TABLE II

X-RAY DATA ON B_4C, $B_{5.66}C$ AND B_7C ($d_{hk.l}$ (Å.))

		1. B_4C		2. $B_{5.66}C$		3. B_7C	
hk.l (hexagonal)	Intensity	Obsd.	Calcd. (from a_0 = 5.61 Å., c_0 = 12.07 Å.)	Obsd.	Calcd. (from a_0 = 5.65 Å., c_0 = 12.15 Å.)	Obsd.	Calcd. (from a_0 = 5.67 Å., c_0 = 12.19. Å)
10.1	3	4.49	4.51	4.52	4.54	4.53	4.55
00.3	4	4.02	4.03	4.04	4.05	4.06	4.06
01.2	7	3.78	3.79	3.81	3.81	3.81	3.82
11.0	3	2.81	2.81	2.82	2.82	2.83	2.83
10.4	8	2.57	2.57	2.59	2.58	2.58	2.59
02.1	10	2.38	2.38	2.40	2.40	2.41	2.41
11.3	1	2.30	2.30	2.32	2.32	2.32	2.32
00.6	1	2.02	2.01	2.04	2.02	...	...
21.1	1	1.82	1.82	1.83	1.83	...	...
20.5	3	1.714	1.713	1.725	1.724	1.730	1.730
11.6	1	1.637	1.635	1.645	1.645	1.651	1.652
10.7	1	1.628	1.625	1.634	1.635	...	...
30.3	2	1.505	1.503	1.516	1.513	1.519	1.518
12.5	3	1.463	1.462	1.474	1.474	1.477	1.477
01.8	3	1.446	1.442	1.455	1.451	1.455	1.455
02.7	3	1.407	1.407	1.416	1.416	...	...
22.0	3	1.403	1.403	1.412	1.412	1.419	1.418
00.9	2	1.345	1.342	1.350	1.350	1.354	1.354
13.1	2	1.342	1.340	1.347	1.348	...	...
22.3	2	1.326	1.325	1.333	1.334	1.339	1.339
20.8	1	1.286	1.283	1.293	1.290	1.296	1.295
30.6	2	1.261	1.263	1.270	1.270	1.273	1.274
04.2	1	1.191	1.191	...	...	1.204	1.204

TABLE III

CHEMICAL AND SPECIFIC GRAVITY DATA ON B_4C, $B_{5.66}C$ AND B_7C

	1. B_4C	2. $B_{5.66}C$	3. B_7C
C, %	21.71	16.18	13.27
B, %	78.29	82.48	83.69
SiO_2, %	...	...	0.42
B_2O_3 (uncombined), %	...	...	0.42
N_2, %	...	...	0.14
Total, %	100.00	98.66	97.94
B/C	4.00	5.66	7.00
Sp. gr. (29/4°)	2.51	2.484	2.47

plained by the substitutional solid solution mechanism.

Assuming substitution of boron atoms for carbon, the theoretical density of B_7C was calculated.

9 B's replace 9 C's in eight rhombohedral cells to give $B_{105}C_{15}$.

$$\text{S. G.} = \frac{[(105)(10.82) + (15)(12.01)][1.66]}{(2.66)(339.38)} = 2.42$$

The experimental density was 2.47.

Clark and Hoard have shown that the B_4C structure is an approximate NaCl type referred to rhombohedral axes, with a compact group of 12 boron atoms substituting for Na^+ and a linear group of 3 carbon atoms for Cl^-. The central carbon atom has as immediate neighbors only the two end carbon atoms. Each end carbon atom has, on the other hand, four immediate neighbors, *i.e.*, three boron atoms and one carbon atom. The central position would seem more favorable for trivalent boron than either end position. Whatever the mechanics of the substitution, it would appear that the bonding strength between boron groups and carbon groups is diminished. This would be the normal accompaniment of increase in size of the unit cell and decreased specific gravity. Decreased Knoop hardness and inferior lapping characteristics attest to diminution of bonding strength within the high-boron boron carbide structure.

Acknowledgments.—The writer was greatly assisted by members of the Norton Company Research Laboratories. Contributions to the experimental work were made by N. W. Thibault, L. J. Beaudin and G. R. Finlay. W. M. Hazel supplied the chemical and specific gravity data. The manuscript was reviewed by S. S. Kistler and A. A. Klein.

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The Solubility and Absorption Spectrum of Iodine in Sulfuric Acid Solutions

BY J. G. BOWER AND R. L. SCOTT

RECEIVED DECEMBER 24, 1952

The colors exhibited by iodine in different solvents have been the subject of extensive interest for more than fifty years. Substances in which iodine dissolves may be put in two general classes; "violet" or "inert" solvents in which iodine has the color of its vapor and "brown" solvents in which the color ranges from brown to dark red. The "brown" solvents have attracted the attention of many investigators since spectroscopic data have been obtained indicating the formation of 1:1 molecular complexes in some of these media. Detailed work on iodine in benzene, substituted benzenes, naphthalene and other aromatic hydrocarbons[1–7] has resulted in the determination of equilibrium constants and in some cases[8] heats of formation for these molecular complexes. A theory of their structure has been expounded in some detail by Mulliken.[9–11]

This interest in iodine and its interaction with various solvents led us to examine its behavior in sulfuric acid solutions. In 1925, Carter[12] measured the solubility of iodine in various concentrations of sulfuric acid and water, and found that the solubility decreased as the acid concentration was increased, and observed that at the same time, the solutions changed from a brown color to a light pink. The present study was undertaken in order to obtain a more quantitative elucidation of the colors by means of the spectrophotometer and to redetermine the solubilities.

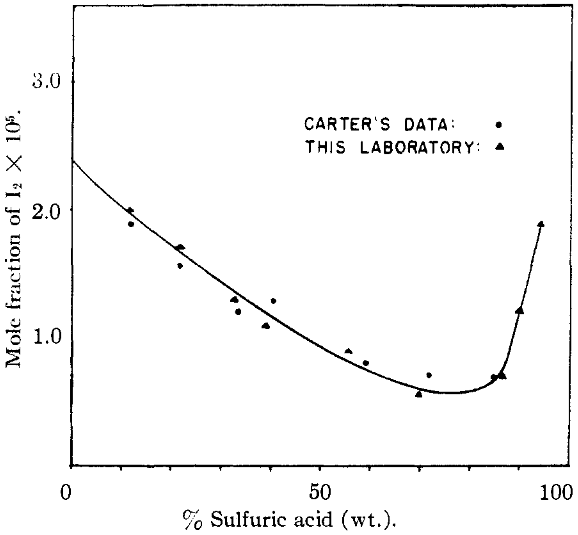

Fig. 1.—Solubility of iodine (expressed as the mole fraction) as a function of the sulfuric acid concentration: ●, Carter's data; ▲, this Laboratory.

Experimental

The iodine used in these determinations was Baker Reagent Grade further purified by resublimation. The sulfuric acid was du Pont C.P., which proved on analysis to be 94.9% H_2SO_4.

Saturated solutions of iodine were prepared by adding an excess of solid iodine to sulfuric acid solutions of varying concentrations heating them to bring about supersaturation and then after partial cooling, immersing in a constant temperature bath at 25.00 ± 0.02°. While in the bath the solutions were agitated to assure complete saturation. The undissolved iodine was filtered off in a sintered glass filter, which was also immersed in the 25° bath.

Immediately following the filtration, part of each solution was sealed into ampules and reserved for spectrophotometric study, while the remainder was analyzed for the iodine content.

Four samples of about 50 g. each were weighed out and the iodine extracted with carbon tetrachloride. The carbon tetrachloride extract was washed with dilute sodium acetate solution to eliminate any residual sulfuric acid, and then titrated with approximately 0.002 *N* sodium thiosulfate, using the color of the carbon tetrachloride layer as indicator.

The spectra of the various solutions were run on a Cary Model 11S recording spectrophotometer, and the optical density of the solutions (relative to distilled water in the reference cell) determined from 210 to 775 mμ. The cell was surrounded by two aluminum blocks through which water at 30.0 ± 0.1° was circulated, after the method of McCullough and Barsh.[13]

Results.—The solubilities determined here and those obtained by Carter are plotted together in Fig. 1. The agreement is rather good over the entire range where there are measurements to be compared. Carter did not determine the solubility in solutions stronger than 87% H_2SO_4 and consequently did not observe the minimum in the solubility. Therefore, to check the enhanced solubility in the 94.9% acid, we made two completely independent determinations, which agreed within 1.5%. The minimum solubility expressed as mole fraction occurs between 75 and 80% acid, but a graph (not shown) of solubility in moles per liter looks quite different. The solubility, which is 1.32 m*M*/l. in pure water falls gradually to a minimum of 0.207 m*M*/l. in 86.5% H_2SO_4 and then rises steeply to 0.423 m*M*/l. at 94.9%.

Spectra of some of the solutions are shown in Fig. 2. The spectra omitted (11.5, 22.0 and 33.4%) are unexceptional, except for the appearance of high peaks at 288 and 350 mμ at concentrations of acid between 5 and 20%. We have evidence to support the belief that these are due to triiodide ion[14] formed in some process greatly accelerated by the high temperatures used in getting the iodine into solution.

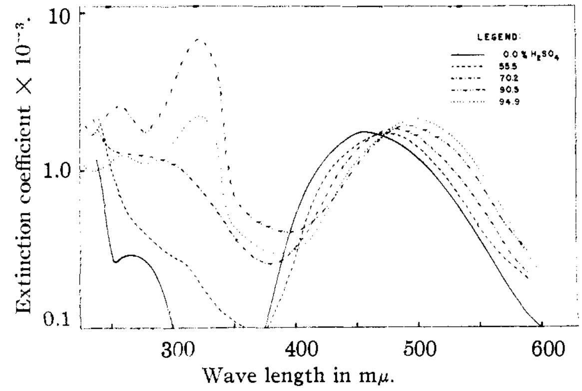

Fig. 2.—Spectra of iodine in solutions of 0.0 to 94.9% sulfuric acid (note that the extinction coefficient is plotted on a logarithmic scale, rather than in the usual manner): —, 0.0% H_2SO_4; ----, 55.5% H_2SO_4; -·-·-, 70.2% H_2SO_4; -··-··-, 90.5% H_2SO_4; ......, 94.9% H_2SO_4.

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(1) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **70**, 2382 (1948).

(2) H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949).

(3) R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 5170 (1950).

(4) N. W. Blake, H. Winston and J. A. Patterson, *ibid.*, **73**, 4437 (1951).

(5) G. Pimental, G. Jura and L. Grotz, *J. Chem. Phys.*, **19**, 513 (1951).

(6) S. Ham, A. Rees and A. Walsh, *ibid.*, **20**, 1336 (1952).

(7) R. M. Keefer and L. J. Andrews, THIS JOURNAL, **74**, 4500 (1952).

(8) T. M. Cromwell and R. L. Scott, *ibid.*, **72**, 3825 (1950).

(9) R. S. Mulliken, *ibid.*, **72**, 600 (1950).

(10) R. S. Mulliken, *J. Chem. Phys.*, **19**, 514 (1951).

(11) R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952).

(12) J. S. Carter, *J. Chem. Soc.*, 2861 (1925).

(13) J. D. McCullough and M. K. Barsh, THIS JOURNAL, **71**, 3029 (1949).

(14) Compare the spectrum of I_3^- reported by A. D. Awtrey and R. E. Connick, *ibid.*, **73**, 1842 (1951). ADDED IN PROOF.—L. I. Katzin, *J. Chem. Phys.*, **21**, 490 (1942), has recently discussed the appearance of the triiodide spectrum in solutions of iodine in water and the alcohols.

As the acid content is increased, the visible peak begins to shift toward that of iodine vapor (520 mμ), a shift which becomes more marked in the region of concentrated acid (see Table I). Note that the molar extinction coefficient is fairly constant, varying by no more than 30% over the entire range.

TABLE I

Concn. of acid, wt. %	$\lambda_{max.}$	$\epsilon_{max.}$
0	460	1.73
11.5	453	1.95
21.9	460	1.56
33.4	465	1.49
38.9	468	1.73
55.5	474	1.43
70.2	481	1.80
79.6	482	1.88
86.5	483	1.78
90.5	493	1.88
94.9	500	2.11

Discussion

The color changes corresponding to the shift of $\lambda_{max.}$ in the visible region may be considered, in terms of the Lewis theory, as arising from two related effects. In the first place, iodine and sulfuric acid are both Lewis acids; consequently, one would expect no electron exchange interaction to occur when these are mixed. In addition, since H_2SO_4 is a stronger acid than I_2 it may displace the halogen from its complex with water. Thus as the acid concentration increases, the color of the solution shifts toward the violet color which one would expect to find in an inert solvent. In the most concentrated sulfuric acid, the visible peak appears at 500 mμ[15] while in typical inert solvents the maximum usually occurs between 510 and 520 mμ. Table II gives values of $\lambda_{max.}$ and molar extinction coefficients, $\epsilon_{max.}$, for iodine in various solvents.

TABLE II

	$\lambda_{max.}$	$\epsilon_{max.}$
Iodine vapor[16]	520	820
n-Heptane[2]	520	910
Carbon disulfide[2]	518	1120
Carbon tetrachloride[2]	517	930
Benzene[2]	500	1040
Mesitylene[2]	490	1185
Diethyl ether[2]	462	880
Water	460	700
Acetone[2]	363	610

Thus the absorption of iodine in concentrated sulfuric acid would lead one to believe that if a complex does exist between iodine and sulfuric acid, it is a relatively weak one.

In general, one might expect sulfuric acid to be an even poorer solvent for non-polar non-electrolytes than water, but any difference is magnified by the fact that the solubility of iodine in water is enhanced by the acid–base interaction which is absent in sulfuric acid. Such an interpretation would account for the steady decrease in solubility from that found in water to that in 80% sulfuric acid; however, the sharp increase in solubility and the high absorption peaks in the ultraviolet observed beyond 90% sulfuric acid do not fit into this picture, and must be due to some as yet unexplained special effect.

NOTE ADDED IN PROOF.—Professor T. F. Young has pointed out to us that our minimum solubility occurs just short of 50 mole per cent. sulfuric acid (84.2% by weight) where he has found the species in solution to be almost exclusively H_3O^+ ond HSO_4^- [*Record Chem. Progress* (*Kresge-Hooker Sci. Lib.*), **12**, 81 (1951)]. At higher concentrations, the amount of undissociated sulfuric acid becomes appreciable, which may account for the increased solubility.

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[15] At the American Chemical Society meeting in Atlantic City, New Jersey, on Sept. 15, 1952, R. E. Buckles and J. F. Mills, THIS JOURNAL, **75**, 552 (1953) reported similar observations on the spectrum of iodine in 96% sulfuric acid and drew essentially the same conclusions which we had drawn from our own research, which was then largely complete.

[16] E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 540 (1936).

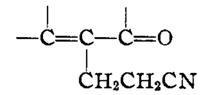
Cyanoethylation of Isophorone

BY HERMAN A. BRUSON AND THOMAS W. RIENER

RECEIVED FEBRUARY 25, 1953

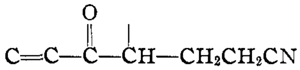
Some time ago it was reported that isophorone resisted cyanoethylation with acrylonitrile.[1] Upon repeating this work with isophorone which had been freed from acidic impurities that poison the alkaline catalyst used for cyanoethylation, namely, benzyltrimethylammonium hydroxide ("Triton B"), it was found possible to obtain mono-, di- and tricyanoethylation products of isophorone.

Infrared analyses were made of these three compounds (1% in chloroform) with a Beckman IR-2T infrared spectrophotometer. Using sodium chloride cells of 16 mil thickness, and maximum gain, spectrograms were obtained covering the range 5.5 to 8.0 μ. A strong absorption peak was observed for all three compounds as well as for isophorone itself, in the neighborhood of 6 μ, ascribed to the conjugated C=C–C=O grouping. For monocyanoethyl isophorone as well as isophorone, this peak occurs at 6.05 μ; whereas for the dicyanoethyl- and tricyanoethyl isophorones the peak occurs at 5.9 μ. Since the grouping



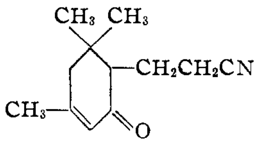
$$-\overset{|}{C}=\underset{\underset{CH_2CH_2CN}{|}}{C}-\overset{|}{C}=O$$

would be expected to show a greater displacement of the isophorone peak than the grouping



$$C=C-\overset{\overset{O}{\|}}{C}-\overset{|}{C}H-CH_2CH_2CN$$

it appears most probable that the monocyanoethylation product has the structure I



I

the dicyanoethylation product the structure II, and the tricyanoethylation product the structure III.

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[1] H. A. Bruson and T. W. Riener, THIS JOURNAL, **64**, 2853 (1942).