

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO₃_AROM2

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NO₃ + C₆H₅CH₃ (Toluene) → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Relative Rate Coefficients</i>			
$\leq 5 \times 10^{-17}$	300	Japar and Niki, 1975	RR (a)
$\leq 3.8 \times 10^{-15}$	300 ± 1	Carter et al., 1981	RR (b)
$(6.7 \pm 2.6) \times 10^{-17}$	298 ± 1	Atkinson et al., 1984a	RR (c)
$(6.75 \pm 1.65) \times 10^{-17}$	298 ± 1	Atkinson et al., 1984b	RR (d)
$(7.81 \pm 0.83) \times 10^{-17}$	296 ± 2	Atkinson and Aschmann, 1988	RR (d)

Comments

- (a) NO₃ radicals were generated from the thermal decomposition of N₂O₅. The experimental data were relative to the equilibrium coefficient K for the NO₃ + NO₂ ↔ N₂O₅ reactions, and are placed on an absolute basis by use of $K = 2.15 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ at 300 K (IUPAC, current recommendation).
- (b) NO₃ radicals were generated from the reaction of O₃ with NO₂ in the presence of toluene and propene (the reference compound). The contribution of the O₃ reaction was taken into account in estimating the amount of propene reacted with NO₃ radicals. The concentrations of toluene and propene were monitored by GC, and the derived rate coefficient ratio is placed on an absolute basis using a rate coefficient of $k(\text{NO}_3 + \text{propene}) = 9.79 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K (IUPAC, current recommendation).
- (c) NO₃ radicals were generated from the thermal decomposition of N₂O₅. The concentrations of toluene and ethene (the reference compound) were measured by GC, and a rate coefficient ratio of $k(\text{NO}_3 + \text{toluene})/k(\text{NO}_3 + \text{ethene}) = 0.32 \pm 0.12$ obtained. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{ethene}) = 2.1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendation).
- (d) NO₃ radicals were generated from the thermal decomposition of N₂O₅. The concentrations of toluene and *n*-heptane (the reference compound) were measured by GC. Rate coefficient ratios of $k(\text{NO}_3 + \text{toluene})/k(\text{NO}_3 + \textit{n}\text{-heptane}) = 0.45 \pm 0.11$ (Atkinson et al., 1984b) and 0.57 ± 0.06 (Atkinson and Aschmann, 1988) were obtained. These rate coefficient ratios are placed on an absolute basis by use of rate coefficients of $k(\text{NO}_3 + \textit{n}\text{-heptane}) = 1.37 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (Atkinson, 1991) and $1.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson and Arey, 2003). Rate coefficient ratios of $k(\text{NO}_3 + \text{C}_6\text{H}_5\text{CD}_3)/k(\text{NO}_3 + \textit{n}\text{-heptane}) = 0.28 \pm 0.05$ and $k(\text{NO}_3 + \text{C}_6\text{D}_5\text{CD}_3)/k(\text{NO}_3 + \textit{n}\text{-heptane}) = 0.25 \pm 0.13$ at 296 ± 2 K were also determined by Atkinson and Aschmann (1988).

Preferred Values

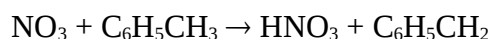
$$k = 7.8 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.25 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The room temperature relative rate measurements of Atkinson et al. (1984a, 1984b) and Atkinson and Aschmann (1988) are in good agreement, and are consistent with the upper limit of Carter et al. (1981). While the upper limit to the rate coefficient obtained by Japar and Niki (1975) relative to the equilibrium constant for the $\text{NO}_3 + \text{NO}_2 \leftrightarrow \text{N}_2\text{O}_5$ reactions is somewhat lower than the rate coefficients of Atkinson et al. (1984a,b) and Atkinson and Aschmann (1988), there are significant uncertainties in the equilibrium constant used for the $\text{NO}_3 + \text{NO}_2 \leftrightarrow \text{N}_2\text{O}_5$ reactions. The preferred 298 K value is based on the most recent study of Atkinson and Aschmann (1988). In that study, rate coefficients were also measured for the reactions of NO_3 radicals with $\text{C}_6\text{H}_5\text{CD}_3$ and $\text{C}_6\text{D}_5\text{CD}_3$, and the significant deuterium isotope effect for the $\text{C}_6\text{H}_5\text{CD}_3$ reaction indicates that the reaction proceeds by H- (or D-) atom abstraction from the CH_3 (or CD_3) substituent group.



This conclusion is consistent with the trend in reaction rate coefficients for the reactions of NO_3 radicals with toluene, the xylenes and the trimethylbenzenes (Atkinson, 1991).

References

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