[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Boron–Nitrogen Compounds. I. Syntheses of B-Aminoborazines[1]

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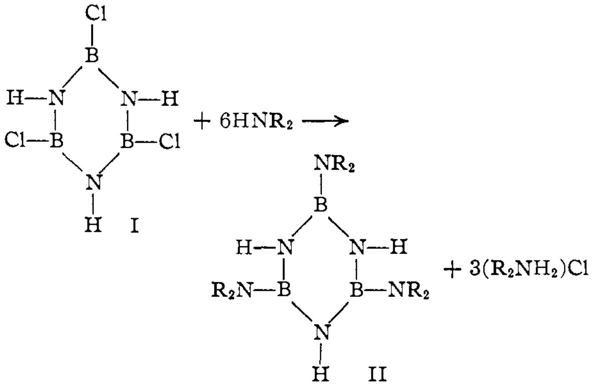
Two basic syntheses of B-aminoborazines, $[-NR-B(NR_2)-]_3$, are reported: the reaction of B-trichloroborazines with amines produces the same type of compounds as the reactions of aminodichloroboranes with anhydrous ammonia or amines. Both of these basic reactions permit several modifications.

B-Aminoborazines of the general formulation $[-NR-B(NR_2)-]_3$ with R = hydrogen, alkyl or aryl have not been thoroughly investigated. The only description of such materials resides in a patent by Gould.[2] According to Gould, the formation of B-aminoborazines occurs through the reaction of B-trichloroborazines with an excess of amines.



This reaction also can be effected by treating stoichiometric amounts of I with amines at elevated temperatures

$$\text{I} + 3HNR_2 \longrightarrow \text{II} + 3HCl$$

The hydrogen chloride does not react with the amine but is expelled as a gas. Even the amine hydrochloride may be used

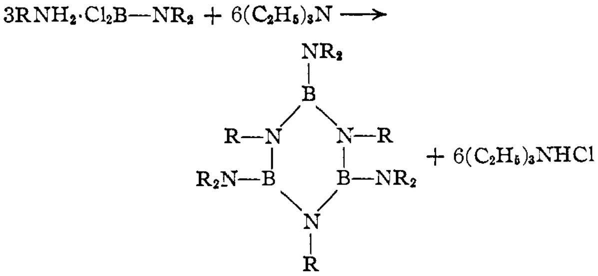
$$\text{I} + 3(R_2NH_2)Cl \longrightarrow \text{II} + 6HCl$$

In this case, however, satisfactory yields have not been obtained.

However, a preformed borazine ring structure *per se* is not required to ensure the formation of B-aminoborazines: the reaction of aminodichloroboranes, R_2N-BCl_2, with an excess of anhydrous ammonia or primary amines likewise produced these compounds

$$3R_2N—BCl_2 + 9NH_3 \longrightarrow \text{II} + 6NH_4Cl$$

When a primary amine was used in this reaction, a two-step synthesis became possible. In the first step, stoichiometric amounts of aminodichloroboranes and primary amines reacted, affording an addition product, $RNH_2{\cdot}Cl_2B-NR_2$. Hydrogen chloride then was removed using the theoretical amount of a tertiary amine, thus providing the expected borazine derivative

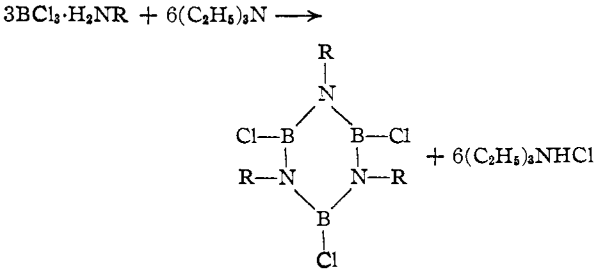


This two-step reaction is particularly advantageous when only small amounts of an aminodichloroborane are available, as the yields of the resulting B-aminoborazines are very good. Its application is, of course, restricted to the preparation of those B-aminoborazines where the nitrogen of the borazine ring structure is substituted by an organic group.

At present these B-aminoborazines have been prepared and described

B-tris-(monomethylamino)-borazine[2]	m.p. 85–105°
B-tris-(dimethylamino)-borazine	m.p. 112°
B-tris-(diethylamino)-borazine	b.p. 149° (7 mm.)
B-tris-(diphenylamino)-borazine	m.p. above 300°
B-tris-(diethylamino)-N-triethylborazine	b.p. 84°
B-tris-(piperidino)-N-triethylborazine	b.p. 95° (3 mm.)

The aminodichloroboranes were synthesized according to the method described by Brown[3] for the preparation of dichloro-(dimethylamino)-borane: the reaction of secondary amines with boron trichloride afforded the addition compounds $R_2NH{\cdot}BCl_3$, which lost hydrogen chloride on treatment with triethylamine. However, the reaction of triethylamine with the addition product of boron trichloride and a primary amine—instead of a secondary one—provided a synthesis for B-trichloro-N-trisubstituted borazines, as illustrated by the equation



A description of this reaction was published recently by Turner and Warne.[4]

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[1] Supported by the Office of Ordnance Research, U. S. Army.

[2] J. R. Gould, U. S. Patent 2,754,177 (July 10, 1956). Gould describes the preparation and properties of B-tris-(dimethylamino)-borazine, B-tris-(diethylamino)-borazine, B-tris-(monomethylamino)-borazine and the B-aminoborazine itself. No properties are given for the latter and its free existence seems to be in doubt.

[3] J. F. Brown, Jr., THIS JOURNAL, **74**, 1219 (1952).

[4] H. S. Turner and R. J. Warne, *Chemistry and Industry*, **18**, 526 (1958).

Experimental

Reaction of B-Trichloroborazine with an Excess of an Amine. 1. B-Trichloroborazine.—B-Trichloroborazine was prepared using minor modifications of the second method of Brown and Laubengayer.[5]

The presence of mercury appears to produce a catalytic effect on the formation of B-trichloroborazine through the reaction of boron trichloride and ammonium chloride; this behavior has been reported for other metals (Fe, Co, Ni) by Emeleus and Videla.[6] Further, in order to prepare larger amounts of B-trichloroborazine, it was found desirable to employ more boron trichloride in the reaction than the amounts recommended by Brown and Laubengayer. Table I indicates that, under the conditions used, the addition of boron trichloride at the rate of 40 cc. per hour is preferred. In the absence of mercury a larger yield of unidentified non-volatile material was obtained.

TABLE I

PREPARATION OF B-TRICHLOROBORAZINE

Reaction time 6 hours, 150 g. ammonium chloride, 1600 cc. chlorobenzene.

Boron trichloride, cc./hr.	20	30	40	50	60	70
B-Trichloroborazine g. (3-4 cc. mercury added)	31	38	74	67	68	59
B-Trichloroborazine, g. (no mercury added)	31	37	58	59	51	47

2. **B-Tris-(dimethylamino)-borazine.**[2]—A solution of 19.4 g. (0.43 mole) of dimethylamine in 200 cc. of dry benzene was placed in a 1-liter, three-necked flask equipped with a mercury-sealed mechanical stirrer, a dropping funnel and a −78° condenser, protected from moisture by a tube containing potassium hydroxide. Stirring was started and a solution of 9.9 g. (0.054 mole) of B-trichloroborazine in 200 cc. of dry benzene was added from the dropping funnel over 15 minutes. Spontaneous evolution of heat and a copious formation of a precipitate were observed. After being stirred for 1.5 hr. at ambient temperature, the reaction mixture was filtered under anhydrous conditions; the precipitate then was extracted with dry benzene. The original filtrate and the extracts were combined and the benzene removed under vacuum, affording 8.2 g. of halogen-free B-tris-(dimethylamino)-borazine. Purification was readily achieved by resublimation at 95°/(2 mm.). The compound appeared as colorless needles, m.p. 112–113°. *Anal.* Calcd. for $B_3H_6C_6H_{21}$: B, 15.5; N, 40.0; C, 34.3; H, 10.1; mol. wt., 209.7. Found: B, 15.8; N, 40.2; C, 33.9; H, 9.8; mol. wt. (cryoscopic in benzene), 211.

Reaction of B-Trichloroborazine with a Stoichiometric Amount of an Amine. B-Tris-(diphenylamino)-borazine.—A solution of 10.14 g. (0.06 mole) of diphenylamine in 400 cc. of dry benzene was added very slowly dropwise over a period of 13–16 hr. to a refluxing solution of 3.68 g. (0.02 mole) of B-trichloroborazine in 300 cc. of dry benzene. Refluxing was continued for another 4 hr. and stopped when the rate of evolution of hydrogen chloride had declined. More than 90% of the calculated hydrogen chloride was collected at this time in a receiver. The reaction mixture was filtered while hot and the nearly colorless crystals were washed several times with hot benzene and hot ether. They were dried *in vacuo* over phosphorus pentoxide and paraffin for 24 hr. The yield of product amounted to 11.8 g. (91%). The compound did not melt below 300°. It is insoluble in water and the usual organic solvents. *Anal.*[7] Calcd. for $B_3N_6C_{36}H_{33}$: B, 5.57; N, 14.43; C, 74.30; H, 5.71. Found: B, 5.22; N, 14.39; C, 68.51; H, 5.80. As we were unable to obtain a molecular weight of the B-tris-(diphenylamino)-borazine because of its insolubility, the infrared spectrum and the analysis are the only proof for its structure. Though the experimental C-value is much too low, calculation by difference provides a value of 74.59% C; (theoretical, 74.30). Furthermore, the infrared spectrum is in accordance with those of other B-aminoborazines (for instance, NH-stretching near 2.9 μ, B–N ring vibration at 6.7 μ).

Reaction of B-Trichloroborazine with an Amine Hydrochloride. B-Tris-(diethylamino)-borazine.—A mixture of 3.7 g. (0.02 mole) of B-trichloroborazine and 5 g. (0.046 mole) of diethylamine hydrochloride (dried over potassium hydroxide) was covered with 100 cc. of dry benzene (distilled over sodium) and 100 cc. of dry, freshly distilled tetrahydrofurane and refluxed for 19 hr.; slow evolution of hydrogen chloride occurred. After cooling, the reaction mixture was filtered. The solvent was removed by distillation, leaving 1.2 g. (22%) of a brown liquid, which was distilled *in vacuo*. The b.p. of the slightly yellow product was 164° (10 mm.) or 149–150° (7 mm.). Redistillation at 120° (2 mm.) did not afford a completely colorless material. *Anal.* Calcd. for $B_3N_6C_{12}H_{18}$: B, 11.05; N, 28.6; C, 49.0; H, 11.34; mol. wt., 293.8. Found: B, 11.2; N, 28.5; C, 49.0; H, 11.33; mol. wt. (cryoscopic in benzene), 295.0.

Reaction of an Aminodichloroborane with an Excess of Ammonia. 1. Dichloro-(diethylamino)-borane.—One hundred cc. of dry benzene was placed in a 2-liter, three-necked flask fitted with a Hershberg stirrer, a dropping funnel and a reflux-condenser and cooled to 0°; 61.5 cc. (0.75 mole) of boron trichloride was dissolved in the benzene with stirring. The flask was cooled with Dry Ice–methyl alcohol and a solution of 76.5 cc. (0.74 mole) of freshly distilled diethylamine in 300 cc. of dry benzene was added dropwise over an hour resulting in the formation of a white precipitate of $BCl_3{\cdot}HN(C_2H_5)_2$. The cooling bath was removed and the reaction mixture warmed to room temperature while being continually stirred.[8] A mixture of 105 cc. of dry freshly distilled triethylamine (0.76 mole) and 200 cc. of dry benzene was added to the suspension of the addition compound with continued stirring. The solid material dissolved and the contents of the flask darkened somewhat. The reaction mixture was heated to reflux and, after some minutes, white crystals precipitated. These proved to be crystals of triethylamine hydrochloride. The reaction mixture was refluxed for 3 hr. and then allowed to stand overnight. It then was filtered and the solvent removed from the filtrate by distillation. The residual dark-brown strongly fuming liquid was distilled through a column affording 93.5 g. (81%) of a colorless liquid b.p., 148° which represents an improvement in yield over and above that noted by Wiberg and Brown.[9] The dichloro-(diethylamino)-borane was subjected to an infrared determination in the liquid phase. A peak at 6.6 μ indicated the characteristic aminoborane B–N double bond. The lack of OH bands in the 3 μ region shows inappreciable hydrolysis. At 3.4 μ, CH stretching and bending appears. The band at 6.85 μ is due to a C-methyl deformation vibration while the bands at 8.73 and 11.9 μ indicate the presence of N–C stretching frequencies. The absorption in the 11.25 μ region apparently reflects the BCl_2-grouping.

2. **B-Tris-(diethylamino)-borazine.**—A 1-liter, three-necked flask was equipped with a Hershberg stirrer, an inlet tube, a reflux condenser and a dropping funnel. Five hundred cc. of dry benzene was placed in the reaction flask and saturated with anhydrous ammonia. The reaction flask was cooled in a Dry Ice–methyl alcohol bath and the addition of ammonia was continued with stirring. A mixture of 15.4 g. (0.10 mole) of dichloro-(diethylamino)-borane and 100 cc. of dry benzene was added dropwise. After the addition was complete, the cooling bath was removed. When the reaction mixture reached room temperature, the addition of ammonia was stopped and the contents of the flask were refluxed for 2 hr. The reaction mixture was allowed to stand overnight and filtered; the solvent was removed by distillation. Vacuum distillation of the residue provided 5.1 g.

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(5) C. A. Brown and A. W. Laubengayer, THIS JOURNAL, **77**, 3699 (1955).

(6) H. J. Emeleus and G. J. Videla, *Proc. Chem. Soc.*, 288 (1957).

(7) Very serious difficulties with the analysis of organo-boron compounds and particularly borazines have been noted previously in the literature. Compare: A. Stock and E. Pohland, *Ber.*, **59**, 2215 (1926); S. D. Rosenberg and E. G. Rochow, WADC Technical Report 54-102, March, 1954, p. 6. We noticed especially that boron–nitrogen compounds containing aryl groups gave unsatisfactory analyses. Thus we had difficulty in obtaining accurate carbon analyses through commercial laboratories for the well-known B-triphenylborazine and for arylated aminoboranes.

(8) It is not necessary to isolate the addition compound in order to prepare the dichloro-(diethylamino)-borane. However, if a separation is desired, the precipitate can be filtered off in a stream of dry nitrogen, washed with a little benzene and dried over phosphorus pentoxide and paraffin *in vacuo*. Highly hygroscopic crystals melting at 118–128° (not sharp) are obtained in a nearly theoretical yield.

(9) E. Wiberg, *FIAT Rev. German Sci.*, Vol. XXIII, Part I, 217; C. A. Brown and R. Osthoff, THIS JOURNAL, **74**, 2378 (1952).

(52%) of slightly yellow B-tris-(diethylamino)-borazine, b.p. 149–150° (7 mm.), identical with the material obtained above.

Reaction of an Aminodichloroborane with an Excess of Amine. B-Tris-(diethylamino)-N-triethylborazine.—To a cooled solution of 27 g. (0.60 mole) of monoethylamine in 500 cc. of dry benzene (or any other inert organic solvent) a mixture of 15.4 g. (0.10 mole) of dichloro-(diethylamino)-borane and 200 cc. of dry benzene was added dropwise accompanied by stirring. The reaction mixture then was warmed slowly to room temperature and finally refluxed for 2 hr. It was then allowed to stand overnight, filtered and the solvent removed. The B-tris-(diethylamino)-N-triethylborazine remained as a liquid, which distilled at 84°. The distillation was accompanied by slight decomposition and afforded 4.6 g. (58%) of the pure borazine compound. *Anal.* Calcd. for $B_3N_6C_{18}H_{45}$: B, 8.57; N, 22.21; C, 57.20; H, 12.00; mol. wt., 378.05. Found: B, 8.52; N, 22.10; C, 57.67; H, 11.07; mol. wt. (cryoscopic in benzene), 374.

The B-tris-(diethylamino)-N-triethylborazine reacts vigorously with alcohols, dilute acids, etc.; it is very hygroscopic. Hydrolysis first produces a splitting of the boron–amino bond, but the borazine ring structure also is attacked very rapidly. It is advisable to avoid contact of the skin with the compound because of its vesicant action.

Reaction of a Tertiary Amine with the Addition Compound of an Aminodichloroborane with a Primary Amine. B-Tris-(diethylamino)-N-triethylborazine.—One hundred fifty cc. of dry ether and 15.4 g. (0.10 mole) of dichloro-(diethylamino)-borane were cooled in an ice-bath and a solution of 4.5 g. (0.10 mole) of monoethylamine in 100 cc. of dry ether was added dropwise with stirring resulting in the formation of a white precipitate. The cooling bath was removed and a mixture of 20.2 g. (0.20 mole) of freshly distilled triethylamine and 50 cc. of dry ether was added. The reaction mixture was stirred for 4 hr. and filtered. The solvent was distilled off, leaving a yellow-brown liquid, which was purified through distillation; 10.8 g. (92%) of a colorless liquid, b.p. 84°, identical with the earlier described B-tris-(diethylamino)-N-triethylborazine, was obtained.

B-Tris-(piperidino)-N-triethylborazine.—The same molar ratios and the same technique as cited above were employed in the reaction between dichloro-(piperidino)-borane[10] and monoethylamine in the presence of triethylamine. The resulting product was obtained in 80.5% yield as a liquid boiling at 94–96° (3 mm.). Calcd. for $B_3N_6C_{21}H_{45}$: B, 7.93; N, 20.28; C, 60.82; H, 10.95; mol. wt., 414.1. Found: B, 7.47; N, 20.26; C, 61.09; H, 11.00; mol. wt. (cryoscopic in benzene), 412.

Reaction of Triethylamine with the Addition Product of Boron Trichloride with a Primary Amine. B-Trichloro-N-trimethylborazine.—To a cooled solution of 58.6 g. (0.50 mole) of boron trichloride in 300 cc. of dry benzene, a cold solution of 15.53 g. (0.34 mole) of monomethylamine in 150 cc. of benzene was mixed with stirring. A mixture of 101.2 g. (1.0 mole) of dry freshly distilled triethylamine and 100 cc. of dry benzene was then added dropwise. The cooling bath was removed and the reaction mixture stirred for 3 hr. at ambient temperature. It then was refluxed for 1.5 hr. and allowed to stand overnight. After filtration, the benzene was removed from the filtrate by distillation, leaving nearly colorless crystals, which were sublimed *in vacuo*. Sublimation afforded 23.7 g. (63%) of white crystals, m.p. 155°, of B-trichloro-N-trimethylborazine in agreement with Turner[4] and others.

Discussion

Though the B-aminoborazines are undergoing further investigation, some additional aspects deserve mention.

If the amino group of the B-aminoborazine is not substituted, the resultant compounds are very unstable. Thus B-aminoborazine itself, the parent substance of this class, could not be isolated. The reaction of B-trichloroborazine with anhydrous ammonia in either liquid ammonia or an inert organic solvent afforded a white precipitate which appeared to be a mixture of B-triaminoborazine and ammonium chloride. All attempts at separation, however, by the method of Klement[11] or by washing out the ammonium chloride with liquid ammonia in a closed system[12] were unsuccessful. The reaction mixture of B-triaminoborazine with ammonium chloride continued to evolve ammonia even *in vacuo* and under anhydrous conditions. After a short time the product, which initially dissolved rapidly in water, required a longer time to dissolve.

Table II

Nitrogen Determination of the Reaction Mixture of B-Trichloroborazine with Anhydrous Ammonia (Calcd. 1 Mole B-Aminoborazine + 3 Moles Ammonium Chloride)

	Nitrogen, %
Calcd. for the mixture	44.1
Found 1 hr. after preparation	43.2
2 hr.	41.7
4 hr.	40.4
7 hr.	37.1
9 hr.	36.8

At the beginning of this investigation, it was believed that B-aminoborazines substituted on the ring nitrogens would show an increased stability toward hydrolysis as compared to those B-aminoborazines where the ring nitrogens are not substituted. The behavior of the B-triamino-N-triphenylborazine indicates that such is not necessarily the case. It was possible to prepare a small amount of the latter crude compound, but it gradually decomposed with the evolution of ammonia. Thus, on the basis of existing evidence, substitution of the nitrogen atoms of the borazine ring does not appear to have any pronounced influence on the stability of the B-amino bond of the side chain.

B-Aminoborazines, alkylated on the amino group, are soluble in anhydrous inert organic solvents without decomposition. They are more stable but still quite sensitive to moisture. As a rule, hydrolysis appears to start on the B–N side chain bond, but hydrolysis of the ring structure occurs almost immediately thereafter. B-Aminoborazines arylated on the amino group seem to be more stable, but apparently are rather insoluble. The increased stability toward hydrolysis might be attributed to a "steric protection" by the large phenyl group. Such behavior is in accordance with that of boroxines: the latter also show an increasing stability with the size of the substituent.[13]

The B-aminoborazines were subjected to an infrared determination. All the spectra show a very strong band at 6.7 μ and the most intensive infrared band of the borazine itself is reported for that same region.[14] There seems no doubt but that this is due to a vibration of the six-membered B-N ring system. According to investigations with phenylated borazines,[15] the B–N ring fre-

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(10) O. C. Musgrave, *J. Chem. Soc.*, 4305 (1956).

(11) R. Klement and O. Koch, *Chem. Ber.*, **87**, 333 (1954).

(12) M. Goehring and K. Niedenzu, *ibid.*, **89**, 1768 (1956).

(13) E. Wiberg, *Experientia Suppl.*, **VII**, 183 (1957).

(14) B. L. Crawford and J. T. Edsall, *J. Chem. Physics*, **7**, 223 (1939); W. C. Price, *et al.*, *Disc. Faraday Soc.*, **9**, 131 (1950).

(15) H. J. Becher and S. Frick, *Z. anorg. allgem. Chem.*, **295**, 83 (1958).

quency has a range for its position from 6.8 μ (N-triphenylborazine) to 7.3 μ (B-trichloro-N-triphenylborazine) and is always the strongest band. However, the B-aminoborazines prepared always showed the strongest band at 6.7 μ. That there is practically no range for the position of this absorption may be explained by the basic structure of the B-aminoborazines, *i.e.*, regardless of other substituents, the boron atoms are always bonded to three nitrogen atoms. Thus the influence of the substituent seems to be greatly reduced and the B–N ring frequency is restricted to a very small range.

It is remarkable that all the B-aminoborazines showed a band in the 7.4 μ region. This might be attributed to the absorption of the bond between the boron atoms and the nitrogen of the side chains.

An infrared band at 2.92 μ is shown by all the B-aminoborazines where the ring nitrogen is not substituted by an organic group. It is typical for a relatively unassociated NH bond, as it is appreciably greater than the value of *ca*. 3 μ for amines. The nuclear magnetic resonance spectrum of the B-tris-(diethylamino)-borazine shows the typical ethyl group structure, CH_2 at 172 cycles and CH_3 at 245 cycles when measured against benzene; diethylamine was run for comparison. The NH of diethylamine is sharp and its position is temperature dependent; sharp because exchange is fast and temperature dependent because of varying degrees of association with temperature. It is hard to find the N–H peak in the n.m.r. spectrum of the B-tris-(diethylamino)-borazine, but it is probably the broad shallow band just to the right of the spikes due to methyl resonance. This suggests that the rate of exchange is relatively slow. The sharpness and high frequency of the infrared N–H band indicated very little association; it is probably too sterically hindered. The long residence time of a given proton on nitrogen allows quadrupole relaxation and thus gives a broad band.

The B-aminoborazines are representatives of a new class of compounds where one boron atom is bonded to three different nitrogen atoms. They may be considered as the first polymerization products of boron triamides, $B(NR_2)_3$. The existence and the preparation of boron triamides has been described elsewhere.[16]

Acknowledgment.—The authors gratefully acknowledge the determination of the infrared and nuclear magnetic resonance spectra by Dr. Keith S. McCallum, Redstone Arsenal Research Division, Rohm and Haas Company, Huntsville, Alabama.

[16] E. Wiberg and K. Schuster, *Z. anorg. allgem. Chem.*, **213**, 77 (1933); A. Dornow and K. H. Gehrt, *ibid.*, **294**, 81 (1958).

DURHAM, NO. CAROLINA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Hydrolytic Polymerization in Boiled Chromic Solutions[1]

BY JOHN A. LASWICK AND ROBERT A. PLANE

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Cationic species present in boiled solutions of chromic perchlorate have been resolved using ion-exchange chromatography. In addition to $Cr(H_2O)_6^{+3}$, which is retained least strongly by Dowex-50 cation-exchange resin, two new species can be isolated. The first is identical in visible absorption spectrum and ion-exchange behavior to the product obtained by oxidation of chromous solutions by O_2 and Tl^{+3} and believed to be dinuclear. The second is apparently more highly polymerized. A small residual fraction of the original chromium seems to be irreversibly sorbed to the resin. Attempts to further characterize the dissolved fractions by reaction with molybdate fail, apparently due to fragmentation of chromic species and depolymerization of molybdate species. The rates of formation of the separable olated ions in boiling 0.05 to 0.10 *M* chromic solutions are followed. The dinuclear species reaches a maximum concentration (11% of the total Cr) within minutes; the next fraction attains a steady value of 12% only after some hours. Approximately 74% remains in the unreacted form. However, very prolonged refluxing causes deposition of nearly all of the chromium as a crystalline solid giving an X-ray pattern identical with that of $HCrO_2$. Addition of base, prior to refluxing, leads to formation of a colloid, which was not detected in any experiment without added base.

The presence of polynuclear complexes in solutions of many relatively highly charged ions has been demonstrated.[2] The chromium(III) system has been studied more intensively than perhaps any other,[3] because of the technical importance of basic chromium solutions in tanning leather. This system is a particularly interesting one for investigation since the changes which chromic species undergo are generally quite slow, thus allowing a variety of techniques for study which are not applicable to labile systems. Indeed, this slow response of chromic species to a change of environment also makes difficult the interpretation of many of the experiments conducted in the past. Nearly all such investigations involved the addition of base, either gradually, or in large increments. Kohlschütter and co-workers have demonstrated that the subsequent behavior of such systems is dependent upon the method of addition of the base,[4] and thus cannot represent an equilibrium situation.

A technique for studying these "olated" chromic solutions which does not involve addition of base was devised by Hall and Eyring.[5] This method, based on conductometric titration of the chromic

[1] From the thesis submitted by John A. Laswick to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Presented in part at the 133rd National Meeting of the American Chemical Society, San Francisco, California, April, 1958.

[2] See, *e.g.*, S. Hietanen and L. G. Sillen, *Acta Chem. Scand.*, **8**, 1607 (1954).

[3] E. Stiasny, "Gerbereichemie," Verlag Theodor Steinkopff, Dresden, 1933, pp. 344–399.

[4] H. W. Kohlschütter and O. Melchior, *Angew. Chem.*, **49**, 865 (1936).

[5] H. T. Hall and H. Eyring, THIS JOURNAL, **72**, 782 (1950).