IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_41

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This data sheet last evaluated: September 2009; last change in preferred values: September 2009.

$$CH_3O_2 + C_2H_5O_2 \rightarrow CH_3O + C_2H_5O + O_2 \quad (1)$$
$$\rightarrow CH_3OH + C_2H_5CHO + O_2 \quad (2)$$
$$\rightarrow HCHO + C_2H_5OH + O_2 \quad (3)$$

$\Delta H°(1) = 20.1$ kJ·mol^{-1}
$\Delta H°(2) = -349.0$ kJ·mol^{-1}
$\Delta H°(3) = -325.0$ 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			
$(2.0 \pm 0.5) \times 10^{-13}$	298	Villenave and Lesclaux, 1996	PLP-AS (a)

Comments

(a) Laser flash photolysis of CH_3Cl-C_2H_6-O_2-N_2 mixtures at 193 nm, with some additional experiments using C_2H_5Cl-CH_4-O_2-N_2 mixtures. The progress of the reaction was followed by time-resolved UV absorption measurements at 235 nm, close to the absorption maximum of both peroxy radicals. The value of k was derived by simulation of, and optimisation to, the absorption profiles, using an explicit chemical mechanism which took account of the well-characterised self reactions of CH_3O_2 and $C_2H_5O_2$ and their reactions with HO_2 formed in the system. The branching ratios of the title reaction could not be determined, but were assigned values based on the arithmetic mean of those for the analogous channels of the self reactions of CH_3O_2 and $C_2H_5O_2$.

Preferred Values

Parameter	Value	T/K
k/cm^3 molecule^{-1} s^{-1}	2.0×10^{-13}	298
Reliability		
$\Delta \log k$	± 0.3	298

Comments on Preferred Values

The preferred value of k is based on the results of the only study of the reaction. As discussed by Villenave and Lesclaux (1996), the value is intermediate to the rate coefficients for the self-reactions of CH_3O_2 and $C_2H_5O_2$ which (in conjunction with data for other reactions reported in the same study) provides some support for estimating rate coefficients for cross-reactions of simple unsubstituted peroxy radicals using a rule based on the geometric mean of the self-reactions of the participating radicals. Independent confirmatory studies of k are required, as are measurements as a function of temperature. Studies of the branching ratios are also required.

References

Villenave, E. and Lesclaux, R.: J. Phys. Chem., 100, 14372, 1996.