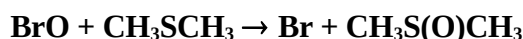


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx76

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This data sheet updated: 31st May 2007.



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(2.65 \pm 0.65) \times 10^{-13}$	298	Barnes et al., 1989	DF-MS
$(2.7 \pm 0.5) \times 10^{-13}$	298 ± 1	Barnes et al., 1991	DF-MS
$1.5 \times 10^{-14} \exp[(845 \pm 175)/T]$	246-320	Bedjanian et al., 1996	DF-MS (a)
$(2.7 \pm 0.2) \times 10^{-13}$	297		
$(4.40 \pm 0.66) \times 10^{-13}$	295 ± 2	Ingham et al., 1999	PLP-A (b)
$1.3 \times 10^{-14} \exp[(1033 \pm 265)/T]$	278-333	Nakano et al., 2001	PLP-CRDS (c)
$(4.60 \pm 0.60) \times 10^{-13}$	300		

Comments

- (a) $\text{CH}_3\text{S(O)CH}_3$ was observed as a reaction product, with a measured formation yield at 320 K and 1.3 mbar (1 Torr) total pressure of 0.94 ± 0.11 .
- (b) BrO radicals were generated by the reaction of O(³P) atoms (formed from 248 nm photolysis of O₃) with Br₂, and detected by absorption at 338.3 nm. Experiments were carried out at 80, 133 and 267 mbar (60, 100 and 200 Torr) total pressure of N₂, with measured rate coefficients of $(4.40 \pm 0.60) \times 10^{-13}$, $(4.40 \pm 0.66) \times 10^{-13}$ and $(4.36 \pm 0.65) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. Formation of $\text{CH}_3\text{S(O)CH}_3$ was observed, with a yield of 1.17 ± 0.34 .
- (c) BrO radicals were generated by the reaction of O(³P) atoms (formed from 266 nm photolysis of O₃) with Br₂, and detected by absorption at 338.5 nm. Experiments were carried out as a function of temperature at 100 Torr (133 mbar) of N₂ diluent, and at 300 K the rate coefficient was independent of the pressure of N₂ diluent over the range 100-200 Torr (133-267 mbar) or of the bath gas (N₂ or SF₆) at 100 Torr (133 mbar) total pressure.

Preferred Values

$k = 4.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.5 \times 10^{-14} \exp(1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270-340 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The recent measurements of the rate coefficient by Ingham et al. (1999) and Nakano et al. (2001) were carried out total pressures of 80-267 mbar of N₂, compared to the earlier measurements of Barnes et al. (1989; 1991) and Bedjanian et al. (1996) which were carried out at 0.5-6.8 mbar pressure. The higher room temperature rate coefficients of Ingham et al. (1999) and Nakano et al. (2001), which are in excellent agreement, may then reflect a pressure dependence of the rate coefficient at pressures below 80 mbar. The temperature dependencies reported by Bedjanian et al. (1996) and Nakano et al. (2001) are of similar magnitude. The preferred values are based on the more atmospherically relevant studies of Ingham et al. (1999) and Nakano et al. (2001). The uncertainty at 298 K is sufficient to encompass the room temperature rate coefficients of Barnes et al. (1989, 1991) and Bedjanian et al. (1996). Clearly, further rate coefficient measurements as a function of pressure and temperature are needed.

The reaction produces CH₃S(O)CH₃ + Br as the dominant, if not only, product under the experimental conditions employed to date (Bedjanian et al., 1996; Ingham et al., 1999; Ballesteros et al., 2002), and Ballesteros et al. (2002) cite "a near unity molar product yield" at 296 ± 3 K and atmospheric pressure.

The reaction is postulated (Bedjanian et al., 1996; Ingham et al., 1999) to proceed by:



This proposed mechanism is consistent with the observation of Ballesteros et al. (2002) of a lack of a deuterium isotope effect in the reactions of BrO radicals with CH₃SCH₃ and CD₃SCD₃, with $k_D/k_H = 1.0 \pm 0.1$ at 296 ± 3 K, and is consistent with the theoretical calculations of Sayin and McKee (2004).

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