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The Charge-transfer Complex and the Photochemical Reactions of Anthracene with Sulfur Dioxide in Various Solvents

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The equilibrium constant, K, of the 1 : 1 charge-transfer complex formation of anthracene with sulfur dioxide has been estimated by spectrophotometric measurements to be 0.33 in carbon tetrachloride at 15°C. The values of ΔH (-4.8 kcal.mol^{-1}) and ΔS° (-19 cal.deg^{-1}mol^{-1}) have been derived. The K value is nearly zero when estimated in the longer wavelength region, indicating that a contact charge-transfer complex is involved. A sort of contact charge-transfer complex of anthracene-SO_2 is also observed in benzene. Irradiations by a high-pressure mercury lamp of anthracene with sulfur dioxide in various solvents have been carried out. In solvents such as *n*-hexane and carbon tetrachloride, which have no interaction with sulfur dioxide, anthracene gives sulfur-containing substances, such as anthracene-9-sulfonic acid (I) and dianthranyl-(9.9′)-sulfonic acid-(10) (II). On the contrary, in benzene or in carbon disulfide, no product such as the sulfonic acid, the dimer or the endoperoxide of anthracene is produced, indicating that the interaction of anthracene with sulfur dioxide is diminished by the solvent - sulfur dioxide interaction. A suggestion was made that the activated intermediate which induced the formation of I and II was of a singlet character.

Comprehensive studies have been made of the photochemical reactions of anthracene, especially of dimerization and oxidation in solutions.[1-3] According to these studies, in such hydrocarbon solvents as benzene and hexane anthracene affords its dimer through an excited singlet state ($^1A^*$), whereas in a heavy atom containing such solvents as carbon tetrachloride, chloroform and carbon disulfide, a transition from $^1A^*$ to ^3A (a triplet state) results in the formation of a cyclic endoperoxide in the presence of oxygen.

Such behavior of anthracene in various solvents has prompted the present authors to investigate the solvent effects of a photochemical reaction in the presence of sulfur dioxide, since the interaction of anthracene and sulfur dioxide has been the subject of considerable interest lately.[4,5]

Weiss[4] has concluded that the complex between anthracene and sulfur dioxide is an ion pair as the result of a complete electron transfer. Lichtin et al.,[5] however, have found that the complex in liquid sulfur dioxide is not a very good conductor, and no evidence has been provided for the ionic nature of the complex, either by conductometry or ultraviolet spectrometry.

In this paper, the electronic spectra of anthracene in various solvent systems involving liquid sulfur dioxide have been examined in order to obtain a greater understanding of the nature of the charge-transfer complex of anthracene - sulfur dioxide, our results will be discussed, together with the photochemical outcomes of the reaction of anthracene with sulfur dioxide in various solvents.

Experimental

Materials.—Liquid sulfur dioxide was dehydrated with phosphorus pentoxide and distilled. Carbon tetrachloride, benzene, *n*-hexane, and ethanol were purified by ordinary methods. A chromatographically-purified anthracene, m. p. 215—215.5°C, was used.

The Measurement of Electronic Spectra. — A Hitachi EPU 2 A-type spectrophotometer equipped with a thermostat was used. A pressure cell made of quartz was used to ensure the measurement in a sulfur dioxide solution; the width of the cell could be adjusted to 0.706 mm. by the insertion of a spacer. Lambert-Beer's law was satisfactorily obeyed throughout the range of the measurements.

The Calculation of the Equilibrium Constant of the Complex-Formation.—The Benesi-Hildebrand equation[6] was used for the estimation of the equilibrium constant.

Since the formation of the complex is shown as:

$$A + SO_2 \rightleftarrows A\cdot SO_2 \text{ (Complex)} \qquad (1)$$

the equilibrium constant can be expressed as:

$$K = \frac{[A\cdot SO_2]}{([A]_0-[A\cdot SO_2])([SO_2]_0-[A\cdot SO_2])} \qquad (2)$$

where $[A\cdot SO_2]$ = the molar concentration of the complex, $[A]_0-[A\cdot SO_2]$ = the molar concentration of free anthracene, and $[SO_2]_0-[A\cdot SO_2]$ = the mole fraction of

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[1] R. M. Hochstrasser and G. B. Porter, *Quarterly Rev.*, **XIV** 2, 146 (1960).

[2] E. J., *Discussions. Faraday Soc.*, **14**, 143 (1953).

[3] E. J. Bowen and D. W. Tanner, *Trans. Faraday Soc.*, **51**, 475 (1955).

[4] J. Weiss, *J. Chem. Soc.*, **1942**, 250.

[5] N. N. Lichtin, R. E. Weston, Jr., and J. D. White, *J. Am. Chem. Soc.*, **74**, 4715 (1952).

[6] H. A. Benesi and J. H. Hildebrand, ibid., **71**, 2703 (1949).

free sulfur dioxide. $[A\cdot SO_2]$ in the last term is expressed in terms of the mole fraction.

Under the experimental conditions,

$$[SO_2]_0 \gg [A\cdot SO_2]$$

and $$[SO_2]_0 - [A\cdot SO_2] \fallingdotseq [SO_2]_0$$

The Benesi-Hildebrand equation is derived as:

$$\frac{l[A]_0}{D} = \frac{1}{\varepsilon_c \cdot K[SO_2]_0} + \frac{1}{\varepsilon_c} \tag{3}$$

where ε_c, D and l are the molecular extinction coefficient of the complex, the optical density of the solution, and the light-path length of the cell respectively. A linear plot of $l[A]_0/D$ vs. $1/[SO_2]_0$ will give $1/\varepsilon_c \cdot K$ and $1/\varepsilon_c$ by the slope and the intercept of the line respectively. K can thus be estimated.

The Estimation of $\Delta G°$, ΔH and $\Delta S°$.—The thermodynamic values, $\Delta G°$ (free energy change), ΔH (enthalpy change), and $\Delta S°$ (entropy change), were calculated by the following relation:

$$R \ln K = \Delta S° - \frac{\Delta H}{T}$$

Apparatus.—The vessel used for the reaction is illustrated in Fig. 1.

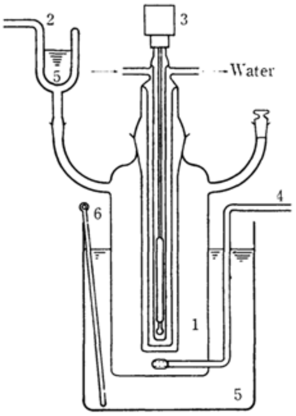


Fig. 1. Reaction vessel.

(1) reaction vessel, (2) cooler, (3) high pressure mercury lamp (which is equipped with double layered surrounding tubes made of quartz to be useful for low temperature experiment), (4) gas-inlet tube, (5) dry ice-trichloroethylene, (6) thermometer

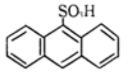
A reaction vessel (1), equipped with a dry ice cooler (2), a 300-Watt high-pressure mercury lamp (3) inside the vessel and an inlet tube for nitrogen or oxygen gas (4), was chilled with dry ice - triclene bath in a Dewar vessel (5) equipped with thermometer (6).

The Procedure of the Reaction.—Anthracene (0.11—1.5 g.) was dissolved in a solvent (liquid sulfur dioxide, carbon tetrachloride, benzene, *n*-hexane or ethanol) in the reaction vessel; then a measured amount of liquid sulfur dioxide was charged into this solution. The atmosphere in the vessel was replaced by pure nitrogen gas several times, under cooling with the dry ice - triclene bath, the temperature of the vessel being kept at −25°C. The mixture was then irradiated for a definite time (1.5—8 hr.) by the mercury lamp. After the reaction, the solvent and /or liquid sulfur dioxide was distilled, and the residue was triturated with ethanol.

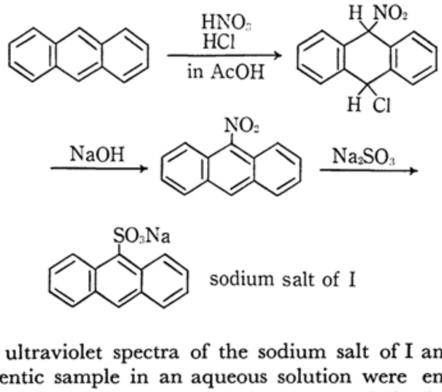
The ethanol-soluble part was evacuated to dryness and extracted with benzene in order to remove the unreacted anthracene. The residual part was added and digested with alcoholic sodium hydroxide until the pH of the solution became 7. The precipitated sodium salt was filtered and dried; thus it was identified as the sodium salt of I.

The ethanol-insoluble part was again extracted with benzene, since the extracts still contained some unreacted anthracene. The benzene-insoluble substance was in the form of dark brown crystals (II).

The Identification of the Products.—*Anthracene-9-sulfonic Acid (I)*.—I was a hygroscopic substance containing sulfur; it was insoluble in a non-polar solvent and soluble in methanol, ethanol and aqueous alkali, and it formed alkaline salts readily. The properties are coincident with the results described in the literature[7] for anthracene-9-sulfonic acid. IR (KBr disk), 3400 cm⁻¹ (ν_{OH}), 1140—1220 cm⁻¹ ($\nu_{as.SO_2}$ of SO_2OH) and 1040 cm⁻¹ ($\nu_{s.SO_2}$ of SO_2OH). An authentic specimen was synthesized by the method of Minajew and Fedorow[8] by the following scheme:

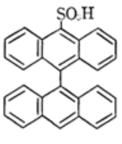


(I)



The ultraviolet spectra of the sodium salt of I and the authentic sample in an aqueous solution were entirely superimposable upon each other: λ_{max} 256 ($\log \varepsilon =$ 4.61), 335 (3.12), 351 (3.37), 370 (3.55) and 390 mμ (3.52). The R value of the salt as determined by thin-layer chromatography (adsorbent, Wako-silica gel B-5, 0.63 mm., elution with water), R=0.56., was coincident with that of the authentic specimen.

Dianthranyl-(9.9)′-sulfonic Acid-(10) (II).—II had a m. p. above 300°C and was sparingly soluble in ordinary solvents. Its infrared spectrum was almost identical with that of anthracene-9-sulfonic acid.



(II)

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[7] Beilstein's "Handbuch," **EII 11**, 110 (1950).

[8] W. Minajew and B. Fedorow, *Ber.*, **62**, 2489 (1929).

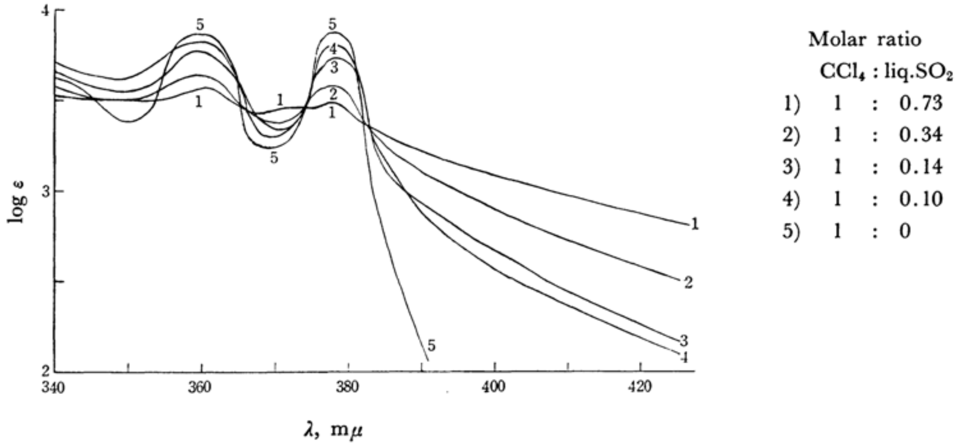
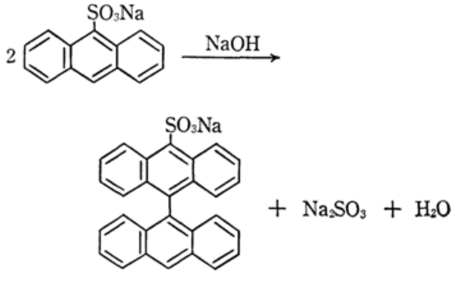


Fig. 2. The electronic spectra of anthracene, CCl_4-SO_2 system, 30°C.

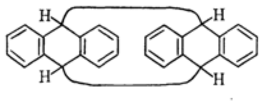
ν_{max}^{KBr} 3400 cm^{-1} (ν_{OH}), 1160—1220 cm^{-1} and 1030 cm^{-1} (sulfur dioxide stretching of sulfonic acid), which disappeared when this compound was heated in a crucible. The sulfur content, 7.36% (calcd., 7.36%), shows that the molar ratio of the SO_3H group to the anthracene ring is 1 : 2. This ratio was confirmed by the alkali titration of II (neutral equivalent 409; calcd., 434). Moreover, the mass spectrum shows the presence of a dianthranyl ring, *m/e*, 354, 178, 127, 80, 64 and 48. The properties obtained here are coincident with the results described in the literature,[9] and so II was confirmed to be dianthranyl-(9.9′)-sulfonic acid-(10).

An authentic specimen was synthesized by the following method:[10]



The infrared spectrum and *R*-value (0.81) as determined by the thin-layer chromatography (adsorbent, Wako-silica gel B-5, 0.30 mm.; elution with 1 : 1 ethanol-water) of the sodium salt of II were coincident with those of the authentic specimen.

9, 9′, 10, 10′-Dianthracene(III).—This compound was sparingly soluble in an organic solvent, m. p. 255—257°C, and a mixed melting point determination with



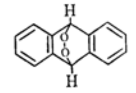
(III)

an authentic dianthracene[11] showed no depression. At the melting point, this compound dissociated to the anthracene-monomer (m. p. 211—212°C). These properties are coincident with those of the photodimers of anthracene derivatives reported by Greene et al.[12] The 725 cm^{-1} band due to the out-of-plane C–H deformation vibration of *ortho*-di-substituted aromatics which is observed in anthracene itself is replaced by a band at 760 cm^{-1} in this compound similar to that proposed for 9.10-dihydroanthracene.[13]

Found: C, 94.26; H, 5.52. Calcd. for $C_{28}H_{20}$: C, 94.38; H, 5.63%.

III was thus confirmed to be 9, 9′, 10, 10′-dianthracene.

9.10-Anthracene-endo-cyclicperoxide (IV).—IV decomposed at 120°C (reported, m. p. (decomp.) 120°C[14]). The active oxygen was analyzed by the spectrophotometric determination of iodine which had been liberated



(IV)

from the ethanolic solution of IV by the addition of potassium iodide. The infrared spectrum showed no absorption at 3450 cm^{-1} due to the ν_{OH} of hydroperoxide. This compound was confirmed by reexamining the method of Bowen and Tanner[3] in the absence of sulfur dioxide.

Results and Discussion

The Interaction of Anthracene with Liquid Sulfur Dioxide. Solvent Effects.—In Fig. 2, the electronic spectra of the anthracene - liquid sulfur dioxide - carbon tetrachloride system are compared at different molar ratios of sulfur dioxide vs. carbon tetrachloride, where a constant amount of anthracene (6.3 mg.) was dissolved in 10 ml. of carbon tetrachloride.

As is shown in Fig. 2, the characteristic fine structure of the absorption of anthracene disappears

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[9] Beilstein's "Handbuch," **EII 11**, 112 (1950).

[10] W. Minajew and B. Fedorow, *Ber.*, **62**, 2493 (1929).

[11] E. Funakubo, Y. Matsumoto and T. Nagai, *Technol. Repts. of Osaka Univ.*, **11**, 409 (1961).

[12] F. D. Greene, S. L. Misrock and J. R. Wolfe, *J. Am. Chem. Soc.*, **77**, 3852 (1955).

[13] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen, London (1958), p. 77.

[14] E. H. Rodd (Editor) "Chem. of Carbon Compound," **IIIB** Elsevier Publishing Co., New York (1956), p. 1365.

as the molar fraction of sulfur dioxide increases, while the absorption of the longer-wave-length region (as far as 470 mμ) of the broad absorption increases. The absorption bands above 400 mμ may obviously be identified as a charge-transfer complex[15] between anthracene and sulfur dioxide, since the absorptions of both anthracene and sulfur dioxide are below 400 mμ in carbon tetrachloride.

Figure 3 shows the Benesi-Hildebrand plot at 0°C; it indicates a 1 : 1 complex formation. This complex formation is also confirmed from the linear Benesi-Hildebrand plots at 15 and 30°C, and by the linear plot in Fig. 4, where a linear correlation between $\ln K$ vs. $1/T$ is visualized.

The equilibrium constants, K, for the complex formation estimated at various wavelengths are listed in Table I.

TABLE I. EQUILIBRIUM CONSTANT OF THE COMPLEX FORMATION

Wavelength	0°C	15°C	30°C
400 mμ	0.581	0.327	0.216
410 mμ	0.188	0	0
420 mμ	0	0	0

The K values are different depending on the wavelengths. The null-values of the K's at the higher wavelengths are of some interest, because these values mean that the interactions are principally due to the contact charge-transfer complex[16] and that the effects of many complexes with different orientations are overlapping to show a broad absorption band.

The small values of the equilibrium constants, K, are due to the fact that there are various mixtures, from the loose forms of the 1 : 1 complexes to the contact-type form. In contrast to this, the K value for the A–I_2 complex in carbon tetrachloride is estimated to be $K_c=52$ (l./mol.)[17] and $K_c=3.7$ (l./mol.).[18] The same tendency is also shown in the K's at 15 and 30°C.

The apparent enthalpy and entropy changes calculated from these K values at 400 mμ are as follows:

$\Delta G^\circ=0.64$ kcal. mol^{-1}, $\Delta H=-4.8$ kcal. mol^{-1} and $\Delta S^\circ=-19$ cal. deg^{-1} mol^{-1}.

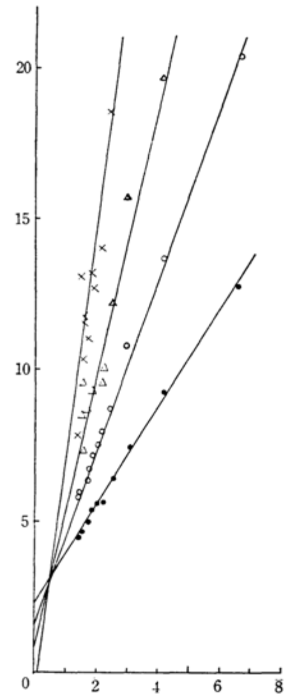

Fig. 3. Benesi-Hildebrand plot, anthracene-SO_2 in CCl_4 at 0°C.
●—● 390 mμ △—△ 410 mμ
○—○ 400 mμ ×—× 420 mμ

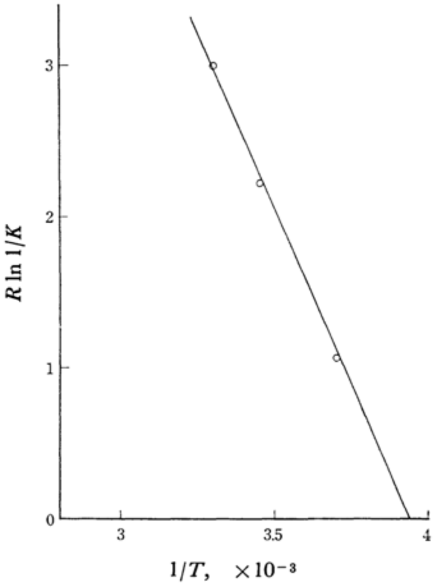

Fig. 4. $R \ln 1/K$ vs. $1/T$ plot. Anthracene-SO_2 in CCl_4

The spectra of liquid sulfur dioxide in various solvents indicate the interaction of the solvents with sulfur dioxide. The maximum of the absorption of sulfur dioxide is observed at 290 mμ (ε 383)[19]; the λ_{max} and ε were almost the same in such solvents as n-hexane and carbon tetrachloride, which show no interaction with sulfur dioxide. However, in benzene, ethanol and methanol the λ_{max} of sulfur dioxide shifts to a shorter wavelength

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[15] R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

[16] L. E. Orgel and R. S. Mulliken, *J. Am. Chem. Soc.*, **71**, 4839 (1957).

[17] B. Bhattacharya and S. Basu, *Trans. Faraday Soc.*, **54**, 1286 (1958).

[18] J. Peters and W. B. Person, *J. Am. Chem. Soc.*, **86**, 10 (1964).

[19] D. Booth, E. S. Dainton and K. J. Ivin, *Trans. Faraday Soc.*, **55**, 1293 (1959).

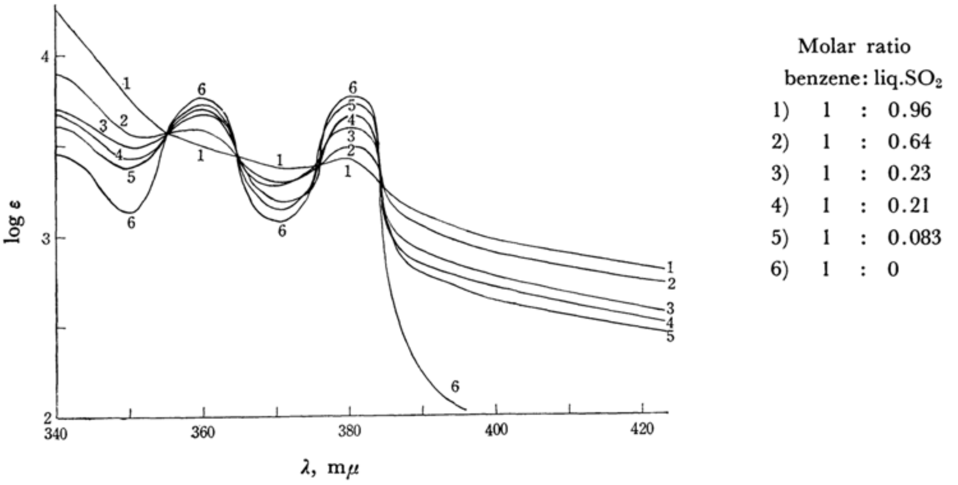

Fig. 5. The electronic spectra of anthracene, benzene-SO_2 system, 30°C.

TABLE II. THE RESULTS OF PHOTOCHEMICAL REACTION

No.	Anthracene $\times 10^{-2}$ mol./l.	Solvent	ml.	Temp. °C	Time hr.	Product %
1	1.33	liq.SO_2	380	−25	3	I (53.1)
						II (9.3)
2	0.43	*n*-Hexane	350	−25	3	I (75.2)
		liq.SO_2	20			II (14.9)
3	1.35	CCl_4	221			I (25.9)
		liq.SO_2	195	−25	3	II (46.6)
4	0.16	Ethanol	450			I trace
		liq.SO_2	40	−25	3	II (39.0)
5	6.48	Benzene	130	20	3	III (31.7)
6	6.39	Benzene	130			
		liq.SO_2	2	20	3	no reaction
7	1.69	Benzene	107			
		liq.SO_2	60	20	8	no reaction
8	1.40	Benzene	222			
		liq.SO_2	180	−25	3	no reaction
9*	1.94	CS_2	233	−10	1.5	IV (9.7)
10*	1.91	CS_2	233	−10	1.5	trace of sulfur
		liq.SO_2	4			compound**
11	1.91	CS_2	233			
		liq.SO_2	4	−10	1.5	no reaction
12*	1.47	liq.SO_2	320	−10	1.5	I (84.4)
						II (4.7)

The yields of the products are in mole percent.

* O_2 was bubbled into the solution.

** m. p. >300°C (sinters at ca. 135°C), IR, 1680 cm^{-1} ($\nu_{C=O}$), 1160 and 1310—1340 cm^{-1} (ν_s and ν_{as} SO_2), UV, λ_{max} 252 mμ. Sulfur content 14.88%. The yield was very small and the structure was not identified.

(280—274 mμ) and the molecular extinction coefficient, ε, also increases (for example, 1390 in benzene),[20] indicating an interaction of some extent. In carbon disulfide, an absorption which might be due to a charge-transfer complex with sulfur dioxide appears. The same trend is seen in benzene, as is shown in Fig. 5, which indicates that the anthracene-sulfur dioxide complex is affected by benzene. The Benesi-Hildebrand plot is scattered, indicating that the anthracene-sulfur dioxide interaction in benzene results in a sort of contact charge-transfer complex.

In ethanol, despite the supposed EtOH - sulfur

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[20] L. J. Andrews and R. N. Keefer, *J. Am. Chem. Soc.*, **73**, 4169 (1951).

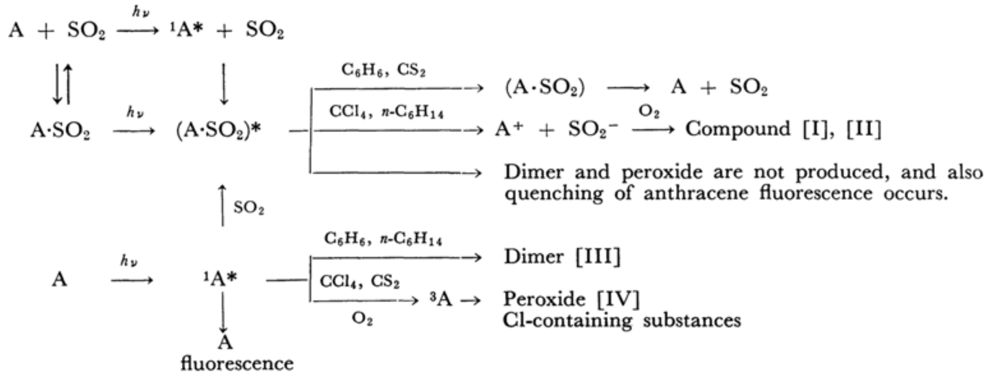

Fig. 6. Reaction schemes.

dioxide interaction, a linear Benesi-Hildebrand plot was observed, indicating that either a loose 1 : 1 complex or a complicated, anthracene - sulfur dioxide - EtOH (for example, a 1:1:1 complex) complex might be formed. Moreover, the absorptions at 610—680 mμ of anthracene due to the S–T transition[21] of anthracene in an approximately saturated solution were not observed in such systems as carbon tetrachloride, carbon disulfide and carbon disulfide - oxygen.

The Irradiation of Anthracene - Sulfur Dioxide Solutions by a High-pressure Mercury Lamp.—In order to obtain further information about the effects of solvents on the interaction between sulfur dioxide and anthracene, irradiation by a high-pressure mercury lamp was attempted. The results are listed in Table II.

The yields of I and II were higher in the presence of *n*-hexane and carbon tetrachloride. According to the findings of Bowen et al., the irradiation of anthracene in carbon tetrachloride gave chlorine-containing compounds,[22] whereas in this anthracene - sulfur dioxide - carbon tetrachloride system sulfur-containing compounds were produced in place of chlorinated compounds.

It has been already established that, in benzene, anthracene dimerizes by an irradiation through an excited singlet state (Exp. No. 5). By the addition of a small amount of sulfur dioxide, regardless of its quantity or the reaction time, the dimerization reaction was inhibited (Exp. No. 6, 7 or 8). In addition, no sulfur compounds were found in the reaction mixture. The results are interpreted as being the consequence of the formation of an anthracene - sulfur dioxide - benzene contact complex. In an ethanol solution (Exp. No. 4), the sulfur content in the products was greatly decreased. In carbon disulfide (Exp. No. 11), also, no sulfur-containing compound was found in the reaction mixture. The previously-recognized formation of endocyclic peroxide through a triplet state by the bubbling of oxygen gas into a carbon disulfide solution of anthracene (Exp. No. 9) was inhibited by the addition of sulfur dioxide in the presence of oxygen; it was replaced by the formation of a small amount of a sulfur compound.

With regard to the influence of oxygen addition to sulfur dioxide (Exp. No. 12), it was demonstrated that formation of I and II was not affected. Thus, it can be assumed that the activated intermediate which induces the formation of I and II is of a singlet character. This assumption is supported by the following facts. i) Neither the disulfone nor the disulfonic acid of anthracene was produced, though expected, if the intermediate was of a triplet state as a result of its radical character. In fact, Squire et al.[23] obtained diphenyl disulfone by the thermal reaction of benzene and sulfur dioxide in the presence of a radical source such as benzoyl peroxide. ii) As has been described above, the sulfur-containing substances were produced in preference to chlorinated compounds in the anthracene - sulfur dioxide - carbon tetrachloride system, though a Cl-radical-abstracting reaction might be expected if the intermediate had a triplet character. Actually, under irradiation by a low-pressure mercury lamp (2537 Å), chlorinated compounds were produced in preference to sulfur-containing compounds, even in the anthracene - sulfur dioxide - carbon tetrachloride system which is similar to that of the photoreaction of anthracene in carbon tetrachloride without sulfur dioxide undertaken by Bowen et al.[22] (A low-pressure mercury lamp does not emit the radiation of the wavelength required for the excitation of anthracene-sulfur dioxide complex.) This behavior differs from the behavior under the irradiation of a high-pressure mercury lamp. iii) Moreover, the absorption at 610—680 mμ of anthracene due to S–T transition was not observed.

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[21] In a CHCl$_3$ solution of anthracene containing acetylacetonate of Fe^{3+}, the absorptions at 610—680 mμ due to the S-T transition of anthracene have been recognized by Chaudhuri et al. (J. N. Chaudhuri and S. Basu, *Trans. Faraday Soc.*, **54**, 1605 (1958)).

[22] E. J. Bowen and K. K. Rohatgi, *Discussions Faraday Soc.*, **14**, 146 (1953).

[23] J. M. Squire and W. A. Waters, *J. Chem. Soc.*, **1962**, 2068.

As has been described above, the photochemical reactions in solutions, the reaction of anthracene with sulfur dioxide are seriously influenced by the solvents used, the interaction between the solvent and sulfur dioxide being of the greatest importance. The reaction schemes are illustrated in Fig. 6. As is shown in the scheme, the various reaction courses in the photochemical influence are presumably founded on the excited anthracene - sulfur dioxide complex $(A \cdot SO_2)^*$, which may be produced by the photo-activation of a charge-transfer complex or by the interaction of sulfur dioxide with photoactivated anthracene rather than by the photoactivated sulfur dioxide.[24]

Dimerization in a benzene solution is thus inhibited, and the quenching[25-28] of anthracene fluorescence occurs by the addition of a small amount of sulfur dioxide. Moreover, in benzene or a carbon disulfide solution, in the presence of sulfur dioxide, I and II are not formed, indicating that the interaction of anthracene with sulfur dioxide is diminished by the solvent-sulfur dioxide interaction.

On the contrary, in a *n*-hexane or in carbon tetrachloride solution, which has no interaction with sulfur dioxide, anthracene interacts with sulfur dioxide as much as in liquid sulfur dioxide, where the electron - transferred complex is stabilized in the excited state by solvation with the surrounding sulfur dioxide. The sulfur-containing compounds, such as sulfonic acid of the aromatic compound, will thus be produced from the excited anthracene-sulfur dioxide complex and an atmospheric oxygen which is probably present slightly in the reaction system. The photochemical formation of sulfonic acid of the aromatic compound gives a new synthetic method.

The authors wish to express their thanks to Mr. Hiroshi Takeuchi of our laboratory for his help in the experimental work.

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[24] In the photochemical gas-phase reactions between sulfur dioxide and olefin or paraffin, the formation of sulfinic acids due to the excitation of sulfur dioxide has been reported by Dainton and Ivin (F. S. Dainton and K. J. Ivin, *Trans. Faraday Soc.*, **46**, 374, 382 (1950)). Thereby, the photochemical products, such as dibenzyl disulfone and benzyl-sulfinic acid, may be expected from sulfur dioxide and toluene if sulfur dioxide is excited, but no photochemical formation is observed under the present conditions. Therefore, the interaction of the photoactivated free anthracene with sulfur dioxide is predominant, rather than that by photo-activated sulfur dioxide, since greater amounts of anthracene than the quantity of the complexed anthracene expected from the calculated value of the equilibrium constant, *K*, are brought into the reaction or inhibition for dimerization. It would be very interesting to know if there is a possibility of a singlet-triplet intersystem crossing of the photoactivated anthracene by sulfur dioxide, due to the spin-orbit coupling. However, no evidence for such a conversion has been obtained.

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