# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx32

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This data sheet last evaluated: 28th June 2007; no revision of preferred values.

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## $NO_3 + CH_3SH \rightarrow$ products

### Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $1.0 \times 10^{-13} \exp[(600 \pm 400)/T]$ | 280-350 | Wallington et al., 1986 | FP-A |
| $(8.1 \pm 0.6) \times 10^{-13}$ | 298 | | |
| $(7.7 \pm 0.5) \times 10^{-13}$ | 298 | Rahman et al., 1988 | DF-MS |
| $1.09 \times 10^{-12} \exp[(0 \pm 50)/T]$ | 254-367 | Dlugokencky and Howard, 1988 | F-LIF |
| $(1.09 \pm 0.13) \times 10^{-12}$ | 298 | | |
| *Relative Rate Coefficients* | | | |
| $(1.00 \pm 0.22) \times 10^{-12}$ | 297 ± 2 | Mac Leod et al., 1986 | RR (a) |

### Comments

(a) $NO_3$ radicals were generated by the thermal decomposition of $N_2O_5$ in $N_2O_5$-$NO_2$-air mixtures at atmospheric pressure. The decay rates of $CH_3SH$ and *trans*-2-butene were monitored by FTIR and GC respectively, and the measured rate coefficient ratio of $k(NO_3 + CH_3SH)/k(NO_3 +$ *trans*-2-butene$) = 2.57 \pm 0.55$ is placed on an absolute basis by use of a rate coefficient of $k(NO_3 +$ *trans*-2-butene$) = 3.89 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson, 1997).

### Preferred Values

$k = 9.2 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, independent of temperature over the range 250-370 K.

*Reliability*

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 400$ K.

*Comments on Preferred Values*

The preferred value at 298 K is the mean of the four studies carried out to date (Wallington et al., 1986; Rahman et al., 1988; Dlugokencky and Howard, 1988), which are in reasonably good agreement. Although a significant negative temperature dependence is indicated by the absolute rate coefficient study of Wallington et al. (1986), this is due to the rate coefficient measured at 350 K, and the rate coefficients at 280 and 298 K are identical (Wallington et al., 1986). The temperature independence of the rate coefficient determined by Dluogokencky and Howard (1988) is accepted. The experimental data indicate that there is no pressure dependence of the rate coefficient, at least over the range ~0.0013-1 bar.

The magnitude of the rate coefficient and the lack of a temperature dependence of the rate coefficient shows that this reaction proceeds by initial addition, followed by decomposition of the adduct to yield $CH_3S$ radicals (see also the data sheet on the $NO_3 + CH_3SCH_3$ reaction)

$$NO_3 + CH_3SH \leftrightarrow [CH_3S(ONO_2)H]^{\ddagger} \rightarrow CH_3S + HNO_3$$

This conclusion is consistent with the product studies carried out by Mac Leod et al. (1986) and Jensen et al. (1992). Jensen et al. (1992) identified $CH_3SO_3H$ (methanesulfonic acid), $SO_2$, HCHO, $CH_3ONO_2$, $CH_3SNO$, and $HNO_3$ as products of the $NO_3$ radical reaction with $CH_3SH$ at 295 ± 2 K and 0.99 ± 0.01 bar (740 ± 10 Torr) total pressure of purified air.

## References


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