

TEMPERATURE DEPENDENCE OF THE REACTION $\text{OH} + \text{SO}_2 + \text{M} \rightarrow \text{HSO}_3 + \text{M}$ FOR $\text{M} = \text{Ar}$ AND SF_6

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Absolute rate constants k_1^{bi} have been determined, using a flash-photolysis-resonance-fluorescence technique, for the atmospherically important reaction of OH radicals with SO_2 for $\text{M} = \text{Ar}$ and SF_6 over the temperature range 298–424 K at total pressures from 98–653 Torr. At ≈ 650 Torr total pressure, the Arrhenius expressions $k_1^{bi}(\text{M} = \text{Ar}) = 1.16 \times 10^{-14} \times \exp[(2370 \pm 300)/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_1^{bi}(\text{M} = \text{SF}_6) = 1.27 \times 10^{-13} \exp[(1495 \pm 300)/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ were obtained where the (negative) activation energies are in cal/mole. The rate constants at 298 K and ≈ 650 Torr are $k_1^{bi}(\text{M} = \text{Ar}) = (6.49 \pm 0.84) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_1^{bi}(\text{M} = \text{SF}_6) = (1.61 \pm 0.22) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. A value of $k_1^{bi}(\text{M} = \text{N}_2) = 4.0 \times 10^{-14} \exp(1900/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at approximately atmospheric pressure was estimated from these results with $k_1^{bi}(\text{M} = \text{N}_2) = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at ≈ 650 Torr total pressure and 298 K, in good agreement with a recent evaluation.

1. Introduction

The reaction of the hydroxyl radical with SO_2 ,



is an important depletion process for SO_2 in the polluted troposphere and in plumes from fossil-fueled power plants [1,2].

Rate constants k_1 for this reaction, which is in the fall-off region between second- and third-order kinetics over the pressure range accessible to laboratory studies, have been obtained, mainly at room temperature, by both absolute [3–6] and relative rate [7–11] techniques. Absolute rate constants k_1 have been determined over significant pressure ranges only for $\text{M} = \text{Ar}$ (20–500 Torr [4] and 25–648 Torr [6] total pressure) and $\text{M} = \text{He}$ (50–500 Torr [4]), while values of k_1 have been obtained, relative to the rate constant for the reaction of OH radicals with CO, at 760 Torr for $\text{M} = \text{N}_2 + \text{O}_2$ by Cox [8,9] and over the range 20–1000 Torr total pressure for $\text{M} = \text{N}_2$ by Castleman and co-workers [10,11]. The sole temperature-dependence study is that of Castleman and Tang [11], carried out in the low-pressure third-order kinetics region.

There is hence a need for the modelling of the troposphere and of power-plant plumes to determine k_1 as a function of temperature at ambient pressure of $\text{M} = \text{N}_2$ and O_2 . However, since these diluent gases cannot be used at high pressure with the flash-photolysis-resonance technique, because of quenching of the $\text{OH}(\text{A } ^2\Sigma^+)$ state, rate constants k_1 have been determined in this work for $\text{M} = \text{Ar}$ and SF_6 up to ≈ 650 Torr total pressure over the temperature range 298–424 K. From these results and analogous data for the reaction of OH radicals with NO_2 [12], the values of k_1 at atmospheric pressure for $\text{M} = \text{N}_2$ can be estimated.

2. Experimental

The apparatus and techniques used have been described previously [6,13]. Hydroxyl radicals were produced by the pulsed vacuum ultraviolet photolysis of H_2O at wavelengths longer than the CaF_2 cutoff ($\geq 1250 \text{ \AA}$). OH radical concentrations were monitored as a function of time after the flash by resonance fluorescence, using a cooled EMI 9659QA photomultiplier fitted with an interference filter transmitting the 3064 Å band of $\text{OH}(\text{A } ^2\Sigma^+, v' = 0 \rightarrow \text{X } ^2\Pi, v'' = 0)$. The intersection of the detection system aperture and the reso-

nance radiation beam defined a fluorescence viewing zone at the center of the reaction vessel whose cross section was ≈ 2 cm in diameter. This region was well separated from the reaction vessel walls, minimizing wall losses of the OH radicals. The reaction cell was enclosed in a furnace which could be held constant to better than ± 1 K over the temperature range 295–475 K, the gas temperature being measured by a chromel/alumel thermocouple mounted inside the reaction vessel.

The flash lamp was typically operated at discharge energies of 20–80 J per flash at repetition rates of one flash in four seconds. Signals were obtained by photon counting in conjunction with multichannel scaling. Decay curves of OH radicals were accumulated from 100–4250 flashes, depending on the signal strengths. OH half-lives ranged from 1.52–92.4 ms and radical concentrations were monitored over at least three half-lives. In all cases the flash duration (≤ 1 μ s) was negligible in comparison to the OH radical half-lives encountered.

In order to avoid the accumulation of photolysis or reaction products, all experiments were carried out under flow conditions so that the gas mixture in the reaction vessel was replenished every few flashes. The partial pressure of H₂O in the reaction cell ranged from 0.05–0.16 Torr. The gases used had the following purity levels according to the manufacturer: Ar $\geq 99.998\%$; SF₆ $\geq 99.99\%$; SO₂ $\geq 99.98\%$ (taken from a cylinder of a 1.06 \pm 0.02% mixture in argon). All flows were monitored by calibrated flowmeters and the gases were premixed before entering the reaction vessel.

3. Results and discussion

The reaction of OH radicals with SO₂ was studied over the temperature range 298–424 K at ≈ 650 Torr total pressure of argon, and over the range 98–653 Torr total pressure of SF₆. Under the experimental conditions used, the pseudo-first-order decays of the OH radical concentrations, [OH], are given by the integrated rate expression

$$[\text{OH}]_0/[\text{OH}]_t = S_0/S_t \\ = \exp \{ (k + k_1^{\text{bi}}[\text{SO}_2])(t - t_0) \}, \quad (1)$$

where [OH]₀ and [OH]_t represent the concentrations of OH at times t_0 and t , respectively, S_0 and S_t are the

corresponding resonance-fluorescence intensities, k is the first-order rate for removal of OH in the absence of added reactant (primarily attributed to diffusion out of the viewing zone and to reaction with impurities), and k_1^{bi} is the bimolecular rate constant for the reaction of OH radicals with SO₂.

For M = Ar at 298 K, and for M = SF₆ at both the lowest temperatures and total pressures, some nonexponentiality in the OH radical decays was observed, as noted in the previous room-temperature study of this reaction in this laboratory [6]. This nonexponentiality was probably caused either by a long-lived chemiluminescence or by enhanced scattering of the resonance lamp radiation by aerosol particles formed subsequent to the initial reaction. Decay rates were obtained under conditions where this effect was negligible for at least two half-lives.

Fig. 1 shows a plot of the OH radical decay rate against SO₂ concentration for the temperatures and total pressures studied for M = Ar, while fig. 2 shows a plot of k_1^{bi} (M = SF₆) against the total SF₆ pressure for the temperatures 298 and 424 K, and table 1 gives the rate constants k_1^{bi} for M = Ar and SF₆ obtained by least-squares analysis of plots such as those shown in fig. 1.

Fig. 3 shows the data at ≈ 650 Torr total pressure for M = Ar and SF₆, and at ≈ 100 Torr total pressure for M = SF₆, plotted in Arrhenius form. Least-squares analysis of these results yields the Arrhenius expressions

$$k_1^{\text{bi}}(\text{M} = \text{Ar}, \approx 650 \text{ Torr}) \\ = 1.16 \times 10^{-14} \exp \{ (2370 \pm 300)/RT \} \\ \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k_1^{\text{bi}}(\text{M} = \text{SF}_6, \approx 100 \text{ Torr}) \\ = 3.72 \times 10^{-14} \exp \{ (1610 \pm 300)/RT \} \\ \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k_1^{\text{bi}}(\text{M} = \text{SF}_6, \approx 650 \text{ Torr}) \\ = 1.27 \times 10^{-13} \exp \{ (1495 \pm 300)/RT \} \\ \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

where the indicated errors in the (negative) activation energy (in cal/mole) are the estimated overall error limits.

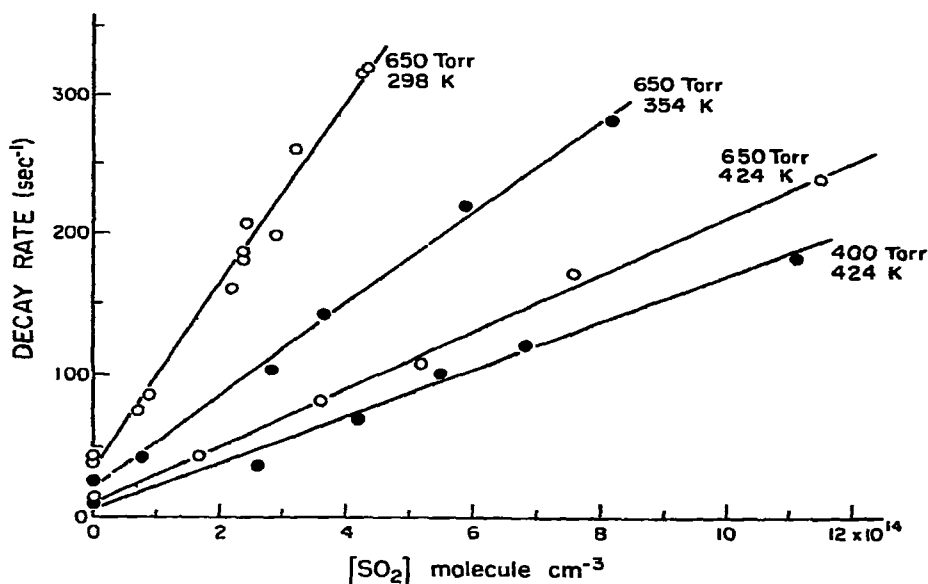


Fig. 1 Plots of OH radical decay rate against SO_2 concentration for $M = \text{Ar}$ at the temperatures and total pressures studied

The present room-temperature rate constant for $M = \text{Ar}$ at 650 Torr total pressure, $(6.49 \pm 0.84) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, is in excellent agreement with the value of $k_1^{\text{bi}}(M = \text{Ar}, 648 \text{ Torr}) = (6.55 \pm 0.66) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ determined in the previous study

Table 1
Rate constants k_1^{bi} for the reaction of OH radicals with SO_2 for $M = \text{Ar}$ and SF_6 . The indicated error limits are the estimated overall error limits which include the least-squares standard deviations (2–8%) as well as the estimated accuracy limits of other parameters such as pressure and reactant concentrations

Temperature (K)	Total pressure (Torr)	$10^{13} \times k_1^{\text{bi}} (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	
$M = \text{Ar}$	298 ± 1	650 ± 4	6.49 ± 0.84
	354 ± 1	650 ± 2	3.22 ± 0.36
	424 ± 1	404 ± 1	1.62 ± 0.28
		653 ± 2	1.98 ± 0.20
$M = \text{SF}_6$	298 ± 1	98 ± 2	5.70 ± 1.18
		203 ± 2	7.83 ± 0.79
		400 ± 2	12.3 ± 1.6
		643 ± 2	16.1 ± 2.2
	354 ± 1	100 ± 1	3.61 ± 0.58
		652 ± 2	10.3 ± 1.6
	424 ± 1	100 ± 1	2.54 ± 0.31
		201 ± 2	3.61 ± 0.58
		408 ± 2	6.00 ± 0.64
		650 ± 2	7.61 ± 0.80

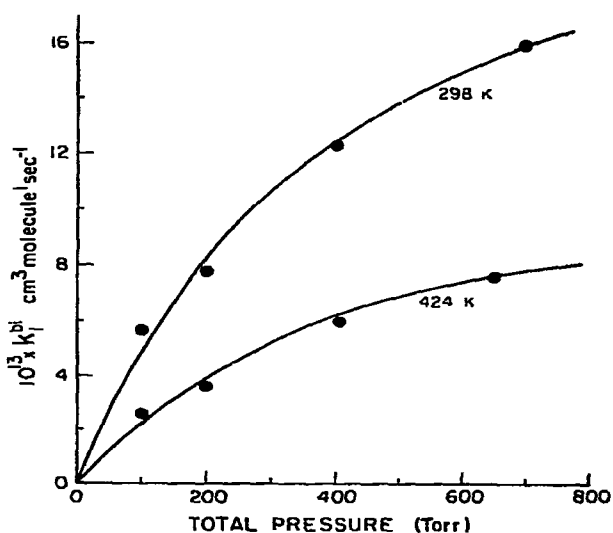


Fig. 2. Plots of k_1^{bi} ($M = \text{SF}_6$) against the total pressure of SF_6 at 298 and 424 K.

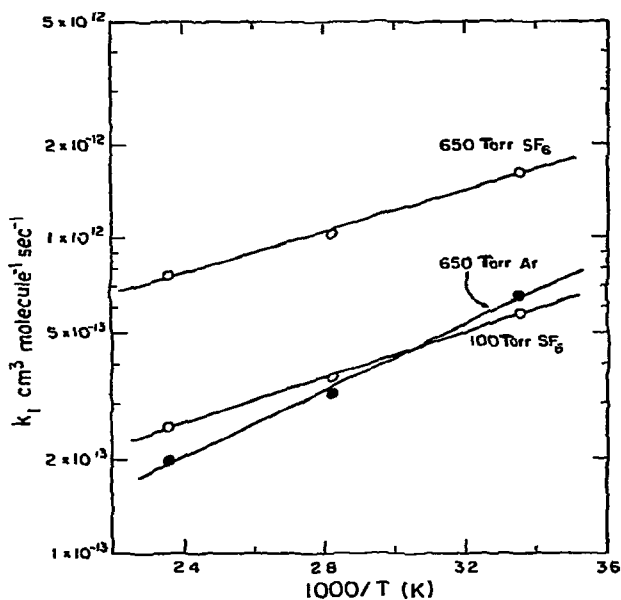


Fig. 3. Arrhenius plot of $\log k_1^{bi}$ against $1000/T(K)$ for $M = Ar$ and SF_6 at ≈ 650 Torr total pressure, and for $M = SF_6$ at ≈ 100 Torr total pressure

in this laboratory [6]. As anticipated, for example by analogy with the reaction of OH radicals with NO_2 [12], SF_6 is a more efficient third body than Ar. However, perhaps surprisingly, the rate constants for $M = SF_6$, as shown in table 1 and fig. 2, have not attained the second-order limiting high-pressure value at ≈ 650 Torr total pressure. From Lindemann plots, the second-order limiting high-pressure rate constants were estimated to be $\geq 3.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and $\geq 1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 424 K.

As seen from fig. 3 the bimolecular rate constants k_1^{bi} have negative temperature dependencies (equivalent to $T^{-3.4}$ for $M = Ar$ at 650 Torr total pressure, and $T^{-2.3}$ and $T^{-2.1}$ for $M = SF_6$ at 100 and 650 Torr total pressure). These temperature dependencies are of a similar size and magnitude to that reported by Anastasi and Smith [12] for the limiting high-pressure bimolecular rate constant for the reaction of OH radicals with NO_2 and provide a further opportunity to test the predictions of RRKM theory against experiment. However, as expected from unimolecular theory, these temperature dependencies are less negative than that determined by Castleman and Tang [11] ($E = -2.8 \text{ kcal mole}^{-1}$) in the low-pressure third-order region, and at

650 Torr total pressure, the temperature dependence for $M = SF_6$ is less negative than that for $M = Ar$.

For tropospheric modelling purposes, the important results are the values of k_1^{bi} for $M = N_2$ and O_2 at atmospheric pressure [1,2]. From the relative efficiencies of Ar, N_2 and SF_6 in the analogous reactions of the OH radical with NO_2 [12], with N_2 being in between Ar and SF_6 in third-body efficiency, values of $k_1^{bi}(M = N_2)$ of $1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, $5.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 354 K and $3.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 424 K can be estimated at ≈ 650 Torr from the present rate-constant results. Hence for tropospheric purposes (since N_2 and O_2 are of comparable third-body efficiency [12]), the Arrhenius expression, applicable to approximately atmospheric pressure,

$$k_1^{bi}(M = N_2) = 4.0 \times 10^{-14} \exp(1900/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

is recommended (the activation energy is in cal/mole). This value for $k_1^{bi}(M = N_2)$ at 298 K and atmospheric pressure, which is derived by interpolation between directly measured rate constants which differ in magnitude by a relatively small amount, is essentially identical with the value recommended recently by Calvert et al. [1] ($k_1^{bi}(M = \text{air}) = (1.1 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) from an evaluation of the existing rate constant data.

References

- [1] J.G. Calvert, F. Su, J.W. Bottenheim and O.P. Strausz, *Atmos Environ* 12 (1978) 197.
- [2] A.E.J. Eggleton and R.A. Cox, *Atmos. Environ.* 12 (1978) 227.
- [3] G.W. Harris and R.P. Wayne, *J. Chem. Soc. Faraday Trans. I* 71 (1975) 610.
- [4] D.D. Davis, A.R. Ravishankara and S. Fischer, *Geophys. Res. Letters* 6 (1979) 113.
- [5] S. Gordon and W.A. Mulac, *Intern. J. Chem. Kinetics* S1 (1975) 289.
- [6] R. Atkinson, R.A. Perry and J.N. Pitts Jr., *J. Chem. Phys.* 65 (1976) 306.

- [7] W A. Payne, L J. Stief and D D Davis, J. Am. Chem Soc. 95 (1973) 7614.
- [8] R A Cox, J Photochem 3 (1974) 291
- [9] R A Cox, Intern J Chem Kinetics S1 (1975) 379.
- [10] A.W Castleman Jr, R E Davis, H R Munkelwitz, I N Tang and W P. Wood, Intern J Chem. Kinetics S1 (1975) 629
- [11] A W. Castleman Jr. and I N Tang, J. Photochem 6 (1977) 349
- [12] C. Anastasi and I W.M. Smith, J. Chem Soc Faraday Trans II 72 (1976) 1459
- [13] R Atkinson, D A Hansen and J N Pitts Jr, J. Chem Phys 62 (1975) 3284; 63 (1975) 1703.