



Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VIII - gas phase reactions of organic species with four, or more, carbon atoms ($\geq C_4$)

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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 ($\geq C_4$) available on the IUPAC website in 2019, including thermal reactions of closed-shell organic species with HO and NO₃ radicals, and their photolysis. 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*



40 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Atmospheric Chemistry superseded the original CODATA Task Group for Atmospheric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
45 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
50 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
55 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
60 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
65 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 NO₃ radicals, and photolysis. The
70 reactions with O₃ are included in a separate volume within this series (Cox et al., 2020), along
with the chemistry of the Criegee intermediates produced.



2 Guide to the gas-phase datasheets

75 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.

80 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
85 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
90 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
95 given in the Comments on Preferred Values section in the datasheets. Rate coefficients are given here in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. 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,
100 298 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
105 summarizing the experimental details. The following abbreviations, relating to experimental techniques, are used in the Techniques and Comments sections:



- A– absorption
- AS – absorption spectroscopy
- 110 CCD – charge coupled detector
- CIMS – chemical ionization mass spectroscopy/spectrometry
- CL – chemiluminescence
- CRDS – cavity ring-down spectroscopy
- DF – discharge flow
- 115 EPR – electron paramagnetic resonance
- F – flow system
- FP – flash photolysis
- FTIR – Fourier transform infrared
- FTS – Fourier transform spectroscopy
- 120 GC – gas chromatography/gas chromatographic
- HPLC – high-performance liquid chromatography
- IR – infrared
- LIF – laser induced fluorescence
- LMR – laser magnetic resonance
- 125 LP – laser photolysis
- MM – molecular modulation
- MS – mass spectrometry/mass spectrometric
- P – steady state photolysis
- PLP – pulsed laser photolysis
- 130 PR – pulse radiolysis
- RA – resonance absorption
- RF – resonance fluorescence
- RR – relative rate
- S – static system
- 135 TDLS – tunable diode laser spectroscopy
- UV – ultraviolet
- UVA – ultraviolet absorption
- VUVA – vacuum ultraviolet absorption

- 140 For measurements of relative rate coefficients, wherever possible the comments contain the

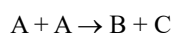


actual measured ratio of rate coefficients together with the rate coefficient of the reference reaction used to calculate the absolute rate coefficient listed in the data table. The absolute value of the rate coefficient given in the table may be different from that reported by the original author owing 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.



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

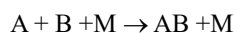
Note that the stoichiometric coefficient for A, i.e. 2, appears in the denominator before the rate of change of [A] (which is equal to $2k[A]^2$) and as a power on the right-hand side. Representations of k as a function of temperature characterize simple “direct” bimolecular reactions. Sometimes it is found that k also depends on the pressure and the nature of the bath



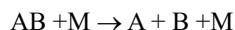
175 gas. This may be an indication of complex-formation during the course of the bimolecular
reaction, which is always the case in combination reactions. In the following sections the
representations of k which are adopted in these cases are explained.

2.3 Treatment of combination and dissociation reactions

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



185 and the reverse dissociation reactions



are composed of sequences of different types of physical and chemical elementary processes.
190 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:

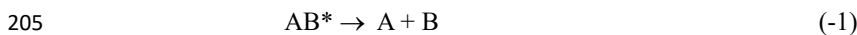
$$\frac{d[AB]}{dt} = k[A][B] \quad \text{Eq. (2)}$$

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

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

200 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,





while the dissociation reactions are characterized by:



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:

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

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while that for the dissociation reaction is given by:

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

220 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
225 pressure and high pressure rate coefficients,

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

230 From this convention, the Lindemann-Hinshelwood equation is obtained

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

It follows that, for combination reactions, $k_0 = k_1 k_2 [M] / k_{-1}$ and $k_\infty = k_1$, while, for dissociation
235 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 $K_c = k_1 k_2 / k_{-1} k_{-2}$.

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
240 “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
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
245 broadening factor F to the Lindemann-Hinshelwood expression (Troe, 1979):

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

The broadening factor F depends on the ratio $x = k_0/k_\infty$, which is proportional to $[M]$, and can
250 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):

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

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

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

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

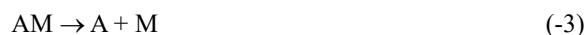
where $x = k_0/k_\infty$, $n = [\ln 2 / \ln(2/F_c)] [0.8 + 0.2 x^q]$, $q = (F_c - 1) / \ln(F_c/10)$ and $\ln = \log_e$ (Troe and
Ushakov, 2014). While the former equation for $\log F$ appears acceptable as long as $F_c \geq 0.6$,
265 the latter equation for F should be used for $F_c \leq 0.6$. With these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

The parameters k_0 , k_∞ , 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
270 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 $\text{HO} + \text{NO}_2 + \text{M}$, 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_∞ . In this case, the apparent values for k_0 , k_∞ , 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_∞ 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_∞ . In the present evaluation, we generally follow the experimentally fitted values for k_0 , k_∞ , 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_∞ 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



which, in the low pressure range, leads to $k_0 = (k_3 / k_{-3})k_4 [\text{M}]$. For some tri- and tetra-atomic adducts AB, e.g., $\text{O} + \text{O}_2 \rightarrow \text{O}_3$ and $\text{HO} + \text{C}_6\text{H}_6 \rightarrow \text{HOC}_6\text{H}_6$, 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_∞ 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.

The dependence of k_0 and k_∞ on the temperature T is represented in the form $k \propto T^{-n}$ except for



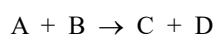
cases with an established energy barrier in the potential. We have used this form of temperature
dependence because it usually gives a better fit to the data over a wider range of temperature
than does the Arrhenius expression. It should be emphasised that the chosen form of the
temperature dependence is often only adequate over limited temperature ranges such as 200–
300 K. Obviously, the relevant values of n are different for k_0 and k_∞ . In this evaluation, values
of k_0 are given for selected examples of third bodies M, and if possible for M = N₂, O₂, or air.

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2.4 Treatment of complex-forming bimolecular reactions

Bimolecular reactions may follow the “direct” pathway

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



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

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

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

335

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



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

340
$$k_{\text{Ass}} = k_1 k_2 [\text{M}] / (k_{-1} + k_2 [\text{M}] + k_5) \quad \text{Eq. (14)}$$

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

Note that k_{Ass} and k_{CA} are dependent on the nature and concentration of the third body M, in
345 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
350 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

355
$$k_{\text{Ass}}^* = k_1 k_2 [\text{M}] / (k_{-1} + k_2 [\text{M}]) \quad \text{Eq. (16)}$$

and

360
$$k_{\text{CA}}^* = k_1 k_5 / (k_2 [\text{M}] + k_5). \quad \text{Eq. (17)}$$

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

365
$$k_{\text{CA}}^* = k_{\text{Ass},\infty} [1 / (1 + x^*)] F_{\text{CA}}^*(x^*) \quad \text{Eq. (18)}$$

with $x^* = k_{\text{Ass},\infty} [\text{M}] / k_{\text{CA},\infty}^*$ and a broadening factor $F_{\text{CA}}^*(x)$ (Stewart et al., 1989). The latter
factor is generally larger than $F_{\text{Ass}}^*(x^*)$ (Troe, 2015). The rate parameters $k_{\text{CA},0}^*$ and $k_{\text{CA},\infty}^*$



370 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
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 $k_{\text{Ass},0}$, $k_{\text{Ass},\infty}$, $F_{\text{Ass},c}$, $k_{\text{CA},0}$, $k_{\text{CA},\infty}$, and $F_{\text{CA},c}$. If
375 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
(for more details, see Troe, 2015).

380 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 $k_{\text{tot}} = k_{\text{Ass}} + k_{\text{CA}}$, i.e., $k_{\text{tot},0} = k_{\text{CA},0} = k_1 k_5 / (k_{-1} + k_5)$, because
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
385 with an increase above a certain temperature. k_{tot} , as given above, may increase with pressure
from $k_{\text{CA},0}$ to k_1 , with $M = \text{H}_2\text{O}$ often being a particularly efficient third body in the pressure -
dependent range. The pressure dependence generally becomes less apparent with increasing
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
390 (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. $M = \text{H}_2\text{O}$ here again may be particularly efficient. Without detailed theoretical
analysis, in general, it will be difficult to disentangle the intrinsic mechanism. Therefore,
reference to theoretical work is given for selected reactions.

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2.5 Photochemical reactions

The datasheets begin with a list of feasible primary photochemical transitions for wavelengths
usually down to 170 nm, along with the corresponding enthalpy changes at 0 K where possible
400 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
experimental data for: (i) absorption cross sections and (ii) quantum yields. These data are



405 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
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
410 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
list of references.

415 2.6 Conventions concerning absorption cross sections

These are presented in the datasheets as “absorption cross sections per molecule, base e.” They
are defined according to the equation:

$$420 \quad I / I_0 = \exp(-\sigma[N]l) \quad \text{Eq. (19)}$$

where I_0 and I are the incident and transmitted light intensities, $[N]$ is the number concentration
of absorber (expressed in molecule cm^{-3}), l is the path length (expressed in cm), and σ is the
absorption cross section (units of $\text{cm}^2 \text{ molecule}^{-1}$). Note that “molecule” is not a unit but is
425 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.
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
430 coefficient, ϵ , is often quoted, particularly in the older literature, and is defined as:

$$\epsilon = \{1/[A]l\} \log_{10}(I_0/I), \quad \text{Eq. (20)}$$

where $[A]$ is the concentration of the absorber expressed in units of moles per liter. While ϵ is
often called an extinction coefficient, the term “extinction” should more properly be used for
the sum of absorption and scattering. To convert from ϵ (base 10, units of $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) to σ
435 (base e, units of $\text{cm}^2 \text{ molecule}^{-1}$) multiply by 3.82×10^{-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:

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

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 $\pm 10\%$ or less are frequently reported in the literature. Unfortunately, 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. 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.



470 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 reliable data. Thus, we do
not feel justified at present in assigning uncertainty limits to the parameters reported for the
photochemical reactions.

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

Reaction number	Reaction	k_{598} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{598}$	Temp. dependence k/cm ³ molecule ⁻¹ s ⁻¹	Temp. range of range/K	$\Delta(E/R)/K^a$
HO reactions based on datasets in Supplement and on the IUPAC website updated in 2019						
HOX_VOC7	HO + CH ₃ CH ₂ CH ₂ CH ₃ → H ₂ O + CH ₃ CH ₂ CH ₂ CH ₂					
	→ H ₂ O + CH ₃ CHCH ₂ CH ₃					
overall		2.35×10^{-12}	± 0.06	$9.8 \times 10^{-12} \exp(-425/T)$	180-300	± 100
HOX_VOC8	HO + CH ₂ =C(CH ₃)CH=CH ₂ (isoprene) → products	1.0×10^{-10}	± 0.06	$2.1 \times 10^{-11} \exp(465/T)$	240-630	± 150
HOX_VOC9	HO + α -pinene → products	5.3×10^{-11}	± 0.08	$1.3 \times 10^{-11} \exp(410/T)$	240-360	± 100
HOX_VOC14	HO + CH ₃ CH ₂ CH ₂ CHO → products	2.3×10^{-11}	± 0.08	$5.8 \times 10^{-12} \exp(410/T)$	250-430	± 250
HOX_VOC15	HO + CH ₂ =C(CH ₃)CHO → products	3.0×10^{-11}	± 0.08	$8.4 \times 10^{-12} \exp(380/T)$	230-380	± 100
HOX_VOC20	HO + CH ₃ C(O)CH ₂ CH ₃ → products	1.1×10^{-12}	± 0.10	$1.5 \times 10^{-12} \exp(-90/T)$	210-300	± 200
HOX_VOC21	HO + CH ₃ C(O)CH=CH ₂ → products	2.0×10^{-11}	± 0.10	$2.6 \times 10^{-12} \exp(610/T)$	230-380	± 200
HOX_VOC22	HO + pinonaldehyde → products	3.9×10^{-11}	± 0.15	$5.2 \times 10^{-12} \exp(600/T)$	230-380	± 300
HOX_VOC27	HO + CH ₃ CH ₂ CH ₂ CH ₂ OH → products	8.5×10^{-12}	± 0.06	$5.3 \times 10^{-12} \exp(140/T)$	260-380	± 200
HOX_VOC28	HO + CH ₃ CH(OH)CH ₂ CH ₃ → products	8.7×10^{-12}	± 0.08			
HOX_VOC29	HO + (CH ₃) ₂ C(OH)CH=CH ₂ → products	6.3×10^{-11}	± 0.08	$8.1 \times 10^{-12} \exp(610/T)$	230-300	± 200
HOX_VOC31	HO + 3-methylfuran → products	9.3×10^{-11}	± 0.15			
HOX_VOC33	HO + (CH ₃) ₂ C(OH)CHO → products	1.4×10^{-11}	± 0.10			
HOX_VOC42	HO + 1-C ₄ H ₉ ONO ₂ → products	1.6×10^{-12}	± 0.06			
HOX_VOC43	HO + 2-C ₄ H ₉ ONO ₂ → products	8.6×10^{-13}	± 0.15			
HOX_VOC46	HO + CH ₃ CH ₂ C(O)CH ₂ ONO ₂ → products	8.2×10^{-13}	± 0.30			
HOX_VOC47	HO + CH ₃ CH(ONO ₂)C(O)CH ₃ → products	1.2×10^{-12}	± 0.30			
HOX_VOC48	HO + CH ₂ =C(CH ₃)C(O)OONO ₂ (MPAN) → products	2.9×10^{-11}	$\pm 0.2-0.5$			
HOX_VOC60	HO + (CH ₃) ₂ CH → H ₂ O + (CH ₃) ₂ C → H ₂ O + (CH ₃) ₂ CHCH ₂					
Overall		2.1×10^{-12}	± 0.04	$5.4 \times 10^{-12} \exp(-285/T)$	210-300	± 150
HOX_VOC61	HO + 2-methylpropene → products	5.1×10^{-11}	± 0.04	$9.4 \times 10^{-12} \exp(505/T)$	290-430	± 200
HOX_VOC62	HO + 1-butene → products	3.1×10^{-11}	± 0.06	$6.6 \times 10^{-12} \exp(465/T)$	290-430	± 150
HOX_VOC63	HO + <i>cis</i> -2-butene → products	5.6×10^{-11}	± 0.10	$1.1 \times 10^{-11} \exp(485/T)$	290-430	± 200
HOX_VOC64	HO + <i>trans</i> -2-butene → products	7.1×10^{-11}	± 0.06	$1.1 \times 10^{-11} \exp(553/T)$	290-430	± 200
HOX_VOC66	HO + CH ₃ C(O)C(O)CH ₃ → products	2.3×10^{-13}	± 0.06	$5.25 \times 10^{-13} \exp(-243/T)$	240-350	± 50
HOX_VOC67	HO + <i>n</i> -C ₄ H ₉ C(O)OH → products	1.8×10^{-12}	± 0.15			
HOX_VOC68	HO + <i>i</i> -C ₄ H ₉ C(O)OH → products	2.6×10^{-11}	± 0.04	$6.8 \times 10^{-12} \exp(410/T)$	240-425	± 60
HOX_VOC69	HO + (CH ₃) ₂ CHCH ₂ OH → products	8.9×10^{-12}	± 0.08	$2.73 \times 10^{-12} \exp(352/T)$	240-370	± 120
HOX_VOC70	HO + (CH ₃) ₂ COH → products	1.1×10^{-12}	± 0.06	$1.6 \times 10^{-12} \exp(-121/T)$	240-314	± 75
HOX_VOC76	HO + C ₂ H ₅ CH(OH)CHO → C ₂ H ₅ CH(OH)CO + H ₂ O → C ₂ H ₅ C(OH)CHO + H ₂ O					
overall		2.4×10^{-11}	± 0.10			
HOX_VOC77	HO + C ₂ H ₅ CH(OH)CH ₂ ONO ₂ → products	7.0×10^{-12}	± 0.20			
HOX_VOC78	HO + C ₂ H ₅ CH(ONO ₂)CH ₂ OH → products	7.4×10^{-12}	± 0.20			
HOX_VOC79	HO + CH ₃ C(O)CH(OH)CH ₃ → H ₂ O + CH ₃ C(O)C(OH)CH ₃ → products					
Overall		9.7×10^{-12}	± 0.10	$1.24 \times 10^{-12} \exp(612/T)$	280-350	± 350
HOX_VOC84	HO + α -terpinene → products	3.5×10^{-10}	± 0.08			



Hox_VOC85	HO + γ -terpinene → products	1.7×10^{10}	± 0.10				
Hox_VOC86	HO + terpinolene → products	2.2×10^{10}	± 0.15				
Hox_VOC87	HO + α -phellandrene → products	3.2×10^{10}	± 0.08				
Hox_VOC88	HO + β -phellandrene → products	1.7×10^{10}	± 0.15				
Hox_VOC89	HO + α -cedrene → products	6.7×10^{11}	± 0.10				
Hox_VOC90	HO + longifolene → products	4.7×10^{11}	± 0.10				
Hox_VOC91	HO + α -copaene → products	9.0×10^{11}	± 0.10				
Hox_VOC92	HO + β -caryophyllene → products	2.0×10^{10}	± 0.15				
Hox_VOC93	HO + α -humulene → products	2.9×10^{10}	± 0.10				
Hox_VOC99	HO + β -pinene → products	7.6×10^{11}	± 0.05				
Hox_VOC100	HO + limonene → products	1.65×10^{10}	± 0.05			$1.62 \times 10^{11} \exp(460/T)$	240-420 ± 150
Hox_VOC101	HO + camphene → products	5.2×10^{11}	± 0.10			$3.41 \times 10^{11} \exp(470/T)$	220-360 ± 150
Hox_VOC102	HO + 2-carene → products	8.0×10^{11}	± 0.15			$4.14 \times 10^{12} \exp(754/T)$	280-320 ± 100
Hox_VOC103	HO + 3-carene → products	8.3×10^{11}	± 0.06			$2.5 \times 10^{11} \exp(357/T)$	230-360 ± 50
Hox_VOC104	HO + β -myrcene → products	2.1×10^{10}	± 0.15			$4.0 \times 10^{11} \exp(579/T)$	310-430 ± 150
Hox_VOC105	HO + β -ocimene → products	2.8×10^{10}	± 0.15				
Hox_VOC106	HO + β -sabinene → products	1.2×10^{10}	± 0.15				
Hox_VOC107	HO + α -farnesene → products	2.2×10^{10}	± 0.30			2.2×10^{10}	298-430 ± 200
Hox_VOC108	HO + β -farnesene → products	2.3×10^{10}	± 0.30			2.3×10^{10}	298-430 ± 200
Hox_VOC109	HO + α -terpineol → products	1.9×10^{10}	± 0.30				
Hox_AROM1	HO + C ₆ H ₆ (benzene) → H ₂ O + C ₆ H ₅ → HOC ₆ H ₅	8×10^{15}	± 0.50			$3.8 \times 10^{11} \exp(-2520/T)$	330-1410 ± 300
Hox_AROM2	Overall HO + C ₆ H ₅ CH ₃ (toluene) → H ₂ O + C ₆ H ₄ CH ₃ → HOC ₆ H ₄ CH ₃	1.2×10^{12} 3.5×10^{13}	± 0.06 ± 0.20			$2.3 \times 10^{12} \exp(-190/T)$ $2.5 \times 10^{11} \exp(-1270/T)$	230-350 ± 200 310-1050 ± 200
Hox_AROM3	Overall HO + <i>m</i> -CH ₃ C ₆ H ₄ OH (<i>m</i> -cresol) → H ₂ O + CH ₃ C ₆ H ₄ O → H ₂ O + CH ₂ C ₆ H ₄ OH → CH ₃ C ₆ H ₄ (OH) ₂	5.6×10^{12}	± 0.06			$1.8 \times 10^{12} \exp(340/T)$	210-350 ± 200
Hox_AROM4	Overall HO + <i>o</i> -CH ₃ C ₆ H ₄ OH (<i>o</i> -cresol) → H ₂ O + CH ₃ C ₆ H ₄ O → H ₂ O + CH ₂ C ₆ H ₄ OH → CH ₃ C ₆ H ₄ (OH) ₂	6.2×10^{11}	± 0.10			$2.4 \times 10^{12} \exp(965/T)$	290-350 ± 600
Hox_AROM5	Overall HO + <i>p</i> -CH ₃ C ₆ H ₄ OH (<i>p</i> -cresol) → H ₂ O + CH ₃ C ₆ H ₄ O → H ₂ O + CH ₂ C ₆ H ₄ OH → CH ₃ C ₆ H ₄ (OH) ₂	4.2×10^{11}	± 0.10			$1.6 \times 10^{12} \exp(970/T)$	290-350 ± 600
Hox_AROM6	Overall HO + C ₆ H ₅ OH (phenol) → H ₂ O + C ₆ H ₅ O → H ₂ O + C ₆ H ₄ OH → HOC ₆ H ₅ O	4.8×10^{11}	± 0.10			$1.9 \times 10^{12} \exp(970/T)$	290-350 ± 600
Hox_AROM7	Overall HO + 1,2-dihydroxybenzene (1,2-C ₆ H ₄ (OH) ₂) → products	2.8×10^{11}	± 0.08			$4.7 \times 10^{13} \exp(1220/T)$	290-350 ± 600
Hox_AROM8	HO + 1,2-dihydroxy-3-methylbenzene → products	1.0×10^{10}	± 0.15				
Hox_AROM9	HO + 1,2-dihydroxy-4-methylbenzene → products	2.0×10^{10}	± 0.15				
		1.5×10^{10}	± 0.15				



Hox_AROM10	HO + 3-methyl-2-nitrophenol → products	3.4 × 10 ⁻¹²	± 0.30		
Hox_AROM11	HO + 4-methyl-2-nitrophenol → products	3.4 × 10 ⁻¹²	± 0.15		
Hox_AROM12	HO + 5-methyl-2-nitrophenol → products	6.4 × 10 ⁻¹²	± 0.20		
Hox_AROM13	HO + 6-methyl-2-nitrophenol → products	2.5 × 10 ⁻¹²	± 0.30		
Hox_AROM14	HO + 1,4-benzoquinone → products	4.6 × 10 ⁻¹²	± 0.15		
Hox_AROM15	HO + methyl-1,4-benzoquinone → products	2.3 × 10 ⁻¹¹	± 0.15		
Hox_AROM16	HO + C ₆ H ₅ NO ₂ (nitrobenzene) → products	1.4 × 10 ⁻¹³	± 0.20	6.0 × 10 ⁻¹³ exp(-440/T)	250-370 ± 300
Hox_AROM17	HO + 3-nitrotoluene → products	1.2 × 10 ⁻¹²	± 0.50		
Hox_AROM18	HO + <i>cis</i> -CHOC=CHCHO → products	5.7 × 10 ⁻¹¹	± 0.20		
Hox_AROM19	HO + <i>trans</i> -CHOC=CHCHO → products	≥ 2 × 10 ⁻¹¹	± 0.20		
Hox_AROM20	HO + 3 <i>H</i> -furan-2-one → products	4.8 × 10 ⁻¹¹	± 0.20		
Hox_AROM21	HO + furan-2,5-dione → products	1.4 × 10 ⁻¹²	± 0.20		
Hox_AROM22	HO + CH ₃ C(O)CH=CHCHO (<i>cis/trans</i> -4-oxopent-2-enal) → products	6.2 × 10 ⁻¹¹	± 0.20		
Hox_AROM25	HO + C ₆ H ₅ CHO (benzaldehyde) → products	1.26 × 10 ⁻¹¹	± 0.08	5.9 × 10 ⁻¹² exp(225/T)	290-350 ± 170
Hox_AROM26	HO + C ₆ H ₅ CH ₂ OH (benzyl alcohol) → products	2.7 × 10 ⁻¹¹	± 0.08		
NO₃ reactions based on datasheets in Supplement and on the IUPAC website updated in 2019					
NO3_VOC26	NO ₃ + 2-methylpropane, (CH ₃) ₃ CH → products	1.1 × 10 ⁻¹⁶	± 0.10	3.0 × 10 ⁻¹² exp(-3050/T)	290-430 ± 300
NO3_VOC27	NO ₃ + 2-methylpropene ((CH ₃) ₂ C=CH ₂) → products	3.4 × 10 ⁻¹³	± 0.10		
NO3_VOC28	NO ₃ + 1-butene → products	1.5 × 10 ⁻¹⁴	± 0.10	3.2 × 10 ⁻¹³ exp(-950/T)	230-480 ± 200
NO3_VOC29	NO ₃ + <i>cis</i> -2-butene → products	3.5 × 10 ⁻¹³	± 0.10		
NO3_VOC30	NO ₃ + <i>trans</i> -2-butene → products	3.9 × 10 ⁻¹³	± 0.08	{ 1.78 × 10 ⁻¹² exp(-530/T) + 1.28 × 10 ⁻¹⁴ exp(570/T) }	200-380
NO3_VOC33	NO ₃ + <i>d</i> -limonene → products	1.2 × 10 ⁻¹¹	± 0.12		
NO3_VOC34	NO ₃ + 2-carene → products	2.0 × 10 ⁻¹¹	± 0.12		
NO3_VOC35	NO ₃ + 3-carene → products	9.1 × 10 ⁻¹²	± 0.12		
NO3_VOC36	NO ₃ + β-pinene → products	2.5 × 10 ⁻¹²	± 0.12		
NO3_VOC37	NO ₃ + myrcene → products	1.1 × 10 ⁻¹¹	± 0.12		
NO3_VOC38	NO ₃ + sabinene → products	1.0 × 10 ⁻¹¹	± 0.10		
NO3_VOC39	NO ₃ + ocimene, <i>cis</i> and <i>trans</i> → products	2.2 × 10 ⁻¹¹	± 0.15		
NO3_VOC40	NO ₃ + α-terpinene → products	1.8 × 10 ⁻¹⁰	± 0.25		
NO3_VOC41	NO ₃ + γ-terpinene → products	2.9 × 10 ⁻¹¹	± 0.12		
NO3_VOC42	NO ₃ + α-phellandrene → products	7.3 × 10 ⁻¹¹	± 0.15		
NO3_VOC43	NO ₃ + terpinolene → products	9.7 × 10 ⁻¹¹	± 0.25		
NO3_VOC46	NO ₃ + camphene → products	6.6 × 10 ⁻¹³	± 0.10		
NO3_VOC47	NO ₃ + β-caryophyllene → products	1.9 × 10 ⁻¹¹	± 0.25		
NO3_VOC48	NO ₃ + α-cedrene → products	8.2 × 10 ⁻¹²	± 0.25		
NO3_VOC49	NO ₃ + α-humulene → products	3.5 × 10 ⁻¹¹	± 0.25		
NO3_VOC50	NO ₃ + α-copaene → products	1.6 × 10 ⁻¹¹	± 0.25		
NO3_VOC51	NO ₃ + longifolene → products	6.8 × 10 ⁻¹³	± 0.25		
NO3_VOC52	NO ₃ + isolongifolene → products	3.9 × 10 ⁻¹²	± 0.25		
NO3_VOC53	NO ₃ + alloisolongifolene → products	1.4 × 10 ⁻¹²	± 0.25		
NO3_VOC54	NO ₃ + α-neodolvene → products	8.25 × 10 ⁻¹²	± 0.25		



NO3_VOC55	NO ₃ + valencene → products	7.9 × 10 ⁻¹²	± 0.25
NO3_VOC56	NO ₃ + α-terpineol → products	1.7 × 10 ⁻¹¹	± 0.25
NO3_AROM1	NO ₃ + C ₆ H ₆ (benzene) → products	< 3 × 10 ⁻¹⁷	
NO3_AROM2	NO ₃ + C ₆ H ₅ CH ₃ (toluene) → products	7.8 × 10 ⁻¹⁷	± 0.25
NO3_AROM3	NO ₃ + <i>m</i> -CH ₃ C ₆ H ₄ OH (<i>m</i> -cresol) → CH ₃ C ₆ H ₄ O + HNO ₃ → other products		
NO3_AROM4	Overall NO ₃ + <i>o</i> -CH ₃ C ₆ H ₄ OH (<i>o</i> -cresol) → CH ₃ C ₆ H ₄ O + HNO ₃ → other products	1.0 × 10 ⁻¹¹	± 0.15
NO3_AROM5	Overall NO ₃ + <i>p</i> -CH ₃ C ₆ H ₄ OH (<i>p</i> -cresol) → CH ₃ C ₆ H ₄ O + HNO ₃ → other products	1.4 × 10 ⁻¹¹	± 0.15
NO3_AROM6	Overall NO ₃ + C ₆ H ₅ OH (phenol) → C ₆ H ₅ O + HNO ₃ → other products	1.1 × 10 ⁻¹¹	± 0.15
NO3_AROM7	Overall NO ₃ + 1,2-dihydroxybenzene (1,2-C ₆ H ₄ (OH) ₂) → products	3.8 × 10 ⁻¹²	± 0.15
NO3_AROM8	NO ₃ + 1,2-dihydroxy-3-methylbenzene → products	9.9 × 10 ⁻¹¹	± 0.15
NO3_AROM9	NO ₃ + 1,2-dihydroxy-4-methylbenzene → products	1.7 × 10 ⁻¹⁰	± 0.15
		1.5 × 10 ⁻¹⁰	± 0.15

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

P23	CH ₃ C(O)C(O)CH ₃ + hv → products
P24	<i>i</i> -C ₃ H ₇ CHO + hv → products
P26	<i>cis</i> /trans-but-2-enedial + hv → products
P27	4-oxopent-2-enedial + hv → products
P28	2-nitrophenol + hv → products
P30	benzaldehyde + hv → products
P31	3-methyl-2-nitrophenol + hv → products
P32	4-methyl-2-nitrophenol + hv → products

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