

Preliminary Note

Transient intermediates in the photochemistry of elemental sulphur in solution[†]

H. L. CASAL and J. C. SCAIANO

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario K1A 0R6 (Canada)

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1. Introduction

Interest in the photochemistry of elemental sulphur goes back to at least 1870 [1]. In spite of this, few of the reaction intermediates involved in these processes have been characterized in any detail. Meyer *et al.* [2 - 4] have identified a few of these in studies of sulphur vapour, liquid sulphur and "photosulphur". In particular S_3 has been established to absorb at 400 - 410 nm, while $S_4(\text{open})$ has a characteristic band at 530 nm. Longer open ("biradical") species are believed to be dark red [5], while small rings and polymeric sulphur absorb in the UV region [6].

We have found only one preliminary report on the flash photolysis of elemental sulphur in solution in the microsecond-millisecond time scale [7]. In this case a transient absorbing at about 420 nm was identified. It was tentatively assigned to $S_8(\text{open})$, in spite of the obvious similarity of the spectrum to that reported for S_3 [4].

The formation of the unstable molecule S_2 resulting from the flash photolysis of elemental sulphur in the gas phase has been reported as has the recombination kinetics of S_2 [8, 9]. S_2 has also been detected from flash photolysis studies of OCS and CS_2 in the gas phase [10, 11].

In this preliminary note we report the preliminary results of a study of the laser photolysis of S_8 in solution. We have been able to identify S_3 and S_4 on the basis of the comparison of our results with those of other studies and of our own observations in the photochemistry of sulphur monochloride.

2. Experimental details

2.1. Materials

Resublimed sulphur was obtained from Fisher and sulphur monochloride (S_2Cl_2) was obtained from Aldrich. All solvents used were spectroscopic grade and were used without further purification. Solutions were typically 10^{-4} - 10^{-3} M and were passed through a 7 mm \times 7 mm cell made of Suprasil quartz. The flow was controlled by a Cole-Parmer model 7520-20 variable peristaltic pump.

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2.2. Laser photolysis

The samples were excited by pulses from a Molectron UV-24 nitrogen laser (337.1 nm, about 8 ns, up to 10 mJ (pulse)⁻¹) or a Lumonics TE800-2 excimer laser (308 nm with Xe-HCl, about 5 ns, up to 80 mJ (pulse)⁻¹). The signals were initially captured by a Tektronix R7912 transient digitizer and then transferred to a PDP 11/23 computer that controlled the experiment and provided suitable storage, hard copy and processing facilities. Further details have been given elsewhere [12].

3. Results and discussion

3.1. Photolysis of S₈

Transient spectra were recorded in deaerated solutions using a flow system; this was essential for these experiments (see below). Figure 1 shows the spectra obtained following 308 nm excitation of a 10⁻³ M solution of S₈ in cyclopentane. Figure 1, spectrum A, shows the "early" spectrum (0 - 800 ns

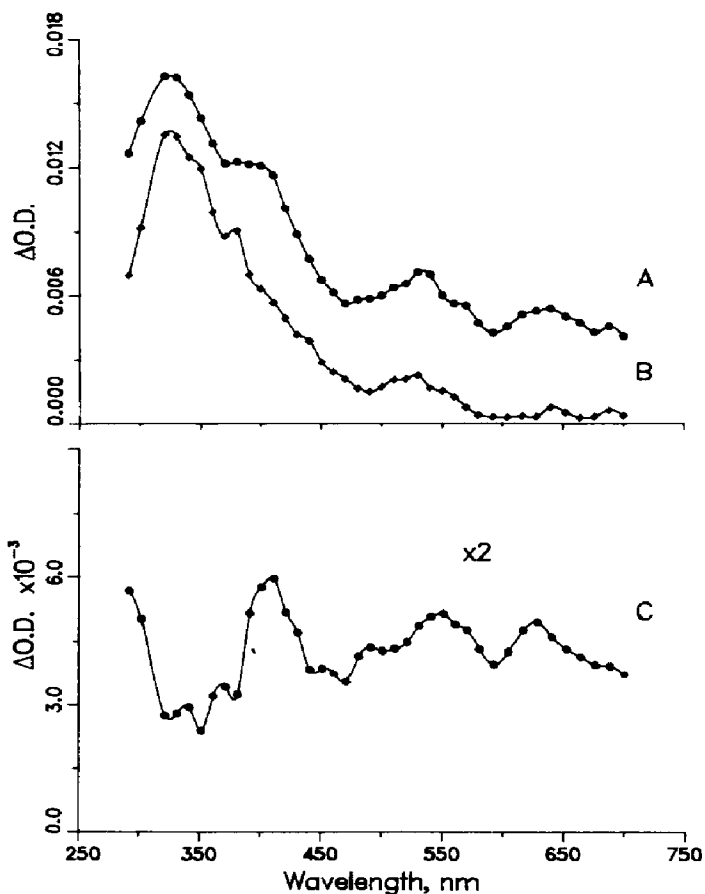


Fig. 1. Transient absorption spectra obtained by laser photolysis of a 10⁻³ M solution of S₈ in cyclopentane: spectrum A, signals detected in the 0 - 800 ns time interval after the 337 nm laser pulse; spectrum B, signals detected between 8 and 17 μs after the laser pulse; spectrum C, difference spectrum obtained by subtracting spectrum B from spectrum A.

after excitation) with four distinguishable regions at 325, 400, 530 and 640 nm. At longer times (Fig. 1, spectrum B, 8 - 17 μ s) the spectrum shows absorptions at about 330 nm and at about 530 nm. Subtraction of the spectra A and B (Fig. 1, curve C) indicates that the main species decaying in this time scale has $\lambda_{\text{max}} = 406$ nm as well as other bands at 530 nm and all the 640 nm absorption.

The 406 nm band can be assigned to S_3 on the basis of the previous characterization of this species by Meyer *et al.* [4]. The same workers also characterized S_4 , from studies of the photochemistry of S_4Cl_2 , as the band absorbing at 530 nm, which appears to be entirely consistent with the band at that wavelength in the laser photolysis of elemental sulphur [3]. The absorption at 640 nm cannot be assigned unequivocally but following earlier suggestions it may be due to S_6 and S_8 open chains [4]. Calculations indicate that longer S_n chains should absorb at longer wavelengths [5]. It is interesting to speculate that S_6 may absorb at 620 - 640 nm, while S_8 (open) probably absorbs at about 750 nm. Weak absorptions in this region were occasionally observed in our experiments.

The signals in the 320 - 380 nm region may be produced by cyclic species and by polymeric sulphur. The latter absorbs at 360 nm [6]. Similar absorption spectra were recorded in other solvents such as ethanol and dichloromethane, although in the case of ethanol no transient absorption at 640 nm was detected.

We note that the data presented above were obtained using high flow rates (about 0.4 ml (pulse) $^{-1}$) which ensure that every laser shot irradiates a fresh portion of solution. Lower rates tend to lead to artifacts. For example, the signal due to S_4 had a growth lifetime of about 24 ns and decayed with $\tau \sim 5$ μ s in cyclopentane; however, when the flow was decreased by a factor of 5 this signal was about 3 - 4 times more intense, it was almost entirely formed during the laser pulse (no longer than 8 ns) and decayed partially with $\tau \sim 20$ ns. We believe that with static samples or low flow rates the laser pulses (308 or 337 nm, usually every 3 s) are exciting long-lived intermediates produced by previous pulses. This seems consistent with the strong absorptions observed in the UV region. Some of these can be readily detected using a conventional spectrometer after completion of the laser experiment; they decay over several hours. If these ideas prove correct and if the absorption at 530 nm induced biphotonically is also caused by S_4 they would require its formation to be more efficient from "photosulphur" or small rings than from S_8 .

The formation of both the 406 and 530 nm signals is a very fast process, occurring in 20 - 40 ns under conditions of fast flow in cyclopentane. Only the signals in the 320 nm region are formed with relatively slow kinetics; for example in ethanol the lifetime for this build-up was about 1.7 μ s. S_3 and S_4 typically decay in the microsecond time scale, *e.g.* 4.8 μ s (S_3) and 5.4 μ s (S_4) in cyclopentane. Under the same conditions the 640 nm band decayed with $\tau \sim 320$ ns, while the 320 nm band decayed in 1 - 2 μ s in cyclopentane but took more than 25 μ s to decay in ethanol.

3.2. Photolysis of sulphur monochloride

The photolysis of S_2Cl_2 in the gas phase has been examined in detail [13]. We have now examined its photochemistry in ethanol. Figure 2 shows the spectrum obtained by 308 nm photolysis of a 2×10^{-4} M solution. The bands at 400 and 530 nm are assigned to S_3 and S_4 respectively. No signals were observed at $\lambda > 600$ nm. Surprisingly, the lifetime of S_3 produced in this manner was only about 200 ns (compared with about 1.4 μ s when obtained from S_8 in the same solvent); the build-up lifetime could not be determined because of interference by fluorescence. Earlier gas-phase work [13] showed the formation of S_3 but not S_4 . In accord with this, Fig. 2 shows the S_3 band as its dominant feature.

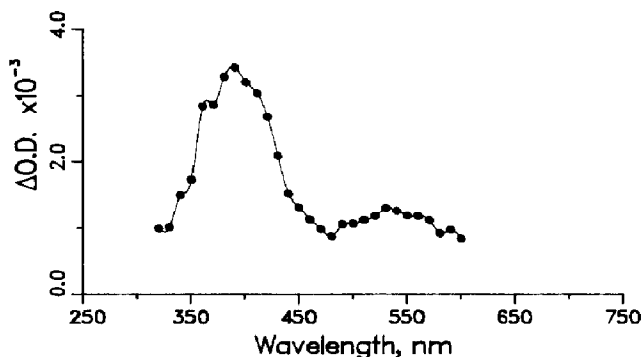


Fig. 2. Transient absorption spectrum obtained by laser photolysis of a 2×10^{-4} M solution of S_2Cl_2 in ethanol. Signals were monitored between 0.5 and 2 μ s after the 308 nm laser pulse.

Additional studies [14] in which we examined S_2Cl_2 in benzene also show the formation of the π complex between chlorine atoms and benzene ($\lambda_{max} = 490$ nm).

4. Conclusions

Over a decade ago Meyer pointed out that more than 44 sulphur allotropes had already been reported [15]. It would be naive to assume that any single study or technique can properly address this sort of problem. However, our preliminary results show that at least S_3 and S_4 are important intermediates in the solution photochemistry of S_8 . Other species, in particular open chains and small rings, are probably involved as well. Further studies are currently in progress to establish reactivity patterns for S_3 and S_4 , the possible importance of two-photon processes and the use of photosensitization techniques.

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