cobalt octacarbonyl was placed in the erlenmeyer flask, the flask attached to the gas buret, the system purged with nitrogen, and the gas volume recorded. The flask was immersed in Dry Ice, and 2.0 g. of piperidine dissolved in 13 ml. of toluene was slowly added to the flask. The Dry Ice bath was removed, the contents of the flask stirred by means of a magnetic stirrer, and the gas volume recorded after the solution had reached room temperature. No evolution of gas occurred. The dark solution turned light red, and a greenish-yellow oil separated. The addition of 20 ml. of water solubilized the oil, and the color changed to light yellow. After 5 minutes of stirring, 50 ml. of nickel *o*-phenanthroline chloride solution was added and the solution stirred for 5 minutes. After acidification with 10 ml. of 6 *N* hydrochloric acid, the solution was filtered. Analysis for cobalt carbonyl anion gave 0.341 g. (1.99 millimoles). This is 92% of the amount of anion predicted by equation (8).

I and Dilute Hydrochloric Acid.—A solution of 10 ml. of xylene containing 1.9680 g. (5.76 millimoles) of dicobalt octacarbonyl was cooled in a Dry Ice-bath as described above, 6.0 g. of piperidine dissolved in 19 ml. of xylene was added, the Dry Ice removed, and the solution allowed to warm to 0° in an ice–water-bath. A solution of 12 ml. of concentrated hydrochloric acid and 40 ml. of water was added slowly with stirring. Upon addition of the acid, the xylene solution turned dark brown, owing to the formation of dicobalt octacarbonyl according to equation (13). The gas evolved (52 ml.) consisted of 4 ml. of hydrogen and 48 ml. (2.14 millimoles) of carbon monoxide; this amounts to only 4.6% of the carbon monoxide present in the dicobalt octacarbonyl.

I and Concentrated Hydrochloric Acid.—To a solution of 10 ml. of xylene containing 1.500 g. (4.38 millimoles) of dicobalt octacarbonyl, cooled in a Dry Ice-bath as described above, was added 4.0 g. of piperidine dissolved in 19 ml. of xylene. The Dry Ice-bath was removed and, after the solution had reached room temperature, a solution of 12 ml. of concentrated hydrochloric acid and 11 ml. of water was rapidly added with stirring. The resulting aqueous layer was pink while the xylene solution was dark brown, indicating the presence of cobalt chloride and dicobalt octacarbonyl; the formation of both of these compounds is postulated in equation (16). The gas evolved (184 ml.) consisted of 20 ml. (0.89 millimole) of hydrogen and 164 ml. (7.32 millimoles) of carbon monoxide. This is 20.9% of the amount of carbon monoxide present in the dicobalt octacarbonyl; equation (16) requires the evolution of 25% of the amount of carbon monoxide in the dicobalt octacarbonyl. If the decomposition of cobalt hydrocarbonyl (equation (14)) had gone to completion, the amount of hydrogen (equation (16)) would have been 0.5 mole per mole of dicobalt octacarbonyl, or 2.19 millimoles. That the amount of hydrogen obtained in this experiment is lower than that predicted by equation (16) is consistent with the fact that cobalt hydrocarbonyl is fairly stable in aqueous solutions even in the presence of acids.[1]

Dicobalt Octacarbonyl and Sodium Amalgam.—To 0.4931 g. (1.44 millimoles) of dicobalt octacarbonyl in 12 ml. of toluene was added 130 g. of sodium amalgam containing approximately 1% sodium, and the mixture was stirred. The benzene solution was decolorized after 1 hour, indicating complete conversion of dicobalt octacarbonyl. Stirring was continued for 1 more hour. No gas was evolved during the reaction. Sixty ml. of water was added and the mixture stirred for 2 hours to decompose excess sodium and dissolve the sodium salt of cobalt hydrocarbonyl, $NaCo(CO)_4$. Analysis of the aqueous solution showed 0.465 g. (2.72 millimoles) of cobalt carbonyl anion (1.89 millimoles of cobalt carbonyl anion per mole of dicobalt octacarbonyl).

Dicobalt Octacarbonyl and Sodium Hydroxide Solution.—To 0.5048 g. (1.48 millimoles) of dicobalt octacarbonyl dissolved in 20 ml. of toluene was added 20 ml. of a 4 *N* sodium hydroxide solution. During the reaction, which was completed in 8 hours, a total of 42 ml. of carbon monoxide was evolved. The toluene solution became colorless, and the aqueous solution turned from light blue-violet at the beginning to light straw-yellow at the end of the reaction. The aqueous solution contained 0.435 g. (2.55 millimoles) of cobalt carbonyl anion (1.72 moles of cobalt carbonyl anion per mole of dicobalt octacarbonyl).

Dicobalt Octacarbonyl and Water.—To 0.54 g. (1.60 millimoles) of dicobalt octacarbonyl dissolved in 25 ml. of benzene, 15 ml. of water was added. Completion of the reaction required 48 hours, and during this time 105 ml. (4.70 millimoles) of carbon monoxide was evolved. The aqueous solution contained 0.405 g. (2.37 millimoles) of cobalt carbonyl anion (1.48 moles of cobalt carbonyl anion per mole of dicobalt octacarbonyl).

BRUCETON, PENNA. RECEIVED AUGUST 21, 1951

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Dimethylaminoboron Dichloride and Difluoride

BY JOHN F. BROWN, JR.

The reaction of triethylamine with dimethylamine–boron trichloride in benzene solution gave a 73% yield of dimethylaminoboron dichloride. Pyridine with dimethylamine–boron trichloride gave mainly a 1:1 adduct. There was no reaction between triethylamine and dimethylamine–boron trifluoride, but when dimethylamine–boron trifluoride was pyrolyzed, it gave a 31% yield of dimethylaminoboron difluoride dimer, along with the disproportionation products trimethylamine–boron trifluoride and tetramethylammonium fluoborate.

Dimethylaminoboron dichloride was first prepared by Wiberg[1] by mixing dimethylamine and boron trichloride. The process was represented by equation 1, although HCl was not found among the products.

$$(CH_3)_2NH + BCl_3 \longrightarrow (CH_3)_2NBCl_2 + HCl \quad (1)$$

Bis-dimethylaminoboron chloride and tris-dimethylaminoboron were also formed, and the yields of the amino dichloride were low.

It has now been found that good yields of dimethylaminoboron dichloride may be obtained by first forming dimethylamine–boron trichloride in benzene solution and then dehydrohalogenating it with triethylamine, according to equations 2 and 3. When the preparation is carried out in this way, no appreciable amounts of bis- or tris-aminoboron compounds appear to be formed, but a brown tar is obtained as a by-product.

$$(CH_3)_2NH + BCl_3 \longrightarrow (CH_3)NHBCl_3 \quad (2)$$

$$(CH_3)_2NHBCl_3 + (C_2H_5)_3N \longrightarrow (CH_3)_2NBCl_2 + (C_2H_5)_3NHCl \quad (3)$$

When pyridine is used instead of triethylamine, little dehydrohalogenation results, but instead a 1:1 dimethylamine–boron trichloride–pyridine adduct is formed.

Dimethylaminoboron difluoride, which does not seem to have been previously described, could not be prepared by this method. There was no evidence of any reaction between dimethylamine–boron trifluoride and triethylamine, even though the

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[1] E. Wiberg and W. Sütterlin, *Z. anorg. Chem.*, **202**, 46 (1931); E. Wiberg and K. Schuster, *ibid.*, **213**, 77 (1933).

corresponding trichloride reacted instantly. When, however, the adduct was refluxed for an hour at 240–295° both the dimer of dimethylaminoboron difluoride and fluoborates were formed, probably according to the equation

$$(CH_3)_2NHBF_3 \xrightarrow{\Delta} (CH_3)_2NBF_2 + (CH_3)_2NH_2BF_4 \quad (4)$$

just as boron nitride and ammonium fluoborate are formed by pyrolysis of ammonia–boron trifluoride.[2] The yield of dimeric dimethylaminoboron difluoride was only 31% and there was some redistribution of the methyl groups, since trimethylamine–boron trifluoride and tetramethylammonium fluoborate were also obtained.

Discussion

This method of synthesizing dimethylaminoboron dichloride suggests the following mechanism for Wiberg's direct substitution process. When dimethylamine is added to boron trichloride, the simple adduct is first formed as in equation 2. This then reacts with more dimethylamine to give dimethylammonium chloride and dimethylaminoboron dichloride. Low yields of the latter are obtained because the excess dimethylamine, which must be present in order to dehydrohalogenate the dimethylamine-boron trichloride, can react further with the dimethylaminoboron dichloride to form adducts[3] and bis- and tris-aminoboron compounds. The marked difference between the behavior of dimethylamine-boron trichloride and that of dimethylamine-boron trifluoride may be related to the greater stability of the boron–fluorine bond and to steric repulsions between chlorines in the trichloride.

It is interesting to compare dimethylaminoboron dichloride with dimethylaminoboron difluoride. Both substances dimerize upon standing, the difluoride much more rapidly than the dichloride. Both dimers are water insoluble solids, having camphor-like odors, and are partially dissociated in the vapor state. However, the difluoride dimer decomposes on standing in dry air, while the dimer of the dichloride is unchanged after several months; and the difluoride dimer dissolves almost instantly in boiling water, while the dichloride dimer requires several hours of refluxing for its hydrolysis, and may even be steam distilled with fair recovery.

Experimental

Dimethylaminoboron Dichloride.—The vapors from 33 ml. (0.50 mole) of dimethylamine were passed into a solution of 41 ml. (0.50 mole) of boron trichloride in 500 ml. of benzene with good stirring and cooling. A white, crystalline precipitate soon began to separate. On one occasion this precipitate (m.p. 127–137°) was filtered off and identified as dimethylamine–boron trichloride.

Anal. Calcd. for $C_2H_7NBCl_3$: Cl, 65.55. Found: Cl, 65.4.

To the slurry of dimethylamine–boron trichloride 70 ml. (0.50 mole) of triethylamine dissolved in 180 ml. of benzene was added with continued stirring and cooling. After standing overnight, the colorless precipitate of triethylamine hydrochloride (57 g., 83%) was filtered off, washed with a little benzene and analyzed.

Anal. Calcd. for $C_6H_{16}NCl$: Cl, 26.0. Found: Cl, 25.8.

The brownish, strongly fuming filtrate was fractionated to give 45.5 g. (73%) of colorless dimethylaminoboron dichloride, b.p. 51–53° (90 mm.). Running the dehydrohalogenation step at 80° gave similar yields, but when the reaction was carried out in chloroform solution the high solubility of the triethylamine hydrochloride complicated the separation of the products and the yield of amino dichloride was 63%.

The dimethylaminoboron dichloride was completely converted to its crystalline dimer after 1–2 days standing at room temperature. However, when this dimer was sublimed in a vacuum, most of it went back to the original monomeric liquid.

The brown color of the crude benzene solution apparently arose from the triethylamine, or from some impurity in it. When triethylamine was added to boron trichloride in benzene, the solution became brown as soon as an excess of triethylamine was present, and the low-melting triethylamine–boron trichloride which crystallized out had a dark brown color.

The Distillation Residue.—Upon standing, the residue from the distillation of dimethylaminoboron dichloride, prepared as above, deposited an additional 4 g. of triethylamine hydrochloride (total yield, 61 g., 89%). The bulk of the residue was a viscous, dark brown oil, soluble in water with complete hydrolysis, and partially soluble in benzene. A similar dark viscous oil was left as the residue from the reaction run in chloroform. These oils contained N:Cl ratios of about 1:2 (45% Cl, 9% N) and upon hydrolysis yielded dimethylamine (identified as the alkali-insoluble *p*-toluenesulfonamide, m.p. 78–79°) but no primary amines. The exact constitution of these residual oils seems obscure.

Dimethylamine–Boron Trichloride–Pyridine Adduct.—Dimethylamine (10 ml., 0.15 mole) was added to boron trichloride (23 ml., 0.28 mole) in 75 ml. of benzene as before, and the solution distilled (distillate, 30 ml.) to remove the excess boron trichloride. To the warm solution, pyridine (12 ml., 0.15 mole) was added with stirring. When all the pyridine had been added, the clear, homogeneous solution suddenly crystallized. The coarse, white crystals of the dimethylamine–boron trichloride–pyridine adduct were filtered off and washed with a little benzene; yield 30.0 g. (83%); m.p. 127–147° with loss of pyridine.

Anal. Calcd. for $C_7H_{12}N_2BCl_3$: Cl, 44.1; dimethylamine, 18.7; pyridine, 32.8. Found: Cl, 43.2; dimethylamine, 18.6; pyridine, 32.6.

The dehydrohalogenation reaction probably did proceed to a small extent, since the freshly prepared adduct had the odor of dimethylaminoboron dichloride dimer and gave a slightly turbid solution in water; and the mother liquors from the crystallization fumed slightly in air.

Dimethylamine–Boron Trifluoride Pyrolysis.—Dimethylamine–boron trifluoride was prepared in 90% yield by passing an equivalent of dimethylamine into commercial boron trifluoride etherate dissolved in three times its volume of benzene. The light brown lower layer was separated, and warmed in a vacuum to remove small amounts of benzene and ether.

The adduct (77.5 g., 0.69 mole) was heated in a flask equipped with an air-cooled reflux condenser. Refluxing commenced when the liquid reached 240°, but the temperature rose, rapidly at first, then more gradually, to 295° at the end of an hour. Meanwhile, 4.8 g. of large white needles collected in the reflux condenser, but no gases were evolved.

The contents of the flask were distilled through a fractionating column. There was 4.7 g. of distillate below 200°, and 16.2 g. in the range 200–245°, mostly at 238°. The residue in the flask was boiling at 362° at the end of the distillation. (Dimethylammonium fluoborate boils at about 355°.) This residue weighed 41.5 g. and the hold-up in the column and head, 10 g. All of the pyrolysis products were solids at room temperature.

The tan-colored residue was dissolved in water, the solution heated to boiling, and decolorized with a little charcoal. When cooled to 0°, it deposited 3.5 g. (0.022 mole) of crude tetramethylammonium fluoborate. The mother liquors, when treated with an excess of potassium chloride, gave 29 g. (0.23 mole) of potassium fluoborate.

The distillate and the needles from the reflux condenser were mixed with chlorobenzene and fractionated. The por-

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

[3] C. A. Brown and R. C. Osthoff, Abstracts of Papers Presented at the 118th Meeting of the American Chemical Society, Chicago, Ill., 1950, p. 100.

tion boiling below 132° was collected, thus separating the dimethylaminoboron difluoride dimer as its azeotrope, b.p. 116°. The distillate and the residue were each mixed with hexane, cooled to 0°, and the crystals filtered off, giving, respectively, 10.0 g. (0.054 mole) of dimethylaminoboron difluoride dimer, subl. 135°, and 13.0 g. (0.10 mole) of crude trimethylamine–boron trifluoride, m.p. 125–135°.

Tetramethylammonium Fluoborate.—Traces of impurities were volatilized from the crude product by heating to 250° at 5 mm. The purified fluoborate melted without decomposition at 415° and did not depress the melting point of an authentic specimen. It could be distilled at 15 mm. a little above its melting point, but decomposed with charring when heated at atmospheric pressure.

Trimethylamine–boron Trifluoride.—The crude product was purified with 90% recovery by three vacuum sublimations at about 100° and 5 mm. The purified sublimate was a white crystalline solid, m.p. 140–146°; b.p. 238°; apparent molecular weight, 213 in an 0.0054 mole-fraction solution in benzene (cryoscopic). Reported constants for trimethylamine–boron trifluoride are m.p. 138°,[4] 139–147°[5]; b.p. 233° (extrapolated[5]); apparent molecular weight 228 in an 0.0054 mole fraction solution in benzene.[4]

Anal. Calcd. for $C_3H_9NBF_3$: N, 11.0. Found: N, 11.3.

Dimethylaminoboron Difluoride Dimer.—The crude product was resublimed and recrystallized from benzene to give colorless crystals having a pleasant camphor-like odor; subl. 135°, m.p. (sealed tube) 167–169° (sl. dec.). The compound was insoluble in hexane and cold water, slightly soluble in cold aromatic solvents, soluble in hot aromatic solvents, and rapidly hydrolyzed by hot water. It formed low boiling azeotropes with chlorobenzene, *m*-xylene, and probably also with benzene.

Mass spectrometric study showed no peaks corresponding to the dimeric formula. The observed parent peaks at masses 91, 92 and 93 suggested the presence of monomeric dimethylaminoboron difluoride, and the interpretation that dissociation of the dimer was complete in the high vacuum.

The compound was unstable upon standing in dry air. It rapidly acquired an unpleasant, pungent odor, the crystals became sticky, and a low melting solid of lesser volatility was formed. Because of this instability, it is doubtful whether any of the analyses were based upon particularly pure specimens of the compound.

Anal. Calcd. for $C_4H_{12}B_2N_2F_4$: C, 25.9; H, 6.5; N, 15.1; mol. wt., 186. Found: C, 24.8; H, 6.5; N, 15.0; mol. wt., 173 (Victor Meyer method at 155°, 747 mm.).

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SCHENECTADY, N. Y. RECEIVED JULY 13, 1951

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(4) J. R. Bright and W. C. Fernelius, THIS JOURNAL, **65**, 735 (1943).

(5) A. B. Burg and Sr. A. A. Green, *ibid.*, **65**, 1838 (1943).

[CONTRIBUTION FROM THE PHYSICS DEPARTMENT, THE UNIVERSITY OF CHICAGO]

A Study of Molecular Complexes Formed by Aniline and Aromatic Nitrohydrocarbons[1,2]

BY J. LANDAUER AND HARDEN MCCONNELL[3]

The equilibrium constants and absorption spectra of the 1:1 complexes formed by aniline and *m*-dinitrobenzene, *p*-dinitrobenzene and *s*-trinitrobenzene have been determined in chloroform solution. Evidence for the existence of 1:2 complexes has also been obtained. It is proposed that an acid-base interaction (in the Lewis sense) is responsible for the formation and coloration of these complexes. Geometrical structures for the complexes are discussed.

I. Introduction

Many investigators have attributed the marked visible coloration exhibited by solutions containing aromatic amines and nitrohydrocarbons to the formation of highly colored molecular complexes. The existence of such complexes in the solid state is well known[4–7] and, in certain cases, their presence in solution has been established by spectroscopic methods.[8]

In spite of the extensive literature on this subject little quantitative information has appeared regarding the absorption spectra of the aromatic amine–polynitrohydrocarbon complexes. Part III of the present communication gives the results of a spectrophotometric determination of the equilibrium constants and absorption spectra of the 1:1 complexes present in chloroform solutions containing aniline and *m*-dinitrobenzene, *p*-dinitrobenzene and *s*-trinitrobenzene. Evidence for the existence of 1:2 complexes in these solutions is also presented.

In contrast to the earlier theories,[4,9] it is now generally recognized that the spectra and stabilities of complexes of the aniline–nitrohydrocarbon type cannot be adequately accounted for in terms of intermolecular interactions involving simple dispersion, polarization, multipole, hydrogen bond[10,11] or strong chemical bond forces.[8,11]

In Part IV it is proposed that an acid–base interaction is responsible for the formation and visible coloration of the aniline–polynitrobenzene complexes. Probable geometrical structures for these complexes are discussed in terms of the theory of acid–base interactions formulated by Mulliken.[12,13]

II. Experimental

Absorption spectra were determined with a model DU Beckman spectrophotometer. Optical densities were reproducible to 2%. Light paths of approximately 1.0, 0.1, 0.03 and 0.01 cm. were employed using 1.0-cm. quartz cells and calibrated quartz spacers. The reference cell always contained pure chloroform.

In several preliminary experiments, solutions containing

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(1) This work was assisted in part by the Office of Naval Research under Task, Order IX of Contract N6ori with the University of Chicago.

(2) Presented at the Symposium on Molecular Structure and Spectroscopy at The Ohio State University, June 11, 1951.

(3) National Research Council Postdoctoral Fellow, 1950–1951.

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