



1 **Evaluated kinetic and photochemical data for atmospheric chemistry:**
2 **Volume IX – gas phase reactions of halogenated alkanes, alkenes, and**
3 **oxygenated compounds**

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22

23 **Abstract.** This article, the ninth in the series, presents kinetic and photochemical data sheets
24 evaluated by the IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation. It
25 covers an extension of the gas phase and photochemical reactions of halogenated alkanes,
26 alkenes, and oxygenated organic compounds implemented on the IUPAC website since 2008.
27 The article consists of a summary table of the recommended kinetic parameters for the
28 evaluated reactions, and a supplement containing the data sheets providing information upon
29 which the recommendations are made.

30

31 **1 Introduction**

32

33 In the mid-1970s it was appreciated that there was a need to establish an international panel to
34 produce a set of critically evaluated rate parameters for reactions of interest for atmospheric
35 chemistry. To this end the CODATA Task Group on Chemical Kinetics, under the auspices of
36 the International Council of Scientific Unions (ICSU), was constituted in 1977, and tasked to
37 produce an evaluation of relevant, available kinetic and photochemical data. The first
38 evaluation by this international committee was published in *J. Phys. Chem. Ref. Data* in 1980
39 (Baulch et al., 1980) and was followed by supplements in 1982 (Baulch et al., 1982) and 1984
40 (Baulch et al., 1984). In 1986 the IUPAC Subcommittee on Gas Kinetic Data Evaluation for



41 Atmospheric Chemistry superseded the original CODATA Task Group for Atmospheric
42 Chemistry. The Subcommittee continued its data evaluation program with supplements
43 published in 1989 (Atkinson et al., 1989), 1992 (Atkinson et al., 1992), 1997 (Atkinson et al.,
44 1997a; Atkinson et al., 1997b), 1999 (Atkinson et al., 1999), and 2000 (Atkinson et al., 2000).
45
46 Starting in 2005, the gas-phase evaluation work was expanded to include heterogeneous
47 reactions of gases on solid (Crowley et al., 2010) and liquid substrates (Ammann et al., 2013).
48 Aqueous-phase reactions of atmospheric importance were added starting in 2015. The
49 IUPAC group's work now includes over 1400 gas-phase, heterogeneous, and aqueous-phase
50 reactions of importance in atmospheric chemistry. Reflecting the broader scope, the group
51 changed its name to the IUPAC Task Group on Atmospheric Chemical Kinetic Data
52 Evaluation in 2013. The history of IUPAC data evaluations and their role in addressing the
53 critical societal challenges of stratospheric ozone loss, tropospheric ozone formation, acid
54 rain, urban air pollution, aerosol formation, and climate change is discussed by Cox et al.
55 (2018).
56
57 In 2000 the evaluation was made available on the worldwide web (<https://iupac.aeris-data.fr/>).
58 The IUPAC website hosts an interactive data base with a search facility and hyperlinks
59 between the summary table and data sheets which can be downloaded as individual PDF files.
60 Work is underway to provide machine readable metadata from the data sheets to enable
61 automatic transfer of IUPAC recommended data into atmospheric models. The IUPAC group
62 continues to update and extend the set of evaluated reactions. To enhance the accessibility of
63 this updated material to the scientific community, the evaluation is being published as a series
64 of articles in Atmospheric Chemistry and Physics (Atkinson et al., 2004, 2006, 2007, 2008;
65 Crowley et al., 2010; Ammann et al., 2013; Cox et al. 2020; Mellouki et al., 2021).
66
67 The fourth article in this series covering small ($\leq C_3$) organic halogen species was published
68 in 2008 (Atkinson et al., 2008). The past two decades have seen increasing concern regarding
69 the presence of long-chain persistent bioaccumulative fluorinated organic pollutants such as
70 perfluorooctanoic acid ($C_7F_{15}C(O)OH$, PFOA), perfluorooctane sulphonic acid
71 ($C_8F_{17}S(O)OH$, PFOS), and per- and polyfluoroalkyl substances (PFAS) in the environment
72 (Giesy and Kannan, 2001; Ellis et al., 2004; Lau et al., 2007; Prevedouros et al., 2006).
73 Concern over the growing contribution of hydrofluorocarbons (HFCs) to radiative forcing of
74 climate change (Velders et al., 2009) led to the recent Kigali Agreement to limit HFC



emissions. Halogenated alkenes and oxygenates have been developed to replace HFCs (Brown, 2009; Burkholder et al. 2015; Wallington et al., 2015) and are used as industrial solvents, synthesis reagents for surface coatings, inhalation agents, fire retardants, fire-fighting foams, and surfactants (Wallington et al., 2017). To provide data relevant to understanding these new issues we have extended the set of evaluated reactions. We present here in Volume IX data sheets for gas-phase and photochemical reactions of halogenated organic species added since publication of Volume IV (Atkinson et al., 2008).

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 all pathways which are considered feasible. The available kinetic data on the reactions are summarized under two headings: (i) Absolute Rate Coefficients, and (ii) Relative Rate Coefficients. Under these headings, we list the published experimental data as absolute rate coefficients. If the temperature coefficient has been measured, the results are given in the temperature dependent form as stated by the authors 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 dependences in alternative forms such as $k = C(T/298 \text{ K})^n \exp(-D/T)$ or $k = ET^2 \exp(-F/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 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 (180-310 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 data sheets. 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 section 2.3 of



109 this guide. Single-temperature data are presented as such and, wherever possible, the rate
110 coefficient at, or close to, 298 K as measured by the original authors is quoted directly. This
111 means that the listed rate coefficient at 298 K may differ slightly from that calculated from the
112 Arrhenius parameters determined by the same authors. Rate coefficients at 298 K marked
113 with an asterisk indicate that the value was calculated by extrapolation of a measured
114 temperature range, which did not include 298 K. The tables of data are supplemented by a
115 series of comments summarizing the experimental details. The following abbreviations,
116 relating to experimental techniques, are used in the Techniques and Comments sections:
117 A – absorption
118 AS – absorption spectroscopy
119 CCD – charge coupled detector
120 CIMS – chemical ionization mass spectroscopy/spectrometry
121 CL – chemiluminescence
122 CRDS – cavity ring-down spectroscopy
123 DF – discharge flow
124 EPR – electron paramagnetic resonance
125 F – flow system
126 FP – flash photolysis
127 FTIR – Fourier transform infrared
128 FTS – Fourier transform spectroscopy
129 GC – gas chromatography/gas chromatographic
130 HPLC – high-performance liquid chromatography
131 IR – infrared
132 LIF – laser induced fluorescence
133 LMR – laser magnetic resonance
134 LP – laser photolysis
135 MM – molecular modulation
136 MS – mass spectrometry/mass spectrometric
137 P – steady state photolysis
138 PLP – pulsed laser photolysis
139 PR – pulse radiolysis



140 RA – resonance absorption

141 RF – resonance fluorescence

142 RR – relative rate

143 S – static system

144 TDLS – tunable diode laser spectroscopy

145 UV – ultraviolet

146 UVA – ultraviolet absorption

147 VUVA – vacuum ultraviolet absorption

148

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

156

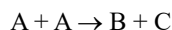
157 The preferred values in the datasheets are based on our consideration of the suitability of
158 experimental method and coverage of applicable parameter space (temperature, total pressure
159 of diluent gas, partial pressure of gas-phase species) within the atmospherically relevant
160 range. The general approach and methods used have been reviewed by Cox (2012). It is
161 recognized that preferred values may change with publication of new data, and such changes
162 are updated at the website. The preferred rate coefficients are presented (i) at a temperature of
163 298 K and (ii) in temperature dependent form over a stated temperature range. This is
164 followed by a statement of the uncertainty limits in $\log k$ at 298 K and the uncertainty limits
165 either in (E/R) or in n , (for systems with power law temperature dependence), for the mean
166 temperature in the range. Some comments on the assignment of uncertainties are given later in
167 this guide to the datasheets. The ‘Comments on Preferred Values’ section describes how the
168 selection was made and give any other relevant information. The extent of the comments
169 depends upon the present state of our knowledge of the reaction in question. The datasheets
170 are concluded with a list of the relevant references.

171

172 **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.

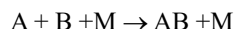


$$-\frac{1}{2} \frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{d[C]}{dt} = k[A]^2 \quad \text{Eq. (1)}$$

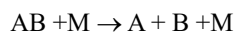
Note that the stoichiometric coefficient for A, i.e. 2, appears in the denominator before the rate of change of [A] (which is equal to $2k[A]^2$) and as a power on the right-hand side. Representations of k as a function of temperature characterize simple “direct” bimolecular reactions. Sometimes it is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



and the reverse dissociation reactions



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:

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



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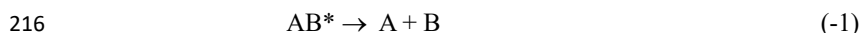
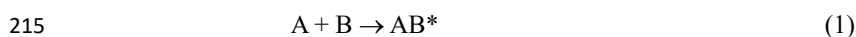
207 while dissociation reactions are described by a formal first-order rate law:

208

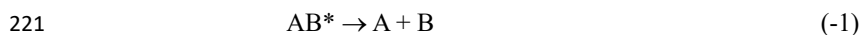
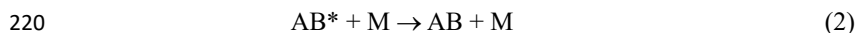
$$209 \quad \frac{-d[AB]}{dt} = k[AB] \quad \text{Eq. (3)}$$

210

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



218 while the dissociation reactions are characterized by:



222 Assuming quasi-stationary concentrations for the highly excited unstable species AB^* (i.e. that
 223 $d[AB^*]/dt \approx 0$), it follows that the rate coefficient for the combination reaction is given by:

224

$$225 \quad k = k_1 \left(\frac{k_2[M]}{k_{-1} + k_2[M]} \right) \quad \text{Eq. (4)}$$

226

227 while that for the dissociation reaction is given by:

228

$$229 \quad k = k_{-2}[M] \left(\frac{k_{-1}}{k_{-1} + k_2[M]} \right) \quad \text{Eq. (5)}$$

230

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

237



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

239

240

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

242

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

244

245 It follows that, for combination reactions, $k_0 = k_1 k_2 [M] / k_{-1}$ and $k_\infty = k_1$, while, for dissociation
 246 reactions, $k_0 = k_{-2} [M]$ and $k_\infty = k_{-1} k_{-2} / k_2$. Since detailed balancing applies, the ratio of the rate
 247 coefficients for combination and dissociation at a fixed T and $[M]$ is given by the equilibrium
 248 constant $K_c = k_1 k_2 / k_{-1} k_{-2}$.

249 Starting from the high-pressure limit, the rate coefficients fall off with decreasing third body
 250 concentration $[M]$ and the corresponding representation of k as a function of $[M]$ is termed the
 251 “falloff curve” of the reaction. In practice, the above Lindemann-Hinshelwood expressions do
 252 not suffice to characterize the falloff curves completely. Because of the multistep character of
 253 the collisional deactivation ($k_2 [M]$) and activation ($k_{-2} [M]$) processes, and energy- and angular
 254 momentum-dependences of the association (k_1) and dissociation (k_{-1}) steps, as well as other
 255 phenomena, the falloff expressions have to be modified. This can be done by including a
 256 broadening factor F to the Lindemann-Hinshelwood expression (Troe, 1979):

257

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

259

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

264

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

266

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

268

269 When F_c decreases, the falloff curve broadens and becomes asymmetric (i.e. $F(k_0/k_\infty) \neq$



270 $F(k_{\infty}/k_0)$). The given equation for F then becomes insufficient and should be replaced, e.g. by

271

$$272 \quad F(x) \approx (1+x)/(1+x^n)^{1/n} \quad \text{Eq. (10)}$$

273

274 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
 275 Ushakov, 2014). While the former equation for $\log F$ appears acceptable as long as $F_c \geq 0.6$,
 276 the latter equation for F is more rigorous when $F_c \leq 0.6$. With these equations, falloff curves
 277 are represented in terms of the three parameters k_0 (being proportional to $[M]$), k_{∞} , and F_c .

278 The parameters k_0 , k_{∞} , and F_c depend on details of the intra- and intermolecular dynamics and
 279 in principle can be calculated. If the required information is not available, one has to obtain
 280 them by fitting experimental falloff curves with the expressions given above. Nevertheless, one
 281 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
 282 B in total have $r = 3, 4, 5$, and 6 external rotational degrees of freedom, respectively (Cobos
 283 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
 284 may be lower, if low frequency vibrations in A or B are relevant in addition to the rotations and
 285 if collisions are inefficient. Over the range 200 – 300 K often one can neglect a temperature
 286 dependence of F_c (for detailed calculations of F_c , including a dependence on the bath gas M,
 287 see e.g. Troe 1983; Troe and Ushakov, 2011, 2014). The accuracy of $F(x)$ as given above is
 288 estimated to be about 10 percent. Larger differences between experimentally fitted F_c often are
 289 an indication for inadequate falloff extrapolations to k_0 and/or k_{∞} . In this case, the apparent
 290 values for k_0 , k_{∞} , and F_c still can provide a satisfactory representation of the considered
 291 experimental data, in spite of the fact that k_0 and/or k_{∞} are not the real limiting values. If falloff
 292 curves are fitted in different ways, changes in F_c require changes in the limiting k_0 and k_{∞} . In
 293 the present evaluation, we generally follow the experimentally fitted values for k_0 , k_{∞} , and F_c ,
 294 provided that F_c does not differ too much from the standard values given above and theoretically
 295 modelled values. If large deviations are encountered, the experimental data are re-evaluated
 296 using F_c -values as given above. One should also note that k_{∞} for combination reactions without
 297 a barrier often have only weak temperature dependences which in many cases can be neglected.

298

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





305 which, in the low-pressure range, leads to $k_0 = (k_3 / k_{-3})k_4 [M]$. For some tri- and tetra-atomic
 306 adducts AB, e.g., $O + O_2 \rightarrow O_3$ and $HO + C_6H_6 \rightarrow HOC_6H_6$, the value of k_0 may exceed that
 307 from the energy-transfer mechanism and show stronger temperature dependences (Luther et al.,
 308 2005; Teplukhin and Babikov, 2016). This mechanism may also influence high pressure
 309 experiments when k_0 from the radical-complex mechanism exceeds k_∞ from the energy-transfer
 310 mechanism (Oum et al., 2003). In this case falloff over wide pressure ranges cannot be
 311 represented by contributions from the energy-transfer mechanism alone, in particular when
 312 measurements at pressures above about 10 bar are taken into consideration.

313

314 The dependence of k_0 and k_∞ on the temperature T is represented in the form $k \propto T^{-n}$ except for
 315 cases with an established energy barrier in the potential. We have used this form of temperature
 316 dependence because it usually gives a better fit to the data over a wider range of temperature
 317 than does the Arrhenius expression. It should be emphasised that the chosen form of the
 318 temperature dependence is often only adequate over limited temperature ranges such as 200–
 319 300 K. Obviously, the relevant values of n are different for k_0 and k_∞ . In this evaluation, values
 320 of k_0 are given for selected examples of third bodies M, and if possible for $M = N_2$, O_2 , or air.

321

322 2.4 Treatment of complex-forming bimolecular reactions

323

324 Bimolecular reactions may follow the “direct” pathway

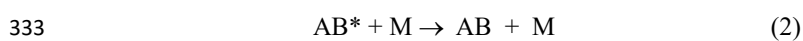
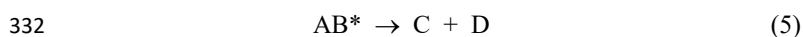
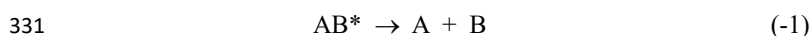
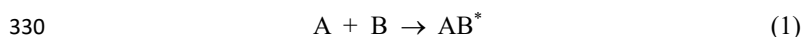
325



327

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

329



334

335 (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

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

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

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

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

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

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

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

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

and

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



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

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

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 $k_{\text{CA},\infty}^*$ 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 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).

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 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 $\text{M} = \text{H}_2\text{O}$ 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 $\text{C} + \text{D}$ 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. $\text{M} = \text{H}_2\text{O}$ 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.



2.5 Photochemical reactions

Tables are provided in the datasheets which summarise the available 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 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: $\log_{10}(\sigma_{T1} / \sigma_{T2}) = B \cdot (T_1 - T_2)$ 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.

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:

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

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 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 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 (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 large systematic errors which are difficult to detect. This is hardly surprising since it is not always possible to study atomic and free radical reactions in isolation, and consequently mechanistic and other difficulties



469 frequently arise. Our assessment of uncertainty limits tends towards the cautious side. Our
470 assessment of uncertainties in the preferred values are not determined by a rigorous, statistical
471 analysis of the database, which is generally too limited to permit such an analysis. Rather, the
472 uncertainties are based on our knowledge of the techniques, the difficulties of the
473 experimental measurements, the potential for systematic errors, and the number of studies
474 conducted and their agreement or lack thereof.

475

476 **Author contribution:** All authors defined the scope of the work. TJW, JNC, and AM developed
477 and drafted the datasheets and manuscript. All authors reviewed, refined, and revised the
478 manuscript and datasheets.

479

480 **Competing interests:** The authors declare that they have no conflict of interest. MA is a
481 member of the editorial board of *Atmospheric Chemistry and Physics*.

482

483 **Acknowledgements.** The members of the Task Group wish to express their appreciation to
484 IUPAC for the financial help which facilitated the preparation of this evaluation. M.A.
485 appreciates support by the Swiss National Science Foundation (grant no. 188662). We also
486 acknowledge financial support from the Office Fédéral de l'Education et de la Science, the
487 Centre National de la Recherche Scientifique-Institut National des Sciences de l'Univers
488 (CNRS-INSU). Support was also obtained from the French Data Terra Research Infrastructure
489 through the AERIS Atmosphere Data and Services Centre. We thank Cathy Boonne, Elliot
490 Richard, and Maroua Soltani for developing and maintaining the website.

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617



618 **Table 1 Summary of recommended rate coefficients^a for organic halogen reactions added since publication**
 619 **of Volume IV**

Datasheet ID ^b	Reaction	$k_{298} / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$\Delta \log k_{298}^c$	$k(T) / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R) / \text{K}^c$
<i>Organic FOx, ClOx, BrOx, and IOx reactions added to the IUPAC website (see Supplementary Material for datasheets)</i>						
<i>Halogenated alkanes</i>						
oFOx72	HO + CF ₃ CH ₂ CH ₃ (HFC-263fb) → products	4.9×10^{-14}	0.15	$3.7 \times 10^{-12} \exp(-1290/T)$	240-370	300
oFOx73	HO + CF ₃ CHFCF ₂ F (HFC-245eb) → products	1.6×10^{-14}	0.15	$1.1 \times 10^{-11} \exp(-1250/T)$	240-380	300
oFOx74	HO + CHF ₂ CHFCF ₂ (HFC-245ea) → products	1.8×10^{-14}	0.15	$1.8 \times 10^{-12} \exp(-1375/T)$	240-380	300
oFOx75	HO + CF ₃ CH ₂ CHF ₂ (HFC-245fa) → products	6.9×10^{-15}	0.12	$6.0 \times 10^{-13} \exp(-1331/T)$	270-370	300
oFOx76	HO + CF ₃ CH ₂ CF ₂ CH ₃ (HFC-365mfe) → products	7.1×10^{-15}	0.20	$1.6 \times 10^{-12} \exp(-1620/T)$	270-380	200
oFOx77	HO + CF ₃ CH ₂ CH ₂ CF ₃ (HFC-356mff) → products	7.8×10^{-15}	0.10	$2.6 \times 10^{-12} \exp(-1734/T)$	260-370	300
oFOx78	HO + CF ₃ CF ₂ CH ₂ CH ₂ F (HFC-356mcf) → products	4.2×10^{-14}	0.15	$1.7 \times 10^{-12} \exp(-1108/T)$	250-370	300
oFOx79	HO + CHF ₂ CF ₂ CF ₂ CHF ₂ (HFC-338pcc) → products	4.3×10^{-15}	0.08	$7.82 \times 10^{-13} \exp(-1548/T)$	230-420	200
oFOx80	HO + CF ₃ CH ₂ CF ₂ CH ₂ CF ₃ (HFC-458mfef) → products	2.6×10^{-15}	0.15	$1.23 \times 10^{-12} \exp(-1833/T)$	270-360	300
oFOx81	HO + CF ₃ CHFCF ₂ CF ₃ (HFC-44-10mcc) → products	3.3×10^{-15}	0.12	$5.68 \times 10^{-13} \exp(-1534/T)$	240-400	300
oFOx82	HO + CF ₃ CF ₂ CH ₂ CH ₂ CF ₃ (HFC-55-10mcf) → products	8.3×10^{-15}	0.20			
oFOx83	HO + CHF ₂ (CF ₃) ₄ CF ₃ (HFC-52-13p) → products	1.8×10^{-15}	0.10	$5.76 \times 10^{-13} \exp(-1726/T)$	250-430	300
oClOx86	HO + C ₂ H ₅ Cl → products	3.7×10^{-13}	0.10	$4.25 \times 10^{-12} \exp(-727/T)$	220-400	200
oClOx87	HO + CH ₂ ClCH ₂ Cl → products	2.4×10^{-13}	0.08	$8.69 \times 10^{-12} \exp(-1070/T)$	290-360	200
oClOx88	HO + CH ₃ CHCl ₂ → products	2.76×10^{-13}	0.10	$2.04 \times 10^{-12} \exp(-596/T)$	290-370	300
oBrOx16	HO + CHBr ₃ → products	2.7×10^{-13}	0.15	$1.0 \times 10^{-12} \exp(-388/T)$	290-370	300
oBrOx17	HO + C ₂ H ₅ Br → products	3.3×10^{-13}	0.15	$2.25 \times 10^{-12} \exp(-576/T)$	230-300	300
oBrOx18	HO + CH ₂ BrCH ₂ Br → products	2.22×10^{-13}	0.10	$7.69 \times 10^{-12} \exp(-1056/T)$	290-370	300
oBrOx19	HO + <i>n</i> -C ₃ H ₇ Br → products	1.0×10^{-12}	0.10	$3.91 \times 10^{-12} \exp(-399/T)$	210-300	300
oBrOx20	HO + CH ₃ CHBrCH ₃ → products	7.58×10^{-13}	0.06	$1.96 \times 10^{-12} \exp(-283/T)$	210-355	200
oBrOx21	HO + <i>n</i> -C ₄ H ₉ Br → products	2.3×10^{-12}	0.20			
oBrOx22	HO + <i>n</i> -C ₅ H ₁₁ Br → products	3.7×10^{-12}	0.20			
oBrOx23	HO + <i>n</i> -C ₆ H ₁₃ Br → products	5.5×10^{-12}	0.20			
oIOx4	HO + CH ₃ CH ₂ I → products	3.43×10^{-13}	0.10	$5.55 \times 10^{-12} \exp(-830/T)$	290-380	200
oIOx5	HO + CH ₃ CH ₂ CH ₂ I → products	1.36×10^{-12}	0.08	$1.86 \times 10^{-11} \exp(-780/T)$	290-380	200
oIOx6	HO + CH ₃ CHICH ₃ → products	1.29×10^{-12}	0.08	$7.64 \times 10^{-11} \exp(-530/T)$	290-380	200
oFOx108	Cl + CHF ₂ CH ₂ CF ₃ (HFC-245fa) → products	6.9×10^{-15}	0.30			
oFOx110	Cl + CF ₃ CHFCF ₃ (HFC-227ea) → products	4.4×10^{-16}	0.15			
oFOx111	Cl + CHF ₃ (HFC-23) → products	3.4×10^{-18}	0.50			
oBrOx24	Cl + CH ₃ Br → products	4.5×10^{-13}	0.05	$1.38 \times 10^{-11} \exp(-1020/T)$	210-300	100
<i>Halogenated alkenes</i>						
oFOx112	HO + CF ₂ =CF ₂ (HFO-1114) → products	1.04×10^{-11}	0.06	$3.84 \times 10^{-12} \exp(297/T)$	250-500	100
oFOx114	HO + CF ₃ CF=CH ₂ (HFO-1234yf) → products	1.12×10^{-11}	0.06	$1.16 \times 10^{-12} \exp(-10/T)$	200-300	100
oFOx115	HO + <i>E</i> -CF ₃ CH=CHF (HFO-1234ze(E)) → products	7.07×10^{-13}	0.06	$6.91 \times 10^{-13} \exp(7/T)$	210-300	100
oFOx117	HO + <i>Z</i> -CF ₃ CH=CHF (HFO-1234ze(Z)) → products	1.21×10^{-12}	0.15	$8.46 \times 10^{-13} \exp(106/T)$	260-300	100
oFOx118	HO + <i>E</i> -CF ₃ CF=CHF (HFO-1225ze(E)) → products	2.2×10^{-12}	0.15			
oFOx119	HO + <i>Z</i> -CF ₃ CF=CHF (HFO-1225ze(Z)) → products	1.2×10^{-12}	0.10	$7.60 \times 10^{-13} \exp(155/T)$	200-300	100
oFOx116	HO + CF ₃ CF ₂ =CF ₂ (FO-1216) → products	2.18×10^{-12}	0.04	$7.38 \times 10^{-13} \exp(322/T)$	240-340	100
oFOx135	HO + <i>E</i> -CF ₃ CH=CHCF ₃ (HFO-1336mzz(E)) → products	1.31×10^{-13}	0.06	$6.94 \times 10^{-13} \exp(-496/T)$	210-380	100
oFOx136	HO + <i>Z</i> -CF ₃ CH=CHCF ₃ (HFO-1336mzz(Z)) → products	4.80×10^{-13}	0.06	$2.46 \times 10^{-13} \exp(199/T)$	210-300	100
oClOx95	HO + CH ₂ =CHCl (vinyl chloride) → products	7.55×10^{-12}	0.08	$2.54 \times 10^{-12} \exp(325/T)$	280-600	100
oFOx120	HO + <i>E</i> -CF ₃ CH=CHCl (HCFO-1233zd(E)) → products	3.53×10^{-13}	0.06	$8.79 \times 10^{-13} \exp(-272/T)$	220-300	100
oFOx121	HO + <i>Z</i> -CF ₃ CH=CHCl (HCFO-1233zd(Z)) → products	9.24×10^{-13}	0.06	$3.61 \times 10^{-13} \exp(280/T)$	220-300	100
oFOx165	HO + <i>E</i> -CF ₃ CF=CHCl (HCFO-1224yd(E)) → products	1.30×10^{-12}	0.08	$1.09 \times 10^{-12} \exp(53/T)$	250-430	100
oFOx166	HO + <i>Z</i> -CF ₃ CF=CHCl (HCFO-1224yd(Z)) → products	5.83×10^{-13}	0.08	$8.03 \times 10^{-13} \exp(-95/T)$	250-430	100



oFOx164	HO + E-CF ₃ CBr=CH ₂ (HBFO-1233xfB) → products	3.84 × 10 ⁻¹²	0.06	1.11 × 10 ⁻¹² exp(370/T)	250-430	100
oFOx154	NO ₃ + CF ₃ =CF ₂ (HFO-1114) → products	< 3 × 10 ⁻¹⁵				
oFOx153	NO ₃ + CF ₃ CF ₂ =CH ₂ (HFO-1234yf) → products	2.6 × 10 ⁻¹⁷	0.15			
oFOx122	NO ₃ + Z-CF ₃ CF=CHF (HFO-1225ze(Z)) → products	4.2 × 10 ⁻¹⁸	0.20			
oFOx123	NO ₃ + CF ₃ CF ₂ =CF ₂ (FO-1216) → products	< 3 × 10 ⁻¹⁵				
oFOx155	NO ₃ + CF ₂ =CF=CF=CF ₂ → products	1.56 × 10 ⁻¹⁵	0.15			
oClOx96	NO ₃ + CH ₂ =CHCl (vinyl chloride) → products	4.6 × 10 ⁻¹⁶	0.10	1.8 × 10 ⁻¹³ exp(-1780/T)	260-380	300
oFOx126	O ₃ + CF ₂ =CF ₂ (HFO-1114) → products	4.8 × 10 ⁻²¹	0.15			
oFOx113	O ₃ + CF ₃ CH=CH ₂ (HFO-1243zf) → products	1.43 × 10 ⁻²⁰	0.08	4.65 × 10 ⁻¹⁶ exp(-3096/T)	290-390	200
oFOx128	O ₃ + CF ₃ CF=CH ₂ (HFO-1234yf) → products	2.67 × 10 ⁻²¹	0.08			
oFOx129	O ₃ + E-CF ₃ CH=CHF (HFO-1234ze(E)) → products	2.50 × 10 ⁻²¹	0.10			
oFOx156	O ₃ + Z-CF ₃ CH=CHF (HFO-1234ze(Z)) → products	1.7 × 10 ⁻²¹	0.15			
oFOx130	O ₃ + CF ₃ CF ₂ =CF ₂ (FO-1216) → products	6.2 × 10 ⁻²²	0.30			
oFOx157	O ₃ + CF ₂ =CF=CF=CF ₂ → products	7.9 × 10 ⁻²¹	0.15	9.51 × 10 ⁻¹⁷ exp(-2800/T)	220-320	200
oFOx127	O ₃ + E-CF ₃ CH=CHCF ₃ (HFO-1336mzz(E)) → products	4.14 × 10 ⁻²²	0.10			
oFOx124	O ₃ + Z-CF ₃ CH=CHCF ₃ (HFO-1336mzz(Z)) → products	7.09 × 10 ⁻²²	0.08			
oClOx97	O ₃ + CH ₂ =CHCl (vinyl chloride) → products	2.5 × 10 ⁻¹⁹	0.15			
oFOx132	O ₃ + E-CF ₃ CH=CHCl (HCFO-1233zd(E)) → products	1.51 × 10 ⁻²¹	0.15			
oFOx131	O ₃ + Z-CF ₃ CH=CHCl (HCFO-1233zd(Z)) → products	1.53 × 10 ⁻²¹	0.15			
oFOx125	O ₃ + CF ₃ CCl=CH ₂ (HCFO-1233xf) → products	3.00 × 10 ⁻²¹	0.08			
Halogenated alcohols						
oFOx84	HO + CH ₂ FCH ₂ OH → products	9.12 × 10 ⁻¹³	0.08	2.23 × 10 ⁻¹² exp(-266/T)	230-300	200
oFOx85	HO + CHF ₂ CH ₂ OH → products	2.61 × 10 ⁻¹³	0.08	1.63 × 10 ⁻¹² exp(-545/T)	220-300	200
oFOx86	HO + CF ₃ CH ₂ OH → products	1.00 × 10 ⁻¹³	0.06	1.25 × 10 ⁻¹² exp(-754/T)	220-300	100
oFOx87	HO + CF ₃ CH ₂ CH ₂ OH → products	9.6 × 10 ⁻¹³	0.10	2.72 × 10 ⁻¹² exp(-305/T)	260-360	100
oFOx88	HO + C ₂ F ₅ CH ₂ OH → products	1.05 × 10 ⁻¹³	0.06	1.28 × 10 ⁻¹² exp(-748/T)	250-430	200
oFOx89	HO + CF ₃ CH(OH)CF ₃ → products	2.43 × 10 ⁻¹⁴	0.12	3.94 × 10 ⁻¹⁵ (T/298) ^{4.57} exp(542/T)	250-430	
oFOx158	HO + (CF ₃) ₂ C(OH)CH ₃ → products	7.71 × 10 ⁻¹⁵	0.12	1.90 × 10 ⁻¹⁸ (T/298) ^{11.5} exp(2476/T)	230-370	
oFOx159	HO + (CF ₃) ₃ COH → products	8.6 × 10 ⁻¹⁶	0.12	3.0 × 10 ⁻²⁰ (T/298) ^{11.3} exp(3060/T)	230-370	
oFOx90	HO + CF ₃ CHFCF ₂ CH ₂ OH → products	1.3 × 10 ⁻¹³	0.12	2.26 × 10 ⁻¹² exp(-848/T)	250-430	200
oFOx91	HO + n-C ₃ F ₇ CH ₂ OH → products	1.11 × 10 ⁻¹³	0.10	6.06 × 10 ⁻¹² exp(-1192/T)	280-370	200
oFOx92	HO + n-C ₄ F ₉ CH ₂ OH → products	9.4 × 10 ⁻¹⁴	0.15			
oFOx93	HO + n-C ₄ F ₉ CH ₂ CH ₂ OH → products	1.0 × 10 ⁻¹²	0.15			
oFOx94	HO + n-C ₆ F ₁₃ CH ₂ CH ₂ OH → products	8.3 × 10 ⁻¹³	0.15			
oFOx95	HO + n-C ₈ F ₁₇ CH ₂ CH ₂ OH → products	9.2 × 10 ⁻¹³	0.15			
oFOx96	HO + CF ₃ CH(OH) ₂ → products	1.2 × 10 ⁻¹³	0.20			
oClOx90	HO + CH ₂ ClCH ₂ OH → products	1.3 × 10 ⁻¹²	0.20			
oClOx91	HO + CCl ₃ CH ₂ OH → products	2.5 × 10 ⁻¹³	0.20			
Halogenated aldehydes						
oFOx97	HO + CHF ₂ CHO → products	1.6 × 10 ⁻¹²	0.15			
oFOx98	HO + C ₂ F ₅ CHO → products	5.2 × 10 ⁻¹³	0.10	2.42 × 10 ⁻¹² exp(-458/T)	250-360	200
oFOx99	HO + n-C ₃ F ₇ CHO → products	5.8 × 10 ⁻¹³	0.08	2.0 × 10 ⁻¹² exp(-369/T)	250-380	200
oFOx100	HO + n-C ₄ F ₉ CHO → products	6.1 × 10 ⁻¹³	0.08	2.0 × 10 ⁻¹² exp(-356/T)	250-380	150
oFOx101	HO + CF ₃ CH ₂ CHO → products	2.7 × 10 ⁻¹²	0.15	7.74 × 10 ⁻¹² exp(-314/T)	260-360	150
oFOx102	HO + n-C ₆ F ₁₃ CH ₂ CHO → products	2.0 × 10 ⁻¹²	0.15			
oFOx103	HO + n-C ₈ F ₁₇ CH ₂ CHO → products	1.8 × 10 ⁻¹²	0.15			
Halogenated ketones						
oFOx104	HO + C ₂ F ₅ C(O)CF(CF ₃) ₂ → products	< 5 × 10 ⁻¹⁶				
oClOx92	HO + CH ₂ ClC(O)CH ₃ → products	4.4 × 10 ⁻¹³	0.15			
oClOx93	HO + CHCl ₂ C(O)CH ₃ → products	4.0 × 10 ⁻¹³	0.15			
oClOx94	HO + CCl ₃ C(O)CH ₃ → products	1.5 × 10 ⁻¹⁴	0.15			
Halogenated acids						
oFOx105	HO + C ₂ F ₅ C(O)OH → products	1.5 × 10 ⁻¹³	0.15			
oFOx106	HO + n-C ₃ F ₇ C(O)OH → products	1.5 × 10 ⁻¹³	0.15			



oFOx107	HO + <i>n</i> -C ₄ F ₉ C(O)OH → products	1.5 × 10 ⁻¹³	0.15			
Halogenated ethers						
oFOx137	HO + CH ₃ OCHF ₂ → products	3.52 × 10 ⁻¹⁴	0.15	1.16 × 10 ⁻¹¹ exp(-1728/T)	290-470	100
oFOx138	HO + CH ₃ OCF ₃ → products	1.29 × 10 ⁻¹⁴	0.10	1.10 × 10 ⁻¹² exp(-1324/T)	290-470	100
oFOx139	HO + CHF ₂ OCHF ₂ → products	2.20 × 10 ⁻¹⁵	0.10	1.04 × 10 ⁻¹² exp(-1836/T)	270-470	100
oFOx140	HO + CHF ₂ OCF ₃ → products	4.57 × 10 ⁻¹⁶	0.10	3.09 × 10 ⁻¹³ exp(-1942/T)	290-400	100
oFOx141	HO + CH ₃ OCHF ₂ CF ₃ → products	1.57 × 10 ⁻¹³	0.10	1.74 × 10 ⁻¹² exp(-716/T)	250-330	100
oFOx142	HO + CH ₃ OCF ₂ CHF ₂ → products	2.24 × 10 ⁻¹⁴	0.10	2.50 × 10 ⁻¹² exp(-1405/T)	240-440	100
oFOx143	HO + CH ₃ OCH ₂ CF ₃ → products	6.24 × 10 ⁻¹³	0.10			
oFOx144	HO + CH ₃ OC ₂ F ₅ → products	1.20 × 10 ⁻¹⁴	0.10	1.84 × 10 ⁻¹² exp(-1499/T)	240-440	100
oFOx145	HO + <i>n</i> -C ₃ F ₇ OCH ₃ → products	1.18 × 10 ⁻¹⁴	0.10	1.98 × 10 ⁻¹² exp(-1526/T)	240-440	100
oFOx146	HO + <i>i</i> -C ₃ F ₇ OCH ₃ → products	1.52 × 10 ⁻¹⁴	0.10	1.86 × 10 ⁻¹² exp(-1432/T)	240-440	100
oFOx147	HO + C ₄ F ₉ OCH ₃ → products	1.19 × 10 ⁻¹⁴	0.08	1.15 × 10 ⁻¹² exp(-1362/T)	250-330	100
oFOx148	HO + CH ₃ OCH(CF ₃) ₂ → products	2.29 × 10 ⁻¹³	0.10	1.08 × 10 ⁻¹² exp(-461/T)	230-340	100
oFOx149	HO + CH ₂ FOCH(CF ₃) ₂ (Sevoflurane) → products	3.32 × 10 ⁻¹⁴	0.15	8.58 × 10 ⁻¹³ exp(-969/T)	230-310	200
oFOx150	HO + CHF ₂ OCHF ₂ CF ₃ (Desflurane) → products	4.08 × 10 ⁻¹⁵	0.10	7.43 × 10 ⁻¹³ exp(-1551/T)	230-300	200
Halogenated vinyl ethers						
oFOx133	HO + CF ₃ OCF=CF ₂ → products	2.96 × 10 ⁻¹²	0.10	1.01 × 10 ⁻¹² exp(320/T)	250-430	100
oFOx134	HO + C ₂ F ₅ OCF=CF ₂ → products	3.0 × 10 ⁻¹²	0.10	6.0 × 10 ⁻¹³ exp(480/T)	200-300	100
Peroxy radicals						
oFOx160	CF ₃ C(O)O ₂ + HO ₂ → CF ₃ C(O)OOH + O ₂ (1)	<i>k</i> ₁ / <i>k</i> = 1.8 ×				
	→ CF ₃ C(O)OH + O ₃ (2)	10 ⁻¹²				
	→ CF ₃ C(O)O + HO (3)	<i>k</i> ₃ / <i>k</i> = 7.6 ×				
		10 ⁻¹²				
		<i>k</i> ₂ / <i>k</i> = 1.12 ×				
		10 ⁻¹¹				
	Overall	2.0 × 10 ⁻¹¹	0.3			
oFOx161	CF ₃ C(O)O ₂ + NO → CF ₃ C(O)O + NO ₂	2.8 × 10 ⁻¹¹	0.2	4.0 × 10 ⁻¹² exp(560/T)	220-340	200
oFOx162	CF ₃ C(O)O ₂ + NO ₂ + M → CF ₃ C(O)O ₂ NO ₂ + M	6.6 × 10 ⁻¹²	0.3			
oFOx163	CF ₃ C(O)O ₂ NO ₂ + M → CF ₃ C(O)O ₂ + NO ₂ + M	5.0 × 10 ⁻²⁰		5.0 × 10 ⁻² exp(-12350/T)	290-330	
		[N ₂] (<i>k</i> ₀ /s ⁻¹)				
		9.9 × 10 ⁻⁵		1.1 × 10 ¹⁷ exp(-14440/T)		
		(<i>k</i> _∞ /s ⁻¹)				
		7.95 × 10 ⁻⁶ (1				
		bar) <i>k</i> /s ⁻¹				
Photochemical reactions added to the IUPAC website (see Supplementary Material for datasheets)						
PF5	CHF ₂ CHO + <i>hν</i> → products					
PF6	C ₂ F ₅ CHO + <i>hν</i> → products					
PF7	<i>n</i> -C ₃ F ₇ CHO + <i>hν</i> → products					
PF8	<i>n</i> -C ₄ F ₉ CHO + <i>hν</i> → products					
PF9	CF ₃ CH ₂ CHO + <i>hν</i> → products					
PF10	<i>n</i> -C ₆ F ₁₃ CH ₂ CHO + <i>hν</i> → products					

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621 a: Rate coefficients are also known as rate constants, both terms are used here.

622 b: See corresponding datasheets in Supplement for further information (e.g., methods used and products

623 formed).

624 c: The cited uncertainty is an expanded uncertainty corresponding approximately to a 95% confidence limit.

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