

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_28

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(2.1 \pm 0.3) \times 10^{-12}$	298	Jenkin et al., 1993	MM-AS (a,b)
<i>Branching Ratios</i>			
$k_2/k = (0.67 \pm 0.11)$	295	Jenkin et al., 1993	P-FTIR (c)
$k_2/k = (0.67 \pm 0.13)$	298	Jenkin et al., 1993	MM-AS (d)

Comments

- k is defined by $-d[\text{CH}_3\text{OCH}_2\text{O}_2]/dt = 2k[\text{CH}_3\text{OCH}_2\text{O}_2]^2$ and has been derived from the measured overall second-order decay of $\text{CH}_3\text{OCH}_2\text{O}_2$ radicals (k_{obs}).
- Molecular modulation study of Cl_2 - CH_3OCH_3 - O_2 - N_2 mixtures together with a pulsed radiolysis study of SF_6 - CH_3OCH_3 - O_2 mixtures. k_{obs} was found to be dependent on the total pressure over the range 23 mbar to 1013 mbar (17 Torr to 760 Torr) and on the composition of the reaction mixture. On the basis of a mechanism involving the generation of H atoms via the reaction $\text{CH}_3\text{OCH}_2\text{O} + \text{M} \rightarrow \text{CH}_3\text{OCHO} + \text{H} + \text{M}$, it was possible to derive the cited pressure-independent value of k .
- FTIR spectroscopic study of the steady-state photolysis of Cl_2 in the presence of CH_3OCH_3 - O_2 - N_2 mixtures over the total pressure range 13 mbar to 930 mbar (10 Torr to 700 Torr). The branching ratio was determined from the yields of CH_3OCHO and $\text{CH}_3\text{OCH}_2\text{OOH}$. Minor amounts of $\text{CH}_3\text{OCH}_2\text{OH}$ were also observed.
- Similar study to that described in Comment (c). The branching ratio and k were derived from a kinetic analysis of the effects of $[\text{O}_2]$ and $[\text{Cl}_2]$ on k_{obs} , based on a mechanism including the production of H atoms from the reaction $\text{CH}_3\text{OCH}_2\text{O} + \text{M} \rightarrow \text{CH}_3\text{OCHO} + \text{H} + \text{M}$.

Preferred Values

$k = 2.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_2/k = 0.67$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The apparent effect of total pressure on k , the first reported for this type of reaction (Dagaut et al., 1989), has been shown to be an artifact by the more recent experiments of Jenkin et al. (1993). This comprehensive study on which the recommendation is based, has shown that the pressure effect was due to secondary chemistry involving H atoms which arise from the reaction $\text{CH}_3\text{OCH}_2\text{O} + \text{M} \rightarrow \text{CH}_3\text{OCHO} + \text{H} + \text{M}$. A kinetic analysis of the molecular modulation system, allowing for secondary chemistry, yielded the preferred rate coefficient. At the same time the derived value of the branching ratio, k_2/k , is in excellent agreement with that obtained from a steady-state photolysis system with FTIR spectroscopic analyses (Jenkin et al., 1993).

References

- Dagaut, P., Wallington, T. J. and Kurylo, M. J.: *J. Photochem. Photobiol.*, 48, 187, 1989.
Jenkin, M. E., Hayman, G. D., Wallington, T. J., Hurley, M. D., Ball, J. C., Nielsen, O. J. and Ellermann, T.: *J. Phys. Chem.*, 97, 11712, 1993.