IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_22

$$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + HCHO + O_2 \qquad (1)$$
$$\rightarrow 2CH_3O + O_2 \qquad (2)$$
$$\rightarrow CH_3OOCH_3 + O_2 \qquad (3)$$

$\Delta H°(1) = -331.0 \text{ kJ·mol}^{-1}$

$\Delta H°(2) = 13.6 \text{ kJ·mol}^{-1}$

$\Delta H°(3) = -146.5 \text{ kJ·mol}^{-1}$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(5.2 \pm 0.9) \times 10^{-13}$	298	Cox and Tyndall, 1980[1]	MM-UVAS (a,b)
$(3.7 \pm 0.7) \times 10^{-13}$	298	Sander and Watson, 1980[2]	FP-UVAS (a,c)
$1.40 \times 10^{-13} \exp[(223 \pm 41)/T]$	250-420	Sander and Watson, 1981[3]	FP-UVAS (a,d)
$(3.0 \pm 0.5) \times 10^{-13}$	298		
$(4.4 \pm 1.0) \times 10^{-13}$	298	McAdam, Veyret, and Lesclaux, 1987[4]	FP-UVAS (a,e)
$1.3 \times 10^{-13} \exp[(220 \pm 70/T)]$	228-380	Kurylo and Wallington, 1987[5]	FP-UVAS (a,f)
$(2.7 \pm 0.45) \times 10^{-13}$	298		
$(3.5 \pm 0.5) \times 10^{-13}$	298	Jenkin *et al.*, 1988[6]	MM-UVAS (a,g)
$(3.6 \pm 0.55) \times 10^{-13}$	300	Simon, Schneider, and Moortgat, 1990[7]	MM-UVAS (a,h)
$1.3 \times 10^{-13} \exp(365/T)$	248-573	Lightfoot, Lesclaux, and Veyret, 1990[8]	FP-UVAS (a,i)
$(4.1 \pm 0.9) \times 10^{-13}$	300		
Branching Ratios			
$k_2/k = 1/\{1 + \exp[(1131 \pm 30)/T]/(17 \pm 5)\}$	223-333	Horie, Crowley, and Moortgat, 1990[9]	P-FTIR (j)
$k_2/k = 0.30$	298		
$k_2/k = 0.41 \pm 0.04$	296	Tyndall, Wallington, and Ball, 1998[10]	P-FTIR (k)
$k_3/k < 0.06$	296		

Comments

(a) k is defined by $-d[CH_3O_2]/dt = 2k[CH_3O_2]^2$ and was derived from the measured overall second-order decay of CH_3O_2 radicals (k_{obs}) by correcting for secondary removal of the CH_3O_2 radicals.

(b) $[CH_3O_2]$ determined by absorption at 250 nm in modulated photolysis of Cl_2-CH_4-O_2 mixtures. $k/\sigma(250 \text{ nm}) = 1.33 \times 10^5$ cm s^{-1}, $\sigma = 3.9 \times 10^{-18}$ cm^2 molecule^{-1} s^{-1} at 250 nm.

(c) Flash-photolysis of $(CH_3)_2N_2$-O_2 and Cl_2-CH_4-O_2 mixtures. $[CH_3O_2]$ monitored by long path UV absorption giving $k/\sigma = (1.06 \pm 0.07) \times 10^5$ cm s^{-1} at 245 nm and $(2.84 \pm 0.36) \times 10^5$ cm s^{-1} at 270 nm. Value quoted is a mean value using σ values obtained by Hochanadel *et al.*[11] Small effects of varying O_2 and adding CO are reported.

(d) Flash-photolysis of Cl_2-CH_4-O_2 mixtures. σ determined from absorption at $t = 0$ extrapolated from decay curves and estimate of $[CH_3O_2]_o$ from change in Cl_2 concentration in flash. $\sigma(250\text{ nm}) = (2.5 \pm 0.4)$ x 10^{-18} cm^2 molecule^{-1} at 298 K, and $k/\sigma(250\text{ nm}) = (5.6 \pm 0.8)$ x 10^4 exp$[(223 \pm 41)/T]$ cm s^{-1} (250 K to 420 K) were obtained.

(e) Flash-photolysis of Cl_2 in the presence of CH_4 and O_2 over the pressure range 169 mbar to 530 mbar (120 Torr to 400 Torr). $[CH_3O_2]$ monitored by UV absorption. $k_{obs}/\sigma(250\text{ nm}) =$ 1.34 x 10^5 cm s^{-1} and $\sigma(250\text{ nm}) = 4.4$ x 10^{-18} cm^2 molecule^{-1} were obtained. k_{obs}/k taken to be 1.35.

(f) Flash-photolysis of Cl_2 in the presence of CH_4-O_2-N_2 mixtures at pressures between 67 mbar and 530 mbar (50 Torr and 400 Torr). $k_{obs} = (1.7 \pm 0.4)$ x 10^{-13} exp$[(220 \pm 70)/T]$ cm^3 molecule^{-1} s^{-1} determined from measured values of $k_{obs}/\sigma(250)$ by taking $\sigma(250) = 3.30$ x 10^{-18} cm^2 molecule^{-1} as previously determined by same authors. Here we have taken $k_{obs}/k =$ 1.35 to calculate k. k_{obs} shown to be independent of pressure over the range 67 mbar to 530 mbar (51 Torr to 403 Torr) at 298 K.

(g) Modulated photolysis of Cl_2 in the presence of CH_4-O_2 mixtures at a total pressure of 1 bar (760 Torr). $k_{obs}/\sigma(250\text{ nm}) = 1.11$ x 10^5 cm s^{-1} and $\sigma(250\text{ nm}) = (4.25 \pm 0.5)$ x 10^{-18} cm^2 molecule^{-1} were obtained leading to $k_{obs} = (4.7 \pm 0.5)$ x 10^{-13} cm^3 molecule^{-1} s^{-1}. Cited value of k obtained by taking $k_{obs}/k = 1.35$ to allow for secondary removal of CH_3O_2.

(h) Modulated photolysis of Cl_2 in the presence of CH_4-O_2 mixtures at pressures of 320 mbar (240 Torr). $k_{obs}/\sigma(250\text{ nm}) = 1.16$ x 10^5 cm s^{-1} and $\sigma(250\text{ nm}) = 4.14$ x 10^{-18} cm^2 molecule^{-1} were obtained, leading to $k_{obs} = (4.8 \pm 0.5)$ x 10^{-13} cm^3 molecule^{-1} s^{-1}. The cited value of k was obtained by taking $k_{obs}/k = 1.35$ to allow for secondary removal of CH_3O_2.

(i) Flash-photolysis of Cl_2 in the presence of CH_4-O_2-N_2 mixtures over the pressure range 270 mbar to 930 mbar (200 Torr to 700 Torr). CH_3O_2 radicals were monitored by UV absorption. The values $k_{obs}/\sigma(210\text{ nm to }260\text{ nm}) = 1.17$ x 10^5 cm s^{-1} and $\sigma(250\text{ nm}) = 4.8$ x 10^{-18} cm^2 molecule^{-1} were obtained. k_{obs}/k taken to be 1.35. At temperatures >373 K, the second-order decays of CH_3O_2 were affected by HO_2 radical reactions. The branching ratio was obtained from the effect of $[HO_2]$ on the CH_3O_2 decays.

(j) Study of the photooxidation of CH_4, initiated by Cl atoms generated from Cl_2, in a slow-flow system under steady-state illumination. Analysis of HCHO, CH_3OH and HCOOH products by FTIR spectroscopy.

(k) Photolysis of $CH_3N_2CH_3$-O_2 and Cl_2-CH_4-O_2 mixtures, with analyses of reactants and products by FTIR spectroscopy.

Preferred Values

$k = 3.5$ x 10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.03$ x 10^{-13} exp$(365/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200 K to 400 K.
$k_2 = 1.3$ x 10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 7.4$ x 10^{-13} exp$(-520/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220 K to 330 K.

Reliability
$\Delta \log k = \pm 0.12$ at 298 K.
$\Delta(E/R) = \pm 200$ K.
$\Delta \log k_2 = \pm 0.15$ at 298 K.
$\Delta(E_2/R) = \pm 300$ K.

Comments on Preferred Values

The room temperature measurements of k_{obs}/σ of Cox and Tyndall (1980), Sander and Watson (1980, 1981), McAdam et al., (1987), Kurylo and Wallington (1987), Jenkin et al., (1988), Simon et al., (1988) and Lightfoot et al. (1990) are in excellent agreement and lead to the recommended value of $k_{obs}/\sigma(250 \text{ nm}) = 1.24 \times 10^5$ cm s^{-1}. The measurements of the absorption cross-section by Simon *et al.*[7] form the basis of our recommendation of $\sigma(250 \text{ nm}) = 3.9 \times 10^{-18}$ cm^2 molecule^{-1}. Thus, we recommend $k_{obs} = 4.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K. Taking the branching ratio of $k_2/k = 0.37$ at 298 K yields the value of k at 298 K given above.

The temperature dependence of k reported by Lightfoot *et al.*[8] is in excellent agreement with the studies of Sander and Watson,[3] Kurylo and Wallington[5] and Jenkin and Cox.[12] Here we have recommended the *E/R* value of Lightfoot *et al.*[8] on the basis of their more extensive temperature range, and the temperature-dependent branching ratio k_2/k. The recommended Arrhenius equation follows from the recommended values of k_{298} and *E/R*.

There have been a number of measurements of the branching ratio, k_2/k, which have been carefully reanalysed by Tyndall *et al.*[10] The values of k_2/k at 298 K range from 0.30 to 0.45. Tyndall *et al.*[10] recommend the average of 0.37 ± 0.06 which is also accepted in the review of Tyndall *et al.*[13] This value is taken as our preferred value at 298 K, with enhanced error limits. The two studies[8,9] of the temperature dependence of the branching ratio involve different temperature ranges. Here we have selected the results of Horie *et al.*[9] over the more atmospherically relevant temperature range of 200 K to 330 K, modified to reproduce our recommended value of k_2/k at 298 K. This has been combined with our recommended expression for k to obtain the preferred expression for k_2. There is no convincing evidence for any contribution from Channel (3).[10]

It should be noted that, from an analysis of their own data[9] together with the results of Lightfoot *et al.*,[8] Anastasi *et al.*,[14] Kan *et al.*,[15] Parkes,[16] Niki *et al.*[17] and Weaver *et al.*,[18] the equation $k_2/k = 1/\{1+[\exp(1330/T)]/33\}$ was obtained by Horie *et al.*[9] for the more extensive temperature range 223 K to 573 K. This equation shows slight non-Arrhenius behaviour. Lightfoot *et al.*[8] observed no pressure dependence of the branching ratio, k_2/k, over the range 0.28 bar to 1 bar.

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