IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oRClOx54

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$$CHCl_2O_2 + CHCl_2O_2 \rightarrow CHCl_2OH + C(O)Cl_2 + O_2 \qquad (1)$$
$$\rightarrow CHCl_2O + CHCl_2O + O_2 \qquad (2)$$
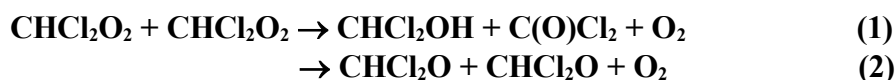
Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
1-10 x 10^{-12}	300	Catoire et al., 1996	FP-UVA (a)
(7.0 ± 1.8) x 10^{-12}	298	Biggs et al., 1999	DF-LIF (b)
Branching Ratios			
$k_2/k \geq 0.85$	305	Sanhueza and Heicklen, 1975	UVP-IR (c)
$k_2/k \geq 0.88$	298	Niki et al., 1980	UVP-FTIR (d)
$k_2/k \geq 0.85$	298	Catoire et al., 1996	UVP-FTIR (e)
$k_2/k \geq 0.9$	250-325		FP-UVA (f)

Comments

(a) Flash photolysis of CHCl$_3$ in the presence of CH$_3$OH-O$_2$-N$_2$ mixtures at a total pressure of 1000 mbar. Decays in transient absorption signals (with contributions from CHCl$_2$O$_2$ and HO$_2$) were recorded in the wavelength range 220 nm to 250 nm. Approximate value of k derived in conjunction with determination of the rate coefficient for the reaction of CHCl$_2$O$_2$ with HO$_2$, using a five reaction mechanism. Authors indicate that best fits were obtained using values of k close to those measured for the self reactions of CH$_2$ClO$_2$ and CCl$_3$O$_2$ (which are almost identical) in the same laboratory (Catoire et al., 1994, 1996), and recommend that k is the average these determinations: 2.6 x 10^{-13} exp[(800 $\pm$ 60)/T] cm^3 molecule^{-1} s^{-1} over the temperature range 273 K to 460 K, with $k = (3.8 \pm 1.4)$ x 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K.

(b) Experiments performed at pressures in the range 1.3 to 4 mbar. CHCl$_2$O$_2$ radicals were produced by the F + CH$_2$Cl$_2$ reaction, with subsequent addition of O$_2$. CHCl$_2$O$_2$ radicals were monitored indirectly by titration to NO$_2$ following reaction with excess NO, with LIF detection of NO$_2$. ClO radicals generated by the secondary chemistry were also titrated to NO$_2$ under the experimental conditions. k values were extracted by numerical simulation of the results, using an 11 reaction scheme to take account possible of secondary reactions.

(c) Photolysis of Cl$_2$ in the presence of CH$_2$Cl$_2$-O$_2$-N$_2$ mixtures. In situ monitoring of products by IR showed formation of CHClO as the dominant product as part of an efficient chain mechanism. C(O)Cl$_2$ was observed as a minor product. Listed quantum yield based on the reported quantum yield of 5.9 for CHClO formation.

(d) Photolysis of Cl$_2$ in the presence of CH$_2$Cl$_2$-O$_2$-N$_2$ mixtures. In situ monitoring of products by FTIR spectroscopy showed formation of CHClO as the dominant product as part of an efficient chain mechanism. C(O)Cl$_2$ was observed as a minor product. Listed quantum yield based on the reported quantum yield of 7.5 for CHClO formation.

(e) Photolysis of Cl$_2$ or F$_2$ in the presence of CH$_2$Cl$_2$-O$_2$-N$_2$ mixtures. In situ monitoring of products by FTIR spectroscopy showed formation of CHClO and C(O)Cl$_2$ with yields of ca. 85% and 5% respectively. No other primary products were detected.

(f) Flash photolysis of Cl_2 in the presence of CH_2Cl_2-O_2-N_2 mixtures over the temperature range 250 K to 325 K demonstrated efficient chain regeneration of $CHCl_2O_2$ in the system.

Preferred Values

$k_2/k = 1.0$ at 298 K.

Reliability
$\Delta(k_2/k) = {}^{+0.0}_{-0.15}$ at 298 K.

Comments on Preferred Values
The reported dominant chain formation of $HC(O)Cl$ from CH_2Cl_2 oxidation in a number of product studies (Sanhueza and Heicklen, 1975; Niki et al., 1980; Catoire et al., 1996) has established that the self-reaction of $CHCl_2O_2$ proceeds almost exclusively via formation of $CHCl_2O$ radicals (channel (2)), which decompose by elimination of Cl. This is also supported by the failure to detect $CHCl_2OH$ in all the product studies, which would otherwise provide evidence for channel (1). The efficient chain regeneration of $CHCl_2O_2$ radicals observed in the Cl_2-CH_2Cl_2-O_2-N_2 flash photolysis experiments of Catoire et al. (1996), is also consistent with the dominance of channel (2) over a wide temperature range.

The reported determinations of k (Catoire et al., 1996; Biggs et al., 1999) are subject to substantial uncertainties, owing to the complexity of the secondary chemistry. Catoire et al. (1996) report only a broad range for k at 300K, based on simulations of a complex system in which competitive removal of $CHCl_2O_2$ by reaction with HO_2 was occurring (see note (a) above). The discharge flow determination of Biggs et al. (1999) was complicated by indirect detection of $CHCl_2O_2$ (which also had contributions from ClO), and possible secondary chain removal of $CHCl_2O_2$ via reactions with Cl and ClO. Consequently, no firm recommendation for k is currently possible, and further kinetics studies are required.

References

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