IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oFOx113

This data sheet last evaluated: June 2017; last change in preferred values: June 2017.

HO + CH_2=CHCl → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
(2–5) x 10^{-12}	296	Howard (1977)	DF-LMR (a)
1.14×10^{-12} exp[(526±151)/T]	299-422	Perry et al. (1977)	FP-RF (b)
(6.60±0.66) x 10^{-12}	299		
2.14×10^{-12} exp[(700±120)/T]	313-1173	Liu et al. (1989)	PR-RA (c)
7.55 x 10^{-12}	313		
2.72×10^{-12} exp[(335±42)/T]	293-730	Yamada et al., 2001	LP-LIF (d)
(8.49±0.40) x 10^{-12}	293		

Comments

(a) The reaction rate coefficient was measured using a discharge flow reactor with laser magnetic resonance detection of HO radicals. HO radicals were produced by the reaction of H atoms with NO_2 in 0.7-7.0 Torr (0.9-9.3 mbar) of helium diluent. The rate coefficient was dependent on total pressure increasing from approximately 2 x 10^{-12} to 5 x 10^{-12} cm^3 molecule^{-1} s^{-1} over the total pressure range 0.7-7.0 Torr.

(b) Flash photolysis of H_2O in 50 or 100 Torr of argon diluent was used as a source of HO radicals. The decay of HO radicals was monitored using resonance fluorescence. There was no discernable effect (<5%) of total pressure over the range studied.

(c) Pulse radiolysis of one atmosphere of argon containing approximately 6 Torr of water vapor was used as a source of HO radicals. Resonance absorption at 308 nm was used to monitor the decay of HO radicals in the presence of vinyl chloride. It was deduced that the predominant reaction channel changes from an addition-initiated reaction at temperatures below 588K to a hydrogen abstraction reaction for temperatures above 723 K. The rate coefficient for the addition reaction was described by the Arrhenius expression $k = 2.14 \times 10^{-12}$ exp[(700±120)/T] while that for the H-abstraction reaction was described by $k = 2.98 \times 10^{-11}$ exp[-(4020±700)/T] cm^3 molecule^{-1} s^{-1}.

(d) Photolysis of HONO at 351 nm in 740 Torr of helium diluent was used as a source of HO radicals. HO radicals were monitored using laser induced fluorescence.

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	7.55 x 10^{-12}	298
k /cm^3 molecule^{-1} s^{-1}	2.54 x 10^{-12} exp (325/T)	280-600
Reliability		
$\Delta \log k$	± 0.08	298
Δ E/R	± 100	280-600

Comments on Preferred Values

Howard (1976) showed that at pressures below 7 Torr of helium diluent the rate of the reaction decreases with total pressure. Perry et al. (1977) reported that at total pressures of 50 Torr of argon diluent and above there is no discernable effect of pressure on the measured rate coefficient. The rate coefficients reported by Perry et al. (1977), Liu et al. (1989), and Yamada et al. (2001) near 298 K measured at, or near, the high pressure limit and are in reasonable agreement. Taking an average of the rate coefficients measured near ambient temperature gives the recommended value at 298 K. The recommended Arrhenius expression is derived from a fit to the data obtained below 600 K by Perry et al. (1977), Liu et al. (1989), and Yamada et al. (2001) with the A factor adjusted to give the recommended rate coefficient at 298 K. The recommended expression describes the high-pressure limiting rate coefficient which is appropriate for atmospheric conditions.

The reaction proceeds via addition of HO to the >C=C< double bond to give $HOCH_2CHCl$ and $CH_2CHClOH$ radicals with the former expected to predominate. Elimination of a Cl atom from the $CH_2CHClOH$ radical will give the enol CH_2=CHOH. Addition of O_2 followed by reaction with NO is expected to give a variety of products including $HOCH_2CHO$, HCHO, and HC(O)Cl.

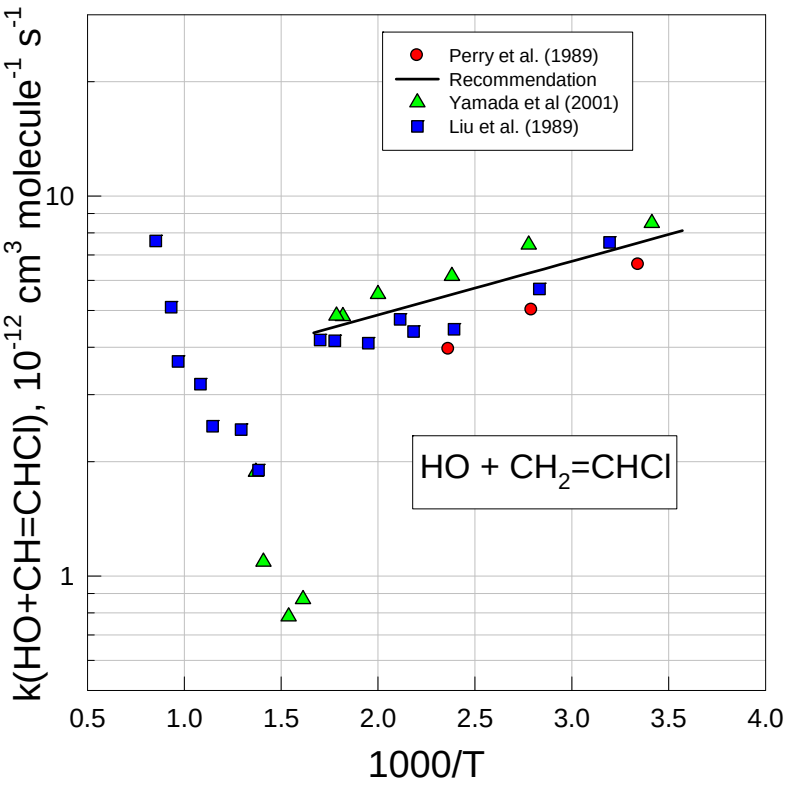
References

Howard, C. J.: J. Chem. Phys., 65, 4771, 1976.

Liu, A.; Mulac, W. A.; and Jonah, C. D., J. Phys. Chem., 93, 4092, 1989.

Perry, R. A.; Atkinson, R.; and Pitts, J. N., Jr., J. Chem. Phys., 67, 458, 1977,

Yamada, T.; Siraj, M.; Taylor, P. H.; Peng, J.; Hu, X.; and Marshall, P., J. Phys. Chem. A, 105, 9436 2001.


Perry et al. (1989)
Recommendation
Yamada et al (2001)
Liu et al. (1989)
HO + CH2=CHCl
k(HO+CH=CHCl), 10-12 cm3 molecule-1 s-1
10
1
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
1000/T