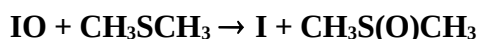


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx77

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This data sheet last evaluated: 4th June 2009. Last change in preferred values: 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>			
$(3.0 \pm 1.5) \times 10^{-11}$	296 ± 2	Barnes et al., 1987	(a)
$(1.5 \pm 0.5) \times 10^{-11}$	298	Martin et al., 1987	DF-MS
$\leq 3.5 \times 10^{-14}$	298 ± 2	Daykin and Wine, 1990	PLP-A (b)
$(1.5 \pm 0.2) \times 10^{-14}$	298	Maguin et al., 1991	DF-MS
$(8.8 \pm 2.1) \times 10^{-15}$	298 ± 1	Barnes et al., 1991	DF-MS
$(1.6 \pm 0.1) \times 10^{-14}$	298	Knight and Crowley, 2001	DF-MS
$1.2 \times 10^{-16} \exp[(2230 \pm 460)/T]$	273-312	Nakano et al., 2003	PLP-CRDS (c)
$(2.5 \pm 0.2) \times 10^{-13}$	298		
$9.6 \times 10^{-12} \exp[-(1816 \pm 397)/T]$	296-468	Gravestock et al., 2005	PLP-LIF (d)
$(2.0^{+0.4}_{-0.6}) \times 10^{-14}$	296		
$3.2 \times 10^{-13} \exp[-(925 \pm 136)/T]$	256-341	Dillon et al., 2006	PLP-LIF (e)
$(1.44 \pm 0.15) \times 10^{-14}$	298		

Comments

- (a) Photolysis of $\text{NO}_2\text{-I}_2\text{-CH}_3\text{SCH}_3\text{-N}_2$ mixtures. Photolytic production of $\text{O}(^3\text{P})$ atoms from NO_2 formed IO radicals via the reaction $\text{O}(^3\text{P}) + \text{I}_2 \rightarrow \text{IO} + \text{I}$. The concentrations of NO, NO_2 , CH_3SCH_3 , and CH_3SOCH_3 were followed as a function of time by FTIR absorption spectroscopy. A computer fit of the measured product yields to a 16-step reaction mechanism yielded the cited rate coefficient.
- (b) IO radicals were generated by the reaction of $\text{O}(^3\text{P})$ atoms (formed from 351 nm photolysis of NO_2) with I_2 , and were monitored by long-pathlength absorption at 427 nm. The total pressure of N_2 , O_2 or air diluent was varied over the range 40-300 Torr (53-400 mbar).
- (c) IO radicals were generated by the reaction of $\text{O}(^3\text{P})$ atoms (formed from 266 nm photolysis of O_3) with CF_3I , and detected by absorption at 435.60 nm. The total pressure (of N_2) was varied over the range 5-200 Torr (6.7-267 mbar) at 298 K, and the measured rate coefficient was observed to increase from $1.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 5 Torr (6.7 mbar) pressure to a high-pressure limit of $2.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 100-200 Torr (133-267 mbar) pressure. Temperature-dependent measurements were carried out at 100 Torr (133 mbar) of N_2 diluent. The cited rate coefficients are for 100 Torr N_2 .
- (d) IO radicals were generated by the reaction of $\text{O}(^3\text{P})$ atoms (formed from 351 nm photolysis of NO_2) with CF_3I and CH_3I . The total pressure of He diluent was varied over the range 5-300 Torr (6.7-400

mbar) at 296 K, and the measured rate coefficient was observed to be independent of pressure over this range. Temperature dependent measurements were carried out at 50 Torr (67 mbar) of He diluent.

- (e) IO radicals were generated by the reaction of O(³P) atoms (formed from 351 nm photolysis of NO₂ or, in selected experiments, from the 248 nm photolysis of O₃) with CF₃I and CH₃I. For product yield experiments, IO radicals were also generated from the 351 nm photolysis of CH₂I₂ in the presence of O₃. The total pressure of N₂ or air diluent was varied over the range 60-363 Torr (80-484 mbar) for the rate coefficient measurements at 298 K, and the measured rate coefficient was observed to be independent of pressure over this range. Temperature-dependent measurements were carried out at 130-140 Torr (173-187 mbar) of air diluent.

Preferred Values

$k = 1.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 3.3 \times 10^{-13} \exp(-925/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250-350 K.

Reliability

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

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

Comments on Preferred Values

In the first two studies of this reaction by Barnes et al. (1987) and Martin et al. (1987), erroneously high values were obtained which are now believed to have been due to features of the secondary chemistry and heterogeneous processes occurring under the conditions used. The later studies of Maguin et al. (1991), Barnes et al. (1991), Knight and Crowley (2001), Gravestock et al. (2005) and Dillon et al. (2006) give much lower values in the range $(0.9\text{-}2.0) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature, and these lower values are supported by the study of Daykin and Wine (1990) in which only an upper limit to the rate coefficient was determined.

The most recent studies of Gravestock et al. (2005) and Dillon et al. (2006) show that the room temperature rate coefficient is independent of pressure over the range 5 Torr of helium to 363 Torr of air or N₂ diluent (6.7-484 mbar). In contrast, Nakano et al. (2003) reported a pronounced pressure dependence of the 298 K rate coefficient below 100 Torr of N₂ diluent, a order of magnitude higher "high-pressure" rate coefficient at 298 K than measured by Gravestock et al. (2005) or Dillon et al. (2006), and a strong negative temperature dependence at 100 Torr pressure [note that at 5 Torr pressure, Nakano et al. (2003) measured a rate coefficient of $(1.0 \pm 0.3) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, of similar magnitude to the discharge flow rate data of Maguin et al. (1991), Barnes et al. (1991) and Knight and Crowley (2001)]. The data reported by Nakano et al. (2003) are clearly inconsistent with those of Daykin and Wine (1990), who reported an upper limit rate coefficient at 40-300 Torr of N₂, O₂ or air of $k \leq 3.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, and Gravestock et al. (2005). The modeling data presented by Gravestock et al. (2005) and the experimental data of Dillon et al. (2006) indicate that secondary chemistry in the Nakano et al. (2003) study led to overestimation of the rate coefficient for the IO + CH₃SCH₃ reaction.

Accordingly, the preferred value at 298 K is an average of the room temperature rate coefficients of Maguin et al. (1991), Barnes et al. (1991), Knight and Crowley (2001), Gravestock et al. (2005) and Dillon et al. (2006), and is consistent with the upper limit to the rate coefficient of Daykin and Wine (1990). Because the kinetic study of Dillon et al. (2006) extended down to 256 K, the preferred temperature dependence is that reported by Dillon et al. (2006), and the A-factor is adjusted to fit the preferred 298 K rate coefficient. The higher temperature dependence obtained by Gravestock et al. (2005) over the temperature range 298-468 K compared to that measured by Dillon et al. (2006) over the range 256-341 K may suggest that the Arrhenius plot exhibits curvature at higher temperatures. Hence the preferred Arrhenius expression should not be used above 350 K.

CH₃S(O)CH₃ has been detected in a number of studies (Barnes et al., 1987, 1991; Martin et al., 1987; Maguin et al., 1991; Knight and Crowley, 2001), and a semi-quantitative measurement of the yield by Barnes et al. (1991) gave a yield of 0.84 ± 0.40 . Dillon et al. (2006) determined the I atom formation yield from IO + CH₃SCH₃ by measuring IO radical decay rates in the presence of O₃, which converts any I atoms formed back to IO radicals. The independence of the measured IO decay rates on the CH₃SCH₃ concentration under these conditions resulted in a calculated I atom formation yield of $0.98^{+0.06}_{-0.08}$ at 298 K.

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