one in Figure 11 and the correlation fails for CH₂CHCl and CH₂CF₂. Carbenes, especially SiCl₂, exhibit a similar ordering of rate constants for this series of olefins.³⁹⁻⁴¹ The increase in rate constants of singlet carbenes with methyl substitution of C2H4 has been interpreted as a consequence of inductive donation of electrons to the π system by methyl. Thus, the π system more readily coordinates with the vacant p orbital of the singlet carbene. Conversely, halogen substitution withdraws electrons from the π system and reduces the rate constants. These rather complicated electronic effects are approximately represented by the trend in ionization energies.⁴¹ This correlation for the rate constants of $NF(a^{1}\Delta)$ confirms a carbenelike reactivity and evidently the π system of the olefin donates an electron pair to the vacant orbital of the $\pi_x^2 - \pi_y^2$ component to initiate the addition reaction of NF(a). Just as for carbene reactions, this step is followed by interaction of the electron pair initially on NF(a) with the olefin to complete the addition reaction.

Conclusions

The room temperature quenching rate constants for NF(a) span a range from $\sim 1 \times 10^{-17}$ for N₂ to 2.6 $\times 10^{-11}$ cm³ s⁻¹ for trimethylamine and trimethylbismuth. In general, the quenching rate constants are not so large as to preclude using NF(a) as a gas-phase energy storage molecule. A comprehensive correlation was found between the quenching rate constants and the proton affinity values for reagent molecules that can act as bases, i.e., those containing oxygen and nitrogen. A less extensive correlation was found between the rate constants and the ionization energies for alkenes. These correlations and the absence of any H/D kinetic isotope effect upon the rate constants strongly suggest that chemical interactions control the quenching rate, rather than a physical E-V quenching mechanism. The correlation of rate constants with base strengths of the reagent implies that the $\pi_x^2 - \pi_y^2$ component of the NF(a) structure is more important than the $\pi_x \pi_y$ biradical component, as is expected from the ordering of the ¹A' and ¹A'' potentials correlating to NF(a¹ Δ) + Q. The quenching rate constants for NO and NO2 are small, which is further evidence that the $\pi_x \pi_y$ component is not very reactive even with radicals. Considerable effort was expended to characterize the bimolecular self-quenching of NF(a), and a rate constant of $(5 \pm 2) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ is favored. Energy pooling to give NF(b) and NF(X) is a minor component to the selfquenching process. The products presumably are N_2 and F_2 (or 2F) or stepwise relaxation giving NF(X) and NF(a). The 2F + HN₃ reaction system was shown to be a suitable source for studies of NF(a) at 200 K, as well as at 300 K.

Acknowledgment. This work was supported by the U.S. Air Force Office of Scientific Research (Grant 88-0279). We thank Professor Dick McDonald for advice on the proton affinity correlation plot.

A Laser Photolysis Study of the Reaction of SO₄⁻ with Cl⁻ and the Subsequent Decay of Cl₂⁻ in Aqueous Solution

W. John McElroy

Central Electricity Generating Board, National Power Division, Technology and Environmental Centre, Kelvin Avenue, Leatherhead, Surrey KT22 7SE, U.K. (Received: July 11, 1988; In Final Form: December 2, 1988)

Kinetic spectroscopic techniques were employed to investigate the reactions of the SO4- and Cl2- radicals following photolysis of $K_2S_2O_8$ -NaCl solutions at 248 nm. The extinction coefficient of SO_4^- was estimated to have a value of $(1.6 \pm 0.1) \times$ 10^3 M⁻¹ cm⁻¹ (base 10) at 450 nm, its wavelength of maximum absorbance. A mechanism is proposed which accounts for the observed decay of Cl_2^- in aqueous solution. Several rate coefficients have been determined at 20 °C: $k(SO_4^- + Cl^-) = (2.7 \pm 0.4) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (at zero ionic strength), $2k(Cl_2^- + Cl_2^-) = (1.4 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (at zero ionic strength), $k(\tilde{C}l_2^- + H_2O) = (1.3 \pm 0.1) \times 10^3 \text{ s}^{-1}$, and $k(\tilde{C}l_2^- + H_2O) = (2.5 \pm 0.2) \times 10^5 \text{ s}^{-1}$.

Introduction

The aqueous oxidation of SO_2 to form sulfuric acid is of fundamental importance in the atmosphere since this process exerts a considerable influence on the composition and, in particular, the acidity of cloud and rainwater.¹ Many uncertainties still remain with regard to the kinetics and mechanisms of SO₂ oxidation,^{2,3} and their elucidation is particularly important if experimental measurements are to be extrapolated to atmospheric conditions which are much more complex than simpler laboratory systems.

It has been proposed that radicals such as SO_3^- , SO_4^- , and $SO_5^$ are key intermediates in the autoxidation of aqueous solutions of SO_2 ⁴ While the available literature on this process is extensive,

the mechanism has yet to be fully resolved.^{3,5} Chloride ion is a major component of cloud and rainwater in maritime air masses. Reaction of the SO₄⁻ radical with Cl⁻ leads to the production of the dichloride ion, $Cl_2^{-.6}$

$$\mathrm{SO}_4^- + \mathrm{Cl}^- \to \mathrm{SO}_4^{2-} + \mathrm{Cl} \tag{1}$$

$$Cl + Cl^{-} \rightleftharpoons Cl_{2}^{-}$$
 (2')

The impact of chloride ion on the rate of SO₂ oxidation is dependent on the subsequent fate of the Cl2- radical and also the mechanism of the autoxidation reaction itself.^{3,5}

Kinetic studies of the reaction of SO_4^- with CI^- have been carried out previously using flash photolysis or pulse radiolysis techniques. $^{6-10}$ Under second-order conditions the accuracy of

⁽³⁹⁾ Safarik, I.; Ruzsicska, B. P.; Jodhan, A.; Strausz, O. P.; Bell, T. N. (40) Cha, J. O.; Beach, D. B.; Jasinski, J. M. J. Phys. Chem. 1987, 91,
 (40) Cha, J. O.; Beach, D. B.; Jasinski, J. M. J. Phys. Chem. 1987, 91,

^{5340.}

⁽⁴¹⁾ Baggott, J. E.; Blitz, M. A.; Frey, H. M.; Lightfoot, P. D.; Walsh, R. J. Chem. Soc. Faraday Trans. 2 1988, 84, 515.

Scire, J. A.; Venkatram, A. Atmos. Environ. 1985, 19, 637.
 Hoffmann, M. R.; Jacob, D. J. SO₂, NO and NO₂ Oxidation Mechanisms: Atmospheric Considerations; Butterworth: Boston, 1984; Chapter 3. (3) McElroy, W. J. Atmos. Environ. 1986, 20, 323.

⁽⁴⁾ Hayon, E.; Treinen, A.; Wilf, J. J. Am. Chem. Soc. 1972, 94, 47.

⁽⁵⁾ Huie, R. E.; Neta, P. Atmos. Environ. 1987, 21, 1743.
(6) Chawla, O. P.; Fessenden, R. W. J. Phys. Chem. 1975, 79, 2693.
(7) Chawla, O. P. An Electron Spin Resonance Study of Photochemical Reactions in Aqueous Solutions. Ph.D. Thesis, Carnegie-Mellon University, Pittsburgh, 1973.



Figure 1. Flow diagram of laser photolysis apparatus.

the absolute value of the rate coefficient is limited by uncertainty regarding the extinction coefficient of SO₄⁻. Literature values^{11,12} extend from 450 to 1600 M^{-1} cm⁻¹ (base 10) at 450 nm, the wavelength of maximum absorbance.

Quantitative rate data for the decay of Cl₂⁻ in aqueous solution have been confined mainly to the self-reaction, for which published rate coefficients (2k₃) range from 7×10^7 to 2×10^{10} M⁻¹ s⁻¹ at 25 °C.13-17

$$Cl_2^- + Cl_2^- \rightarrow Cl_2 + 2Cl^- \tag{3}$$

An alternative mechanism has recently been proposed¹⁷ to account in part for the loss of Cl_2^{-} .

$$Cl_2^- \rightleftharpoons Cl + Cl^-$$
 (2)

$$Cl + H_2O \rightleftharpoons H^+ + HOCl^-$$
 (4)

$$HOCI^- \rightleftharpoons OH + CI^-$$
 (5)

Experimental observations¹⁷ are not entirely consistent with this mechanism, particularly the apparent absence of any dependence on pH.

In the present work, the extinction coefficient of SO_4^- at 450 nm has been measured by using laser photolysis of aqueous $K_2S_2O_8$ solutions at 248 nm as a radical source. Kinetic spectroscopic techniques have been employed to obtain a direct determination of the rate coefficient for reaction 1. The subsequent decay of Cl_2^- has been investigated.

Experimental Section

Laser Photolysis Apparatus. A Lambda Physik Excimer Multigas laser (EMG 101) operating at 248 nm (KrF) has been

 (9) Slama-Schwok, A.; Rabini, J. J. Phys. Chem. 1986, 90, 1176.
 (10) Wine, P. H.; Tang, Y.; Thorn, R. P.; Wells, J. R.; Davis, D. D. J. Geophys. Res., in press

used as the photolysis source. This laser system produces an optimum output of 250 mJ per pulse (equivalent to a peak power of 15 MW), with a pulse half-width of 16 ns and a beam crosssectional area of 250 mm².

The laser irradiated a low-fluorescence quartz cell of internal dimensions $10 \times 11 \times 4$ mm (length \times height \times width) mounted in a thermostated aluminum block and connected so that the reagent solution could flow through the cell (Figure 1). Typical flow rates were in the range $5-15 \text{ mL min}^{-1}$. The body of the cell was blackened so that only the windows were transparent to radiation. The optical path length with respect to the laser beam was 4 mm and the center of the cell was 30 cm from the laser window. Absence of any dead volume and the flat density profile of the laser beam ensured uniform irradiation of reactant solutions.

Transient species produced as a consequence of photolysis of reactant solutions were monitored in absorption by kinetic spectrophotometry. A high-pressure xenon arc lamp (Thorn EMI XE/D 250 watt) with a regulated power supply (iREM E2X20P) was used as the light source. Collimated light from the arc passed through the photolysis cell onto the entrance slit of an Applied Photophysics M300 high-radiance monochromator which is an f/4 200 mm focal length symmetrical Czerny-Turner Unit operated in the first order with a slit width of 0.25 mm and a spectral resolution of 4 nm mm⁻¹.

Absorbance signals were detected by means of an RCA IP28 photomultiplier tube having an S-5 spectral response. The tube was typically run at 500-600 V with the output developed across a 5-k Ω anode load resistor before being biased and fed to a fast analog to digital converter (Datalab Transient Recorder Model DL905) with a maximum sampling speed of 5 MHz. A time constant of $\sim 3 \,\mu s$ was measured for the complete detection circuit. The self-masking design of the cell together with the narrow bandwidth of the monochromator resulted in a negligible amount of scattered light from the laser falling on the photomultiplier. A flexible plastic bellows connected the laser to the cell housing so that the laser beam was totally enclosed and mechanical noise generated by the laser gas circulation fan was decoupled from the detection system.

A trigger pulse from the laser control circuit initiated the recording cycle. Data from the transient recorder were transferred via a 1-MHz bus to a BBC Master Series Microcomputer which was capable of signal accumulation at a rate in excess of two experiments per second. Averaged signals were stored on floppy disk for subsequent analysis. Unless otherwise stated, all experiments were an average of 128 single events and were carried out at 20 °C. A laser repetition rate of 1 Hz ensured that the entire volume of the cell was swept out after two pulses. The extent

⁽⁸⁾ Kim, K.-J.; Hamill, W. H. J. Phys. Chem. 1976, 80, 2320.

⁽¹¹⁾ Dogliotti, L.; Hayon, E. J. Phys. Chem. 1967, 71, 2511

⁽¹²⁾ Roebke, W.; Renz, M.; Henglein, A. Int. J. Radiat. Phys. Chem. 1969, 1, 39.

⁽¹³⁾ Ross, A. B.; Neta, P. Natl. Bur. Stand. (U.S.), Natl. Stand. Ref. Data Ser. NSRDS-NBS-65 1979.

⁽¹⁴⁾ Navaratnam, S.; Parsons, B. J.; Swallow, A. J. Radiat. Phys. Chem. 1980, 15, 159

⁽¹⁵⁾ Gogolev, A. V.; Makarov, I. E.; Pikaev, A. K. High Energy Chem. 1984, 18, 496.

⁽¹⁶⁾ Lierse, C.; Sullivan, J. C.; Schmidt, K. H. Inorg. Chem. 1987, 26, 1408

⁽¹⁷⁾ Wagner, I.; Karthäuser, J.; Strehlow, H. Ber. Bunsen-Ges. Phys. Chem. 1986, 90, 861.

of photolysis of $K_2S_2O_8$ was less than 0.1% per pulse. Laser discharge voltages were in the range 27-33 kV.

Reagents. Solutions were prepared using water with resistivity >18 M Ω . K₂S₂O₈ (Fluka puriss. p.a., >99.5%; <0.005% Cl⁻), NaCl (BDH AnalaR grade, >99.9%) HCl (BDH Convol, >99.9%), and N₂O (Matheson Research Grade >99.5%) were used without further purification. Argon (Air Products high-purity grade) was passed through a rare gas purifier (BOC Mk 4).

The major impurity in all available sources of $K_2S_2O_8$ is sulfuric acid and it was this which predominantly controlled the pH in all experiments where HCl was not used. A 4 × 10⁻¹ M solution of $K_2S_2O_8$ had a pH of ~3.8 which is equivalent to an H_2SO_4 content of ~0.2%.

Determination of Extinction Coefficients. The extinction coefficient of the sulfate radical anion, ϵ_{SO_4} , was determined by comparison with that of Cl₂⁻. The absorption of SO₄⁻ at 450 nm was monitored following the photolysis of a 2 × 10⁻² M K₂S₂O₈ solution. Similarly the absorption of Cl₂⁻ was monitored at 340 nm following the photolysis of a solution containing 1 × 10⁻³ M NaCl and 2 × 10⁻² K₂S₂O₈. Laser pulse energies were identical in both experiments and each experiment was repeated six times. Absorbances were measured 10 μ s after the laser pulse. The effect on ϵ_{SO_4} of varying both the S₂O₈²⁻ and Cl⁻ concentrations was investigated over the ranges (1-4) × 10⁻² and (1-10) × 10⁻³ M, respectively.

Determination of Rate Coefficients. The reaction of SO_4^- with Cl⁻ was investigated by monitoring the decay of the sulfate radical at 480 nm following photolysis of 2×10^{-2} M K₂S₂O₈ in the presence of 5×10^{-5} M NaCl. The effect on the second-order rate constant of doubling both the S₂O₈²⁻ and Cl⁻ concentrations was also examined. A total of 40 experiments were performed. The absorption of Cl₂⁻ at 340 nm was monitored in an attempt to obtain a value for the rate coefficient from the product buildup kinetics. A laser discharge voltage of 30 kV was employed in all studies of this reaction.

The decay of Cl_2^- produced by the reaction of SO_4^- with $Cl^$ was studied over a wide range of conditions ($S_2O_8^{2-}$ (1 × 10⁻² to 4 × 10⁻² M, Cl^- (5 × 10⁻⁵ to 1 × 10⁻⁴ M), pH (2.2-3.9), ionic strength (0.03–0.24 M), and laser discharge voltage (27–33 kV)). In excess of 140 experiments were performed to investigate the dependence of the observed decay on the initial Cl_2^- concentration, pH, [Cl^-], [$S_2O_8^{2-}$], and ionic strength of the solution. Experiments were also carried out using N₂O- and Ar-saturated solutions to examine the influence of solvated electrons and molecular oxygen, respectively.

Results and Discussion

The Extinction Coefficient of SO_4^- at 450 nm. The optical spectrum of the SO_4^- radical anion has been characterized in a number of previous investigations.^{4,11,18} Absorption extends from 280 to 570 nm and has a maximum at 450 nm.

In this study the SO_4^- radical anion was generated by photolysis of the peroxodisulfate ion, $S_2O_8^{2^-}$, which absorbs strongly below 260 nm ($\epsilon_{248 \text{ nm}} \approx 20 \text{ M}^{-1} \text{ cm}^{-1}$). The absorption of SO_4^- was monitored at 450 nm.

$$S_2 O_8^{2-} + h\nu \rightarrow 2SO_4^{-} \tag{6}$$

A plot of the optical density profile following photolysis of 2.0 $\times 10^{-2}$ M K₂S₂O₈ is shown in Figure 2a. Existing literature data on the decay of SO₄⁻ in aqueous solution¹³ suggest that sinks for this species are negligible on a time scale of 10 μ s for an initial optical density of 2 $\times 10^{-3}$. The absorption at this point is expected to be very similar to that immediately following the laser pulse.

The extinction coefficient of SO_4^- was determined by comparing the absorbance of SO_4^- as described above with that of Cl_2^- at 340 nm produced by the reaction of the sulfate radical with chloride ion. For an NaCl concentration of 10^{-3} M the half-lives of reactions 1 and 2 are approximately 3.0 μ s and 50 ns, respectively, based on available rate data.¹³ Although reaction 3

(18) Lesigne, B.; Ferradini, C.; Pucheault, J. J. Phys. Chem. 1973, 77, 2156.



Figure 2. (a, upper curve) Absorption at 450 nm following the photolysis of $K_2S_2O_8$ (0.02 M). (b, lower curve) Absorption at 340 nm following the photolysis of $K_2S_2O_8$ (0.02 M) in the presence of NaCl (0.001 M).

is in effect an equilibrium $(K_3 = 1.9 \times 10^5 \text{ M}^{-1})$,¹⁹ the concentration of chlorine atoms is negligible at this chloride ion concentration.

Figure 2b shows the decay of Cl_2^- resulting from the addition of 10^{-3} M to a 2 × 10^{-2} M K₂S₂O₈ solution for the same laser pulse energy as in Figure 2a. After 10 μ s reactions 2 and 3 are essentially complete and the concentration of Cl_2^- is expected to be the same as that of SO₄⁻ in the absence of chloride ion, assuming loss processes are again negligible on this time scale.

The dichloride radical anion is a particularly strong absorber in the ultraviolet. Extinction coefficients for this species were determined for the range 230–450 nm in a detailed pulse radiolysis study by Jayson, Parsons, and Swallow.¹⁹ The value obtained at 340 nm, the wavelength of maximum absorbance, was (8.8 ± 0.5) × 10³ dm³ mol⁻¹ cm⁻¹ (base 10). From this, the peak Cl₂⁻ concentration in Figure 2b is calculated to be $(1.4 \pm 0.1) \times 10^{-6}$ M. Based on the data in Figure 2a the extinction coefficient of SO₄⁻ at 450 nm is then $(1.6 \pm 0.1) \times 10^{3}$ M⁻¹ cm⁻¹ (base 10). Varying the concentrations of S₂O₈²⁻ over the range $(1-4) \times 10^{-2}$ M and increasing Cl⁻ by as much as an order of magnitude had no effect on $\epsilon_{SO_4^-}$, confirming that under the conditions employed the reaction of SO₄⁻ with Cl⁻ leads quantitatively to the formation of Cl₂⁻.

This result is in agreement with the work of Chawla and Fessenden⁶ who also obtained a value of 1600 M⁻¹ cm⁻¹ for ϵ_{SO_4} at 450 nm by comparison with (SCN)₂⁻. However, it is somewhat higher than those of 450 and 1100 M⁻¹ cm⁻¹ respectively determined by Dogliotti and Hayon¹¹ and Roebke, Renz, and Henglein.¹² While Chawla and Fessenden⁶ do not provide full details of their experiments, the extinction coefficient of (SCN)₂⁻ is well established and the absorbance of both transient species was monitored immediately after a 1 μ s radiolysis pulse.

In the study of Dogliotti and Hayon¹¹ the extinction coefficient of SO₄⁻ was calculated by comparison with that of CO₃⁻. By use of a similar approach to that employed in this study, CO₃⁻ was produced by the reaction of SO₄⁻ with HCO₃⁻. However, the optical densities of SO₄⁻ and CO₃⁻ were not observed until approximately 40 and 80 μ s, respectively, after the initiation of the photolysis flash. A major loss mechanism in the early stages of the decay of both species is the second-order self-reaction. Rate coefficients (2k) for CO₃⁻ + CO₃⁻ and SO₄⁻ + SO₄⁻ are 3.4 × 10⁷ and 8.8 × 10⁸ M⁻¹ s⁻¹, respectively.^{4,11} Since the initial radical concentration was ~3 × 10⁻⁵ M, a lower limit of 52% depletion of SO₄⁻ would have occurred by the time at which the optical density was monitored, compared with only 8% in the case of CO₃⁻. This may account for a large part of the discrepancy with the value reported in this study.

The value of 1100 M^{-1} atm⁻¹ assigned to ϵ_{SO_4} at 450 nm by Roebke et al.¹² was obtained from a study of the pulse radiolysis of aqueous solutions of N₂O-saturated H₂SO₄ (2 M) and Ar-

⁽¹⁹⁾ Jayson, G. G.; Parsons, B. J.; Swallow, A. J. J. Chem. Soc., Faraday Trans. 1 1973, 69, 1597.



Figure 3. Second-order plot of the decay of SO_4^- at 480 nm following the photolysis of $K_2S_2O_8$ (0.02 M) in the presence of NaCl (5 × 10⁻⁵ M).

saturated $S_2O_8^{2-}$ (4 × 10⁻⁵ M). In the case of sulfuric acid it was assumed that the source of SO_4^- was due to the reaction of OH with HSO₄⁻.

$$OH + HSO_4^- \rightarrow H_2O + SO_4^-$$
(7)

As the initial SO_4^- yield was a factor of 30 higher than in the present study, a significant loss (>20%) might have occurred by the time the spectrum was monitored, which was 5 μ s after the radiolysis pulse.

In the radiolysis of $S_2O_8^{2-}$ solutions it was assumed that the yield of SO_4^- was the same as that of the hydrated electron in pure water under identical experimental conditions.

$$e_{aq}^{-} + S_2 O_8^{2-} \rightarrow SO_4^{2-} + SO_4^{-}$$
 (8)

Since the concentration of $S_2O_8^{2-}$ employed was relatively low, it is feasible that a significant fraction of the hydrated electrons reacted with other transient species, particularly hydroxyl radicals. This would have resulted in a significant underestimate of ϵ_{SO_4} , even if the initial hydrated electron concentration was in the micromolar range.

Tang et al.²⁰ have recently determined the product of the quantum yield for SO_4^- production from photolysis of $S_2O_8^{2-}$ at 266 nm (Φ) and the extinction coefficient of SO_4^- at 443 nm (ϵ). They reported a value for $\Phi\epsilon$ of 2770 ± 280 M⁻¹ cm⁻¹. Since $\epsilon_{SO_4^-}$ at 443 nm is very similar to that at 450 nm this results in a quantum yield for SO_4^- production of 266 nm of ~1.75 based on the value of $\epsilon_{SO_4^-}$ determined in the present study. The Reaction of SO_4^- with Cl⁻. In the present study the decay

The Reaction of SO_4^- with $C\Gamma$. In the present study the decay of SO_4^- in the presence of $C\Gamma^-$ was monitored at 480 nm to avoid any contribution from the tail of the Cl_2^- absorption which is present at 450 nm due to reaction 2. The extinction coefficient of SO_4^- at 480 nm was estimated to be 1350 M⁻¹ cm⁻¹ (base 10).

The half-life of SO_4^- produced by the photolysis of a 2×10^{-2} M $S_2O_8^{2^-}$ solution is ~160 μ s in the absence of chloride ion. Following the addition of 5×10^{-5} M Cl⁻ to this solution the half-life is reduced to ~30 μ s. A typical second-order plot of the decay of SO_4^- in the presence of Cl⁻ is shown in Figure 3 corresponding to ~3 half-lives. Increasing the chloride ion concentration to 1.0×10^{-4} M had no effect on the observed second-order constant. This confirms that under these conditions loss processes for SO_4^- other than reaction with Cl⁻ make a negligible contribution to the decay. At higher chloride concentrations (>2 × 10^{-4} M) the decay became too fast to monitor due to the time constant of the photomultiplier circuit and the bandwidth of the analogue to digital converter.

The rate coefficient for the reaction of SO₄⁻ with Cl⁻ was determined to be $(6.6 \pm 1.6) \times 10^8$ M⁻¹ s⁻¹ at 20 °C and pH 3.8 $([S_2O_8^{2-}] = 4 \times 10^{-2}$ M, $[Cl^-] = 5 \times 10^{-5}$ M, I = 0.12, 10 experiments). At lower laser pulse energies and higher chloride ion concentrations $(2 \times 10^{-4}$ M) where the decay of SO₄⁻ was pseudo first order, a similar second-order rate coefficient was

obtained. On changing the monitoring wavelength to 450 nm the apparent value of k_1 was reduced to $(5.8 \pm 1.0) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ which was due to the interference of the Cl₂⁻ absorption discussed earlier. Any Cl atoms produced by reaction 1 are immediately converted to Cl₂⁻ by reaction 2 ($k_2 = 2.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).¹³ The formation of Cl₂⁻ was monitored at 340 nm, although there was some contribution from SO₄⁻ at this wavelength (10% at the peak absorbance). With an extinction coefficient¹⁹ of 8800 M⁻¹ cm⁻¹ the maximum Cl₂⁻ concentration was less than 30% of the initial yield of SO₄⁻. Cl₂⁻ was apparently removed at a rate approaching that of its formation via reactions 2 and 3. Thus product buildup kinetics could not be employed to measure k_2 .

In a previous direct determination of k_1 Chawla and Fessenden⁶ obtained a value of 3.1×10^8 M⁻¹ s⁻¹ at pH 6.8 with 1 mM phosphate buffer and 10 mM *tert*-butyl alcohol to scavenge OH produced by the radiolysis pulse. No error limits for k_1 were given and the chloride ion concentrations were not specified, although the decay of SO₄⁻⁻ was monitored at 480 nm to eliminate absorption by Cl₂⁻⁻. The limited information provided by Chawla and Fessenden⁶ suggests that the ionic strength was a factor of 12 lower than that used in the present study. For a reaction between two ions, Debye-Hückel theory predicts a simple dependence of log k on the square root of the ionic strength, I.²¹

$$\log k = \log k_0 + 1.018 Z_{\rm A} Z_{\rm B} I^{1/2}$$

 Z_A and Z_B are the ionic charges and k_0 is the rate constant at infinite dilution. The value of $k_1 = 6.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (I = 0.12 M) determined in this study is then equivalent to a rate coefficient of $3.7 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$ when I is reduced to 0.01 M.

This provides a satisfactory explanation of the difference between the value of k_1 reported here and that obtained by Chawla and Fessenden.⁶ Indeed, a 2-fold reduction in the concentration of K₂S₂O₈ to 2×10^{-2} M in the present study resulted in a decrease of k_1 to $(4.7 \pm 0.6) \times 10^8$ M⁻¹ s⁻¹. This corresponds to a second-order rate coefficient of $(2.7 \pm 0.4) \times 10^8$ M⁻¹ s⁻¹ for the reaction of SO₄⁻ with Cl⁻ at infinite dilution. In a recent direct determination of k_1 under pseudo-first-order conditions, Wine et al.²⁰ reported a value of 2.6×10^8 M⁻¹ s⁻¹ at infinite dilution in excellent agreement with the present study.

Two other determinations of k_1 have been reported based on indirect methods. Kim and Hamill⁸ obtained a value of $1.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ from the product buildup kinetics of Cl_2^- . As discussed above, this procedure underestimates the rate coefficient in the case of the reaction of SO_4^- with Cl^- . In an earlier study by Chawla⁷ a value for k_1 of $1.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ was obtained by competition kinetics with fumarate ion. The effect of solute concentration on the fumarate- SO_4^- adduct was monitored by electron spin resonance spectroscopy. This study was not referred to in later publications.⁴

The Decay of Cl_2^- in Aqueous Solution. Nagarajan and Fessenden²² have demonstrated that the photolysis of $S_2O_8^{2-}$ solutions at 248 nm and the subsequent oxidation of Cl⁻ by SO₄⁻ is an efficient and clean source of the dichloride radical anion, Cl_2^- . For chloride concentrations in excess of 10⁻³ M the half-life for Cl₂⁻ formation is very much shorter than that associated with loss mechanisms. The observed rise of the absorption at 340 nm was controlled by the time constant of the detection circuit. $\tau_{Cl_2^-}$, the true rise time for Cl₂⁻, is a factor of 20 faster than τ_{obs} for a chloride concentration of 10^{-2} M.

$$\tau_{\text{Cl}_2^-} = \frac{1}{k_1[\text{Cl}^-]} = \frac{1}{6.6 \times 10^8[\text{Cl}^-]}$$

Experiments were performed to investigate the dependence of the initial yield of Cl_2^- on precursor concentration (i.e., $[S_2O_8^{2-}]$) and laser pulse energy. In both cases a linear relationship was established.

When the initial Cl_2^- concentration was low (<1 μ M) the observed decay was essentially first order. However, as the laser

⁽²¹⁾ Moore, W. J. Physical Chemistry, 5th ed.; Longman: London, 1972. (22) Nagarajan, V.; Fessenden, R. W. J. Phys. Chem. 1985, 89, 2330.



Figure 4. First-order component of the decay of Cl₂⁻ at 340 nm following the photolysis of $K_2S_2O_8$ (0.04 M) in the presence of NaCl (0.01 M).

TABLE I: First- and Second-Order Rate Coefficients for the Decay of Dichloride Ion (Cl₂⁻) in Aqueous Solution at 20 °C and pH 3.8

		-			
[S ₂ O ₈ ²⁻], M	[Cl ⁻], M	<i>I</i> , M	$k_1(\times 10^{-3}),$ s ⁻¹	$2k_2(\times 10^{-9}),$ M ⁻¹ s ⁻¹	no. expts
$\begin{array}{r} 4 \times 10^{-2} \\ 4 \times 10^{-2} \\ 2 \times 10^{-2} \\ 1 \times 10^{-2} \\ 4 \times 10^{-2} \\ 4 \times 10^{-2} \\ 2 \times 10^{-2} \\ 4 \times 10^{-2} \\ 4 \times 10^{-2} \end{array}$	$ \begin{array}{c} 10^{-2} \\ 10^{-2} \\ 10^{-2} \\ 10^{-2} \\ 10^{-1} \\ 10^{-3} \\ 10^{-3} \\ 10^{-4} \\ 5 \times 10^{-5} \end{array} $	0.130 0.130 0.070 0.040 0.220 0.121 0.061 0.120 0.120	$1.3 \pm 0.1 \\ 1.3 \pm 0.1 \\ 1.2 \pm 0.1 \\ 1.2 \pm 0.1 \\ 1.3 \pm 0.1 \\ 2.6 \pm 0.1 \\ 2.7 \pm 0.1 \\ 12 \pm 1^{b} \\ 14 + 1^{b}$	$3.1 \pm 0.1 3.0 \pm 0.1 2.8 \pm 0.1 2.3 \pm 0.1 3.5 \pm 0.1 3.1 \pm 0.1 2.8 \pm 0.1 c$	24 5° 6 10 5 5 10
				-	

^a pH = 2.2. ^b For [Cl⁻] < 5 × 10⁻³ M the risetime for Cl_2^- formation becomes significant with respect with respect to the rate of loss. The decay at 340 nm was only processed beyond the point at which SO₄⁻ had decayed by >95% of its initial concentration as monitored at 480 nm. "The second-order component was negligible under these conditions and a rate coefficient could not be extracted from the data. k_1 and k_2 are the evaluated first- and second-order rate coefficients (Appendix).

energy and $S_2O_8^{2-}$ was increased, thereby increasing the yield of Cl2⁻, significant deviation from first-order behavior was observed. At the highest laser pulse energy ($[Cl_2^-]_0 > 5 \times 10^{-6} \text{ M}$) there was a significant second-order component associated with the bimolecular decay of Cl₂⁻. This has been established in previous studies.23-25

$$\operatorname{Cl}_{2}^{-} + \operatorname{Cl}_{2}^{-} \to \operatorname{Cl}_{3}^{-} + \operatorname{Cl}^{-}$$

$$(9)$$

 Cl_3^- has a very low stability constant $(K_{10} = 0.18 \text{ M}^{-1})^{26}$ and rapidly dissociates to produce chlorine.

$$\mathrm{Cl}_{3}^{-} \rightleftharpoons \mathrm{Cl}_{2} + \mathrm{Cl}^{-} \tag{10}$$

By use of a combined first- and second-order fitting procedure (Appendix) second- and first-order coefficients of $2k_9 = (3.1 \pm$ $(0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{first}} = (1.3 \pm 0.1) \times 10^3 \text{ s}^{-1}$ were extracted over 3-4 half-lives from a set of more than 40 experiments in which the ionic strength was maintained at 0.13 M ($K_2S_2O_8 = 0.04$ M, NaCl = 0.01 M, laser discharge voltage range 27-33 kV). The high signal to noise ratio achieved by using signal averaging over 128 single events resulted in experimental error limits in the rate coefficients of less than 5%, corresponding to two standard deviations. Figure 4 shows a plot of the first-order component of the decay for an initial Cl_2^- concentration of 5.24 \times 10⁻⁶ M. The observed rate coefficients were independent of the laser pulse energy which confirms that this is an efficient method of producing Cl_2^-

The influence of pH on the decay of Cl₂⁻ was investigated by replacing sodium chloride with hydrochloric acid to give a pH of 2.2. No effect was observed (Table I). Similarly, the observed kinetics were identical in argon-, N2O- and air-saturated solutions, eliminating any involvement of O_2 in the reaction mechanism and the production of free electrons in the photolysis step.

First- and second-order rate coefficients extracted from dichloride ion decays for a range of K₂S₂O₈ and NaCl concentrations are listed in Table I. The least-squares correlation over a minimum of 3 half-lives was always greater than 0.990 and approached 0.999 for the highest signal to noise ratios.

The variation of $2k_9$ with ionic strength is consistent with expectations for a reaction between two singly charged negative ions. Deviation from the linear relationship between $\log k$ and $I^{1/2}$ is observed at the highest ionic strengths employed where simple Debye-Hückel theory cannot be applied. Extrapolation to infinite dilution gives a rate constant of $2k_9 = (1.4 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This is comparable to a value of $2k_9 = 2.3 \times 10^9$ M⁻¹ s⁻¹ calculated for the diffusion-controlled bimolecular reaction between two dichloride ions assuming a diffusion constant of 0.7 \times 10⁻⁵ cm² s⁻¹ and a distance of closest approach of 3.5 Å as suggested by Wagner, Karthäuser, and Strehlow.¹⁷

The rate coefficients determined in early investigations of the self-reaction of Cl2⁻ using direct kinetic methods¹³ are generally an order of magnitude higher than those reported in this study and are up to 5 times faster than the diffusion-controlled limit. This was because no allowance had been made for the contribution of the first-order component in these earlier studies. Low signal to noise ratios had generally only allowed rate constants to be evaluated over 1-2 half-lives. Langmuir and Hayon²³ did observe that the decay of Cl_2^- following photolysis of HgCl₂ was first order, but reported a value of $2k_9 = 1.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ based on photolysis studies of NaCl and HgCl₄²⁻. If data obtained in the present study are processed over 1 half-life assuming only second-order kinetics, the resulting rate coefficient is very similar to the higher values reported hitherto.13

In more recent direct studies of the self-reaction of Cl_2^- , rate constants have been obtained¹⁴⁻¹⁶ which are consistent with the present investigation. However, Wagner et al.¹⁷ have reported a very low value for $2k_9$ of 7×10^7 M⁻¹ s⁻¹. This was obtained indirectly by using a numerical model to obtain the best fit for seven rate coefficients to observed changes in conductivity following flash photolysis of Cl⁻ in acid solutions. Such methods are prone to large errors.

A mechanism has been proposed¹⁷ which could account for the apparent first-order component of the Cl2- decay. This is essentially the reverse scheme to that proposed by Jayson et al.¹⁹ for the formation of Cl_2^- following the pulse radiolysis of N₂Osaturated chloride solutions.

$$Cl_2^- \rightleftharpoons Cl + Cl^-$$
 (2)

$$Cl + H_2O \rightleftharpoons H^+ + HOCl^-$$
 (4)

$$HOCI^- \rightleftharpoons OH + CI^-$$
 (5)

Rate coefficients obtained by Jayson et al.¹⁹ were $k_2 = 1.1 \times 10^5$ s^{-1} , $k_2' = 2.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $k_4 = 1.3 \times 10^3 \text{ s}^{-1}$, $k_4' = 2.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $k_5 = 6.1 \times 10^9 \text{ s}^{-1}$, and $k_5' = 4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, where k_i' is the rate coefficient of the *i*th back reaction. k_2' was estimated assuming the back reaction was diffusion controlled, and k_2 was then obtained by using the measured equilibrium constant (K_2) = 5.3 × 10⁻⁶ M). Nagarajan and Fessenden²² have recently determined k_2' directly, obtaining a value of $8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, so that k_2 becomes 4.2×10^4 s⁻¹. The overall process is described by reaction 11 which is consistent with a pseudo-first-order loss mechanism for Cl_2^{-} .

$$Cl_2^- + H_2O \Rightarrow OH + H^+ + 2Cl^-$$
 (11)

While this equilibrium mechanism supports the dependence of the first-order rate constant on chloride ion concentration (Table I) it is inconsistent with the absence of a dependence on $[H^+]$. Furthermore, the data of Jayson et al.¹⁹ suggest that in acid solutions the equilibrium lies far to the left ($K_{11} = 4.7 \times 10^{-13}$ M^3) so that this process should be an unimportant sink for Cl_2^{-1} for the conditions employed in the current study. If, however,

⁽²³⁾ Langmuir, M. E.; Hayon, E. J. Phys. Chem. 1967, 71, 3803.
(24) Ward, J. F.; Kuo, I. Adv. Chem. Ser. 1968, 81, 368.
(25) Wu, D.; Wong, D.; Di Bartolo, B. J. Photochem. 1980, 14, 303.
(26) Zimmerman, G.; Strong, F. C. J. Am. Chem. Soc. 1957, 79, 2063.



Figure 5. First-order rate coefficient for the loss of Cl_2^- as a function of Cl^- concentration.

reaction 4 leads to the formation of HOCIH which subsequently undergoes rapid decomposition to give H⁺ and HOCI⁻ such that k_{12} [CI][H₂O] $\gg k_{12}'$ [HOCIH], the predicted pH dependence of the Cl₂⁻ decay would be small. This is consistent with the findings of Wagner et al.¹⁷ who also reported the absence of an [H⁺] dependence.

$$Cl + H_2O \rightleftharpoons HOClH$$
 (12)

$$HOC|H \rightleftharpoons HOC|^{-} + H^{+}$$
(13)

A simple computer model incorporting reactions 1, 9, 2, 4, and 5 was used to examine the above mechanism in more detail. A significant $[H^+]$ effect was predicted over the pH range 2-4, although above pH 6 the rate of the reverse reaction 4 becomes sufficiently small to eliminate the influence of $[H^+]$ on the rate of removal of Cl_2^- . Furthermore, under the range of conditions listed in Table I the predicted rate of loss of Cl_2^- by the first-order rate was too low to compete with the second-order process (reaction 9). Only when the forward rate coefficient for the reaction of Cl with H₂O, k_4 , was increased by a factor of ~100 was an adequate first-order rate obtained. Under these conditions it was still necessary to invoke reactions 12 and 13 to account for the observed absence of an $[H^+]$ dependence.

The dependence of the observed first-order rate coefficient on chloride ion concentration is illustrated in Figure 5. Under all experimental conditions the ratio $[Cl_2^-]/[Cl] > 10 (K_2 \simeq 5.3 \times 10^{-6} \text{ M})^{19}$ so that the absorption of chlorine atoms was negligible at 340 nm ($\epsilon_{Cl} = 3800 \text{ M}^{-2} \text{ cm}^{-1}$ (base 10) at 340 nm).²² The contribution from HOCl⁻ is also expected to be minimal. At high chloride ion concentrations, a stable equilibrium between dichloride ion and chlorine atoms is rapidly achieved. Based on the above mechanism the first-order component in the decay of Cl_2^- should be attributable to the reaction of chlorine atoms with water, reaction 12, and the first-order rate coefficient (Table I) should show an inverse dependence on the chloride ion concentration. This is not observed however.

While the first-order rate coefficient increases markedly for chloride ion concentrations below 10^{-3} M, a lower limit is obtained for Cl⁻ concentrations above 10^{-2} M. This is indicative of an alternative loss process involving the direct reaction of Cl_2^- in the rate-determining step. This is most likely attributable to the reaction of dichloride ion with H₂O such that $k_{14} = (1.3 \pm 0.1) \times 10^3$ s⁻¹.

$$Cl_2^- + H_2O \Rightarrow HClOH + Cl^-$$
 (14)

Assuming a value¹⁹ of $K_2 = 5.3 \times 10^{-6}$ M, it is then possible to calculate the value for k_{12} from the increase in the observed first-order rate coefficient for the loss of Cl_2^- as the Cl^- concentration is reduced.

$$k_{12} = (k_{obs} - k_{14})[Cl^{-}]/K_2$$

For chloride concentrations of 10^{-3} , 10^{-4} , and 5×10^{-5} M respective values for k_{12} of 2.5×10^5 , 2.0×10^5 , and 1.2×10^5 s⁻¹ are obtained. As the chloride ion concentration is reduced, equilibrium

 K_2 is no longer achieved and this accounts for the apparent decrease in k_{12} for [Cl⁻] > 10⁻⁴ M. The most reliable estimate of k_{12} is $(2.5 \pm 0.2) \times 10^5 \text{ s}^{-1}$ obtained for [Cl⁻] = 10⁻³ M, since equilibrium was fully established in this case. This is consistent with a recent estimate²⁷ of $k_{12} = 1.6 \times 10^5 \text{ s}^{-1}$, although it is not apparent how this value was derived.

These results were further confirmed by use of a simple computer model of the proposed reaction scheme (reactions 1, 9, 2, 12, and 14) to simulate the optical density profile following the laser pulse. Comparison with observed profiles confirmed that these were consistent with the derived values of k_1 , k_9 , k_{12} , and k_{14} over the entire range of experimental conditions.

A direct consequence of the above mechanism, if it is to fit the observed lack of an $[H^+]$ dependence, is that equilibrium K_{12} should lie to the right, i.e., $k_{12} \gg k_{12}'$. Since $k_{12} = 2.5 \times 10^5 \text{ s}^{-1}$ it follows that k_{12}' is quite small, i.e., $<10^3 \text{ s}^{-1}$. The mechanism as it stands is apparently unable to account for the observed rate of formation of Cl_2^- following the pulse radiolysis of acidic NaCl solutions.¹⁹ (From ref 19 the first-order rate constant for the formation of Cl_2^- for $1 \times 10^{-2} \text{ M H}^+$ and Cl^- is $1.4 \times 10^6 \text{ s}^{-1}$.)

This problem is resolved if the reverse of reaction 14 is the major pathway leading to Cl_2^- production. A computer model of the detailed reaction mechanism confirms that, as k_{14}' approaches the diffusion-controlled limit, the predicted rate of Cl_2^- formation from OH is comparable that observed by Jayson et al.¹⁹ and shows the expected [H⁺] dependence. Even at low Cl⁻ concentrations the mechanism is consistent with the present analysis for $Cl_2^$ disappearance. The reason for this lies in the low predicted concentration of HClOH during the decay of Cl_2^- , such that even when $k_{14}' > 10^9 \text{ M}^{-1} \text{ s}^{-1}$ this reaction is too slow to perturb the lack of an [H⁺] dependence. (Simple deprotonation reactions are generally very rapid and a value of $k_{13} = 1 \times 10^8 \text{ s}^{-1}$ was assumed in the case of HClOH.) Pulse radiolysis experiments are required to resolve the issues raised concerning the formation of Cl_2^- from OH and the rate constant for reaction 14' in particular.

Implications for Cloud and Precipitation Chemistry. The roles of SO₄⁻ and Cl₂⁻ as chain carriers in the autoxidation of SO₂ in cloudwater have been reviewed.^{3,5} Chloride is a major ion in cloudand rainwater, particularly in maritime air masses. The results of the present study confirm that reaction with chloride is a more important sink for the sulfate radical than reaction with the bisulfite ion ($k_{15} = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)⁵. For pH = 4, T = 293 K, [SO_{2]g} = 5 ppb, and [Cl⁻] = 5 × 10⁻⁴ M the rate of reaction 1 is approximately an order of magnitude greater than reaction 15.

$$\mathrm{SO}_4^- + \mathrm{Cl}^- \to \mathrm{SO}_4^{2-} + \mathrm{Cl} \tag{1}$$

$$SO_4^- + HSO_3^- \rightarrow HSO_4^- + SO_3^-$$
 (15)

Since measured chloride ion concentrations in cloud over the UK and North Sea are typically 5×10^{-4} M, Cl is rapidly converted to Cl_2^- via reaction 1. Currently the reactions of both Cl and Cl_2^- with H₂O (reaction 12 and 14) are not included in models of cloud and precipitation chemistry. The value of k_{12} reported above suggests that reaction 12 could be a dominant loss mechanism for Cl_2^- in the atmosphere. The autoxidation of SO₂ would then be propagated by the hydroxyl radical (the product of reaction 5) rather than the dichloride ion as had been suggested hitherto.³

Acknowledgment. The author thanks P. G. Wallis and Miss E. Shaw (CEGB Scholar) who carried out much of the experimental work.

Appendix

Combined First- and Second-Order Fitting Procedure. For a species X which is removed by both first- and second-order processes the rate of removal is given by eq A1. k_1 and k_2 are

$$-\frac{d[X]}{dt} = 2k_2[X]^2 + k_1[X]$$
(A1)

⁽²⁷⁾ Klanning, U. K.; Wolff, T. Ber. Bunsen-Ges. Phys. Chem. 1985, 89, 243.

$$-\frac{dx}{dt} = 2k_2x^2 + k_1x$$
$$\int_{x_0}^x \frac{dx}{2k_2x^2 + k_1x} = -\int_0^t dt$$

Let

$$n = 2k_2/k_1$$

then

$$\int_{x_0}^{x} \frac{dx}{nx^2 + x} = -\int_0^t k_1 dt$$
$$\int_{x_0}^{x} \frac{dx}{x} - n \int_{x_0}^{x} \frac{dx}{1 + nx} = -\int_0^t k_1 dt$$
$$[\ln x]_{x_0}^x - [\ln (1 + nx)]_{x_0}^x = -k_1 t$$

thus

$$\ln\left[\frac{x_0 + nxx_0}{x + nxx_0}\right] = k_1 t \tag{A2}$$

The optical density of the solution (OD) at time t, assuming only species X absorbs, is given by the Beer-Lambert Law (eq A3). ϵ is the extinction coefficient (base 10) of species X, l is

$$OD = \log \frac{I_0}{I_1} = \epsilon x l \tag{A3}$$

the absorption path length, I_0 is the incident light intensity, and I_t is the transmitted light intensity, x and x_0 are then given by eq A4 and A5, respectively.

$$x = \frac{\text{OD}}{\epsilon l} \tag{A4}$$

$$x_0 = \frac{(\text{OD})_{t=0}}{\epsilon l} \tag{A5}$$

Substituting for x and x_0 in eq A2 gives eq A6

$$\ln\left[\frac{\epsilon l(\text{OD})_{t=0} + n(\text{OD})(\text{OD})_{t=0}}{\epsilon l(\text{OD}) + n(\text{OD})(\text{OD})_{t=0}}\right] = k_1 t \qquad (A6)$$

The value of n is adjusted so that a plot of the left-hand side of eq A6 versus time is linear and passes through the origin. Since the second-order component is most significant in the early part of the decay it is important that the fit is optimized in this region. k_1 is then given by the slope and $2k_2 = nk_1$.

In the present study the linear least-squares correlation coefficient was always greater than 0.990 over more than 3 half-lives for the best fit to the data and rose to 0.999 for those experiments with the highest signal to noise ratio. Obviously the value of nis particularly sensitive to errors in ϵ , which is consistent with the normal expectation for second-order rate constants obtained from absorbance measurements. Indeed, results are frequently expressed as the ratio k/ϵ to eliminate this dependence.

The results obtained by using the above method were verified by transferring the data from a number of experiments to a mainframe computer where a three-parameter nonlinear leastsquares fitting procedure was used to determine x_0 , $2k_2$, and k_1 .

Registry No. SO₄⁻, 14808-79-8; Cl⁻, 16887-00-6; Cl₂⁻, 12595-89-0; Cl, 22537-15-1; H₂O, 7732-18-5.

Kinetic Isotope Effects in the Electronic Quenching of OD/OH($A^2\Sigma^+, \nu=0$) at $296 \pm 4 \text{ K}$

R. D. Kenner,[†] F. P. Capetanakis, and F. Stuhl*

Physikalische Chemie I, Ruhr-Universität Bochum, 4630 Bochum 1, Federal Republic of Germany (Received: June 30, 1989; In Final Form: October 10, 1989)

Electronic quenching of $OD/OH(A^2\Sigma^+, v=0)$ by a number of collision partners has been investigated at 296 ± 4 K. The excited hydroxyl radicals were generated in the pulsed photolysis of nitric acid in the presence of a large amount of Ar as a relaxing gas. The current results are in agreement with most values in the recent literature and show that there is no isotope effect for many collision partners. However, a significant isotope effect has been found for quenching by CO, NO, and CF_2Cl_2 .

Introduction

The hydroxyl radical, in both its first electronically excited state, $A^{2}\Sigma^{+}$, and its ground state, $X^{2}\Pi$, is one of the best studied simple radicals. The connecting $(A \rightarrow X)$ transition generates a spectrum with relatively wide rotational spacing, which is easily accessible in the UV.¹ By theoretical methods, potential surfaces of OH in collisions with simple molecules can be mapped with increasing accuracy.^{2,3} The current interest in this radical stems partly from the key role it plays in combustion⁴ and air chemistry.⁵

Our interest in the properties of OD(A) originates from a systematic study of the collisional properties of electronically excited hydrides which is currently underway in several labora-tories including ours.⁶ In contrast to the knowledge accumulated for OH(A), not much was known about the collisional properties of OD(A) when the present work was initiated. During this study, we became aware of the extensive work on the quenching of OD(A) performed by Vaghjiani and Ravishankara.⁷ While the current results are in very good agreement with those of ref 7, comparisons with the cross sections for quenching of OH(A) given in the literature suggested an isotopic dependence of the quenching

- (4) Combustion Chemistry; Gardiner Jr., W. C., Ed.; Springer-Verlag: Berlin, 1984. (5) Warneck, P. Chemistry of the Natural Atmosphere; Academic:
- London, 1988.
- (6) Crosley, D. R. J. Phys. Chem. 1989, 93, 6273.

[†]Present address: 3417 Patricia Ave. Apt. 26, Montreal, Quebec, H4B 1Y9, Canada.

⁽¹⁾ Watson, W. W. Astrophys. J. 1924, 60, 145.

^{(2) (}a) Farantos, S. C.; Vegiri, A. J. Phys. Chem. 1988, 92, 2719. (b) Vegiri, A.; Farantos, S. C.; Papagiannakopoulos, P.; Fotakis, C. In Selectivity in Chemical Reactions; Whitehead, C., Ed.; Reidel: Dordrecht, 1988.

⁽³⁾ Staemmler, V. Private communication

⁽⁷⁾ Vaghjiani, G. L.; Ravishankara, A. R. J. Chem. Phys. 1987, 87, 7050.