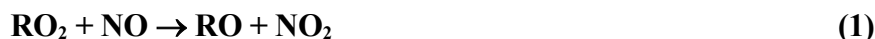


# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation: halogenated peroxy radical + NO (+M) reactions

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

This data sheet updated: 12<sup>th</sup> July 2006.



(R = CH<sub>2</sub>F, CHF<sub>2</sub>, CF<sub>3</sub>, CH<sub>2</sub>FCHF, CHF<sub>2</sub>CF<sub>2</sub>, CF<sub>3</sub>CHF, CF<sub>3</sub>CF<sub>2</sub>, CHFCl, CF<sub>2</sub>Cl, CFCl<sub>2</sub>, CH<sub>3</sub>CFCl, CF<sub>2</sub>ClCH<sub>2</sub>, CFCl<sub>2</sub>CH<sub>2</sub>, CF<sub>3</sub>CCl<sub>2</sub>, CH<sub>2</sub>ClCH<sub>2</sub>, CH<sub>2</sub>Cl, CCl<sub>3</sub>, CH<sub>2</sub>Br, CHBr<sub>2</sub>)

## 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>			
R = CH <sub>2</sub> F			
$(1.25 \pm 0.13) \times 10^{-11}$	295	Sehested et al., 1993	PR-AS (a)
R = CHF <sub>2</sub>			
$(1.26 \pm 0.16) \times 10^{-11}$	295	Sehested et al., 1993	PR-AS (a)
R = CF <sub>3</sub>			
$(1.78 \pm 0.36) \times 10^{-11}$	295	Plumb and Ryan, 1982	DF-MS (b)
$1.45 \times 10^{-11} (T/298)^{(1.2 \pm 0.2)}$	230-430	Dognon et al., 1985	PLP-MS (c)
$(1.45 \pm 0.2) \times 10^{-11}$	298		
$(1.53 \pm 0.30) \times 10^{-11}$	290	Peeters et al., 1992	DF-MS (d)
$(1.68 \pm 0.26) \times 10^{-11}$	295	Sehested and Nielsen, 1993	PR-AS (a)
$(1.53 \pm 0.20) \times 10^{-11}$	297	Bevilacqua et al., 1993	F-CIMS (e)
$(1.57 \pm 0.38) \times 10^{-11}$	298	Turnipseed et al., 1994	PLP-LIF (f)
$(1.57 \pm 0.31) \times 10^{-11}$	293	Bhatnagar and Carr, 1994	FP-MS (g)
$(1.76 \pm 0.35) \times 10^{-11}$	298	Bourbon et al., 1996	DF-LIF (h)
$(1.6 \pm 0.3) \times 10^{-11}$	298	Louis et al., 1999	DF-MS (i)
R = CH <sub>2</sub> FCHF			
$>8.7 \times 10^{-12}$	296	Wallington et al., 1994	PR-AS (a)
R = CHF <sub>2</sub> CF <sub>2</sub>			
$>(9.7 \pm 1.3) \times 10^{-12}$	295	Sehested et al., 1993	PR-AS (a)
R = CF <sub>3</sub> CHF			
$(1.28 \pm 0.36) \times 10^{-11}$	298	Wallington and Nielsen, 1991	PR-AS (a)
$(1.31 \pm 0.30) \times 10^{-11}$	324	Bhatnagar and Carr, 1995	FP-MS (j)
R = CF <sub>3</sub> CF <sub>2</sub>			
$>(1.07 \pm 0.15) \times 10^{-11}$	295	Sehested et al., 1993	PR-AS (a)
R = CHFCl			
$(1.31 \pm 0.20) \times 10^{-11}$	299	Bhatnagar and Carr, 1996	FP-MS (k)
R = CF <sub>2</sub> Cl			
$1.6 \times 10^{-11} (T/298)^{(1.5 \pm 0.4)}$	230-430	Dognon et al., 1985	PLP-MS (c)
$(1.6 \pm 0.3) \times 10^{-11}$	298		
$(1.31 \pm 0.12) \times 10^{-11}$	295	Sehested et al., 1993	PR-AS (a)
R = CFCl <sub>2</sub>			
$(1.6 \pm 0.2) \times 10^{-11}$	298	Lesclaux and Caralp, 1984	PLP-MS (l)
$1.45 \times 10^{-11} (T/298)^{(1.3 \pm 0.2)}$	230-430	Dognon et al., 1985	PLP-MS (c)

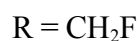
$(1.45 \pm 0.2) \times 10^{-11}$	298		
R = CH <sub>3</sub> CFCl			
$2.0 \times 10^{-11} (T/300)^{-(1.8 \pm 0.3)}$	263-321	Wu and Carr, 1996	FP-MS (m)
$1.9 \times 10^{-11}$	298		
R = CF <sub>2</sub> ClCH <sub>2</sub>			
$(1.18 \pm 0.10) \times 10^{-11}$	295	Sehested et al., 1993	PR-AS (a)
R = CFCl <sub>2</sub> CH <sub>2</sub>			
$(1.28 \pm 0.11) \times 10^{-11}$	295	Sehested et al., 1993	PR-AS (a)
$1.3 \times 10^{-11} (T/300)^{-(1.5 \pm 0.2)}$	263-321	Wu and Carr, 1996	FP-MS (m)
$1.25 \times 10^{-11}$	298		
R = CF <sub>3</sub> CCl <sub>2</sub>			
$(1.5 - 2.0) \times 10^{-11}$	298	Hayman et al., 1994	PLP-AS (n)
R = CH <sub>2</sub> ClCH <sub>2</sub>			
$(9.7 \pm 1.2) \times 10^{-12}$	298	Patchen et al. (2005)	F-CIMS (o)
R = CH <sub>2</sub> Cl			
$(1.87 \pm 0.20) \times 10^{-11}$	295	Sehested et al., 1993	PR-AS (a)
R = CCl <sub>3</sub>			
$(1.86 \pm 0.28) \times 10^{-11}$	295	Ryan and Plumb, 1984	DF-MS (p)
$1.7 \times 10^{-11} (T/298)^{-(1.0 \pm 0.2)}$	230-430	Dognon et al., 1985	PLP-MS (c)
$(1.7 \pm 0.2) \times 10^{-11}$	298		
R = CH <sub>2</sub> Br			
$(1.07 \pm 0.11) \times 10^{-11}$	295	Sehested et al., 1993	PR-AS (a)
R = CHBr <sub>2</sub>			
$(1.74 \pm 0.16) \times 10^{-11}$	296	Bayes et al., 2005	PLP-RF (q)
<i>Branching Ratios</i>			
R = CF <sub>3</sub>			
$k_2/k = (0.0167 \pm 0.0027)$	295	Nishida et al., 2004	P-FTIR (r)

### Comments

- (a)  $k$  determined from  $+d[\text{NO}_2]/dt$  at a total pressure of 1 bar.
- (b)  $k$  was independent of pressure over the range 2.5-6.8 mbar.
- (c) No significant pressure dependence in  $k$  over the range 1.3-13 mbar was observed.
- (d) Fast-flow system with molecular beam sampling MS at a total pressure of 2.7 mbar.  $k$  was derived from decay of CF<sub>3</sub>O<sub>2</sub> and appearance of NO<sub>2</sub>.
- (e)  $k$  determined from decay of CF<sub>3</sub>O<sub>2</sub> in the presence of NO; pressure range 1.1-2.7 mbar.
- (f) Photolysis of CF<sub>3</sub>Br in the presence of O<sub>2</sub> and NO at 93 mbar total pressure.  $k$  was obtained by fitting the measured CF<sub>3</sub>O radical temporal profile, with formation through CF<sub>3</sub>O<sub>2</sub> + NO and loss through CF<sub>3</sub>O + NO.
- (g) Photolysis of (CF<sub>3</sub>CO)<sub>2</sub>O in the presence of O<sub>2</sub>, N<sub>2</sub> and NO at 2.7-40 mbar total pressure.  $k$  obtained from the kinetics of CF<sub>3</sub>O<sub>2</sub> removal and CF<sub>3</sub>O formation.  $k$  was independent of pressure in the studied range.
- (h) CF<sub>3</sub>O<sub>2</sub> generated from F + CHF<sub>3</sub> reaction, with  $k$  determined from the formation kinetics of CF<sub>3</sub>O when NO added; pressure range 1.1-4.0 mbar.
- (i) CF<sub>3</sub>O<sub>2</sub> generated from F + CHF<sub>3</sub> reaction, with  $k$  determined from the removal kinetics of CF<sub>3</sub>O<sub>2</sub> when NO added; pressure range 0.9-4.0 mbar.
- (j) Photolysis of Cl<sub>2</sub> in the presence of CF<sub>3</sub>CH<sub>2</sub>F, O<sub>2</sub>, N<sub>2</sub> and NO at 16-33 mbar total pressure.  $k$  was obtained from the formation kinetics of NO<sub>2</sub>.  $k$  was independent of pressure in the studied range.
- (k) Photolysis of Cl<sub>2</sub> in the presence of CH<sub>2</sub>FCl, O<sub>2</sub>, N<sub>2</sub> and NO at 8-33 mbar total pressure.  $k$  was obtained from the formation kinetics of NO<sub>2</sub>.  $k$  was independent of pressure in the studied range.

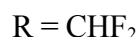
- (l) Measurements were made at 2.7 mbar total pressure.
- (m) Photolysis of  $\text{CH}_3\text{CFCl}_2$  in the presence of  $\text{O}_2$ ,  $\text{N}_2$  and  $\text{NO}$  at 11-27 mbar total pressure.  $k$  for both  $\text{CH}_3\text{CFCIO}_2$  and  $\text{CFCl}_2\text{CH}_2\text{O}_2$  were extracted simultaneously from the removal kinetics of  $\text{NO}$  and formation kinetics of  $\text{CFCl}_2\text{CH}_2\text{O}$ .  $k$  was independent of pressure in the studied range.
- (n)  $k$  derived from computer fit of transient absorption traces based on a mechanism of 9 reactions. Experiments performed at 1 bar pressure.
- (o)  $\text{CH}_2\text{ClCH}_2\text{O}_2$  generated from the  $\text{C}_2\text{H}_4 + \text{Cl}$  reaction, with  $k$  determined from pseudo-first order decay  $\text{CH}_2\text{ClCH}_2\text{O}_2$  in the presence of  $\text{NO}$ . Measurements made at 130 mbar pressure.
- (p)  $k$  independent of pressure over the range 2.3-7.2 mbar.
- (q) Photolysis of  $\text{CHBr}_3$  in the presence of  $\text{O}_2$  and  $\text{NO}$  at 2.7-13 mbar.  $k$  was obtained from the formation kinetics of secondary Br atoms, generated from the prompt decomposition of  $\text{CHBr}_2\text{O}$ .  $k$  was independent of pressure in the studied range.
- (r)  $\text{CF}_3\text{O}_2$  generated from the UV photolysis of  $\text{CF}_3\text{N}_2\text{CF}_3$  in excess  $\text{NO}$ ,  $\text{N}_2$  and  $\text{O}_2$  at 930 mbar. Branching ratio determined from the relative yields of  $\text{CF}_3\text{ONO}_2$  and  $\text{COF}_2$ .

### Preferred Values



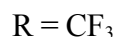
$k = 1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$\Delta \log k = \pm 0.3$  at 298 K.



$k = 1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$\Delta \log k = \pm 0.3$  at 298 K.



$k = 1.6 \times 10^{-11} (T/298)^{-1.2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230-430 K.

$\Delta \log k = \pm 0.1$  at 298 K.

$\Delta n = \pm 0.5$ .



$k > 9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.



$k > 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.



$k = 1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$\Delta \log k = \pm 0.2$  at 298 K.



$k > 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.



$k = 1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

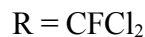
$\Delta \log k = \pm 0.3$  at 298 K.



$k = 1.5 \times 10^{-11} (T/298)^{-1.5} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230-430 K.

$\Delta \log k = \pm 0.2$  at 298 K.

$\Delta n = \pm 0.5$ .



$k = 1.5 \times 10^{-11} (T/298)^{-1.3} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230-430 K.

$\Delta \log k = \pm 0.2$  at 298 K.

$\Delta n = \pm 0.5$ .



$k = 2.0 \times 10^{-11} (T/298)^{-1.8} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 260-320 K.

$\Delta \log k = \pm 0.3$  at 298 K.

$\Delta n = \pm 0.5$ .



$k = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$\Delta \log k = \pm 0.3$  at 298 K.



$k = 1.3 \times 10^{-11} (T/298)^{-1.5} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 260-320 K.

$\Delta \log k = \pm 0.2$  at 298 K.

$\Delta n = \pm 0.5$ .



$k = 1.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$\Delta \log k = \pm 0.3$  at 298 K.



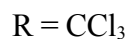
$k = 9.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$\Delta \log k = \pm 0.3$  at 298 K.



$k = 1.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$\Delta \log k = \pm 0.3$  at 298 K.



$k = 1.8 \times 10^{-11} (T/298)^{-1.0} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230-430 K.

$\Delta \log k = \pm 0.2$  at 298 K.

$\Delta n = \pm 0.5$ .



$k = 1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$\Delta \log k = \pm 0.3$  at 298 K.



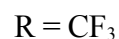
$k = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$\Delta \log k = \pm 0.3$  at 298 K.

### *Comments on Preferred Values*



The preferred values are the rounded-off rate coefficients determined by Sehested et al. (1993).



The preferred values are based on the temperature dependent data of Dognon et al. (1985),

adjusted to fit a  $k_{298}$  value based on the determinations of Plumb and Ryan (1982), Dognon et al. (1985), Peeters et al. (1992), Sehested and Nielsen (1993), Bevilacqua et al. (1993), Turnipseed et al. (1994), Bhatnagar and Carr (1994), Bourbon et al., (1996) and Louis et al. (1999).



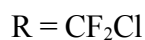
The preferred value is the rounded-off lower limit of Wallington et al. (1994).



The preferred value is the rounded-off rate coefficient determined by Wallington and Nielsen (1991).



The preferred value is the rounded-off rate coefficient determined by Bhatnagar and Carr (1996).



The preferred values are based on the temperature dependent data of Dognon et al. (1985), adjusted to fit the average value of  $k_{298}$  from the data of Sehested et al. (1993) and Dognon et al. (1985).



The preferred values are based on the temperature dependent data of Dognon et al. (1985), adjusted to fit the average value of  $k_{298}$  from the data of Lesclaux and Caralp (1984), and Dognon et al. (1985)-



The preferred values are based on the temperature dependent data of Wu and Carr (1996).



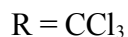
The preferred value is the rounded-off average of the rate coefficients determined by Sehested et al. (1993) and Wu and Carr (1996).



The preferred value is the mid-point of the range of values determined by Hayman et al. (1994).



The preferred value is the rate coefficient determined by Patchen et al. (2005).



The preferred values are based on the temperature dependent data of Dognon et al. (1985), adjusted to fit the average value of  $k_{298}$  from the data of Ryan and Plumb (1984) and Dognon et al. (1985).



The preferred value is the rounded-off rate coefficient determined by Bayes et al. (2005).

The temperature dependence expressions are given in the form favoured by Dognon et al. (1985), and subsequently adopted by others, which best describe the measured data. Comparison of the reported rate coefficients with those for the corresponding alkyl peroxy

radicals,  $\text{CH}_3\text{O}_2$  and  $\text{C}_2\text{H}_5\text{O}_2$ , indicates that the presence of a  $\alpha$ -halogen substituent typically enhances  $k_{298}$  by a factor of about 1.5 – 2, with the reactions also possessing a similar dependence on temperature where comparison is possible. Although not so marked, it appears that additional  $\alpha$ -halogen substituents result in further slight enhancements to  $k_{298}$ . Similarly to small alkyl peroxy radicals, the observations indicate that the reactions are dominated by the RO-forming channel (1). Dognon et al. (1985) measured quantum yields for  $\text{NO}_2$  greater than unity for all the  $\text{RO}_2$  radicals studied; suggesting that the  $\text{RO}_2 + \text{NO}$  reactions mainly form RO and  $\text{NO}_2$ , with additional  $\text{NO}_2$  being produced from secondary chemistry. Recently, Nishida et al. (2004) have observed formation of a small yield ( $1.7 \pm 0.3$ ) % of  $\text{CF}_3\text{ONO}_2$  from the reaction of  $\text{CF}_3\text{O}_2$  with NO, confirming the existence of channel (2) at 930 mbar pressure. This suggests that the reactions of the  $\text{C}_1$  and  $\text{C}_2$  halogenated  $\text{RO}_2$  radicals will generally have minor channels forming  $\text{RONO}_2$ , but additional studies are required to confirm this.

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