BF_3, leading to a value of 13 kcal. for its heat of dissociation.

6. The heat of formation of $Me_2O:BF_3$ has been determined calorimetrically as 13.9 kcal. and that of $Et_2O:BF_3$ as 12.5 kcal. The heats of solution of boron trifluoride in water and diethyl ether have been determined.

7. Molecular weight determinations made cryoscopically in benzene indicate that the etherates are monomeric.

8. Dipole moment measurements on these etherates have been carried out in benzene. The results indicate that the contribution of the donor–acceptor bond to the total dipole moment is small.

ITHACA, NEW YORK RECEIVED NOVEMBER 17, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

Donor-Acceptor Bonding. II. An Electron Diffraction Investigation of the Structure of Dimethyl Ether–Boron Trifluoride

BY S. H. BAUER, G. R. FINLAY AND A. W. LAUBENGAYER

With the establishment of the correct molecular formula by the vapor density method[1] for the product of the reaction $BF_3(g) + (CH_3)_2O(g)$, an investigation of the structure of that association product became possible. The apparent molecular weight of the gaseous dimethyl ether–boron trifluoride has been determined over the temperature range 25–130°. At the lower portion of this interval the molecules present do have a molecular weight very near to 114 units; together with the analytical data this leads to the formula $(CH_3)_2O:BF_3$. Below 40° the extent of dissociation is under 10%.

In this report we are presenting electron diffraction data obtained on the vapor of the associated compound at about 40°. The photographs permitted a structure determination.

The Photographs

For the electron diffraction studies the clear liquid of density 1.246 (20°), b. p. 126.6° (760 mm.), n_D 1.302, was heated to about 65° during the run, so that sufficient vapor be available. However, condensation took place in the long lead tube to the electron diffraction nozzle; it is, therefore, doubtful whether the temperature of the vapor at the point of diffraction was much above 40°. The construction of the nozzle is such as to maintain the pressure at the instant of diffraction as high as possible over a very small volume.[2] Thus, although it is difficult to estimate the actual pressure at the point of diffraction, we can safely state that the amount of dissociation was negligible. This assumption is in agreement with our previous experience, and was borne out by the resulting electron diffraction photographs. Both light and dense pictures were obtained, the latter showing six maxima. The visual appearance of the pattern is sketched as curve Vis, Fig. 2; the s_0 values for the maxima and minima and their relative intensities as determined visually from five of the best photographs are given in Table I.

TABLE I

DIMETHYL ETHER–BORON TRIFLUORIDE

Max.	Min.	s_0	$I_{av.}$	$s_{0(calcd.)}/s_{0(obs.)}$ IVb	IVc	Va
1		3.22	7	1.012	1.020	1.056
	2	4.44	−5	0.991	0.990	1.016
2		5.76	10	1.005	1.010	1.024
	3	7.61	−6	1.012	1.016	1.016
3		8.88	4.2	1.033	1.038	1.036
	4	10.07	−3	1.025	1.031	1.029
4		11.32	3.5	1.003	1.012	1.007
	5	12.68	−2.8	1.006	1.018	1.019
5		14.08	2.2	1.004	1.012	1.018
	6	15.24	−1.5	1.015	1.020	1.043
6		16.43	1	1.003	1.020	1.075
		Average		1.010	1.017	1.031
		Mean deviation		0.0086	0.0082	0.0158
Interatomic distances deduced, Å.		B–F		1.404	1.414	1.433
		B–O		1.555	1.505	1.485
		C–O		1.434	1.444	1.464

A radial distribution calculation[3] resulted in the curve R.D. of Fig. 1; the indicated distances are

1.40 Å.	interpreted as a superposition of B–F, C–O, B–O
2.36	interpreted as a superposition of F–F, B–C, C–C
2.84 3.61	interpreted as a superposition of variable F–C, C–H, B–H
4.58	possibly due to the longer F–H and stray maxima arising from the incomplete integration.

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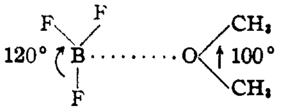
[1] A. W. Laubengayer and G. R. Finlay, THIS JOURNAL, **65**, 884 (1943).

[2] Nozzle design similar to that described by E. H. Eyster, R. H. Gillette and L. O. Brockway, *ibid.*, **62**, 3236 (1940).

[3] J. Walter and J. Y. Beach, *J. Chem. Phys.*, **8**, 601 (1940)

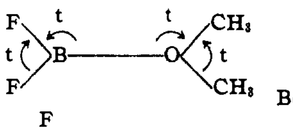
In interpreting a radial distribution curve such as this one, wherein the superposition of various contributions to each peak introduces considerable confusion, we found it very helpful to compare the R.D. computed from the data with a number of "synthetic" distribution curves which represent the ideal R.D.'s for various models.[4] Some of the curves for the six basic configurations are given in Fig. 1.

I. 

B–F 1.30 Å.
C–O 1.42
C–H 1.09
B–O very large (no association)

II. Configuration as I; plane of F's perpendicular to B–O bond, whose length was taken to be 1.50 Å.

III. Configuration as II; B–F stretched to 1.39 Å. B–O remained at 1.50

IV. 

B–F 1.39 Å.
C–O 1.42
C–H 1.09
B–O 1.45
Boron valence angles tetrahedral
Oxygen valence angles tetrahedral

V. Configuration as in IV; ∠BOC = 125°, ∠COC = 110°

VI. Configuration as in IV; all oxygen valence angles 120°

The dotted lines under the individual curves in Fig. 1 indicate the contributing components, using an average temperature factor $a_{ij} = 0.042$. The effects of internal rotation assumed to be free, are indicated approximately. Comparison of the "synthetic" with the experimental curves immediately eliminates models II and III, and consequently also I. To decide which of the remaining three structures best agree with the photographs we computed a large number of intensity curves, some of which are reproduced in Fig. 2.

In our preliminary set of computations for Model IV the variable selected was the B–F/B–O ratio. Using the simple expression

$$I = \sum_{ij} Z_i Z_j \sin l_{ij}s/l_{ij}s$$

for the intensity, assuming that the dimethyl ether part of the molecule remains unchanged, that all the *variable* H–H, C–H, B–H and F–H are negligible, and that the *staggered* configuration (C's with respect to F's) was the most probable, six curves were calculated for which the ratio B–F/B–O ranged from 0.869 to 1.000. Qualitatively all these curves appear to be alike, and all agree with the observed intensity pattern. (Figure 2, curves IVa and IVf are the extremes.) It is indeed unfortunate that an accurate estimation of the intensities of the minima is not possible as that would be of considerable aid in selecting a model. The quantitative fit can best be judged from curve B, Fig. 3, which shows how the mean deviation for the rings observed changes with the above ratio (Table I). Interpolating, the value of B–F/B–O for which the quantitative fit appears to be best is 0.925. The dimensions of the best model may then be obtained from curve A, Fig. 3, for which the average values of $s_{0(\text{calcd.})}/s_{0(\text{obs.})}$ were plotted against B–F/B–O. At B–F/B–O = 0.925, $s_{0(\text{calcd.})}/s_{0(\text{obs.})} = 1.016$. One may thus conclude that within the approximations enumerated above, structure IV with the dimensions B–F 1.41 Å.; B–O 1.52 Å.; and the dimethyl ether part of the molecule remaining unchanged is in excellent agreement with the data. Also from a theoretical point of view this is the most acceptable configuration since the oxygen atom in $(CH_3)_2O{:}BF_3$ thus becomes analogous to the nitrogen atom of an amine. The eclipsed configuration of IV was not considered.[5]

Our next step was an attempt to eliminate model V. Since in going from IV to V the C–B and C–F distances are stretched, the following dimensions were selected so that the distances in Va bracket those of IVc which we knew were satisfactory: B–F = 1.39; B–O = 1.44; C–F = 2.80 and 3.62; the minimal and maximal values were given equal weight since no particular orientation of the methyl groups with respect to the fluorine atoms seems more probable than the others. The resulting curve (Va, Fig. 2) is not as satisfactory both from a quantitative standpoint (Table I), and qualitatively in the region of the last peak, as are the best curves for model IV. The qualitative feature may be improved by neglecting the C–F interactions completely (Vb) but the mean deviation for the various rings is thus increased. The intensity distribution assuming free rotation about the B–O bond would best be represented by a curve somewhere between Va and Vb. Since we have already found that the general form of the pattern is not affected in this case by alteration of the B–F/B–O ratio, no further models for configuration V were computed. Presumably, the undesirable feature sug-

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(4) The equations used are those given by P. Debye, *J. Chem. Phys.*, **9**, 55 (1941).

(5) J. Y. Beach and K. J. Palmer, *ibid.*, **6**, 639 (1938).

gesting a very weak sixth peak and an intense seventh peak, which we did not observe, would be retained. One may thus conclude that model V does not give as satisfactory agreement with the data as does IV, but it *cannot be eliminated entirely*. It is clear that model VI is in the same category as V.

It is of interest to note that models IV and V could not be distinguished even when the more complete and somewhat lengthy intensity calculations were made, using structure and temperature factors, and the expressions derived by Debye[4] for atoms whose separations change due to free rotation about a bond.

The final attempt to determine whether the structure of $(CH_3)_2O:BF_3$ is more nearly like IV, V, or VI was made through the use of the analytic method.[6] Indeed, a pattern such as was obtained here is ideal for the application of this method, since the final selection is to be based entirely on the shift in the position of the peaks rather than on slight changes in their form. As a first approximation we took model IVc; and for the unknowns, the small increments to be made in the following four interatomic separations in order to reduce the mean deviation to a minimum: B–F, B–O, C–O, and C–B; C–C = 2.32 Å., C–H = 1.09 Å., carbon and boron valence angles tetrahedral, were assumed. The positions of the 1–5th maximum and 2–6th minimum were treated by least squares. The following best values were thus obtained

B–F	1.48 Å.	C–O	1.23 Å.
B–O	1.45 Å.	C–B	2.17 Å.

The intensity pattern expected for this model (VII) is indicated by the top curve of Fig. 2.

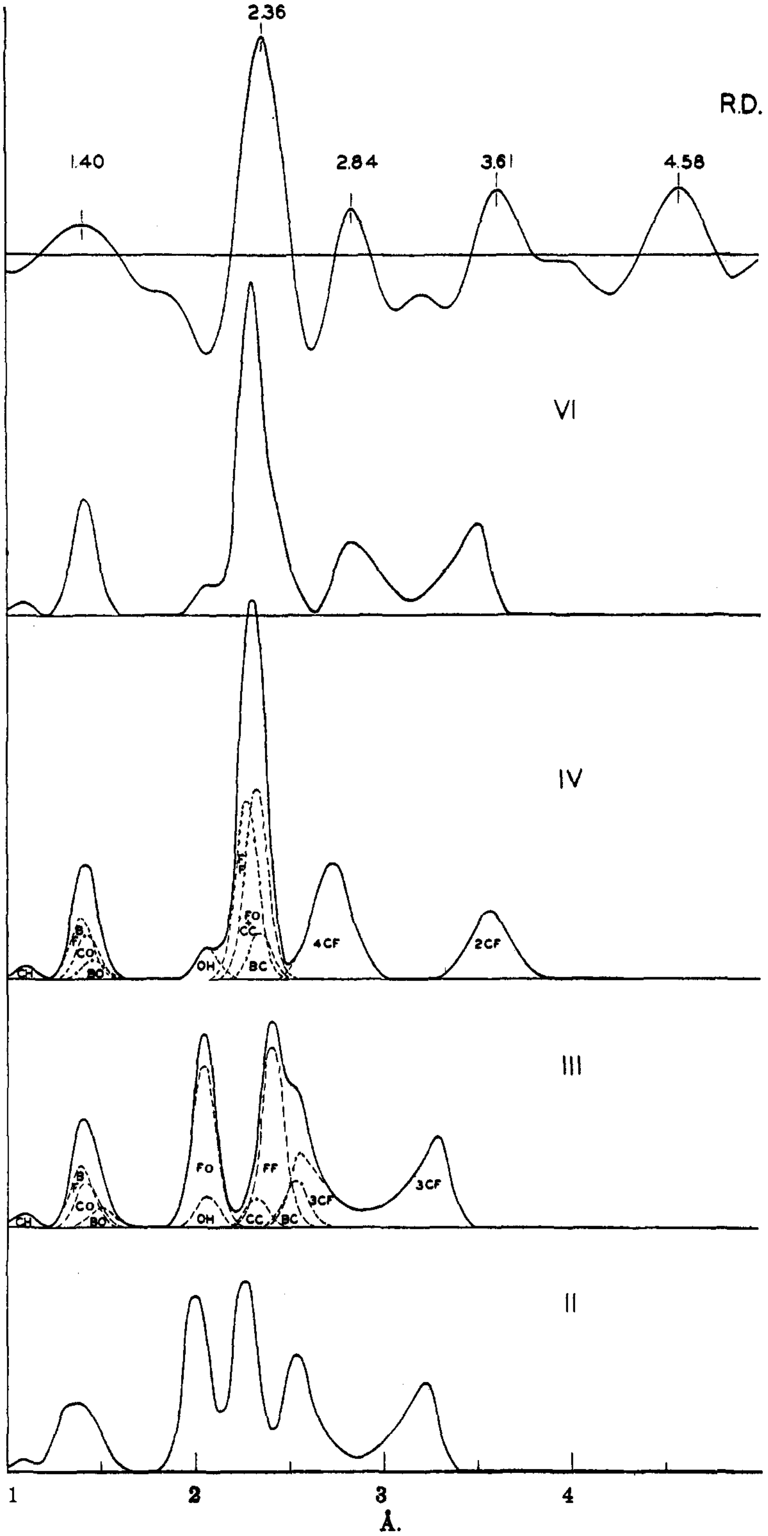

Fig. 1.—Radial distribution curves for $(CH_3)_2O:BF_3$. The curve marked R.D. is that obtained from the data using the method of Walter and Beach. The others are "synthetic" curves, computed for the models described in the text. The C–F contributions (assuming free rotation about B–O) were roughly estimated.

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[6] S. H. Bauer, *J. Chem. Phys.*, **4**, 406 (1936).

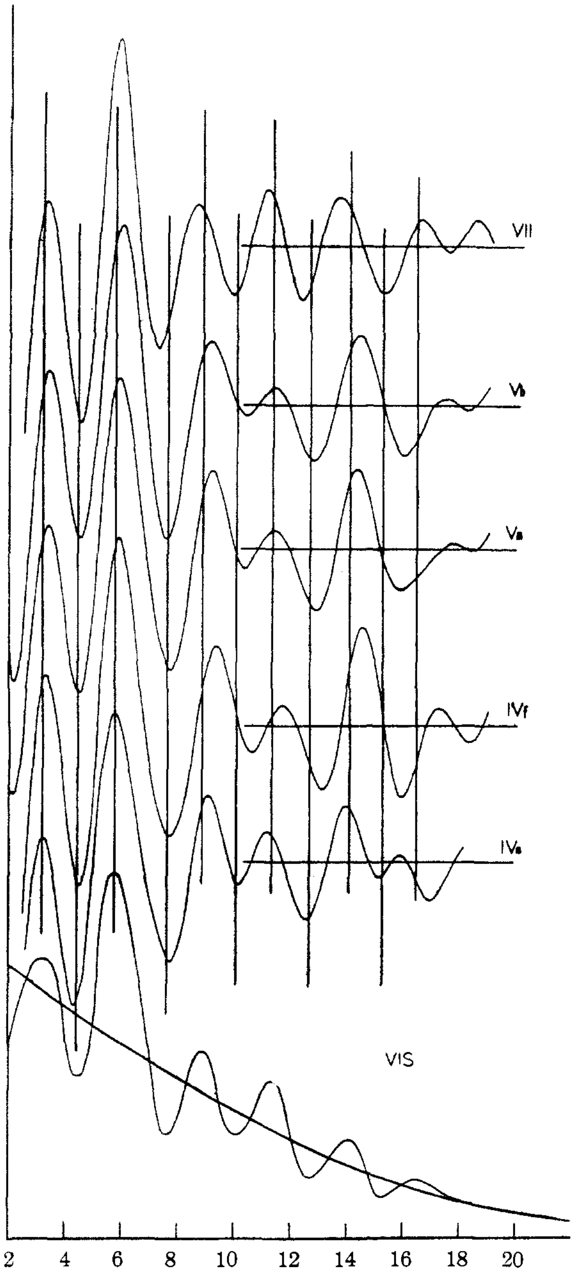

Fig. 2.—Intensity curves for $(CH_3)_2O:BF_3$. Curve "Vis" is a sketch of the visual appearance of the photographs; the smooth curve indicates the supposed background above and below which the intensities of the maxima and minima were estimated. IVa and IVf are theoretical intensity curves of model IV with B–F 1.39, B–O 1.60 and 1.39, respectively, and are the extremes of the range covered. The other curves are described in the text.

It is decidedly unacceptable qualitatively, and the quantitative agreement between the predicted and observed positions of the maxima and minima is not particularly good either. This instance emphasizes the unreliability of the analytical method when applied to data obtained visually. Whereas in the analytic procedure one implicitly assumes that the data are of high precision, the St. John and other psychologic effects inherent to the visual method of estimating ring diameters precludes such a possibility. Thus, although a clear-cut elimination of structures V and VI for $(CH_3)_2O:BF_3$ is not possible, the configuration in which both the boron and oxygen valence angles are tetrahedral, with B–F = 1.41 ± 0.02 Å. and B–O = 1.52 ± 0.06 Å. is in somewhat better agreement with the data than are the above two.

Chemical evidence indicates that the carbon–oxygen bond is considerably activated, since the associated $(CH_3)_2O:BF_3$ is an excellent methylating agent. Unfortunately, our present electron diffraction techniques are not able to demonstrate the occurrence of a small change in a fairly large molecule. Columns IVb and IVc of Table I do suggest a slight lengthening of the C–O separation, possibly from 1.42 to 1.44 Å.

Discussion

To determine whether the oxygen valence bonds are non-planar one might attempt to resolve the optical antipodes of ethyl methyl ether–boron trifluoride. The failure of such an attempt, however, would be significant only if one could show that there is a fair expectation that the rate of inversion of non-planar oxygen valence bonds was sufficiently low in a convenient temperature range. Following the method of Kincaid and Henriques,[7] we computed the barrier height hindering inversion in the above compound to be around 17 kcal.; therefore, the difficulties encountered here would be at least comparable to, if not greater than, those met with in the numerous attempts to resolve the trialkyl amines.[8]

(7) J. F. Kincaid and F. C. Henriques, This Journal, **62**, 1474 (1940).

(8) In the above computation we used B–O = 1.52 Å., O–C = 1.44 Å., tetravalent bond angles for oxygen, and an estimated value of 1 × 10^{-5} for the "force constant" that would be characteristic of the symmetric deformation vibration of a trivalent oxygen possessing a positive formal charge, were that constant defined as $k = 4\pi^2\omega_6^2\mu c^2/N$, ω_6 being the observed frequency. To arrive at that value we considered the "force constants" for the series $(CH_3)_3NH^+$, $(CH_3)_3CH$, $(CH_3)_3N$, and assumed that the trend was roughly parallel to that in the series $(CH_3)_2NH_2^+$, $(CH_3)_2CH_2$, $(CH_3)_2NH$, and $(CH_3)_2O$. The data were taken from K. W. F. Kohlrausch, "Der Smekal-Raman Effect," Ergänzungsband, 1938. Parenthetically, we might point out that the method of Kincaid and Henriques very likely gives values which are too high for the energy required to flatten pyramidal molecules. For example, if one uses the four term potential function as given by J. B. Howard and E. B. Wilson, Jr. (*J. Chem. Phys.*, **2**, 630, (1934)), an energy for the flattening of phosphorus trichloride equal to about 42 kcal. is obtained as compared with the 57 kcal. computed by K. and H.

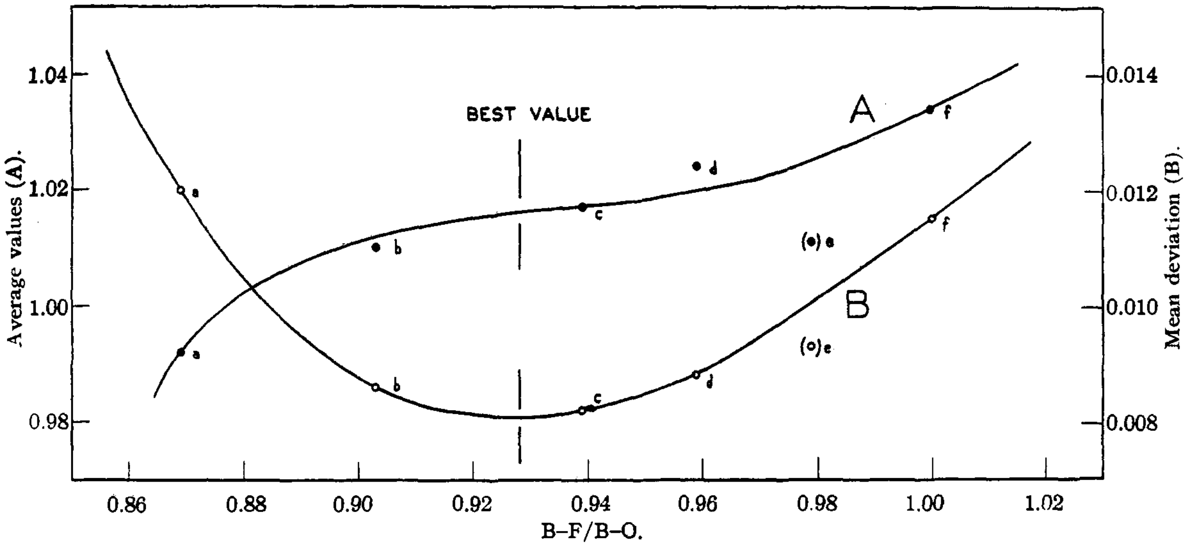

Fig. 3.—A. Average values of $s_{calcd.}/s_{obs.}$ for the maxima and minima, plotted against the B–F/B–O ratio for models IV. B. Mean deviations for $s_{calcd.}/s_{obs.}$ of individual maxima and minima from their average values, plotted against the B–F/B–O ratio for models IV. Point (e) is not comparable to the others, since it was computed for a slightly different C–O distance.

The boron–fluorine and boron–oxygen separations observed in dimethyl ether–boron trifluoride agree, within the experimental error, with corresponding distances in compounds in which boron is tetrahedrally bonded to fluorine or oxygen. Thus in the alkali fluoborates an approximate value for the B–F separation is 1.43 Å.,[9] while in boron arsenate ($BAsO_4$) the average B–O distance is 1.49 Å.[10] It has also been reported[11] on the basis of X-ray powder photographs that $NaBF_4$ and $NaOH \cdot BF_3$ are isomorphous; this strongly indicates that when hydroxyl ion acts as the donor, the boron–oxygen bond distance is close to (probably no more than 0.05 Å. greater than) the B–F separation.

It is clear that in the association process, the boron trifluoride unit (B–F = 1.30 Å., boron valence bonds at 120°),[12] in contrast with the dimethyl ether unit, undergoes rather drastic structural changes, of the type discussed in the preceding paper.[1] Since the single bond distances predicted according to the method of Schomaker and Stevenson[13] (B–F = 1.39 Å., B–O = 1.45 Å.) agree with the values reported here, we may conclude that the B–F and B–O bonds are of unit bond order in dimethyl ether–boron trifluoride.

Remarks on the Nature of Donor-Acceptor Bonding

The mode of description of a bond such as is formed between boron trifluoride and a compound to which it adds has been a point of some debate. In the language of atomic orbitals it may be appropriately described as "donor-acceptor" in the sense that an unshared pair of electrons belonging to one molecule eventually become shared by the two molecules. The bond distance is expected to be (and in the cases measured has been found to be) that of a normal covalent bond of the same coördination number.[14] From dipole moment data it appears that there is only a partial electron transfer[1] so that the coefficients of the ionic terms must be quite large. The occurrence of "saturation of valencies" and well-defined bond angles so characteristic of ordinary bonds is equally striking for "donor-acceptor" bonds. From this point of view, the stretching and bending of the B–F bonds and the formation of the B–O bond may be interpreted as a transition from a case of sp^2 bonds resonating with the three excited structures $F_2B^-::{}^+F$ of BF_3,[12,13b] wherein a certain amount of double bond character is introduced, to the case of sp^3 single bonds in $(CH_3)_2O:BF_3$.

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[9] J. L. Hoard and V. Blair, THIS JOURNAL, **57**, 1985 (1935): Rb^+ and NH_4^+ salts; C. Finbak and O. Hassel, *Z. physik. Chem.*, **B32**, 433 (1936).

[10] G. E. R. Schultze, *ibid.*, **B24**, 215 (1934).

[11] L. J. Klinkenberg, *Rec. trav. chim.*, **56**, 36 (1937).

[12] H. A. Levy and L. O. Brockway, THIS JOURNAL, **59**, 2085 (1937).

[13] (a) V. Schomaker and D. P. Stevenson, *ibid.*, **63**, 37 (1941); (b) S. H. Bauer and J. Y. Beach, *ibid.*, **63**, 1394 (1941).

[14] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 159.

On the other hand, various investigators have argued that the assumption of electron-pair-bond formation in the association process is unnecessary. Thus, as the B–F bonds are bent back, the BF_3 unit assumes a dipole moment estimated at 1.5 *D*. Dipole–dipole interactions and the mutual polarization of the acid and base molecules will, therefore, be appreciable. It should be obvious that both modes of description are approximations, and that when the neglected terms in each are fully considered the two will reduce to the same expression. Such terms will have to be taken into account, for instance, in order to explain the effects of substituents on the acid–base strength of the atoms directly involved in this type of linkage.

It occurred to us that one method of deciding which of these approximations is the more suitable for general considerations is to estimate the energy required to rupture the newly formed bond leaving the two molecules in the "valence states" they were in when in the associated unit. Although the assumptions which we have to make are rather crude, they nevertheless permit us to estimate an order of magnitude.

To begin with, the energies of "donor–acceptor" bonds may be set equal to the measured ΔH values for the respective dissociation reactions *plus* the energy (designated by ΔE) which must be put into the donor and acceptor molecules to transform their electron configurations to that appropriate for the associated unit. In the specific case of the etherate, one should add to the ΔH for the reaction[1,15]

$$(CH_3)_2O:BF_3(g) = BF_3(g) + (CH_3)_2O(g),\ \Delta H = 13\ \text{kcal.}$$

a ΔE of magnitude sufficient to transform the electron configuration of the boron trifluoride from that appropriate for a planar trigonal structure to one in which the B–F bonds are 0.11 Å. longer and tetrahedral to one another, and to activate to some extent the C–O bonds in the ether, resulting in a slight increase in the interatomic distance, of perhaps 0.02 Å. Below we shall outline two methods for estimating this ΔE; in the first it is assumed that ΔE is measured merely by the energy needed to produce the observed geometrical distortions in a molecule whose structure is intermediate between the original and final states, while in the second ΔE is approximated by estimating the resonance energy of boron trifluoride.

Bailey and collaborators[16] pointed out that Badger's rule[17] holds for boron trifluoride; presumably, it also holds to a sufficient accuracy for $X:BF_3$ and for the stages intermediate to the initial and final configurations. If an $r_e = 1.36$ Å. is selected for the average B–F separation during the association, the force constant for the stretching motion, K, is equal to 0.59 megadynes/cm., and the interaction constant, k, equals roughly 0.09 megadynes/cm. On substituting the observed increment in bond distance and these constants in a potential function, such as was used by Bailey and collaborators,[16] an energy slightly greater than 20 kcal. per mole is deduced. One might also wish to consider the energy needed to decrease symmetrically the boron valence angles from 120° to an angle such that a further decrement will cause the molecule to snap over to the tetrahedral configuration. However, the energy of bending the boron valence bonds enters only into the discussion of the energy of activation but not into the heat of reaction, since in the absence of pertinent data one can do nothing but assume that sp^2 and sp^3 single bonds are of equal stability (ref. 14, p. 88). The energy of stretching the two C–O bonds is 0.3 kcal. per mole, so that the first estimate leads to $\Delta E = 21$ kcal. It follows that the main contribution toward ΔE is derived from the drastic changes suffered by the boron trifluoride unit.

The second method of arriving at the magnitude of ΔE is based on the point of view that in the association process the graphite type resonance present in the planar configuration is removed; this leads to a weakening of the B–F bonds which shows up experimentally as an increase in bond length. The energy of formation of boron trifluoride from the gaseous atoms is 467–507 kcal.[18]; we estimate the strength of a single B–F bond to be 130–140 kcal.[19]; a resonance energy of 70–80

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(15) H. C. Brown and R. M. Adams, This Journal, **64**, 2557 (1942).

(16) C. R. Bailey, J. B. Hale and J. W. Thompson, *Proc. Roy. Soc.* (London), **A161**, 107 (1937).

(17) R. M. Badger, *J. Chem. Phys.*, **3**, 710 (1935).

(18) The heat of formation of gaseous boron trifluoride from the elements in their standard states has been given variously as 257 kcal. (F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936, p. 105) and 297 kcal. (W. A. Roth and E. Borger, *Ber.*, **70B**, 48, 1937). Combining these with the heat of sublimation of boron and dissociation energy of fluorine, one obtains

$$B(g) + 3F(g) = BF_3(g),\quad \Delta H = -467,\ -507\ \text{kcal.}$$

(19) Three lines of reasoning suggest the value quoted. (a) As a first rough guess, one might say that the strength of the B–F bond is slightly less than that of the H–F bond. The accepted value

kcal. consequently may be deduced. Thus values for ΔE range from 21 to 80 kcal., and, therefore, the estimated energy of rupture of the newly formed B–O bond in the etherate ranges from 34 to 93 kcal. In similar fashion, one may deduce from the observed heat of reaction

$$C_5H_5N:BF_3(g) = BF_3(g) + C_5H_5N(g),\ \Delta H = 51\ \text{kcal.}^{20}$$

that the energy of rupture of the B–N bond is somewhere between 72 and 130 kcal. These values, rough as they are, clearly demonstrate that the bonds formed in this type of association reaction are comparable in strength to those of normal covalent bonds between the corresponding atoms.[21] In contrast, the maximum dipole–dipole energy, say for dimethyl ether–boron trifluoride, is around 15 kcal. Thus, unless it is shown that the magnitude of the ordinary polarization forces is several times that of the dipole–dipole interaction, the view that a definite chemical bond is formed is distinctly favored, and in a number of cases appears to be the only one which is acceptable; one such example is the association of two $Al(CH_3)_2X$ molecules to produce a unit of zero moment.

Summary

An electron diffraction investigation of the compound dimethyl ether–boron trifluoride $[(CH_3)_2O:BF_3]$ led to the following structure for this molecular compound: the boron valence angles are tetrahedral; B–F = 1.41 ± 0.02 Å.; B–O = 1.52 ± 0.06 Å.; the dimethyl ether part of the molecule remains essentially unaffected; at most, the C–O separation being stretched from 1.42 to 1.44 Å. Although the available photographs agree best with the assumption that the oxygen valence angles are tetrahedral, the possibility that the ∠BOC's and even ∠COC are 120° cannot be definitely eliminated.

The energetics of the association reaction is discussed and, on the basis of values estimated, it is suggested that the bond formed in the association process be regarded as being due to an electron pair rather than to dipole–dipole interaction.

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for the latter is 147 kcal. (ref. 14, p. 53). (b) From the structural data, and the curve proposed by Pauling (ref. 14, p. 164), the bond order in boron trifluoride is roughly 0.3. If the strength of a double bond is assumed to be about 1.7 times that of a single bond, one gets 130–140 kcal. for the strength of the B–F single bond, depending on the ΔH selected for the energy of formation of BF_3. (c) On combining the equation given in ref. 18 with the following

$F(g) + e^- = F^-(g)$, $\Delta H = -95$ kcal. (ref. 14, p. 322)
$B(g) + e^- = B^-(g)$, the electron affinity of boron must be less than 5 kcal., and hence negligible in the following argument
$BF_3(g) + F^-(g) = BF_4^-(g)$, $\Delta H = -71$ kcal.

(J. H. de Boer and J. A. M. van Liempt, *Rec. trav. chim.*, **46**, 124 (1927) one may deduce

$$B(g) + 3F(g) + F^-(g) = BF_4^-(g),\ \Delta H = -577\ \text{kcal.}$$
$$B^-(g) + 4F(g) = BF_4^-(g),\ \Delta H = -670\ \text{kcal.}$$

Now, the strength of the B–F single bond is one-fourth of a value somewhere between the two given above, being closer to the first than to the second. A judicious guess is 600/4 = 150 kcal.

[20] P. A. van der Meulen and H. A. Heller, THIS JOURNAL, **54**, 4404 (1932). Doctoral Dissertation by G. R. Finlay

$$BF_3(g) + NH_3(g) = H_3N:BF_3(s),\ \Delta H = -42\ \text{kcal.}$$

which checks with the value given, when a reasonable energy of sublimation is added to the 42 kcal.

[21] One should not forget that the donating and accepting properties of the atoms involved and thus the bond strength will depend on the nature and steric factors of the groups attached to them. For instance, compare the ΔH given for the association of ammonia–boron trifluoride with

$$B(CH_3)_3(g) + NH_3(g) = H_3N:B(CH_3)_3(g),\ \Delta H = -8\ \text{to}\ -10\ \text{kcal.}$$

Computed from data of A. Stock and F. Zeidler, *Ber.*, **54**, 531 (1921). The influence of steric factors is discussed in ref. 15.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Disproportionation of *o*-Tolyldiphenylmethyl

BY P. W. SELWOOD AND RALPH F. PRECKEL

Marvel[1] and his co-workers have recently in several publications drawn attention to the disproportionation of hexaarylethanes to form substituted methanes and olefinic compounds, with the consequent disappearance of the free radical. A previous communication[2] by the authors points out the significance of disproportionation toward colorimetric and ebullioscopic determinations of free radical concentration. In an effort to learn more of the mechanism of the disproportionation reaction the following work was undertaken. It consists of parallel magnetic, spectroscopic, and ebullioscopic measurements on di-*o*-tolyltetraphenylethane undergoing disproportionation in benzene solution.

Experimental

The magnetic measurements and the preparation of the free radicals have already been described.[2] Again the

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[1] Marvel, Rieger and Mueller, THIS JOURNAL, **61**, 2769 (1939), *et seq.*

[2] Preckel and Selwood, *ibid.*, **63**, 3397 (1941).