# Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VIII - gas phase reactions of organic species with four, or more, carbon atoms (≥ C₄)

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**Abstract.** This article, the eighth in the series, presents kinetic and photochemical datasheets evaluated by the IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation. It covers the gas phase thermal and photochemical reactions of organic species with four, or more, carbon atoms (≥ C₄) available on the IUPAC website in 2019, including thermal reactions of closed-shell organic species with HO and NO₃ radicals, and their photolysis. The present work is a continuation of Volume II (Atkinson et al., 2006) with new reactions and updated datasheets for reactions of HO (77 reactions) and NO₃ (36 reactions) with ≥ C₄ organics including alkanes, alkenes, dienes, aromatics, oxygenated, organic nitrates and nitro compounds in addition to photochemical processes for 9 species. The article consists of a summary table, containing the recommended kinetic parameters for the evaluated reactions, and a supplement containing the datasheets, which provide information upon which the recommendations are made.

## 1 Introduction

In the mid-1970s it was appreciated that there was a need for the establishment of an international panel to produce a set of critically evaluated rate parameters for reactions of interest for atmospheric chemistry. To this end the CODATA Task Group on Chemical Kinetics,

under the auspices of the International Council of Scientific Unions (ICSU), was constituted in 1977, and tasked to produce an evaluation of relevant, available kinetic and photochemical data. The first evaluation by this international committee was published in J. Phys. Chem. Ref. Data in 1980 (Baulch et al., 1980), followed by Supplements in 1982 (Baulch et al., 1982) and 1984 (Baulch et al., 1984). In 1986 the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry superseded the original CODATA Task Group for Atmospheric Chemistry. The Subcommittee continued its data evaluation program with Supplements published in 1989 (Atkinson et al., 1989), 1992 (Atkinson et al., 1992), 1997 (Atkinson et al., 1997a), 1997 (Atkinson et al., 1997b), 1999 (Atkinson et al., 1999), and 2000 (Atkinson et al., 2000).

The gas-phase evaluation work was expanded to include heterogeneous reactions of gases on solid and liquid substrates in 2005. Aqueous-phase reactions of atmospheric importance were added in 2015. The IUPAC group's work now includes over 1400 gas-phase, heterogeneous, and aqueous-phase reactions of importance in atmospheric chemistry. Reflecting the broader scope the group changed its name to the IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation in 2013. Cox (2012) and Cox et al. (2018) discuss the history of IUPAC data evaluations and their role in addressing the critical societal challenges of stratospheric ozone loss, tropospheric ozone formation, acid rain, urban air pollution, aerosol formation, and climate change.

In 2000 the evaluation was made available on the worldwide web (since 2016, http://iupac.pole-ether.fr). The IUPAC website hosts an interactive data base with a search facility and hyperlinks between the summary table and the datasheets, both of which can be downloaded as individual Word and PDF files. Work is underway to convert the datasheets to machine readable xml files which will enable automatic transfer of IUPAC recommended data into atmospheric models. The IUPAC group continues to update and extend the set of evaluated reactions. To enhance the accessibility of this updated material to the scientific community, the evaluation is being published as a series of articles in Atmospheric Chemistry and Physics (Atkinson et al., 2004, 2006, 2007, 2008; Crowley et al., 2010; Ammann et al., 2013). We present here in Volume VIII new datasheets for gas-phase thermal and photochemical initiation reactions of organic species with four, or more, carbon atoms. The coverage of this volume includes evaluation of the thermal reactions of the organic species with HO and $NO_3$ radicals, and photolysis. The reactions with $O_3$ are included in a separate volume within this series (Cox et al., 2020), along

with the chemistry of the Criegee intermediates produced. The coverage of the evaluation was previously limited to the reactions of $\leq C_3$ organics, selected larger species (*n*-butane, isoprene, 2-methyl-but-3-en-2-ol and $\alpha$-pinene) and some related oxygenated products (Atkinson et al., 2006). This has been substantially increased to include all $C_4$ alkanes and alkenes, benzene and toluene, monoterpenes and sesquiterpenes, and related oxygenated products. This volume therefore presents evaluations for 97 new reactions, and updates for 25 reactions, of organic species with four, or more, carbon atoms.

## 2 Guide to the datasheets

For each reaction covered in this volume, a datasheet with details about e.g. experimental methods and a justification of the choice of preferred value is available in the supplementary information. The datasheets covering gas-phase reactions are principally of two types: (i) those for individual thermal reactions and (ii) those for the individual photochemical reactions.

### 2.1 Thermal reactions

The datasheets begin with a statement of the reactions including known / potential product channels when this information is available. The available kinetic data on the reactions are summarized under two headings: (i) Absolute Rate Coefficients, and (ii) Relative Rate Coefficients. Under both headings, we list the published experimental data as absolute rate coefficients. If the temperature coefficient has been measured, the results are given in a temperature dependent form over a stated temperature range. For bimolecular reactions, the temperature dependence is usually expressed in the normal Arrhenius form, $k = A \exp(-B/T)$, where B = E/R. For a few bimolecular reactions, we have listed temperature dependencies in alternative forms such as $k = C(T/298 \text{ K})^n \exp(-D/T)$ or $k = ET^2\exp(-F/T)$ where the original authors have found that alternative expressions give a better fit to the data. In our recommendations we seek to provide simple Arrhenius expressions that describe the kinetics over the atmospherically relevant temperature range (200-300 K). More complex expressions which are often needed to describe the kinetic behaviour over larger ranges of temperature are given in the Comments on Preferred Values section in the datasheets. Rate coefficients are given here in units of $cm^3$ molecule$^{-1}$ s$^{-1}$. Note that "molecule" is not a unit, but is included for clarity. For pressure dependent combination and dissociation reactions, the non-Arrhenius temperature dependence is used. This is discussed more fully in a subsequent section of this guide. Single temperature data are presented as such and wherever possible the rate coefficient at, or close to, 298 K is quoted directly as measured by the original authors. This means that the listed rate coefficient at 298 K may differ slightly from that calculated from the Arrhenius parameters determined by the same authors. Rate coefficients at 298 K marked with an asterisk indicate that the value was calculated by extrapolation of a measured temperature range which did not include 298 K. The tables of experimental data are supplemented by a series of comments summarizing the experimental details. The following abbreviations, relating to experimental techniques, are used in the Techniques and Comments sections:

115      A – absorption

API – atmospheric pressure ionization

AS – absorption spectroscopy

CCD – charge coupled detector

120      CEAS – cavity enhanced absorption spectroscopy

CIMS – chemical ionization mass spectroscopy/spectrometry

CL – chemiluminescence

CRDS – cavity ring-down spectroscopy

DF – discharge flow

125      EPR – electron paramagnetic resonance

F – flow system

FP – flash photolysis

FTIR – Fourier transform infrared

FTS – Fourier transform spectroscopy

130      GC – gas chromatography/gas chromatographic

HPLC – high-performance liquid chromatography

IBBCEAS – incoherent broad band cavity enhanced absorption spectroscopy

IR – infrared

LIF – laser induced fluorescence

135      LMR – laser magnetic resonance

LP – laser photolysis

MM – molecular modulation

MS – mass spectrometry/mass spectrometric

P – steady state photolysis

140      PLP – pulsed laser photolysis

PR – pulse radiolysis

RA – resonance absorption

RF – resonance fluorescence

RR – relative rate

145      S – static system

TDLS – tunable diode laser spectroscopy

ToF – time of flight

UV – ultraviolet

UVA – ultraviolet absorption

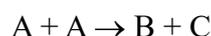
VUVA – vacuum ultraviolet absorption

For measurements of relative rate coefficients, wherever possible the comments contain the actual measured ratio of rate coefficients together with the rate coefficient of the reference reaction used to calculate the absolute rate coefficient listed in the data table. The absolute value of the rate coefficient given in the table may be different from that reported by the original author owing to a different choice of rate coefficient of the reference reaction. Whenever possible the reference rate coefficient data are those preferred in the present evaluation.

The preferred values in the datasheets are based on our consideration of the suitability of experimental method and coverage of applicable parameter space (temperature, total pressure of diluent gas, partial pressure of gas-phase species) within the atmospherically relevant range. The general approach and methods used have been reviewed recently by Cox (2012). It is recognized that preferred values may change with publication of new data, and such changes are updated at the website. The preferred rate coefficients are presented (i) at a temperature of 298 K and (ii) in temperature dependent form over a stated temperature range. This is followed by a statement of the uncertainty limits in log $k$ at 298 K and the uncertainty limits either in (E/R) or in n, for the mean temperature in the range. Some comments on the assignment of uncertainties are given later in this guide to the datasheets. The Comments on Preferred Values describe how the selection was made and give any other relevant information. The extent of the comments depends upon the present state of our knowledge of the particular reaction in question. The datasheets are concluded with a list of the relevant references.

## 2.2 Conventions concerning rate coefficients

All of the reactions in the table are elementary processes. Thus the rate expression is derived from a statement of the reaction, e.g.

$$A + A \rightarrow B + C$$

$$-\frac{1}{2}\frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{d[C]}{dt} = k[A]^2 \qquad \qquad \text{Eq. (1)}$$

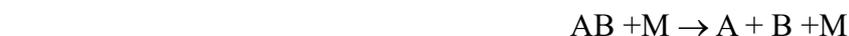
Note that the stoichiometric coefficient for A, i.e. 2, appears in the denominator before the rate of change of [A] (which is equal to $2k[A]^2$) and as a power on the right-hand side. Representations of $k$ as a function of temperature characterize simple "direct" bimolecular reactions. Sometimes it is found that $k$ also depends on the pressure and the nature of the bath gas. This may be an indication of complex-formation during the course of the bimolecular reaction, which is always the case in combination reactions. In the following sections the representations of $k$ which are adopted in these cases are explained.

**2.3 Treatment of combination and dissociation reactions**

Unlike simple bimolecular reactions such as those considered in Sect. 2.2, combination reactions

$$A + B + M \rightarrow AB + M$$

and the reverse dissociation reactions

$$AB + M \rightarrow A + B + M$$

are composed of sequences of different types of physical and chemical elementary processes. Their rate coefficients reflect the more complicated sequential mechanism and depend on the temperature, $T$, and the nature and concentration of the third body, M. In this evaluation, the combination reactions are described by a formal second-order rate law:

$$\frac{d[AB]}{dt} = k[A][B] \qquad\qquad \text{Eq. (2)}$$

while dissociation reactions are described by a formal first-order rate law:

$$\frac{-d[AB]}{dt} = k[AB] \qquad\qquad \text{Eq. (3)}$$

In both cases, $k$ depends on the temperature and on the concentration of M, i.e., [M]. To rationalize the representations of the rate coefficients used in this evaluation, we first consider the Lindemann-Hinshelwood reaction scheme. The combination reactions follow an elementary

mechanism of the form,

$$A + B \rightarrow AB^* \qquad (1)$$

$$AB^* \rightarrow A + B \qquad (-1)$$

$$AB^* + M \rightarrow AB + M \qquad (2)$$

while the dissociation reactions are characterized by:

$$AB + M \rightarrow AB^* + M \qquad (-2)$$

$$AB^* + M \rightarrow AB + M \qquad (2)$$

$$AB^* \rightarrow A + B \qquad (-1)$$

Assuming quasi-stationary concentrations for the highly excited unstable species AB* (i.e. that d[AB*]/dt $\approx$ 0), it follows that the rate coefficient for the combination reaction is given by:

$$k = k_1 \left( \frac{k_2[M]}{k_{-1} + k_2[M]} \right) \qquad \text{Eq. (4)}$$

while that for the dissociation reaction is given by:

$$k = k_{-2}[M] \left( \frac{k_{-1}}{k_{-1} + k_2[M]} \right) \qquad \text{Eq. (5)}$$

In these equations the expressions before the parentheses represent the rate coefficients of the process initiating the reaction, whereas the expressions within the parentheses denote the fraction of reaction events which, after initiation, complete the reaction to products. In the low pressure limit ([M] $\rightarrow$ 0) the rate coefficients are proportional to [M]; in the high pressure limit ([M] $\rightarrow$ $\infty$) they are independent of [M]. It is useful to express $k$ in terms of the limiting low pressure and high pressure rate coefficients,

$$k_0 = \lim k([M]) \text{ for } [M] \rightarrow 0 \text{ and } k_\infty = \lim k([M]) \text{ for } [M] \rightarrow \infty \qquad \text{Eq. (6)}$$

From this convention, the Lindemann-Hinshelwood equation is obtained

$$k = \frac{k_0 k_\infty}{k_0 + k_\infty} \qquad \text{Eq. (7)}$$

It follows that, for combination reactions, $k_0 = k_1 k_2[M] / k_{-1}$ and $k_\infty = k_1$, while, for dissociation

reactions, $k_0 = k_{-2}[M]$ and $k_\infty = k_{-1}k_{-2} / k_2$. Since detailed balancing applies, the ratio of the rate coefficients for combination and dissociation at a fixed $T$ and [M] is given by the equilibrium constant $K_c = k_1k_2 / k_{-1}k_{-2}$.

250  Starting from the high-pressure limit, the rate coefficients fall off with decreasing third body concentration [M] and the corresponding representation of $k$ as a function of [M] is termed the "falloff curve" of the reaction. In practice, the above Lindemann-Hinshelwood expressions do not suffice to characterize the falloff curves completely. Because of the multistep character of the collisional deactivation ($k_2[M]$) and activation ($k_{-2}[M]$) processes, and energy- and angular

255  momentum-dependences of the association ($k_1$) and dissociation ($k_{-1}$) steps, as well as other phenomena, the falloff expressions have to be modified. This can be done by including a broadening factor $F$ to the Lindemann-Hinshelwood expression (Troe, 1979):

$$k = \frac{k_0 k_\infty}{k_0 + k_\infty} F = k_0 \left(\frac{1}{1+x}\right) F = k_\infty \left(\frac{x}{1+x}\right) F \qquad \text{Eq. (8)}$$

260

The broadening factor $F$ depends on the ratio $x = k_0/k_\infty$, which is proportional to [M], and can be used as a measure of "reduced pressure". The first factors on the right-hand side represent the Lindemann-Hinshelwood expression and the additional broadening factor $F$, at not too high temperatures, is approximately given by (Troe, 1979):

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$$\log F \cong \frac{\log F_c}{1 + [\log(k_0/k_\infty)/N]^2} \qquad \text{Eq. (9)}$$

where $\log = \log_{10}$ and $N \approx [0.75 - 1.27 \log F_c]$.

270  When $F_c$ decreases, the falloff curve broadens and becomes asymmetric (i.e. $F(k_0/k_\infty) \neq F(k_\infty/k_0)$). The given equation for $F$ then becomes insufficient and should be replaced, e.g. by

$$F(x) \approx (1+x)/(1+x^n)^{1/n} \qquad \text{Eq. (10)}$$

275  where $x = k_0/k_\infty$, $n = [\ln 2 / \ln(2/F_c)] [0.8 + 0.2 x^q]$, $q = (F_c - 1) / \ln(F_c/10)$ and $\ln = \log_e$ (Troe and Ushakov, 2014). While the former equation for $\log F$ appears acceptable as long as $F_c \geq 0.6$, the latter equation for $F$ should be used for $F_c \leq 0.6$. With these equations, falloff curves are represented in terms of the three parameters $k_0$ (being proportional to [M]), $k_\infty$, and $F_c$.

The parameters $k_0$, $k_\infty$, and $F_c$ depend on details of the intra- and intermolecular dynamics and in principle can be calculated. If the required information is not available, one has to obtain them by fitting experimental falloff curves with the expressions given above. Nevertheless, one may estimate $F_c$ to be typically of the order of 0.49, 0.44, 0.39, and 0.35, if the reactants A and B in total have $r = 3, 4, 5$, and 6 external rotational degrees of freedom, respectively (Cobos and Troe, 2003; for the reaction HO + NO$_2$ + M , e.g. one would have $r = 5$ and $F_c \approx 0.39$); $F_c$ may be lower, if low frequency vibrations in A or B are relevant in addition to the rotations and if collisions are inefficient. Over the range 200 – 300 K often one can neglect a temperature dependence of $F_c$ (for detailed calculations of $F_c$, including a dependence on the bath gas M, see e.g. Troe 1983; Troe and Ushakov, 2011, 2014). The accuracy of $F(x)$ as given above is estimated to be about 10 percent. Larger differences between experimentally fitted $F_c$ often are an indication for inadequate falloff extrapolations to $k_0$ and/or $k_\infty$. In this case, the apparent values for $k_0$, $k_\infty$, and $F_c$ still can provide a satisfactory representation of the considered experimental data, in spite of the fact that $k_0$ and/or $k_\infty$ are not the real limiting values. If falloff curves are fitted in different ways, changes in $F_c$ require changes in the limiting $k_0$ and $k_\infty$. In the present evaluation, we generally follow the experimentally fitted values for $k_0$, $k_\infty$, and $F_c$, provided that $F_c$ does not differ too much from the standard values given above and theoretically modelled values. If large deviations are encountered, the experimental data are re-evaluated using $F_c$ -values as given above. Values of $k_\infty$ for combination reactions without a barrier often have only weak temperature dependences which in practice can be neglected.

Besides the energy-transfer mechanism, i.e., reactions (1), (-1), and (2), a second mechanism may become relevant for some reactions considered here. This is the radical-complex (or chaperon) mechanism

$$A + M \rightarrow AM \qquad\qquad (3)$$

$$AM \rightarrow A + M \qquad\qquad (-3)$$

$$B + AM \rightarrow AB + M \qquad\qquad (4)$$

which, in the low pressure range, leads to $k_0 = (k_3 / k_{-3})k_4$ [M]. For some tri- and tetra-atomic adducts AB, e.g., O + O$_2$ → O$_3$ and HO + C$_6$H$_6$ → HOC$_6$H$_6$, the value of $k_0$ may exceed that from the energy-transfer mechanism and show stronger temperature dependences (Luther et al., 2005; Teplukhin and Babikov, 2016). This mechanism may also influence high pressure experiments when $k_0$ from the radical-complex mechanism exceeds $k_\infty$ from the energy-transfer mechanism (Oum et al., 2003). In this case falloff over wide pressure ranges cannot be

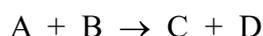
represented by contributions from the energy-transfer mechanism alone, in particular when measurements at pressures above about 10 bar are taken into consideration.

315     The dependence of $k_0$ and $k_\infty$ on the temperature $T$ is represented in the form $k \propto T^{-n}$ except for cases with an established energy barrier in the potential. We have used this form of temperature dependence because it usually gives a better fit to the data over a wider range of temperature than does the Arrhenius expression. It should be emphasised that the chosen form of the temperature dependence is often only adequate over limited temperature ranges such as 200–

320     300 K. Obviously, the relevant values of $n$ are different for $k_0$ and $k_\infty$. In this evaluation, values of $k_0$ are given for selected examples of third bodies M, and if possible for M = $N_2$, $O_2$, or air.

**2.4 Treatment of complex-forming bimolecular reactions**

325     Bimolecular reactions may follow the "direct" pathway

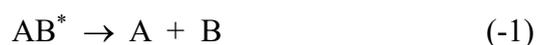
$$A + B \rightarrow C + D$$

and/or involve complex-formation, in the simplest way characterized by the steps

330

$$A + B \rightarrow AB^* \qquad\qquad (1)$$

$$AB^* \rightarrow A + B \qquad\qquad (-1)$$

335     $$AB^* \rightarrow C + D \qquad\qquad (5)$$

$$AB^* + M \rightarrow AB + M \qquad\qquad (2)$$

(there may be additional pathways following from AB*; direct and complex-forming pathways

340     may or may not be coupled). Assuming quasi-stationary concentrations of AB* (i.e. that $d[AB^*]/dt \approx 0$ as in section 2.3), a Lindemann-Hinshelwood type analysis leads to

$$d[AB]/dt = k_{Ass} [A] [B] \qquad\qquad \text{Eq. (11)}$$

$$d[C]/dt = d[D]/dt = k_{CA} \, [A] \, [B] \qquad\qquad \text{Eq. (12)}$$

$$d[A]/dt = - \, (\, k_{Ass} + k_{CA} \,) \, [A] \, [B] \qquad\qquad \text{Eq. (13)}$$

The rate constants for association ($k_{Ass}$) and for chemical activation leading to product formation ($k_{CA}$) then are given by

$$k_{Ass} = k_1 \, k_2 \, [M] \, / (\, k_{-1} + k_2 \, [M] + k_5) \qquad\qquad \text{Eq. (14)}$$

$$k_{CA} = k_1 \, k_5 \, / (\, k_{-1} + k_2 \, [M] + k_5) \qquad\qquad \text{Eq. (15)}$$

Note that $k_{Ass}$ and $k_{CA}$ are dependent on the nature and concentration of the third body M, in addition to their temperature dependence. In reality, as for combination and dissociation reactions, the given expressions for $k_{Ass}$ and $k_{CA}$ have to be extended by suitable broadening factors $F$ to account for the multistep character of processes (2) and the energy- and angular momentum-dependences of processes (1), (-1), and (5). These broadening factors, however, generally differ for $k_{Ass}$ and $k_{CA}$; also they generally differ from those of simple combination reactions described in section 2.3. One should note that association and chemical activation here are coupled such that their joint treatment is complicated. Some simplification is reached when the processes first are treated separately and the coupling is introduced at the end (Troe, 2015). The corresponding rate constants of the separated processes are denoted by $k_{Ass}*$ and $k_{CA}*$ and are given by

$$k_{Ass}* = k_1 \, k_2 \, [M] \, / \, (k_{-1} + k_2 \, [M]) \qquad\qquad \text{Eq. (16)}$$

and

$$k_{CA}* = k_1 \, k_5 \, / \, (k_2 \, [M] + k_5). \qquad\qquad \text{Eq. (17)}$$

$k_{Ass}*$ then corresponds to the rate constant of a combination reaction described in section 2.3 and has a broadening factor $F_{Ass}*(x*)$. $k_{CA}*$ has to be treated in a different way and is expressed in the form

$$k_{CA}* = k_{Ass,\infty} \, [\, 1/ \, (1 + x*)] \, F_{CA}*(x^*) \qquad\qquad \text{Eq. (18)}$$

380 with $x^* = k_{Ass,\infty}$ [M] $/ k_{CA,\infty}^*$ and a broadening factor $F_{CA}^*(x)$ (Stewart et al., 1989). The latter

factor is generally larger than $F_{Ass}^*(x^*)$ (Troe, 2015). The rate parameters $k_{CA,0}^*$ and $k_{CA,\infty}^*$

depend on the molecular parameters and can be calculated theoretically or fitted experimentally

(after the coupling between association and chemical activation has been accounted for). In

practice one may try to represent the rate constants in the form of rate constants of separated

385 processes $k_{Ass}^*$ and $k_{CA}^*$. Coupling these rate constants then leads to a full representation of the

rate constants in terms of the six rate parameters $k_{Ass,0}$, $k_{Ass,\infty}$, $F_{Ass,c}$, $k_{CA,0}$, $k_{CA,\infty}$, and $F_{CA,c}$. If

one neglects the coupling and fits these parameters directly from the experiments (Miller and

Klippenstein, 2001), however, one has to be aware of the fact that the values obtained do not

correspond to those of separated, single-channel, association and chemical activation processes

390 (for more details, see Troe, 2015).

As a consequence of the multistep character of complex-forming bimolecular reactions, a

variety of temperature - and pressure – dependences of $k_{Ass}$ and $k_{CA}$ are observed. The low

pressure limit of the total rate constants $k_{tot} = k_{Ass} + k_{CA}$, i.e., $k_{tot,0} = k_{CA,0} = k_1 k_5 / (k_{-1} + k_5)$, because

395 of different energy – and angular momentum – dependences of the specific rate constants $k_1$,

$k_{-1}$, and $k_5$, may increase or decrease with temperature, the latter with the possibility to a change

with an increase above a certain temperature. $k_{tot}$, as given above, may increase with pressure

from $k_{CA,0}$ to $k_1$, with M = $H_2O$ often being a particularly efficient third body in the pressure –

dependent range. The pressure dependence generally becomes less apparent with increasing

400 temperature. Finally, the further fate of an addition product AB is of importance. It may be

collisionally reactivated to energies where $k_5 \gg k_{-1}$, such that formation of C + D is enhanced

(in comparison to energies where $k_5 \ll k_{-1}$). There is also the possibility that A-M  (or B-M)

complexes are formed which react in a chaperon mechanism with B (or A) and then form

products. M = $H_2O$ here again may be particularly efficient. Without detailed theoretical

405 analysis, in general, it will be difficult to disentangle the intrinsic mechanism. Therefore,

reference to theoretical work is given for selected reactions.

## 2.5 Photochemical reactions

410 The datasheets begin with a list of feasible primary photochemical processes for wavelengths

usually down to 185 nm, along with the corresponding enthalpy changes at 0 K where possible

or alternatively at 298 K. Calculated threshold wavelengths corresponding to these enthalpy changes are also listed, bearing in mind that the values calculated from the enthalpy changes at 298K are not true "threshold values". This is followed by tables which summarise the available

415      experimental data for: (i) absorption cross sections and (ii) quantum yields. These data are supplemented by a series of comments. The next table lists the preferred absorption cross section data and the preferred quantum yields at appropriate wavelength intervals. For absorption cross sections the intervals are usually 1 nm, 5 nm or 10 nm. Any temperature dependence of the absorption cross sections is also given where possible. The aim in presenting

420      these preferred data is to provide a basis for calculating atmospheric photolysis rates. For absorption continua the temperature dependence is often represented by Sulzer-Wieland type expressions (Astholz et al., 1981). Alternately a simple empirical expression of the form: $\log_{10}(\sigma_{T1}/\sigma_{T2}) = B*(T_1-T_2)$ is used. The comments again describe how the preferred data were selected and include other relevant points. The photochemical datasheets are concluded with a

425      list of references.

**2.6 Conventions concerning absorption cross sections**

These are presented in the datasheets as "absorption cross sections per molecule, base e." They

430      are defined according to the equation:

$$I / I_0 = \exp(-\sigma[N]l) \hspace{3cm} \text{Eq. (19)}$$

where $I_0$ and $I$ are the incident and transmitted light intensities, [N] is the number concentration

435      of absorber (expressed in molecule $cm^{-3}$), $l$ is the path length (expressed in cm), and $\sigma$ is the absorption cross section (units of $cm^2$ $molecule^{-1}$). Note that "molecule" is not a unit but is included here for clarity. Other definitions and units are frequently quoted. The closely related quantities "absorption coefficient" and "extinction coefficient" are often used, but care must be taken to avoid confusion in their definition, see Calvert (1990) for definitions and discussion.

440      It is always necessary to know the units of concentration and of path length and the type of logarithm (base e or base 10) corresponding to the definition. The decadic molar absorption coefficient, $\varepsilon$, is often quoted, particularly in the older literature, and is defined as:

$$\varepsilon = \{1/([A]l)\}\log_{10}(I_0/I), \hspace{3cm} \text{Eq. (20)}$$

where [A] is the concentration of the absorber expressed in units of moles per liter. While $\varepsilon$ is

often called an extinction coefficient, the term "extinction" should more properly be used for the sum of absorption and scattering. To convert from $\varepsilon$ (base 10, units of $dm^3$ $mol^{-1}$ $cm^{-1}$) to $\sigma$ (base e, units of $cm^2$ $molecule^{-1}$) multiply by $3.82 \times 10^{-20}$.

**2.7 Assignment of uncertainties**

Under the heading "reliability," estimates have been made of the absolute accuracies of the preferred values of $k$ at 298 K and of the preferred values of E/R over the quoted temperature range. The accuracy of the preferred rate coefficient at 298 K is quoted as the term $\Delta \log k$, where $\Delta \log k = d$ and $d$ is defined by the equation, $\log k = c \pm d$. This is equivalent to the statement that $k$ is uncertain to a factor of $f$, where $d = \log f$. The accuracy of the preferred value of E/R is quoted as the term $\Delta(E/R)$, where $\Delta(E/R) = g$ and $g$ is defined by the equation E/R = $h \pm g$. $d$ and $g$ are uncertainties corresponding approximately to 95% confidence limits. For second-order rate coefficients listed in this evaluation, an estimate of the uncertainty at any given temperature within the recommended temperature range may be obtained from the equation:

$$\Delta \log k(T) = \Delta \log k(298 \text{ K}) + 0.4343\{\Delta E/R(1/T - 1/298 \text{ K})\} \qquad \text{Eq. (21)}$$

The assignment of these absolute uncertainties in $k$ and E/R is our subjective assessment. They are not determined by a rigorous, statistical analysis of the database, which is generally too limited to permit such an analysis. Rather, the uncertainties are based on our knowledge of the techniques, the difficulties of the experimental measurements, the potential for systematic errors, and the number of studies conducted and their agreement or lack thereof. Experience shows that for rate measurements of atomic and free radical reactions in the gas phase, the precision of the measurement, i.e. the reproducibility, is usually good. Thus, for single studies of a particular reaction involving one technique, standard deviations, or even 95% confidence limits, of ±10% or less are frequently reported in the literature. However, when we compare data for the same reaction studied by more than one group of investigators and involving different techniques, the rate coefficients sometimes differ by a factor of 2 or even more. This can only mean that one or more of the studies has involved large systematic uncertainty which is difficult to detect. The differences between various measurements could be due to multiple reasons, such as insufficient purity of compounds, unknown/unexpected impurities, wall

adsorption and decomposition, insufficient time resolution for the initial elementary step, opposing and parallel reactions or unexpected decomposition products from the primary product. This is hardly surprising since, unlike molecular reactions, it is not always possible to study atomic and free radical reactions in isolation, and consequently mechanistic and other difficulties frequently arise. On the whole, our assessment of uncertainty limits tends towards the cautious side. Thus, in the case where a rate coefficient has been measured by a single investigation using one particular technique and is unconfirmed by independent work, we typically suggest an uncertainty of a factor of 2.

In contrast to the usual situation for the rate coefficients of thermal reactions, where inter-comparison of results of a number of independent studies permits a realistic assessment of reliability, for many photochemical processes there is a scarcity of data. Thus, we do not feel justified at present in assigning uncertainty limits to the parameters reported for the photochemical reactions.

**Author contribution**: All authors defined the scope of the work. AM, TJW, JNC, MEJ and RAC developed and drafted the data sheets and manuscript. All authors reviewed, refined, and revised the manuscript and data sheets.

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## References

510

Ammann, M., Cox, R. A., Crowley, J. N., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VI – heterogeneous reactions with liquid substrates, Atmos. Chem. Phys., 13, 8045-8228, 2013.

515 Astholz, D. C., Brouwer, L. and Troe, J.: High-temperature ultraviolet-absorption spectra of polyatomic molecules in shock waves, Ber. Bunsenges. Phys. Chem., 85, 559–564, 1981.

Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, Jr., R. F., Kerr, J. A., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement III, IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, J. Phys. Chem.

520 Ref. Data, 18, 881–1097, 1989.

Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, Jr., R. F., Kerr, J. A. and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement IV, IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, J. Phys. Chem. Ref. Data, 21, 1125–1568, 1992.

525 Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, Jr., R. F., Kerr, J. A., Rossi, M. and Troe, J.: Evaluated kinetic, photochemical, and heterogeneous data for atmospheric chemistry: Supplement V, IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, J. Phys. Chem. Ref. Data, 26, 521–1011, 1997a.

Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, Jr., R. F., Kerr, J. A., Rossi, M. J. and Troe,

530 J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement VI, IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, J. Phys. Chem. Ref. Data, 26, 1329–1499, 1997b.

Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, Jr., R. F., Kerr, J. A., Rossi, M. J. and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement VII,

535 IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, J. Phys. Chem. Ref. Data, 28, 191–393, 1999.

Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, Jr., R. F., Kerr, J. A., Rossi, M. J. and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry, Supplement VIII, IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, J. Phys.

540 Chem. Ref. Data, 29, 167–266, 2000.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J. and Troe, J.: Evaluated kinetic and photochemical data for atmospheric

chemistry: Volume I - gas phase reactions of $O_x$, $HO_x$, $NO_x$, and $SO_x$ species, Atmos. Chem. Phys., 4, 1461-1738, 2004.

545    Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J. and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II - gas phase reactions of organic species, Atmos. Chem. Phys., 6, 3625-4055, 2006.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin,
550    M. E., Rossi, M. J. and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume III - gas phase reactions of inorganic halogens, Atmos. Chem. Phys., 7, 981-1191, 2007.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J. and Wallington, T. J.: Evaluated kinetic and photochemical data
555    for atmospheric chemistry: Volume IV - gas phase reactions of organic halogen species, Atmos. Chem. Phys., 8, 4141-4496, 2008.

Baulch, D. L., Cox, R. A., Hampson, Jr., R. F., Kerr, J. A., Troe, J. and Watson, R. T.: Evaluated kinetic and photochemical data for atmospheric chemistry, CODATA Task Group on Chemical Kinetics, J. Phys. Chem. Ref. Data, 9, 295–471, 1980.

560    Baulch, D. L., Cox, R. A., Crutzen, P. J., Hampson, Jr., R. F., Kerr, J. A., Troe, J. and Watson, R. T.: Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement I, CODATA Task Group on Chemical Kinetics, J. Phys. Chem. Ref. Data, 11, 327–496, 1982.

Baulch, D. L., Cox, R. A., Hampson, Jr., R. F., Kerr, J. A., Troe, J. and Watson, R. T.: Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement II, CODATA Task
565    Group on Gas Phase Chemical Kinetics, J. Phys. Chem. Ref. Data, 13, 1259–1380, 1984.

Calvert, J. G.: Glossary of atmospheric chemistry terms, Pure & App. Chem., 62, 2167-2219, 1990.

Cobos, C. J. and Troe, J.: Prediction of reduced falloff curves for recombination reactions at low temperatures, Z. Phys. Chem., 217, 1–14, 2003.

570    Cox, R. A.: Evaluation of laboratory kinetics and photochemical data for atmospheric chemistry applications, Chem. Soc. Rev., 41, 6231-6246, 2012.

Cox, R. A., Ammann, M., Crowley, J. N., Herrmann, H., Jenkin, M. E., McNeill, V. F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.: IUPAC in the (real) clouds: 40 years of evaluating atmospheric chemistry data, Chemistry International, 40, 52, 2018.

575    Cox, R. A., Ammann, M., Crowley, J. N., Herrmann, H., Jenkin, M. E., McNeill, V. F., Mellouki, A., Troe, J. and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric

chemistry: Volume VII – Criegee intermediates, Atmos. Chem. Phys., 20, 13497–13519, 2020.

Crowley, J. N., Ammann, M., Cox, R. A., Hynes, R. G., Jenkin, M. E., Mellouki, A., Rossi, M.
580     J., Troe, J. and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume V – heterogeneous reactions on solid substrates, Atmos. Chem. Phys., 10, 9059-9223, 2010.

Luther, K., Oum, K. and Troe, J.: The role of the radical-complex mechanism in the ozone recombination/dissociation reaction, Phys. Chem. Chem. Phys., 7, 2764-2770, 2005.

585     Miller, J. and Klippenstein, S. J.: The reaction between ethyl and molecular oxygen: Further analysis, Int. J. Chem. Kinet. 33, 654– 668, 2001.

Oum, K., Sekiguchi, K., Luther, K. and Troe, J.: Observation of unique pressure effects in the combination reaction of benzyl radicals in the gas to liquid transition region, Phys. Chem. Chem. Phys., 5, 2931–2933, 2003.

590     Stewart, P. H., Larson, C. W. and Golden, D. M.: Pressure and temperature dependence of reactions proceeding via a bound complex. 2. An application to $2 \, CH_3 \rightarrow C_2H_5 + H$, Combust. Flame, 75, 25 – 31, 1989.

Teplukhin, A. and Babikov, D.: A full-dimensional model of ozone forming reaction: the absolute value of the recombination rate coefficient, its pressure and temperature
595     dependencies, Phys. Chem. Chem. Phys., 18, 19194 – 19206, 2016.

Troe, J.: Predictive possibilities of unimolecular rate theory, J. Phys. Chem., 83, 114 – 126, 1997.

Troe, J.: Theory of thermal unimolecular reactions in the fall-off range. I. Strong collision rate constants, Ber. Bunsenges. Phys. Chem., 87, 161-169, 1983.

600     Troe, J. and Ushakov, V. G.: Revisiting falloff curves of thermal unimolecular reactions, J. Chem. Phys., 135, 054304, 2011.

Troe, J. and Ushakov, V. G.: Representation of "Broad" Falloff Curves for Dissociation and Recombination Reactions, Z. Phys. Chem., 228, 1 – 10, 2014.

Troe, J.: Simplified representation of partial and total rate constants of complex-forming
605     bimolecular reactions, J. Phys. Chem. A, 119, 12159 – 12165, 2015.

**Table 1. Summary of recommended rate coefficients for organic ($\geq C_4$) reactions**

| Reaction number | Reaction | $k_{298}$ cm³ molecule⁻¹ s⁻¹ | $\Delta \log k^a_{298}$ | Temp. dependence of $k$/cm³molecule⁻¹ s⁻¹ | Temp. range/K | $\Delta(E/R)/K^a$ |
|---|---|---|---|---|---|---|
| *HO reactions based on datasheets in Supplement and on the IUPAC website updated in 2019* | | | | | | |
| HOx_VOC7 | HO + *n*-butane → H₂O + CH₂CH₂CH₂CH₃ | | | | | |
| | → H₂O + CH₃CHCH₂CH₃ | | | | | |
| | **Overall** | $2.35 \times 10^{-12}$ | ± 0.06 | $9.8 \times 10^{-12}\exp(-425/T)$ | 180-300 | ± 100 |
| HOx_VOC8 | HO + isoprene → products | $1.0 \times 10^{-10}$ | ± 0.06 | $2.1 \times 10^{-11}\exp(465/T)$ | 240-630 | ± 150 |
| HOx_VOC9 | HO + $\alpha$-pinene → products | $5.3 \times 10^{-11}$ | ± 0.08 | $1.3 \times 10^{-11}\exp(410/T)$ | 240-360 | ± 100 |
| HOx_VOC14 | HO + *n*-butanal → products | $2.3 \times 10^{-11}$ | ± 0.08 | $5.8 \times 10^{-12}\exp(410/T)$ | 250-430 | ± 250 |
| HOx_VOC15 | HO + methacrolein → products | $3.0 \times 10^{-11}$ | ± 0.08 | $8.4 \times 10^{-12}\exp(380/T)$ | 230-380 | ± 100 |
| HOx_VOC20 | HO + 2-butanone → products | $1.1 \times 10^{-12}$ | ± 0.10 | $1.5 \times 10^{-12}\exp(-90/T)$ | 210-300 | ± 200 |
| HOx_VOC21 | HO + methyl vinyl ketone → products | $2.0 \times 10^{-11}$ | ± 0.10 | $2.6 \times 10^{-12}\exp(610/T)$ | 230-380 | ± 200 |
| HOx_VOC22 | HO + pinonaldehyde → products | $3.9 \times 10^{-11}$ | ± 0.15 | $5.2 \times 10^{-12}\exp(600/T)$ | 230-380 | ± 300 |
| HOx_VOC27 | HO + 1-butanol → products | $8.5 \times 10^{-12}$ | ± 0.06 | $5.3 \times 10^{-12}\exp(140/T)$ | 260-380 | ± 200 |
| HOx_VOC28 | HO + 2-butanol → products | $8.7 \times 10^{-12}$ | ± 0.08 | | | |
| HOx_VOC29 | HO + 2-methyl-3-buten-2-ol → products | $6.3 \times 10^{-11}$ | ± 0.08 | $8.1 \times 10^{-12}\exp(610/T)$ | 230-300 | ± 200 |
| HOx_VOC31 | HO + 3-methylfuran → products | $9.3 \times 10^{-11}$ | ± 0.15 | | | |
| HOx_VOC33 | HO + 2-hydroxy-2-methylpropanal → products | $1.4 \times 10^{-11}$ | ± 0.10 | | | |
| HOx_VOC42 | HO + 1-butyl nitrate → products | $1.6 \times 10^{-12}$ | ± 0.06 | | | |
| HOx_VOC43 | HO + 2-butyl nitrate → products | $8.6 \times 10^{-13}$ | ± 0.15 | | | |
| HOx_VOC46 | HO + 1-nitrooxy-2-butanone → products | $8.2 \times 10^{-13}$ | ± 0.30 | | | |
| HOx_VOC47 | HO + 3-nitrooxy-2-butanone → products | $1.2 \times 10^{-12}$ | ± 0.30 | | | |
| HOx_VOC48 | HO + 2-Methyl-1-(nitroperoxy)-2-propen-1-one → products | $2.9 \times 10^{-11}$ | $^{+0.2}_{-0.5}$ | | | |
| HOx_VOC60 | HO + 2-methylpropane → H₂O + (CH₃)₃C | | | | | |
| | → H₂O + (CH₃)₂CHCH₂ | | | | | |
| | **Overall** | $2.1 \times 10^{-12}$ | ± 0.04 | $5.4 \times 10^{-12}\exp(-285/T)$ | 210-300 | ± 150 |
| HOx_VOC61 | HO + 2-methylpropene → products | $5.1 \times 10^{-11}$ | ± 0.04 | $9.4 \times 10^{-12}\exp(505/T)$ | 290-430 | ± 200 |
| HOx_VOC62 | HO + 1-butene → products | $3.1 \times 10^{-11}$ | ± 0.06 | $6.6 \times 10^{-12}\exp(465/T)$ | 290-430 | ± 150 |
| HOx_VOC63 | HO + *cis*-2-butene → products | $5.6 \times 10^{-11}$ | ± 0.10 | $1.1 \times 10^{-11}\exp(485/T)$ | 290-430 | ± 200 |
| HOx_VOC64 | HO + *trans*-2-butene → products | $7.1 \times 10^{-11}$ | ± 0.06 | $1.1 \times 10^{-11}\exp(553/T)$ | 290-430 | ± 200 |
| HOx_VOC66 | HO + biacetyl → products | $2.3 \times 10^{-13}$ | ± 0.06 | $5.25 \times 10^{-13}\exp(-243/T)$ | 240-350 | ± 50 |
| HOx_VOC67 | HO + *n*-butanoic acid → products | $1.8 \times 10^{-12}$ | ± 0.15 | | | |
| HOx_VOC68 | HO + *i*-butanal → products | $2.6 \times 10^{-11}$ | ± 0.04 | $6.8 \times 10^{-12}\exp(410/T)$ | 240-425 | ± 60 |
| HOx_VOC69 | HO + 2-methyl-1-propanol → products | $8.9 \times 10^{-12}$ | ± 0.08 | $2.73 \times 10^{-12}\exp(352/T)$ | 240-370 | ± 120 |
| HOx_VOC70 | HO + 2-methyl-2-propanol → products | $1.1 \times 10^{-12}$ | ± 0.06 | $1.6 \times 10^{-12}\exp(-121/T)$ | 240-314 | ± 75 |
| HOx_VOC76 | HO + 2-hydroxybutanal → C₂H₅CH(OH)CO + H₂O | | | | | |
| | → C₂H₅C(OH)CHO + H₂O | | | | | |
| | **Overall** | $2.4 \times 10^{-11}$ | ± 0.10 | | | |
| HOx_VOC77 | HO + 1-nitrooxy-2-butanol → products | $7.0 \times 10^{-12}$ | ± 0.20 | | | |
| HOx_VOC78 | HO + 2-nitrooxy-1-butanol → products | $7.4 \times 10^{-12}$ | ± 0.20 | | | |
| HOx_VOC79 | HO + 3-hydroxy-2-butanone | | | | | |
| | → H₂O + CH₃C(O)C(OH)CH₃ | | | | | |
| | → products | | | | | |
| | **Overall** | $9.7 \times 10^{-12}$ | ± 0.10 | $1.24 \times 10^{-12}\exp(612/T)$ | 280-350 | ± 350 |

| | | | | | |
|---|---|---|---|---|---|
| HOx_VOC84 | HO + α-terpinene → products | $3.5 \times 10^{-10}$ | $\pm 0.08$ | | |
| HOx_VOC85 | HO + γ-terpinene → products | $1.7 \times 10^{-10}$ | $\pm 0.10$ | | |
| HOx_VOC86 | HO + terpinolene → products | $2.2 \times 10^{-10}$ | $\pm 0.15$ | | |
| HOx_VOC87 | HO + α-phellandrene → products | $3.2 \times 10^{-10}$ | $\pm 0.08$ | | |
| HOx_VOC88 | HO + β-phellandrene → products | $1.7 \times 10^{-10}$ | $\pm 0.15$ | | |
| HOx_VOC89 | HO + α-cedrene → products | $6.7 \times 10^{-11}$ | $\pm 0.10$ | | |
| HOx_VOC90 | HO + longifolene → products | $4.7 \times 10^{-11}$ | $\pm 0.10$ | | |
| HOx_VOC91 | HO + α-copaene → products | $9.0 \times 10^{-11}$ | $\pm 0.10$ | | |
| HOx_VOC92 | HO + β-caryophyllene → products | $2.0 \times 10^{-10}$ | $\pm 0.15$ | | |
| HOx_VOC93 | HO + α-humulene → products | $2.9 \times 10^{-10}$ | $\pm 0.10$ | | |
| HOx_VOC99 | HO + β-pinene → products | $7.6 \times 10^{-11}$ | $\pm 0.05$ | $1.62 \times 10^{-11}\exp(460/T)$ | 240-420 | $\pm 150$ |
| HOx_VOC100 | HO + limonene → products | $1.65 \times 10^{-10}$ | $\pm 0.05$ | $3.41 \times 10^{-11}\exp(470/T)$ | 220-360 | $\pm 150$ |
| HOx_VOC101 | HO + camphene → products | $5.2 \times 10^{-11}$ | $\pm 0.10$ | $4.14 \times 10^{-12}\exp(754/T)$ | 280-320 | $\pm 100$ |
| HOx_VOC102 | HO + 2-carene → products | $8.0 \times 10^{-11}$ | $\pm 0.15$ | | |
| HOx_VOC103 | HO + 3-carene → products | $8.3 \times 10^{-11}$ | $\pm 0.06$ | $2.5 \times 10^{-11}\exp(357/T)$ | 230-360 | $\pm 50$ |
| HOx_VOC104 | HO + β-myrcene → products | $2.1 \times 10^{-10}$ | $\pm 0.15$ | | |
| HOx_VOC105 | HO + β-ocimene → products | $2.8 \times 10^{-10}$ | $\pm 0.15$ | $4.0 \times 10^{-11}\exp(579/T)$ | 310-430 | $\pm 150$ |
| HOx_VOC106 | HO + β-sabinene → products | $1.2 \times 10^{-10}$ | $\pm 0.15$ | | |
| HOx_VOC107 | HO + α-farnesene → products | $2.2 \times 10^{-10}$ | $\pm 0.30$ | $2.2 \times 10^{-10}$ | 298-430 | $\pm 200$ |
| HOx_VOC108 | HO + β-farnesene → products | $2.3 \times 10^{-10}$ | $\pm 0.30$ | $2.3 \times 10^{-10}$ | 298-430 | $\pm 200$ |
| HOx_VOC109 | HO + α-terpineol → products | $1.9 \times 10^{-10}$ | $\pm 0.30$ | | |
| HOx_AROM1 | HO + benzene → $H_2O + C_6H_5$ | $8 \times 10^{-15}$ | $\pm 0.50$ | $3.8 \times 10^{-11}\exp(-2520/T)$ | 330-1410 | $\pm 300$ |
| | → $HOC_6H_6$ | | | | |
| | **Overall** | $1.2 \times 10^{-12}$ | $\pm 0.06$ | $2.3 \times 10^{-12}\exp(-190/T)$ | 230-350 | $\pm 200$ |
| HOx_AROM2 | HO + toluene → $H_2O + C_6H_5CH_2$ | $3.5 \times 10^{-13}$ | $\pm 0.20$ | $2.5 \times 10^{-11}\exp(-1270/T)$ | 310-1050 | $\pm 200$ |
| | → $HOC_6H_5CH_3$ | | | | |
| | **Overall** | $5.6 \times 10^{-12}$ | $\pm 0.06$ | $1.8 \times 10^{-12}\exp(340/T)$ | 210-350 | $\pm 200$ |
| HOx_AROM3 | HO + m-cresol → $H_2O + CH_3C_6H_4O$ | | | | |
| | → $H_2O + CH_2C_6H_4OH$ | | | | |
| | → $CH_3C_6H_4(OH)_2$ | | | | |
| | **Overall** | $6.2 \times 10^{-11}$ | $\pm 0.10$ | $2.4 \times 10^{-12}\exp(965/T)$ | 290-350 | $\pm 600$ |
| HOx_AROM4 | HO + o-cresol → $H_2O + CH_3C_6H_4O$ | | | | |
| | → $H_2O + CH_2C_6H_4OH$ | | | | |
| | → $CH_3C_6H_4(OH)_2$ | | | | |
| | **Overall** | $4.2 \times 10^{-11}$ | $\pm 0.10$ | $1.6 \times 10^{-12}\exp(970/T)$ | 290-350 | $\pm 600$ |
| HOx_AROM5 | HO + p-cresol → $H_2O + CH_3C_6H_4O$ | | | | |
| | → $H_2O + CH_2C_6H_4OH$ | | | | |
| | → $CH_3C_6H_4(OH)_2$ | | | | |
| | **Overall** | $4.8 \times 10^{-11}$ | $\pm 0.10$ | $1.9 \times 10^{-12}\exp(970/T)$ | 290-350 | $\pm 600$ |
| HOx_AROM6 | HO + phenol → $H_2O + C_6H_5O$ | | | | |
| | → $H_2O + C_6H_4OH$ | | | | |
| | → $HOC_6H_5OH$ | | | | |
| | **Overall** | $2.8 \times 10^{-11}$ | $\pm 0.08$ | $4.7 \times 10^{-13}\exp(1220/T)$ | 290-350 | $\pm 600$ |
| HOx_AROM7 | HO + 1,2-dihydroxybenzene → products | $1.0 \times 10^{-10}$ | $\pm 0.15$ | | |
| HOx_AROM8 | HO + 1,2-dihydroxy-3-methylbenzene → products | $2.0 \times 10^{-10}$ | $\pm 0.15$ | | |

| | | | | | |
|---|---|---|---|---|---|
| HOx_AROM9 | HO + 1,2-dihydroxy-4-methylbenzene → products | $1.5 \times 10^{-10}$ | ± 0.15 | | |
| HOx_AROM10 | HO + 3-methyl-2-nitrophenol → products | $3.4 \times 10^{-12}$ | ± 0.30 | | |
| HOx_AROM11 | HO + 4-methyl-2-nitrophenol → products | $3.4 \times 10^{-12}$ | ± 0.15 | | |
| HOx_AROM12 | HO + 5-methyl-2-nitrophenol → products | $6.4 \times 10^{-12}$ | ± 0.20 | | |
| HOx_AROM13 | HO + 6-methyl-2-nitrophenol → products | $2.5 \times 10^{-12}$ | ± 0.30 | | |
| HOx_AROM14 | HO + 1,4-benzoquinone → products | $4.6 \times 10^{-12}$ | ± 0.15 | | |
| HOx_AROM15 | HO + methyl-1,4-benzoquinone → products | $2.3 \times 10^{-11}$ | ± 0.15 | | |
| HOx_AROM16 | HO + nitrobenzene → products | $1.4 \times 10^{-13}$ | ± 0.20 | $6.0 \times 10^{-13}\exp(-440/T)$ 250-370 ± 300 | |
| HOx_AROM17 | HO + 3-nitrotoluene → products | $1.2 \times 10^{-12}$ | ± 0.50 | | |
| HOx_AROM18 | HO + cis-but-2-enedial → products | $5.7 \times 10^{-11}$ | ± 0.20 | | |
| HOx_AROM19 | HO + trans-but-2-enedial → products | $\geq 2 \times 10^{-11}$ | | | |
| HOx_AROM20 | HO + 3H-furan-2-one → products | $4.8 \times 10^{-11}$ | ± 0.20 | | |
| HOx_AROM21 | HO + furan-2,5-dione → products | $1.4 \times 10^{-12}$ | ± 0.20 | | |
| HOx_AROM22 | HO + cis/trans-4-oxopent-2-enal → products | $6.2 \times 10^{-11}$ | ± 0.20 | | |
| HOx_AROM25 | HO + benzaldehyde → products | $1.26 \times 10^{-11}$ | ± 0.08 | $5.9 \times 10^{-12}\exp(225/T)$ 290-350 ± 170 | |
| HOx_AROM26 | HO + benzyl alcohol → products | $2.7 \times 10^{-11}$ | ± 0.08 | | |

***$NO_3$ reactions based on datasheets in Supplement and on the IUPAC website updated in 2019***

| | | | | | |
|---|---|---|---|---|---|
| NO3_VOC26 | $NO_3$ + 2-methylpropane → products | $1.1 \times 10^{-16}$ | ± 0.10 | $3.0 \times 10^{-12}\exp(-3050/T)$ 290-430 ± 300 | |
| NO3_VOC27 | $NO_3$ + 2-methylpropene → products | $3.4 \times 10^{-13}$ | ± 0.10 | | |
| NO3_VOC28 | $NO_3$ + 1-butene → products | $1.3 \times 10^{-14}$ | ± 0.10 | $3.2 \times 10^{-13}\exp(-950/T)$ 230-480 ± 200 | |
| NO3_VOC29 | $NO_3$ + cis-2-butene → products | $3.5 \times 10^{-13}$ | ± 0.10 | | |
| NO3_VOC30 | $NO_3$ + trans-2-butene → products | $3.9 \times 10^{-13}$ | ± 0.08 | $\{1.78\times10^{-12}\exp(-530/T) + 1.28\times10^{-14}\exp(570/T)\}$ 200-380 | |
| NO3_VOC33 | $NO_3$ + d-limonene → products | $1.2 \times 10^{-11}$ | ± 0.12 | | |
| NO3_VOC34 | $NO_3$ + 2-carene → products | $2.0 \times 10^{-11}$ | ± 0.12 | | |
| NO3_VOC35 | $NO_3$ + 3-carene → products | $9.1 \times 10^{-12}$ | ± 0.12 | | |
| NO3_VOC36 | $NO_3$ + β-pinene → products | $2.5 \times 10^{-12}$ | ± 0.12 | | |
| NO3_VOC37 | $NO_3$ + myrcene → products | $1.1 \times 10^{-11}$ | ± 0.12 | | |
| NO3_VOC38 | $NO_3$ + sabinene → products | $1.0 \times 10^{-11}$ | ± 0.10 | | |
| NO3_VOC39 | $NO_3$ + ocimene, cis and trans → products | $2.2 \times 10^{-11}$ | ± 0.15 | | |
| NO3_VOC40 | $NO_3$ + α-terpinene → products | $1.8 \times 10^{-10}$ | ± 0.25 | | |
| NO3_VOC41 | $NO_3$ + γ-terpinene → products | $2.9 \times 10^{-11}$ | ± 0.12 | | |
| NO3_VOC42 | $NO_3$ + α-phellandrene → products | $7.3 \times 10^{-11}$ | ± 0.15 | | |
| NO3_VOC43 | $NO_3$ + terpinolene → products | $9.7 \times 10^{-11}$ | ± 0.25 | | |
| NO3_VOC46 | $NO_3$ + camphene → products | $6.6 \times 10^{-13}$ | ± 0.10 | | |
| NO3_VOC47 | $NO_3$ + β-caryophyllene → products | $1.9 \times 10^{-11}$ | ± 0.25 | | |
| NO3_VOC48 | $NO_3$ + α-cedrene → products | $8.2 \times 10^{-12}$ | ± 0.25 | | |
| NO3_VOC49 | $NO_3$ + α-humulene → products | $3.5 \times 10^{-11}$ | ± 0.25 | | |
| NO3_VOC50 | $NO_3$ + α-copaene → products | $1.6 \times 10^{-11}$ | ± 0.25 | | |
| NO3_VOC51 | $NO_3$ + longifolene → products | $6.8 \times 10^{-13}$ | ± 0.25 | | |
| NO3_VOC52 | $NO_3$ + isolongifolene → products | $3.9 \times 10^{-12}$ | ± 0.25 | | |
| NO3_VOC53 | $NO_3$ + alloisolongifolene → products | $1.4 \times 10^{-12}$ | ± 0.25 | | |
| NO3_VOC54 | $NO_3$ + α-neoclovene → products | $8.25 \times 10^{-12}$ | ± 0.25 | | |

| | | | |
|---|---|---|---|
| NO3_VOC55 | NO$_3$ + valencene → products | $7.9 \times 10^{-12}$ | ± 0.25 |
| NO3_VOC56 | NO$_3$ + α-terpineol → products | $1.7 \times 10^{-11}$ | ± 0.25 |
| | | | |
| NO3_AROM1 | NO$_3$ + benzene → products | $< 3 \times 10^{-17}$ | |
| NO3_AROM2 | NO$_3$ + toluene → products | $7.8 \times 10^{-17}$ | ± 0.25 |
| NO3_AROM3 | NO$_3$ + m-cresol → CH$_3$C$_6$H$_4$O + HNO$_3$ | | |
| | → other products | | |
| | **Overall** | $1.0 \times 10^{-11}$ | ± 0.15 |
| NO3_AROM4 | NO$_3$ + o-cresol → CH$_3$C$_6$H$_4$O + HNO$_3$ | | |
| | → other products | | |
| | **Overall** | $1.4 \times 10^{-11}$ | ± 0.15 |
| NO3_AROM5 | NO$_3$ + p-cresol → CH$_3$C$_6$H$_4$O + HNO$_3$ | | |
| | → other products | | |
| | **Overall** | $1.1 \times 10^{-11}$ | ± 0.15 |
| NO3_AROM6 | NO$_3$ + phenol → C$_6$H$_5$O + HNO$_3$ | | |
| | → other products | | |
| | **Overall** | $3.8 \times 10^{-12}$ | ± 0.15 |
| NO3_AROM7 | NO$_3$ + 1,2-dihydroxybenzene → products | $9.9 \times 10^{-11}$ | ± 0.15 |
| NO3_AROM8 | NO$_3$ + 1,2-dihydroxy-3-methylbenzene → products | $1.7 \times 10^{-10}$ | ± 0.15 |
| NO3_AROM9 | NO$_3$ + 1,2-dihydroxy-4-methylbenzene → products | $1.5 \times 10^{-10}$ | ± 0.15 |

*Photochemical reactions based on datasheets in Supplement and on the IUPAC website updated in 2019*

| | |
|---|---|
| P8 | butanone + h$v$ → products |
| P23 | biacetyl + h$v$ → products |
| P24 | i-butyraldehyde + h$v$ → products |
| P26 | cis-/trans-but-2-enedial + h$v$ → products |
| P27 | 4-oxopent-2-enedial + h$v$ → products |
| P28 | 2-nitrophenol + h$v$ → products |
| P30 | benzaldehyde + h$v$ → products |
| P31 | 3-methyl-2-nitrophenol + h$v$ → products |
| P32 | 4-methyl-2-nitrophenol + h$v$ → products |

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[a] The cited uncertainty corresponds approximately to 95% confidence limits.