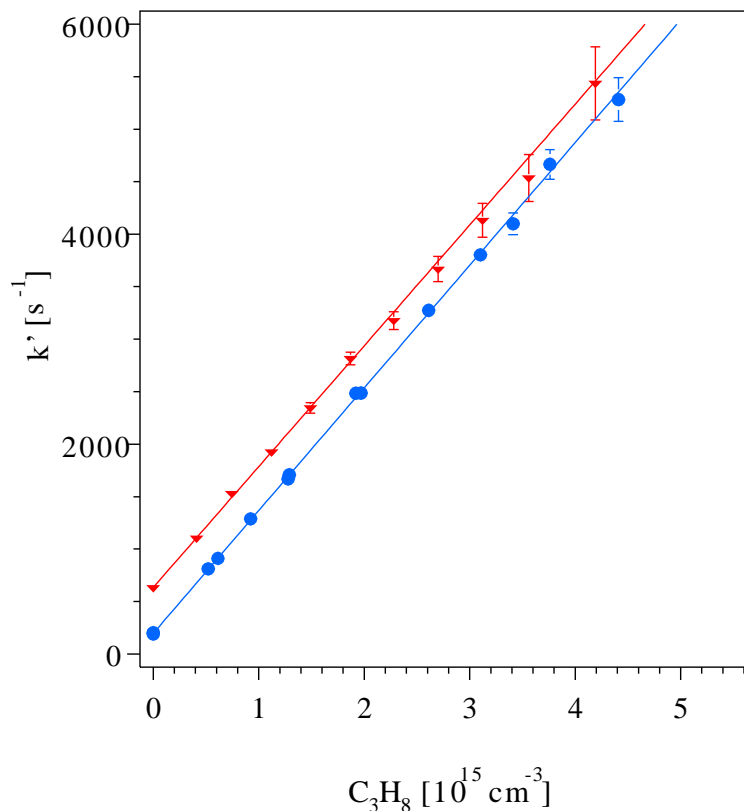
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Fig. 2. Plot of pseudo-first order decay constant of OH versus [propane]. Circles represent data obtained using 248 nm photolysis of HNO_3 as OH source, triangles are data points obtained using the two-photon (439.44 nm) dissociation of NO_2 in the presence of H_2 as OH source. The rate constants obtained are $(1.17 \pm 0.01) \times 10^{-12}$ and $(1.15 \pm 0.03) \times 10^{-12} cm^3 s^{-1}$, respectively (2σ precision).

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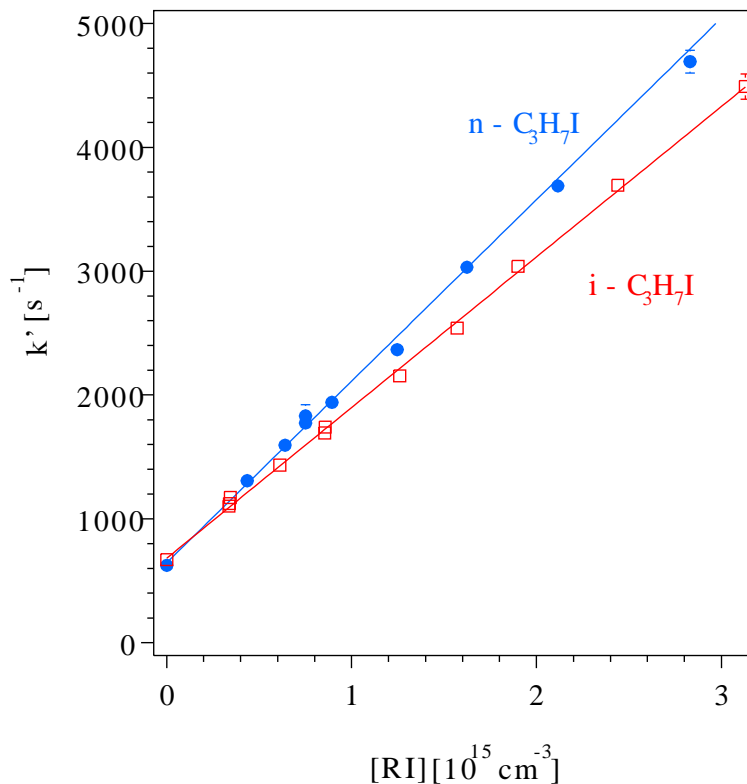
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Fig. 3. Plot of pseudo-first order decay constant of OH versus [propyl-iodide]. Solid circles, $n\text{-C}_3\text{H}_7\text{I}$ ($k_{298} = 1.47 \pm 0.02 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$); open squares, $i\text{-C}_3\text{H}_7\text{I}$ ($k_{298} = 1.22 \pm 0.01 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$), 2σ precision. Overall errors in the rate constants are estimated as $\approx 5\%$, related mainly to errors in the absorption cross sections of $n\text{-C}_3\text{H}_7\text{I}$ and $i\text{-C}_3\text{H}_7\text{I}$.

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