

200. *The Parachor and Chemical Constitution. Part XVIII. Additive Compounds of Boron Trifluoride.*

By SAMUEL SUGDEN and MICHAEL WALOFF.

THE additive compounds of boron trifluoride with ethers and other compounds are of special interest in connexion with the electronic theory of valency, and we have therefore determined the parachors of a number of these substances. We are much indebted to Prof. G. T. Morgan and Mr. R. Taylor for supplying the first five substances listed in the table below.

The substances examined can all be formulated as shown in (I), in which the link between boron and oxygen is a "co-ordinate link" or a semipolar double bond. An allowance of -1.6 units was therefore made for this link in the calculation of the parachor. The constant used for boron was 16.4 (Etridge and Sugden, *J.*, 1928, 989), and for fluorine the new value of 25.0 was employed (Allen and Sugden, this vol., p. 760).

The experimentally determined parachors agree in general well with the calculated values (Table I). Substances Nos. 2 and 6 show small negative anomalies which have been verified by examination of two independently prepared specimens; the smaller deviations found for the other substances are of the order of magnitude to be expected from the small constitutional effects which are known to influence the parachor.

TABLE I.

No.	Additive compound of BF_3 with	$[P]$ obs.	$[P]$ calc.	Diff.	k .
1	Methyl formate	228.4	227.8	+0.6	1.4
2	Ethyl formate	262.7	266.8	-4.1	2.0
3	Methyl acetate	269.8	266.8	+3.0	2.5
4	Ethyl acetate	303.1	305.8	-2.7	2.0
5	Dimethyl ether	220.6	222.0	-1.4	1.7
6	Diethyl ether	294.6	300.0	-5.4	1.9
7	Methylacetanilide	453.2	452.5	+0.7	2.8

The last column of the table gives the Ramsay-Shields coefficient, k . The significance of this constant is somewhat doubtful, but it may be taken to indicate that these substances, with the exception of No. 1, are "normal" liquids. The low value for the methyl formate compound is remarkable, especially in view of the fact that the parachor is normal.

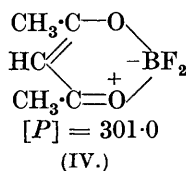
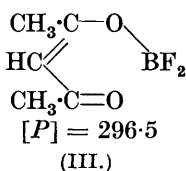
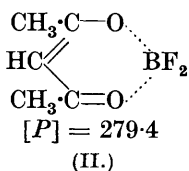
The theoretical interest of these results is concerned with two points involved in the structure shown in formula (I). These are (a) that two more than the normal number of electrons are shared, and (b) that the valency shell of the boron atom has increased from six to eight electrons. It was shown by one of us (Sugden, J., 1929, 323; "The Parachor and Valency," pp. 110, 133) that all the parachor anomalies ascribed to singlet linkages could be accounted for on another hypothesis, *viz.*, that the sharing of an electron was accompanied by a contraction of -11.6 units. This hypothesis can only be tested in compounds in which an element exhibits a valency higher than the normal valency (Sugden, *loc. cit.*), since in normal compounds any contraction on sharing is automatically allowed for in computing the atomic constants. Certain compounds of mercury and thallium of suitable constitution were examined and showed no contraction on sharing, and the hypothesis was therefore discarded.

The observations on the thallium compounds have been criticised by Sidgwick and Sutton (J., 1930, 1461) on the ground that these substances are highly associated in solution. In our view this criticism does not affect the main point, for associated liquids usually give parachors a few units lower than the calculated value. Any effect of association would therefore be to increase the expected negative anomaly of -23 units; since no appreciable negative anomaly was found, the hypothesis of a contraction on sharing cannot be maintained. Sippel (*Ber.*, 1930, 63, 2185) has, however, revived this hypothesis and used it as a basis for the interpretation of parachors. The data recorded above for the boron trifluoride compounds give further evidence against this view. The sharing of two electrons more than the normal number should give an anomaly of -23.2 units, and none of the substances shows anything like this value.

The second point concerns another hypothesis which has been advanced to account for the anomalies ascribed by one of us to singlet linkages. Sidgwick ("The Electronic Theory of Valency," p. 128; see also Sidgwick and Barkworth, J., 1931, 807; Sidgwick and Bayliss, J., 1930, 2027; further, see Simons, *J. Physical Chem.*, 1931, 35, 2118) suggests that when the valency shell of an atom is increased above its normal value there is a contraction in the

volume of the molecule due to the greater screening effect of the larger shell upon the electrostatic field of the atomic nuclei. This effect is considered to vary from atom to atom and ranges from -12 for a co-ordinated hydrogen atom with a shell of four electrons to -26 for a quinquevalent phosphorus atom with a shell of ten electrons. In both cases the outer shell contains two more than the normal number. This is true also for the boron trifluoride compounds in Table I; since these substances do not show any considerable negative anomaly, it is clear that the hypothesis of a parachor defect due to an enlarged valency shell must also be abandoned. The hypothesis of singlet linkages remains as the only one which accounts in a simple manner for the negative parachor anomalies found in higher halides, derivatives of β -diketones, and other compounds.

In an earlier paper (Sugden, J., 1929, 321) it was shown that acetylacetone borondifluoride gave a parachor which was inconsistent with the singlet structure (II) and it was therefore concluded that it had the open-chain structure (III). By analogy with the boron trifluoride addition compounds, it is now evident that the chelate ring may be completed by a semipolar double bond as in (IV). The calculated parachors are shown below the formulæ; it will be seen that (IV) gives a value in excellent agreement with the observed parachor of 300.6.



[. indicates a singlet link.]

In the course of this work the action of boron trifluoride on a number of amines and amides was investigated. Aniline, methylaniline, dimethylaniline, and *p*-toluidine gave precipitates when mixed with the trifluoride in ethereal solution; the products were very hygroscopic and/or decomposed on melting, so they were not further examined. Definite *compounds* with acetanilide and methylacetanilide were prepared and analysed; of these only the latter proved suitable for the determination of its parachor.

EXPERIMENTAL.

The tables below are set out in the same manner as in earlier papers of this series and need no further description. All temperatures recorded are corrected for thermometer error and for exposed stem.

Methyl formate boron trifluoride, $C_2H_4O_2, BF_3$, $M = 128$; m. p. 23.5° , b. p. 92.5° . Densities determined: $D_4^{31.5^\circ} 1.409$, $D_4^{43.5^\circ} 1.398$, $D_4^{51^\circ} 1.391$, $D_4^{59.5^\circ} 1.385$, $D_4^{66.5^\circ} 1.377$, whence $D_4^0 = 1.450 - 0.00128t$.

t	32°	37.5°	46.5°	54°	59°
γ , dynes/cm. ...	39.30	38.61	37.99	37.41	36.58
D , g./c.c.	1.409	1.402	1.390	1.381	1.374
$[P]$	227.4	227.6	228.6	229.2	229.1
				Mean	228.4

Ethyl formate boron trifluoride, $C_3H_6O_2, BF_3$, $M = 142$; m. p. 3° , b. p. 103° . Densities determined (specimen 1): $D_4^{19^\circ} 1.323$, $D_4^{29.5^\circ} 1.310$, $D_4^{38.5^\circ} 1.299$, $D_4^{52.5^\circ} 1.282$, whence $D_4^0 = 1.346 - 0.00122t$.

Specimen 1.					
t	14.5°	23°	33°	43.5°	52.5°
γ	36.16	34.93	33.71	32.57	31.60
D	1.329	1.318	1.306	1.293	1.282
$[P]$	262.0	261.8	262.0	262.3	262.5
Specimen 2.					
t	16.5°	36°	47°	57°	
γ	35.62	34.26	33.01	31.70	
D	1.326	1.302	1.289	1.276	
$[P]$	261.7	263.9	264.0	264.0	
	Mean of all observations = 262.7.				

Methyl acetate boron trifluoride, $C_3H_6O_2, BF_3$, $M = 142$; m. p. 61.5° . Densities determined: $D_4^{61.5^\circ} 1.253$, $D_4^{64^\circ} 1.249$, $D_4^{68^\circ} 1.244$, $D_4^{73^\circ} 1.237$, $D_4^{81^\circ} 1.229$, $D_4^{87.5^\circ} 1.221$, whence $D_4^0 = 1.324 - 0.00117t$.

t	64°	70°	75°	81°	87°
γ	31.71	31.30	30.39	29.80	28.88
D	1.249	1.242	1.236	1.229	1.222
$[P]$	269.7	270.3	269.7	270.0	269.3
	Mean 269.8				

Ethyl acetate boron trifluoride, $C_4H_8O_2, BF_3$, $M = 156$; m. p. 31° , b. p. 123° . Densities determined: $D_4^{42^\circ} 1.223$, $D_4^{48^\circ} 1.217$, $D_4^{53.5^\circ} 1.210$, $D_4^{61.5^\circ} 1.200$, $D_4^{70^\circ} 1.190$, whence $D_4^0 = 1.276 - 0.00123t$.

t	39.5°	45°	59°	66°	
γ	31.92	30.85	29.87	29.45	
D	1.227	1.213	1.203	1.196	
$[P]$	302.2	303.1	303.2	303.8	Mean 303.1

Dimethyl ether boron trifluoride, C_2H_6O, BF_3 , $M = 114$; b. p. 128° . Densities determined: $D_4^{30^\circ} 1.241$, $D_4^{35.5^\circ} 1.233$, $D_4^{43^\circ} 1.222$, $D_4^{50.5^\circ} 1.218$, $D_4^{59^\circ} 1.207$, whence $D_4^0 = 1.264 - 0.00116t$. Gasselin (*Ann. Chim. Phys.*, 1894, 3, 30) gives $D_4^0 = 1.141$.

t	20.5°	27.5°	34.5°	41°	59°
γ	33.03	32.10	31.38	30.91	28.84
D	1.240	1.232	1.224	1.216	1.195
$[P]$	220.3	220.2	220.4	221.0	221.0
	Mean 220.6				

Diethyl ether boron trifluoride, $C_4H_{10}O, BF_3$, $M = 142$, was prepared as described by Gasselin (*loc. cit.*), and purified by fractional

distillation; b. p. 126—127°/777 mm. Densities determined (specimen 1): $D_4^{13^\circ}$ 1.135, $D_4^{24.5^\circ}$ 1.122, $D_4^{30^\circ}$ 1.117, $D_4^{47.5^\circ}$ 1.109, $D_4^{77.5^\circ}$ 1.098, whence $D_4^t = 1.150 - 0.00108t$. Gasselin gives $D_4^t = 1.154$.

Specimen 1.				
t	15.5°	25.5°	37.5°	54.5°
γ	30.15	29.31	27.89	26.79
D	1.133	1.122	1.109	1.091
[P].....	293.7	294.5	294.4	296.2

Specimen 2.					
t	19.5°	30°	37°	45.5°	57.5°
γ	30.05	29.05	28.30	27.62	26.50
D	1.133	1.121	1.113	1.102	1.089
[P].....	293.3	294.1	294.3	295.4	295.8

Mean of all results = 294.6.

Methylacetanilide boron trifluoride, $C_9H_{11}ON, BF_3$, $M = 217$. This substance was prepared in 75% yield by pouring a solution of 10 g. of methylacetanilide in dry ether into an ethereal solution of boron trifluoride prepared from a mixture of 14 g. of boric anhydride, 28 g. of calcium fluoride and 90 c.c. of concentrated sulphuric acid. It is essential to add the anilide solution to the trifluoride, otherwise the product is impure and cannot be purified. The substance is insoluble in benzene, toluene, ether, and *isopropyl* ether, and very soluble in acetone and alcohol; the solutions in the last two solvents turn yellow and finally pink on standing or, more rapidly, on heating. The *compound* was purified by dissolving it in the minimum amount of dry acetone and precipitating it by addition of two volumes of dry *isopropyl* ether [Found: N (Dumas), 6.40. $C_9H_{11}ON, BF_3$ requires N, 6.45%]; m. p. 114°. Densities determined: $D_4^{14^\circ}$ 1.193, $D_4^{20.5^\circ}$ 1.189, $D_4^{28^\circ}$ 1.182, $D_4^{35.5^\circ}$ 1.176, $D_4^{50.5^\circ}$ 1.164, whence $D_4^t = 1.205 - 0.00083(t - 100)$.

t	118.5°	128.5°	139°	150°	
γ	38.06	37.10	36.03	34.90	
D	1.190	1.181	1.173	1.164	
[P].....	452.9	453.6	453.2	453.1	Mean 453.2

Acetanilide boron trifluoride, C_8H_9ON, BF_3 , $M = 203$, was prepared and purified in a similar manner to the methyl derivative. It is insoluble in benzene, ligroin, ether, and *isopropyl* ether, and is very soluble in acetone and alcohol. Unlike the methyl derivative, it is not hygroscopic. It was analysed by hydrolysing it with caustic alkali, distilling over the aniline, and estimating it by titration with standard nitrite [Found: $C_6H_5 \cdot NH_2$, 45.5. C_8H_9ON, BF_3 requires $C_6H_5 \cdot NH_2$, 45.8%]; m. p. 133°. It decomposed just above the m. p. and was therefore unsuitable for parachor determinations.

Co-ordination Compounds of Boron Trifluoride and Organic Esters.

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WE had found that the action of boron trifluoride on methyl and ethyl esters of formic and acetic acids resulted in the formation of crystalline products $R \cdot CO_2X, BF_3$ (where $R = H$ or CH_3 and $X = CH_3$ or C_2H_5) and had supplied Dr. Sugden with this series of compounds for researches on the parachor of boron (Sugden and Waloff, *v. supra*) when the appearance of a paper by Bowlus and Nieuwland (*J. Amer. Chem. Soc.*, 1931, **53**, 3835) rendered superfluous any detailed account of our experiments. To the note which has already appeared (*Chem. and Ind.*, 1931, **50**, 869) we now wish to make the following additions.

Methyl benzoate boron trifluoride, $C_6H_5 \cdot CO_2Me, BF_3$, separated from a mixture of its generators, on cooling, in colourless tabular crystals, m. p. 40—55° (decomp.) (Found: C, 46.2; H, 4.1; B, 5.3. $C_8H_8O_2, BF_3$ requires C, 47.1; H, 3.95; B, 5.3%).

Boron trifluoride and methyl salicylate interacted with evolution of hydrogen fluoride. The pale yellow, crystalline product, after being washed successively with methyl salicylate and petroleum (b. p. 40—60°), sublimed under 20 mm. pressure to yield colourless feathery crystals, m. p. 128°. The analytical numbers approximated to $C_8H_8O_3, BF_2$, which suggested partial replacement of fluorine by hydroxylic oxygen and co-ordination of the residual BF_2 with the ester group, so that the compound had a composition analogous to that of the condensation products of boron trifluoride and the β -diketones (Morgan and Tunstall, *J.*, 1924, **125**, 1963).

Boron trifluoride and methyl glycolate interacted with but slight evolution of hydrogen fluoride, and the product when distilled at 62—66°/4 mm. gave a colourless liquid, b. p. 60°/3 mm., approximating in composition to a simple additive compound $C_3H_6O_3, BF_3$.

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