ELSEVIER

Journal of Molecular Structure 348 (1995) 183–186

Journal of
MOLECULAR
STRUCTURE

Time-resolved UV/VIS Diode Array Absorption Spectroscopy of SO_x^-(x=3, 4, 5) Radical Anions in Aqueous Solution

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1. BACKGROUND AND EXPERIMENTAL

In the present study radicals were generated by excimer-laser photolysis and monitored by time-resolved UV/VIS-broadband diode array absorption spectroscopy. The apparatus combines spectral sensitivity in the wavelength range 210-750 nm with time resolution down to 100 ns. It has been developed as a universal tool for the study of kinetics and spectroscopy of free radicals in solution. More details of the experimental methods applied for the investigations of the sulfur radical anions SO_x^- can be found elsewhere [1]. A schematic representation of the experimental set-up is shown in Fig. 1.

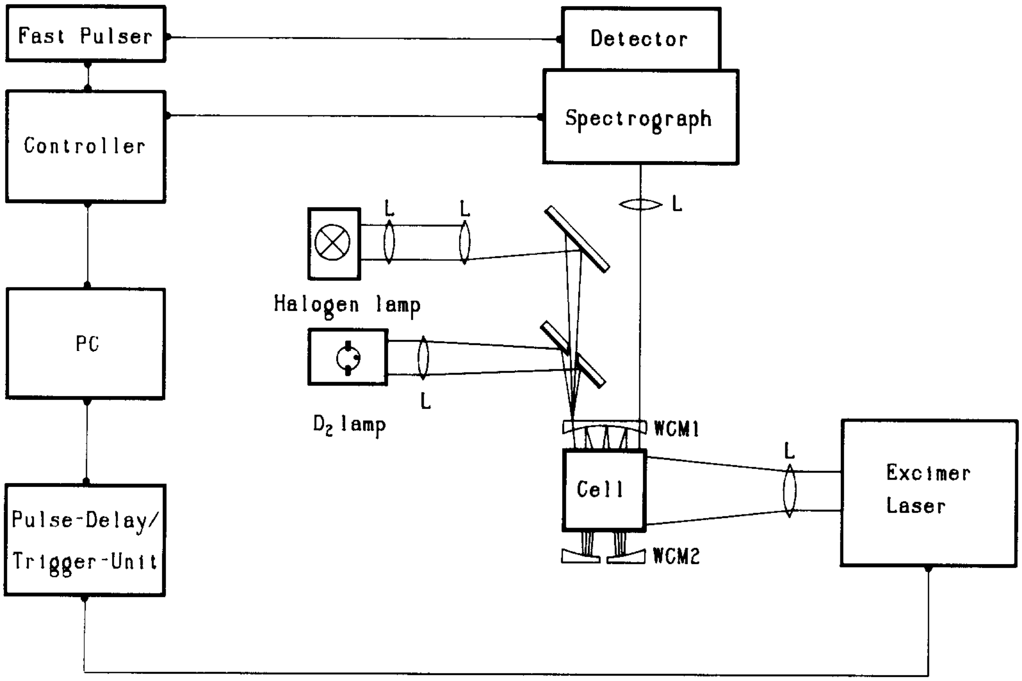

Figure 1. Schematic representation of the experimental set-up

0022-2860/95/$09.50
SSDI 0022-2860(95)08619-6

2. RESULTS AND DISCUSSION

2.1. Absolute decadic absorption coefficients for the sulfite (SO_3^-) and peroxymonosulfate (SO_5^-) radical anions

To calculate the absolute decadic absorption coefficients of the above radical anions the measured absorption spectra of SO_3^- and SO_5^- were standardized by the absolute absorption coefficients published by Buxton et al. [2,3]. These authors obtained maximum absorption coefficients of ε_{250}= (1090±20) $l\,mol^{-1}cm^{-1}$ for SO_3^- and of ε_{260}= (740±18) $l\,mol^{-1}cm^{-1}$ for SO_5^-. The absolute absorption coefficients derived from the current investigation are listed in Table 1 as a function of wavelength in intervals of 5 nm. An error of 5% is estimated for these data based on the errors of the literature data [2,3] and additional experimental errors in the present study. Absorption coefficients for smaller wavelength intervals are in preparation [4].

Table 1

Absolute decadic absorption coefficients for the sulfite radical anion (SO_3^-) and the peroxymonosulfate radical anion (SO_5^-).

λ [nm]	ε (SO_3^-) [l/mol cm]	ε (SO_5^-) [l/mol cm]
230 - 235		320
235 - 240	710	340
240 - 245	770	390
245 - 250	880	460
250 - 255	990	560
255 - 260	1070	660
260 - 265	1090	730
265 - 270	1060	740
270 - 275	990	710
275 - 280	900	650
280 - 285	790	560
285 - 290	680	460
290 - 295	590	360
295 - 300	500	270
300 - 305	440	190
305 - 310	390	130
310 - 315	340	90
315 - 320	300	70
320 - 325	270	50
325 - 330	240	30
330 - 335	220	20
335 - 340	190	10
340 - 345	160	
345 - 350	140	
350 - 355	130	
355 - 360	120	
360 - 365	110	
365 - 370	100	
370 - 375	80	
375 - 380	60	
380 - 385	40	
385 - 390	10	

2.2 Results for the study of SO_4^- - kinetics

In this part of the study the decay of SO_4^- due to reactions (R-1) and (R-2), viz.

$$SO_4^- + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^- \qquad \text{(R-1)}$$

$$SO_4^- + H_2O \rightarrow HSO_4^- + OH \qquad \text{(R-2)}$$

has been investigated as a function of the peroxodisulfate concentration which was varied in the range from $5 \cdot 10^{-5}$ to $5 \cdot 10^{-4}$ $mol\,l^{-1}$. At 293 K and pH=5 rate constants $k_1 = (6.3 \pm 1.5) \cdot 10^5$ $l\,mol^{-1}s^{-1}$ (for $I \rightarrow 0$) and of $k_2 = (6.6 \pm 0.4) \cdot 10^2$ s^{-1} have been determined. The obtained kinetic data are in good agreement with the available literature data. From T-dependent measurements the expression

$$k_2(T) = (4.7 \pm 0.2) \cdot 10^2 \exp[-(1110 \pm 60)/T] \cdot l\,mol^{-1}s^{-1} \qquad (1)$$

with $E_A = (9.2 \pm 0.5)$ kJ/mol was derived. Data on the T-dependence of reaction (R-2) are currently not available from the literature. For the recombination reaction (R-3):

$$SO_4^- + SO_4^- \rightarrow S_2O_8^{2-} \qquad \text{(R-3)}$$

a rate constant of $k_3 = (1.6 \pm 0.4) \cdot 10^8$ $l\,mol^{-1}s^{-1}$ has been obtained. The result is in good agreement with literature data by Huie et al. [5] and Tang et al. [6], whereas the rate constant published by McElroy et al. [7] is larger than our value by a factor 3.

In another part of our study the possible formation reaction (R-4) of OH-radicals in atmospheric droplets has been investigated

$$SO_4^- + OH^- \rightarrow SO_4^{2-} + OH \qquad \text{(R-4)}$$

By variation of the OH^-- concentration in the range $3 \cdot 10^{-6}$ to $1 \cdot 10^{-4}$ $mol\,l^{-1}$ we investigated the dependence of the first-order rate coefficient for the decay of SO_4^- on the OH^--concentration for reaction (R-4). At 298 K a rate constant of $k_4 = (1.4 \pm 0.2) \cdot 10^7$ $l\,mol^{-1}s^{-1}$ (for $I \rightarrow 0$) has been determined. This value is somewhat smaller than currently available literature data.

2.3. Results for the study of the SO_5^- - kinetics

For the self-reaction of the peroxymonosulfate radical anion, viz.

$$SO_5^- + SO_5^- \rightarrow 2\,SO_4^- + O_2 \qquad \text{(R-5a)}$$

$$\rightarrow S_2O_8^{2-} + O_2 \qquad \text{(R-5b)}$$

a rate constant of $k_5=(1.3\pm0.3)\cdot10^8\ \mathrm{l\,mol^{-1}s^{-1}}$ (for I→ 0) was found at 298 K and pH=4. This result is in good agreement with currently available literature data, e.g. $k_5=(9.3\pm0.1)\cdot10^7\ \mathrm{l\,mol^{-1}s^{-1}}$ [8] and $k_5=1\cdot10^8\ \mathrm{l\,mol^{-1}s^{-1}}$ [5]. The second order rate coefficient for reaction (R-5) has also been measured in the temperature range from 288 to 320 K. The temperature dependence is best described by

$$k_2(T)=(1.1\pm0.1)\cdot10^{12}\exp[-(2600\pm1000)/T]\ \mathrm{l\,mol^{-1}s^{-1}} \qquad (2)$$

corresponding to an activation energy of $E_A=(22\pm9)$ kJ/mol. To our knowledge, data on the temperature dependence of reaction (R-5) are currently not available from the literature.

From the direct detection of the formation of sulfate radical anions due to reaction (R-5a) an upper limit for the branching ratio of the two channels of reaction (R-5), viz.

$$\frac{k_{5a}}{k_{5a}+k_{5b}} \leq 0.04 \qquad (3)$$

could be established. This value is not inconsistent with a recent determination by Warneck [9], where a branching ratio of $k_{5a}/k_{5b}=0.04$ has been determined.

The spectroscopic and kinetic data from the present investigation provide information for a better understanding of the oxidation of S(IV) in tropospheric aquatic systems where, according to present knowledge, reaction chains involving free-radical play a substantial role. Future work will apply modelling techniques to describe these chemical systems.

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