quent intervals in order to accumulate any quantity of this key intermediate compound proved very tedious.

During the past five years numerous small variations in the preparation have been given a trial. Several of the changes proved distinctly advantageous and their combination led to a procedure which is less time consuming, cheaper and which can be carried out easily on a larger scale. These improvements are the result of the following three major changes: (a) reduction of the amount of zinc chloride and acetone to one-third of the quantities originally used, (b) decrease of the reaction time from nineteen hours to approximately two hours and (c) the use of a better solvent (butyl ether instead of petroleum ether) for the isolation and crystallization of the diacetone *d*- or *l*-mannitol.

Experimental

Two hundred and seventy grams of zinc chloride sticks (Analytical reagent, Mallinckrodt) is dissolved in 1350 cc. of dry acetone. After the solution has cooled to room temperature and the insoluble matter has settled out, the slightly turbid supernatant liquid is decanted and added to 170 g. of finely powdered *d*- or *l*-mannitol which has been passed through a 200-mesh sieve. The mixture, protected against intrusion of moisture, is either shaken or vigorously stirred until most of the mannitol is dissolved. This operation usually requires about two hours at a room temperature of 19 to 20°. The solution is then filtered (recovering approximately 40 g. of unreacted mannitol) and the filtrate is immediately processed as follows.

In a 5-liter round-bottomed flask equipped with an efficient mechanical stirrer, reaching nearly to the bottom of the flask, are dissolved 340 g. of potassium carbonate (anhydrous) in 340 cc. of water; this solution is covered with 1350 cc. of dry ether.[14] The mixture is vigorously stirred while the filtered acetone-zinc chloride solution is poured in as rapidly as possible. The success of the preparation depends to a large extent upon the speed with which the reactants are brought together; thus the rate of addition and the efficiency of stirring are influential factors. The stirring is continued for a period of thirty to forty minutes, after which the ether-acetone solution is decanted and the zinc carbonate pellets are washed with several portions (totalling 300 to 400 cc.) of a 1:1 acetone–ether mixture. The combined solutions are dried by stirring with 340 g. of calcined potassium carbonate for thirty minutes. The solution is filtered and the carbonate is washed with several portions of a 1:1 acetone–ether mixture (totalling 300 cc. to 400 cc.). The combined filtrate and washings are evaporated under reduced pressure. The residue is finally dried *in vacuo* at 60 to 70° (water-bath) for two hours. The distilling flask is transferred to an oil-bath, 400 cc. of *n*-butyl ether added and the temperature of the bath raised to 135°. The hot solution is filtered rapidly, using a hot water funnel. Another 75-cc. portion of hot butyl ether is used to rinse the flask and filter. The filtrate, which solidifies immediately, is kept in ice for several hours. The precipitate is filtered with suction, washed with low boiling petroleum ether and dried *in vacuo*. The yield of 1,2,5,6-diacetone *d*- or *l*-mannitol is as high as 103 g. (55% of the theoretical amount based on the amount of mannitol in solution). The products melt from 117 to 119°. Recrystallization from water in which both acetone mannitols are very soluble occasions an appreciable loss but gives very pure products in the form of long, fine needles melting at 122°. Products, however, melting from 117 to 119° are pure enough for most purposes. Mixed melting points of 1,2,5,6-diacetone *d*- or *l*-mannitol thus prepared with corresponding enantiomorphs prepared by other methods give no depression. Both compounds on oxidation with lead tetraacetate and subsequent hydrolysis yield quantitatively *d*- or *l*-glyceraldehyde, respectively.[15,16]

Anal. 1,2,5,6-Diacetone *d*-mannitol $C_{12}H_{22}O_6$ (262.2). Calcd.: C, 54.9; H, 8.6. Found: C, 54.8; H, 8.5. 1,2,5,6-Diacetone *l*-mannitol $C_{12}H_{22}O_6$ (262.2). Calcd.: C, 54.9; H, 8.6. Found: C, 54.9; H, 8.5.

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[14] The ether was freed from ethanol and water before use.

[15] E. Baer, J. M. Grosheintz and H. O. L. Fischer, This Journal, **61**, 2607 (1939).

[16] E. Baer and H. O. L. Fischer, *ibid.*, **61**, 761 (1939).

DEPARTMENT OF CHEMISTRY
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On the Structure of Dimethyl Ether–Boron Trifluoride

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

Brown and Adams[1] called attention to a discrepancy in the data on the dissociation of dimethyl ether–boron trifluoride.[2] We reëxamined the data in question and agree that these are not self-consistent; it is likely that the dissociations we calculated for the lower temperature range are too low. Since our experimental method was such that no direct observation of the completeness of vaporization could be made, it is possible that in this lower temperature range the sample was not entirely in the vapor phase, as was assumed in our calculations. Consequently, the percentage dissociation we assumed in interpreting our electron diffraction photographs of dimethyl ether–boron trifluoride[3] was incorrect; instead of the negligible 10% dissociation for the saturated vapor at about 40° we should have taken a value close to 57% deduced from the combined data of Brown and Adams[4] and of Laubengayer and Finlay. We have therefore reconsidered our electron diffraction results assuming more extensive dissociation.

As will be recalled, our study began with a radial distribution computation. This approach is basic, since no assumption need be made regarding the structure or composition of the diffracting sample. The interatomic distances which must occur in the diffracting sample are indicated in Fig. 1a, curve R.D. Extensive experience has shown that the peaks which lie below 1 Å. or above 4 Å. cannot be trusted, due to the fact that the incomplete integrations introduce spurious oscillations in these regions; those peaks found between 1 and 2 Å., and between 3 and 4 Å. are within 3% of the interatomic distances obtained by more extensive analysis, while the range 2 to 3 Å. is most accurately represented (to 1–2%). Since in the unassociated molecules no interatomic distances above 2.36 Å. are present, the occurrence of peaks

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[1] H. C. Brown and R. M. Adams, This Journal, **65**, 2253 (1943).

[2] A. W. Laubengayer and G. R. Finlay, *ibid.*, **65**, 887 (1943).

[3] S. H. Bauer, G. R. Finlay and A. W. Laubengayer, *ibid.*, **65**, 889 (1943).

[4] H. C. Brown and R. M. Adams, *ibid.*, **64**, 2559 (1942).

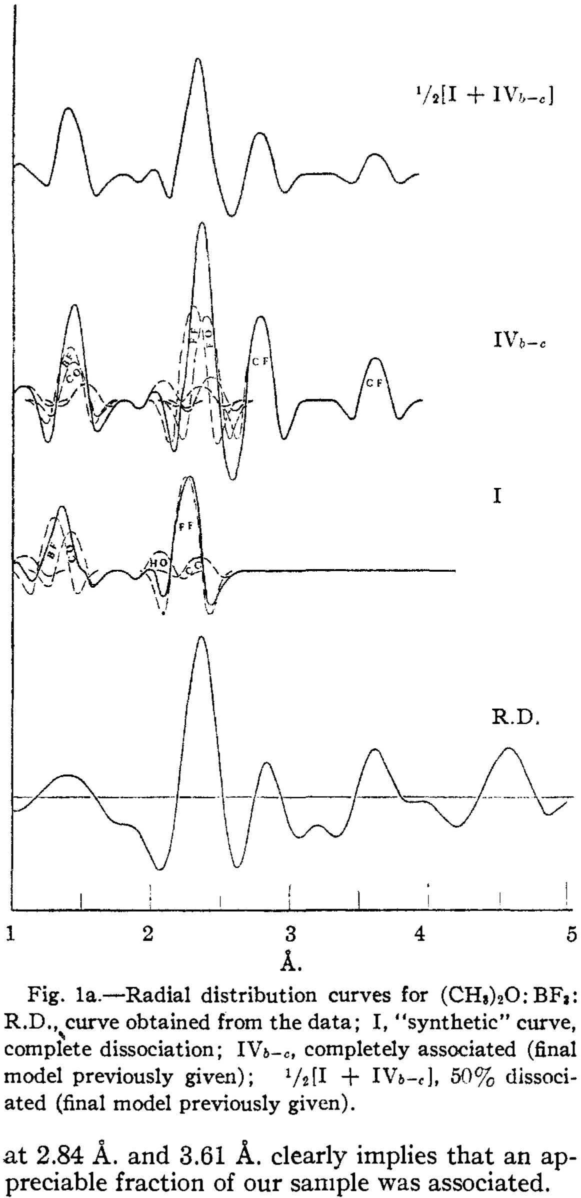

Fig. 1a.—Radial distribution curves for $(CH_3)_2O:BF_3$: R.D., curve obtained from the data; I, "synthetic" curve, complete dissociation; IV$_{b-c}$, completely associated (final model previously given); $^1/_2$[I + IV$_{b-c}$], 50% dissociated (final model previously given).

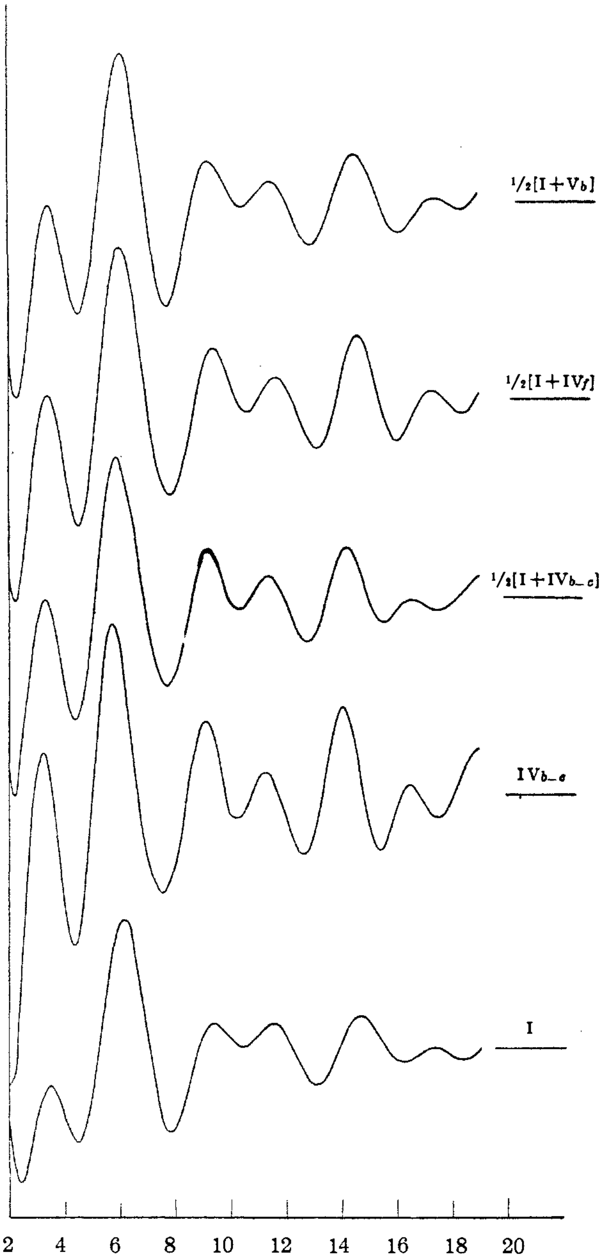

Fig. 2a.—Theoretical intensity curves for $(CH_3)_2O:BF_3$: I, completely dissociated; IV$_{b-c}$, completely associated (final model previously given); $^1/_2$[I + IV$_{b-c}$]; $^1/_2$[I + IV$_f$]; $^1/_2$[I + V$_b$]: models previously discussed, 50% dissociated.

at 2.84 Å. and 3.61 Å. clearly implies that an appreciable fraction of our sample was associated.

It is instructive to compare "synthetic" radial distribution curves for various models [I (unassociated); IV (0% dissociated–final model given previously[2]); and (I + IV)/2 (50% dissociated–final model)] with the one obtained from the photographs (Fig. 1a). Although it appears that a clear cut distinction cannot be made between 50 and 0% dissociation, the case of 100% dissociation and our previously designated models II and III may still be unquestionably eliminated. And, as has been pointed out in our original communication, the only question which remains is what configuration of IV, V or VI is in best agreement with the data. Further, the correct model must be essentially like IV, V or VI, since these give the critical peaks, due to the C–F interactions at the observed positions 2.8 Å. and 3.6 Å., and allow the F–F and F–O separations (which are the principal components of the large peak at 2.36 Å.) to come close to one another. This is emphasized by the similarity of the curves in Fig. 1a, below 2.5 Å.; the F–F separations in the associated molecule have to be rather close to those in the unassociated BF$_3$, in spite of the formation of the new B–O bond, and consequent changes in ∠FBF's. This can only be accomplished by the simultaneous elongation of B–F to about 1.4 Å.

Our next consideration was to note how the curves in Fig. 3, reference 2, change, when one assumes an appreciable amount of dissociation. Theoretical intensity curves were therefore computed for models IVa, IVd, IVf, and IVb-c (final model previously given); also for V_a and V_b, assuming in each case that 50% of the sample was dissociated[5] (Fig. 2a). The resulting curves differ only slightly from those in which no dissociation was assumed (except for model IVa, which is no longer admissible); this is due to the fact that the amplitude of the intensity curve for the dissociated part of the sample, for S > 8, is only about half of the amplitude of the pattern of the associated molecules, while in the region S < 8 all the curves show the same qualitative features. The quantitative comparison is presented in Table Ia.

TABLE Ia

DIMETHYL ETHER–BORON TRIFLUORIDE

				s_0(calcd.)/s_0(obs.)				
				0% dissociated	50% dissociated			
Max.	Min.	s_0	I_{Av}	IV_{b-c}	IV_{b-c}	IV_d	IV_f	V_b
1		3.22	7	1.003	1.025	1.037	1.056	1.068
	2	4.44	−5	0.982	0.991	1.009	1.013	1.018
2		5.76	10	.993	1.021	1.035	1.042	1.052
	3	7.61	−6	.992	1.012	1.024	1.026	1.022
3		8.88	4.2	1.028	1.036	1.048	1.056	1.038
	4	10.07	−3	1.016	1.029	1.039	1.051	1.036
4		11.32	3.5	.996	1.005	1.019	1.028	1.016
	5	12.68	−2.8	.999	1.009	1.023	1.035	1.020
5		14.08	2.2	1.000	1.010	1.026	1.037	1.031
	6	15.24	−1.5	1.012	1.021	1.039	1.051	1.058
6		16.43	1	1.004	1.010	1.036	1.049	1.059
Average				1.002	1.015	1.030	1.040	1.038
Mean deviation				0.0093	0.0100	0.0094	0.0115	0.0155
Interatomic distances deduced			B–F	1.41	1.43	1.432	1.446	1.443
			B–O	1.52	1.54	1.493	1.446	1.495
			C–O	1.44	1.46	1.483	1.498	1.495

On replotting the average deviations for models IV, the minimum (0.0093) is found to be shifted from (B–F)/(B–O) = 0.925 to (B–F)/(B–O) = 0.955 with the average value for $s_{\text{calcd.}}/s_{\text{obs.}} = 1.028$. Hence the structure which is in best qualitative and quantitative agreement with the data—assuming 50% dissociation—is:

Boron and oxygen valence angles tetrahedral

B–F = 1.43 ± 0.03 Å. (previously 1.41 ± 0.02 Å.)

B–O = 1.50 ± 0.06 Å. (previously 1.52 ± 0.06 Å.)

C–O = 1.45 ± 0.03 Å. (previously 1.44 ± 0.03 Å.)

The situation also remains unchanged with regard to models V and VI; quantitatively these are not as satisfactory as the above model, but they cannot be eliminated. Due to the introduction of another variable, the degree of dissociation of the diffracting sample, the limits of error imposed on the final B–F distance is of necessity increased.

The case of dimethyl ether–boron trifluoride turned out to be more favorable for a structure determination than we had anticipated, due to the apparent insensitivity to the degree of dissociation of the complex. A similar electron diffraction attempt to determine the structure of the methyl cyanide–boron trichloride complex in the vapor phase clearly showed that the compound was completely dissociated at 95°, and this was substantiated by vapor density measurements.[6]

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(5) The exact per cent. dissociation in the sample doing the diffracting is not known. It probably was around 60%, as can be judged from the heights of the peaks at 2.84 Å. and 3.16 Å. of the R.D. curve. We assumed 50% dissociation rather than the somewhat larger value only because the computations are thus greatly simplified. We have shown below that the conclusions regarding the final structure are not sensitive to the fraction postulated.

(6) A. W. Laubengayer and D. C. Sears, THIS JOURNAL, **67**, 164 (1945).

ITHACA, N. Y. RECEIVED JUNE 1, 1944

The Production of a Poison for Nickel Catalysts in the Absorption of Oxygen by Fieser's Solution[1]

BY W. B. BURFORD, III, AND J. C. W. FRAZER

In the early stages of work on the poisoning of nickel hydrogenation catalysts by water vapor[2] an attempt was made to remove oxygen from the ethylene by means of alkaline hydrosulfite in the form of Fieser's solution number 2,[3] using an equivalent amount of potassium hydroxide in place of the sodium hydroxide specified. Highly erratic results followed which suggested that the solution might be introducing some impurity into the ethylene. This was confirmed by the disappearance of the effect when purification by means of a precatalyst tube was substituted for the Fieser's solution.

The odor of exhausted solutions strongly indicated a sulfur containing compound. Tests for sulfur dioxide and hydrogen sulfide were both negative, but a positive test for carbon disulfide was obtained by the procedure of Vogel.[4] This consists of passing the gases into alcoholic potassium hydroxide and precipitating any xanthate formed with copper sulfate as the dark yellow-green insoluble copper xanthate.

Tests were made by bubbling gas through the hydrosulfite solution at about 55 ml. per min. for one-half to one hour and passing the exit gases through alcoholic potassium hydroxide. The yellow-green color of the precipitate formed was observed readily against filter paper after filtration.

Using ethylene containing 2% oxygen a positive test was obtained in fifteen minutes. However, with 0.1% oxygen at least half an hour was required and it was necessary to heat the hydrosulfite. A faint positive test was obtained when air alone was passed through for fifteen minutes but none if pure nitrogen was used.

Various brands and purities of reagents produced no change in these observations.

It is concluded that the action of ethylene–oxygen mixtures or of air on Fieser's solution pro-

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(1) Original manuscript received January 27, 1943.

(2) W. B. Burford, III, and J. C. W. Frazer, THIS JOURNAL, **67**, 331 (1945).

(3) L. F. Fieser, *ibid.*, **46**, 2639 (1924).

(4) Vogel, *Ann.*, **86**, 369 (1853).