[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Molecular Addition Compounds. I. The Interaction of Ammonia with Ammonia-Boron Trifluoride at Low Temperatures[1]

BY HERBERT C. BROWN AND SIDNEY JOHNSON[2]

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The ammonia–boron trifluoride system has been examined at −78.6°, −45.9°, as well as at 28°. At 28° the existence of a single 1:1 addition compound ($H_3N:BF_3$) is indicated, in accordance with the conclusions of previous workers. However, at lower temperatures the vapor pressure–composition data reveal the existence of three additional compounds with the composition: $2NH_3 \cdot BF_3$, $3NH_3 \cdot BF_3$, $4NH_3 \cdot BF_3$. It is proposed that the three hydrogen atoms of the ammonia molecule in the 1:1 compound, $H_3N:BF_3$, are rendered sufficiently acidic by the boron trifluoride group to permit them to bind up to three additional ammonia molecules through hydrogen bonding: $H_3N \cdots HNH_2:BF_3$; $(H_3N)_2 \cdots H_2NH:BF_3$; $(H_3N)_3 \cdots H_3N:BF_3$. A similar investigation of the dimethylamine–boron trifluoride system at 0° and −64° did not reveal any tendency for the simple 1:1 compound, $HN(CH_3)_2:BF_3$, to bind in a similar manner an additional molecule of dimethylamine. The different behavior of dimethylamine is attributed to its large steric requirements.

Ammonia reacts with boron trifluoride to form a simple 1:1 addition compound[3] which has received careful characterization.[4] With regard to the existence of products containing higher ratios of ammonia to boron trifluoride, the literature is confused and contradictory.

Gay-Lussac[3] reported that the two gases reacted in the molar ratio of $2NH_3 \cdot BF_3$ as well as 1:1. Davy confirmed Gay-Lussac's observations and claimed the existence of an additional compound, $3NH_3 \cdot BF_3$.[5] Later Rideal also reported the existence of these higher ammoniates, $2NH_3 \cdot BF_3$ and $3NH_3 \cdot BF_3$.[6] However, Laubengayer and Condike concluded that only the 1:1 compound exists in this system.

In the course of studies of other 1:1 addition compounds of ammonia and Lewis acids we have observed that excess ammonia can frequently be removed from such compounds only with difficulty, suggesting a strong interaction between the base and the addition compounds. In certain of these systems evidence was obtained for the existence of definite compounds containing 1, 2 or 3 additional molecules of ammonia. Accordingly, it appeared desirable to investigate the ammonia–boron trifluoride system over a range of temperatures in order to settle the question of the possible existence of higher ammoniates of boron trifluoride.

Results and Discussion[7]

At 28° a measured amount of boron trifluoride was treated with varying amounts of ammonia. From the residual pressures, the ratio of the two gases which reacted could be estimated. Typical data are summarized in Table I.

TABLE I

REACTION OF AMMONIA AND BORON TRIFLUORIDE AT 28°

Molar ratio NH_3/BF_3	Residual press., mm.	Reactants NH_3/BF_3
0.0	165.0	
.277	120.4	1.025
.527	79.0	1.010
.755	40.3	0.999
.956	10.1	1.018
1.020	5.6	0.986
1.269	46.5	0.987
1.551	87.8	1.019
1.771	127.1	1.000
1.962	159.5	0.995
2.390	223.4	1.037

The results fully confirm the observations of Laubengayer and Condike. At room temperature and ammonia pressures up to 200 mm. there is no evidence for the existence of ammoniates other than the 1:1 compound. We therefore examined the system at lower temperatures.

At −45.9° the vapor pressure–composition data definitely establish the existence of higher ammoniates. In addition to the stable 1:1 compound, plateaus were observed corresponding to the existence of 2:1, 3:1 and less, certainly, 4:1 compounds. These products are relatively unstable. Thus the dissociation pressure of the $2NH_3 \cdot BF_3$ compound at −45.9° is in the range 44–46 mm., and that for the $3NH_3 \cdot BF_3$ product lies in the range 123–125 mm. Although the data appeared to indicate the existence of a 4:1 compound, the dissociation pressures in this range were so high (240–250 mm.) that it was decided to investigate the system at −78.6° to ob-

TABLE II

VAPOR PRESSURE–COMPOSITION DATA FOR THE AMMONIA–BORON TRIFLUORIDE SYSTEM

−45.9°		−78.6°	
Molar ratio NH_3/BF_3	Press., mm.	Molar ratio NH_3/BF_3	Press., mm.
6.09	274.6	5.85	33.5
5.15	269.3	5.57	33.6
4.09	264.0	5.32	32.6
3.85	251.1	4.98	32.6
3.46	247.7	4.78	30.0
3.29	244.4	4.35	28.5
3.06	206.0	4.16	5.2
2.82	122.8	3.93	2.5
2.59	122.9	3.71	2.0
2.12	125.1	3.24	1.3
1.91	46.0	2.56	1.3
1.09	44.0	2.32	1.1
1.01	.01	2.26	0.1

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[1] Based upon a thesis submitted by Sidney Johnson in partial fulfillment of the requirements for the degree of Doctor of Philosophy

[2] A.E.C. Fellow at Purdue University, 1951–1953.

[3] J. L. Gay-Lussac and J. L. Thenard, *Mem. phys. chim. Soc. d'Arcueil*, **2**, 210 (1809); Gmelin's "Handbuch der anorganischen Chem.," Verlag Chemie, Berlin, 8th ed., 1926, Vol. 13, p. 114.

[4] A. W. Laubengayer and G. F. Condike, THIS JOURNAL, **70**, 2274 (1948).

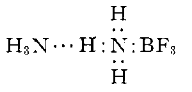
[5] J. Davy, *Phil. Trans.*, **102**, 352 (1812).

[6] S. Rideal, *Ber.*, **22**, 992 (1889).

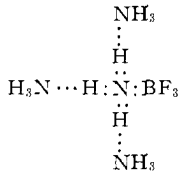
[7] The apparatus and experimental procedures are similar to those described in earlier papers in this series. See H. C. Brown, L. P. Eddy and R. Wong, THIS JOURNAL, **75**, 6275 (1953).

tain verification of the existence of this product. At this temperature the data revealed a sharp increase in pressure at a mole ratio NH_3/BF_3 of 4 to 1, establishing the existence of a total of four ammoniates in this system. Typical data are given in Table II.

It is of interest to consider the probable structures of these higher ammoniates. The powerful electron-withdrawing character of the boron trifluoride group must greatly increase the polar character of the three nitrogen–hydrogen bonds, resulting in a greatly increased ability to form hydrogen bonds with donor molecules. It is suggested that the stable 1:1 addition compound binds the 1, 2 and 3 additional ammonia molecules through a corresponding number of hydrogen bonds.



$$H_3N\cdots H:\overset{H}{\underset{H}{\ddot{\underset{\cdot\cdot}{N}}}}:BF_3$$



$$H_3N\cdots H:\overset{\overset{NH_3}{\vdots}}{\overset{H}{}}\!\!\!\!\underset{\underset{NH_3}{\vdots}}{\underset{H}{}}\!\!\ddot{\underset{\cdot\cdot}{N}}:BF_3$$

We attempted to test this interpretation by investigating the dimethylamine–boron trifluoride system. Since the 1:1 addition compound here contains but one nitrogen–hydrogen bond, the 1:1 product should be capable of uniting with a maximum of but one additional molecule of dimethylamine. However, the vapor pressure–composition data at 0° and at −64.0° showed no evidence for the existence of compounds other than the stable 1:1 product. It is probable that the accumulation of two methyl groups together with the bulky boron trifluoride group on a single nitrogen atom results in a serious steric barrier to hydrogen bonding involving the relatively bulky base, dimethylamine.

It therefore appears that compounds of higher order are quite possible in systems known to yield stable 1:1 addition compounds and the existence of such compounds of higher order presumably accounts for the difficulties frequently encountered in removing excess base in the presence of the 1:1 products.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Formation of Formaldehyde in the Photo-oxidation of Acetone[1,2]

BY MARGARET I. CHRISTIE

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The reactions with oxygen of the radicals formed in the photolysis of acetone have been further investigated at low oxygen pressures at 120 and 175°. Quantum yields of formaldehyde formation have been determined colorimetrically. One molecule of formaldehyde, in addition to one molecule of either carbon monoxide or of carbon dioxide, results from the formation of each methyl radical in the acetone–oxygen system. It is suggested that methyl radicals react as follows: $CH_3 + O_2 + CH_3COCH_3 = CH_2O + H_2O + CH_2COCH_3$ (without implying that this reaction necessarily occurs in a single step). The acetonyl radicals would then be responsible for carbon monoxide and for carbon dioxide formation. By use of acetone labeled with carbon-14 in the end carbons it is shown that most if not all of the carbon dioxide comes from these carbon atoms.

Introduction

Acetone decomposes photochemically to methyl and acetyl radicals. When methane is formed, acetonyl radicals must also be formed. Marcotte and Noyes,[3] in an investigation of the photochemical oxidation of acetone at low oxygen pressures, measured the quantum yields of methane, carbon monoxide and carbon dioxide formed and of oxygen consumed. At temperatures of 120° and over and at oxygen pressures up to 2 mm., the quantum yield of oxygen disappearance was approximately constant at 4.0 ± 0.5. The sum of the yields of carbon monoxide and of carbon dioxide was about three irrespective of methane formation under conditions such that the dissociation of acetyl radicals was complete. After correction for carbon monoxide formed by dissociation of acetyl radicals, the CO_2/CO ratio was found to be proportional to the oxygen pressure. A mechanism consistent with the facts was based on the formation of formyl radicals by reaction of both methyl and acetonyl radicals with oxygen. It did not predict large yields of formaldehyde.

It is doubtful if formyl radicals are oxidized to carbon dioxide since this is not a major product in the photochemical oxidation of formaldehyde.[4,5] Other authors[6,7] favor the reaction $HCO + O_2 = CO + HO_2$. The photo-oxidation of dimethylmercury and of methyl iodide give CO_2/CO ratios almost independent of oxygen pressure.[8]

Formaldehyde has recently been identified[9] as a product in the acetone–oxygen system.

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[2] The author wishes to express her gratitude to the Celanese Corporation of America for a postdoctoral fellowship for the year 1952–1953. Present address: Newnham College, University of Cambridge, England.

[3] F. B. Marcotte and W. A. Noyes, Jr., *Discussions Faraday Soc.*, **10**, 236 (1951); THIS JOURNAL, **74**, 783 (1952).

[4] J. E. Carruthers and R. G. W. Norrish, *J. Chem. Soc.*, 1036 (1936).

[5] E. C. A. Hormer, Ph.D. Thesis, King's College, University of London, 1951.

[6] K. Faltings, W. Groth and P. Harteck, *Z. physik. Chem.*, **41B**, 15 (1938).

[7] G. von Elbe and B. Lewis, *J. Chem. Phys.*, **7**, 717 (1939).

[8] R. B. Martin and W. A. Noyes, Jr., THIS JOURNAL, **75**, 4183 (1953).

[9] D. E. Hoare, *Trans. Faraday Soc.*, **49**, 1292 (1953).