

# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO\_50

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## Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(9^{+9}_{-4.5}) \times 10^{-12}$	298	Stevens et al., 1999	DF-LIF (b)
$(2.5 \pm 0.5) \times 10^{-11}$	295	Reitz et al., 2002	PLP-LIF (c)
$(1.1 \pm 0.8) \times 10^{-11}$	300	Chuong et al., 2001	DF-LIF (d)
$(9 \pm 3) \times 10^{-12}$	298	Zhang et al., 2003	DF-CIMS (e)
$(8.8 \pm 1.2) \times 10^{-12}$	298	Miller et al., 2004	DF-CIMS (f)
$(9 \pm 3) \times 10^{-12}$	298	Park et al., 2004	PLP-LIF (g)
$(8.1^{+3.4}_{-2.3}) \times 10^{-12}$	298	Ghosh et al., 2010	PLP-LIF (h)
<i>Branching ratios</i>			
$k_2/k \approx 0.08\text{--}0.14$ (987 mbar)	298	Tuazon and Atkinson, 1990	UVP-FTIR (i)
$k_2/k = 0.044 \pm 0.008$ (991 mbar)	298	Chen et al., 1998	UVP-GC-CL (j)
$k_2/k = 0.15 \pm 0.10$ (133 mbar)	298	Chuong et al., 2001	DF-LIF (d)
$k_2/k = 0.12 \pm 0.07$ (1000 mbar)	297	Sprengnether et al., 2002	DF-FTIR (k)
$k_2/k = 0.08 \pm 0.06$ (593 mbar)			
$k_2/k = 0.07 \pm 0.03$ (133 mbar)	298	Patchen et al., 2007	DF-CIMS (l)
$k_2/k = 0.07^{+0.025}_{-0.015}$ (1013 mbar*)	295	Lockwood et al., 2010	UVP-GC-CL (m)
$k_2/k = 0.09^{+0.04}_{-0.03}$ (993 mbar)	297	Xiong et al., 2015	UVP-CIMS (n)
$k_2/k = 0.13 \pm 0.04$ (993 mbar)	297	Teng et al., 2017	UVP-CIMS (o)

## Comments

- (a) HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> is used here to represent the set of isomeric peroxy radicals formed from sequential addition of HO and O<sub>2</sub> to isoprene (2-methyl-but-1,3-diene).
- (b) HO radicals generated from the reaction of F atoms with H<sub>2</sub>O, following production of F from microwave discharge of CF<sub>4</sub>-He mixtures. HO monitored by LIF. HO concentration-time profiles, when added to isoprene-NO-O<sub>2</sub>-He mixtures, used to investigate the kinetics of HO removal and recycling at a total pressure of 2.7 mbar (2 Torr). Value of  $k$  determined from optimisation of simulated HO profiles to those observed, using a 9 reaction mechanism.
- (c) Laser flash photolysis of H<sub>2</sub>O<sub>2</sub>-isoprene-O<sub>2</sub>-NO-N<sub>2</sub> mixtures at 248 nm, with HO monitored by LIF. HO concentration-time profiles used to investigate the kinetics of HO removal and recycling at a total pressure of 4–5.3 mbar (3–4 Torr). Value of  $k$  determined from optimisation of simulated HO profiles to those observed, using a 7 reaction mechanism.

- (d) HO radicals generated from the reaction of F atoms with H<sub>2</sub>O, following production of F from microwave discharge of CF<sub>4</sub>-He mixtures. HO monitored by LIF. HO concentration-time profiles, when added to isoprene-NO-O<sub>2</sub>-Ar mixtures, used to investigate the kinetics of HO removal and recycling, in a high pressure turbulent flow system at total pressures between 133 mbar and 200 mbar (100–150 Torr). Values of  $k$  and  $k_2/k$  determined from optimisation of simulated HO profiles to those observed, using an explicit reaction mechanism containing over 50 reactions.
- (e) HO radicals generated from the reaction of H atoms with NO<sub>2</sub>, following production of H from microwave discharge of H<sub>2</sub>-He mixtures. HOC<sub>5</sub>H<sub>8</sub>O<sub>2</sub> radicals generated in HO-isoprene-O<sub>2</sub>-NO-N<sub>2</sub> mixtures in a flow system at 1.3 – 2.7 mbar (1–2 Torr), and monitored as a negative ion following reaction with SF<sub>6</sub><sup>-</sup>. The HOC<sub>5</sub>H<sub>8</sub>O<sub>2</sub> concentration displayed complex kinetic behaviour, indicative of chain regeneration of HOC<sub>5</sub>H<sub>8</sub>O<sub>2</sub>. Value of  $k$  determined from optimisation of simulated HOC<sub>5</sub>H<sub>8</sub>O<sub>2</sub> profiles to those observed, using a 12 reaction mechanism.
- (f) HO radicals generated from the reaction of F atoms with H<sub>2</sub>O, following production of F from microwave discharge of CF<sub>4</sub>-He mixtures. HOC<sub>5</sub>H<sub>8</sub>O<sub>2</sub> radicals generated in HO-isoprene-O<sub>2</sub>-N<sub>2</sub> mixtures in a high pressure turbulent flow system at 133 mbar (100 Torr), and monitored via proton transfer following reaction with H<sup>+</sup>(H<sub>2</sub>O)<sub>n</sub>. Kinetics determined under pseudo-first order conditions by sequential addition of an HO scavenger (but-1-ene) followed by the reagent NO. The HO scavenger was added at a sufficient excess concentration to preclude significant regeneration of HOC<sub>5</sub>H<sub>8</sub>O<sub>2</sub> under the experimental conditions, which was confirmed through simulations of the system using a 10 reaction mechanism.
- (g) Laser flash photolysis of H<sub>2</sub>O<sub>2</sub>-isoprene-O<sub>2</sub>-NO-N<sub>2</sub> mixtures at 248 nm, with HO monitored by LIF. HO concentration-time profiles used to investigate the kinetics of HO recycling at a total pressure of 5.3 mbar (4 Torr). Value of  $k$  determined from optimisation of simulated HO profiles to those observed, using an explicit reaction mechanism containing 14 reactions. Result reported to be insensitive to adopted value of  $k_2/k$ , which was subsequently fixed at 0.05 for the experimental conditions.
- (h) Laser flash photolysis of 2-iodo-2-methylbut-3-en-1-ol-O<sub>2</sub>-NO-Ar mixtures at 248 nm., with production and cycling of HO monitored by LIF. Photolysis of 2-iodo-2-methylbut-3-en-1-ol generates the HOC<sub>5</sub>H<sub>8</sub> isomer which corresponds to the major channel for HO addition to isoprene, and subsequently a targeted subset of the HOC<sub>5</sub>H<sub>8</sub>O<sub>2</sub> isomers. HO concentration-time profiles used to investigate the kinetics of HO production and recycling at a total pressure of 66 mbar (50 Torr). Value of  $k$  determined from optimisation of simulated HO profiles to those observed, using an explicit reaction mechanism containing 25 reactions. Result reported to be insensitive to adopted value of  $k_2/k$ , which was subsequently fixed at 0.15 for the experimental conditions.
- (i) Blacklight photolysis of CH<sub>3</sub>ONO-isoprene-NO-air mixtures in a 7.9 m<sup>3</sup> chamber. The total yield of isoprene nitrates relative to isoprene consumed was estimated on the basis of IR band strengths for –ONO<sub>2</sub> groups, as quantified previously for alkyl nitrates.
- (j) Blacklight photolysis of (CH<sub>3</sub>)<sub>2</sub>CHONO-isoprene-NO-air mixtures in a 5 m<sup>3</sup> chamber. Formation of 7 isoprene nitrate isomers was detected through separation in a capillary chromatographic column and quantification by pyrolytic conversion to NO<sub>2</sub>, followed by chemiluminescent reaction of NO<sub>2</sub> with luminol. One isoprene nitrate isomer reported to dominate the distribution, accounting for 45–65% of the total. Reported value of  $k_2/k$  based on the total yield of isoprene nitrate isomers relative to isoprene consumed (measured using GC-FID)..
- (k) HO<sub>2</sub> radicals generated from the reaction of H atoms with O<sub>2</sub>, following production of H from microwave discharge of H<sub>2</sub>-He mixtures. HO<sub>2</sub> added to isoprene-NO-air mixtures in a

high pressure wall-less flow system at 593 or 1000 mbar (445 Torr or 750 Torr). HO formation from reaction of HO<sub>2</sub> with excess NO allows consumption of isoprene to be initiated. Products quantified by long-path FTIR spectroscopy at small consumptions of isoprene by a procedure involving modulating the radical source to obtain difference spectra. With support from DFT calculations, IR band strengths for the -ONO<sub>2</sub> groups in isoprene nitrates were based on that quantified for (CH<sub>3</sub>)<sub>2</sub>CHONO<sub>2</sub>.

- (l) HO radicals generated from the reaction of F atoms with H<sub>2</sub>O, following production of F from microwave discharge of CF<sub>4</sub>-He mixtures. HO added to isoprene-NO-air mixtures in a high pressure turbulent flow system at 133 mbar (100 Torr). Products monitored via proton transfer following reaction with H<sup>+</sup>(H<sub>2</sub>O)<sub>n</sub>. Relative flux through channels (1) and (2) determined from the measured formation of isoprene nitrates and NO<sub>2</sub>. The latter was corrected for secondary formation, which was typically calculated to account for about 30% of the observed total NO<sub>2</sub> on the basis of simulations using a 10 reaction mechanism.
- (m) Blacklight photolysis of isoprene-HONO-NO-NO<sub>2</sub>-air mixtures in a 5.5 m<sup>3</sup> chamber. Formation of 8 isoprene nitrate isomers was detected using GC-ECD, with three isomers positively identified using synthesised standards. The total isoprene nitrate yield was quantified by a procedure involving pyrolytic conversion to NO<sub>2</sub>, photolytic conversion of NO<sub>2</sub> to NO, and chemiluminescent reaction of NO with ozone. The 4,3, 1,2 and 4,1 isomers were reported to account for 90% of the total yield. Reported value of k<sub>2</sub>/k based on the total yield of isoprene nitrate isomers relative to isoprene consumed (measured using GC-FID).
- (n) Blacklight photolysis of (CH<sub>3</sub>)<sub>2</sub>CHONO-isoprene-NO-air mixtures in a 5.5 m<sup>3</sup> chamber. Isoprene nitrate isomers were detected using CIMS through reaction with I(H<sub>2</sub>O)<sub>n</sub><sup>-</sup> to form iodide clusters. The signals were calibrated using synthesised standards of the 4,3 and 1,4 isomers, with the sensitivity of other β-OH and δ-OH isomers inferred from those calibrations. Reported value of k<sub>2</sub>/k based on the total yield of isoprene nitrate isomers relative to isoprene consumed, measured using proton-transfer reaction linear ion trap mass spectrometry.
- (o) Blacklight photolysis of CH<sub>3</sub>ONO-isoprene-NO-air mixtures in a 0.85 m<sup>3</sup> chamber. Individual isoprene nitrate isomers were detected using CIMS through reaction with CF<sub>3</sub>O<sup>-</sup>, following chromatographic separation. The CIMS sensitivities of the individual isomers were determined independently by simultaneous measurement of NO<sub>2</sub> by thermal-dissociation LIF (Lee et al., 2014). Reported value of k<sub>2</sub>/k based on the total yield of isoprene nitrate isomers relative to isoprene consumed (measured using GC-FID).

### Preferred Values

Parameter	Value	T/K
k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	8.8 × 10 <sup>-12</sup>	298
k <sub>1</sub> /k	0.89 (at 1013 mbar)	298
k <sub>2</sub> /k	0.11 (at 1013 mbar)	298
<i>Reliability</i>		
Δ log k	± 0.1	298
Δ k <sub>1</sub> /k	± 0.05	298
Δ k <sub>2</sub> /k	± 0.05	298

### *Comments on Preferred Values*

The sequential addition of HO and O<sub>2</sub> to isoprene generates a set of six structurally isomeric peroxy radicals, of which four possess β-hydroxy groups and two possess δ-hydroxy groups. Each of the δ-hydroxy peroxy radicals may also exist in *E*- and *Z*- forms. With the exception of the recent study of Ghosh et al. (2010), the reported determinations of *k* have considered reaction of NO with the entire population of HOC<sub>5</sub>H<sub>8</sub>O<sub>2</sub> radicals formed following addition of HO to isoprene. Through use of a specific iodo-substituted precursor (see comment (h)), Ghosh et al. (2010) selectively studied the subset of peroxy radicals formed from the addition of HO at carbon 1 in isoprene (i.e., 2-methyl-buta-1,3-diene); leading to a population containing one β-hydroxy isomer and one δ-hydroxy isomer, with the latter present in *E*- and *Z*- forms.

The preferred value of *k* is based on the results of Miller et al. (2004), in which the time dependence of the HOC<sub>5</sub>H<sub>8</sub>O<sub>2</sub> isomer population was monitored directly under pseudo-first order conditions. However, with the exception of the results of Reitz et al. (2002), the preferred value is consistent with the other reported values, which were all determined by optimising simulations of chain recycling of HO or HOC<sub>5</sub>H<sub>8</sub>O<sub>2</sub> using an explicit mechanism. The higher rate coefficient reported by Reitz et al. (2002) is taken to be superseded by that of Park et al. (2004), from the same laboratory, which employed a very similar methodology. The lack of evidence of differential reactivity for the HOC<sub>5</sub>H<sub>8</sub>O<sub>2</sub> isomers in any of the studies, and particularly the consistent value reported by Ghosh et al. (2010) for a targeted subset of the population, suggests that the preferred value of *k* can reasonably be assigned to the reactions of each of the individual HOC<sub>5</sub>H<sub>8</sub>O<sub>2</sub> isomers. This is also generally consistent with the wider kinetics database of reactions of NO with hydrocarbon-derived RO<sub>2</sub> radicals, which generally show little sensitivity to the size or structure of the organic group (e.g., see discussion in Miller et al., 2004).

The preferred values of the branching ratios are based on a least squares fit to the Sprengnether et al. (2002), Patchen et al. (2007), Xiong et al. (2015) and Teng et al. (2017) determinations of *k*<sub>2</sub>/*k*, assuming a relative pressure dependence equivalent to that recommended for peroxy radicals containing six heavy atoms in the organic group (Arey et al., 2001; Teng et al., 2015; Jenkin et al., 2019). This leads to a value of 0.11 at 1013 mbar (760 Torr), falling to about 0.045 at 133 mbar (100 Torr). It is noted that the preferred value of *k*<sub>2</sub>/*k* at 1013 mbar is also consistent with those reported in a number of chamber evaluations of isoprene oxidation in which detailed mechanisms have been optimised, which lie in the range 0.09–0.12 (Carter and Atkinson, 1996; Pinho et al., 2005; Paulot et al., 2009). However, the reported determinations show some variability and further studies are clearly required to reduce the uncertainties in this parameter. Systematic studies as a function of temperature and pressure would also be valuable.

In contrast to the kinetics discussed above, the broader database of peroxy radical reactions indicates that the branching ratio for organic nitrate formation can be sensitive to the structure of the organic group and to the presence of oxygenated functional groups. Given that the HOC<sub>5</sub>H<sub>8</sub>O<sub>2</sub> isomers can be primary, secondary or tertiary, possess allyl functionalities and either β- or δ-hydroxy groups, it is possible that *k*<sub>2</sub>/*k* varies from one HOC<sub>5</sub>H<sub>8</sub>O<sub>2</sub> isomer to another. Some studies tend to confirm this (e.g. Paulot et al., 2009; Lockwood et al., 2010), although the recent appraisal of Wennberg et al. (2018) suggests that the variability may be as low as ~0.02, based on the speciated observations of Teng et al. (2017). The preferred value thus represents a weighted average value for the peroxy radical population. Further determinations of *k*<sub>2</sub>/*k* for specific isomers (or subsets of isomers) would therefore be informative.

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