

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO32

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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> (3.3 ± 0.3) $\times 10^{-13}$	298	Adachi and Basco, 1982 ¹	FP-UVAS (a,b)

Comments

- (a) k is defined by $-d[n\text{-C}_3\text{H}_7\text{O}_2]/dt = 2k[n\text{-C}_3\text{H}_7\text{O}_2]^2$ and has been derived from the measured overall second order decay of $n\text{-C}_3\text{H}_7\text{O}_2$ radicals (k_{obs}) by correcting for secondary removal of the $n\text{-C}_3\text{H}_7\text{O}_2$ radicals.
- (b) The monitoring wavelength for $n\text{-C}_3\text{H}_7\text{O}_2$ radicals was 260 nm, with $\sigma = 3.15 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. The rate coefficient was derived from $k_{\text{obs}} = (3.84 \pm 0.33) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ on the basis of a mechanism with 12 secondary reactions.

Preferred Values

$k = 3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The recommended rate coefficient is the rounded-off value from the study of Adachi and Basco.¹ The room temperature rate coefficient requires substantiation along with a determination of the temperature coefficient.

The recommended value of k_{298} is in line with the rate coefficients of the analogous reactions of the CH_3O_2 and $\text{C}_2\text{H}_5\text{O}_2$ radicals. On the other hand, the recommended rate coefficient for the self-reaction of the $i\text{-C}_3\text{H}_7\text{O}_2$ radical is considerably lower ($k_{298} = 1.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and that reported² for the $t\text{-C}_4\text{H}_9\text{O}_2$ radical is even lower still ($k_{298} = 2.3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). This trend is in keeping with that observed in the liquid phase for the RO_2 radical interactions,³ i.e., $k(\text{primary RO}_2) > k(\text{secondary RO}_2) > k(\text{tertiary RO}_2)$.

References

- ¹ H. Adachi and N. Basco, *Int. J. Chem. Kinet.* **14**, 1125 (1982).
- ² C. Anastasi, I. W. M. Smith, and D. A. Parkes, *J. Chem. Soc. Faraday Trans. 1*, **74**, 1693 (1978).
- ³ J. E. Bennett, D. M. Brown, and B. Mile, *Trans. Faraday Soc.* **66**, 386 (1970).