range 0.5 to 27*M*; consequently great accuracy cannot be expected from the method. Even so, the fact that their results are all low suggests that the cell reaction is not simply

$$HgO(s) + H_2(g) \longrightarrow H_2O(l) + Hg$$

but may be affected by such factors as partial adsorption of water by the electrode material with formation of hydroxides of mercury, or allotropic changes in the mercuric oxide as the concentration changes.

Acknowledgment.—The author wishes to acknowledge of the kind assistance of Dr. R. A. Robinson throughout the course of this work.

Summary

From isopiestic measurements at 25° on concentrated solutions of sodium hydroxide and sulfuric acid, values of the water activities and activity coefficients of sodium hydroxide have been calculated between 2 and 29*M*.

AUCKLAND, NEW ZEALAND RECEIVED JULY 17, 1945

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE STATE UNIVERSITY OF IOWA]

Solvate Formation by Certain Tetrahalides in Liquid Sulfur Dioxide

BY P. A. BOND AND WM. E. BELTON

Studies which have been made on the solubilities of the tetrahalides of the fourth periodic group in sulfur dioxide have resulted in the discovery of several systems where two liquid phases are in equilibrium with a single gas phase. Bond and Beach,[1] Bond and Stephens[2] and Bond and Crone[3] have reported upon systems formed by stannic chloride, stannic bromide, carbon tetrachloride, titanium tetrachloride and titanium tetrabromide with sulfur dioxide and have described these systems in terms of solubility and temperature. For each of these solutes the two liquid layers are well defined with the exception of those for stannic chloride which were found to be metastable. A solution of zirconium chloride did not form two liquid layers but gave a crystalline solvate having the composition $ZrCl_4 \cdot SO_2$.

Presence of this solvate suggested the possible occurrence of similar compounds of other tetrahalides with sulfur dioxide. These were found and this paper concerns itself with their isolation and the determination of their composition.

Analyses of the lower or heavy layers separated at a temperature slightly above the quadruple point gave the same composition as that of the respective solvates. These results do not, however, agree with those obtained previously by Bond and co-workers. In each case the composition of the lower layer as formerly reported showed a higher percentage of the tetrahalide than indicated for the solvates here investigated. For $TiCl_4$–SO_2 the percentages were 94.5 against 85.6, for $TiBr_4$–SO_2 96 against 92, and for $SnBr_4$–SO_2 94.07 against 93.2. The last two values are rather close. The fairly easy formation of metastable phases in the case of the titanium tetrahalide systems might have led to inaccuracy in tracing the curves, but this does not seem to be a complete explanation, for in the system $SiCl_4$–SO_2, Bond and Stephens,[2] no reasonable composition could be given for a solvate which would contain 99% $SiCl_4$ as required by the determined quadruple point. Further research on these systems is indicated, with especial attention to the possibility of the lowering of the melting point of the solvate by dissolved tetrahalide and the occurrence of a eutectic point between the quadruple point and the melting point of the tetrahalide.

Some research has also been done upon the vapor pressures of the solvates and their solutions. The results are incomplete and are not here reported.

Experimental

The liquid sulfur dioxide and the tetrahalides were prepared and purified according to the methods used by Bond and co-workers.[1,2,3] All apparatus used in the preparation of solutions and in the analyses of the compounds was designed to prevent the absorption of water from the air as was done in previous investigations.

The apparatus used to determine the composition of the solid phase is shown in Fig. 1. The flask A was prepared by closing one end of a 25-mm. glass tube 9.5 cm. in length and attaching an additional piece of glass rod to the sealed end to give additional weight and thus allow it to sink in a bath of acetone–solid carbon dioxide. A hollow ground glass stopper, C, was provided which served also as an inlet tube for the sulfur dioxide. Its elongated open tip extended well into the tube A so that the gas was delivered below the exit tube D.

After cleaning and drying at 110°, the flask was weighed while submerged in a bath of acetone cooled with solid carbon dioxide. This was accomplished by suspending it by a fine nichrome wire from the stirrup of an analytical balance placed above the bath. When the weight of the flask had been determined, it was removed from the bath and a portion of pure tetrahalide added. The flask was then closed and weighed in the bath at the same temperature. In order to ensure the largest possible contact of the solidified tetrahalide with the solvent, the flask was rotated and cooled slowly so that the solidified material was distributed on the sides as well as the bottom of the tube.

Pure dry sulfur dioxide was now passed through the center tube, C, and liquefied in the flask which had been replaced in the bath. When sufficient sulfur dioxide had been liquefied, the flask was detached, stoppered, removed from the bath and allowed to warm slightly until solution had occurred. It was then replaced in the bath and permitted to come to equilibrium at the desired temperature

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(1) Bond and Beach, THIS JOURNAL, **48**, 348 (1926).

(2) Bond and Stephens, *ibid.*, **51**, 2910 (1929).

(3) Bond and Crone, *ibid.*, **56**, 2028 (1934).

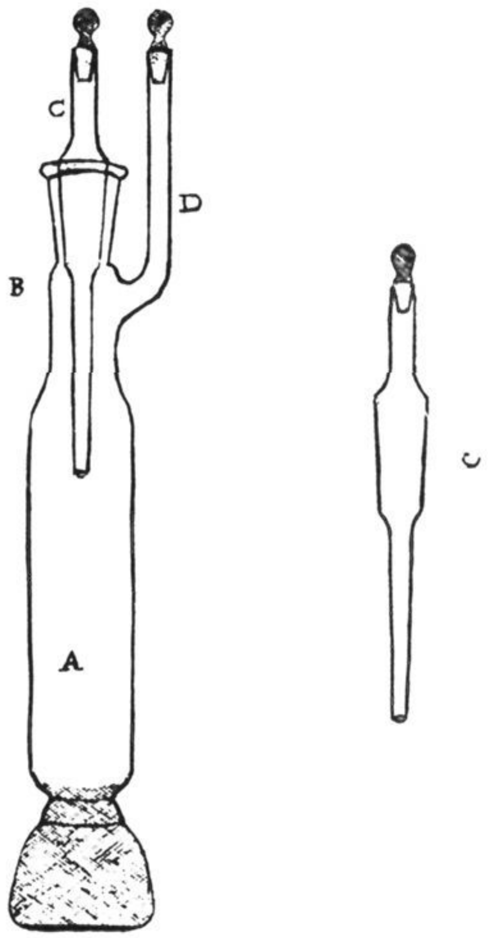


Fig. 1.

in order that precipitation of the solid phase might occur. The excess of sulfur dioxide was now evaporated by connecting tube D in series with a wash bottle containing a concentrated solution of sodium hydroxide, to a water aspirator. The air admitted to sweep out the sulfur dioxide was dried by passing it through a calcium chloride tube and a sulfuric acid wash bottle arranged in series attached to the tube C. To check the complete evaporation of the sulfur dioxide, the wash bottle containing the sodium hydroxide was from time to time replaced by another containing 25 ml. of distilled water to which three drops of standard iodine solution had been added. When no reaction with the iodine solution was obtained, it was assumed that the free sulfur dioxide had been completely removed.

The wash bottle was then replaced by another which contained a known volume of standard iodine solution. The temperature of the bath was gradually increased up to room temperature and finally, to ensure complete decomposition of the solvate, the flask containing it was placed in a beaker of hot water. Tests for the complete removal of the combined sulfur dioxide were made as before. These test portions were combined with the main solution, the excess iodine was titrated with standard thiosulfate solution, and from the volume of standard iodine required to react with it the amount of combined sulfur dioxide was obtained.

Due to the fact that it was difficult to get the weight of the sample by the method used, it was checked by a halogen determination on each sample. The method outlined above was used for all the systems investigated.

TABLE I

THE SYSTEM TIN TETRABROMIDE–SULFUR DIOXIDE AT −35°

$SnBr_4$, g.	SO_2, g.	Moles, $SnBr_4$	Moles, SO_2	Moles, SO_2 / Moles, $SnBr_4$
0.1010	0.0076	0.000230	0.000118	0.515
.1375	.0093	.000313	.000145	.463
.2823	.0210	.000644	.000328	.508
.2084	.0153	.000475	.000239	.501
.1863	.0135	.000425	.000211	.496
.1650	.0120	.000376	.000187	.497

TABLE II

THE SYSTEM TITANIUM TETRABROMIDE–SULFUR DIOXIDE AT 0°

$TiBr_4$, g.	SO_2, g.	Moles, $TiBr_4$	Moles, SO_2	Moles, SO_2 / Moles, $TiBr_4$
0.5225	0.0451	0.00142	0.000704	0.494
.8607	.0730	.00234	.00114	.498
.4180	.0355	.00113	.00055	.487
.3120	.0266	.000848	.000415	.489
.2873	.0248	.000782	.000388	.495
.2193	.0188	.000597	.000294	.492

TABLE III

THE SYSTEM TITANIUM TETRACHLORIDE–SULFUR DIOXIDE AT −35°

$TiCl_4$, g.	SO_2, g.	Moles, $TiCl_4$	Moles, SO_2	Moles, SO_2 / Moles, $TiCl_4$
0.2125	0.0376	0.00112	0.000587	0.524
.1250	.0239	.000659	.000373	.565
.1705	.0297	.00090	.000465	.515
.3600	.0604	.00189	.000943	.499
.1620	.0277	.000854	.000432	.506
.1870	.0318	.000985	.000496	.503
.1420	.0251	.000748	.000392	.524

The results show quite definitely that below the concentrations required for the formation of the two liquid system, the solubility curves are those of the solvates $SnBr_4 \cdot {}^1/_2\ SO_2$, $TiCl_4 \cdot {}^1/_2\ SO_2$ and $TiBr_4 \cdot {}^1/_2\ SO_2$.

The nature of the heavier liquid layer was investigated by separating a portion of it and determining its composition. The apparatus for this operation is illustrated in Fig. 2.

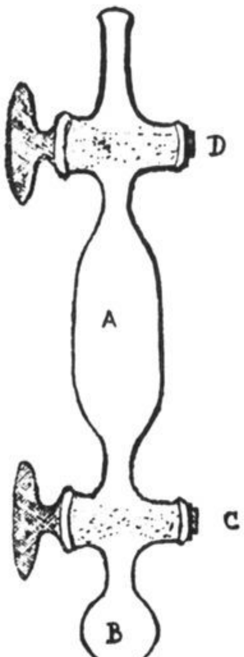


Fig. 2.

Tin tetrabromide was added to the large bulb A, the stopcock D was closed and the bulb placed in a constant temperature bath containing acetone–solid carbon dioxide. When time had been given for the apparatus and contents to cool, liquid sulfur dioxide was added to the tetrabromide in A. The stopcock D was closed and the apparatus was removed from the acetone bath and placed in a constant temperature water-bath set at the temperature required for the formation of the two phases. When this had occurred, the apparatus was rotated in order that the liquid tetrabromide might be thoroughly mixed with the liquid sulfur dioxide. Finally the temperature was kept constant for a considerable time in order that equilibrium could be obtained before a portion of the heavier phase was drawn into the smaller bulb. The temperature of the bath used in the case of the tin tetrabromide was 17° which is 0.45° above the quadruple point. A similar differential was used for the other tetrahalides. When a portion of the bottom phase had been separated, the large compartment A was emptied and washed free from all traces of tin tetrabromide and sulfur dioxide. The amount of the sulfur dioxide present in the lower layer was determined by attaching the stopcock E in series with a wash bottle containing a known volume of standard iodine solution and an aspirator. In order to ensure complete removal of the sulfur dioxide, the apparatus was placed in a beaker of hot water. The excess iodine was determined by titration with thiosulfate solution.

TABLE IV

THE DETERMINATION OF THE HEAVY PHASE $SnBr_4$–SO_2; QUADRUPLE POINT, 16.55°

Wt., $SnBr_4$	Wt., SO_2	Moles, $SnBr_4$	Moles, SO_2	Moles, SO_2 / Moles, $SnBr_4$
1.5420	0.1153	0.003518	0.001801	0.512
2.0675	.1520	.004717	.002355	.499
2.2427	.1643	.005117	.002567	.501
1.7934	.1314	.004092	.002051	.501

TABLE V

THE DETERMINATION OF THE HEAVY PHASE $TiCl_4$–SO_2; QUADRUPLE POINT, –31.4°

Wt., $TiCl_4$	Wt., SO_2	Moles, $TiCl_4$	Moles, SO_2	Moles, SO_2 / Moles, $TiCl_4$
0.6240	0.1056	0.003297	0.001650	0.501
.8342	.1413	.004393	.002207	.502
.7642	.1276	.004028	.001994	.495
.7284	.1235	.003839	.001930	.502

TABLE VI

THE DETERMINATION OF THE HEAVY PHASE $TiBr_4$–SO_2; QUADRUPLE POINT, 29.4°

Wt., $TiBr_4$	Wt., SO_2	Moles, $TiBr_4$	Moles, SO_2	Moles, SO_2 / Moles, $TiBr_4$
1.1961	0.1050	0.00325	0.00164	0.502
0.9620	.0845	.00261	.00132	.504
1.2500	.1095	.00340	.00171	.502
1.3520	.1185	.00368	.00185	.503
0.7230	.0633	.00199	.00099	.496

The results in each case show that at a temperature slightly above the quadruple point the lower layer has the same composition as that of the solvate determined previously as shown in Tables IV, V and VI.

As a further check on the molten material, portions of the crystalline solvates were separated, dried by decanting the liquid phase and allowed to stand until no evidence of liquid could be seen. The melting points were then determined. Results were consistently accurate and coincided within experimental accuracy with the temperature at which the liquid phases appeared.

Summary

The systems titanium tetrachloride–sulfur dioxide, tin tetrachloride–sulfur dioxide and titanium tetrabromide–sulfur dioxide have been investigated and solvates have been found.

The composition of the solvates has been determined and each has been found to contain one-half molecule of sulfur dioxide per molecule of the tetrahalide.

Comparison of the properties of the heavy layers with those of the solvated tetrahalides at temperatures slightly above the quadruple point indicates that within experimental error they are the same.

IOWA CITY, IOWA

RECEIVED JUNE 9, 1945

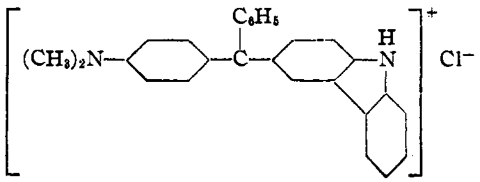
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Spectra of Two Diaminotriphenylmethane Dyes Derived from Carbazole

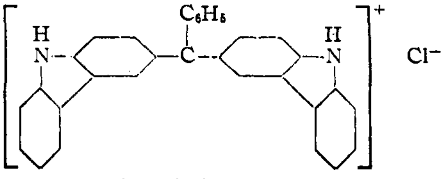
BY G. E. K. BRANCH, B. M. TOLBERT AND WARREN LOWE

Brooker, Sprague and co-workers[1] have shown that the wave length of the principal band of a cyanine dye in which the two amino groups have very different basicities is less than the arithmetic or harmonic mean of the wave lengths of the principal bands of the two symmetrical dyes of which the dye in question is a structural hybrid. Phenylation of one of the amino groups of diaminotriphenylmethane dyes gives small deviations.[2] Thus λ_x for N-phenyl-N′-dimethyl-*p,p*′-diaminotriphenylmethyl chloride is only 6 mμ less than the arithmetic mean of the λ_x values of the parent dyes, viridine green and malachite green.

The above unsymmetrical dye is a derivative of diphenylamine and dimethylaniline, the former base being a weaker base than the latter. But carbazole is a weaker base than diphenylamine, so one might expect the Brooker deviation for a dye derived from carbazole and dimethylaniline to be much greater than 6 mμ. To test this prediction we prepared N-dimethyl-*p*-aminophenyl-3-carbazylphenylmethyl chloride and 3,3′-dicarbazylphenylmethyl chloride, the former being the structural hybrid of the latter and malachite green. Throughout this article we have called the two carbazyl derivatives the monocarbazyl dye and the dicarbazyl dye, respectively. Their structures can be represented by formulas I and II



I



II

The monocarbazyl dye was prepared by condensing N-dimethyl-*p*-aminobenzophenone with carbazole using phosphorus oxychloride as the condensing agent. The dicarbazyl dye was pre-

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(1) For a summary see L. G. S. Brooker, *Rev. Mod. Phys.*, **14**, 275 (1942).

(2) Tolbert, Branch and Berlenbach, THIS JOURNAL, **67**, 887 (1945).