The Charge-transfer Complex and Photochemical Reaction of 9-Anthraldehyde Hydrazone in Sulphur Dioxide–Oxygen

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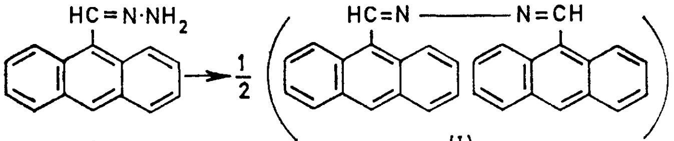
The 1 :1 charge-transfer complex of 9-anthraldehyde hydrazone with sulphur dioxide is not ionic in the ground state. Photolysis of the hydrazone in liquid sulphur dioxide or in liquid sulphur dioxide–carbon tetrachloride yielded 9-anthraldehyde azine (I) and nitrogen *via* N–N scission only. The quantum yield for formation of compound (I) varied with solvent and the concentrations of sulphur dioxide and oxygen. Quenching experiments indicated the intermediacy of a triplet charge-transfer complex between the hydrazone and sulphur dioxide. The rate constant for quenching of the complex, k_a *ca.* 3·0 × 10^8 l mol^{-1} s^{-1}, and the equilibrium constant for formation of the complex, K_3 *ca.* 1·7 × 10^2 l mol^{-1}, were evaluated from experiments in the presence of air. Addition of oxygen caused a large increase in the quantum yield for formation of compound (I), suggesting that it is formed from an ionic intermediate *via* the triplet charge-transfer complex.

WHEN there is sufficient energy gain through solvation, photodissociation of a charge-transfer (C-T) complex may occur even at room temperature. Leonhardt and Weller[1] reported that in non-polar media excited C-T complexes of perylene with aniline derivatives fluoresce, whereas in polar media the complexes may dissociate into solvated ions without direct contact between the reaction partners.

We have previously investigated[2] the photochemical reaction of sulphur dioxide with anthracene. The formation of anthracene-9-sulphonic acid and 9,9′-bianthranyl-10-sulphonic acid either in n-hexane or liquid sulphur dioxide may arise *via* the sulphur dioxide–anthracene C-T complex, which could yield the observed products by subsequent aerial oxidation. In this reaction, we assumed that the C-T complex dissociated into ions solvated by sulphur dioxide molecules.



A

(I)

This paper deals with the nature of the ground state of 9-anthraldehyde hydrazone in sulphur dioxide and the photochemical reaction of the hydrazone in liquid sulphur dioxide–oxygen.

RESULTS AND DISCUSSION

Interaction of 9-*Anthraldehyde Hydrazone with Sulphur Dioxide in the Ground State.*—The electronic spectra of 9-anthraldehyde hydrazone (A) in sulphur dioxide–carbon tetrachloride were measured at various $SO_2 : CCl_4$ ratios. The C-T band of compound A with sulphur dioxide and the ^1L_a band of A overlap one another.

The Ketelaar equation[3] may be derived from expressions (1)—(3). When $(SO_2)_0 \gg (A)_0$, equation (4) is obtained. $(A)_0$ Is the initial concentration of A, l is the cell length (cm), D_a and ε_a, the observed optical density and molecular absorption coefficient, respectively,

$$A + SO_2 \overset{K}{\rightleftharpoons} (A \cdots SO_2) \qquad (1)$$

$$K = (A \cdots SO_2)/[(A)_0 - (A \cdots SO_2)][(SO_2)_0 - (A \cdots SO_2)] \qquad (2)$$

$$D_a = (A \cdots SO_2)\varepsilon_c l + [(A)_0 - (A \cdots SO_2)]\varepsilon l \qquad (3)$$

$$1/(\varepsilon_a - \varepsilon) = 1/K(\varepsilon_c - \varepsilon)(SO_2)_0 + 1/(\varepsilon_c - \varepsilon) \qquad (4)$$

and ε and ε_c, the respective molecular absorption coefficients of A and $(A \cdots SO_2)$. Linear plots of $1/(\varepsilon_a - \varepsilon)$ against $1/(SO_2)_0$ were obtained. The derived K values are in Table 1. The variation of K implies either co-existence of several complexes with sulphur dioxide or competition between carbon tetrachloride[4,5] and sulphur dioxide for compound A.

TABLE 1

Equilibrium constants for complex formation between A and SO_2 in CCl_4 at 30 °C

Wavelength (nm)	K/l mol^{-1}
460	0·31
470	0·22
480	0·18
490	0·15
500	0·14

A solution of compound A in liquid sulphur dioxide gives no e.s.r. signal either at room temperature or −196 °C. In the n.m.r. spectrum peaks ascribed to NH and aromatic protons are shifted to lower field by 0·23 and 0·06—0·10 p.p.m., respectively, compared with those in deuteriochloroform solution. These data suggest that ionic species are not involved in the ground state of the $(A \cdots SO_2)$ complex (Scheme 1). This was further supported by the fact that styrene was not polymerized in this system.

The chemical shifts indicate that sulphur dioxide molecules interact mainly with the amino-group of compound A, so that irradiation at the frequency of the spectral band due to the C-T complex should dis-

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[1] H. Leonhardt and A. Weller, *Ber. Bunsengesellschaft Phys. Chem.*, 1963, **67**, 791.

[2] T. Nagai, K. Terauchi, and N. Tokura, *Bull. Chem. Soc. Japan*, 1966, **39**, 868.

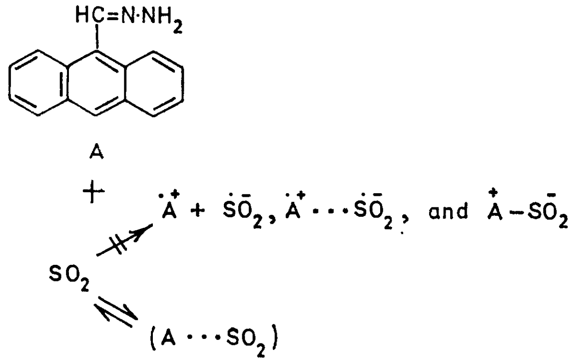
[3] J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit, and W. Dzcubas, *Rec. Trav. chim.*, 1952, **71**, 1104.

[4] D. P. Stevenson and G. M. Coppinger, *J. Amer. Chem. Soc.*, 1962, **84**, 149.

[5] K. M. C. Davis and M. F. Farmer, *J. Chem. Soc.* (*B*), 1967, 28.

sociate it into ionic species including the amino-radical cation.

Photochemical and Thermal Reactions of Compound A in Liquid Sulphur Dioxide.—The results are summarized in Table 2.



SCHEME 1 Ground-state interaction of the hydrazone A with sulphur dioxide

The product, 9-anthraldehyde azine (I), was isolated and characterized spectroscopically (see Experimental section). Photolysis of the hydrazone A in liquid sulphur dioxide gave the azine in nearly quantitative yield, but the yield was negligible in benzene. Addition of benzene to sulphur dioxide decreased the formation of the azine, presumably by reducing formation of the C-T complex due to an interaction of sulphur dioxide with benzene.[6,7] However, compound (I) was formed in good yield by the addition of sulphur dioxide to carbon tetrachloride with which it does not interact.

In the dark, compound (I) was formed in benzene–sulphur dioxide but it was not formed in benzene alone. Formation of compound (I) was almost independent of the presence of oxygen and the reaction temperature.

These results suggest that the C-T complex between the hydrazone A and sulphur dioxide is involved in the formation of compound (I) in the photochemical and thermal reactions, and that carbon tetrachloride–sulphur dioxide is a suitable solvent system for the reaction.

TABLE 2

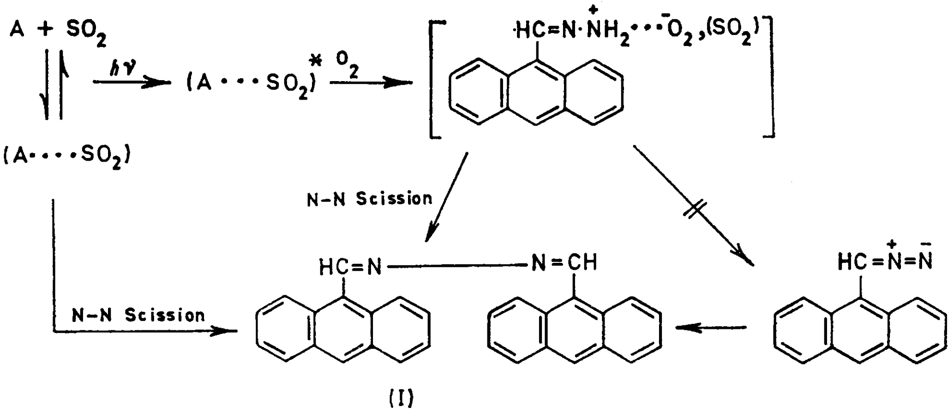
Photochemical and thermal reactions of A *

Expt.	[A]/ mol l^{-1}	Solvents	Reaction time (h)	Yield of (I) (%)
1	0·12	Liquid SO_2 [a]	5	97
2	0·15	C_6H_6 [a]	5	*ca.* 0
3	0·034	CCl_4–SO_2 [a] (92·9 : 7·1)	2	67
4	0·078	C_6H_6–SO_2 [a] (68 : 32)	5	85
5	0·096	Liquid SO_2 [b]	5	22
6	0·091	C_6H_6 [b,c]	5	30
7	0·091	C_6H_6 [b,c]	5	27
8	0·27	Liquid SO_2 [b,d]	5	36

* Reactions were performed in Pyrex vessels, solvents (50—100 ml) being used without degassing. The reaction temperature was controlled at 0° except for experiment 7 (80°). The light source was a Halōs PIH 300 W high-pressure mercury lamp.

[a] Irradiation. [b] Dark reaction. [c] Gaseous SO_2 was bubbled into the solvent. [d] Degassed solvent was used.

Compound (I) may possibly be formed from a diazo-intermediate. However, in the analogous photolysis of benzaldehyde hydrazone the corresponding azine was obtained nearly quantitatively without concomitant formation of stilbene,[8] which means that the formation of the azine (I) from compound A proceeds by N–N scission [9,10] (Scheme 2). The formation of nitrogen was confirmed by mass spectrometry; it may arise from the dimerization of nitrene, $:\dot{N}H$.[11]



SCHEME 2 The reaction of compound A with sulphur dioxide

Character of the Intermediate.—*Effects of solvents and quenchers.* Quantum yields for the formation of compound (I) in sulphur dioxide–carbon tetrachloride and -benzene were taken in air at 20° using filtered light of wavelength 350—450 nm (virtually no absorption by sulphur dioxide [12]). The photolyses were

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[6] H. Takeuchi, T. Nagai, and N. Tokura, *Tetrahedron*, 1967, **23**, 1783.

[7] H. Takeuchi, T. Nagai, and N. Tokura, *Bull. Chem. Soc. Japan*, 1967, **40**, 2375.

[8] W. Kirmse, 'Carbene Chemistry,' Academic Press, New York, 1964.

[9] S. D. Carson, *J. Org. Chem.*, 1970, **35**, 2734.

[10] R. W. Binkley, *J. Org. Chem.*, 1970, **35**, 2796.

[11] A. F. Marcantonio and J. T. Thekkekandam, *J. Amer. Chem. Soc.*, 1971, **93**, 1524.

[12] R. B. Carton and A. B. F. Dancan, *J. Amer. Chem. Soc.*, 1968, **90**, 1945.

carried out for 6 min, the dark reaction and the inner filter effect of compound (I) being negligibly small in this period. Figure 1 shows the effect of added sulphur dioxide on the quantum yields for the formation of compound (I) in benzene and carbon tetrachloride. The addition of a small amount of sulphur dioxide to carbon tetrachloride increased the quantum yield, but the addition of a large amount caused a decrease in the quantum yield. However, the effect of added sulphur dioxide in benzene is unclear. The results of quenching experiments with piperylene (penta-1,3-diene) (Figure 2) indicate that the azine (I) derives from a triplet state. The increase in the quantum yield for compound (I) upon addition of sulphur dioxide indicates that an activated C-T complex between compound A and sulphur dioxide takes part in the reaction. Furthermore, the quenching effect of a large amount of sulphur dioxide can be readily accounted for by the triplet–triplet energy transfer[13] from the activated intermediate to sulphur dioxide having a triplet energy level at 380—460 nm.[12] Quenching with sulphur dioxide is less likely

$$^3(\mathrm{A}\cdots\mathrm{SO_2})^* + \mathrm{SO_2} \xrightarrow{k_a} (\mathrm{A}\cdots\mathrm{SO_2}) + {}^3\mathrm{SO_2}^* \quad (5)$$

$$^3(\mathrm{A}\cdots\mathrm{SO_2})^* + \text{Piperylene} \xrightarrow{k_q} (\mathrm{A}\cdots\mathrm{SO_2}) + {}^3\text{Piperylene}^* \quad (6)$$

than with piperylene, because its triplet level is higher than that of piperylene. It appears, therefore, that the triplet C-T complex between compound A and sulphur dioxide is responsible for product formation.

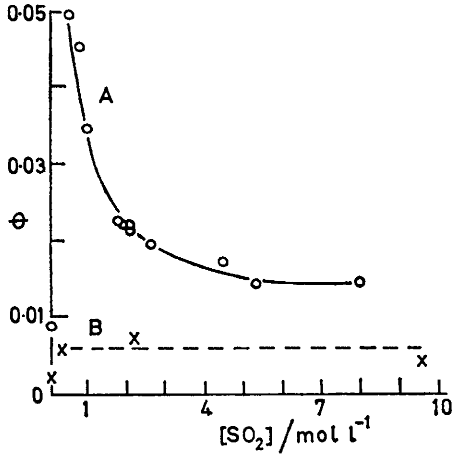


FIGURE 1 Quantum yield Φ for the formations of the azine (I) in the photolysis of the hydrazone A at 20 °C in A, sulphur dioxide–carbon tetrachloride and B, sulphur dioxide–benzene

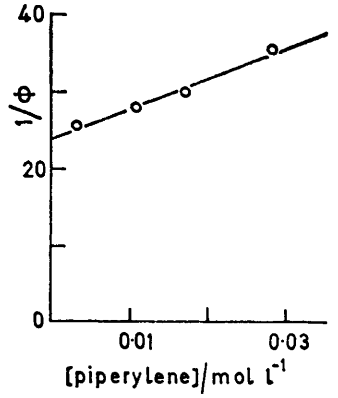
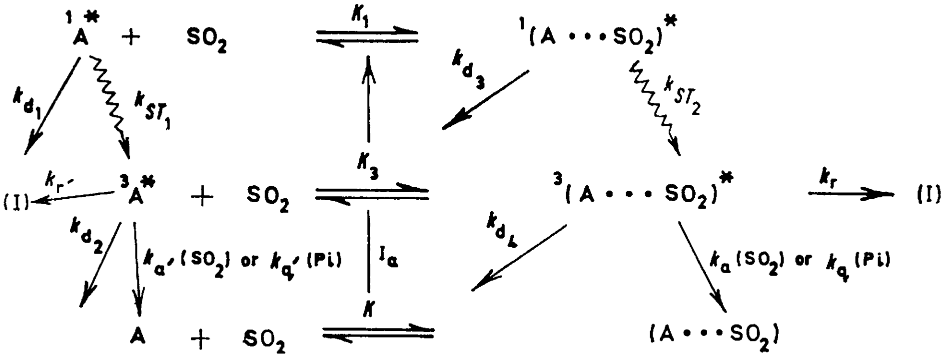


FIGURE 2 Relationship between [piperylene] and 1/Φ in the photolysis of the hydrazine A in sulphur dioxide (*ca.* 0·5 mol l^{-1})–carbon tetrachloride at 20 °C

An alternative possibility is the coexistence of two complexes, $(\mathrm{A}\cdots\mathrm{SO_2})$ and $(\mathrm{A}\cdots\mathrm{CCl_4})$, but the latter can probably be neglected in view of the low complex formation constant of amines with carbon tetrachloride.[4,5]



SCHEME 3 Photolysis of compound A in sulphur dioxide–carbon tetrachloride; k_{d_1}—k_{d_4} = rate constants of emission and radiation less transitions

If the rate constants for the various steps of the photolysis are as in Scheme 3, equations (7)—(14) can be derived for the sulphur dioxide–carbon tetrachloride system. The rate of light absorption is given by equation (7) where $[^1\mathrm{A}^*]$ and $[^1(\mathrm{A}\cdots\mathrm{SO_2})^*]$ are the concentrations

$$I_a = (k_{d_1} + k_{ST_1})[^1\mathrm{A}^*] + (k_{d_3} + k_{ST_2})[^1(\mathrm{A}\cdots\mathrm{SO_2})^*] \quad (7)$$

of the excited singlets of the hydrazone and the complex,

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[13] K. Sandrous and H. L. J. Backstrom, *Acta Chem. Scand.*, 1962, **16**, 958.

respectively, assuming the steady state for the excited singlets. The quantum yield (Φ) for the formation of compound (I) from $^3(\mathrm{A}\cdots\mathrm{SO_2})^*$ and $^3\mathrm{A}^*$ in liquid sulphur dioxide–carbon tetrachloride is given by equation (8). Assumption of steady states in the triplet states [$^3\mathrm{A}^*$ and $^3(\mathrm{A}\cdots\mathrm{SO_2})^*$], gives equation (9). Combining equations (8) and (9) gives equation (10). From $K_1 = [^1(\mathrm{A}\cdots\mathrm{SO_2})^*]/[^1\mathrm{A}^*][\mathrm{SO_2}]$ and $K_3 = [^3(\mathrm{A}\cdots\mathrm{SO_2})^*]/[^3\mathrm{A}^*][\mathrm{SO_2}]$ we obtain equation (11)

Since simple energy considerations show[1] that electronically excited molecules have a lower ionization potential than molecules in the ground state, the values of K_1 and K_3 may be sufficiently high to give the relations $K_1 \gg k_{ST_1}/k_{ST_2}[\mathrm{SO_2}]$ and $K_3 \gg k_{r'}/k_r[\mathrm{SO_2}]$ in the presence of sulphur dioxide (*ca.* 0·5—2 mol l^{-1}), thus giving equation (12). From the linear relationship of $1/\Phi$ *vs.* [SO$_2$], k_{d_2}/k_rK_3 is negligible, so that equation (13) is obtained. If piperylene (Pi) and sulphur dioxide act as quenchers, we get equation (14).

$$\Phi = \frac{k_{r'}[^3\mathrm{A}^*] + k_r[^3(\mathrm{A}\cdots\mathrm{SO_2})^*]}{(k_{d_1} + k_{ST_1})[^1\mathrm{A}^*] + (k_{d_3} + k_{ST_2})[^1(\mathrm{A}\cdots\mathrm{SO_2})^*]} \quad (8)$$

$$k_{ST_1}[^1\mathrm{A}^*] + k_{ST_2}[^1(\mathrm{A}\cdots\mathrm{SO_2})^*] = \{k_{d_2} + k_{r'} + k_{a'}[\mathrm{SO_2}]\}[^3\mathrm{A}^*] + \{k_{d_4} + k_r + k_a[\mathrm{SO_2}]\}[^3(\mathrm{A}\cdots\mathrm{SO_2})^*] \quad (9)$$

$$1/\Phi = \frac{(k_{d_1} + k_{ST_1})[^1\mathrm{A}^*] + (k_{d_3} + k_{ST_2})[^1(\mathrm{A}\cdots\mathrm{SO_2})^*]}{k_{ST_1}[^1\mathrm{A}^*] + k_{ST_2}[^1(\mathrm{A}\cdots\mathrm{SO_2})^*]} \times \frac{\{k_{d_2} + k_{r'} + k_{a'}[\mathrm{SO_2}]\}[^3A^*] + \{k_{d_4} + k_r + k_a[\mathrm{SO_2}]\}[^3(A\cdots\mathrm{SO_2})^*]}{k_{r'}[^3\mathrm{A}^*] + k_r[^3(\mathrm{A}\cdots\mathrm{SO_2})^*]} \quad (10)$$

$$1/\Phi = \left[1 + \frac{k_{d_1} + k_{d_3}K_1[\mathrm{SO_2}]}{k_{ST_1} + k_{ST_2}K_1[\mathrm{SO_2}]}\right] \left[1 + \frac{k_{d_2} + k_{a'}[\mathrm{SO_2}] + \{k_{d_4} + k_a[\mathrm{SO_2}]\}K_3[\mathrm{SO_2}]}{k_{r'} + k_rK_3[\mathrm{SO_2}]}\right] \quad (11)$$

$$1/\Phi = (1 + k_{d_3}/k_{ST_2})\{1 + k_{d_4}/k_r + k_a[\mathrm{SO_2}]/k_r + k_{d_2}/k_rK_3[\mathrm{SO_2}] + k_{a'}/k_rK_3\} \quad (12)$$

$$1/\Phi = (1 + k_{d_3}/k_{ST_3})(1 + k_{d_4}/k_r + k_d/k_rK_3 + k_a[\mathrm{SO_2}]/k_r\} \quad (13)$$

$$1/\Phi = (1 + k_{d_2}/k_{ST_2})(1 + k_{d_4}/k_r + k_{q'}/k_rK_3 + k_q[\mathrm{Pi}]/k_r + k_{a'}/k_rK_3 + k_a[\mathrm{SO_2}]/k_r) \quad (14)$$

Using the data shown in Figure 1, expression (13) was plotted for two concentration limits of sulphur dioxide (0·5 and 2 mol l^{-1}). The reciprocal quantum yields when plotted against [SO$_2$] yielded a straight line, and as shown in Figure 2, a plot of $1/\Phi$ *vs.* [piperylene] also gave a straight line.

Thus from the slope of the linear dependence on $1/\Phi$ and [SO$_2$] or [Pi], we evaluated the ratio $k_a/k_r : k_q/k_r$ as 18·3 : 410. If the quenching rate constant with piperylene of the triplet C-T complex is controlled by the diffusion step,[14] the k_q value is nearly $6{\cdot}7 \times 10^9$ l mol^{-1} s^{-1}. Therefore, these slopes and intercepts show that $K_3 = 1{\cdot}7 \times 10^2$ l mol^{-1} from the assumptions $k_q = k_{q'}$ and $k_a = k_{a'}$ and $k_a = 3{\cdot}0 \times 10^8$ l mol^{-1} s^{-1}. The fact that K_3 is greater than K and k_a is less than k_q is consistent with our view.

Effect of oxygen. In general, oxygen is a good quencher of triplet states. However, the presence of oxygen in liquid sulphur dioxide–carbon tetrachloride caused a significant increase in the quantum yield for the azine (Table 3).

TABLE 3

The effect of oxygen in the photolysis of A (*ca.* 1×10^{-3} mol l^{-1}) at 20°

Solvents *ca.* 4·5 ml)	[SO$_2$]/ mol l^{-1}	Surrounding gas conditions	Quantum yield Φ for (I)
CCl$_4$	0·79	Degassed	0·012
CCl$_4$	0·68	Aerial	0·046
CCl$_4$	3·16	O$_2$ alone	0·070
CCl$_4$	9·37	Degassed	0·002
CCl$_4$	7·9	Aerial	0·021
C$_6$H$_6$	3·5	Degassed	*ca.* 0
C$_6$H$_6$	9·6	Aerial	0·005

This could be interpreted by assuming that the sulphur dioxide–oxygen system rapidly accelerates the transformation of the triplet C-T complex into the ionic intermediate rather than that oxygen acts as the quencher of the triplet level. In this case, the C-T complex of the hydrazone A with oxygen may be ignored in favour of the C-T complex of the hydrazone with sulphur dioxide, as the ability of oxygen to form C-T complexes with anilines is weak.[15]

$$^3(\mathrm{A}\cdots\mathrm{SO_2})^* \xrightarrow{\mathrm{SO_2-O_2}} \overset{\bullet+}{\mathrm{A}}\ \overset{-\bullet}{\mathrm{O_2}}(\mathrm{SO_2}) \longrightarrow (\mathrm{I}) \quad (15)$$

Electron transfer from ground state molecules to liquid sulphur dioxide–oxygen has recently been recognized in the polymerization of styrene[16] and *N*-vinylcarbazole,[17] and in the transformation of diarylethylenes[18] and the trityl radical[19] into the corresponding radical cations and the trityl cation. Thus equation (15) is compatible with all the evidence.

Conversely, oxygen had no effect on the dark reaction of the hydrazone A with sulphur dioxide (Table 2). This is consistent with the notion that the azine (I) is formed directly from the ground state C-T complex between compound A and sulphur dioxide and not *via* the ionic species derived from the C-T complex. Generally,[1] electronically excited molecules have a lower ionization potential than molecules in the ground state, so that electron transfer is more favoured by

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[17] T. Nagai, T. Miyazaki, and N. Tokura, *J. Polymer Sci., Part B-2, Polymer Letters*, 1968, **6**, 346.

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liquid sulphur dioxide–oxygen in the excited molecules than in the ground state (Figure 3).

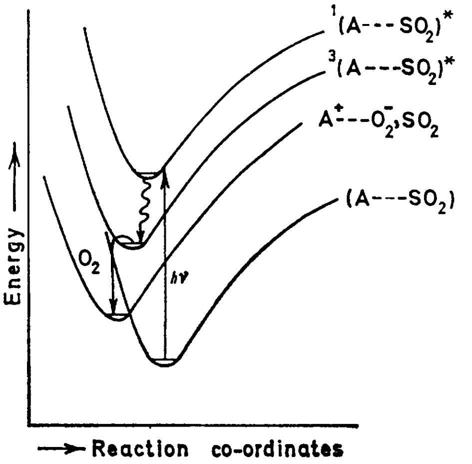

FIGURE 3 Potential diagram for the photoionization of the hydrazone A in sulphur dioxide–oxygen

EXPERIMENTAL

Materials.—Benzene and carbon tetrachloride were purified by ordinary methods. Liquid sulphur was dehydrated with phosphorus(V) oxide and distilled. Piperylene was obtained commercially. 9-Anthraldehyde hydrazone A was prepared from 9-anthraldehyde according to Nakaya *et al.*[20] Benzaldehyde hydrazone was synthesized by the method of Curtius.[21]

Measurement of C-T Complex Formation.—A Hitachi EPU 2A type spectrometer was used with a 1·0 cm quartz pressure cell.

Photochemical and Thermal Reactions of Compound A.—The light source was a Halōs PIH 300 W high-pressure mercury lamp. All photochemical and thermal reactions were carried out in a Pyrex pressure vessel under the conditions given in Table 2. The reaction mixture was then distilled under reduced pressure, and the product was crystallized from chloroform–benzene to give 9-anthraldehyde azine (I), m.p. 270—272°, τ ($CDCl_3$) $-0{\cdot}15$ (-CH=N-, 2H) and 1·0—2·7 (ArH, 18H), *m/e* 408, 204, and 177, $\lambda_{max.}$ (CCl_4) 430 nm (log ε 4·26) (Found: C, 87·8; H, 4·85; N, 6·65. Calc. for $C_{26}H_{20}N_2$: C, 88·2; H, 4·95; N, 6·85%). Besides the product (I), nitrogen was formed; this was confirmed by the mass spectrum of the reaction mixture produced under the degassed conditions of experiment 1 in Table 2. The n.m.r. spectra were obtained with a JEOL spectrometer. The mass spectra were recorded on a Hitachi RMU-6E spectrometer.

Irradiation of Benzaldehyde Hydrazone in Liquid Sulphur Dioxide.—In the experiment using benzaldehyde hydrazone in place of A, benzaldehyde azine was formed, but not stilbene. The product, m.p. 93°, was recrystallized from 95% ethanol, and was identical (n.m.r. and i.r. spectra) with an authentic sample.[22] Benzaldehyde hydrazone remained unchanged when benzene was used as the solvent in place of sulphur dioxide.

Actinometry.—A Halōs PIH 300 W high-pressure mercury arc was centred at the focus of an aluminium reflector. The light was filtered by two quartz cells (1 cm width) containing the filter solution mounted on an optical bench. The apparatus was enclosed in a protective shield. The light input of the photolysis solution (*ca.* 4·5 ml) was monitored with the quartz cell (1·0 cm thick and 1·0 cm lateral width) containing the actinometer. The samples and the light input cells were interchanged twice during the irradiation period (6 min) at 20°. The light transmitted by the sample was measured by the actinometer cell set behind the photolysis solution. Potassium ferrioxalate actinometry was employed, and a quantum yield of 1·15 was assumed.[23] Formation of compound (I) was followed by u.v. spectrometry.

The observed optical density is expressed in equation (16)

$$D = \varepsilon_A(1 - x)c_0l + (\tfrac{1}{2})\varepsilon_{(I)}c_0xl \qquad (16)$$

where ε_A, $\varepsilon_{(I)}$, c_0, l, and x are the molecular extinction coefficient of *A* and of (I), the initial molar concentration of A (*ca.* $1{\cdot}0 \times 10^{-3}$ mol l^{-1}), the light path length of the photolysis cell, and the fraction of the reaction completed, respectively. For the case where $l = 1$ cm, equation (17)

$$x = (D/c_0 - \varepsilon_A)/\{(\tfrac{1}{2})\varepsilon_{(I)} - \varepsilon_A\} \qquad (17)$$

is obtained. At 480 nm ε_A, $\varepsilon_{(I)}$, and D were measured. Before each experiment, the values of ε_A and $\varepsilon_{(I)}$ were measured at various concentrations of sulphur dioxide in carbon tetrachloride or in benzene.

Filter Solutions.[24,25]—$NaBr,2H_2O$ (65 g) and $Pb(NO_3)_2$ (0·3 g) were dissolved in water (100 ml); $CuSO_4,5H_2O$ (4·4 g) was dissolved in aqueous 2·7M-NH_4OH (100 ml). This filter combination was used to give a light beam in the 350—450 nm region.

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