IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx47

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HO + C_2Cl_4 → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
(1.70 ± 0.34) x 10^{-13}	296	Howard, 1976	DF-LMR
9.44 x 10^{-12} exp[-(1199 ± 55)/*T*]	297-420	Chang and Kaufman, 1977	DF-RF
(1.69 ± 0.07) x 10^{-13}	297		
5.53 x 10^{-12} exp[-(1034 ± 13)/*T*]	301-433	Kirchner, 1983; Kirchner et al., 1990	DF-MS
(1.73 ± 0.17) x 10^{-13}	301		
1.93 x 10^{-22} $T^{3.2}$ exp[(660.8 ± 54.6)/*T*]	296.5-714	Tichenor et al., 2000	PLP-LIF (a)
(1.45 ± 0.16) x 10^{-13}	296.5		
1.53 x 10^{-12} exp[-(688.2 ± 67.5)/*T*]	293-720	Tichenor et al., 2001	PLP-LIF
(1.52 ± 0.17) x 10^{-13}	293		
Relative Rate Coefficients			
(2.2 ± 0.7) x 10^{-12}	305 ± 2	Winer et al., 1976	RR (b)

Comments

(a) Tichenor et al. (2000) also fit their data to an Arrhenius expression, obtaining k = 1.68 x 10^{-12} exp[-(764.2 ± 79.1)/T] cm^3 molecule^{-1} s^{-1} over the same temperature range of 296.5-714 K.

(b) HO radicals were generated by the photolysis of NO_x-organic-air mixtures at ~1 bar of air. Tetrachloroethene and 2-methylpropene (the reference compound) were monitored by GC. The measured rate coefficient ratio k(HO + tetrachloroethene)/k(HO + 2-methylpropene) = 0.044 (±30%) is placed on an absolute basis by use of a rate coefficient of k(HO + 2-methylpropene) = 4.94 x 10^{-11} cm^3 molecule^{-1} s^{-1} at 305 K (Atkinson, 1997).

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	1.6 x 10^{-13}	298
k /cm^3 molecule^{-1} s^{-1}	3.5 x 10^{-12} exp(-920/T)	290-420
Reliability		
Δ log k	± 0.10	298

$\Delta(E/R)$	± 300

Comments on Preferred Values

The room temperature absolute rate coefficients of Howard (1976), Chang and Kaufman (1977), Kirchner (1983), Kirchner et al. (1990) and Tichenor et al. (2000, 2001) are in good agreement. The relative rate coefficient of Winer et al. (1976) at 305 K is an order of magnitude higher, presumably in part because of the large difference in reactivities of tetrachloroethene and the 2-methylpropene reference compound. The preferred 298 K value is derived from the mean of the values of Howard (1976), Chang and Kaufman (1977), Kirchner et al. (1990), Tichenor et al. (2000) and Tichenor et al. (2001). The temperature dependence of the rate coefficient is the average of the Arrhenius activation energies reported by Chang and Kaufman, Kirchener et al. (1990), Tichenor et al. (2000) and Tichenor et al. (2001), with the pre-exponential factor being adjusted to fit the 298 K preferred value. No rate coefficients are available below 290 K, and additional studies involving measurements down to ≤ 220 K are clearly needed.

The reaction proceeds by initial HO radical addition to form the $HOCCl_2CCl_2$ radical, which under atmospheric conditions leads to the formation of Cl atoms, $C(O)Cl_2$ and other, as yet unidentified, products (Tuazon et al., 1988). The molar formation yield of $C(O)Cl_2$ was measured by Tuazon et al. (1988) to be ~0.5 in both the presence and absence of a Cl atom scavenger.

References

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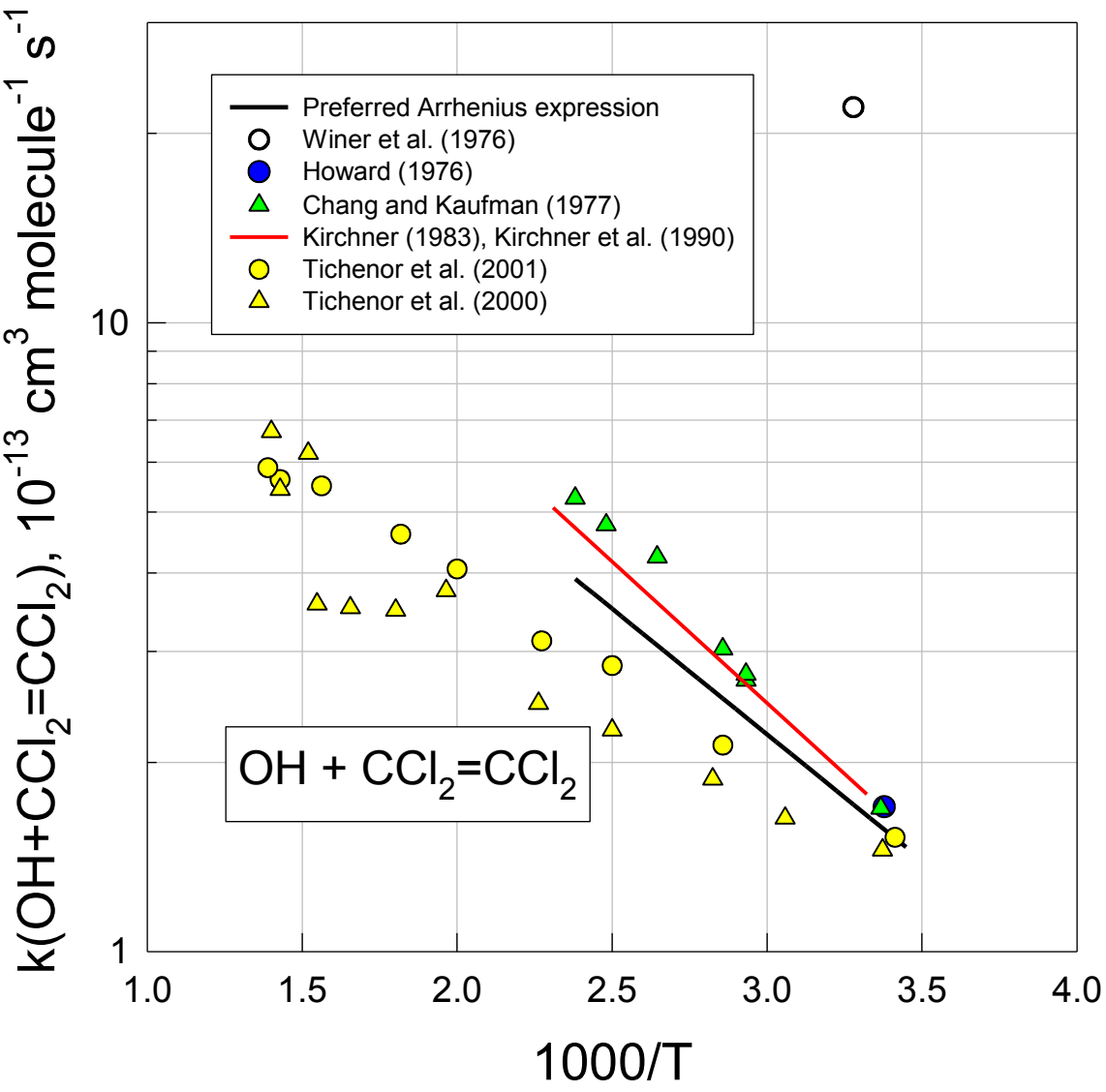
Preferred Arrhenius expression
Winer et al. (1976)
Howard (1976)
Chang and Kaufman (1977)
Kirchner (1983), Kirchner et al. (1990)
Tichenor et al. (2001)
Tichenor et al. (2000)
OH + CCl2=CCl2
k(OH+CCl2=CCl2), 10-13 cm3 molecule-1 s-1
1000/T
10
1
1.0
1.5
2.0
2.5
3.0
3.5
4.0