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Primary Photochemical Process of Sulfur in Solution

Chiho Nishijima,* Nobuaki Kanamaru,** and Katsumi Kimura
Physical Chemistry Laboratory, Institute of Applied Electricity, Hokkaido University, Sapporo 060

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Synopsis. A photochemical intermediate possibly attributed to linear S_8 has been found with a flash-photolysis technique and a rigid-glass technique. The decay behavior of transient in ethanol at room temperature between 10 and 100 ms may be interpreted in terms of the dimerization and polymerization of the linear S_8.

Since a very early work by Lallemand,[1] several groups[2] have studied the phenomenon of photopolymerization of sulfur in solution. Previously, the photoproduct has been explained in terms of allotropes and called "photosulfur". However, no studies on its reaction mechanism and intermediate species have been published so far. In the present work we considered it interesting to study the primary process of the formation of photosulfur in solution by means of a flash photolysis technique as well as a low-temperature UV-irradiation technique.

Experimental

Sulfur (Wako Chemical 99.999%) was recrystallized from carbon disulfide. Low temperature photolysis experiments of sulfur were carried out in EPA glass (2 : 2 : 5) by UV light in the region 250—350 nm using a high-pressure mercury lamp combined with a filter system which consists of an aqueous $NiSO_4$ solution and a Toshiba UV-D25 glass filter. In the low-temperature experiments, absorption spectrum measurements were carried out with a Cary Model 15 spectrophotometer, a quartz cell of 1-cm path length being used. Flash photolysis experiments were carried out with degassed solutions of sulfur in ethanol at room temperature using a flash photolysis apparatus described previously[3] and using a quartz cell of 15 cm long.

Results and Discussion

Sulfur in EPA glass at 77 K shows absorption peaks at 262 and 278 nm ($\varepsilon \approx 6 \times 10^3$ l/mol cm), as shown by Curve 1 in Fig. 1. When an EPA glass containing sulfur (4×10^{-4} M) at 77 K was irradiated by the 250—350 nm light for about 2—3 min, the absorption spectrum shown by Curve 2 was obtained, indicating a new absorption band peaking at 420 nm with an optical density of 0.15 which disappears by warming.[7] Meyer *et al.*[4–6] have recently published the visible absorption bands of S_2, S_3, and S_4 photolytically produced from S_2Cl_2, S_3Cl_2, and S_4Cl_2, respectively, in rigid matrices. The photo-induced 420 nm band in Fig. 1 more or less differs from those of S_2, S_3, and S_4. As far as each S_8 molecule is trapped in EPA glass at 77 K, it may be difficult to consider that a further dissociation forming $S+S_7$, S_2+S_6, S_3+S_5, or $2S_4$ takes place in the 77-K matrix. Therefore, the photo-induced spectrum (Curve 2, Fig. 1) may be assigned to the linear S_8 biradical formed by ring opening.

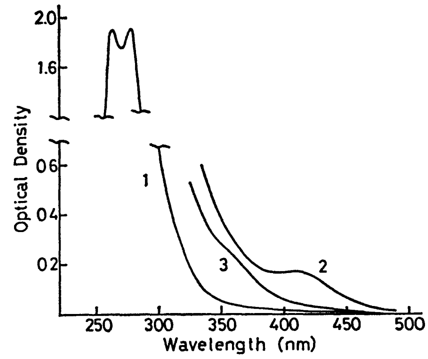

Fig. 1. Electronic absorption spectra before and after the Hg-lamp irradiation of sulfur in EPA glass at 77 K, shown by Curves 1 and 2, respectively. Curve 3 is the spectrum obtained when the irradiated glass was warmed up to room temperature.

$$S_8 \xrightarrow{h\nu} \cdot S_8 \cdot \text{ (linear)} \qquad (1)$$

The flash UV-irradiation of a degassed ethanol solution of sulfur (1×10^{-5} M) at room temperature gave rise to the transient spectra shown in Fig. 2 in which the upper spectra (Curves 1—3) were obtained within about 30 μs after flash, while the lower spectrum was obtained at 10 ms that resembles the low-temperature spectrum (Curve 2, Fig. 1). However, transient spectra taken within about 30 μs are somewhat complicated, suggesting several short-lived transients. Under non-degassed conditions, no transients were detected (possibly because of quenching by oxygen).

The second- and first-order plots of the absorbances of the transients against the time (t) at various wave-

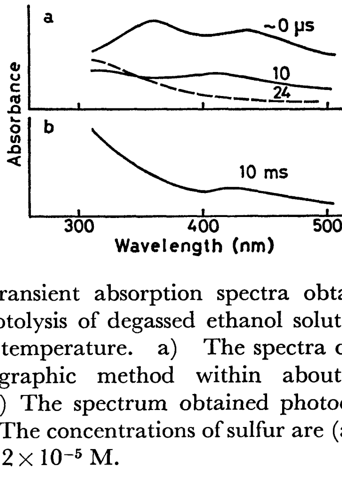

Fig. 2. Transient absorption spectra obtained by the flash photolysis of degassed ethanol solutions of sulfur at room temperature. a) The spectra obtained with a photographic method within about 30 μs after flash. b) The spectrum obtained photoelectrically at 10 ms. The concentrations of sulfur are (a) 1×10^{-5} M and (b) 2×10^{-5} M.

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* Present address: Kagawa Nutrition College, 251 Chiyoda, Sakado-machi, Saitama

** Present address: The Institute of Physical and Chemical Research, Wako-shi, Saitama.

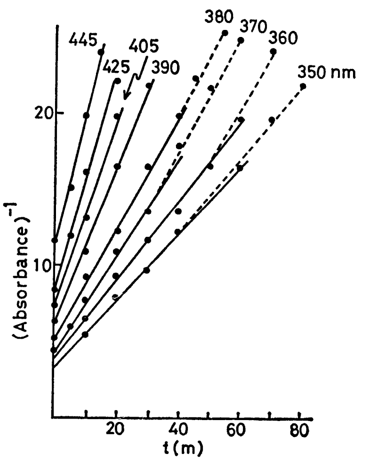

Fig. 3. Second-order decay plots of the transient absorbances obtained at various wavelengths at room temperature under degassed conditions. (An ethanol solution of 2×10^{-5} M sulfur was used.)

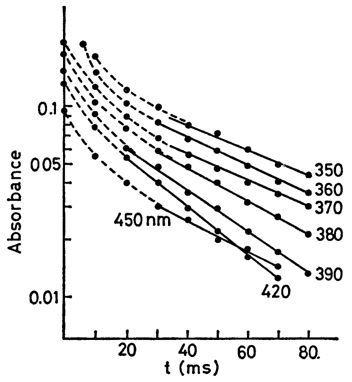

Fig. 4. First-order decay plots of the transient absorbances obtained at various wavelengths at room temperature under degassed conditions. (An ethanol solution of 2×10^{-5} M sulfur was used.)

lengths are shown in Figs. 3 and 4, respectively, suggesting that the 350—450 nm absorption may be ascribed to a single species in the time scale 10—100 ms with a minor contribution from other species. The rate of second-order decay obtained from the plots of the 350—380 nm and 440—450 nm absorptions in Fig. 3 is $C_0k_2=75\pm10\ \mathrm{s}^{-1}$, where C_0 is the initial concentration of the transient species. (There is some anomaly in the region 390—430 nm) Similarly, we obtained the rate of first-order decay $k_1=16\ \mathrm{s}^{-1}$, using the plots of the 350—380 nm and 440—450 nm absorptions in Fig. 4.

From the present experimental results, it may be suggested that the intense flash irradiation of sulfur in ethanol solution gives rise to the linear S_8 as well as its some decomposed species (such as S and S_7) which decay much faster than the linear S_8. The observed second- and first-order decays in the range 10—100 msec may be interpreted in terms of the dimerization and polymerization of the linear S_8,

$$2S_8 \longrightarrow S_{16} \qquad (2)$$

$$S_8 + S_{8n} \longrightarrow S_{8(n+1)} \qquad (3)$$

where $n\geq2$. Such mechanisms seem to be consistent with the formation of photosulfur which has been understood as a polymeric substance of sulfur for a long time.[2]

The main conclusion obtained here is that the decay of transient species around 10—40 ms may be interpreted mainly in terms of the dimerization of the linear S_8 biradical, whereas the decay observed after about 40 ms may be explained mainly with the polymerization of the linear S_8.

References

1) M. A. Lallemand, *Compt. Rend.*, **70**, 182 (1870).

2) For instance, see B, Meyer, *Chem. Rev.*, **64**, 429 (1964).

3) N. Kanamaru and K. Kimura, *Mol. Photochem.*, **5**, 427 (1973).

4) B. Meyer, T. V. Oommen, and D. Jensen, *J. Phys. Chem.*, **75**, 912 (1971).

5) B. Meyer, T. Stroyer-Hansen, D. Jensen, and T. V. Oommen, *J. Am. Chem. Soc.*, **93**, 1034 (1971).

6) B. Meyer, T. Stroyer-Hansen, and T. V. Oommen, *J. Mol. Spectrosc.*, **42**, 335 (1972).

7) It should also be mentioned that a further UV-irradiation at 77 K for a much longer time, *e.g.*, about 30 min, gives rise to another spectrum (with absorption maxima at about 370 and 420 nm) which disappears at higher temperature. The 370-nm band may be possibly due to some photo-decomposed species such as S and S_7.