[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

The Interaction of Sulfur Dioxide with Aromatic Substances

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Solutions of sulfur dioxide in benzene and certain of its substitution products show absorption maxima in the wave length region 278–305 mμ which are regarded as characteristic of 1:1 sulfur dioxide-aromatic addition compounds. By spectrophotometric procedures used previously, in studying halogen–aromatic interactions, equilibrium constants for reactions to form these addition compounds have been evaluated. The stabilities of the complexes are enhanced by the presence of substituents on the aromatic nucleus which increase the electron density on the ring. Possible structures for the complexes are discussed in the light of structures proposed earlier for related aromatic molecular addition compounds.

The capacity of sulfur dioxide to undergo molecular association with the aromatic nucleus has been demonstrated on the basis of low temperature phase diagram studies[1] and of viscosity measurements[2] of solutions of sulfur dioxide in benzene and certain of its derivatives. The results of Locket suggest that increasing methyl substitution on the benzene ring results in an enhanced affinity for sulfur dioxide. This observation parallels those made in regard to the tendency for interaction of benzene derivatives with picric acid,[3] tetranitromethane,[4] aromatic nitro compounds,[5] silver ion,[6] and halogens,[7] hydrogen chloride[8] and hydrogen fluoride–boron trifluoride mixtures.[9]

It has seemed desirable to have available more quantitative information concerning the relative tendencies for benzene and certain of its derivatives to interact with sulfur dioxide. Now this has been obtained by the use of essentially the same spectrophotometric procedure that was employed in the investigation of the halogens.[7] It has been found that solutions of sulfur dioxide in aromatic solvents display absorption maxima in the ultraviolet which, though not nearly so pronounced as those encountered in the halogen studies, are best interpreted as being characteristic of 1:1 complexes. Equilibrium constants for the formation of sulfur dioxide complexes of several benzene derivatives in carbon tetrachloride solution have been evaluated. The relative magnitudes of these constants for the various aromatic substances studied are in accord with the basicity series previously established for benzene and certain of its substitution products.[3–8]

Experimental

The Aromatic Compounds.—Eastman Kodak Co. white label mesitylene was further purified by the method of Smith and Cass.[10] A sample of b.p. 164.5–165.5°, $n^{25}\text{D}$ 1.4970, was used in the experiments reported. The remaining materials were samples purified in connection with previous work.[6,7b]

Solvents.—A previously purified sample of carbon tetrachloride[7b] was used. The cyclohexane was Eastman Kodak Co. white label material. A U.S.P. grade of chloroform was used. The methanol was Baker and Adamson reagent grade. Eastman Kodak Co. white label dibutyl ether was dried over sodium and distilled, b.p. 141.5–142.0°. Eastman Kodak Co. cyclohexene (100 g.) was treated with 0.1 mole of methylmagnesium iodide in 40 cc. of ether to remove traces of oxygenated compounds.[11] The recovered cyclohexene was fractionated, b.p. 82.8–83.0°.

Sulfur Dioxide Solutions.—Solutions of sulfur dioxide in the various organic solvents were prepared from sulfuric acid-washed tank sulfur dioxide. The solutions were diluted to about 0.05 *M* sulfur dioxide concentration before analysis. Samples removed for analysis were shaken with water or excess standard sodium hydroxide solution. These aqueous solutions were then titrated according to the established acidimetric–alkalimetric procedures.[12]

The Absorption Spectrum Measurements.—Solutions of sulfur dioxide in various solvent mixtures of carbon tetrachloride and the aromatic substance under investigation were prepared at 25° and measured on the Beckman model DU spectrophotometer using the solvent mixture as a blank. The cell housing was maintained at 25°. Optical density measurements were made from the lowest attainable wave length up to 360 mμ. All optical densities were corrected for the cell blanks as determined from measurements in which both cells contained pure carbon tetrachloride.

Results

The ultraviolet absorption spectrum of sulfur dioxide in a variety of polar and non-polar solvents was investigated. In all cases an absorption maximum was observed in a region varying from 274 mμ (methanol) to 305 mμ (mesitylene). The wave lengths and extinction coefficients for these maxima are listed in Table I. In the non-basic solvents, carbon tetrachloride, cyclohexane and chloroform[13] the maximum occurs at about 290 mμ, and the extinction coefficients are relatively low. With the oxygenated solvents, dibutyl ether and methanol, the absorption maximum is shifted further into the ultraviolet, and the extinction coefficients are considerably larger than those observed for the non-basic solvents. It is possible that this is indicative of interaction between sulfur dioxide and the basic oxygen atoms in the oxygenated solvents. It is significant in this regard that Moede and Curran[13] have observed a high absorption peak in the neighborhood of 270 mμ for *n*-butyl chloride solutions of the trimethylamine–sulfur dioxide addition compound. They suggest that the strong absorption of this complex may stem from the fact that the unshared electrons of the sulfur atom are loosened in forming a coördinate bond between the nitrogen and sulfur atoms.

In aromatic solvents the wave lengths of the absorption maxima range from 280–305 mμ and are shifted toward the visible with increasing methyla-

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(1) (a) Mazzetti and de Carli, *Gazz. chim. ital.*, **56**, 34 (1926); (b) de Carli, *Atti accad. Lincei*, [6] **4**, 460, 533 (1926).

(2) Locket, *J. Chem. Soc.*, 1501 (1932).

(3) (a) Dimroth and Bamberger, *Ann.*, **438**, 67 (1924); (b) Moore, Shepherd and Goodall, *J. Chem. Soc.*, 1447 (1931).

(4) (a) Hammick and Young, *ibid.*, 1463 (1936); (b) Davies and Hammick, *ibid.*, 763 (1938).

(5) Hamilton and Hammick, *ibid.*, 1350 (1938).

(6) Andrews and Keefer, THIS JOURNAL, **71**, 3644 (1949); **72**, 3113, 5034 (1950).

(7) (a) Benesi and Hildebrand, *ibid.*, **70**, 3978 (1948); **71**, 2703 (1949). (b) Keefer and Andrews, *ibid.*, **72**, 4677, 5170 (1950). (c) Andrews and Keefer, *ibid.*, **73**, 462 (1951).

(8) Brown and Brady, *ibid.*, **71**, 3573 (1949).

(9) McCaulay and Lien, Abstracts of Papers, Detroit Meeting of the American Chemical Society, Chicago, Ill., Sept. 1950.

(10) Smith and Cass, THIS JOURNAL, **54**, 1606 (1932).

(11) Frederick, Cogan and Marvel, *ibid.*, **56**, 1815 (1934).

(12) Scott, "Standard Methods of Chemical Analysis," Vol. I, Fifth Edition, D. Van Nostrand Co., New York, N. Y., 1939, p. 927.

(13) *Cf.* Moede and Curran, THIS JOURNAL, **71**, 852 (1949).

tion of the benzene ring. With the exception of that for chlorobenzene the extinction coefficients range from about 1400–2000. The large magnitude of the extinction coefficient in these solvents as compared to that for solvents such as carbon tetrachloride is regarded as an indication of the existence of an interaction between sulfur dioxide and aromatic solvent molecules which is lacking in the nonbasic solvents.

TABLE I

ABSORPTION MAXIMA AND EXTINCTION COEFFICIENTS OF SULFUR DIOXIDE IN VARIOUS SOLVENTS

Solvent	(SO_2) mole/liter × 10^3	$\lambda_{max.}$ mμ	$\epsilon_{max.}$ [a]
Carbon tetrachloride	2.70	290	271
Cyclohexane	2.31	292	328
Chloroform	2.34	289	350
Di-*n*-butyl ether	2.29	284	620
Methanol	1.68	274	810
Benzene	0.570	280	1390
Toluene–CCl_4 [b]	.402	284	1540
m-Xylene–CCl_4 [b]	.429	296	1780
p-Xylene–CCl_4 [b]	.400	296	1550
o-Xylene–CCl_4 [b]	.458	296	1730
Mesitylene–CCl_4 [b]	.596	305	1960
Chlorobenzene–CCl_4 [b]	1.065	288	830
Cyclohexene–CCl_4 [b]	0.688	*ca.* 292	920

[a] Based on total sulfur dioxide in solution. [b] The mole fractions of aromatic or unsaturated substance in these mixed solvents were as follows: toluene, 0.900; *m*-xylene, 0.845; *p*-xylene, 0.845; *o*-xylene, 0.849; chlorobenzene, 0.825; mesitylene, 0.735; cyclohexene, 0.832.

For each of the aromatic compounds investigated a series of measurements of the optical density, *d*, at the absorption maximum were made for solutions of varying composition of sulfur dioxide and aromatic substance in carbon tetrachloride at 25°. These values were used to calculate equilibrium constants for 1:1 complex formation according to equation (1)

$$A + SO_2 = A{\cdot}SO_2 \quad K = (A{\cdot}SO_2)/(A)(SO_2) \qquad (1)$$

assuming initially that the concentration (*C*) of the complex in these solutions is given by equation (2)

$$\log I_0/I = d = (C)\epsilon_c l \qquad (2)$$

where ϵ_c is the molecular extinction coefficient of the complex and *l* is the light path length, 1 cm. in these studies. The condition that $(A) \gg (SO_2)_i$, where $(SO_2)_i$ represents the concentration of both free and complexed sulfur dioxide, was imposed in all of these experiments. It therefore follows that

$$K = \frac{(C)}{[(SO_2)_i - (C)]N_A} \qquad (3)$$

where N_A is the mole fraction of aromatic substance in the solvent, and that

$$\frac{(SO_2)_i l}{d} = \frac{1}{K\epsilon_c} \cdot \frac{1}{N_A} + \frac{1}{\epsilon_c} \qquad (4)$$

A plot of $(SO_2)_i l/d$ against $1/N_A$ should yield a straight line from the intercept and slope of which ϵ_c and *K* values for the complex may be calculated. The assumptions made in treating the data by this method are essentially those discussed in connection with the corresponding work on the halogens[7]: namely, that N_A is equal to the activity of A; that $(C)/[(SO_2)_i - (C)]$ is equal to the ratio of the activities of $A{\cdot}SO_2$ and SO_2; and that ϵ_c for a particular complex remains constant as the solvent composition is varied.

Since the *K* values for formation of these complexes were not large, the measured optical densities included not only the absorption of the complex but, particularly in solutions of low concentration of aromatic substance, also included appreciable absorption of free sulfur dioxide. The plots of the data according to equation (4) using the measured optical densities thus deviated to some extent from linearity, particularly in the region in which $1/N_A$ values were large. The initial slopes of the curves obtained were used to determine *K* values as first approximations. The concentrations of free and complexed sulfur dioxide were then determined, on the basis of these approximate *K* values, from equation (3). The contributions of the free and complexed sulfur dioxide to the measured optical density were calculated on the assumption that the free sulfur dioxide had the same extinction coefficient in these solutions as in carbon tetrachloride. The data were then replotted according to equation (4) using the calculated optical density of the complexed sulfur dioxide. The points thus obtained conformed well to a straight line. The data were then recalculated on the basis of the new *K* value, and the approximation process was repeated until the *K* values on two successive approximations remained constant to the second decimal place.

TABLE II

MAXIMUM OPTICAL DENSITIES FOR THE AROMATIC–CARBON TETRACHLORIDE SOLUTIONS OF SULFUR DIOXIDE (25°)

$1/N_A$	$(SO_2)_i$ mole/liter × 10^4	$d_{max.}$	$1/N_A$	$(SO_2)_i$ mole/liter × 10^4	$d_{max.}$
	Benzene			Toluene	
1.000	5.70	0.793	1.110	3.50	0.526
1.092	4.55	.607	1.220	6.43	.973
1.368	7.15	.825	2.10	3.85	.427
1.92	10.00	.935	2.83	4.81	.456
2.53	12.50	.960	5.40	7.70	.476
4.69	10.80	.582	8.70	9.64	.490
7.44	18.78	.791			
	m-Xylene			*p*-Xylene	
1.182	4.29	0.764	1.182	4.00	0.620
2.271	4.29	.584	2.278	4.00	.457
4.178	4.90	.473	4.19	9.15	.753
6.08	10.30	.824	6.10	9.60	.656
9.90	12.88	.783	9.92	12.00	.649
	o-Xylene			Mesitylene	
1.179	4.58	0.792	1.361	5.96	1.17
2.245	4.58	.602	2.442	3.72	0.597
4.12	5.22	.492	4.61	4.26	.480
6.00	10.98	.867	6.77	5.96	.533
9.74	13.72	.840	11.09	7.45	.496
	Chlorobenzene				
1.211	10.65	0.883			
2.055	8.00	.512			
4.16	16.00	.734			

The experimental data on which these calculations were based are given in Table II, and the resultant *K* and ϵ_c values appear in Table III. Accurate values for chlorobenzene could not be obtained, as the data for solutions in which the $1/N_A$

TABLE III

EQUILIBRIUM CONSTANTS FOR FORMATION OF THE SULFUR DIOXIDE-AROMATIC COMPLEXES (25°)

	ϵ_c[a]	K
Benzene	3850	0.47
Toluene	3450	0.79
m-Xylene	2940	1.49
p-Xylene	2640	1.34
o-Xylene	2700	1.65
Mesitylene	3230	2.11
Chlorobenzene	2500–3300	0.27–0.39

[a] The extinction coefficient of the 1:1 complex.

values were large even after several reapproximations did not conform to linearity according to equation (4). Thus an insufficient number of points were obtained to establish with certainty the best straight line to fit the data. It is presumed that the deviation from linearity noted in this case resulted from the fact that the K value for chlorobenzene is small so that small errors in estimating the amount of free sulfur dioxide in the solutions introduced appreciable error in the calculation of the optical density of the complex.

The Structure and Stability of the Complexes.—The effects of ring substituents on the equilibrium constants (Table III) for aromatic–sulfur dioxide complexes are very similar to those noted in other studies[3–7] in which the availability of electrons on the aromatic nucleus governs the extent of complex formation. Increasing methyl substitution of the aromatic ring results in an increased affinity for sulfur dioxide, while a chlorine substituent has a deactivating effect. The fact that the numerical values of K for sulfur dioxide complex formation of benzene, toluene and the three xylenes are all within close limits one-tenth those for the corresponding iodine monochloride complexes[7b] is an indication of the close parallel in the roles assumed by sulfur dioxide and the halogens in the aromatic interaction process.

Mulliken has recently summarized current opinion regarding the structural nature of molecular complexes. These sulfur dioxide–aromatic interaction products very likely fall into a group of molecular complexes described by Mulliken as "loose compounds of a base with a Lewis acid."[14] The binding forces operative in the sulfur dioxide complex are probably primarily of the van der Waals type modified by contributions from structures of the type $C_6H_6{}^+SO_2{}^-$. The term "intermolecular semipolar bond" suggested by Woodward[15] might well be adopted to describe this type of coördinate link.[16]

In connection with a discussion of bond strengths it is of interest to compare the electron acceptor strength of sulfur dioxide with those of the halogens.[7] The equilibrium constants for formation of the benzene complexes indicate that the ability of these compounds to function as acids increases in the order $Cl_2 < SO_2 < Br_2 < I_2 < ICl$.

Figure 1 presents the absorption spectra of certain of the aromatic–sulfur dioxide complexes. These curves, which represent only the absorption of the complexed sulfur dioxide, were derived from experimental data by use of the equilibrium constants for formation of the complexes in much the same manner as was employed in evaluating the corresponding spectra of the iodine monochloride complexes.[7b] These curves resemble in shape and in the position of the absorption maxima those of the halogen complexes, although the extinction coefficients at the maxima are considerably lower for the sulfur dioxide complexes than for those of halogen.[7b,c]

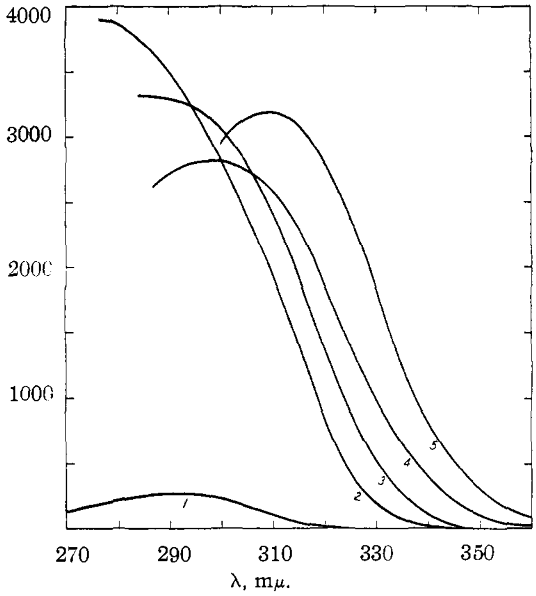

Fig. 1.—The absorption spectra of the sulfur dioxide complexes: curve 1, sulfur dioxide in carbon tetrachloride; curve 2, the benzene complex in pure benzene; curve 3, the toluene complex in toluene–CCl_4 solution (N toluene = 0.900); curve 4, the *o*-xylene complex in *o*-xylene–CCl_4 (N*o*-xylene = 0.849); curve 5, the mesitylene complex in mesitylene–CCl_4 (N mesitylene = 0.735).

The benzene–iodine absorption maximum in the 300 mμ region has been characterized as an intermolecular charge transfer spectrum[14,17] characteristic of the 1:1 molecular complex and resulting from the partial transfer of an electron from the benzene to the iodine. The spectrum of the sulfur dioxide complex may be of this same type. On the other hand, since these complexes show major absorption very close to the absorption maximum of uncomplexed sulfur dioxide, the complex absorption may be intensified sulfur dioxide absorption. This latter picture is similar to that suggested by Mulliken[17] as a possible explanation for the absorption of the benzene–iodine complex near 500 mμ.

The spatial orientation of the aromatic nucleus with respect to the electron acceptor molecule in these molecular complexes has not been generally established. For the benzene–iodine complex Mulliken prefers a structure in which the iodine molecule lies with its center on the sixfold symmetry axis of the benzene molecule and its axis parallel to

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(14) Mulliken, Abstracts of the American Chemical Society Meeting, Chicago, Illinois, September, 1950, Symposium on Generalized Acids and Bases.

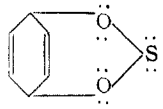
(15) Woodward, THIS JOURNAL, **64**, 3058 (1942).

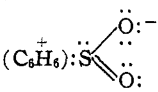
(16) Professor Mulliken has indicated in a private communication that he agrees with the general idea of Woodward and will shortly publish a more precise quantum mechanical treatment of this viewpoint.

(17) Mulliken, THIS JOURNAL, **72**, 605 (1950).

the plane of the ring rather than one[7b,c] in which the axis of the halogen molecule is coincident with the sixfold symmetry axis of the ring. His preference is based on group theory-symmetry considerations and on the argument that van der Waals forces will be greater for the more compact model. For the benzene–silver ion complex similar considerations as based on group theory lead Mulliken to the conclusion that the most favorable location for silver ion is off the six-fold symmetry axis of the ring.[14,16] This conclusion is borne out by preliminary interpretation of X-ray crystallographic measurements of $AgClO_4 \cdot C_6H_6$.[18]

In considering the question of the relative configurations in space of the two molecules contributing to the sulfur dioxide complex two structural types patterned after those discussed previously and in keeping with the non-linear structure of the inorganic component of the complex[19] are sufficiently interesting to deserve specific mention. The first is spatially similar to that proposed by Mulliken for the iodine complex[17] and involves an O–S–O bridge between para positions of the ring with the center of the sulfur atom on a line through the center and perpendicular to the plane of the ring.



One would suspect, however, that the sulfur rather than the oxygen atoms resides nearest the aromatic nucleus in the complex.[20] A structure in which the sulfur dioxide molecule again lies above the plane of the ring but with the sulfur atom making the closest approach to that plane seems preferable. Small contributions from ionic forms such as  would contribute to the stability of such a complex.

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(18) Rundle and Goring, THIS JOURNAL, **72**, 5337 (1950).

(19) See for example Schomaker and Stevenson, *ibid.*, **62**, 1270 (1940).

(20) This reasoning is in keeping with the observation that conjugated dienes react with sulfur dioxide to form cyclic sulfones. Grummitt, Ardis and Fick, *ibid.*, **72**, 5167 (1950), present a discussion of the mechanism of this reaction which is of considerable interest in relation to the results of the present study.

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[CONTRIBUTION NO. 73 FROM THE INSTITUTE FOR ATOMIC RESEARCH, IOWA STATE COLLEGE]

The Hydrogen Positions in Uranium Hydride by Neutron Diffraction[1]

BY R. E. RUNDLE

The hydrogen positions in UD_3 have been determined by neutron diffraction, showing that the bridge structure previously proposed is incorrect. The hydrogens lie in distorted tetrahedra, equidistant from four uranium atoms, with U–D = 2.32 A. There are two types of uranium atoms in the structure, each with twelve nearest D atoms at this distance. The structure is illustrated.

Introduction

Uranium hydride, UH_3, has a primitive cubic lattice, a_0 = 6.63 kX., and a metal arrangement like that of β-tungsten, *i.e.*, $2U_I$ at 000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $6U_{II}$ at $\pm\frac{1}{4}0\frac{1}{2}$ↄ.[2] It has been suggested that the hydrogen atoms lie at the midpoints of the ligands between U_I and U_{II}, so that the hydrogen atom would form two interatomic links to uranium, presumably with one electron pair.[2] In support of the above structure Pauling and Ewing[3] pointed out that the U–H distances given by the proposed structure are in excellent agreement with those calculated from Pauling's rule and metallic radii.[4]

Structures in which hydrogen bridges two atoms together with one electron pair have become quite popular as explanations of electron deficient bonding. The cases where this type of bonding has been verified experimentally are, however, still very few in number, and none of the verified cases include metallic hydrides. For several reasons it seemed important to check the proposed structure of UH_3. This is possible only by neutron diffraction.

Because of the higher coherent scattering factor and lower spin diffuse scattering of deuterium for neutrons,[5] UD_3 rather than UH_3 was used for neutron diffraction study. The results show without question that the suggested bridge structure is incorrect, and provide a different and more complex structure for the hydride.

Structure Determination

Preparation of the Deuteride.—UD_3 was made from uranium metal and deuterium gas. D_2 was prepared from D_2O by Newton's method,[6] which in the final step involves decomposition of UD_3, and furnishes deuterium very free of oxygen, carbon and nitrogen. The D_2O, furnished by the A. E. C., contained less than 0.2% of the hydrogen as H.

Neutron Diffraction Data.—The powder diffraction data (Fig. 1) were obtained by C. G. Shull using the apparatus and method described by Wollan and Shull.[5] Integration across the diffraction maxima, (hkl), gives the power, P_{hkl},

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(1) Presented in part at the Am. Chem. Soc. Convention, San Francisco, Calif., April, 1949.

(2) R. Rundle, THIS JOURNAL, **69**, 1719 (1947).

(3) L. Pauling and F. J. Ewing, *ibid.*, **70**, 1660 (1948).

(4) L. Pauling, *ibid.*, **69**, 542 (1947).

(5) E. O. Wollan and C. G. Shull, *Phys. Rev.*, **73**, 830 (1948).

(6) F. Spedding, A. Newton, J. Warf, O. Johnson, R. Nottorf, I. Johns and A. Daane, *Nucleonics*, **4**, 4 (1949).