IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_VOC21

This data sheet last evaluated 16th October 2007 (with no revision of preferred values).

HO + $CH_3C(O)CH=CH_2$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$3.85 \times 10^{-12} \exp[(456 \pm 73)/T]$	298-424	Kleindienst et al., 1982	FP-RF
$(1.79 \pm 0.28) \times 10^{-11}$	298		
$2.67 \times 10^{-12} \exp[(612 \pm 49)/T]$	232-378	Gierczak et al., 1997	PLP-LIF
$(2.03 \pm 0.17) \times 10^{-11}$	298		
$(1.73 \pm 0.21) \times 10^{-11}$	300	Chuong and Stevens, 2003	DF-RF/LIF (a)
$(1.78 \pm 0.08) \times 10^{-11}$	300	Chuong and Stevens, 2004	DF-LIF (b)
$(1.86 \pm 0.12) \times 10^{-11}$	298 ± 2	Holloway et al., 2005	PLP-LIF (c)
Relative Rate Coefficients			
1.48×10^{-11}	300	Cox et al., 1980	RR (d)
$(1.96 \pm 0.15) \times 10^{-11}$	299 ± 2	Atkinson et al., 1983	RR (e)

Comments

(a) At 300 K no measurable variation in the rate coefficient was observed over the pressure range 2.7-6.7 mbar (2-5 Torr) of He diluent; the cited rate coefficient is that obtained at 6.7 mbar (5 Torr) of He diluent. However, at the other temperatures studied (328, 361, 390 and 422 K) the measured rate coefficients increased with increasing pressure over the range 2.7-6.7 mbar of He, showing that the reaction was in the fall-off regime under these temperature and pressure conditions. Problems ascribed to reversible wall adsorption of methyl vinyl ketone and heterogeneous wall reactions were observed; these were avoided or minimized by addition of ~10% O_2 or by conditioning the reactor with high F atom concentrations

(b) At 133 mbar (100 Torr) of N_2 diluent, using a turbulent flow reactor.

(c) The pulsed laser photolysis of 3-methyl-2,4-dione at 248 nm was used to generate HO radicals.

(d) Relative rate study carried out at atmospheric pressure of air. The concentrations of methyl vinyl ketone and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio is placed on an absolute basis by using a rate coefficient of k(HO + ethene) = 8.44×10^{-12} cm^3 molecule^{-1} s^{-1} at 300 K and atmospheric pressure of air (Atkinson, 1997).

(e) Relative rate study carried out at atmospheric pressure of air. The concentrations of methyl vinyl ketone and propene (the reference compound) were measured by GC. The measured rate coefficient ratio k(HO + methyl vinyl ketone)/k(HO + propene) = 0.747 ± 0.055 is placed on an absolute basis by using a rate coefficient of k(HO + propene) = 2.62×10^{-11} cm^3 molecule^{-1} s^{-1} at 299 K and atmospheric pressure of air (Atkinson, 1997).

Preferred Values

$k = 2.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.6 \times 10^{-12} \exp(610/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230-380 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The room temperature rate coefficients of Kleindienst et al. (1982), Atkinson et al. (1983), Gierczak et al. (1997), Chuong and Stevens (2003, 2004) and Holloway et al. (2005) are in good agreement, but are higher by ~20-35% than the earlier relative rate measurement of Cox et al. (1980). The preferred 298 K rate coefficient is based on the room temperature rate coefficients of Atkinson et al. (1983), Gierczak et al. (1997) and Holloway et al. (2005). The temperature dependence measured by Gierczak et al. (1997) is accepted and the pre-exponential factor is calculated from the preferred 298 K rate coefficient and the temperature dependence.

The products of the reaction of HO radicals with methyl vinyl ketone in the presence of NO have been investigated by Tuazon and Atkinson (1989). The reaction proceeds by initial addition of the HO radical to the carbon atoms of the C=C bond, forming (in the presence of NO) the intermediate hydroxyalkoxy radicals $CH_3C(O)CH(O)CH_2OH$ and $CH_3C(O)CH(OH)CH_2O$, which decompose by the pathways:

$$CH_3C(O)CH(O)CH_2OH \rightarrow CH_3C(O)CHO + CH_2OH$$
$$CH_3C(O)CH(O)CH_2OH \rightarrow CH_3CO + HOCH_2CHO$$
and
$$CH_3C(O)CH(OH)CH_2O \rightarrow HCHO + CH_3C(O)CHOH$$

followed by reactions of CH_2OH and $CH_3C(O)CHOH$ radicals with O_2 to form HCHO + HO_2 and $CH_3C(O)CHO + HO_2$, respectively. The first generation products are therefore HCHO + $CH_3C(O)CHO$ and $HOCH_2CHO + CH_3CO$ (with the acetyl radical reacting to form peroxyacetyl nitrate [$CH_3C(O)OONO_2$; PAN] or HCHO (Tuazon and Atkinson, 1989; IUPAC, 2007)). Tuazon and Atkinson (1989) measured formation yields of methylglyoxal and glycolaldehyde of 25 ± 8% and 64 ± 16%, respectively, showing that initial HO radical addition occurs mainly at the terminal CH_2 group (Tuazon and Atkinson, 1989).

References

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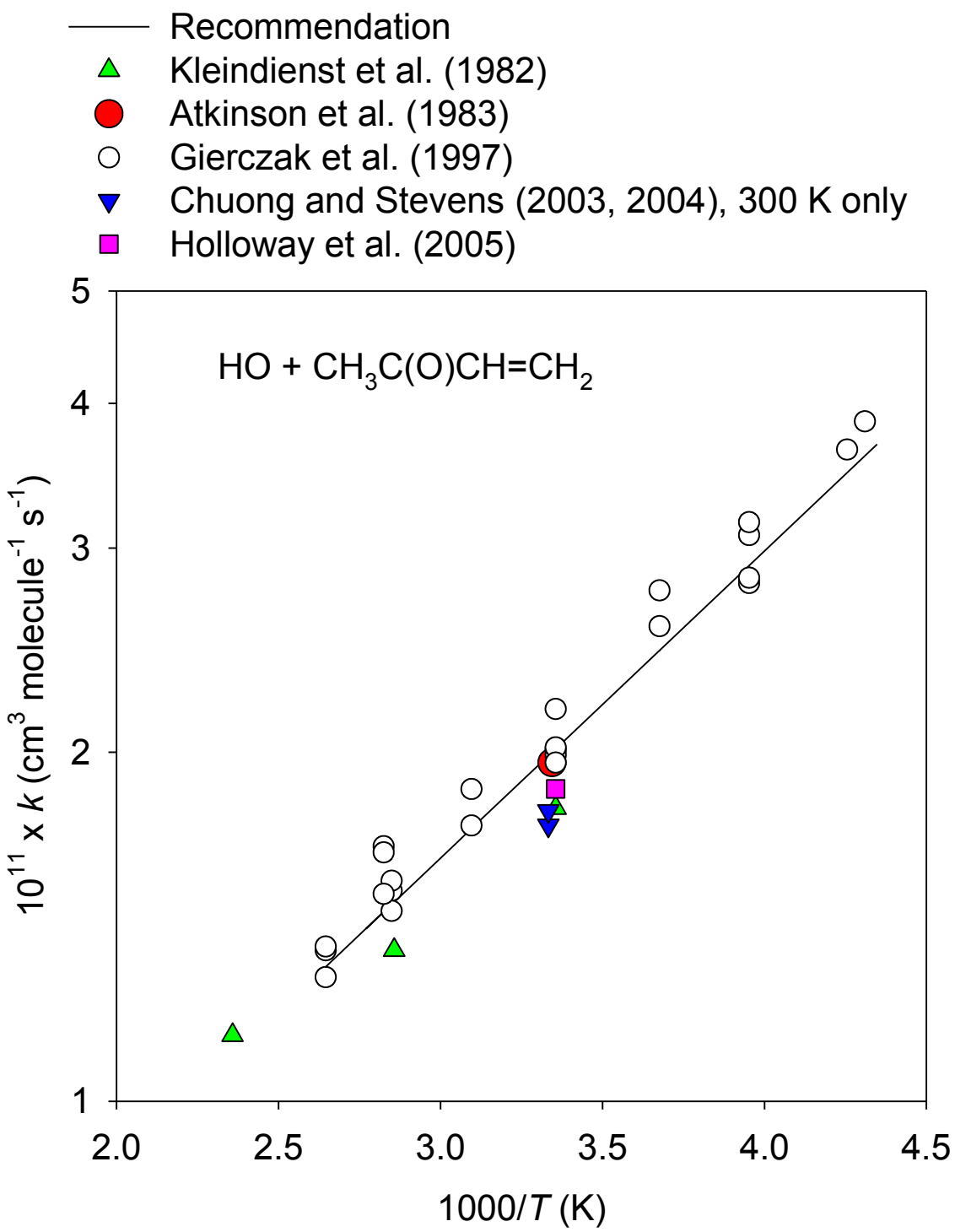
Recommendation
Kleindienst et al. (1982)
Atkinson et al. (1983)
Gierczak et al. (1997)
Chuong and Stevens (2003, 2004), 300 K only
Holloway et al. (2005)
HO + CH3C(O)CH=CH2
10^11 x k (cm^3 molecule^-1 s^-1)
1000/T (K)
1
2
3
4
5
2.0
2.5
3.0
3.5
4.0
4.5