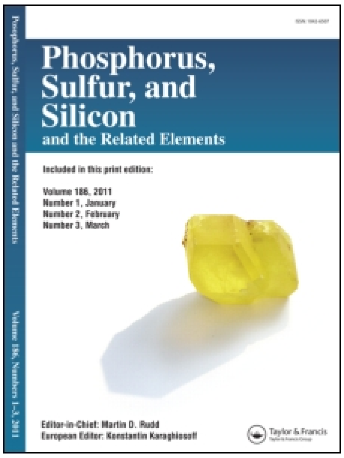

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A STUDY OF THE PHOTOPHYSICAL AND PHOTOCHEMICAL PROPERTIES OF THE S_8 MOLECULE Photochemical Reactions in the S_8 Liquid Methanol System with and without Sensitizers: Benzene, Naphthalene and Pyrene. II

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A STUDY OF THE PHOTOPHYSICAL AND PHOTOCHEMICAL PROPERTIES OF THE S_8 MOLECULE

Photochemical Reactions in the S_8 + Liquid Methanol System with and without Sensitizers: Benzene, Naphthalene and Pyrene. II

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The photochemical reactions occurring in the system S_8 + CH_3OH in the liquid phase were investigated, in the presence of, and without sensitizers. The experimental conditions were identical with those employed in studying the quenching of fluorescence.[1]

The decay of S_8 is more rapid in the presence of sensitizers (the quantum yield and the degree of conversion are higher). In the system studied irradiation by UV light ($\lambda \sim 254$ nm) causes the formation of $(CH_3)_2S$ and of trace amounts of CH_4 and C_2H_6. The process of S_8 decay is of a mixed kinetic character—a pseudo 1st order process predominating, with a contribution from a 2nd order reaction. A possible reaction scheme, associated with excitation energy transfer from sensitizers to S_8 is discussed.

INTRODUCTION

Part I of this work was devoted to establishing the nature of the excited state and determining its energy. The quenching of benzene, naphthalene and pyrene fluorescence by S_8 was discussed, and the process of energy transfer from the S_1 states of the individual sensitizers to the S_0 state of the acceptor, S_8, elucidated.

The present paper is devoted to a photochemical investigation of the S_8 + CH_3OH system, with and without sensitizers. The experiments were carried out under identical conditions to those described in Part I, concerned with the quenching of fluorescence. The disappearance of S_8 molecules was monitored spectrophotometrically and, in parallel, gas chromatography was employed to follow the formation of the photo-product, $(CH_3)_2S$. The results were used to obtain kinetic data for both processes on the basis of which a reaction scheme is proposed to account for the observations.

RESULTS AND DISCUSSION

One of the reasons for investigating photochemical reactions in the S_8 + CH_3OH system, brought about by irradiation with $\lambda \sim 254$ nm, in the presence of sensitizers and without them, was to demonstrate the interdependence between the process of excitation energy transfer from the sensitizers to S_8 and the influence of the sensitizers on the photochemical reactions of S_8. This influence is exemplified by changes in the quantum yield, Φ, for the disappearance of S_8 molecules (followed spectrophotometrically) and also by changes of Φ for that part of the above process which is attributable to the formation of the product, $(CH_3)_2S$ (followed by gas chromatography). Since the disappearance of S_8 and the appearance of the product are closely connected, S_8 being the sole source of sulphur in the product, sulphur is expressed as S_8 throughout the paper.

The reactions were normally followed until the degree of conversion of S_8 reached about 30%. When sensitizers were present and long periods of irradiation were employed, the degree of conversion could be higher. The concentrations of the donors and of the acceptor were selected so as to maximize light absorption by the donors.

In spectrophotometric measurements on the disappearance of S_8 in the system S_8 + CH_3OH, with and without a sensitizer, benzene was used as the donor. The following concentrations were found to be most suitable: $S_8 = 3.0 \times 10^{-4}$ mole·l^{-1}; $C_6H_6 = 4.7 \times 10^{-2}$ mole·l^{-1}. This gave 85% absorption of the incident radiation by the benzene. Partial

TABLE I

The disappearance of S_8 molecules in methanol, at 20°C (spectrophotometric measurements)

	Without sensitizer			With sensitizer (benzene)		
Time of irradiation (min)	The disappearance of $S_8 \times 10^{-4}$ (mol·l^{-1})	Degree of conversion of S_8 %	Quantum yield for the disappearance of S_8[a]	The disappearance of $S_8 \times 10^{-4}$ (mol·l^{-1})	Degree of conversion of S_8 %	Quantum yield for the disappearance of S_8[a]
5	0.15 ± 0.01	5	0.39 ± 0.04	0.24 ± 0.02	8	0.51 ± 0.05
10	0.23 ± 0.02	8		0.53 ± 0.045	17	
15	0.32 ± 0.025	10		0.90 ± 0.08	30	
20	0.43 ± 0.035	13		1.29 ± 0.10	43	
30	0.90 ± 0.08	30		2.05 ± 0.15	68	

[a] Values of ϕ from an extrapolation to zero conversion of S_8.

absorption by S_8 was corrected for in calculating the value of Φ for the disappearance of S_8 and the degree of conversion of S_8. The irradiation ($\lambda \sim$ 254 nm) of benzene in CH_3OH without S_8, at a concentration identical with that when S_8 was present, did not bring about any changes in the absorption spectrum of the benzene (within the limits of experimental error of about 4%).

In following the appearance of the product, $(CH_3)_2S$ by gas chromatography (and thus the disappearance of S_8 corresponding to the formation of the product) without and in the presence of benzene, naphthalene and pyrene sensitizers, the same concentrations of benzene and S_8 were used as for the spectrophotometric method. Naphthalene and pyrene were used at concentrations of 1.5×10^{-2} mole·l^{-1} and 8.3×10^{-4} mole·l^{-1} respectively. These concentrations made it possible to obtain 96% absorption of the incident radiation for naphthalene and 85% absorption for pyrene. Pyrene was used at a much lower concentration here in order to avoid interferences, which could be caused by the formation of excimers in more concentrated solutions.[2–4] For both donors, when Φ values and the degree of conversion were calculated, corrections were made for the fact that the observed absorption was due to not only the sensitizer, but also in part to S_8. In the case of solutions of pyrene in methanol, no appreciable changes (±5%) were observed in the absorption spectrum after irradiation by $\lambda \sim 254$ nm. The same can be taken to be true of naphthalene. Naphthalene and pyrene show numerous similarities in structure and other properties. Direct spectroscopic measurements on the absorption spectrum of naphthalene in such relatively concentrated methanolic solutions were not possible.

The results obtained spectrophotometrically for the disappearance of S_8 in methanolic solutions, at 20°C with and without C_6H_6 sensitizer, are presented in Table I.

It is evident, that in the S + CH_3OH system the disappearance of S_8 has an appreciable higher quantum yield and the degree of conversion in the presence of the benzene sensitizer. The results obtained by gas chromatography also gave a clear indication that the presence of sensitizers leads to increased yields for the disappearance of S_8 in connection with the formation of the product, $(CH_3)_2S$. The data are presented in Table II.

From the degree of conversion and the values of the quantum yield it can be seen that the effect of all three sensitizers on the course of the reaction is similar. The quantum yield for the case of sensitization by naphthalene is not given. The concentration of naphthalene—1.5×10^{-2} mole·l^{-1} for all experiments—gave too intense absorption. In addition to $(CH_3)_2S$, trace amounts of CH_4 and C_3H_6 were detected by gas chromatography. No other reaction products were found. However, taking into account the values of Φ for the disappearance of S_8 (Table I) and for the disappearance of S_8 connected with the formation of $(CH_3)_2S$ (Table II)—it is clear that other sulphur-containing products should be present in the system. These could not be detected using the present methods.

For $\lambda \sim 254$ nm the absorption by benzene in S_8 + methanol (total absorption = 1.07) is about 6 times greater than the absorption by S_8 + methanol alone (absorption = 0.158).

The efficiency of the energy transfer process from C_6H_6 in the excited singlet state to S_8 in the ground state:

TABLE II

The disappearance of S_8 molecules associated with the formation of $(CH_3)_2S$, at 20°C (results from gas chromatography)

Without sensitizer				With sensitizer							
Time of irradiation (min)	The concentration of sulphur combined in $(CH_3)_2S$, in terms of $S_8 \times 10^{-4}$ (mol·l^{-1})	Degree of conversion of S_8 (%)	Quantum yield for the disappearance of S_8 (Amount of sulphur combined in $(CH_3)_2S$ calculated in terms of S_8)[a]	The concentration of sulphur combined in $(CH_3)_2S$, in terms of $S_8 \times 10^{-4}$ (mol·l^{-1})			Degree of conversion of S_8 (%)			Quantum yield for the disappearance of S_8 (Amount of sulphur combined in $(CH_3)_2S$ calculated in terms of S_8)[a]	
				Benzene	Naphthalene	Pyrene	Benzene	Naphthalene	Pyrene	Benzene	Pyrene
5	0.03 ± 0.003	1	0.05 ± 0.005	0.06 ± 0.005	0.06 ± 0.005	0.07 ± 0.005	2	2	2.5	0.12 ± 0.015	0.13 ± 0.015
10	0.07 ± 0.006	2		0.15 ± 0.01	0.13 ± 0.01	0.16 ± 0.01	5	4.5	5.5		
15	0.12 ± 0.01	4		0.25 ± 0.015	0.20 ± 0.015	0.27 ± 0.02	8	6.5	8.5		
30	0.30 ± 0.02	10		0.40 ± 0.035	0.37 ± 0.03	0.40 ± 0.035	13.5	12.5	13.5		
60	0.50 ± 0.04	16.5									

[a] Values of ϕ from an extrapolation to zero conversion of S_8.

$$C_6H_6(S_1) + S_8(S_0) \rightarrow C_6H_6(S_0) + S_8(S_1)$$

estimated from the relationship: $k_q \cdot \tau_D[Q]$ and the present data indicates that the above process is several times faster than all other processes, taken together, by which C_6H_6 in the S_1 state can be quenched (besides the quenching process by S_8). This leads one to suppose that increased photochemical conversion of S_8 in the system containing S_8 and C_6H_6 is caused by increased light absorption, and high efficiency of the energy transfer process.

The results on the disappearance of S_8 as in connection with the formation of $(CH_3)_2S$ in the presence of naphthalene and pyrene (Table II) indicate that a similar mechanism operates as for benzene.

Increased quantum yield for the disappearance of S_8 (to 0.51 ± 0.05) in the presence of benzene is probably caused by the formation of the complex (S_8 C_6H_6).* There is, however, also the possibility that the increased quantum yield is associated with the participation of the triplet state of S_8. The concentration of S_8 in the T state may be increased, compared to a system with no sensitizer, through energy transfer from the T state of C_6H_6 to a T state of S_8. A proportion of C_6H_6 molecules in the S_1 state may be able to pass to a T state, as a result of intersystem crossing, $S_1 \rightarrow T_1$.

Increased quantum yield for the disappearance of S_8 in the presence of the sensitizer (benzene) is confirmed by increased quantum yield for the disappearance of S_8 associated with the formation of $(CH_3)_2S$ in the presence of sensitizers (benzene and pyrene).

The kinetics of both processes were investigated. The reaction was followed at temperatures between 10°C and 40°C (Tables III and IV). The extent of the disappearance of S_8 increases with time of irradiation. With initial concentration of S_8 (a) and that after time t (x) plots of $\log(a - x)$ v.t. obtained taking into account low absorption by the reactants indicated that the disappearance of S_8 (followed spectrophotometrically) and that part of it which is attributable to the formation of $(CH_3)_2S$ (followed by gas chromatography) is of mixed order, pseudo first order predominating, with a contribution from a second order process. The values of the rate constant, k, for the first order reaction increase with increasing temperature. The relatively low value of the activation energy for the disappearance of S_8 indicates that this is a highly probable process. The disappearance of S_8 associated with the formation of $(CH_3)_2S$ requires a somewhat higher activation energy (Table IV). The temperature coefficients deduced for both processes are low, which is characteristic of photochemical reactions. For the disappearance of S_8, these coefficients, for the temperature range used, lie between 1.17 and 1.28 and for the disappearance of S_8 to form $(CH_3)_2S$, between 1.28 and 1.45.

TABLE III

The kinetics of disappearance of S_8 molecules in methanol, at different temperatures

Temperature of the system °C	Reaction rate constant, $k_1{}^a \times 10^{-2}$ (min^{-1})	Activation energy (kcal·mol^{-1})
10	5.3 ± 0.4	4.0 ± 0.35
20	6.8 ± 0.6	
30	8.5 ± 0.7	
40	10.0 ± 0.8	

[a] Reaction rate constants obtained from a pseudo first order rate equation, $\log(a - x) = f(t)$, using the method of least squares; a—initial concentration of S_8; x—concentration of S_8 after irradiation for time t.

TABLE IV

The kinetics of disappearance of S_8 molecules associated with the formation of $(CH_3)_2S$, at different temperatures

Temperature of the system °C	Reaction rate constants, $k_1{}^a \times 10^{-3}$ (min^{-1})	Activation energy (kcal·mol^{-1})
10	2.4 ± 0.2	5.6 ± 0.5
20	3.5 ± 0.3	
30	4.5 ± 0.4	
40	6.3 ± 0.6	

[a] Reaction rate constants obtained from a pseudo first order rate equation, $\log(a - x) = f(t)$, using the method of least squares; a—initial concentration of S_8; x—concentration of S_8 corresponding to sulphur combined in $(CH_3)_2S$, after irradiation for time t.

The results can be taken to indicate that, without the presence of sensitizers, the following reactions can take place in the S_8 + CH_3OH system:

$$S_8 \xrightarrow[\lambda \sim 254\ \mathrm{nm}]{h\nu} S_8^* \longrightarrow \cdot S{-}S_x{-}S\cdot\ ^{5-10} \qquad (1)$$

$$S_8^* + CH_3OH \longrightarrow (S_8CH_3OH)^* \begin{cases} \longrightarrow S_8 + {}^{\cdot}CH_3 + {}^{\cdot}OH & (2) \\ \longrightarrow S_8 + CH_3OH & (3) \end{cases}$$

$$\cdot S{-}S_x{-}S\cdot + CH_3OH \longrightarrow \cdot S{-}S_x{-}S{-}CH_3 + {}^{\cdot}OH \qquad (4)$$

or also:

$$\cdot S{-}S_x{-}S\cdot + CH_3OH \longrightarrow \cdot S{-}S_x{-}S{-}OH + {}^{\cdot}CH_3 \quad (5)$$

$$\cdot S{-}S_x{-}S\cdot + {}^{\cdot}CH_3 \longrightarrow CH_3S^{\cdot} + \cdot S{-}S_x \quad (6)$$

$$CH_3S^{\cdot} + {}^{\cdot}CH_3 \longrightarrow (CH_3)_2S \quad (7)$$

$$^{\cdot}CH_3 + CH_3OH \longrightarrow CH_4 + {}^{\cdot}CH_2OH\ ^{11} \quad (8)$$

$$2\,{}^{\cdot}CH_3 \longrightarrow C_2H_6{}^{12} \quad (9)$$

The S_8 molecule, on absorbing ($\varepsilon_{254}^{S_8} = 5250$ $l \cdot mol^{-1} \cdot cm^{-1}$) a quantum of the incident radiation passes to the excited state (1). The energy corresponding to absorption at $\lambda \sim 254$ nm, is 112.7 kcal·mole^{-1}, [13–17] breaks and a free radical, open-S–S bond in the S_8 molecule, with a bond energy 33 kcal·mole^{-1},[13–17] breaks and a free radical, open-chain form of sulphur (1)[5–10] forms, which is capable of reacting with other components of the system. CH_3OH molecules do not absorb at the wavelength in question.

Excited S_8* can give a short lived complex with the CH_3OH molecules of the surrounding medium. Within this complex, an energy rearrangement can take place, energy passing from the sulphur radical to the methanol, as a result of which the CH_3OH molecule breaks up (2). Independently of this process, the free radical form of sulphur, $\cdot S{-}S_x{-}S\cdot$ (1), can, through direct collisions with CH_3OH molecules initiate reactions with the formation of intermediate products (4) and (5). The formation of CH_4 and C_2H_6 in this system shows that CH_3OH does break up. CH_4 forms, most probably, as a result of hydrogen abstraction from CH_3OH molecules by $^{\cdot}CH_3$ radicals (8).[11] The formation of C_2H_6 is most likely a result of the recombination of $^{\cdot}CH_3$ radicals (9).[12] The deactivation of S_8* (3) and reaction (6), leading to the formation of sulphur species smaller than S_8[5,9,10] can run in parallel with reaction (2).

The free radical CH_3 reacts with the sulphur in the chain $\cdot S{-}S_x{-}S\cdot$ giving the radical $CH_3S^{\cdot}$ (6), which can then interact with a second $^{\cdot}CH_3$ radical to give the product, $(CH_3)_2S$, in the secondary process (7). This product does not absorb the incident radiation. The $(CH_3)_2S$ is present in a low concentration and accounts only for a small proportion of the sulphur present in the system (Table II)—in comparison with the total $S_8 \cdot$ I can therefore suppose that in addition to the product considered, trace amounts of other sulphur species can form, such as CH_3SH, which could arise from the process:

$$2CH_3S^{\cdot} \rightarrow CH_3SH + CH_2S^{\cdot}\ ^{18-20}$$

and certain quantities of polymeric forms of sulphur,[21] which, however, were not detected using the present methods. In spite of the presence of oxygen in the alcoholic OH group, oxygen could not be detected in any other combination.

Because of difficulties in detecting, in the liquid phase, short lived sulphur-containing intermediates and because of the absence of sufficient literature data, it is not easy to propose a fully documented reaction mechanism. The formation of stable products in the system considered indicates that further investigations particularly of fast reactions might be worthwhile, and that flash methods could be useful here.

EXPERIMENTAL

Some of the experimental data have already been given in Part I and these will not be repeated here.

Reagents

Cyclohexane (analytical grade) made by POCh–Gliwice, was purified by shaking with sulphuric acid, washing with distilled water, drying with KOH and distilling twice, the fraction boiling at 80.7°C being collected.

Uranyl sulphate (analytical grade) made by Chemapol-Praque was used without additional purification.

Methane and ethane, made by Fluka, were also used directly.

Apparatus

Reaction products were identified using gas chromatography. The chromatograph employed was Pye Unicam, type 104, with columns packed mainly with Triton X-305, on Diatomite C 100/120 mesh, but also polyethylene glycol 4000 and 400 and silicone oil OV 101.

Quantum yield, Φ, was determined with the aid of an actinometer—this consisted of uranyl sulphate solution (0.01 mole·l^{-1}) and oxalic acid solution (0·05 mole·l^{-1}) mixed in 1 : 1 ratio by volume. The average light intensity emitted by the mercury NK 6/20 lamp and absorbed by S_8 in CH_3OH was $5.2 \pm 0.5 \times 10^{-2}$ mE·h^{-1}·ml^{-1} (determination of Φ for the disappearance of S_8).

Procedure

S_8 in CH_3OH solutions were used at a concentration of 3.0×10^{-4} mole·l^{-1}. This gave high concentration of photoproducts without any precipitation of colloidal sulphur, making it possible to use spectrophotometry to follow directly any changes in the S_8 concentration. The experimental solutions were introduced into a quartz reactor. The low pressure Hg lamp was placed inside the reactor, always in identically the same position. Air was then removed from the system by sweeping with de-oxygenized helium. The whole reactor, together with the lamp, was kept in a thermostat at one of the following temperatures:

10, 20, 30 and 40°C (accurate to ± 0.5°C). For comparison, observations were carried out on the same system without irradiation. In this case no reaction products could be detected.

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