

# DIRECT AND SENSITIZED PHOTOLYSIS OF DIMETHYL SULPHOXIDE IN SOLUTION

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## ABSTRACT

Excitation ( $2537 \text{ \AA} = 112 \text{ kcal/mole}$ ) of dimethyl sulphoxide (DMSO) in solution leads to singlet excited DMSO ( $E_S = 105 \text{ kcal/mole}$ ) that undergoes three primary reactions: fragmentation to methyl and methanesulphinyl radicals, a bimolecular disproportionation reaction to dimethyl sulphone and dimethyl sulphide by a reaction with a ground state DMSO molecule at higher DMSO concentrations, and deactivation to DMSO ground state molecules. The triplet state of DMSO ( $E_T = 83 \pm 3 \text{ kcal/mole}$ ), if formed at all, appears to be chemically inert. At relatively dilute DMSO solutions, the fragmentation ( $D_{c-s} = 53 \text{ kcal/mole}$ ) occurs with a quantum yield of 0.14 which is independent of the nature of the solvent (acetonitrile, alcohols, water), of the viscosity of the solvents as well as of the pH of the solvents. No H/D and  $^{16}\text{O}/^{18}\text{O}$  exchanges take place thermally or photochemically under the reaction conditions applied.

In acetonitrile, the radicals formed in the primary reactions abstract hydrogen atoms from the solvent; in water, electron transfer from methanesulphinyl radical to methyl radical proceeds thereby producing solvated ions, whereas both these reactions occur in alcohols depending upon the alcohols' ability to stabilize such ions. Methanesulphinyl radicals are able to undergo various reactions: they abstract hydrogen from acetonitrile and alcohols, they dimerize in neat DMSO, they transfer an electron to methyl radicals in water, and they add to an aromatic system such as benzene. Methyl radicals, however, were found to undergo exclusively hydrogen abstraction except in water where they accept an electron from the methanesulphinyl radical. DMSO proved itself as a very poor hydrogen donor. Only during photolysis of neat DMSO was the appearance of 'dimsyl' radicals,  $\text{CH}_3\text{SO}\dot{\text{C}}\text{H}_2$ , apparent; their major reaction under these conditions is fragmentation to formaldehyde and methanesulphenyl radicals. A qualitative as well as a quantitative analysis of all the products formed in neat DMSO and in various solvents has been made; the reaction sequences that are assumed to follow the primary processes can quantitatively account for all the products observed such as methane, methanesulphonic acid, dimethyl disulphide, dimethyl sulphide, and methyl methanethiolsulphonate.

Photolysis of DMSO can be sensitized by benzene and toluene whereas *p*-cymene, tetralin, mesitylene, acetone, and benzophenone are incapable of doing so. Fluorescence quenching of benzene by DMSO and the inefficiency of cyclohexene to quench the benzene-sensitized photolysis of DMSO show that singlet-singlet energy transfer and decomposition of the singlet excited DMSO take place. The kinetics of the methane formation (methanesulphinyl

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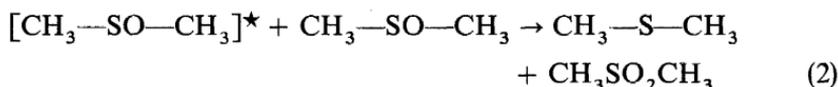
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radicals are quantitatively trapped by benzene) reveal that singlet benzene excimers are involved in the energy transfer process besides the singlet excited benzene monomers. The question, whether these energy transfer reactions lead to the formation of a singlet excited DMSO molecule or to a singlet benzene-DMSO exciplex that subsequently decomposes to methyl and methanesulphinyl radicals, cannot be settled at present.

## INTRODUCTION

Despite the fundamental importance of organic sulphoxides as sulphur analogues of ketones, rather little is known of their photochemistry<sup>1</sup>. Irradiation of neat dimethyl sulphoxide (DMSO) was reported to yield carbon monoxide, methane, and ethane<sup>2</sup> whereas trimethylsulphonium methanesulphonate was found if the irradiation was carried out in the presence of iodine<sup>3</sup>. Sulphinyl radicals assumed to be rather stable intermediates during certain C—S bond cleavage reactions of sulphoxides had not been detected or trapped<sup>1</sup>.

Recently, we reported that direct photolysis of DMSO in water, acetonitrile, and alcohols results in the cleavage of the C—S bond to give a CH<sub>3</sub> and a CH<sub>3</sub>SO fragment which on reaction with the solvents afford methane and a series of sulphur-containing compounds such as methanesulphonic acid, dimethyl sulphide, methyl methanethiolsulphonate, and dimethyl disulphide, respectively<sup>4,5</sup>. Formation of dimethyl sulphone (and a corresponding amount of dimethyl sulphide) could be accounted for by assuming that a bimolecular disproportionation reaction takes place beside the C—S cleavage reaction<sup>4,5</sup>.



## EXPERIMENTAL

Dimethyl sulphoxide (DMSO, Fluka A.G.) was dried (molecular sieve, 4 Å) and distilled (b.pt.<sub>12</sub> 90°). For spectroscopic purposes, DMSO was purified by low-temperature zone melting. For analytical purposes, dimethyl sulphide and dimethyl disulphide were purchased (Fluka); methyl mercaptan was prepared from thiourea and methylbromide; dimethyl sulphone was obtained by oxidation of DMSO with potassium permanganate; hydrolysis of methanesulphonyl chloride yielded methanesulphonic acid; oxidation of dimethyl disulphide with two equivalents of sodium periodate gave methyl methanethiolsulphonate. Methanol, ethyl alcohol and isopropyl alcohol (Merck, p.a.) were distilled over lithium aluminium hydride (LiAlH<sub>4</sub>) (transparency at 254 nm > 90 per cent). Hydrocarbons (pentane, octane,

decane, and hexadecane) (Fluka) were distilled and filtered over alumina ( $\text{Al}_2\text{O}_3$ ) (basic, activity I) for sufficient transparency at 254 nm. Benzene and acetonitrile (Uvasol, Merck) were used without further purification. Tetralin, mesitylene, and *p*-cymene were obtained peroxide-free by washing them with sulphuric acid (Care: Peroxides may react violently). Cyclohexene was distilled over maleic anhydride to remove cyclohexadiene. DMSO- $d_6$  and the *O*-deuterated alcohols were purchased from Merck,  $\text{H}_2^{18}\text{O}$  from Miles and Yeda, xenon from Matheson.

The vacuum u.v. spectrum of DMSO was obtained with a McPherson Model 225 spectrometer. Routine u.v. spectra were recorded on a Bausch and Lomb Spectronic 505 spectrometer. For emission spectra, a Perkin-Elmer MPF-2A spectrometer was used.

A Rayonet RPR 100 Srinivasan-Griffin reactor (Southern New England Ultraviolet Company) equipped with 16 2537Å-mercury low-pressure Vycor lamps or with 3000Å-lamps was used for irradiating solutions at 25° to 60° in 20, 50 or 100 ml cylindrical quartz vessels. The 100 ml vessels could be equipped with 'cooling fingers'; the other vessels were surrounded by quartz tubes through which a stream of cold air was pumped which made it possible to keep the temperature in the solution during irradiation at any desired level between 30° and 60°. Oxygen was removed by conventional freeze-pump-thaw procedures at 77°K on a mercury-free vacuum system.

After irradiation, the samples were frozen to liquid nitrogen temperatures and the non-condensable gases were pumped off by a Toepler pump and measured in a McLeod gauge. Thawing and refreezing were repeated until no non-condensable gas was measured. Condensable gases were measured accordingly by cooling the samples to temperatures of -50° to -90° with a mixture of methanol and liquid nitrogen.

If non-aqueous solutions were used, the gases and the liquid phases could be analysed directly by gas chromatography. Aqueous solutions, however, were extracted with carbon tetrachloride after the gaseous products were pumped off, and the organic phase was then analysed by v.p.c. for methyl mercaptan, dimethyl sulphide and dimethyl disulphide which are hardly soluble in water. In order to analyse for water-soluble or partly water-soluble products such as dimethyl sulphone and methyl methanethiolsulphonate, the aqueous solution was extracted with methylene chloride.

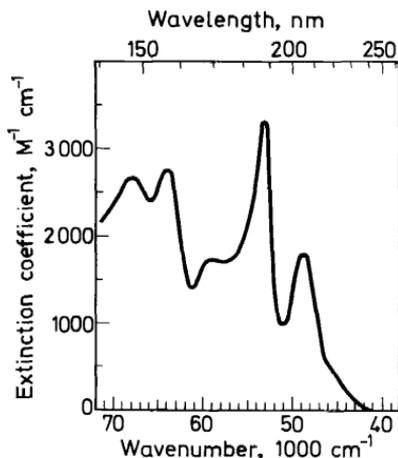
Gas chromatography was performed on a Perkin-Elmer gas chromatograph F-7; calcium-aluminium-silicate (molecular sieve, 5 Å), 80°:  $\text{CH}_4$ ,  $\text{H}_2$ , CO; silica gel, 100°: ethane and higher hydrocarbons; polyethylene glycol (K), polypropylene glycol (R) and silicone oil DC 200 (C), 40°-60°: mercaptans, dialkyl sulphides, dialkyl disulphides,  $\text{SO}_2$ , alcohols, aldehydes and ketones; carbowax 20M, 150°: dimethyl sulphone and methyl methanethiolsulphonate; quantitative determinations by using the solvent or DMSO as internal standard after calibration of the detector of the v.p.c. apparatus.

Methanesulphonic acid was quantitatively determined by potentiometric titration with 0.01 N sodium hydroxide.

For quantum yield determinations, actinometry was performed at 25° using the uranyl oxalate actinometer. The amount of oxalate decomposition (quantum yield at 2537 Å =  $0.62 \pm 0.02$ ) was measured by titration of undecomposed oxalate with potassium permanganate.

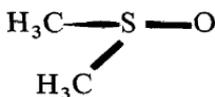
## ABSORPTION SPECTRA, FRONTIER MOLECULAR ORBITALS, ENERGIES OF LOWEST EXCITED SINGLET AND TRIPLET STATES, AND DISSOCIATION ENERGIES

The absorption spectrum of DMSO taken in the gas phase at 0.5 Torr and 25° is shown in *Figure 1*. Absorption at 188 nm is assumed to be connected with a  $\pi \rightarrow \pi^*$ -transition in the S—O group<sup>6</sup> whereas absorption at 205 nm is considered to be due to  $n \rightarrow \sigma^*$  or  $n \rightarrow d$  transitions<sup>6-8</sup>. A weak absorption band occurs at about 220 nm which may be attributed to a  $n \rightarrow \pi^*$  transition. However, if transition of an electron from a *localized* n-orbital occurs, the excited electron may originate from an n-orbital at sulphur or oxygen.



*Figure 1.* Vacuum u.v. absorption spectrum of DMSO in the gas phase at 0.5 Torr and 25°.

For ketones, rather simple MO schemes may be drawn and much of their photochemistry is well understood by considering  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions in the C=O group in which the lone-pair electrons are localized at oxygen. Unfortunately, no such simple scheme appears to be applicable for sulphoxides since the d-orbitals of the sulphur atom may participate in forming the MOs. Applying the CNDO/2 method and using the following parameters<sup>9</sup> we found considerable delocalization of all molecular orbitals of DMSO. *Figure 2* shows the calculated electron densities in the frontier orbitals of DMSO, of which the upper five occupied orbitals have very recently been characterized<sup>10</sup> as  $n_s$ ,  $\pi_{SO}$ ,  $\sigma_{SO}$ ,  $\sigma_{SC}$  and  $n_O$ .



$$\begin{aligned} d_{\text{S-O}} &= 1.48 \text{ \AA} \\ d_{\text{S-C}} &= 1.81 \text{ \AA} \\ d_{\text{C-H}} &= 1.09 \text{ \AA} \end{aligned}$$

$$\begin{aligned} \angle \text{C-S-C} &= 96.4^\circ \\ \angle \text{C-S-O} &= 106.7^\circ \\ \angle \text{S-C-H} &= 107.5^\circ \end{aligned}$$

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The electron configuration of ground state DMSO indicates a polarized S—O bond as well as polarized H—C bonds. The lowest unoccupied MOs are highly localized at sulphur. Compared to the HOMO, in LUMO the electron density at sulphur is enhanced by 0.22 unit whereas it is decreased by 0.08 at oxygen. There is also an electron density enhancement at the hydrogens by 0.01 and a decrease by 0.11 at the carbons. In LUMO + 1, the electron densities at H and C remain nearly unaltered if compared with the HOMO, but the electron density at S is increased by 0.23 and decreased

Electron densities in frontier orbitals of DMSO at

Molecular orbital	3H	C	S	O
LUMO+2	0.02	0.16	0.55	0.07
LUMO+1	0.01	0.08	0.79	0.04
LUMO	0.05	0.00	0.78	0.12
HOMO	0.01	0.11	0.56	0.20
HOMO-1	0.03	0.17	0.25	0.36
HOMO-2	0.04	0.06	0.22	0.58
HOMO-3	0.12	0.14	0.18	0.30
HOMO-4	0.02	0.06	0.28	0.57

Electron configuration in ground state DMSO:  
 $H(s^{0.95})C(s^{1.1}p^{3.0})S(s^{1.7}p^{2.9}d^{1.2})O(s^{1.8}p^{4.5})$

Figure 2. Electron densities in frontier molecular orbitals of DMSO.

by 0.16 at O compared with the HOMO. Excitation of an electron from one of the upper occupied frontier orbitals to one of the lower unoccupied frontier orbitals should thus involve an increase of electron density at sulphur and a decrease at oxygen, but with the negative end of the S—O dipole of the electronically excited DMSO still at the oxygen atom.

This result is in agreement with the observed hypsochromic shift of the absorption maximum of DMSO from 215 nm ( $\epsilon \approx 2000$ ) in cyclohexane to 212 nm in methanol and 206 nm in water. Assuming that this shift is mainly due to stabilization of the DMSO ground state by formation of a hydrogen bond,  $(CH_3)_2S=\overset{\delta-}{O} \cdots H-OH$ , the strength of this bond is calculated to be about 6 kcal/mole.

Application of the CNDO/2 method also allowed us to calculate the dipole moment of ground state DMSO to be 3.9 Debye and the energy of the triplet state of DMSO to be 90 kcal/mole whereas 4.3 Debye<sup>11</sup> and  $83 \pm 3$  kcal/mole (see below) were obtained experimentally.

Since DMSO showed neither fluorescence nor phosphorescence emission, the energies of the first excited singlet and triplet states of DMSO were estimated from the onset of the u.v. absorption spectrum and from the onset of the xenon-catalysed  $S_0 \rightarrow T_1$ -absorption spectrum, respectively. Figure 3 shows the absorption spectra of neat DMSO in the absence and presence of xenon in the longest wavelength absorption region. Xenon exerts a heavy-atom effect and thus catalyses the spin-forbidden singlet-triplet absorp-

tion<sup>12,13</sup>. Extrapolation of the absorption curves leads to onsets at 36–37000  $\text{cm}^{-1}$  for the  $S_0 \rightarrow S_1$  and at  $29000 \pm 1000 \text{ cm}^{-1}$  for the  $S_0 \rightarrow T_1$  transitions which correspond to a singlet energy of  $E_S \approx 105 \text{ kcal/mole}$  and a triplet energy of  $E_T \approx 83 \pm 3 \text{ kcal/mole}$ , respectively.

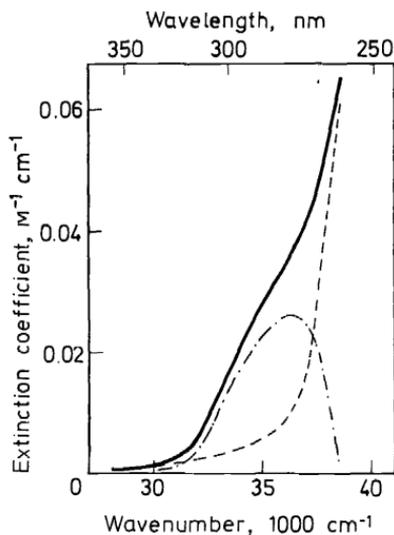


Figure 3. Longest wavelength region absorption spectra of neat DMSO and of DMSO in the presence of xenon.

----- : neat DMSO; ——— : DMSO + 0.15 M xenon;  
 - · - · - : 'Difference' spectrum indicates triplet absorption ( $S_0 \rightarrow T_1$ ).

From an energetic point of view, dissociation of electronically excited DMSO into dimethyl sulphide plus oxygen atom [ $D(S-O) = 89$  to  $90 \text{ kcal/mole}^{14}$ ] could occur only from the excited singlet state, whereas dissociation into methyl plus methanesulphinyl radicals [ $D(C-S) = 52.6 \text{ kcal/mole}^{15}$ ] could occur from the excited singlet as well as from the triplet state of DMSO.

## DIRECT PHOTOLYSIS OF DMSO

### Product analysis

The molar decadic extinction coefficient of DMSO at 254 nm varies between  $0.1 \text{ M}^{-1} \text{ cm}^{-1}$  (water) and  $0.2 \text{ M}^{-1} \text{ cm}^{-1}$  (acetonitrile). Irradiations of oxygen-free (and mercury-free) neat DMSO or 1 to 2 M DMSO solutions at 2537 Å were carried out for one or two hours during which 0.5 to 1 per cent of the starting amounts of DMSO were decomposed. In such low-conversion runs, the yields of all products increased linearly with time since the absorption conditions remained virtually the same.

Table 1 shows the products formed in units of  $10^{-6}$  moles. The limits of error are about  $\pm 10$  per cent for all products.

In alcoholic solvents, rather high amounts of hydrogen and oxidized

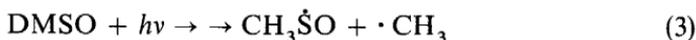
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solvents are formed. As we showed with isopropyl alcohol, irradiation for one hour in the absence of DMSO produced about  $400 \times 10^{-6}$  moles of hydrogen and the same amount of acetone, probably via disproportionation of  $2 \text{CH}_3\dot{\text{C}}(\text{OH})\text{CH}_3$  radicals<sup>16</sup>. In addition, DMSO is able to oxidize alcohols thermally to the corresponding carbonyl compounds<sup>17</sup>. Production of rather large quantities of dimethyl sulphide in methanol may be due to such a reaction. Therefore, most of the further studies on the direct photolysis of DMSO were performed by using acetonitrile and water as solvents.

**Photodissociation and disproportionation reactions**

According to the results obtained for direct photolyses of DMSO in acetonitrile and in water, photodissociation of a C—H bond may be excluded because of the absence of hydrogen among the photolysis products. Similarly, photodissociation of the S—O bond to give dimethyl sulphide and oxygen atom seems to be rather unlikely, although dimethyl sulphide is one of the main products. If this process were occurring, the fate of most of the oxygen atoms would remain unaccounted for since only minor amounts of their most likely reaction product, dimethyl sulphone, are formed. As shown below, the kinetics of dimethyl sulphone production together with those for methane formation disfavour such an S—O bond-breaking process.

To account for products such as methane, methanesulphonic acid, and dimethyl disulphide, a C—S bond cleavage of DMSO has to be considered. If this cleavage occurs as an  $\alpha$ -split reaction



the methyl radicals may abstract hydrogen from either the solvent or DMSO

Table 1. Irradiation of DMSO†

Conditions: Products	2 M in CH <sub>3</sub> CN 1h	2 M in H <sub>2</sub> O 2h	neat 1h	2 M in CH <sub>3</sub> OH 1h	1 M in C <sub>2</sub> H <sub>5</sub> OH 1h	1 M in <i>i</i> -C <sub>3</sub> H <sub>7</sub> OH 1h
CH <sub>4</sub>	170	190	180	160	160	200
H <sub>2</sub>	t‡	t	t	120	250	300
CO	t	t	t	t	t	t
C <sub>2</sub> H <sub>6</sub>	t	t	6	t	t	t
CH <sub>3</sub> SO <sub>3</sub> H	65	110	150	60	50	60
CH <sub>3</sub> SCH <sub>3</sub>	110	90	300	340	120	140
CH <sub>3</sub> SO <sub>2</sub> CH <sub>3</sub>	20	60	100	30	40	30
CH <sub>3</sub> SSCH <sub>3</sub>	55	30	120	+¶	+	+
CH <sub>3</sub> SO <sub>2</sub> SCH <sub>3</sub>	t	10	t	t	t	t
CH <sub>3</sub> SH	t	t	t	t	t	t
(SO) <sub>x</sub>	t	t	t	t	t	t
(CH <sub>3</sub> SOCH <sub>2</sub> ) <sub>2</sub>	—§	—	—	—	—	—
CH <sub>2</sub> O	—	—	160	—	—	—
R—CO—R (H) from alcohol	—	—	—	+	100	670

† At 2537 Å; irradiation of  $4 \times 10^{-2}$  or  $2 \times 10^{-2}$  moles DMSO/20 ml solution; products in units of  $10^{-6}$  moles.

‡ t denotes traces; § — indicates qualitative analysis: negative; ¶ + indicates qualitative analysis: positive, no quantitative analysis performed.

molecules. Since practically no ethane or any other product is obtained that may be derived from reactions of methyl radicals, hydrogen abstraction should be the only reaction of  $\cdot\text{CH}_3$  in the system besides a possible cage recombination reaction to give ground state DMSO. The quantum yield of methane production  $\Phi_{\text{CH}_4}$ , should thus equal the quantum yield of the  $\alpha$ -split,  $\Phi_\alpha$ . Using 1 to 2-molar DMSO solutions,  $\Phi_{\text{CH}_4}$  was found to be 0.14, independent of the nature of the solvents used (all solvents of *Table 1*). If, however,

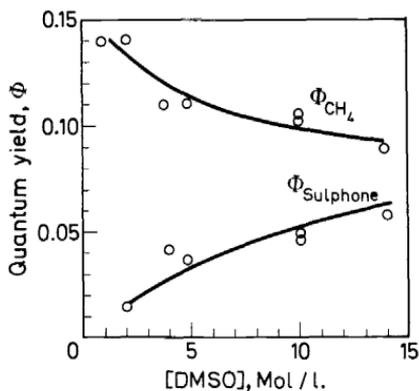
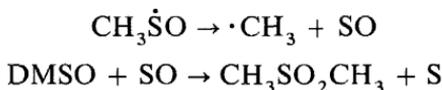


Figure 4. Direct photolysis of DMSO in solution. Quantum yields of methane and dimethyl sulphone production as a function of DMSO concentration.

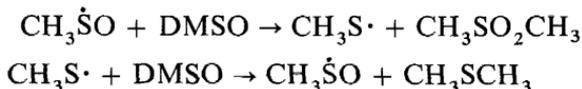
the concentration of DMSO was raised,  $\Phi_{\text{CH}_4}$  dropped to 0.09 for neat DMSO. Again, the quantum yields were independent of whether the photolysis took place in acetonitrile or water. The results presented in *Figure 4* show that DMSO quenches the  $\alpha$ -split reaction to an extent that is obviously related to an increase in the quantum yield of dimethylsulphone formation,  $\Phi_{\text{sulphone}}$ .

Dimethyl sulphone formation according to



is excluded since practically no  $(\text{SO})_x$  and sulphur were found.

Dimethyl sulphone formation according to



as discussed for sulphone formation when thiolsulphinates,  $\text{R}-\text{SO}-\text{S}-\text{R}$ , are photolysed<sup>18</sup>, or sulphone production according to a mechanism as discussed above



or as occurring as a disproportionation reaction according to



should be considered.

Since DMSO is a very poor H-donor even for methyl radicals (see below), one would expect that, with methanesulphinyl and methanesulphenyl radicals being practically incapable of abstracting hydrogen from DMSO, dimethyl sulphone formation should exceed methane formation when neat DMSO is photolysed. This, however, is not so and therefore renders dimethyl sulphone production via sulphinyl and sulphenyl radicals rather unlikely.

In order to allow DMSO to quench the methane formation (see *Figure 4*), the  $\alpha$ -split should occur from an electronically excited DMSO molecule which possesses a long enough lifetime to suffer quenching in a bimolecular process:



Since the quantum yields  $\Phi_{\text{CH}_4}$  and  $\Phi_{\text{sulphone}}$  do not add up to unity, decaying of  $\text{DMSO}^*$  to its ground state should efficiently compete with the chemical reactions.



If dimethyl sulphone formation occurred according to equations (4) and (5), one had to make the additional assumptions (9) and (10)

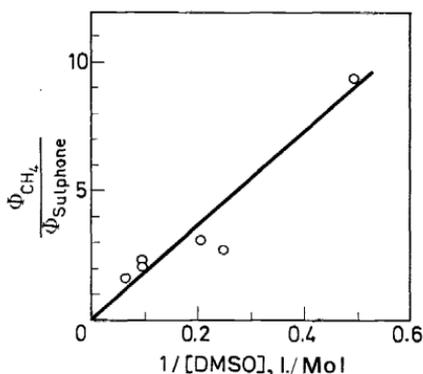


with X being a substrate that is oxidized by O atoms, in order to explain the observed dependence of  $\Phi_{\text{CH}_4}$  and  $\Phi_{\text{sulphone}}$  on  $[\text{DMSO}]$ .

According to these assumptions,

$$\Phi_{\text{CH}_4} / \Phi_{\text{sulphone}} = (k_7/k_4)(1 + k_{10}[\text{X}]/k_5[\text{DMSO}]) \quad (11)$$

is derived which should give  $k_7/k_4 \neq 0$  (and according to *Table 1*, see yields of  $\text{CH}_4$  and  $\text{CH}_3\text{SCH}_3$ , certainly  $> 1$ ), and  $k_7k_{10}[\text{X}]/k_4k_5$  as a slope.



*Figure 5.* Direct photolysis of DMSO in solution.  $\Phi_{\text{CH}_4} / \Phi_{\text{Sulphone}}$  as a function of the reciprocal DMSO concentration.

With reactions (6), (7) and (8), however, and without any further assumption,

$$\Phi_{\text{CH}_4}/\Phi_{\text{sulphone}} = k_7/k_6 [\text{DMSO}] \quad (12)$$

A plot of  $\Phi_{\text{CH}_4}/\Phi_{\text{sulphone}}$  versus  $1/[\text{DMSO}]$  should result in a straight line that passes through the origin of the coordinate system for  $1/[\text{DMSO}]$  extrapolated to zero. The slope of the curve then represents  $k_7/k_6$ .

Figure 5 shows the results which are only compatible with the assumption that dimethyl sulphone production occurs via the disproportionation reaction (6). The slope is found to be 18 M, which means that in 1-molar DMSO solutions, the  $\alpha$ -split is about twenty times faster than the disproportionation reaction.

### The reacting electronically excited state

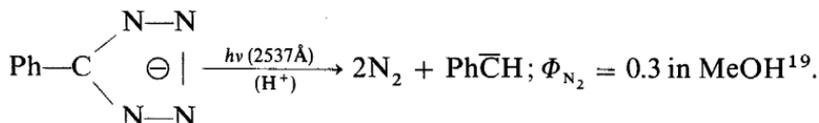
In order to establish the nature of the electronically excited state from which the primary processes (6) and (7) occur, a number of experiments were made which show that these reactions occur directly from the electronically excited *singlet* state of DMSO.

Whereas neat DMSO does not absorb light at 3000 Å, DMSO in the presence of 0.15 M xenon absorbs about 65 per cent of this light if it passes through a 2 cm cell (see Figure 3). Irradiation of such a solution, however, produced methane with a quantum yield of only about 0.004. If the absorption is due to an  $S_0 \rightarrow T_1$  transition as discussed, the triplet-DMSO undergoes the  $\alpha$ -split to an extent that is about 4.5 per cent of that of the excited state reached by direct absorption at 2537 Å.

Since olefins and dienes absorb considerable amounts of light at 2537 Å, quenching of the  $\alpha$ -split reaction and dimethyl sulphone production was carried out by using molecular oxygen. Irradiation of 1-molar DMSO solutions saturated with oxygen (about  $2 \times 10^{-3}$  M oxygen) reduced  $\Phi_{\text{CH}_4}$  from 0.14 to 0.12 whereas the small value of  $\Phi_{\text{sulphone}}$  of about 0.01 remained unchanged within the limits of error.

Sensitization of both primary processes (6) and (7) was not achieved with such efficient triplet sensitizers as benzophenone ( $E_T = 68$  kcal/mole) or acetone ( $E_T = 80$  kcal/mole). If  $E_T$  of DMSO is indeed  $83 \pm 3$  kcal/mole as discussed in the preceding paragraphs, the energy transfer should have a very low probability. Use of benzene as a sensitizer ( $E_T = 85$  kcal/mole), resulted in the formation of methane. However, sensitization is completely due to singlet-singlet energy transfer as will be shown in the next section. In favour of a singlet-singlet energy transfer is the observation that DMSO quenches the benzene fluorescence, and the inefficiency of olefins such as cyclohexene to quench the energy transfer process as well as the  $\alpha$ -split of DMSO certainly argues against a triplet mechanism.

Tetra-*n*-butylammonium-5-phenyl tetrazolide is photolysed in protic solvents such as alcohols exclusively via its triplet state to give nitrogen and phenyl carbene<sup>19, 20</sup>



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Small amounts of 2,4-hexadiene quench the yield of nitrogen rather efficiently.

Irradiation of 0.05 M tetrazolide ( $\epsilon = 9700 \text{ M}^{-1} \text{ cm}^{-1}$ ) in methanol at 2537 Å for one hour yielded  $430 \times 10^{-6}$  mole nitrogen, which means that  $590 \times 10^{-6}$  mole of tetrazolide-triplets were formed during the irradiation period since  $\Phi_{\text{isc}} = 0.41^{19,20}$  and two moles of nitrogen are produced from one mole of tetrazolide-triplets.

DMSO quenches the decomposition of the tetrazolide; quenching obviously obeys a Stern-Volmer mechanism according to

$$\Phi_{\text{N}_2}^0 / \Phi_{\text{N}_2} = 1 + K[\text{DMSO}] \quad (13)$$

where  $\Phi_{\text{N}_2}^0$  and  $\Phi_{\text{N}_2}$  are the quantum yields of nitrogen in the absence and presence of DMSO, respectively, and  $K$  denotes  $k_q \tau_{\text{exc, state}}$ , where  $k_q$  is the rate constant of quenching by DMSO and where  $\tau_{\text{exc, state}}$  is the lifetime of the unquenched excited state tetrazolide.

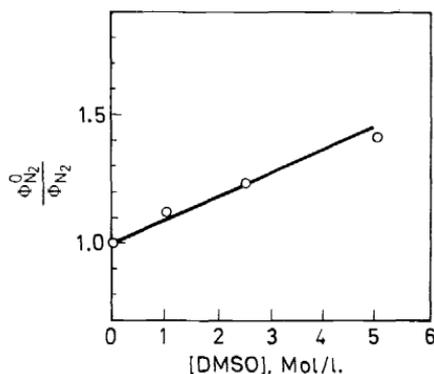


Figure 6. Photolysis of phenyl tetrazolide at 2537 Å. Quenching of nitrogen formation by DMSO.

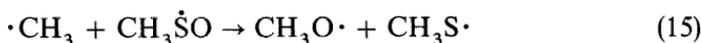
The kinetics are compatible with quenching of a singlet or a triplet state of the tetrazolide. However, if DMSO quenches the singlet-tetrazolide and if this process is connected with an energy transfer, a singlet state of DMSO should be formed and thus should give rise to methane production since direct excitation of DMSO also results in methane formation. In the presence of 5 M DMSO, nitrogen evolution is reduced to about 70 per cent of the original amount. This means,  $590 \times 10^{-6} \times 0.3 = 180 \times 10^{-6}$  mole methane should have been produced if singlet quenching were involved. However, although methane amounts as low as  $0.5 \times 10^{-6}$  mole could be determined by the procedure applied, no methane formation was detected. Thus, we conclude that the quenching observed is due only to triplet quenching. In accord with this conclusion is the rather low efficiency of the quenching process (high amounts of DMSO are needed) since  $E_T$  of DMSO is higher by only about 3 kcal/mole as compared with  $E_T$  of the tetrazolide. The triplet-DMSO if simultaneously formed in the quenching process exerts chemical stability, in accord with our other observations. Therefore, the primary processes (6) and (7) occur with all probability from the excited singlet state of DMSO.

## Reactions subsequent to the primary fragmentation reaction

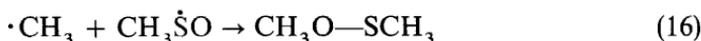
Cage-recombination reactions to give DMSO



or to result in either disproportionation



or in formation of methyl methanesulphenate



with subsequent photolytic cleavage to radicals  $\text{CH}_3\text{O}\cdot$  and  $\text{CH}_3\text{S}\cdot$  are rather unlikely since no methanol was found† as would be expected if  $\text{CH}_3\text{O}\cdot$  were formed, and since the quantum yield of methane formation during photolysis of methyl isoamyl sulphoxide was found to be independent of the viscosities of the solvents used (Table 2). Methyl isoamyl sulphoxide was applied because DMSO was rather insoluble in *n*-alkanes; its use seems to be justified since  $\Phi_{\text{CH}_4}$  equals one half that of DMSO as may be expected from a  $\text{CH}_3-\text{SO}-\text{CH}_2\text{R}$ -molecule.

Table 2. Irradiation of 1 M methyl isoamyl sulphoxide in *n*-alkanes†. Dependence of  $\text{CH}_4$  formation on solvent viscosity

Solvent	Viscosity [cP]	Temperature [°C]	Yield of $\text{CH}_4$ [ $10^{-6}$ mole <sup>4</sup> ]	$\Phi_{\text{CH}_4}$
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	0.2	30	126	~0.07
<i>n</i> -C <sub>8</sub> H <sub>18</sub>	0.47	30	128	
<i>n</i> -C <sub>10</sub> H <sub>22</sub>	0.77	30	115	
<i>n</i> -C <sub>16</sub> H <sub>34</sub>	1.5	60	137	

† At 2537 Å; irradiation of  $2 \times 10^{-2}$  moles of methyl isoamyl sulphoxide/20 ml solution for one hour.

Another cage-reaction during which hydrogen transfer takes place to give a sulphin and methane



as discussed in the case of certain cyclic sulphoxides<sup>23, 24</sup> is excluded since neither formaldehyde nor sulphur is produced during DMSO photolysis. Both these products would be expected since sulphins are known to decompose into sulphur and the corresponding carbonyl compounds<sup>23-26</sup>. Furthermore, methyl radicals give rise to methane exclusively by hydrogen abstraction from the solvent (see below).

Dimerization of methyl radicals as well as of methanesulphinyl radicals to give ethane and methyl methanethiolsulphonate, respectively, are rather unimportant (see Table 1); in direct photolysis of neat DMSO, however, the latter reaction seems to be the only one which the methanesulphinyl radicals are able to undergo. The origin of the traces of methyl methanethiolsulphonate that appear during photolysis of DMSO in various solvents seems to be

† Diisopropyl and di-*t*-butyl sulphoxides, however, afford the corresponding alcohols<sup>21, 22</sup>.

due to other reactions than dimerization of the sulphinyl radicals (see below).

From an energetic point of view, hydrogen abstraction from alcohols and acetonitrile appears to be possible with methyl as well as with methanesulphinyl radicals; however, only methyl radicals might be able to abstract hydrogen from benzene, and none of the radicals should abstract hydrogen atoms from water†.

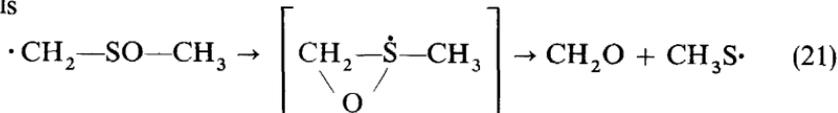


In accord with the energetic considerations, methane and methanesulphonic acid (the oxidation product of the methanesulphonic acid) are observed during photolysis of DMSO in acetonitrile or alcohols; in benzene, however, only methane is found. That the fourth hydrogen does originate exclusively from the solvent molecules is shown by the fact that DMSO- $d_6$  photolysis in non-deuterated solvents results in the formation of  $\text{CHD}_3$  with only traces (much less than one per cent) of  $\text{CD}_4$ ‡, as was determined mass spectroscopically.

Hydrogen abstraction from DMSO itself thus appears to be energetically unfavourable; however, in neat DMSO, methane formation seems to be due exclusively to hydrogen abstraction from DMSO thereby yielding 'dimethyl' radicals according to



Rather little is known about the reactions of dimethyl radicals<sup>29</sup>. However, the appearance of rather high amounts of formaldehyde and the absence of  $\text{CH}_3\text{—SO—CH}_2\text{—CH}_2\text{—SO—CH}_3$  during photolysis of neat DMSO can be accounted for qualitatively as well as quantitatively by assuming that dimethyl radicals decompose to give formaldehyde and methanesulphenyl radicals



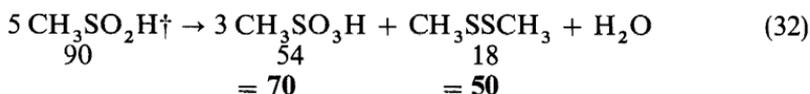
The unusually high amount of dimethyl disulphide produced during photolysis of neat DMSO is then due to its additional formation via dimerization of  $\text{CH}_3\text{S}\cdot$  radicals. Decomposition of dimethyl radicals to give methyl mercaptan and formyl radicals as well as dimerization of  $\text{CH}_3\text{—SO—}\dot{\text{C}}\text{H}_2$  are

† The following values were either taken from refs. 27 and 28 or calculated from the enthalpies of formation<sup>15</sup>.

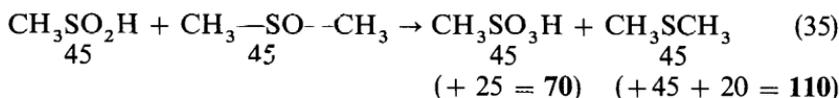
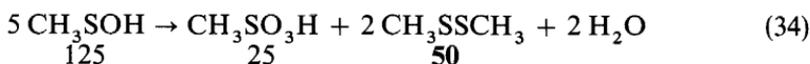
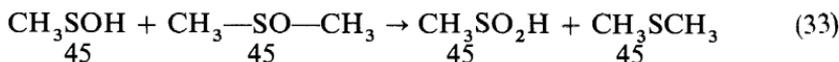
‡ No H/D exchange occurs in non-irradiated solutions at room temperature or slightly elevated temperatures.



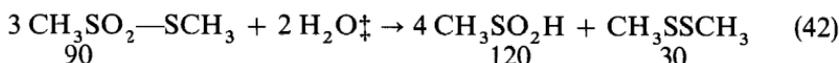
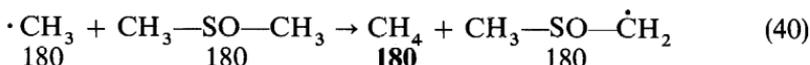
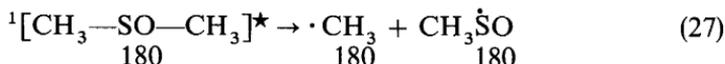
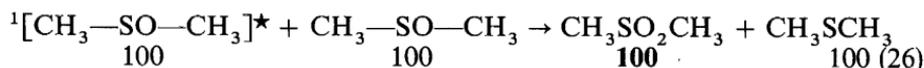
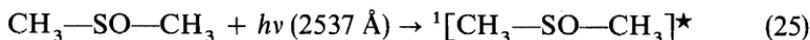
## PHOTOLYSIS OF DIMETHYL SULPHOXIDE IN SOLUTION



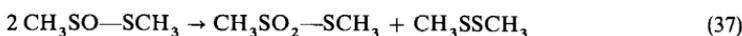
The amounts of products calculated (bold type) and found (Table 1) are in good agreement. However, if it is assumed that methanesulphinic acid is exclusively oxidized by DMSO to give methanesulphonic acid, reactions (30), (31) and (32) are replaced by reactions (33), (34) and (35):



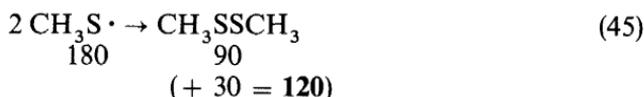
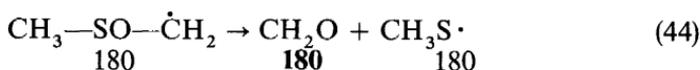
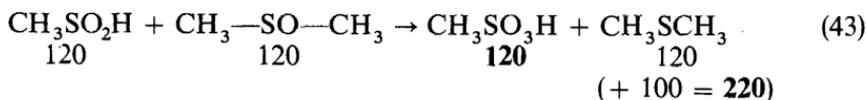
Again, the material balances calculated and found are in good agreement. The proposed reaction sequences occur (at least partly) also in alcoholic solutions if we take into account the side reactions that lead to greater amounts of hydrogen and carbonyl compounds as was already discussed.

*Direct photolysis of neat DMSO:*


† The overall reactions (31) and (32) are composed of the reaction sequences (36), (37), (38) and (39)/(38), respectively;



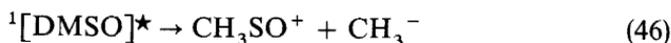
‡ DMSO is very hygroscopic. Thus, the water amount necessary for reaction (42) is certainly present in neat DMSO.



*Direct photolysis of DMSO in water:*

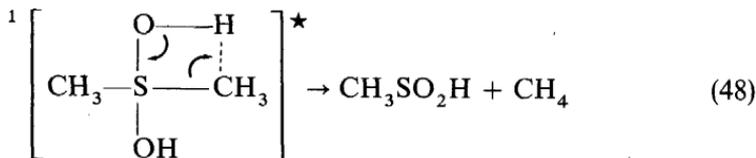
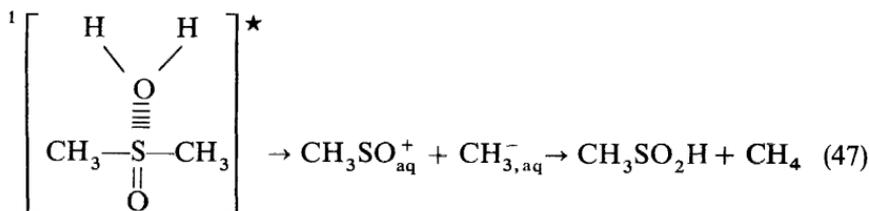
Irradiation of DMSO in water leads qualitatively and quantitatively to the same products as are found during photolysis of DMSO in acetonitrile. Furthermore, if DMSO-d<sub>6</sub> (2 M) is photolysed in water, methane, formed with a quantum yield of  $\Phi_{\text{CH}_4} = 0.14$ , consists only of CHD<sub>3</sub>, as was determined mass spectroscopically; thus, the fourth hydrogen originates totally from water molecules. Since no H/D exchange takes place when DMSO-d<sub>6</sub> is dissolved in water as was observed mass spectroscopically with recovered DMSO-d<sub>6</sub>, and since neither methyl nor methanesulphinyl radicals are able to abstract hydrogen atoms from water, a number of 'non-radical pathways'<sup>5</sup> should be considered:

(1) direct ionic  $\alpha$ -split according to

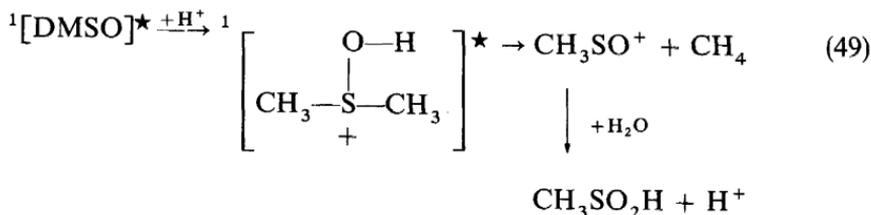


followed by reaction with water to give CH<sub>3</sub>SO<sub>2</sub>H + CH<sub>4</sub>;

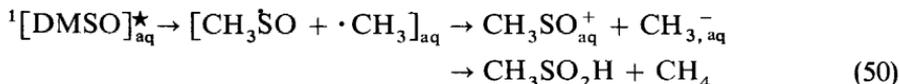
(2) direct ionic or molecular  $\alpha$ -split of DMSO/H<sub>2</sub>O complexes such as



(3) acid-catalysed  $\alpha$ -split according to



or (4) electron transfer between the primary radicals according to

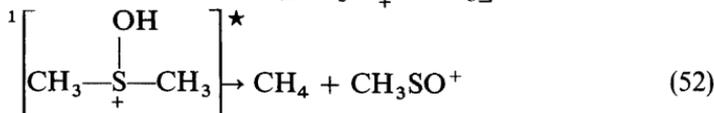
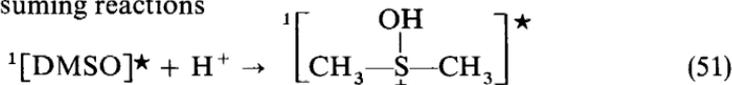


Reaction (46) is excluded since 216 kcal/mole<sup>15</sup> are required for this type of heterolysis whereas only 112 kcal/mole are available by irradiation with 2537 Å†.

Reaction (47) may be energetically feasible if the solvation energies exceed about 110 kcal/mole. However, reaction (47) as well as reactions (48) and (49) should not necessarily occur with the same quantum yield with which the  $\alpha$ -split in acetonitrile occurs; furthermore, small amounts of benzene should not inhibit the formation of methanesulphinic acid as they in fact do (see below).

According to reaction (48), a <sup>16</sup>O/<sup>18</sup>O exchange in DMSO is expected to occur when DMSO is photolysed in H<sub>2</sub><sup>18</sup>O. No such exchange occurs thermally in neutral aqueous solution<sup>32</sup> as we found by means of mass spectroscopy. When DMSO was irradiated in H<sub>2</sub><sup>18</sup>O/H<sub>2</sub><sup>16</sup>O mixtures (1:1) for four hours at 2537 Å, again no <sup>16</sup>O/<sup>18</sup>O exchange was detected in the recovered DMSO. If, however, the same solution was treated with concentrated sulphuric acid and heated to 100° for four hours, a statistical distribution of <sup>16</sup>O and <sup>18</sup>O was found, in agreement with the observation by Oae and co-workers<sup>33, 34</sup>.

According to the latter authors,  $\text{CH}_3-\overset{\text{OH}}{\underset{+}{\text{S}}}-\text{CH}_3$  (ground state) is formed in strongly acidic solution. The cation adds to H<sub>2</sub>O and thus <sup>16</sup>O/<sup>18</sup>O exchange occurs. If we assume that such an exchange would also take place with a singlet excited cation,  ${}^1\left[\text{CH}_3-\overset{\text{OH}}{\underset{+}{\text{S}}}-\text{CH}_3\right]^{\star}$  as formulated in (49), the absence of a <sup>16</sup>O/<sup>18</sup>O exchange excludes reaction (49) as a possible 'non-radical pathway'. Furthermore, according to reaction (49), the  $\alpha$ -split and thus the quantum yield of methane formation should depend on the pH of the solution. Assuming reactions



† Heterolysis to give  $\text{CH}_3\text{SO}^- + \text{CH}_3^+$  requires 245 kcal/mole<sup>15</sup> and is therefore excluded. Furthermore,  $\text{CH}_3^+$  in water should give methanol which was not observed.

a plot of  $\log (1 - \Phi_{\text{CH}_4})/\Phi_{\text{CH}_4}$  versus pH should result in a straight line with a slope of unity since

$$\log (1 - \Phi_{\text{CH}_4})/\Phi_{\text{CH}_4} = \text{pH} + \log K \quad [\text{with } K = k_8(k_{52} + k_{53})/k_{51} \times k_{52}]. \quad (54)$$

However,  $\Phi_{\text{CH}_4}$  is practically independent of the pH between zero and about five, and it decreases only very slightly with increasing pH as is indicated by a slope of 0.07 in the neutral and alkaline region (see Figure 7).

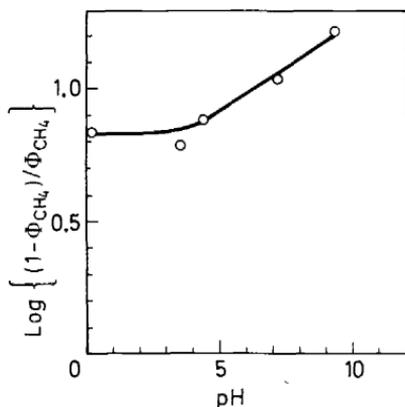


Figure 7. Direct photolysis of DMSO in water. Dependence of the methane quantum yield on the pH of the solution.

The observations made so far are all easily explained if we assume that (1) C—S bond cleavage of excited singlet DMSO to give  $\text{CH}_3$  and  $\text{CH}_3\text{SO}$  radicals is independent of the nature of the solvent used, and that (2) electron transfer between the radicals takes place to give  $\text{CH}_3\text{SO}_{\text{solv}}^+$  and  $\text{CH}_3^{\text{solv}-}$  if the solvent is able to stabilize the ions by solvation, as is indicated by reaction sequence (50).

One would expect then that, using alcohols as solvents, competition between hydrogen atom abstraction by radicals and electron transfer from  $\text{CH}_3\text{SO}$  to  $\cdot\text{CH}_3$  occurs that depends on the solvating power of the alcohols for ions. Using alcohols  $\text{RR}'\text{CH—OD}$ , hydrogen abstraction by  $\cdot\text{CH}_3$  should result in  $\text{CH}_4$  formation, whereas electron transfer to give  $\text{CH}_3^{\text{solv}-}$  followed by reaction with the *O*-deuterated alcohol should afford  $\text{CH}_3\text{D}$ . Formation of  $\text{CH}_3\text{D}$  via deuterium abstraction by methyl radicals should be negligible at room temperature according to the latest data available<sup>28c</sup>.

Table 3. Irradiation of 1 M DMSO† in *O*-deuterated alcohols

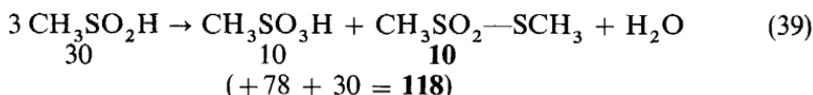
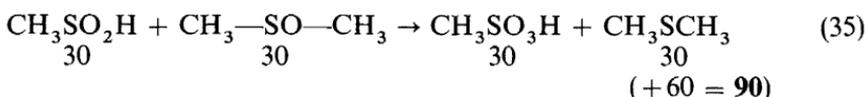
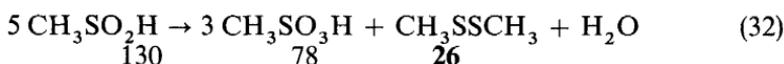
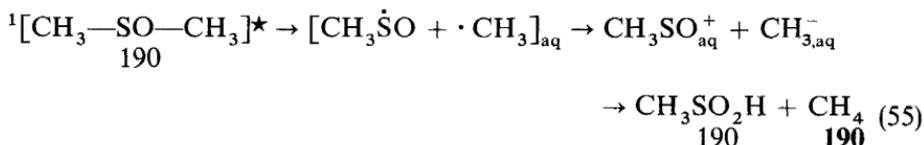
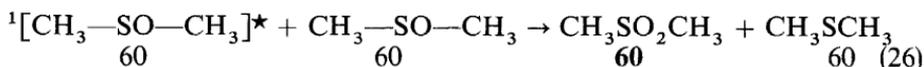
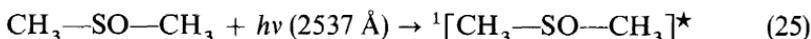
Solvent	Molar ratio $\text{CH}_4:\text{CH}_3\text{D}$	% 'Non-radical pathway'
$\text{CH}_3\text{OD}$	1:1	50
$\text{CH}_3\text{CH}_2\text{OD}$	3:1	25
$(\text{CH}_3)_2\text{CHOD}$	11:1	8

† At 2537 Å; irradiation of  $2 \times 10^{-2}$  moles of DMSO/20 ml solution for one hour.

Table 3 shows the results obtained with *O*-deuterated methanol, ethanol and isopropanol. The quantum yield of methane ( $\text{CH}_4 + \text{CH}_3\text{D}$ ) formation is 0.14 in each case, whereas the ratio of  $\text{CH}_4 : \text{CH}_3\text{D}$  varies with the solvent in the expected manner.

Still another support for the assumed mechanism [equation (50)] is obtained from the benzene-sensitized photolysis of DMSO in water/methanol mixtures. If the DMSO photolysis is sensitized by hexadeutero-benzene in  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  (1:1), only  $\text{CH}_4$  is observed. This indicates that benzene does not serve as a hydrogen donor. If then photolysis of DMSO (4 M) is sensitized by benzene (0.5 M) in  $\text{D}_2\text{O}/\text{CH}_3\text{OD}$  (1:1), methane produced with a quantum yield of 0.01 consists of 95 per cent of  $\text{CH}_4$  and only 5 per cent of  $\text{CH}_3\text{D}$ . This means that the fourth hydrogen of methane originates practically exclusively from the methyl group of methanol. In addition, none of the other products such as  $\text{CH}_3\text{SO}_3\text{H}$ ,  $\text{CH}_3\text{SCH}_3$  etc. are observed; instead, polymeric sulphur-containing products are obtained. Since benzene sensitization leads to  $^1[\text{DMSO}]^*$  (see next paragraph), singlet excited DMSO dissociates to give  $\text{CH}_3$  and  $\text{CH}_3\text{SO}$  radicals, the latter of which are immediately trapped by benzene and thus cannot take part in an electron transfer reaction. Therefore, only methyl radicals (but no methyl anions) remain that abstract hydrogen from the methyl group of  $\text{CH}_3\text{OD}$  to give  $\text{CH}_4$ .

We can now account qualitatively as well as quantitatively for all products formed during direct photolysis of DMSO in water:



## BENZENE-SENSITIZED PHOTOLYSIS OF DMSO

### Product analysis and quantum yields

No chemical change of DMSO is observed when triplet sensitizers such as acetone, propiophenone or benzophenone with energies below 80 kcal/mole are used. However, with benzene ( $\epsilon_{254} = 250$ ) as a sensitizer, decomposition of DMSO occurs as is indicated by the formation of methane. In con-

trast to direct photolysis of DMSO in various solvents, sulphur-containing products such as methanesulphonic acid, dimethyl sulphide, dimethyl sulphone etc. were found either not at all or only in traces when the benzene-sensitized photolysis of DMSO was carried out in neat DMSO, acetonitrile or methanol/water mixtures. Thus, disproportionation between an excited DMSO molecule and an unexcited DMSO molecule to give dimethyl sulphone and dimethyl sulphide is completely suppressed, and the methanesulphinyl radicals are totally trapped by benzene as is indicated by the polymeric sulphur-containing material obtained in benzene-sensitized reactions. As already shown, hydrogen abstraction by methyl radicals occurs only with solvent molecules since hexadeutero-benzene-sensitized photolysis of DMSO in  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  leads exclusively to  $\text{CH}_4$ .

One might assume that part of the methyl radicals formed are also trapped by benzene. When DMSO is photolysed in neat benzene, the fourth hydrogen of methane originates from benzene; methyl radicals are able to abstract hydrogen from the aromatic compound. Photolysis of DMSO in toluene which possesses more easily abstractable hydrogen atoms in the methyl group gives rise to methane formation with the same quantum yield as is found for the benzene-sensitized reaction. We therefore conclude that all methyl radicals formed abstract hydrogen from either the aromatic compound (if the photolysis is carried out in neat aromatic solution) or from solvent molecules (acetonitrile, alcohols if the photolysis is benzene-sensitized in dilute solutions) rather than add to the aromatic sensitizers. Thus,  $\Phi_{\text{CH}_4}$  is considered to represent the quantum yield of the  $\alpha$ -split,  $\Phi_\alpha$ , as it does in direct DMSO photolysis.

In benzene-sensitized photolysis of DMSO, the quantum yield of the methane formation is a function of the DMSO concentration (Figure 8) as well as of the sensitizer (benzene) concentration (Figure 9).

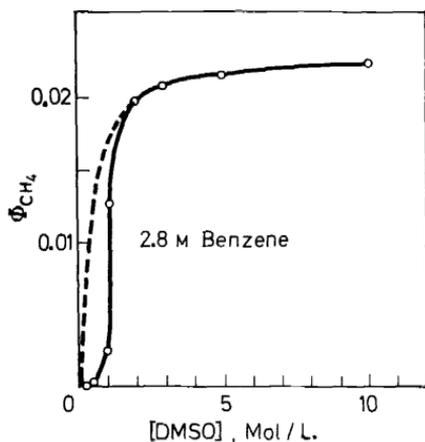


Figure 8. Benzene-sensitized photolysis of DMSO. Dependence of the methane quantum yield on the DMSO concentration.

—; experimental curve; - - -: curve calculated by assuming energy transfer from singlet-excited benzene monomers to DMSO exclusively.

## PHOTOLYSIS OF DIMETHYL SULPHOXIDE IN SOLUTION

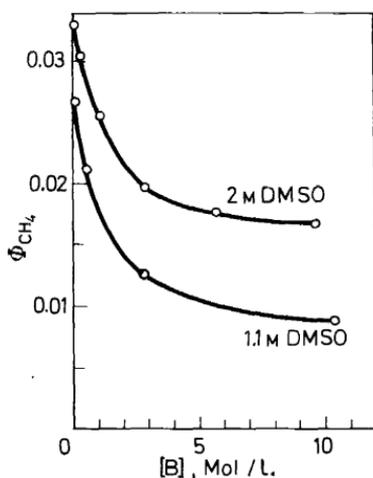


Figure 9. Benzene-sensitized photolysis of DMSO. Dependence of the methane quantum yield on the benzene concentration.

**Energy transfer from singlet excited benzene to DMSO**

From an energetic point of view, energy transfer from benzene ( $E_S = 108$  kcal/mole<sup>35</sup>,  $E_T = 85$  kcal/mole<sup>36</sup>) to DMSO can occur as singlet-singlet as well as triplet-triplet energy transfer. Methane formation as a consequence of an  $\alpha$ -split of a triplet-excited DMSO molecule is rather unlikely as was discussed in the preceding paragraph. Thus, methane formation should occur via a singlet-excited DMSO molecule which in turn should be produced by an energy transfer from singlet-excited benzene (excluding exciplex formation etc. for the present discussion).

Olefins are known to quench the excited singlet as well as the triplet state of benzene<sup>37-40</sup>; however, rather high concentrations of olefins are needed to quench singlet benzene. When 1.1 M DMSO in benzene or 1.1 M DMSO in acetonitrile in the presence of 0.1 M benzene is photolysed in the presence

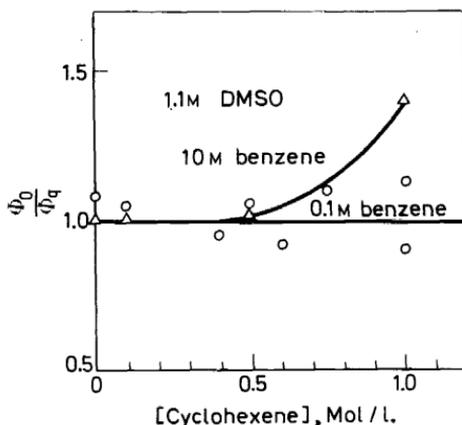


Figure 10. Benzene-sensitized photolysis of DMSO; quenching by cyclohexene.

of cyclohexene as a quencher, a rather inefficient quenching of methane formation is observed only at relatively high cyclohexene concentrations (Figure 10), in agreement with the assumption that only singlet states (of benzene and of DMSO) are involved in the dissociation process.

Singlet energy transfer from benzene to DMSO requires that the fluorescence of benzene is quenched by DMSO. Irradiation of 2.8 M benzene in diethyl ether in the presence of various amounts of DMSO led to a decrease of the fluorescence quantum yield of benzene with increasing DMSO concentration as is shown by the Stern-Volmer plot (Figure 11, curve 2).

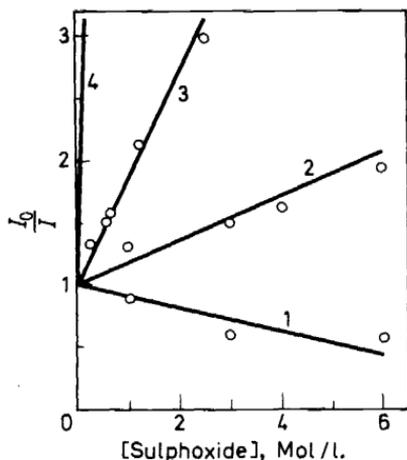


Figure 11. Quenching of the fluorescence of aromatic compounds by sulphoxides as a function of the sulphoxide concentration.

1: 2 M tetralin or mesitylene in the presence of DMSO; 2: 2.8 M benzene in the presence of DMSO; 3: 2.8 M benzene or 2 M mesitylene in the presence of diisopropyl sulphoxide; 4: 2.8 M benzene or 2 M mesitylene in the presence of di-*t*-butyl sulphoxide.

$$\lambda_{\text{exc.}} = 2537 \text{ \AA}; \lambda_f(\text{benzene}) = 283 \text{ nm}; \lambda_f(\text{tetralin, mesitylene}) = 293 \text{ nm}.$$

The fluorescence of *p*-cymene, tetralin and mesitylene ( $E_s = 103 \text{ kcal/mole}^{35}$ ) is not quenched by DMSO; in accord with this result, no methane formation is observed during the attempted photolysis of DMSO by these aromatic sensitizers<sup>†</sup>. However, if di-isopropyl sulphoxide or di-*t*-butyl sulphoxide (both sulphoxides possess  $E_s < 105 \text{ kcal/mole}$  as was estimated from their u.v. spectra) were used, the  $\alpha$ -split as well as the quenching of the fluorescence of benzene, *p*-cymene, tetralin and mesitylene were observed. With benzene as the sensitizer, the concentration of the sulphoxide at which the quantum yield of benzene fluorescence is reduced to one half that of the unquenched value is found to be 5.7 M for DMSO, 1.2 M for di-isopropyl sulphoxide, and 0.1 M for di-*t*-butyl sulphoxide. In agreement with the increasing power of these sulphoxides for fluorescence quenching, the quantum yields of the  $\alpha$ -splits increase in the order DMSO < di-isopropyl

<sup>†</sup> Rather high concentrations of DMSO had to be applied; thus, the physical properties of the solvent (ether) such as viscosity, polarity etc. are changed and this may lead to the otherwise unexpected slight negative slope of curve 1.

sulphoxide < di-*t*-butyl sulphoxide affording methane, propane/propene, and isobutane/isobutene, respectively.

### Kinetic results

Applying a simple Stern–Volmer mechanism according to reactions:



with B and  ${}^1B^*$  denoting benzene in its singlet ground state and singlet-excited state, respectively, yields

$$\Phi_{\text{CH}_4}^0 / \Phi_{\text{CH}_4} = 1 + k_{sq}^m [B] / \{k_0^m + (k_q^m + k_{ET}^m) [\text{DMSO}]\} \quad (63)$$

where  $\Phi_{\text{CH}_4}^0$  is the quantum yield of methane formation extrapolated to zero benzene concentration.

Equation (63) describes qualitatively the observation that  $\Phi_{\text{CH}_4}$  increases with increasing DMSO concentration (Figure 8) but decreases with increasing benzene concentration (Figure 9).

However, if  $\Phi_{\text{CH}_4}^0 / \Phi_{\text{CH}_4}$  is plotted versus  $[B]$ , no linear relation between the ratio of the  $\Phi$ -values and the benzene concentration is obtained (Figure 12).

A better agreement between the assumed mechanism and the experimental

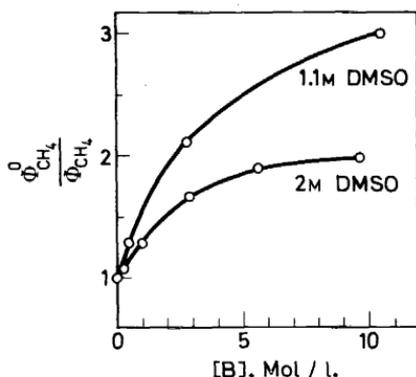
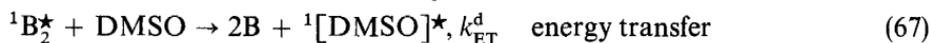


Figure 12. Benzene-sensitized photolysis of DMSO. Dependence of the methane quantum yield on the benzene concentration; plot of  $\Phi_{\text{CH}_4}^0 / \Phi_{\text{CH}_4}$  versus benzene concentration.

results is observed if, in addition to the reactions discussed above, the reversible formation of a benzene excimer<sup>35, 41-46</sup>



and its reactions



are taken into account. This mechanism leads to

$$\frac{\Phi_{\text{CH}_4}}{\Phi_{\text{CH}_4}^0 - \Phi_{\text{CH}_4}} = \frac{k_{\text{ET}}^m}{0.55 (k_{\text{ET}}^m \tau_m / \tau_d - k_{\text{ET}}^d)} \times \frac{1}{[\text{B}]} \quad (68)$$

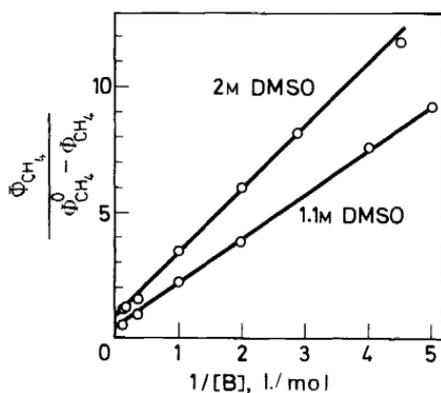
$$+ \frac{k_{\text{ET}}^d}{k_{\text{ET}}^m \cdot \tau_m / \tau_d - k_{\text{ET}}^d}$$

with

$$1/\tau_m = k_0^m + (k_q^m + k_{\text{ET}}^m) [\text{DMSO}] \quad (70)$$

$$1/\tau_d + k_0^d + (k_q^d + k_{\text{ET}}^d) [\text{DMSO}]. \quad (71)$$

A plot of  $\Phi_{\text{CH}_4}/(\Phi_{\text{CH}_4}^0 - \Phi_{\text{CH}_4})$  versus  $1/[\text{B}]$  should result in straight lines the slopes of which as well as their intercepts with the ordinate should depend on the DMSO concentrations applied. *Figure 13* shows the results.



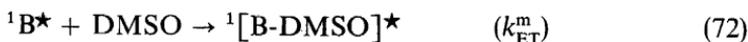
*Figure 13.* Benzene-sensitized photolysis of DMSO. Dependence of the methane quantum yield on the benzene concentration; plot of  $\Phi_{\text{CH}_4}/(\Phi_{\text{CH}_4}^0 - \Phi_{\text{CH}_4})$  versus reciprocal benzene concentration.

Extrapolation to  $[\text{B}] \rightarrow 0$  shows that energy transfer from monomeric singlet-excited benzene to DMSO occurs with a quantum yield of 0.22, since  $\Phi_{\text{CH}_4}([\text{B}] \rightarrow 0) = 0.033 = \Phi_{[\text{B}]_{\text{ET}0}}^m \times \Phi_q$  (see *Figure 9*). This value is in good agreement with the recently determined quantum yield of energy transfer from singlet-excited benzene to carbonyl sulphide<sup>47</sup>.

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Using the rate constant for the radiationless decay of monomeric singlet excited benzene and of the singlet excimer of benzene<sup>45</sup>, the quantitative treatment of the kinetic results shown in *Figure 11* and *Figure 13* (see Appendix) leads to rate constants for these species with DMSO that are about  $10^{-3}k_{\text{diff}}$ . For the bimolecular reaction of monomeric singlet-excited benzene with DMSO, such a small rate constant may be expected because of the closeness of the energy levels of  $^1\text{B}^*$  and  $^1\text{DMSO}^*$ . However, if the energy level of the singlet benzene excimer is about 6 kcal/mole below that of the singlet excited benzene monomer as reported<sup>43</sup>, one would expect that  $k_{\text{ET}}^{\text{d}}$  and  $k_{\text{q}}^{\text{d}}$  should be much smaller than the corresponding rate constants  $k_{\text{ET}}^{\text{m}}$  and  $k_{\text{q}}^{\text{m}}$ , since energy transfer from and quenching of the excimer by DMSO should be endothermic.

Our results indicate that either the energy levels of the singlet excited monomer and the excimer of benzene are closer than reported, or, if the energy difference between the two species is indeed as large as six kcal/mole, energy transfer from both singlet-excited benzene species leads to the same exciplex,  $^1[\text{B-DMSO}]^*$ , which decomposes to give  $\dot{\text{C}}\text{H}_3 + \text{CH}_3\dot{\text{S}}\text{O}$  (and thus finally  $\text{CH}_4$ ) or which deactivates to  $\text{B} + \text{DMSO}$ :



The same kinetics as before will be observed if these reactions (72) to (74) replace reactions (59) to (62) and (66), (67); however, no numerical values of  $k_{\text{ET}}^{\text{m}}$  and  $k_{\text{ET}}^{\text{d}}$  can be evaluated since  $k_{\text{p}}/(k_{\text{p}} + k_{\text{0}})$  can no longer be assumed to equal  $\Phi_{\alpha}$  (= 0.14) as determined for direct photolysis of DMSO in solution.

## APPENDIX

From the slopes and intercepts of the curves with the ordinate of *Figure 13* and applying

$$\Phi_{\text{CH}_4} = (\Phi_{\text{ET}}^{\text{m}} + \Phi_{\text{ET}}^{\text{d}}) \Phi_{\alpha} \quad (75)$$

where  $\Phi_{\alpha} = 0.14$  (from direct photolysis of DMSO), and  $\Phi_{\text{ET}}^{\text{m}}$  and  $\Phi_{\text{ET}}^{\text{d}}$  are the quantum yields of energy transfer to DMSO from singlet-excited benzene monomer and singlet benzene excimer, respectively, given by

$$\Phi_{\text{ET}}^{\text{m}} = \frac{k_{\text{ET}}^{\text{m}} [\text{DMSO}]}{\tau_{\text{m}}^{-1} + 0.55 [\text{B}] \tau_{\text{d}}^{-1}} \quad (76)$$

and

$$\Phi_{\text{ET}}^{\text{d}} = \frac{0.55 [\text{B}] k_{\text{ET}}^{\text{d}} [\text{DMSO}]}{\tau_{\text{m}}^{-1} + 0.55 [\text{B}] \tau_{\text{d}}^{-1}} \quad (77)$$

it is found that  $k_{ET}^m/k_{ET}^d = 2$ ,  $\tau_m/\tau_d = 1.17$  at 2 M DMSO and 1.67 at 1.1 M DMSO, and  $\Phi_{ET}^m/\Phi_{ET}^d = 3.6/[B]$ . Thus, methane production via sensitization by monomeric singlet-excited benzene according to

$$\Phi_{ET}^m \times \Phi_\alpha = \Phi_{CH_4} 3.6/(3.6 + [B]) \quad (78)$$

and methane production via sensitization by the benzene excimer according to

$$\Phi_{ET}^d \times \Phi_\alpha = \Phi_{CH_4} [B]/(3.6 + [B]) \quad (79)$$

may be calculated for 1.1 M DMSO (Figure 14) and 2 M DMSO (Figure 15).

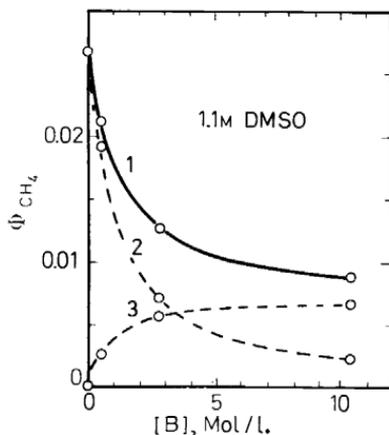


Figure 14. Benzene-sensitized photolysis of DMSO. Participation of singlet-excited benzene monomers (2) and singlet benzene excimers (3) in the sensitization process as a function of the benzene concentration. — denotes experimental quantum yield of methane formation; - - - indicates the calculated quantum yields by sensitization via singlet-excited benzene monomers (2) and via singlet benzene excimers (3). [DMSO] = 1.1 M.

Figures 14 and 15 allow us to obtain  $\Phi_{ET}^m$  and  $\Phi_{ET}^d$  as a function of  $[B]$  and thus to determine  $\Phi_{ET}^{m,0}/\Phi_{ET}^m$ , given by

$$\Phi_{ET}^{m,0}/\Phi_{ET}^m = 1 + 0.55 (\tau_m/\tau_d) [B] \quad (80)$$

with  $\Phi_{ET}^{m,0}$  denoting the quantum yield of energy transfer from monomeric singlet excited benzene extrapolated to  $[B] \rightarrow 0$ , as a function of  $[B]$ , and further, to determine  $1/\Phi_{ET}^d$  as a function of  $1/[B]$  at 1.1 M and 2 M DMSO. Figures 16 and 17 show the results; from the intercepts of the curves of Figure 17 with the ordinate,

$$\begin{aligned} 1/\Phi_{ET}^d &= 20 \text{ for 1.1 M DMSO and } 1/[B] \rightarrow 0 \\ &= 11 \text{ for 2 M DMSO and } 1/[B] \rightarrow 0 \end{aligned}$$

This leads to  $k_0^d/k_{ET}^d = 20$ , and since  $k_0^d = 3.7 \times 10^7 \text{ sec}^{-1}$ <sup>45</sup>, the rate constants of the energy transfer processes are calculated to be

$$k_{ET}^d = 1.9 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$$

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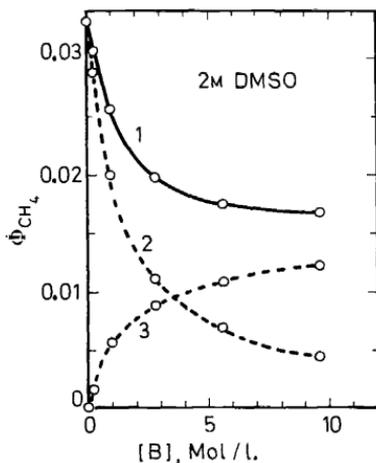


Figure 15. Benzene-sensitized photolysis of DMSO. Participation of singlet-excited benzene monomers (2) and singlet benzene excimers (3) in the sensitization process as a function of the benzene concentration. — denotes experimental quantum yield of methane formation; - - - - indicates the calculated quantum yields by sensitization via singlet-excited benzene monomers (2) and via singlet benzene excimers (3).  $[DMSO] = 2 M$ .

and

$$k_{ET}^m = 3.8 \times 10^6 M^{-1} sec^{-1}$$

which in turn allow determination of the lifetimes of monomeric singlet excited benzene and the singlet benzene excimer molecules to be

$$\tau_m = 4.0 \times 10^{-8} \text{ sec at } 1.1 M \text{ DMSO}$$

$$\tau_d = 2.4 \times 10^{-8} \text{ sec at } 1.1 M \text{ DMSO}$$

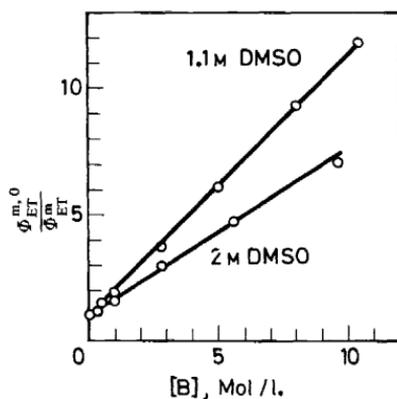


Figure 16. Benzene-sensitized photolysis of DMSO. Quantum yield of sensitization by singlet-excited benzene monomers as a function of the benzene concentration.

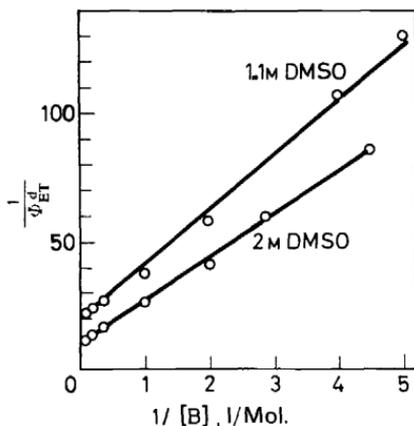


Figure 17. Benzene-sensitized photolysis of DMSO. Quantum yield of sensitization by singlet benzene excimers as a function of the benzene concentration.

and

$$\tau_m = 2.8 \times 10^{-8} \text{ sec at 2 M DMSO}$$

$$\tau_d = 2.4 \times 10^{-8} \text{ sec at 2 M DMSO}$$

According to the mechanism proposed,

$$\Phi_F^0/\Phi_F = 1 + \frac{k_q^m + k_{ET}^m + 0.55 [B] (k_q^d + k_{ET}^d)}{k_0^m + 0.55 [B] k_0^d} [\text{DMSO}] \quad (81)$$

where  $\Phi_F^0$  and  $\Phi_F$  are the quantum yields of benzene monomer fluorescence in the absence and presence of DMSO, respectively. From the slope of curve 2 of Figure 11 ( $= 0.18 \text{ M}^{-1}$ ),  $k_0^m = 3.13 \times 10^7 \text{ sec}^{-1}$ <sup>45</sup>,  $[B] = 2.8 \text{ M}$ , and  $k_q^d$ ,  $k_{ET}^d$ ,  $k_{ET}^m$  as given above, and the assumption that DMSO deactivates both excited benzene species at similar rates, it is found that  $k_q^m = k_q^d = 3 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ .

Thus, quenching of  ${}^1\text{B}_1^*$  and  ${}^1\text{B}_2^*$  seems to occur with similar rate constants that are about  $10^{-3}$  to  $10^{-4}$  times that of a diffusion-controlled rate constant at room temperature ( $k_{\text{diff}} \approx 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ ).

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