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FREE-RADICAL REACTIONS INVOLVING SULPHUR COMPOUNDS—III

PHOTOLYSIS OF AROMATIC DISULPHIDES

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Abstract—Dimesityl disulphide (MS-SM) proved to be a particular suitable model compound for investigating the photo-dissociation reaction of aromatic disulphides. The rate and mechanism of the photo-dissociation of MS–SM in the presence of an active hydrogen donor such as 9,10-dihydroanthracene was studied in a plurality of solvents. Generally, rate constants were found to decrease with increasing kinematic viscosity of the solvent.

In the formation of thiols upon irradiation of solutions of disulphides,[1] the solvent is generally thought to function as the hydrogen donor.[2] It has now been found, however, that thiols are also formed on irradiation of solutions of diphenyl disulphide *in hydrogen-free solvents*,[3] their amount increasing with time (Table 1). The formation of thiophenol could not be detected in the dark, however, even in the presence of an active hydrogen donor as, for example, 9,10-dihydroanthracene.

Table 1. Photolysis of 0·06 m solutions of diphenyl disulphide at 25°, in a nitrogen atmosphere. Standardized irradiation by fluorescent lamps

Solvent	Duration of irradiation (hr)	% S converted into thiol
Toluene	66	16
Dimethyl phthalate	66	16
Carbon tetrachloride	66	9
Tetrachloro ethene	66	8
Toluene	18	7
Toluene	42	13
Toluene	66	17
Toluene	90	22
Toluene	70	18·4[a]
Paraffin oil	66	9·3[b]

[a] Mean equivalent weight of thiols formed 170.
[b] Mean equivalent weight of thiols formed 169.

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[1] W. E. Lyons, *Nature, Lond.* **162**, 1004 (1948).

[2] C. Walling and R. Rabinowitch, *J. Amer. Chem. Soc.* **81**, 1137 (1959).

[3] See also Y. Schaafsma, *Chem. Weekblad* **54**, 61 (1958).

Presumably, a light-induced rearrangement of diphenyl disulphide occurs, for instance by the following reactions:

$$C_6H_5\text{–S–S–}C_6H_5 \xrightarrow{h\nu} 2C_6H_5\text{–S}\cdot \qquad (1)$$

$$C_6H_5\text{–S}\cdot + C_6H_5\text{–S}\cdot \longrightarrow C_6H_5\text{–S–}C_6H_4\text{–SH} \qquad (2)$$

$$C_6H_5\text{–S}\cdot + C_6H_5\text{–S–}C_6H_4\text{–SH} \longrightarrow C_6H_5\text{–SH} + C_6H_5\text{–S–}C_6H_4\text{–S}\cdot \qquad (3)$$

$$C_6H_5\text{–S–}C_6H_4\text{–S}\cdot + C_6H_5\text{–S}\cdot \longrightarrow \text{disulphides} \qquad (4)$$

This reaction scheme is supported by the mean equivalent weight of the thiols in the reaction product, which is 170, a value intermediate between 110 for thiophenol and 218 for the (*o*, *p*)-mercaptodiphenyl sulphide formed in reaction (2).

It is obvious that reactions (2), (3) and (4) interfere seriously with the following—otherwise appropriate—methods for investigating disulphide dissociation, viz. (a) photolysis in the presence of the stable free radical 1,1-diphenyl-2-picrylhydrazyl (P·),[4] which moreover reacts readily with thiols;[5] (b) photolysis in the presence of a suitable hydrogen donor.

We have succeeded in completely preventing reactions of type (2) by blocking all *ortho* and *para* positions of diphenyl disulphide by methyl groups. In dimesityl disulphide (MS–SM) therefore, we have a compound which is pre-eminently suitable for investigating the photo-dissociation of aromatic disulphides.

In the present preliminary account of our work, some reactions with this compound are reported.

(a) *The photochemical reaction of dimesityl disulphide with the stable free radical* 1,1-*diphenyl-2-picrylhydrazyl*

This reaction was thought to provide independent chemical evidence of the transient existence of free thiyl radicals.[4] The reactions occurring in this system are:

$$\text{MS–SM} \longrightarrow 2\text{MS}\cdot \qquad k_1 \qquad (5)$$

$$2\text{MS}\cdot \longrightarrow \text{MS–SM} \qquad k_2 \qquad (6)$$

$$\text{MS}\cdot + \text{P} \longrightarrow \text{product} \qquad k_p \qquad (7)$$

Presumably $k_2 \gg k_p$ and with the disulphide present in large excess the decay of P· is given by:

$$-\ln[\text{P}\cdot] = K\cdot t\cdot[\text{MS–SM}]^{1/2} - \ln[\text{P}_0\cdot]$$

In accordance with this equation a first order decay of [P·] is found (Table 2).

TABLE 2. REACTION OF 1,1-DIPHENYL-2-PICRYLHYDRAZYL [P·] AND DIMESITYL DISULPHIDE [MS–SM] ON IRRADIATION AT 25° IN CCl_4 SOLUTION

[P·] (mmole/l.)	[MS SM] (mmole/l.)	Fluorescent lamps	Duration (hr)	Conversion of P·	$K\sqrt{[\text{MS SM}]}$ s^{-1}	K $l^{1/2}s^{-1}\,mol^{-1/2}$
0·092	7·26	(in the dark)	20	nil	—	—
0·071	–	8 × 20 Watt	2	~5%	—	–
0·064	1·26	2 × 8 Watt	2	~80%	$0{\cdot}175 \times 10^{-3}$	$4{\cdot}9 \times 10^{-3}$
0·068	5·24	2 × 8 Watt	1	~80%	$0{\cdot}33 \times 10^{-3}$	$4{\cdot}5 \times 10^{-3}$

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[4] J. A. Barltrop, P. M. Hayes and M. Calvin, *J. Amer. Chem. Soc.* 76, 4348 (1954).

[5] K. E. Russell, *J. Phys. Chem.* 58, 437 (1954).

(b) *Hydrogen abstraction by dimesityl disulphide*

Radicals MS·, produced photolytically from MS-SM, are converted into mesitylenethiol, MSH, by reaction with a hydrogen-donor molecule, e.g., 9,10-dihydroanthracene, HAH. Depending on the ratio of MS-SM to HAH one or two hydrogen atoms may be abstracted from the latter. For instance, employing equimolar amounts, a 77·5 per cent conversion of disulphide sulphur to MSH and a 83 per cent conversion of HAH was obtained, anthracene (A) and anthracene-dimer (A-A) being the main products. By doubling the amount of HAH—other conditions being the same as in the foregoing experiment—the same yield of MSH and the same conversion of HAH were obtained, 9,9′10,10′-tetrahydrobianthryl (HA-AH) being predominantly formed. Whereas HAH and HA-AH proved to be stable towards the light used, A was converted into A-A.

The possible action of A as a photosensitizer was separately investigated by using it as an additive in an experiment with 9-methoxyfluorene as the hydrogen donor. No accelerating influence was observed, however.

HA-AH can act as a hydrogen donor as well, being converted mainly into A-A. Since in the dark the reaction of HA-AH with MS· radicals (generated from MSH by 2-cyano-2-propyl radicals[6]) produced monomeric anthracene exclusively, the formation of A-A in our irradiated system is obviously due to the well-known photodimerization of anthracene.

The photochemical dehydrogenation of HAH by MS-SM may now be represented as follows:

$$\text{MS-SM} \xrightarrow{h\nu} 2\text{MS}\cdot \qquad k_1 \qquad (5)$$

$$2\text{MS}\cdot \longrightarrow \text{MS-SM} \qquad k_2 \qquad (6)$$

$$\text{MS}\cdot + \text{HAH} \longrightarrow \text{MS-H} + \cdot\text{AH} \qquad k_3 \qquad (8)$$

$$2\cdot\text{AH} \longrightarrow \text{HA-AH} \qquad k_4 \qquad (9)$$

$$\text{MS}\cdot + \text{HA-AH} \longrightarrow \text{MS-H} + \text{A} + \cdot\text{AH} \qquad k_5 \qquad (10)$$

$$2\text{A} \xrightarrow{h\nu} \text{A-A} \qquad (11)$$

By employing a large excess of HAH, e.g. a molar ratio of HAH to MSSM of 20 : 1, thiol formation was found to be first-order with respect to disulphide. In this case (8) competes effectively with (6): virtually all MS· radicals formed are captured by the hydrogen donor and hence equation (12) obtains:

$$\frac{d[\text{MS}\cdot]}{dt} = 2k_1[\text{MS-SM}] - k_3[\text{MS}\cdot][\text{HAH}] = 0 \qquad (12)$$

$$\frac{d[\text{MSH}]}{dt} = k_3[\text{MS}\cdot][\text{HAH}] = 2k_1[\text{MS-SM}] \qquad (13)$$

$$k_1 t = -\ln(1 - x) \qquad (14)$$

where x denotes the fraction of MS-SM converted to MSH. This photochemical hydrogen-abstraction reaction only proceeds if the wavelength of the light used is

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[6] P. Bruin, A. F. Bickel and E. C. Kooyman, *Rec. Trav. Chim.* 71, 1115 (1952).

[7] J. L. Franklin and H. E. Lumpkin, *J. Amer. Chem. Soc.* 74, 1023 (1952); S. Sunner, *Acta Chem. Scand.* 9, 837 (1955).

shorter than 5000 Å, i.e. the energy of the light should exceed 57 kcal/mole of photons. In view of the strength of the S–S bond in disulphides which is estimated to be smaller than about 70 kcal/mole,[4,7] this seems to be a plausible wavelength limit.

(c) *Photo-dissociation of* MS–SM *in various solvents*

According to (14) the rate constant k_1 of photo-dissociation of MSSM can be obtained from measurements of thiol formation as a function of time in solutions of MSSM and a large excess of hydrogen donor, e.g. HAH. Of course, k_1 depends on the intensity of irradiation I and should properly be written $k_1 = k_1'.I$. Since all measurements were performed under standardized irradiation conditions, k_1-values may be used to describe the relative rates of the dissociation reaction. Quite pronounced differences were found upon varying the solvent, though in each case thiol formation was first-order with respect to disulphide. Comparison of many pure solvents and solvent mixtures revealed that no direct relationships exist between the rates of dissociation and such solvent properties as dipole moment, polarizability or dielectric constant. Generally, rate constants k_1, were found to decrease with increasing kinematic viscosity of the solvent. Such a relationship seems plausible as the dissociation of a molecule is only complete when both fragments diffuse apart into the solution. Presumably, the dissociating molecule has to cope with the van der Waals forces in the solvent and actually, a fair correlation was found to exist between reaction

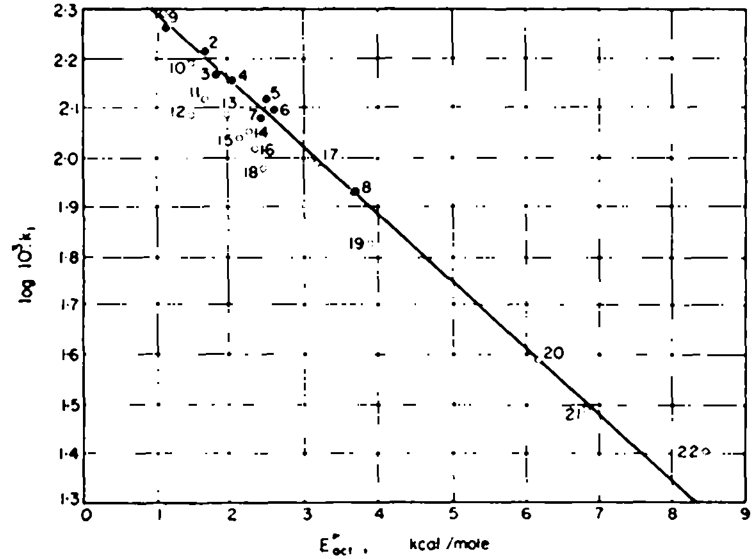

FIG. 1. Logarithm of the rate constant k_1 of photochemical dissociation of dimesityl disulphide vs. activation energy of kinematic viscous flow of the solvent; 25°C. 1 –pentane; 2—heptane; 3 –2,2,4-trimethyl pentane; 4 –toluene; 5 –decane; 6—toluene/hexadecane (37·5%v/62·5%v); 7- heptane/hexadecane (50%v/50%v); 8 –hexadecane; 9– carbon disulphide; 10 – acetone; 11- methyl acetate; 12 —chloroform; 13- chlorobenzene; 14- equal parts by volume of heptane, toluene, hexadecane, chloroform, chlorobenzene, bromobenzene, carbon tetrachloride, cyclohexanone; 15- bromobenzene; 16 -carbon tetrachloride; 17 cyclohexanone; 18—chlorobenzene + 5%w of polystyrene; 19 –ethyl-*p*-ethylbenzoate; 20 –hexadecane/dioctyl phthalate (37·5%v/62·5%v); 21- dimethyl phthalate; 22- dioctyl phthalate.

rates k_1 and the activation energy of kinematic viscous flow, calculated from the Arrhenius type equation for the temperature dependence of viscosity: $\log \nu = \log \nu_0 + E^{\nu}_{act}/2{\cdot}3\, RT$, as is illustrated by Fig. 1.

TABLE 3. RELATION BETWEEN VISCOSITY AND EQUILIBRIUM CONSTANT OF HEXAPHENYLETHANE DISSOCIATION

Solvent	Equilibrium constant at 20° log (K.10^4)	Act. energy of kin. viscous flow E_{act}, kcal/mole
Carbon disulphide	1·28	1·08
Chloroform	0·84	1·43
Benzene	0·61	2·30
1,2-Dibromoethane	0·59	2·63
Bromobenzene	0·57	2·10
1,4-Dioxane	0·40	2·85
Acetophenone	0·23	3·09
Ethylbenzoate	0·22	3·54
Propionitrile	0·08	1·55

The same relationship was found to hold for the equilibrium constants of the thermal dissociation of hexaphenylethane, measured by Ziegler,[8] propionitrile being a notable exception, as is shown in Table 3.

[8] K. Ziegler and L. Ewald, *Liebigs Ann.* **473**, 163 (1929).