1027. *Sulphur Dioxide. Part I. Phase Diagrams of Some Aromatic Hydrocarbon–Sulphur Dioxide Binary Mixtures*

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Phase-diagram studies show the existence of the following compounds: C_6H_6,SO_2, incongruent m. p. $-58°$; $(MeC_6H_5)_2, SO_2$, m. p. $-95°$; (o-$Me_2C_6H_4)_2,SO_2$, incongruent m. p. $-59°$; (m-$Me_2C_6H_4)_2,SO_2$, incongruent m. p. $-71°$; (p-$Me_2C_6H_4)_2,SO_2$, incongruent m. p. $-17°$; and 1,3,5-$Me_3C_6H_3,SO_2$, m. p. $-46°$.

SULPHUR DIOXIDE is a well-known electron acceptor. The stoicheiometry of the molecular addition compounds formed by onium donors with sulphur dioxide appears to depend on the number of donor sites available. For example, acetone, diethyl sulphide, and pyridine form 1 : 1 addition compounds whereas dioxan forms 1 : 1 and 1 : 2 addition compounds with sulphur dioxide.[1,2] The evidence for compound formation between π donors and sulphur dioxide is confused.[3] The application of phase diagram techniques, which indicate specific interactions in the solid state, to binary mixtures of benzene, toluene, *o*-, *m*-, and *p*-xylenes, and mesitylene with sulphur dioxide, is reported here.

RESULTS

M. p.s of binary mixtures of aromatic hydrocarbons with sulphur dioxide are recorded in Tables 1—6. Concentrations are expressed in terms of the mole fraction, x, of sulphur dioxide. M. p. determinations were repeated at least once and are considered to be accurate to $\pm 0{\cdot}2°$. Thermochroism, which occurs in binary mixtures of aromatic hydrocarbons with dinitrogen tetroxide,[4] is not observed.

TABLE 1

Benzene

SO_2 (x)	M. p. (°C)
0·0000	5·6
0·1090	−2·2
0·2023	−9·0
0·2565	−12·8
0·2957	−15·4
0·3546	−20·0
0·3839	−22·3
0·4561	−28·7
0·4858	−32·0
0·5442	−37·5
0·5946	−43·0
0·6467	−49·0
0·7007	−55·7
0·7565	−60·5
0·7995	−63·5
0·8518	−68·4
0·8997	−76·3
0·9492	−74·0
1·0000	−72·5

TABLE 2

Toluene

SO_2 (x)	M. p. (°C)
0·0000	−95·0
0·1015	−96·8
0·1938	−100·5
0·2464	−96·9
0·2916	−95·8
0·3529	−95·7
0·3991	−97·7
0·4562	−101·1
0·5167	−100·7
0·5357	−98·3
0·6045	−92·2
0·6313	−90·3
0·7078	−85·3
0·8009	−80·0
0·8969	−76·0
0·9493	−74·0
1·0000	−72·5

TABLE 3

o-Xylene

SO_2 (x)	M. p. (°C)
0·0000	−25·2
0·0444	−26·8
0·0853	−29·0
0·1789	−33·8
0·2400	−37·5
0·3109	−42·0
0·3563	−46·0
0·3762	−47·5
0·4471	−54·5
0·5066	−59·0
0·5277	−59·5
0·6106	−61·5
0·6568	−63·0
0·7073	−65·5
0·7543	−69·5
0·8130	−75·0
0·8560	−78·5
0·9029	−79·0
0·9523	−76·5
1·0000	−72·5

TABLE 4

m-Xylene

SO_2 (x)	M. p. (°C)
0·0000	−48·0
0·0713	−49·8
0·1960	−56·5
0·2758	−62·3
0·3345	−68·2
0·3906	−72·5
0·4480	−77·7
0·5000	−87·0
0·5229	−91·8
0·5982	−93·3
0·6401	−90·0
0·6977	−86·6
0·7899	−81·5
0·8909	−76·5
0·9487	−74·3
1·0000	−72·5

TABLE 5

p-Xylene

SO_2 (x)	M. p. (°C)
0·0000	13·0
0·1010	8·5
0·1716	4·5
0·2725	−2·0
0·3343	−5·5
0·3742	−8·8
0·4166	−12·0
0·4775	−16·8
0·5469	−22·0
0·5658	−23·5
0·6106	−28·5
0·6578	−33·5
0·7182	−40·0
0·7655	−45·8
0·7963	−49·8
0·8436	−57·2
0·9030	−68·5
0·9511	−78·5
1·000	−72·5

TABLE 6

Mesitylene

SO_2 (x)	M. p. (°C)
0·0000	−52·7
0·0912	−58·0
0·1176	−61·0
0·1693	−64·0
0·2465	−56·2
0·2951	−52·0
0·3559	−49·0
0·4368	−46·5
0·5440	−47·5
0·6631	−53·0
0·7875	−61·8
0·9074	−71·5
0·9258	−72·8
0·9416	−74·8
0·9760	−74·0
1·0000	−72·5

DISCUSSION

The benzene–sulphur dioxide phase diagram indicates the formation of an addition compound of incongruent m. p. —58° with a probable 1 : 1 composition. This system has been investigated previously by three groups. Terres and Doerges obtained a similar

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[1] N. F. Albertson and W. C. Ferneleus, *J. Amer. Chem. Soc.*, 1943, **65**, 1687.

[2] K. R. Hoffman and C. A. vanderWerf, *J. Amer. Chem. Soc.*, 1946, **68**, 997.

[3] L. J. Andrews, *Chem. Rev.*, 1954, **54**, 713.

[4] C. C. Addison and J. C. Sheldon, *J.*, 1956, 1941.

distribution of experimental points [5] but the possibility of compound formation was ignored. A further report that no compound is formed [6] was based on observations of only five mixtures which are insufficient to define the phase diagram. No evidence was obtained for the existence of the reported 1 : 1, 1 : 2, and 1 : 3 compounds having congruent m. p.s.[7]

Toluene and sulphur dioxide form a 2 : 1 addition compound of congruent m. p. −95°. This confirms an earlier report, for which the experimental results are missing.[5] No evidence was obtained for the existence of the reported 1 : 2 and 1 : 3 compounds having congruent m. p.s.[8] It was stated that freezing points could not be determined over a large concentration range for this system because mixtures containing more than 0·46 mol. toluene become viscous at low temperatures,[8] but difficulties of this type did not occur during the present work.

Phase diagrams of *o*- and *m*-xylenes with sulphur dioxide indicate the formation of 2 : 1 compounds of incongruent m. p.s −59° and −71°, respectively. The phase diagram for the *p*-xylene–sulphur dioxide system is less well defined, but it appears that a similar 2 : 1 addition compound of incongruent m. p. −17° is formed. It has been reported that compound formation does not occur in these systems.[9]

Mesitylene and sulphur dioxide form a 1 : 1 addition compound of congruent m. p. −46°. This confirms an earlier report of compound formation, although the low reported m. p. −49·5° and yellow solutions [8] were probably caused by the use of impure mesitylene. Mixtures of mesitylene and sulphur dioxide are colourless at low concentrations of sulphur dioxide and pale yellow at higher concentrations. A deep yellow colour is caused by traces of water, and orange, red, and violet colorations develop in air.[8,10] Hoffman and vanderWerf observed similarly that anhydrous pyridine–sulphur dioxide mixtures are pale yellow [2] and that orange solutions [11] are obtained in the presence of moisture.

The formation of solid addition compounds indicates the presence of specific interactions. The structures of the addition compounds are unknown, but it seems likely that the molecules are arranged in layers in the solid state. It has been suggested that the sulphur atom in benzene–sulphur dioxide lies above the centre of the ring, with the oxygen atoms inclined so that the plane of the sulphur dioxide molecule makes a small angle with the plane of the benzene ring.[12] In addition to satisfying electronic forces, crystallisation should result in an economical packing in the crystal lattice. The presence of one methyl group increases the electron density of the aromatic ring but also introduces a steric factor so that a well-defined 2 : 1 compound is formed between toluene and sulphur dioxide. It is evident from the phase diagrams that the enhanced donor power resulting from the substitution of a second methyl group is insufficient to overcome the crystal lattice requirements, and the solid compounds formed by the xylenes all dissociate below their m. p.s. The substitution of a third methyl group provides a further increase in donor power and electronic and crystal forces are satisfied by a stable 1 : 1 mesitylene–sulphur dioxide structure, in which the m. p. is higher than that of either component. The formation of 2 : 1 compounds by toluene and the xylenes is of interest in view of spectrophotometric studies in which new peaks in the ultraviolet spectra of solutions of aromatic hydrocarbons and sulphur dioxide in carbon tetrachloride were attributed to the formation of 1 : 1 addition compounds.[3,13] This assumption may be valid when applied to the liquid state, from which crystal lattice forces are absent.

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[5] E. Terres and A. Doerges, *Brennstoff-Chem.*, 1956, **37**, 385.

[6] W. F. Sayer and W. S. Peck, *J. Amer. Chem. Soc.*, 1930, **52**, 14.

[7] C. Mazzetti and F. de Carli, *Gazzetta*, 1926, **56**, 34.

[8] F. de Carli, *Atti Accad. naz. Lincei. Rend. Classe Sci. fis. mat. nat.*, 1926, [6], **4**, 460, 523.

[9] W. F. Sayer, K. Martin, and L. Hodnett, *J. Amer. Chem. Soc.*, 1937, **59**, 362.

[10] F. de Carli, *Gazzetta*, 1927, **57**, 347.

[11] Cf. A. E. Hill and T. B. Fitzgerald, *J. Amer. Chem. Soc.*, 1935, **57**, 250.

[12] J. D. Dunitz, *Acta Cryst.*, 1956, **9**, 579; P. A. D. de Maine, *J. Chem. Phys.*, 1957, **26**, 1036, 1042.

[13] L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, 1951, **73**, 4169.

EXPERIMENTAL

Materials.—Aromatic hydrocarbons, except toluene, were distilled from sodium. Sulphur dioxide was purified by slow passage through a drying tower (P_2O_5) and by fractional distillation in a vacuum line. Physical constants agreed closely with accepted literature values.

Mixtures.—Suitable quantities of aromatic hydrocarbon were added by means of a syringe pipette to a series of glass tubes with thin-walled bulbs blown in the ends. The tubes were attached to a high vacuum apparatus, sulphur dioxide was condensed into the bulbs, and the tubes were sealed under vacuum. The amount of each component was obtained by weighing. The volume above the liquid in each bulb was small, and it was considered unnecessary to make corrections for the volume of vapour.

Melting Points.—The tubes were cooled until crystallisation began. They were then immersed and agitated continuously in a low-temperature solvent bath which was allowed to warm slowly. The m. p. was taken as the temperature at which the last crystal disappeared. Errors due to supercooling, which are inherent in freezing-point measurements,[4] are eliminated by this method. The alcohol thermometer was calibrated against a standard mercury-in-glass thermometer at higher temperatures, and against a sulphur dioxide vapour pressure thermometer at low temperatures.

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