

## 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>			
$(3.3 \pm 0.3) \times 10^{-13}$	298	Adachi and Basco, 1982 <sup>1</sup>	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 ( $k_{\text{obs}}$ ) 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.<sup>1</sup> 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  $\text{CH}_3\text{O}_2$  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 reported<sup>2</sup> 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  $\text{RO}_2$  radical interactions,<sup>3</sup> i.e.,  $k(\text{primary RO}_2) > k(\text{secondary RO}_2) > k(\text{tertiary RO}_2)$ .

## References

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