[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF BRITISH COLUMBIA]

Systems of Sulfur Dioxide and Hydrogen Derivatives of Benzene

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Introduction

The solvent action of liquid sulfur dioxide on hydrocarbons affords an interesting study of solution processes. This is exemplified by the behavior of this substance with benzene and its hydrogen derivatives, dihydro, tetrahydro and hexahydrobenzene or cyclohexane, in which there are, respectively, three, two, one and no double bonds. Cyclohexane is only partially miscible below 14° with liquid sulfur dioxide,[1] while benzene[2] is miscible in all proportions above the freezing point curve with the same solvent. It therefore became of interest to discover how the two compounds intermediate in saturation behaved with the sulfur dioxide.

Experimental

Purity of Compounds.—The cyclohexene, tetrahydrobenzene b. p. 82–84°, was obtained from the Eastman Kodak Company. Before using, it was carefully refluxed over metallic sodium for some hours and then fractionated, the middle portion being retained. The sulfur dioxide was the C. P. product supplied by Baker in small iron tanks. Before using, it was bubbled through several wash bottles of sulfuric acid and then over phosphorus pentoxide drying tubes.

Much difficulty was encountered at the outset in an attempt to get the freezing point curve of sulfur dioxide and tetrahydrobenzene or cyclohexene. Whenever sulfur dioxide was allowed to condense in a vessel already containing cyclohexene, a white precipitate formed immediately, which failed to dissolve in an excess of either reagent. The white compound, however, formed only in limited quantities and all efforts to convert the entire amount of the cyclohexene into the insoluble compound were at first fruitless. If the gas were introduced into the hydrocarbon at room temperatures a considerable amount of heat developed with a concomitant charring effect so that upon evaporation of the residual liquid only an asphalt-like substance remained.

It became apparent that some impurity existed in the cyclohexene which brought about reaction with the sulfur dioxide to give the white compound. It also seemed that a reaction took place only just so long as the impurity existed. Upon observing that those samples of the cyclohexene which had been standing the longest after purification by distillation over sodium yielded the most compound, it was decided to try freshly distilled cyclohexene which had been refluxed over sodium for some hours. Even in this case sufficient precipitate formed to interfere with the freezing point determination but from the small amount which did form it was at once obvious that by working in an inert or oxygen-free atmosphere, reaction between the sulfur dioxide and the cyclohexene could be prevented entirely.

Preparation of Insoluble Compound.—Another fact that supported the surmise that oxygen was the instigator of the reaction was that if this gas were first bubbled through the cyclohexene before the addition of sulfur dioxide, the yield of the unknown compound was materially increased. It was mentioned before that the reaction after a

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(1) Seyer and Dunbar, *Trans. Roy. Soc. Can.*, XLV, 307 (1922).

(2) Seyer and Peck, THIS JOURNAL, **52**, 19 (1930).

short time always ceased even with an excess of sulfur dioxide, indicating that the oxygen had been used up in the formation of the precipitate. By alternate treatments of oxygen and sulfur dioxide any amount could be transformed. The presence of small quantities of water seemed to facilitate the reaction. Therefore the procedure adopted for the preparation of sufficient amounts of the compound for examination was as follows: oxygen was bubbled through moist cyclohexene for some minutes at room temperatures; next the liquid was cooled to −30° and sulfur dioxide introduced. When the desired product ceased to form, water was added to remove the excess of sulfur dioxide from the cyclohexene. If this were not done charring would begin to take place when the temperature rose above 0°. The aqueous solution always contained besides sulfurous acid, a small amount of sulfuric acid. The white precipitate was thoroughly washed with water and then lixiviated with hot alcohol to remove traces of water and cyclohexene. The alcohol was itself removed by allowing the solid material to stand for some time in an evacuated desiccator over calcium chloride.

Properties of the Unknown Compound.—The purified substance was a white amorphous compound having no definite melting point. It decomposed at about 250° with the liberation of sulfur dioxide. The solubility was practically zero for all of the most common organic solvents except chloroform. Even in this case the amount dissolved at room temperature was not large enough to allow a freezing point determination to be made. At the boiling point of chloroform, reaction took place as could be seen from the color of the solution, which became dark brown. This fact and the low solubility at the freezing point of chloroform made it impractical to obtain the molecular weight by the ordinary methods. When a chloroform solution was allowed to evaporate at room temperatures a transparent semi-elastic solid was left behind.

Anal. Purified compound. Calcd. for $(C_6H_{10}SO_2)_x$: C, 49.8; H, 6.9; S, 21.8. Found: C, 48.55, 48.24; H, 7.22, 7.00; S, 20.5, 20.8.

The analytical data and the physical chemical properties of the substance indicated that it must be a condensation product of cyclohexene and sulfur dioxide with the empirical formula $(C_6H_{10}SO_2)_x$.

Determination of the Freezing Point Curve of Cyclohexene and Sulfur Dioxide.—Having found that oxygen played a very important part in the formation of the heteropolymer, it was next decided to attempt the determination of the freezing point curve of cyclohexene and sulfur dioxide in the absence of this catalyst. It was soon found that this was no simple matter as the cyclohexene dissolved the ordinary stopcock grease and reacted with phosphorus pentoxide and such other substitutes as were tried. After numerous failures the apparatus described below was found to function satisfactorily, as bulbs filled by means of it stood for almost a year without the slightest sign of reaction.

Procedure.—The cyclohexene was refluxed over sodium for five hours in an atmosphere of nitrogen. For this purpose a long-necked distilling flask was used whose outlet tube had been shortened and sealed. At the end of the refluxing period the sealed end of the outlet tube was broken off and connected to a short condenser and receiving flask. During these changes a stream of nitrogen was continually passed through the distilling apparatus to remove any excess air. The cyclohexene was then distilled through a long fractionating column and collected into three fractions, the middle one, having a refractive index of n^{20}_{D} 1.44601 being retained (Beilstein and "International Critical Tables" give n^{20}_{D} 1.4451) in the vessel (a) see diagram below (Fig. 1).

The next problem was to introduce the hydrocarbon into the freezing point bulbs. These were of about 15 cc. volume and their stems were about 15 cm. in length. The bulb (b), capped with a rubber tube and glass stopper, was weighed and then slipped onto the apparatus as shown in the diagram. The stopcock at (d) was opened and that at (c) closed, thus allowing nitrogen to sweep out the air in the tube (b) through the exit (e). The air having been displaced, cyclohexene was forced into the tube (b) by merely closing the stopcock (d) and opening (c). The tube was then removed, quickly capped and weighed.

A contrivance similar to that illustrated was used to introduce the sulfur dioxide; only in this case the tube was sealed before weighing. Proceeding in this way, it was possible to get mixtures of cyclohexene and sulfur dioxide in the freezing point bulbs without any compound formation. Tubes standing for almost a year showed no signs of reaction.

In all, twenty freezing point determinations were made. The freezing points were found by first forming crystals in the bulb and then allowing the temperature of the bath to rise slowly until all but a few crystals were melted. The temperature of the bath was then kept constant for some time to ensure equilibrium in the bath, after which it was raised a few tenths of a degree to melt all the solid phase. This point was taken as the freezing point of the solution. All the temperatures were measured by a standard resistance thermometer and the freezing points can be taken to be correct to one-half a degree.

The bath itself consisted of a three-liter Dewar tube set into a cylinder fitted with a rubber band to give an air-tight seal. This contained calcium chloride which kept the air within dry, so that no moisture condensed to interfere with the observations. The bath liquid was a low boiling point petroleum ether and was kept cool with liquid air from a metal container. The container had special attachments by means of which it was possible, with the help of a dry air pressure, to force over into the bath any desired quantity of the liquid air. A slight alteration of air pressure was sufficient to either raise or lower the temperature. The results are given in the table. The freezing point of the cyclohexene was found to be −103.9°, which agrees well with that given in the "International Critical Tables," −103.7°; that of sulfur dioxide was taken as −75.43°, a value obtained in a recent investigation. After the freezing points had been obtained the contents of the bulbs were analyzed by absorbing the sulfur dioxide in an alkaline solution of known concentration.

TABLE I

FREEZING POINTS OF MIXTURES OF CYCLOHEXENE AND SULFUR DIOXIDE

C_6H_{10}, g.	C_6H_{10} + SO_2, g.	Mols C_6H_{10} in 100 mols. of soln.	F. p., °C.	C_6H_{10}, g.	C_6H_{10} + SO_2, g.	Mols C_6H_{10} in 100 mols. of soln.	F. p., °C.
0.0580	2.537	1.80	−75.9	2.026	2.812	66.9	− 84.3
3.2500	31.69	8.22	−77.5	1.502	1.860	76.7	− 89.7
0.1849	1.169	12.8	−77.8	0.8834	1.095	77.8	− 90.3
.7348	3.393	17.5	−78.2	.8653	1.029	80.5	− 93.9
.2277	0.8615	20.0	−78.5	1.823	2.137	81.5	− 97.2
.6291	1.533	35.5	−79.0	1.732	1.932	87.3	−103.4
.4511	0.9237	42.7	−79.6	1.234	1.370	87.7	−106.7
.8935	1.759	44.6	−79.9	2.380	2.599	89.5	−110.1
.5146	0.8623	53.6	−81.7	2.776	2.924	93.5	−107.1
1.263	1.982	57.9	−82.2	2.079	2.151	95.7	−106.5

As there is only one eutectic point when concentration is plotted against freezing point as in Fig. 1, there is apparently no compound formation under these conditions of experimentation.

Cyclohexadiene, C_6H_8, and Sulfur Dioxide.—The physical properties of cyclohexadiene are very similar to those of cyclohexene. Hence it was thought that a mode of operation similar to the one described was all that was required to obtain the freezing point curve of this hydrocarbon and sulfur dioxide.

Preparation of 1,3-Cyclohexadiene.—Cyclohexadiene may exist in two forms, one having a quinone structure, the other a conjugated bond. As the 1,3 isomer is the most stable and, as shown in the method of preparation, more likely to be pure, it was decided to use this compound for our experiment. After studying the methods of preparation described by Baeyer,[3] Crossly[4] and Harries[5] it was decided to use the method of the latter for it appeared to give the purest compound. The starting point is the dibromide of cyclohexene, which is easily prepared from the cyclohexene itself, if the directions of Baeyer are followed in detail.[6] Harries' method required large amounts of silver oxide, trimethylamine and absolute alcohol. Moreover, the reaction has to be carried on in a sealed tube. The chief difficulty encountered was that upon opening the tube, contrary to the statements of Harries, no liquid could ever be obtained unless the contents of the tube were heated to about 50°. This liquid when treated further gave no indication of yielding pure cyclohexadiene. Consequently, this method was discarded in favor of that of Crossly and by his method about 50 cc. of hydrocarbon was prepared.

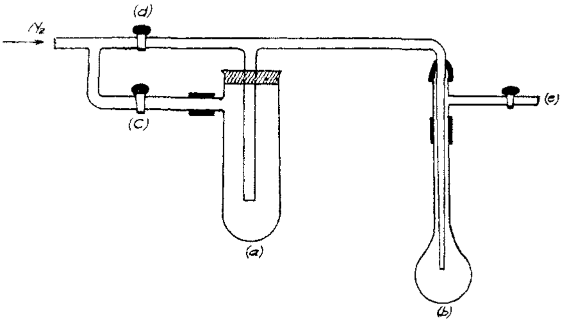

Fig. 1.—Diagram of apparatus for filling bulbs.

The boiling point of the hydrocarbon, as well as the refractive index, was found to be low compared to the values given by Harries, Perkin and others. These low values were probably due to the presence of some cyclohexene and to remove this the product was distilled through a laboratory rectifying column described by Marshall[7] and separated into three fractions. Of these the middle one had the highest refractive index and density which were, respectively, n_{D}^{20} 1.46972 and d_4^{20} 0.8409. Harries' compound had a refractive index of $n_{\mathrm{D}}^{20.5}$ 1.47506 and a density of d_4^{20} 0.8406, which indicates that even after distillation some cyclohexene still remained. However, for the purpose in mind, the material was considered to be of sufficient purity.

Cyclohexadiene was found to react even more readily with sulfur dioxide than cyclohexene to form a white amorphous compound. As has been pointed out in the case of the latter, it was necessary, after the first preliminary reaction, to treat the remaining portion again with oxygen before any more of the precipitate could be induced to form. With cyclohexadiene no such inducement was required, as the condensation product kept on forming as long as sulfur dioxide was added. Immediately upon the addition of the gas to the hydrocarbon the solution took on a yellowish-green color and a white precipitate separated out even at temperatures below −50°. The physicochemical properties of this compound were almost identical with those obtained from the cyclohexene, except that it was slightly more soluble in chloroform.

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(3) Baeyer, *Ann.*, **278**, 94 (1894).

(4) Crossly, *J. Chem. Soc.*, 1416 (1904).

(5) Harries, *Ber.*, **1**, 809 (1912).

(6) Baeyer, *Ann.*, **278**, 108 (1894).

(7) Marshall, *Ind. Eng. Chem.*, **19**, 753 (1927).

Anal. Calcd. for $(C_6H_8SO_2)_x$: C, 50.0; H, 5.5; S, 22.2. Found: C, 49.50, 49.50; H, 5.38, 5.52; S, 20.0, 20.8.

These figures suggested the formula $(C_6H_8SO_2)_x$. Calculated on this basis the sulfur content comes to 22.2, hydrogen to 5.5 and carbon to 50.0. The found sulfur content as in the previous case is somewhat low. The formation of such a condensation product is not altogether unexpected because De Bruin had already found isoprene to condense with sulfur dioxide to give the compound $(C_5H_8SO_2)_x$.[8]

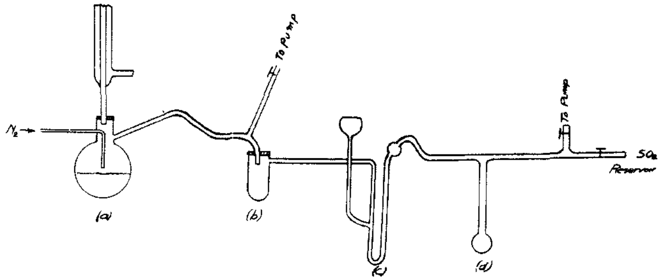

Fig. 2

Attempts to Obtain the Freezing Point Curve of Cyclohexadiene and Sulfur Dioxide.—The method of filling the bulbs described previously was unsuccessful, as the white compound formed even with the utmost precaution in regard to the exclusion of oxygen. To make this exclusion still more rigorous the apparatus described in Fig. 2 was built. Here (a) was a flask containing cyclohexadiene, (b) a receiver, (c) a mercury

TABLE II

DENSITY AND SURFACE TENSION OF CYCLOHEXENE

Temp., °C.	Density corr. to vac.	Density liquid minus vapor	Corr. height, cm.	Surf. tension in dynes	Mol. surface energy, ergs	Total surf. energy in ergs	Parachor
70	0.7630	0.7610	3.63	20.38	460.7	63.59	229.1
60	.7730	.7719	3.75	21.54	482.7	63.49	229.4
50	.7826	.7820	3.915	22.78	506.2	63.47	229.0
40	.7921	.7817	4.07	23.98	520.0	63.41	229.6
30	.8017	.8015	4.23	25.22	551.6	63.39	230.4
20	.8109	.8108	4.40	26.54	576.1	63.46	229.6
10	.8202		4.57	27.89	600.0	63.49	229.7
0	.8296		4.74	29.25	625.6	63.64	229.9
−10	.8382		4.94	30.30	648.7	63.44	230.0
−20	.8482		5.07	31.99	666.8	63.96	229.8
−30	.8569		5.22	33.28	696.3	63.89	229.9

Eötvös constant −30 to 0°, 2.4; 0 to 30°, 2.4; 30 to 70°, 2.3. Parachor found, average 229.6. Freezing point −103.9°. "Int. Crit. Tables" −103.7°. Parachor calculated 229.7.

DENSITY AND SURFACE TENSION OF CYCLOHEXADIENE

60	0.7966	0.7954	3.74	22.22	479.1	64.51	218
40	.8181	.8176	4.05	24.74	537.2	64.49	218.3
20	.8409	.8407	4.35	27.32	569.4	64.53	218.2

Eötvös constant 2.1. Freezing point −49.7°. Parachor calcd. 219.7.

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(8) De Bruin, *Chem. Abstracts*, **9**, 623 (1915).

trap which could be cooled with liquid air and (d) the bulb to be filled. Bulbs filled with this apparatus gave the same results; hence it was concluded that no oxygen was required to induce condensation of cyclohexadiene and sulfur dioxide.

Some Physical Properties of Cyclohexene and Hexadiene.—As the writers anticipated some correlation between the physical properties and behavior of the three hydrocarbons toward sulfur dioxide, it was necessary to measure some of those properties which were not recorded in the literature. These measurements included the densities and surface tensions of the two hydrocarbons and the freezing point of the latter. In the case of cyclohexadiene only three measurements of density and surface tension were made as the purity of the cyclohexadiene was not as desired. From these an approximate calculation of the parachor could be made. The differential capillary rise method was used for measuring the surface tensions and in the case of cyclohexene, where sufficient material was available, the densities were found by measuring the loss in weight of a quartz sinker whose volume was 3.6313 cc. at 20°.

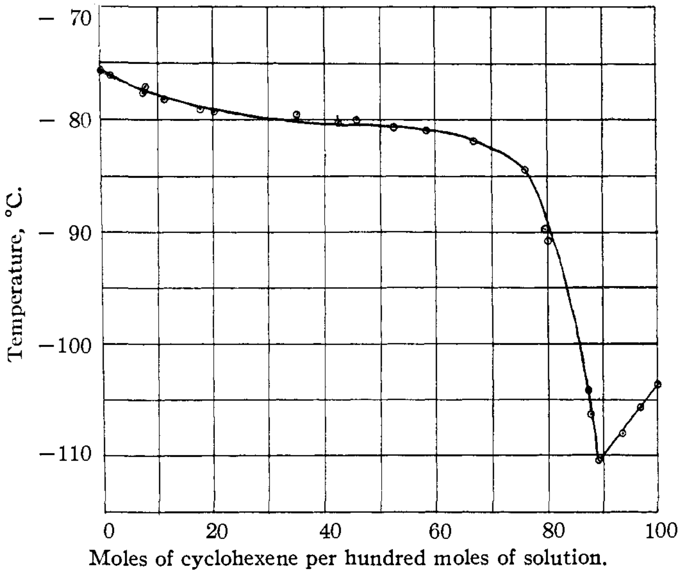


Fig. 3.

If one now observes the curves in Fig. 4 which depict the behavior of mixtures of sulfur dioxide and the different hydrocarbons at various temperatures and considers the value of the ordinary physical constants given in Table III of the various components, one is impressed with the fact that there appears to be no single physical property of the hydrocarbons by

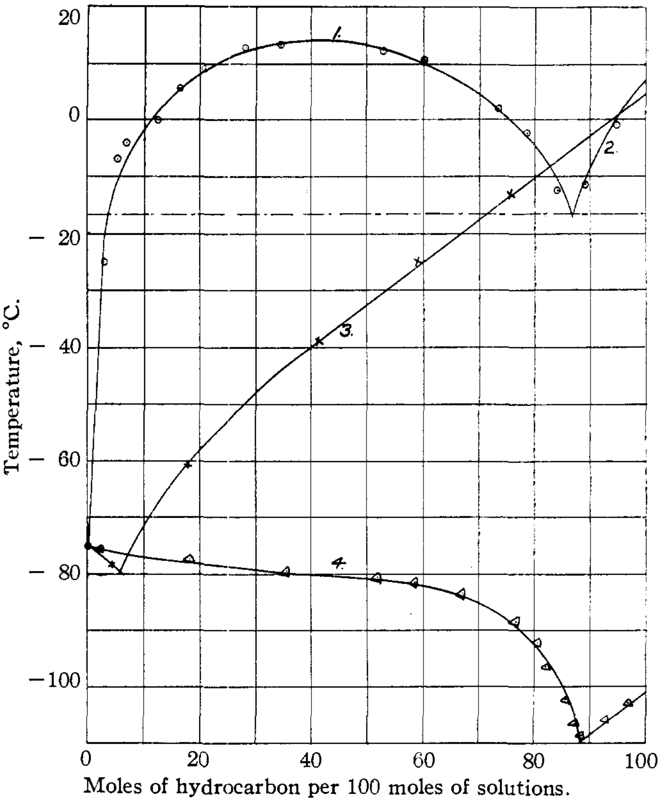
TABLE III

SOME PHYSICAL CONSTANTS OF BENZENE DERIVATIVES

	B. p., °C.	F. p., °C	T. S. E. at 20°
C_6H_{12}	80.75	6.4	62.18
C_6H_{10}	80.1	−103.9	63.46
C_6H_8	83.6	− 49.7	64.53
C_6H_6	80.15	5.4	67.20

means of which their behavior with sulfur dioxide could be predicted. Some of the physical properties are listed in Table III.

The dielectric constants are quite close together and must all lie between 1.8 and 2.3. The boiling points all fall at about 80°. Cyclohexane with a freezing point of 6.4° and a limited miscibility is in sharp contrast to benzene with almost the same freezing and boiling points and complete miscibility. The total surface energy of the first two members of the series differs by only 1.18 ergs, yet at the b. p. −10° of sulfur dioxide the solubility of the saturated hydrocarbon in this solvent is very small; whereas with cyclohexene it is miscible in all proportions.



Moles of hydrocarbon per 100 moles of solutions.

1 Miscibility limits of liquid C_6H_{12} and liquid SO_2 } Seyer and Dunbar
2 Freezing point curve of C_6H_{12} in SO_2 } Seyer and Dunbar
3 Freezing point curve of C_6H_6 and SO_2—Seyer and Peck
4 Freezing point curve of C_6H_{10} and SO_2

Fig. 4.

Thus total surface energy by itself can hardly be considered as a measure of solubility (compare Hildebrand, "Solubility," pp. 110–115). It is apparent that the presence or absence of the double bond far outweighs any physical factor in the determination of solubility of the hydrocarbons in sulfur dioxide. The problem thus becomes largely one of chemical properties of the components and the solution process must then be regarded as a formation of a series of complexes between solvent and solute.

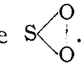
The action of sulfur dioxide toward unsaturated hydrocarbons may probably be due to its similarity to that of ozone. According to Mellor[9] many chemists in order to explain the activity have ascribed to it a ring structure . Rankine and Smith[10] from viscosity measurements of the gas concluded that the formula O═S═O corresponded best with the facts. Wierl,[11] in his investigation dealing with electron dispersion and molecular structure, came to the opposite conclusion, *viz.*, that sulfur dioxide must have the triangular form. In this he is supported by the results of Ghosh and Mohanti[12] as a result of the examination of refractive index and dielectric properties of the oxide. An additional support for the assumption of the ring structure is forthcoming in the parachor as calculated from the data of Seyer and Peck.[13] The value of the parachor for a number of temperatures is listed in the table below.

TABLE IV

PARACHOR OF SO_2 AT VARIOUS TEMPERATURES

Temperature	Parachor	Temperature	Parachor	Temperature	Parachor
100	101.4	50	100.3	0	100.7
90	100.7	40	100.4	−10	100.5
80	100.4	30	100.6	−20	100.5
70	100.5	20	100.7	−30	100.0
60	100.5	10	100.7	−40	99.1

The average value between 100 and −20° is 100.6. Below −20° the sulfur dioxide appears to be associated and consequently the parachor would be expected to change.

Taking the figures 20.0 for oxygen, 48.2 for sulfur and Sugden's[14] latest mean value for the triple ring, the parachor comes to 105.2; whereas if the structure is assumed to be O═S═O with two double bonds a value of 134.6 is obtained, which is obviously too great a divergence from the found average value of 100.6. The first value is, of course, also too high, but as pointed out by Sugden the parachor is not quite additive in the case of the triple ring, for the values obtained by him varied by almost 4 units from the mean. A suggestion prompted by the formula of ozone, championed by Brühl,[15] in which the oxygen atoms are considered to be

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(9) Mellor, "A Comprehensive Treatise on Inorganic Chemistry," Vol. X, p. 235.

(10) Rankine and Smith, *Proc. Phys. Soc.*, **35**, 33 (1922).

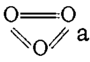
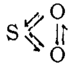
(11) Wierl, *Ann. Physik*, **8**, 521–564 (1931).

(12) Mohanti, *Z. Physik*, **30**, 531–537 (1929).

(13) Seyer and Peck, THIS JOURNAL, **52**, 14 (1930).

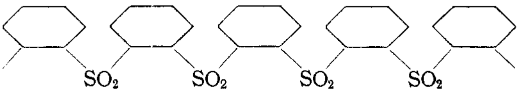
(14) Sugden and Wilkins, *J. Chem. Soc.*, **127**, 1, 140 (1927).

(15) Brühl, *Ber.*, **28**, 2864 (1895).

tetravalent is that a similar condition prevails in the sulfur dioxide molecule *viz.*,  and .

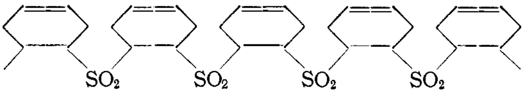
If the proviso is also made that the bonds are semi-polar (Sugden) or coördinate (Sidgwick) between sulfur and oxygen then the above value of the parachor must be reduced by a value 3 × 1.6 = 4.8, giving 100.4, a reasonably good agreement with experience. Such a structure would also allow a ready formation of complexes in solution[16] or condensates.

Benzene, of the four hydrocarbons, appears to be the only one stable in the presence of sulfur dioxide. If cyclohexane, saturated with the gas, is kept in a corked flask a slow reaction takes place and after several months crystals are deposited as well as some asphaltic material, the nature of which has not been investigated. The product formed with cyclohexene may provisionally be given the structural formula



It is possible that in some molecules the benzene rings are directly linked together, which would account for the low value of S found on the basis of the formula $(C_6H_{10}SO_2)_x$.

The stability of the condensate toward alkalies and acids would tend to rule out any linkage through oxygen. On similar grounds the heteropolymer formed from cyclohexadiene having the empirical structure $(C_6H_8SO_2)_y$ would be



As has been pointed out, the presence of oxygen was found to be essential for the condensation process to take place in the case of cyclohexene. As it does not appear to be bound either to the SO_2 or the C_6H_{10} its action must be purely catalytic and its removal from the field of reaction was probably due to the side reaction $SO_2 + {}^1/_2O_2 = SO_3$ which gave rise to the traces of sulfuric acid always noted. It is probable that the formation of a peroxide of cyclohexene preceded polymerization, as its presence was indicated by various tests performed. Such a peroxide has been reported by Birch and Stanfield[17] and Stephens.[18]

Cyclohexadiene is so unstable that apparently no catalyst is required to induce the reaction. The stability of benzene stands out in sharp contrast, for here no reaction was observed after heating it with an equal volume of sulfur dioxide in a sealed tube at a temperature of 100° for ten hours.

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(16) Sidgwick, "The Electronic Theory of Valency," pp. 137 and 149.

(17) Birch and Stanfield, *Nature*, **123**, 491 (1929).

(18) Stephens, THIS JOURNAL, **50**, 568 (1928).

Summary

1. Cyclohexene forms a heteropolymer with sulfur dioxide in the presence of oxygen to form a compound with the approximate formula $(C_6H_{10}SO_2)_x$.

2. Cyclohexadiene forms the compound $(C_6H_8SO_2)_x$ without the presence of oxygen.

3. The freezing point of curve cyclohexene and sulfur dioxide only shows one eutectic.

4. Evidence is presented supporting the ring structure for sulfur dioxide.

5. The ordinary physical properties cannot, in general, be used to predict the behavior of sulfur dioxide with the various hydrocarbons.

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The Effect of Curvature of Surface on Surface Energy. Rate of Evaporation of Liquid Droplets. Thickness of Saturated Vapor Films

BY DOROTHY J. WOODLAND AND EDWARD MACK, JR.

Lord Kelvin[1] derived an equation relating the escaping tendency at a curved surface with magnitude of surface energy. In this equation

$$(RT/M)\ln(p/p_0) = \pm(2\sigma/d)(1/r - 1/r_0) \qquad (1)$$

R is the gas constant; T is the absolute temperature; M the molecular weight; σ the surface energy; d the density of the liquid (or solid); p the escaping tendency of the substance in a surface with radius of curvature r; and p_0 the escaping tendency in a surface with radius of curvature r_0, where r_0 may be infinitely large, namely, in a flat surface. Where the surface is convexly curved the whole right-hand side of the equation has a *plus* sign set before it, and, where the surface is concave, the sign is *minus*. This is, of course, another way of saying that at a convex surface the escaping tendency is greater, and at a concave surface is less, than at a flat surface.

Although the Kelvin equation itself has never received an adequate experimental confirmation, there seems to be no valid reason why it would not hold, if only it could be given a fair test in a suitable experimental setting. In addition to the extensive application of the equation to the calculation of surface energy of solid particles, by making use of the data of solubility as a function of particle size, several attempts have also been made to use the equation for calculation of capillary pore radii in porous bodies, by Zsigmondy[2] and his collaborators, by Williams,[3] Lowry and

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(1) *Phil. Mag.*, [4] **42,** 448 (1871); also, *Proc. Roy. Soc.* (Edinburgh), Session 1869–1870, p. 63.

(2) Zsigmondy, *Z. anorg. Chem.*, **71,** 356 (1911); Anderson, *Z. physik. Chem.*, **88,** 191 (1914).

(3) Williams, *Proc. Roy. Soc.* (London), **A96,** 287 (1919).