$HO + CH_2=C(CH_3)CHO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$1.77 \times 10^{-11} \exp[(175 \pm 52)/T]$	300-423	Kleindienst et al., 1982	FP-RF
$(3.14 \pm 0.49) \times 10^{-11}$	300		
$7.73 \times 10^{-12} \exp[(379 \pm 46)/T]$	234-373	Gierczak et al., 1997	PLP-LIF
$(2.79 \pm 0.12) \times 10^{-11}$	298		
$9.8 \times 10^{-13} \exp[(1050 \pm 120)/T]$	300-422	Chuong and Stevens, 2003	DF-RF/LIF (a)
$(3.23 \pm 0.36) \times 10^{-11}$	300		
$(3.22 \pm 0.10) \times 10^{-11}$	300	Chuong and Stevens, 2004	DF-LIF (b)
Relative Rate Coefficients			
$(2.96 \pm 0.24) \times 10^{-11}$	299 ± 2	Atkinson et al., 1983	RR (c)
$(3.90 \pm 0.31) \times 10^{-11}$	298 ± 2	Edney et al., 1986	RR (d)

Comments

(a) No variation in the rate coefficient was observed over the pressure range 2.7-6.7 mbar (2-5 Torr) of He diluent at any of the temperatures studied (300-422 K). The cited temperature-dependent rate expression uses data at 6.7 mbar pressure of He (Chuong and Stevens, 2003). Problems ascribed to reversible wall adsorption of methacrolein 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) Relative rate study carried out at atmospheric pressure of air. The concentrations of methacrolein and propene (the reference compound) were measured by GC. The measured rate coefficient ratio k(HO + methacrolein)/k(HO + propene) = 1.13 ± 0.09 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).

(d) Relative rate study carried out at atmospheric pressure of air. The concentrations of methacrolein and propene and *trans*-2-butene (the reference compounds) were measured by GC. The measured rate coefficient ratios are placed on an absolute basis by using rate coefficients of k(HO + propene) = 2.63×10^{-11} cm^3 molecule^{-1} s^{-1} and k(HO + *trans*-2-butene) = 6.40×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure of air (Atkinson, 1997). The indicated uncertainty is one standard deviation (Edney et al., 1986).

Preferred Values

k = 2.9×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 8.0 \times 10^{-12} \exp(380/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230-380 K.
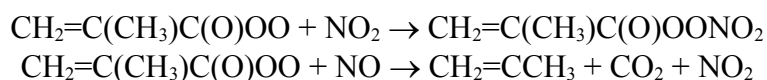
Reliability
$\Delta \log k = \pm 0.10$ at 298 K.
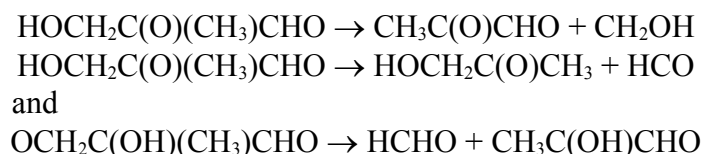$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The room temperature rate coefficients of Kleindienst et al. (1982), Atkinson et al. (1983), Gierczak et al. (1997) and Chuong and Stevens (2003, 2004) are in good agreement, with the relative rate measurement of Edney et al. (1986) being ~20-30% higher. The temperature dependencies obtained by Kleindienst et al. (1982) [300-423 K] and Chuong and Stevens (2003) [300-422 K] are respectively lower and higher than that determined by Gierczak et al. (1997) over the wider temperature range of 234-373 K. In the Chuong and Stevens (2003) study, the rate coefficients at 300, 328 and 361 K are in good agreement with the rate expression of Gierczak et al. (1997); those at 390 and 422 K (Chuong and Stevens, 2003) are lower than predicted from the Arrhenius expression of Gierczak et al. (1997). Because of the wider temperature range used by Gierczak et al. (1997) and the fact that it extends below room temperature, the temperature dependence of Gierczak et al. (1997) is accepted. The preferred 298 K rate coefficient is based on the room temperature rate coefficients of Atkinson et al. (1983) and Gierczak et al. (1997), 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 methacrolein in the presence of NO have been investigated by Tuazon and Atkinson (1990) and Orlando and Tyndall (1999). The reaction proceeds by two pathways: H-atom abstraction from the CHO group, and initial addition of the HO radical to the carbon atoms of the C=C bond. H-atom abstraction from the CHO group accounts for 50-55% of the overall reaction at room temperature (Tuazon and Atkinson, 1990; Orlando and Tyndall, 1999), forming the acyl radical CH_2=C(CH$_3$)CO which then adds O$_2$ to form the acyl peroxy radical CH_2=C(CH$_3$)C(O)OO. This acyl peroxy radical reacts with NO$_2$, to form the peroxyacyl nitrate CH_2=C(CH$_3$)C(O)OONO$_2$ (MPAN), or with NO (Tuazon and Atkinson, 1990; Orlando and Tyndall, 1999):

$$CH_2=C(CH_3)C(O)OO + NO_2 \rightarrow CH_2=C(CH_3)C(O)OONO_2$$
$$CH_2=C(CH_3)C(O)OO + NO \rightarrow CH_2=CCH_3 + CO_2 + NO_2$$

The CH_2=CCH$_3$ radical reacts with O$_2$ to form HCHO, CO and CO$_2$ (Orlando and Tyndall, 1999).

Initial HO radical addition to the C=C bond leads (in the presence of NO) to the intermediate hydroxyalkoxy radicals HOCH$_2$C(O)(CH$_3$)CHO and OCH$_2$C(OH)(CH$_3$)CHO, which decompose by the pathways (Tuazon and Atkinson, 1990; Orlando and Tyndall, 1999):

$$HOCH_2C(O)(CH_3)CHO \rightarrow CH_3C(O)CHO + CH_2OH$$
$$HOCH_2C(O)(CH_3)CHO \rightarrow HOCH_2C(O)CH_3 + HCO$$
$$\text{and}$$
$$OCH_2C(OH)(CH_3)CHO \rightarrow HCHO + CH_3C(OH)CHO$$

followed by reactions of CH$_2$OH and CH$_3$C(OH)CHO radicals with O$_2$ to form HCHO + HO$_2$ and CH$_3$C(O)CHO + HO$_2$, respectively. The OH radical addition reaction appears to be in the high-pressure region above ~2.7 mbar (2 Torr) pressure (Gierczak et al., 1997; Chuong and Stevens, 2003). The first generation products from the HO radical addition pathways are

therefore HCHO + $CH_3C(O)CHO$ and $HOCH_2C(O)CH_3$ + CO (the CO arising from reaction of HCO with O_2). The studies of Tuazon and Atkinson (1990) and Orlando and Tyndall (1999) measured formation yields of methylglyoxal and hydroxyacetone of 8.4% and 44%, respectively, showing that initial HO radical addition occurs mainly at the terminal CH_2 moiety (Tuazon and Atkinson, 1990).

References

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Legend:
— Recommendation
▲ Kleindienst et al. (1982)
● Atkinson et al. (1983)
▽ Edney et al. (1986)
○ Gierczak et al. (1997)
◆ Chuong and Stevens (2003, 2004)

y-axis: $10^{11} \times k$ (cm^3 molecule^{-1} s^{-1})

x-axis: $1000/T$ (K)

HO + CH$_2$=C(CH$_3$)CHO