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A PULSE RADIOLYSIS AND FLASH PHOTOLYSIS STUDY OF THE RADICALS SO_2^- , SO_3^- , SO_4^- AND SO_5^-

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Abstract—Pulse radiolysis and laser-flash photolysis have been used to generate the radicals SO_2^- , SO_3^- , SO_4^- and SO_5^- . Optical absorption spectra for these radicals and rate constants for their self-reactions have been derived. The decay of SO_2^- , SO_3^- and SO_4^- follow simple second-order kinetics; the decay of SO_5^- is slower and does not follow a second-order rate law when the radical is generated by the pulse radiolysis of an oxygenated sulfite or bisulfite solution, but is second-order when generated by the flash photolysis of an oxygenated dithionate solution. SO_2^- reacts rapidly with O_2 and a rate constant of $2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was derived. SO_3^- also reacts rapidly with O_2 and a rate constant of $1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was derived for this reaction. The rate constant for the reaction of H with SO_2 was determined to be $2.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

INTRODUCTION

The radical anions derived from the reactions of dissolved sulfur dioxide (SO_2^- , SO_3^- , SO_4^- and SO_5^-) and their interactions with molecular oxygen are of considerable importance in the mechanism of SO_2 oxidation in the atmosphere, in the behaviour of flue-gas scrubbers, and in the biological impact of ingested SO_2 . Spectra have been reported for SO_2^- (Eriksen, 1974), SO_3^- (Hayon *et al.*, 1972), SO_4^- (Hayon *et al.*, 1972) and SO_5^- (Hayon *et al.*, 1972) but the spectrum of SO_2^- was derived under conditions where its u.v. absorption would be masked and the spectrum of SO_5^- was only taken down to 250 nm and no maximum found. Only a limiting rate constant has been reported for the reaction of SO_2^- with O_2 (Creutz and Sutin, 1974) and the rate constant for the reaction of SO_3^- with O_2 was derived from an indirect study (Huie and Neta, 1984). There have been a few studies of the self-reaction of SO_2^- (Creutz and Sutin, 1974; Lambeth and Palmer, 1973; Eriksen, 1975) but none making use of its strong u.v. absorption (see below). The self-reaction of SO_3^- has been more thoroughly studied (Hayon *et al.*, 1972; Chawla *et al.*, 1973; Behar and Fessenden, 1972; Subhani and Kauser, 1978; Sadat-Safai *et al.*, 1981; Behar *et al.*, 1982), but there is some lack of consistency in the rate constants. The kinetics of the self-reaction of SO_4^- has also been reported by several investigators (Dogliotti and Hayon, 1967; Hayon and McGarvey, 1967; Subhani and Kauser, 1978; Lesigne *et al.*, 1973), but the rate constants also are not completely consistent.

Although the decay of SO_5^- has been investigated (Hayon *et al.*, 1972), the decay rate was found not to follow a simple kinetic order and no rate constant was reported.

Since these radicals are of such importance in the autoxidation of SO_2 solutions, we have carried out an investigation of both their spectra and the kinetics of their self-reactions. Also, rate constants for the reactions of the radicals SO_2^- and SO_3^- with O_2 have been determined along with the rate constant for the reaction of H atoms with SO_2 . Both pulse radiolysis and laser-flash photolysis have been employed for radical production.

EXPERIMENTAL

The radiation source for the pulse radiolysis experiments was a 4 MeV Van de Graaff accelerator, manufactured by High Voltage Engineering,[†] and typically operating at 2.8 MeV. Its pulser has been highly modified and provides 0.5, 1.5, or 5 μs pulses at essentially any repetition rate desired. Relative doses are monitored by measuring the current produced in a toroid located just before the reaction cell. To minimize the impact of dark current on the reaction mixture, a deflection coil was added to the upper part of the Van de Graaff drift tube. Energizing this coil deflected the electron beam from the reaction cell, allowing any dark current from the Van de Graaff to be excluded from the cell. The coil was de-energized just before the pulse, making use of the delay and gate generators discussed below.

The optical train consists of a Varian 300 W xenon arc lamp, separated from the reaction cell by a shutter, and appropriate quartz lenses to focus the light through the cell and onto the entrance slit of a Kratos monochromator. (The wavelength setting of the monochromator could be changed remotely.) A

[†]Certain commercial equipment, instruments, or materials are identified in this paper in order to specify adequately the experimental procedure. Such identification does not imply recognition or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment is identified are necessarily the best available for the purpose.

filter can be installed before the reaction cell to minimize photolysis of the sample and to prevent the transmission of higher order light through the monochromator. The contribution to the measured signal from scattered light within the monochromator becomes significant below about 250 nm. Its magnitude is determined with an appropriate filter in the light path and subtracted from subsequent measurements. The light is detected by a RCA 4840 photomultiplier.

The output from a xenon arc lamp is quite unstable compared to the absorbance we are often measuring, but the period of this instability is long compared to a typical experiment. To allow for this instability while increasing the sensitivity of the system to small absorbance changes, the signal from the photomultiplier is measured relative to the signal determined before the pulse. To do this, the signal from the photomultiplier is recorded just before the pulse by a sample-and-hold circuit, the output of which is fed into one half of a differential amplifier. The other half of the differential amplifier receives the signal directly from the photomultiplier. After the pulse, then, the output of the differential amplifier corresponds to the changes in light detected by the photomultiplier. The output of the differential amplifier is then monitored by a Biomation 8100 transient recorder.

Data from the transient analyzer are read into a Tektronix 4052A computer, which also controls the experiment. The computer starts an individual experiment by opening and closing a switch on the digital I/O module of a Hewlett-Packard 3488A switch control unit. This starts a battery of delay and gate generators which: arm the transient analyzer, boost the lamp output, open the shutter, trigger the sample-and-hold circuit and then the dose monitor, and finally, simultaneously fire the blocking oscillator and trigger the transient analyzer. The blocking oscillator turns on a light-emitting-diode and the light is transmitted through a plastic rod to a photomultiplier in the Van de Graaff pulser. The transient analyzer is operated in the pre-trigger mode. After the transient analyzer has completed its sweep, the computer reads the dose and the absolute voltage recorded by the sample-and-hold circuit, making use of a relay multiplexer module on the switch control unit and a digital voltmeter, and then collects the data from the transient analyzer. If the dose measured is outside some predetermined range, the data are rejected. The voltage signal is converted into transmittance, assuming that the voltage measured prior to the pulse corresponds to 100% transmittance. This cycle is repeated until a set number of valid pulses have been recorded. The absorbance is then calculated and the computer presents an averaged curve for analysis. The curves can be digitally filtered to remove signal resulting from Cherenkov radiation, then fitted to first- or second-order rate equations by weighted linear least-squares routines. (For the self-reaction $A + A \rightarrow P$, the second-order rate constant is determined from

the equation $1/A = 1/A_0 + 2kt$ and reported as k , not $2k$.)

The 2 cm long reaction cell is constructed from 1 cm² quartz tubing with 1/16 in thick optical-grade (suprasil) quartz windows sealed on the ends. The reaction mixture is pumped through the cell by a Rainin Rabbit multichannel peristaltic pump and, where necessary, solutions can be mixed just before the cell. Solenoid pinch valves allow us to select up to six mixtures.

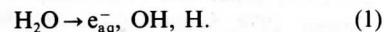
The dose per pulse was calibrated by measuring the absorbance arising from O_2^- , which is converted to an absolute concentration employing the published absorptivity for this stable radical (Bielski *et al.*, 1985). The O_2^- was produced through the pulse radiolysis of an air-saturated formate solution in 0.1 M NaOH.

The laser-flash photolysis apparatus employs the same electronics and optical train as the Van de Graaff system. A Lambda Physik EMG 201 MSC eximer laser, providing optical pulses of 20–40 ns duration and pulse energies of 150–500 mJ, is located 3 m from the reaction cell. Photolysis was carried out at 193 (ArF) and 248 nm (KrF). A 4 cm long quartz reaction cell was used, masked so that only the central 2.5 cm was illuminated by the laser. (The laser beam is about 3 cm wide at the cell face.) As with the Van de Graaff, the laser was fired under computer control and the results of multiple flashes averaged to produce a better curve.

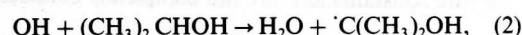
RESULTS AND DISCUSSION

SO_2^-

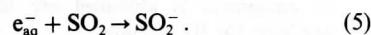
The SO_2^- radical was generated by the pulse radiolysis of a solution containing from 1 to 5 mM SO_2 , 0.05 to 0.1 M i-C₃H₇OH, in 0.1 M HClO₄ or 0.005 to 0.5 M H₂SO₄. The solution was formed immediately before the reaction cell by mixing a solution of acid and alcohol with a HSO_3^- solution. Both solutions were vigorously bubbled with UHP nitrogen prior to mixing and the region of the peristaltic pump and the connecting tubing bathed with nitrogen. The pulse radiolysis of water produces the hydroxyl radical and the hydrated electron in similar concentrations, along with smaller yield of hydrogen atoms



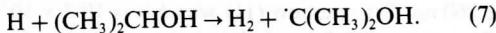
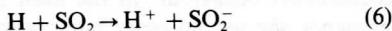
In the above solution, the OH will react with the 2-propanol ($k = 2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) (Farhataziz and Ross, 1977), and the resulting $\cdot C(CH_3)_2OH$ radical will rapidly ($k = 2.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) (Neta *et al.*, 1987) reduce SO_2



The electrons will react with both H^+ and SO_2



Since the rate constant for the former reaction is about $2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ (Anbar *et al.*, 1973; Ross, 1975), it will dominate under our experimental conditions. The H atoms can react with both SO_2 and $\text{i-C}_3\text{H}_7\text{OH}$



The rate constant for the latter reaction has been reported to be about $1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ (Anbar *et al.*, 1975), but there appears to be no reported value for the former. To determine if reaction (6) is rapid, we replaced 2-propanol with 2-methyl-2-propanol, which forms a non-reducing radical upon reaction with OH and which would not be expected to react with SO_2 . Therefore, only reaction (6) would be expected to be a source of SO_2^- . Under these conditions, the yield of SO_2^- was halved, but it was still formed rapidly, indicating that reaction (6) is fast. We determined the rate constant for this reaction by measuring the rate of formation of SO_2^- ($\lambda = 255$ and 320 nm) at SO_2 concentrations from 1 to $5 \times 10^{-4} \text{ M}$ (Fig. 1). A rate constant of $2.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ was derived.

The absorption spectrum of the SO_2^- radical over the wavelength range 230 – 400 nm was determined with a 0.1 M perchloric acid solution containing SO_2 . From 10 to 50 pulses were needed for each point, depending upon the signal strength. The curves were fit to a second-order equation and the maximum absorptivity taken as the calculated absorbance of SO_2^- at the time of the pulse. The spectrum we determined for SO_2^- is shown in Fig. 2. A maximum absorptivity of $1770 \text{ M}^{-1}\text{cm}^{-1}$ at 255 nm was obtained. At 360 nm and above, the absorbance decayed to zero at long time; at 290 nm, the absorbance also decayed to zero. At other wavelengths, however, there was a residual absorbance at long time. At 320 nm, this residual absorbance was at a relative maximum of about one-half or less of the initial SO_2^- absorbance. Below 290 nm, this residual absorbance

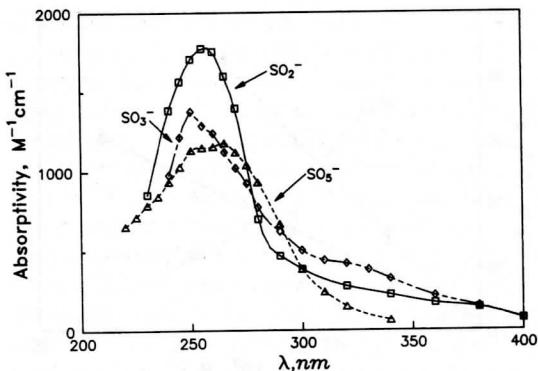
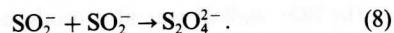


Fig. 2. Absorption spectra for SO_2^- , SO_3^- and SO_5^- determined by pulse radiolysis. For conditions, see text.

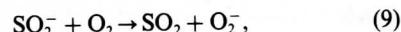
again increased, and at 230 nm, the final absorbance was again about one-half the initial absorbance. We ascribe this residual absorbance to the formation of dithionite, which absorbs strongly at 320 nm and below 250 nm (Lorenz and Samuel, 1931).



In the region of the absorption maximum (255 nm), second-order rate constants have been determined in both perchloric acid and sulfuric acid solutions. The ionic strength was raised by adding sodium bisulfate. (An attempt to use sodium perchlorate to raise the ionic strength was unsuccessful due to a breakdown of the tubing used in the peristaltic pump.) Over the pH range 0.3 – 1.2 and the ionic strength range 0.08 – 0.8 , both calculated from the pK's of H_2SO_4 , the decay rate was essentially invariant ($k = 9.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$). This value is similar to those previously measured by pulse radiolysis (Erikson, 1974, 1975) and somewhat less than those derived from the monomerization of dithionite (Creutz and Sutin, 1974; Lambeth and Palmer, 1973).

The behaviour of the absorbance at 320 nm was somewhat more complicated. Although the absorbance decreased in perchloric acid solutions, in sulfuric acid/sodium bisulfate solutions the absorption increased. The magnitude of the increase became greater as the pH was raised. Frequently, a small "foot" was observed: the absorbance would decrease or remain constant before increasing. At longer time, the absorbance appeared to decay, although this behaviour was not completely consistent. If fit to a second-order equation, the derived rate constant for the increase in absorption was erratic; if fit to a first-order equation, however, consistent results were obtained with an average value of about $1.5 \times 10^4 \text{ s}^{-1}$, independent of reaction conditions. The reason for this behaviour became clear during the flash photolysis studies and is discussed later.

The rate constant for the reaction of SO_2^- with O_2



was determined by monitoring the decrease in absorption at 260 nm in solutions saturated with $\text{N}_2\text{O}:\text{O}_2$

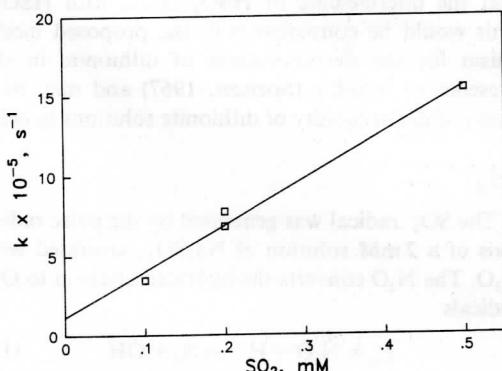


Fig. 1. First-order rate constant for the reaction $\text{H} + \text{SO}_2 \rightarrow \text{H}^+ + \text{SO}_2^-$ as a function of SO_2 concentration. Pulse radiolysis of an N_2 saturated solution containing 0.1 M HClO_4 and 1 mM t-butanol.

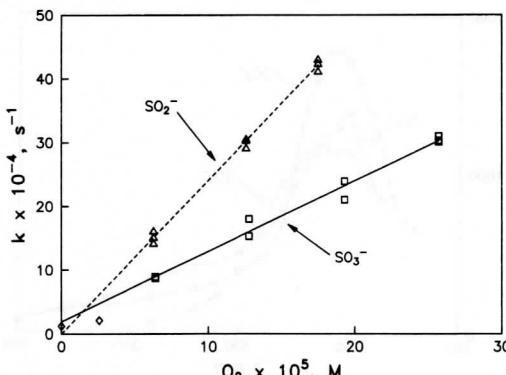
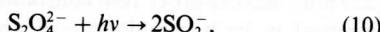


Fig. 3. First-order rate constants for the reactions $\text{SO}_2^- + \text{O}_2 \rightarrow \text{SO}_2 + \text{O}_2^-$ and $\text{SO}_3^- + \text{O}_2 \rightarrow \text{SO}_5^-$ as a function of O_2 concentration. Pulse radiolysis of a solution containing N_2 , 1 mM SO_2 , 0.1 M HClO_4 , and 0.1 M i-propanol and flash photolysis of a 0.2 mM solution of $\text{Na}_2\text{S}_2\text{O}_6$.

mixtures. From a plot of the first-order rate constant against O_2 concentration (Fig. 3), a second order rate constant of $2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was derived.

The SO_2^- radical was also produced by the flash photolysis of solutions containing 0.05 mM sodium dithionite, $\text{Na}_2\text{S}_2\text{O}_4$, at 193 nm



and the loss of SO_2^- due to self-reaction monitored at several wavelengths. The self-reaction did not appear to be simple reformation of the starting material. At short times ($< 40 \mu\text{s}$), the absorbance signal went negative at most wavelengths; at longer time ($\sim 2 \text{ ms}$), the signal returned to the baseline. (A negative absorption means that the solution has been bleached.) This is illustrated for 350 nm in Fig. 4. The exact behavior did depend on wavelength: at 245 and 250 nm, the signal started positive and then went slightly negative before returning to the baseline; at 260 and 270 nm, the signal remained slightly positive (on the $40 \mu\text{s}$ time scale). From 290 to 350 nm, the signal starts negative and becomes more negative, with a maximum negative signal at 320 nm. Below 290 nm, the signal at $t = 0$ was positive, with a maximum at about 260 nm. Experiments were carried out both at the natural pH of the solution (4.6) and with a small amount of added base (pH 7.3), with similar results. At pH 4.6, the rate constant for the return to the baseline was $3.3 \times 10^3 \text{ s}^{-1}$; at pH 7.3 it was $2.4 \times 10^3 \text{ s}^{-1}$.

The initial bleaching of the solution between 290 and 350 nm is easily understood as resulting from the stronger absorption of the precursor, $\text{S}_2\text{O}_4^{2-}$, at these wavelengths than the radical SO_2^- . We interpret the bleaching subsequent to the flash to suggest that the self-reaction of SO_2^- does not simply reform the normal sulfur-bonded $\text{S}_2\text{O}_4^{2-}$, but rather first forms an isomeric form, possibly with a sulphur-oxygen bond.



The return to the baseline, then, corresponds to reaction (12). The formation of this intermediate also explains the kinetic behaviour observed at 320 nm in the pulse radiolysis experiments, particularly the "foot" observed in some of the curves and the poor second-order behaviour. In the flash photolysis experiments, the second-order rate constant measured at 260 nm for reaction (11) was $k/\epsilon = 10.3 \times 10^5$; at 270 nm, $k/\epsilon = 9.3 \times 10^5$. We have not been able to determine an absorptivity under the less acid conditions of the flash-photolysis experiments, but the absorption due to the radical appeared to be somewhat weaker and red-shifted. If we assume the absorptivity is only slightly weaker, the derived second-order rate constant is about twice as large as found in the pulse-radiolysis experiments in strongly acid solutions. This value would be more in line with those derived from the monomerization of dithionite.

The difference in the spectra between the flash (neutral) and pulse (acid) solutions suggests that the spectrum derived in strong acid at least partly arises from the protonated radical, HSO_2 . The protonation of SO_2^- near pH 0 has been suggested before based on an electrochemical study (Neta *et al.*, 1987). This conclusion is further supported by the observation that the second-order rate constant does not show an ionic strength dependence in strong acid. We did not determine the ionic strength dependence in the flash photolysis experiments due to the possible photolysis of the added anion.

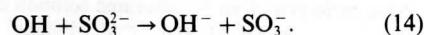
A major difference between the results from the two sets of experiments is that in acid, our experimentally observed yield of $\text{S}_2\text{O}_4^{2-}$ from the self-reaction of SO_2^- appears to be relatively low. Indeed, the decrease in absorbance at 320 nm in the perchloric acid solutions suggests very little $\text{S}_2\text{O}_4^{2-}$ is formed. Even in the sulfuric acid/sodium sulfate solutions, the yield was less than expected. This suggests that either the protonated radical HSO_2 reacts with SO_2^- to produce an additional intermediate which decomposes rather than rearranging to $\text{S}_2\text{O}_4^{2-}$, or that the intermediate formed has an acid-catalyzed decomposition path. Another possibility is that the intermediate or HSO_2 reacts with HSO_3^- . This would be consistent with the proposed mechanism for the decomposition of dithionite in the presence of bisulfite (Spencer, 1967) and may be a cause of the instability of dithionite solutions in acid.

SO_3^-

The SO_3^- radical was generated by the pulse radiolysis of a 2 mM solution of Na_2SO_3 , saturated with N_2O . The N_2O converts the hydrated electron to OH radicals



which react rapidly ($k = 5.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) with SO_3^{2-} (Huie and Neta, 1987)



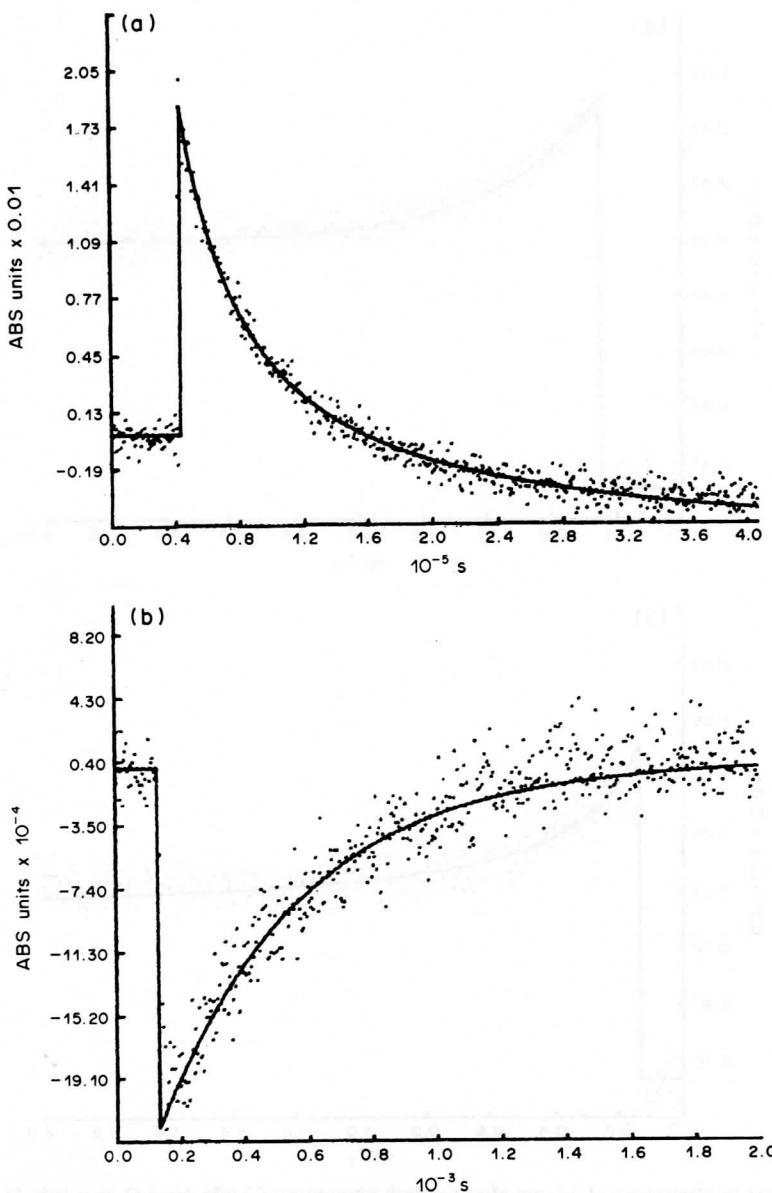


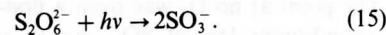
Fig. 4. Absorbance at 350 nm as a function of time after the flash photolysis of 0.05 M $\text{Na}_2\text{S}_2\text{O}_4$. (a) 40 μs full scale; (b) 1 ms full scale. Note that the vertical scale on (b) is expanded about 10 times compared to (a).

The absorption spectrum of the SO_3^- radical was determined over the wavelength range 240–400 nm, employing from 10 to 100 pulses per point, depending upon the signal strength (Fig. 2). The absorbances were normalized to constant pulse intensity and converted to absorptivities by comparison with O_2^- . Since the H atoms, formed in small ($\sim 10\%$) yield, should not react in this system, but do react to produce O_2^- in the calibration system, the calculated yield of SO_3^- was adjusted accordingly. A maximum absorptivity of $1380 \text{ M}^{-1} \text{ cm}^{-1}$ at 250 nm was obtained. The spectrum is very similar to that reported previously (Hayon *et al.*, 1972).

Second-order rate constants were determined for the decay of SO_3^- at 250, 225 and 260 nm. An average

value of $5.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ was obtained. This value is similar to results reported by several other workers. We obtained no information on the products of the reaction, which have been reported to vary from mostly dithionite at low pH, to mostly sulfite and sulfate at high pH (Eriksen, 1974).

The SO_3^- radical also was produced by the laser-flash photolysis of dithionite, $\text{S}_2\text{O}_6^{2-}$ at 193 nm.



Rate constants for the self-reaction of SO_3^- were determined at $\text{S}_2\text{O}_6^{2-}$ concentrations of 1–3.7 mM (ionic strength 1.5–5.5 mM) and an average value of $4.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ derived with no apparent trend with concentration or ionic strength over this limited

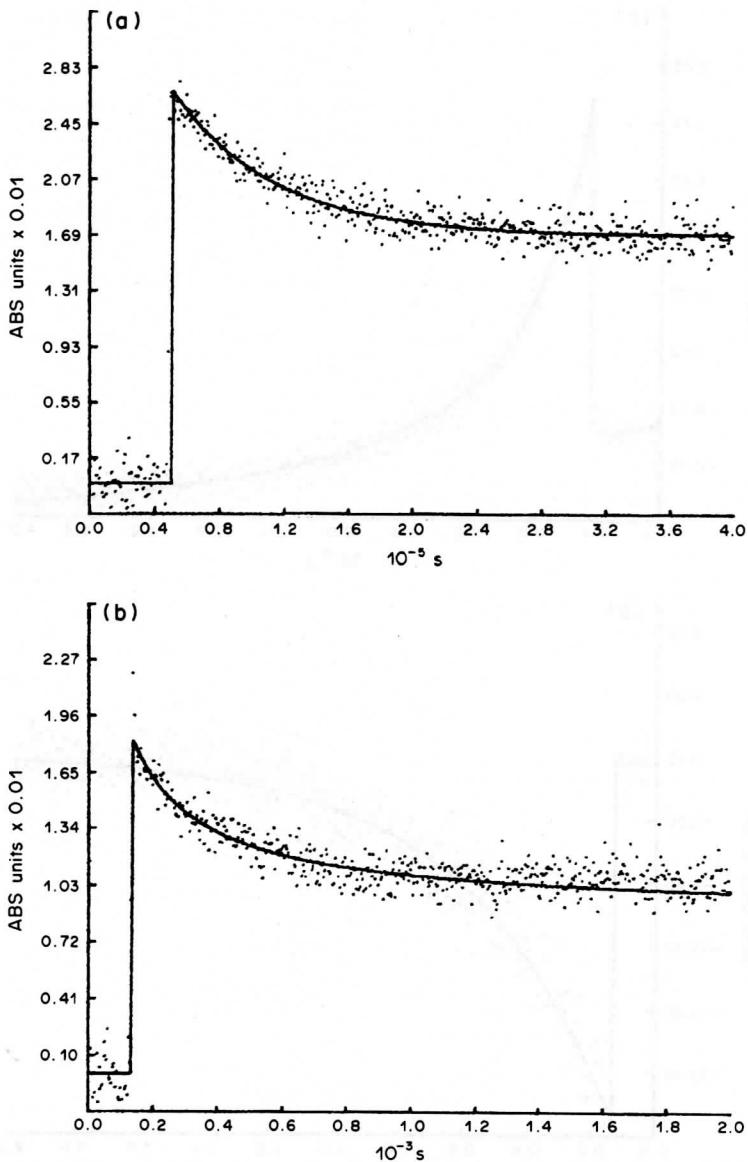
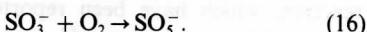


Fig. 5. Decay of absorbance at 245 nm after the flash photolysis of 2 mM $\text{Na}_2\text{S}_2\text{O}_6$ in a 10% O_2 solution.
 (a) 40 μ s full scale; (b) 2 ms full scale.

range. (In these experiments, no mask was being used and a path length of 3 cm has been assumed.)

Upon the addition of O_2 , the absorption at 245 nm decreased due to the reaction (Fig. 5a)



Mixtures containing from 2 to 20% O_2 in N_2 were bubbled through the solution and first order rate constants derived, with the results included in Fig. 3. The point at no O_2 was from a first-order fit to the second-order loss of SO_3^- due to self-reaction. At 26 μM O_2 , the decay of SO_3^- was obviously of mixed order and the first-order fit was poor. Neither point was used in the least-squares fit. From the other points, a rate constant of $1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was derived. This value can be compared to the value we

obtained previously of $1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ by modeling a complex system (Huie and Neta, 1984). The agreement is certainly very satisfactory.



The SO_4^- radical was generated by the laser-flash photolysis at 193 nm of persulfate



The spectrum of the radical is given in Fig. 6 and agrees quite well with that reported by Hayon, *et al.* (1972). When we attempted to fit the decay curve starting at $t = 0$, the second-order fit was not as good as the quality of the data suggested it should be. Upon closer examination, there appeared to be a small, fast initial decay. This initial decay was high-

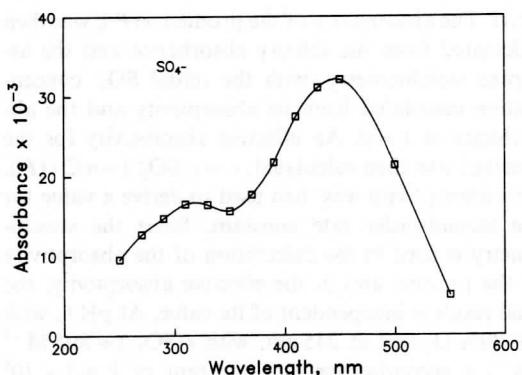


Fig. 6. Spectrum of SO_4^- from the flash photolysis of 0.1 mM $\text{Na}_2\text{S}_2\text{O}_8$ saturated with N_2 .

lighted by starting the second-order fit about 10–50 μs after the flash (Fig. 7). By subtracting this calculated second-order curve from the experimental data and fitting the remainder, a first-order rate constant for the fast, initial decay of about $1 \times 10^5 \text{ s}^{-1}$ was obtained. Attempts to eliminate this initial decay by changing the water source, including the use of HPLC water, were unsuccessful. Reducing the $\text{S}_2\text{O}_8^{2-}$ concentration from 1 to 0.1 mM did not appear to reduce the absolute contribution of this decay, but appeared to increase its relative contribution, due to a lower initial SO_4^- concentration.

The effect of flash energy was investigated by locating a 1 cm quartz cuvette containing 0.1, 0.5 and 1.0 mM $\text{Na}_2\text{S}_2\text{O}_8$ in front of the reaction cell to

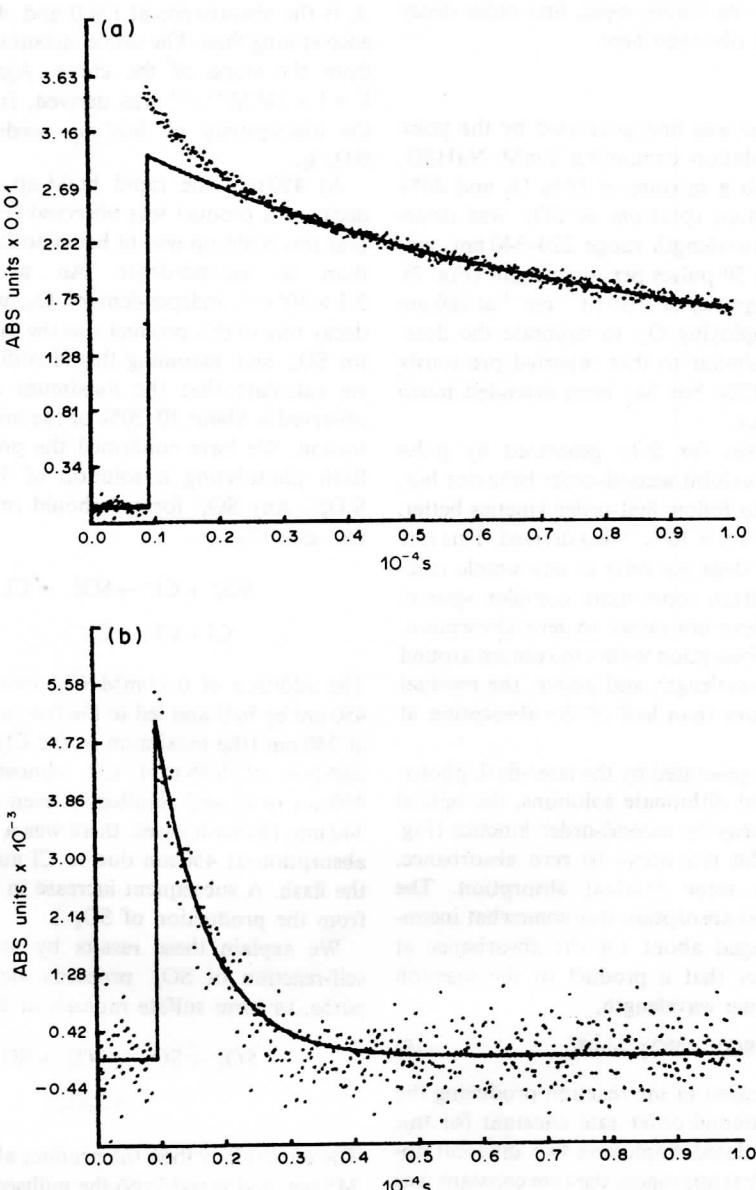


Fig. 7. Decay of absorbance at 450 nm after the flash photolysis of 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$. (a) 400 μs full scale, second-order fit starting 50 μs after the flash; (b) 100 μs full scale, first order fit to the difference between the calculated curve of (a) and actual data.

attenuate the flash. With a 0.5 mM Na₂S₂O₈ solution, little variation in the second-order rate constant was found. At the higher flash energies, the fast first-order component did seem to be more pronounced. This suggests that the first-order decay might be due to a process nonlinear in the flash energy, possibly the formation of an excited state of SO₄⁻.

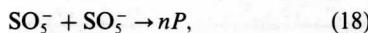
Absolute second-order rate constants for the self-reaction of SO₄⁻ were calculated by taking the absorptivity at 450 nm to be 1100 M⁻¹ cm⁻¹ (Hayon *et al.*, 1972). From the studies at various flash energies, a rate constant of 1.9 × 10⁸ M⁻¹ s⁻¹ was derived. Similar values were derived with 1.0 mM S₂O₈²⁻ at wavelengths from 325 to 500 nm. This value is about a factor of two lower than that reported in Hayon *et al.* (1972), which may reflect a contribution in the earlier work from the initial, rapid, first-order decay in the absorbance observed here.

SO₅⁻

The SO₅⁻ radical was first generated by the pulse radiolysis of a solution containing 2 mM NaHSO₃ and saturated with a mixture of 60% O₂ and 40% N₂O. The absorption spectrum of SO₅⁻ was determined over the wavelength range 220–340 nm, employing from 5 to 50 pulses per wavelength (Fig. 2). A maximum absorptivity of 1030 M⁻¹ cm⁻¹ at 260 nm was obtained, employing O₂⁻ to calibrate the dose. The spectrum is similar to that reported previously (Hayon *et al.*, 1972), but has been extended much further into the u.v.

The decay curves for SO₅⁻ generated by pulse radiolysis did not exhibit second-order behavior but, rather, appeared to follow first-order kinetics better. A rate constant of 1.6 × 10³ s⁻¹ was derived. This rate constant certainly does not refer to any simple reaction, but results from some more complex system. The SO₅⁻ signal does not decay to zero absorption, but to a residual absorption with a maximum around 275 nm. At this wavelength and above, the residual absorption is greater than half of the absorption at *t* = 0.

When SO₅⁻ was generated by the laser-flash photolysis of oxygenated dithionate solutions, the optical absorption did decay by second-order kinetics (Fig. 5b). The signal did not decay to zero absorbance, however, but to some residual absorption. The amount of residual absorption was somewhat inconsistent, but averaged about 1/4 the absorbance at *t* = 0. This implies that a product of the reaction absorbs at the same wavelength,

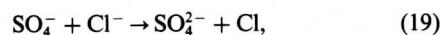


where *n* is the fraction of the reaction producing the product *P*. The second-order rate constant for this reaction was calculated employing two different approaches. In the first approach, the rate constant was calculated simply by first subtracting the absorbance at long time from the data and fitting the remainder to a regular second-order equation, 1/A = 1/A₀ +

2*k*/ε*t*. The absorptivity of the product, ε(*P*), was then calculated from the infinity absorbance and the assumed stoichiometry, with the initial SO₅⁻ concentration calculated from its absorptivity and the absorbance at *t* = 0. An effective absorptivity for the reaction was then calculated, ε = ε(SO₅⁻) - *n*/2 ε(*P*). This absorptivity was then used to derive a value for the second-order rate constant. Since the stoichiometry is used in the calculation of the absorptivity of the product and in the effective absorptivity, the final result is independent of its value. At pH 6, with 10–20% O₂ and at 245 nm, with ε(SO₅⁻) = 805 M⁻¹ cm⁻¹, a second-order rate constant of *k* = 1 × 10⁸ M⁻¹ s⁻¹ was determined.

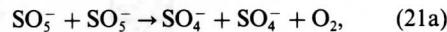
The second approach was to fit the data to the equation (A₀ - A_∞)/(A - A_∞) = 1 + 2[SO₅⁻]₀*kt*, where A₀ is the absorbance at *t* = 0 and A_∞ is the absorbance at long time. The rate constant is then calculated from the slope of the curve. Again, a value of *k* = 1 × 10⁸ M⁻¹ s⁻¹ was derived. In this case, only the absorptivity of SO₅⁻ is needed, to calculate [SO₅⁻]₀.

At 450 nm, the rapid build-up, and subsequent decay of a product was observed (Fig. 8). We found that this build-up was fit better to first-order kinetics than to second-order. An average value of 3.5 × 10⁴ s⁻¹, independent of O₂, was derived. The decay rate of this product was the same as that found for SO₄⁻ and, assuming this identification is correct, we calculate that the maximum amount of SO₄⁻ observed is about 10–20% of the initial SO₅⁻ concentration. We have confirmed the product is SO₄⁻ by flash photolyzing a solution of NaCl and 5 mM S₂O₆²⁻. Any SO₄⁻ formed should react with the Cl⁻ and give Cl₂⁻.

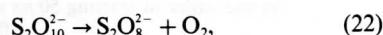


The addition of 0.13 mM Cl⁻ reduced the peak at 450 nm by half and led to the formation of a product at 340 nm (the maximum in the Cl₂⁻ spectrum). The addition of 0.48 mM Cl⁻ almost eliminated the 450 nm peak and resulted in even more product at 340 nm. (In both cases, there was a significant initial absorption at 450 nm due to Cl atoms produced in the flash. A subsequent increase in absorption arose from the production of SO₄⁻.)

We explain these results by assuming that the self-reaction of SO₅⁻ proceeds along two reaction paths, to form sulfate radicals or a tetroxide



The tetroxide is then the product absorbing at about 245 nm, and is stable on the millisecond time scale. It may subsequently decompose to S₂O₈²⁻



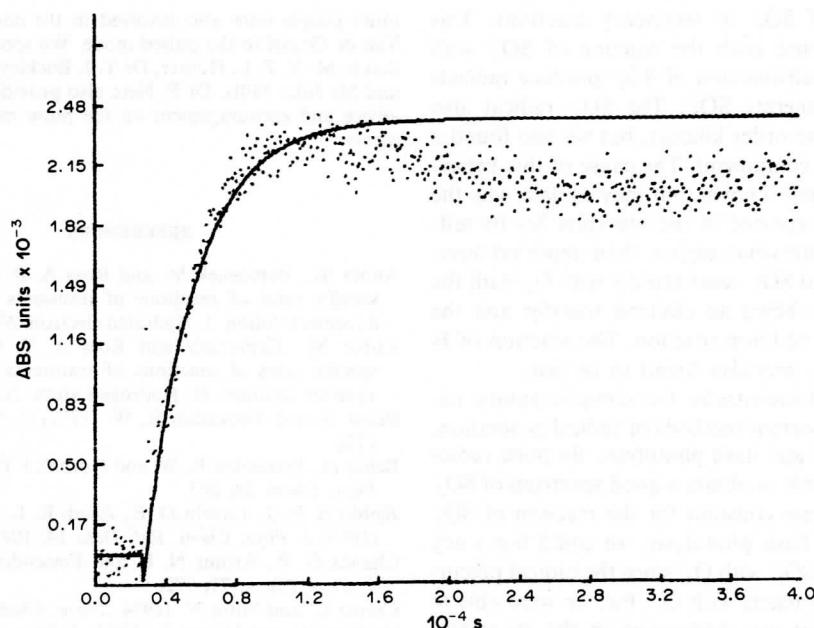
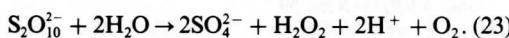


Fig. 8. Build-up of the absorption at 450 nm after the flash photolysis of 2 mM $\text{Na}_2\text{S}_2\text{O}_6$ with 10% O_2 .

or hydrolyze to SO_4^{2-} and H_2O_2 ,



We have not been able to arrive at definitive conclusions on the branching ratio of reaction 21. If we assume the ratio is 1:1, modeling calculations predict roughly the apparent yield of SO_4^- observed ($\sim 20\%$), and also predict that it will appear to be formed more rapidly than the rate at which SO_5^- decays. This is due to the loss of SO_4^- to recombination. The predicted rate of formation of SO_4^- , however, still does not appear to be quite as fast as observed experimentally. With this assumed yield, we derive an absorptivity of about $820 \text{ M}^{-1}\text{cm}^{-1}$ for the tetroxide.

SUMMARY

The major observations from this work are summarized in Table 1 and Figs 2 and 6. The spectra we have obtained here for SO_3^- , SO_4^- and SO_5^- are in substantial agreement with those obtained in earlier work from other laboratories, but with the spectrum for SO_5^- extended substantially further into the ultraviolet. For SO_2^- , we have found a relatively strong u.v. absorption which had not been observed previously. This u.v. absorption appears weaker and

red-shifted in less acid solutions, suggesting an important contribution from HSO_2^- . The spectra of SO_2^- , SO_3^- and SO_5^- are somewhat similar, with SO_2^- the strongest absorber. Fortunately, the difference in absorptivity between SO_3^- and SO_5^- was just enough to permit the determination of the rate constant for the formation of SO_5^- , when signal averaging was employed to enhance the signal. The spectrum of SO_4^- is quite different from the other three, with an absorption maximum in the visible.

The kinetic behavior of SO_3^- observed in this work confirms the observations of several previous workers. The other radicals, however, appear to behave somewhat differently than reported previously. In neutral solutions, the SO_2^- radical does not simply recombine to $\text{S}_2\text{O}_4^{2-}$; rather, the reaction appears to proceed through an intermediate which rearranges to $\text{S}_2\text{O}_4^{2-}$. In an acid, bisulfite, solution, there also appears to be an intermediate formed, but the amount of $\text{S}_2\text{O}_4^{2-}$ ultimately formed appears to be much lower than expected. The behavior of the SO_5^- radical is less clear, although it does appear to form an intermediate which absorbs in the u.v., the fate of this product is not known. The decay of SO_5^- follows second-order kinetics when it is produced in the absence of HSO_3^- or SO_3^{2-} . The kinetic behavior in the presence of HSO_3^- or SO_3^{2-} is probably due to the

Table 1. Summary of results for the SO_x^- radical anions

λ_{\max} (nm)	$\epsilon_{\max}(\text{M}^{-1}\text{cm}^{-1})$	$k(\text{R} + \text{O}_2)(\text{M}^{-1}\text{s}^{-1})$	$k(\text{R} + \text{R})(\text{M}^{-1}\text{s}^{-1})$
SO_2^-	255	1770	2.4×10^9
SO_3^-	250	1380	1.1×10^9
SO_4^-	450	1100^b	—
SO_5^-	260	1030	—

^aIn acid. The rate constant appears to be about a factor of two greater in neutral solution. ^bSee Hayon *et al.* (1972).

regeneration of SO_5^- in secondary reactions. This comes about since both the reaction of SO_5^- with SO_3^{2-} and the self-reaction of SO_5^- produce radicals which can regenerate SO_5^- . The SO_4^- radical also decays by second-order kinetics, but we also found a fast, first-order component. The cause of this behavior is not presently known, but may explain why the rate constants reported in the literature for its self-reaction are somewhat higher than reported here.

Both SO_2^- and SO_3^- react rapidly with O_2 , with the former reaction being an electron transfer and the latter being an addition reaction. The reaction of H atoms with SO_2 was also found to be fast.

This paper demonstrates the complementary nature of two important methods of radical generation: pulse radiolysis and flash photolysis. By pulse radiolysis, we were able to obtain a good spectrum of SO_2^- in acid and a rate constant for the reaction of SO_2^- with O_2 . With flash photolysis, we could not study the reaction of SO_2^- with O_2 , since the radical precursor, $\text{S}_2\text{O}_4^{2-}$, also reacts with O_2 . But we were able to understand what was happening in the recombination reaction better. For SO_3^- and SO_5^- , also, the use of the two techniques provided complementary information. From pulse radiolysis, we were able to derive spectra and absolute absorptivities for the radicals. Flash photolysis proved better for obtaining the kinetics of the reaction of SO_3^- with O_2 . Meaningful kinetic information on the self-reaction of SO_5^- could only be obtained when the radicals were generated by flash photolysis.

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Many people have assisted in the development of the techniques and instruments we are using for the study of the kinetics and spectra of the transient species. We particularly want to recognize the contribution made Mr Julian Whittaker both to the conversion of the Van de Graaff accelerator to operate in the pulsed mode and in the design of many of the electronic circuits we have employed. Several

other people were also involved in the conversion of the Van de Graaff to the pulsed mode. We specifically wish to thank: Mr E. P. L. Hunter, Dr T. J. Buckley, Dr C. E. Dick and Mr John Mills. Dr P. Neta also provided considerable advice and encouragement on the pulse radiolysis experiments.

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