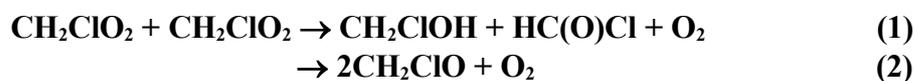


# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oRCIOx53

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This data sheet updated: 27<sup>th</sup> January 2006.



## 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>			
$k_{\text{obs}} = 3.1 \times 10^{-13} \exp[(735 \pm 95)/T]$	228-380	Dagaut et al., 1988	FP-UVA (a,b)
$k_{\text{obs}} = (3.78 \pm 0.45) \times 10^{-12}$	298		
$1.95 \times 10^{-13} \exp[(874 \pm 26)/T]$	251-600	Catoire et al., 1994	FP-UVA (c)
$(4.2 \pm 0.4) \times 10^{-12}$	298		
$(3.3 \pm 0.7) \times 10^{-12}$	298	Biggs et al., 1999	DF-LIF/RF (d)
<i>Branching Ratios</i>			
$k_2/k \approx 1.0$	305	Sanhueza and Heicklen, 1975	UVP-IR (e)
$k_2/k \approx 1.0$	298	Niki et al., 1980	UVP-FTIR (f)

## Comments

- $k_{\text{obs}}$  is based on the measured overall second-order decay of  $\text{CH}_2\text{ClO}_2$ , defined by  $-\text{d}[\text{CH}_2\text{ClO}_2]/\text{dt} = 2k_{\text{obs}}[\text{CH}_2\text{ClO}_2]^2$ . As described in detail by Lesclaux (1997),  $\text{HO}_2$  radicals formed from the subsequent chemistry of  $\text{CH}_2\text{ClO}$  (formed from channel (2)) are expected to lead to secondary removal of  $\text{CH}_2\text{ClO}_2$ . The true value of  $k$  is expected to fall in the range  $k_{\text{obs}}/(1+\alpha) < k < k_{\text{obs}}$ , where  $\alpha = k_2/k$ .
- Flash photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{Cl}-\text{O}_2-\text{N}_2$  mixtures at total pressures of 33-533 mbar at 298 K and of 133 mbar ( $\text{N}_2$ ) from 228-380 K. Peroxy radical concentrations were monitored by UV absorption with  $\sigma_{250 \text{ nm}} = (3.14 \pm 0.45) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ .
- Flash photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{Cl}-\text{O}_2-\text{N}_2$  mixtures at a total pressure of 1000 mbar. Peroxy radical concentrations were monitored by UV absorption in the wavelength range 205 to 290 nm, with  $\sigma_{250 \text{ nm}} = (3.40 \pm 0.20) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  in the temperature range 251 to 393 K (decreasing at higher temperatures). Values of  $k_{\text{obs}}/\sigma_{250 \text{ nm}}$  are in excellent agreement with those of Dagaut et al. (1988) over the common temperature range. Observed decays in transient absorption were found to be distorted from second order kinetics at wavelengths < 250 nm where  $\text{HO}_2$  absorbs significantly, allowing  $k$  and the rate coefficient for the reaction of  $\text{HO}_2$  with  $\text{CH}_2\text{ClO}_2$  to be extracted via an iterative procedure.
- Experiments performed at pressures in the range 1.3 to 4 mbar.  $\text{CH}_2\text{ClO}_2$  radicals were produced by the  $\text{F} + \text{CH}_3\text{Cl}$  reaction, with subsequent addition of  $\text{O}_2$ .  $\text{CH}_2\text{ClO}_2$  radicals were monitored by titration to  $\text{NO}_2$  following reaction with excess  $\text{NO}$ , with LIF detection of  $\text{NO}_2$ .  $\text{HO}_2$  radicals generated the subsequent chemistry of  $\text{CH}_2\text{ClO}$  (formed from channel (2)) were also titrated to  $\text{NO}_2$  under the experimental conditions, but were independently measured through detection of simultaneously formed  $\text{OH}$ , by RF.  $k$  values were extracted by numerical simulation of the results, using an 8 reaction scheme.
- Photolysis of  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{Cl}-\text{O}_2$  mixtures. In situ monitoring of products by IR showed exclusive formation of  $\text{HCl}$  and  $\text{HC(O)Cl}$  as the initial products.

- (f) Photolysis of Cl<sub>2</sub> in the presence of CH<sub>3</sub>Cl-air mixtures. In situ monitoring of reactants and products by FTIR spectroscopy showed 90-95% conversion of CH<sub>3</sub>Cl to HC(O)Cl. Tentative observation of CH<sub>2</sub>ClOOH at yields up to ca. 10%, and H<sub>2</sub>O<sub>2</sub>, is indicative of the occurrence of partial reaction of HO<sub>2</sub> with CH<sub>2</sub>ClO<sub>2</sub> in competition with the HO<sub>2</sub> self reaction.

### Preferred Values

$k = 3.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 1.9 \times 10^{-13} \exp(870/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250-600 K.

$k_2/k = 1.0$  at 298 K.

### Reliability

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

$\Delta(E/R) = \pm 200$  K.

$\Delta(k_2/k) = {}^{+0.0}_{-0.1}$  at 298 K.

### Comments on Preferred Values

The results of the product studies (Sanhueza and Heicklen, 1975; Niki et al., 1980) are consistent with the radical-forming channel (2) being essentially exclusive for the self-reaction of CH<sub>2</sub>ClO<sub>2</sub> radicals.

The preferred value of  $k$  at 298 K is the average of the results of Catoire et al. (1994) (based on their Arrhenius expression) and Biggs et al. (1999), which allowed extraction of  $k$  from full appraisal of the reaction mechanism. The preferred Arrhenius expression for  $k$  is based on the  $E/R$  value from the comprehensive temperature dependence study of Catoire et al. (1994), combined with a pre-exponential factor adjusted to give the preferred value of  $k$  at 298 K. As noted above, the earlier  $k_{\text{obs}}$  data of Dagaut et al. (1988) are also in excellent agreement with those of Catoire et al. (1994) when both sets of data are analyzed by a simple second-order treatment from results derived at  $\lambda = 250$  nm, and are therefore also consistent with this recommendation.

### References

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