

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx46

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This data sheet last evaluated: June 2015; last change in preferred values: November 2003.

HO + C₂HCl₃ → products

Rate coefficient data

k/cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
(2.0 ± 0.4) × 10 ⁻¹²	296	Howard, 1976	DF-LMR
5.32 × 10 ⁻¹³ exp[(445 ± 41)/T]	234-420	Chang and Kaufman, 1977	DF-RF
(2.37 ± 0.10) × 10 ⁻¹²	296		
2.11 × 10 ⁻¹²	305	Kirchner, 1983	DF-MS
7.80 × 10 ⁻¹³ exp[(241 ± 61)/T]	300-459	Kirchner et al., 1990	DF-MS
(1.76 ± 0.17) × 10 ⁻¹²	300		
9.73 × 10 ⁻¹³ exp[(158.7 ± 44.0)/T]	291-650	Tichenor et al., 2000, 2001	PLP-LIF (a)
1.66 × 10 ⁻¹²	298		
<i>Relative Rate Coefficients</i>			
(4.3 ± 1.3) × 10 ⁻¹²	305 ± 2	Winer et al., 1976	RR (b)
(2.64 ± 0.37) × 10 ⁻¹²	296	Edney et al., 1986	RR (c)
2.65 × 10 ⁻¹²	300	Klöpffer et al., 1986	RR (d)

Comments

- This study was stated to supersede the earlier study of Jiang et al. (1993). Tichenor et al. (2001) conducted experiments in 986 mbar of He over the temperature range 291 – 752 K. The Arrhenius expression $k = 9.73 \times 10^{-13} \exp[(158.7 \pm 44.0)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ describes the data obtained over the temperature range 291-650 K.
- HO radicals were generated by the photolysis of NO_x-organic-air mixtures at ~1 bar of air. Trichloroethene and 2-methylpropene (the reference compound) were monitored by GC. The measured rate coefficient ratio $k(\text{HO} + \text{trichloroethene})/k(\text{HO} + \text{2-methylpropene}) = 0.088 (\pm 30\%)$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{2-methylpropene}) = 4.94 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 305 K (Atkinson, 1997).
- HO radicals were generated by the photolysis of CH₃ONO–NO-air mixtures at ~1 bar of air. Trichloroethene and *n*-butane (the reference compound) were monitored by GC. The measured rate coefficient ratio $k(\text{HO} + \text{trichloroethene})/k(\text{HO} + \textit{n}\text{-butane})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \textit{n}\text{-butane}) = 2.33 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (Atkinson, 2003).
- HO radicals were generated by the photolysis of NO_x-organic-air mixtures at ~1 bar of air. Trichloroethene and toluene (the reference compound) were monitored by GC. The measured rate coefficient ratio $k(\text{HO} + \text{trichloroethene})/k(\text{HO} + \text{toluene})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{toluene}) = 5.58 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K (Calvert et al., 2002).

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	2.0×10^{-12}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$3.0 \times 10^{-13} \exp(565/T)$	230-300
<i>Reliability</i>		
$\Delta \log k$	± 0.10	298
$\Delta(E/R)$	± 200	

Comments on Preferred Values

There is a significant degree of scatter in both the measured room temperature rate coefficients and the temperature dependence of the rate coefficient, with the room temperature relative rate coefficient from the Winer et al. (1976) study being much higher than those measured in the other studies (possibly because of the disparity between the reactivities of trichloroethene and the reference compound used). An Arrhenius plot of the rate coefficients of Howard (1976), Chang and Kaufman (1977) and Tichenor et al. (2001) suggests curvature [as also concluded by Tichenor et al. (2000)]. Accordingly, the absolute rate coefficients at ≤ 650 K from the studies of Howard (1976), Chang and Kaufman (1977) and Tichenor et al. (2001) were fitted to the three parameter expression $k = C T^2 \exp(-D/T)$, resulting in $k = 6.06 \times 10^{-19} T^2 \exp(1084/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 234-650 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 260 K and is obtained from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$. The room temperature rate coefficients measured by Kirchner (1983), Edney et al. (1986), Klöpffer et al. (1986) and Kirchner et al. (1990), which are not used in the derivation of the preferred values, are in general agreement with the preferred values, and the temperature dependence reported by Kirchner et al. (1990) over the temperature range 300-459 K of $B = -241 \pm 61$ K is in reasonable agreement with the value of $B = -364$ K derived from the preferred three parameter expression centered at 360 K.

The reaction proceeds by initial HO radical addition to form the HOCHClCCl₂ and HOCCl₂CHCl radicals, which under atmospheric conditions lead to the formation of Cl atoms, HC(O)Cl, C(O)Cl₂ and other, as yet unidentified, products (Tuazon et al., 1988; Kleindienst et al., 1989).

References

- Atkinson, R.: J. Phys. Chem. Ref. Data, 26, 215, 1997.
 Atkinson, R.: Atmos. Chem. Phys., 3, 2233, 2003.
 Calvert, J. G., Atkinson, R., Becker, K. H., Kamens, R. M., Seinfeld, J. H., Wallington, T. J. and Yarwood, G.: The Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons, Oxford University Press, New York, NY, 2002.
 Chang, J. S. and Kaufman, F.: J. Chem. Phys., 66, 4989, 1977.
 Edney, E. O., Kleindienst, T. E. and Corse, E. W.: Int. J. Chem. Kinet., 18, 1355, 1986.
 Howard, C. J.: J. Chem. Phys., 65, 4771, 1976.
 Jiang, Z., Taylor, P. H. and Dellinger, B.: J. Phys. Chem., 97, 5050, 1993.
 Kirchner, K.: Chimia, 37, 1, 1983.
 Kirchner, K., Helf, D., Ott, P. and Vogt, S.: Ber. Bunsenges. Phys. Chem., 94, 77, 1990.
 Kleindienst, T. E., Shepson, P. B., Nero, C. and Bufalini, J. J.: Int. J. Chem. Kinet., 21, 863, 1989.
 Klöpffer, W., Frank, R., Kohl, E.-G. and Haag, F.: Chemiker-Zeitung, 110, 57, 1986.
 Tichenor, L. A. B., Lozada-Ruiz, A. J., Yamada, T., El-Sinawi, A., Taylor, P. H., Peng, J., Hu, X. and Marshall, P.: Proc. Combustion Institute, 28, 1495, 2000.
 Tichenor, L. B., El-Sinawi, A., Yamada, T., Taylor, P. H., Peng, J., Hu, X. and Marshall, P.:

Chemosphere, 42, 571, 2001.

Tuazon, E. C., Atkinson, R., Aschmann, S. M., Goodman, M. A. and Winer, A. M.: Int. J. Chem. Kinet., 20, 241, 1988.

Winer, A. M., Lloyd, A. C., Darnall, K. R. and Pitts, J. N., Jr.: J. Phys. Chem., 80, 1635, 1976.

