IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet IV.A2.75 oClOx1

 The citation for this data sheet is: Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and Wallington, T. J.: Atmos. Chem. Phys., 8, 4141, 2008; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr.
This datasheet last evaluated: June 2015; last change in preferred values: June 2013.

$O(^1D) + CHF_2Cl$ (HCFC-22) $\rightarrow O(^3P) + CHF_2Cl$ (1)
$\rightarrow ClO + CHF_2$ (2)
$\rightarrow$ other products (3)

$\Delta H°(1) = -190$ kJ mol^{-1}
$\Delta H°(2) = -92$ kJ mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(0.95 \pm 0.3) \times 10^{-10}$	173-343	Davidson et al., 1978	PLP (a)
$(1.08 \pm 0.20) \times 10^{-10}$	298	Warren et al., 1991	PLP-RF
$(1.04 \pm 1.1) \times 10^{-10} \exp[(0 \pm 100)/T]$	217-373	Baasandorj et al., 2013	PLP-CR (b)
$(9.96 \pm 0.74) \times 10^{-11}$	296		
Branching Ratios			
$k_1/k = 0.28 \pm 0.06$	298	Warren et al., 1991	PLP-RF (c)
$k_2/k = 0.55 \pm 0.10$	298	Addison et al., 1979	PLP-UVA (d)
$k_2/k = 0.56 \pm 0.03$	296	Feierabend et al., 2010	PLP-CRDS (e)
Relative Rate Coefficients			
$k_2 + k_3 = (9.3 \pm 2.3) \times 10^{-11}$	297	Green and Wayne, 1976	RR (f)
$k_2 + k_3 = (8.69 \pm 1.72) \times 10^{-11}$	298	Nilsson et al., 2012	RR (g)
$k_2 + k_3 = (7.70 \pm 0.13) \times 10^{-11}$	296	Baasandorj et al., 2013	RR (h)

Comments

(a) Pulsed laser photolysis of O_3 at 266 nm. $O(^1D)$ atoms were monitored by time-resolved emission at 630 nm.

(b) Pulsed laser photolysis competitive kinetics method used. $O(^1D)$ atoms were produced by 248 nm pulsed laser (KrF eximer) photolysis of O_3 in the presence of CHF_2Cl and n-C_4H_{10}. $O(^1D)$ atoms react with n-C_4H_{10} to give HO radicals which were monitored by LIF. The initial rate of rise of the HO radical concentration provides a measure of the pseudo-first order loss of $O(^1D)$ in the system from which the rate coefficient for loss of $O(^1D)$ atoms by reaction with CHF_2Cl was determined.

(c) Branching ratio was determined from the ratio of the $O(^3P)$ yield from $O(^1D) + CHF_2Cl$ relative to that for $O(^1D) + N_2$.

(d) Quantitative yields of ClO were determined via the (5,0) band of the $A^2\pi \leftarrow X^2\pi$ system.

(e) $O(^1D)$ produced by laser photolysis of O_3 at 248 nm. ClO radicals were monitored using cavity ring-down differential absorption spectroscopy near the peak and valley of the 10-0 transition band head

at 279.67 and 279.56 nm of the $A^2\pi \leftarrow X^2\pi$ system. Experiments were performed in 400 – 800 mbar of helium diluent.

(f) $O(^1D)$ produced by photolysis of NO_2 at 229 nm. $\Delta(CHF_2Cl)/\Delta(N_2O)$ monitored by IR absorption spectroscopy. Measured rate coefficient ratio of $(k_2+ k_3)/k(O(^1D) + N_2O) = 0.8 \pm 0.2$ is placed on an absolute basis using $k(O(^1D) + N_2O) = 1.16 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current evaluation). The cited rate coefficient refers to chemical reaction only and does not include physical quenching.

(g) $O(^1D)$ atoms were produced by the 254 nm photolysis of O_3 in the presence of CH_4 and CHF_2Cl. The loss of CH_4 and CHF_2Cl was monitored using FTIR spectroscopy and chemical modeling was used to account for the secondary loss of CH_2F_2 via reaction with HO radicals produced in the system.

(h) $O(^1D)$ atoms were produced by 248 nm pulsed laser (KrF eximer) photolysis of O_3 in the presence of CHF_2Cl and NF_3. The loss of CHF_2Cl and NF_3 were monitored by FTIR and a reactive rate coefficient ratio of $k(O(^1D)+ CHF_2Cl)/k(O(^1D)+ NF_3) = 3.50\pm 0.06$ was measured. Using the reactive rate coefficient $k(O(^1D)+ NF_3) = (2.21 \pm 0.33) \times 10^{-11}$ (Baasandorj et al., 2012) gives a reactive rate coefficient $k(O(^1D)+ CHF_2Cl) = k_2 + k_3 = (7.70 \pm 0.13) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	1.0×10^{-10}	170-350
k_1/k	0.25	298
k_2/k	0.55	298
k_3/k	0.20	298
Reliability		
$\Delta \log k$	± 0.04	170-350
$\Delta(k_1/k)$	± 0.05	298
$\Delta(k_2/k)$	± 0.05	298
$\Delta(k_3/k)$	± 0.05	298

Comments on Preferred Values

The values of k reported by Davidson et al. (1978), Warren et al. (1991), and Baasandorj et al. (2013) are in excellent agreement. The preferred value is an average of the results reported near 298 K. The studies by Davidson et al. (1978) and Baasandorj et al. (2013) show that there is no discernible dependence of k on temperature over the range 170 – 350 K. The preferred value of the branching ratio k_1/k is based upon the values of 0.28 ± 0.06 reported by Warren et al. (1991) and 0.23 ± 0.06 reported by Baasandorj et al. (2013). The preferred value of the branching ratio k_2/k is based on the results from Addison et al. (1979) and Feierabend et al. (2010) which are in excellent agreement. Baasandorj et al. (2013) measured $k_2/k + k_3/k = 0.77 \pm 0.06$ from which a value of $k_3/k = 0.23 \pm 0.06$ can be inferred. The results from the relative rate studies by Green and Wayne (1976) and Nilsson et al. (2012) are consistent with the preferred values.

References

Addison, M. C., Donovan, R. J., and Garraway, J.: J. Chem. Soc. Faraday Discuss., 67, 286, 1979.
Baasandorj, M., Fleming, E. L., Jackman, C. H., and Burkholder, J. B.: J. Phys. Chem., 117, 2434, 2013.
Baasandorj, M., Hall, B. D., and Burkholder, J. B.: Atmos. Chem. Phys. 12, 11753, 2012.
Davidson, J. A., Schiff, H. I., Brown, T. J., and Howard, C. J.: J. Chem. Phys., 69, 4277, 1978.
Feierabend, K.J, Papanastasiou, D.K., and Burkholder, J. B.: J. Phys. Chem. A, 114, 12052, 2010.
Green, R. G. and Wayne, R. P.: J. Photochem. 6, 371, 1976.

Nilsson, E. J. K., Andersen, V. F., Nielsen, O. J., Johnson, M. S.: Chem. Phys. Lett., 554, 27, 2012
Warren, R., Gierczak, T., and Ravishankara, A. R.: Chem. Phys. Lett., 183, 403, 1991.