agreement with the generally observed dependence of exchange equilibrium constant upon ionic radius.

The study of the calcium–nickel exchange was carried out with solutions containing calcium and nickel chlorides at an approximately constant ionic strength of unity, *i.e.*, a molarity of approximately 0.33. The exchange constants calculated from the results of this study are plotted in Fig. 12. The K_a values were calculated with no allowance for electrolyte adsorption by the resin. The appropriate expressions are

$$K = \frac{c_{\mathrm{Ni}^{++}} N_{\mathrm{CaRes2}}}{c_{\mathrm{Ca}^{++}} N_{\mathrm{NiRes2}}}, \text{ and } K_a = K_c \cdot \left(\frac{\gamma_{\pm \mathrm{NiCl2}}}{\gamma_{\pm \mathrm{CaCl2}}}\right)^3 \cdot \frac{f_{\mathrm{CaRes2}}}{f_{\mathrm{NiRes2}}}$$

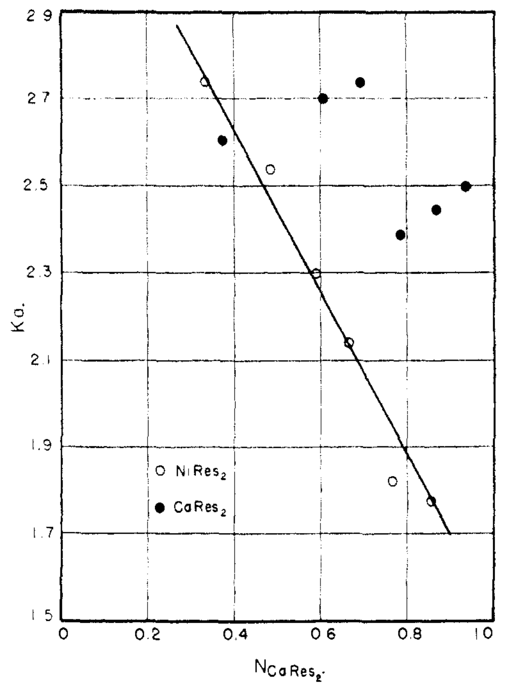

Fig. 12.—Calcium–nickel exchange.

Because of the difficulties inherent in the analytical methods for the two ions concerned, arising principally from coprecipitation, the precision of the results, particularly in the experiments with calcium resin as initial exchanger, is relatively low. Nevertheless, the rather large apparent hysteretic effect, of the order of that observed in the nickel–hydrogen exchange, seems to indicate that the magnitude of hysteresis depends more on difference in bond type than on difference in valence, since the two ions here involved have the same valence but differ in bonding character. As is to be expected, the range of K_a values is intermediate between those for the nickel–hydrogen and the calcium–hydrogen exchanges. A semi-quantitative correlation may again be observed in the triangular relationship among the three systems; the K_a values corresponding to equimolar equilibrium resin mixtures were chosen for the reasons given earlier. The results are

$$K_1 = \frac{(\mathrm{NiRes_2})(\mathrm{H^+})^2}{(\mathrm{HRes})^2(\mathrm{Ni^{++}})} = 13.4$$

$$K_2 = \frac{(\mathrm{CaRes_2})(\mathrm{Ni^{++}})}{(\mathrm{NiRes_2})(\mathrm{Ca^{++}})} = 2.58$$

$$K_3 = \frac{(\mathrm{CaRes_2})(\mathrm{H^+})^2}{(\mathrm{HRes})^2(\mathrm{Ca^{++}})} = 42.4 \text{ (obsd.)}$$

$$K_1 \times K_2 = K_3 = 34.6 \text{ (calcd.)}$$

The agreement between observed and calculated K_a values, within 20% of the observed value, is not so good as in the thallous–ammonium–hydrogen system. In view, however, of the experimental difficulties encountered in analysis, this agreement may be regarded as further validation for the treatment of the exchange results by mass law methods.

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LAWRENCE, KANSAS RECEIVED SEPTEMBER 11, 1950

[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Condensation Products of Ethylene Chlorohydrin and Boron Trichloride[1]

BY DONALD RAY MARTIN AND LEONA SCHAFER MAKO*[1]

When one mole of anhydrous ethylene chlorohydrin is added dropwise with vigorous stirring to one mole of boron trichloride at −78°, boron (III) bis-(β-chloroethoxy)-chloride and tris-(β-chloroethyl)-borate are obtained in yields of 15 and 38 per cent., respectively. Boron (III) bis-(β-chloroethoxy)-chloride is a colorless liquid which forms a glass upon cooling. The liquid density, vapor pressure, heat of vaporization, boiling point, Trouton's constant and percentage composition of this compound were determined. A few chemical properties are reported. Tris-(β-chloroethyl)-borate was prepared by a new procedure.

Berzelius[2] observed that boron trichloride reacts with ethanol to yield a volatile product possessing an ether-like odor. Later Councler[3] observed that hydrogen chloride is evolved when boron trichloride reacts with allyl alcohol, benzyl alcohol or ethylene glycol. More recently, Wiberg and co-workers[4] synthesized the series of compounds $\mathrm{ROBCl_2}$, $\mathrm{(RO)_2BCl}$ and $\mathrm{(RO)_3B}$ (in which R is a methyl or an ethyl group) by allowing the alcohol to react with boron trichloride at −90 to −60°. Similarly, boron (III) bis-(isoamyloxy)-chloride has been prepared.[5]

This investigation was undertaken to observe if

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[1] Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society on September 6, 1950, at Chicago, Illinois.

[2] J. J. Berzelius, *Ann. Physik.*, **78**, 113–150 (1824).

[3] C. Councler, *Ber.*, **10**, 1655–1657 (1877); **11**, 1106–1109 (1878); *J. prakt. Chem.*, [2] **18**, 371–402 (1878).

[4] E. Wiberg and W. Ruschmann, *Ber.*, **70B**, 1393–1402 (1937); E. Wiberg and H. Smedsrud, *Z. anorg. Chem.*, **225**, 204–208 (1935); E. Wiberg and W. Sütterlin, *ibid.*, **202**, 1–21 (1931); **202**, 31–36 (1931).

[5] C. R. Kinney, H. T. Thompson and L. C. Cheney, THIS JOURNAL, **57**, 2396–2397 (1935).

substituted alcohols would react in an analogous manner.

Experimental

Preparation of Boron(III) (β-Chloroethoxy)-chlorides.—The reactor was a three-necked flask fitted with a glass stirrer with a mercury seal, a water-cooled condenser to which was attached a drying tube containing barium oxide, and a gas inlet tube. All connections were made with dry, standard taper joints inasmuch as Lubriseal and Silicone stopcock greases are attacked by the reaction products.

After the desired quantity of boron trichloride had been condensed into the reactor (cooled with a slush of Dry Ice and acetone), the gas inlet tube was replaced quickly by a dropping funnel.

Ethylene chlorohydrin (dried with anhydrous calcium sulfate and subsequently distilled) was added dropwise with constant stirring. Slow addition of ethylene chlorohydrin, vigorous stirring and a cooled reactor are very necessary to prevent decomposition of the products. The temperature of the reactor was not allowed to rise above −78° at any time during the course of the reaction. The conditions for typical syntheses were

BCl_3, g.	ClC_2H_4OH, g.	ClC_2H_4OH addn. time, minutes
75	51	75
180	115	135
375	240	240

During the reaction, hydrogen chloride was evolved in accordance with the reactions

$$2ClC_2H_4OH + BCl_3 \longrightarrow (ClC_2H_4O)_2BCl + 2HCl$$

$$3ClC_2H_4OH + BCl_3 \longrightarrow (ClC_2H_4O)_3B + 3HCl$$

Purification of Boron(III) (β-Chloroethoxy)-chlorides.—The reactivity and thermal instability of the reaction products made necessary the use of a distilling apparatus designed to operate at low pressures. The distillation was conducted in a column (20 × 500 mm.) packed with glass beads (6 mm. dia.). The column was heated by a nichrome tape and surrounded by an air jacket. The reflux ratio was controlled by use of capillary tubing in the usual manner. The temperature of the still head was indicated on a recording potentiometer connected to a copper–constantan thermocouple.

The reaction products were placed in the stillpot and cooled in liquid air. While cold, the stillpot was sealed quickly to the column. The apparatus was rinsed with dry air ten times and then maintained at reduced pressure. Then the stillpot was allowed to warm slowly. This operation was accompanied by the evolution of hydrogen chloride and boron trichloride. These gases were collected in a trap immersed in liquid air.

A fraction was obtained which boiled below room temperature and condensation in an ampoule on a fraction separator was incomplete. The portion not condensed in the ampoule was collected in the trap immersed in liquid air.

The stillpot and column were heated carefully and a second fraction consisting of boron(III) bis-(β-chloroethoxy)-chloride was obtained. Larger yields of a third fraction (tris-(β-chloroethyl)-borate) were obtained easily. The approximate yields (expressed in volume percentage) of the above fractions were: first fraction 8.8, $(ClC_2H_4O)_2BCl$ 15.2, $(ClC_2H_4O)_3B$ 38.0, BCl_3 4.3, HCl 3.8 and impure $(ClC_2H_4O)_2BCl$ in trap 29.9.

Properties of Reaction Products.—Boron(III) bis-(β-chloroethoxy)-chloride. Purified boron(III) bis-(β-chloroethoxy)-chloride is a colorless liquid which solidifies as a translucent glass. A melting point could not be obtained but the glass becomes sufficiently soft at about −75° to begin to flow in a tube inclined at an angle of about 60°.

By use of a pycnometer,[6] the liquid density was observed to be d^{20}_4 1.2770 and d^0_4 1.3367 g./ml. On the assumption that the density changes uniformly with temperature, these data fit the equation $d^t_4 = 1.3367 - 0.00199t$, in which t is degrees centigrade.

The vapor pressure data were obtained between 39 and 90° by the static procedure. The isoteniscope was observed with a cathetometer.[7] The data are best represented by the equation: $\log_{10} p(\text{mm.}) = 8.6263 - 2759/T$. By application of the Clausius–Clapeyron equation, the heat of vaporization is calculated to be 12.63 kcal./mole or 61.41 cal./g. Inasmuch as this compound decomposes at about 90° under its own vapor pressure, its calculated boiling point of 207.0° is of theoretical interest only. The value of Trouton's constant of 26.3 is abnormally high, because it is calculated from data obtained at pressures much less than one atmosphere.

Samples for analysis were obtained by redistillation of purified boron(III) bis-(β-chloroethoxy)-chloride into small vials sealed to a fraction separator. The weighed sample was hydrolyzed in a sodium hydroxide solution (1–2 N) and aliquot portions used for the analyses. Chlorine was determined by the Volhard procedure and boron by the mannitol method. The percentage composition was found to be 51.91 and 5.47 compared with the theoretical values of 51.90 and 5.27 for chlorine and boron, respectively.

Boron(III) bis-(β-chloroethoxy)-chloride reacts with Lubriseal stopcock grease, de Khotinsky cement, cork and rubber. It is soluble in ethanol and diethyl ether. It readily hydrolyzes in air, water and a solution of sodium hydroxide. In the last solution, a sweet smelling product is formed which burns with a blue flame.

Tris-(β-chloroethyl) borate. This compound has been prepared previously by refluxing ethylene chlorohydrin with boric oxide at about 200° for five hours, after which the water formed was removed with anhydrous cupric sulfate.[8]

Although the vapor pressure of this compound has not been reported, the boiling points observed in this study agree with values previously observed,[8] thus: reported 156° (25 mm.), 175° (50 mm.); observed 156° (25 mm.), 172° (48 mm.), 193–194° (100 mm.) (°C).

By the usual microanalytical procedures, the percentage composition of this compound was found to be 28.87 carbon, 4.92 hydrogen and 42.63 chlorine compared with the theoretical values of 28.92, 4.86 and 42.70, respectively.

Tris-(β-chloroethyl) borate is soluble in ethanol and diethyl ether and hydrolyzes in water and sodium hydroxide solution.

Discussion

Beta substitution of chlorine for hydrogen in the alcohol apparently reduces the thermal stability of this type of compound. Presumably the highly electronegative chlorine atom in the beta position causes the electron cloud to shift from the oxygen atom toward the chlorine atom, thus weakening the O–H bond. Similarly, the O–B bond would be expected to be weaker in $(ClC_2H_4O)_2BCl$ than in $(C_2H_5O)_2BCl$.

Under one atmosphere boron(III) ethoxydichloride decomposes at 50° whereas boron(III) β-chloroethoxydichloride was not isolated under reduced pressure. Boron(III) bis-(β-chloroethoxy)-chloride begins to decompose at about 90° under about 11 mm. pressure whereas boron(III) bis-(ethoxy)-chloride is stable at 100° under one atmosphere. Tris-(β-chloroethyl) borate, like its ethyl analog, is not decomposed below its normal boiling point.

As shown above, larger amounts of tris-(β-chloroethyl) borate than of boron(III) bis-(β-chloroethoxy)-chloride were obtained when the crude reaction products were distilled. On several occasions while distilling the reaction products, a white sublimate, presumably boron oxychloride,[4] was formed. It sublimed during distillation between the first fraction and the second fraction

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[6] H. S. Booth and C. V. Herrmann, THIS JOURNAL, **58**, 62–66 (1936).

[7] H. S. Booth, H. M. Elsey and P. E. Burchfield, *ibid.*, **57**, 2064–2069 (1935).

[8] W. J. Jones, L. H. Thomas, E. H. Pritchard and S. T. Bowden, *J. Chem. Soc.*, 824 (1946).

containing boron(III) bis-(β-chloroethoxy)-chloride. This white solid was quite soluble in boron(III) bis-(β-chloroethoxy)-chloride. Wiberg and Sütterlin[4] observed the formation of boron oxychloride when boron(III) ethoxydichloride decomposed as follows

$$C_2H_5OBCl_2 \longrightarrow C_2H_5Cl + BOCl$$
$$3BOCl \longrightarrow B_2O_3 + BCl_3$$

URBANA, ILLINOIS RECEIVED AUGUST 11, 1950

[CONTRIBUTION FROM RESEARCH LABORATORIES OF SCHOOL OF PHARMACY, UNIVERSITY OF WISCONSIN]

Behaviors of Several Compounds as Indicators in Lithium Aluminum Hydride Titration of Functional Groups[1]

BY T. HIGUCHI AND DONALD ANTON ZUCK[2]

An investigation has been made on behaviors of several possible indicators which may be useful in alkalimetric determination of very weak acids and other oxygenated compounds including alcohols, esters, phenols, ketones, aldehydes, etc., which react with lithium aluminum hydride. The possible mode of action of the indicators and experimental results for a number of compounds are presented. The data indicate that the method presented provides a simple and rapid means of determining the combined oxygen content of any of the above listed compounds or their mixtures. The possible value of these indicators in organic synthesis involving the use of lithium aluminum hydride is pointed out. Recently it was shown that various functional groups which react with lithium aluminum hydride including hydroxyl, carbonyl, ester, etc., can be determined volumetrically. The titration end-point in the method described was established potentiometrically, there being a large difference in the reduction potential of a system in presence and absence of unreacted lithium aluminum hydride.[3-6] In the present study an investigation has been carried out on the behaviors of possible chemical indicators for detection of this end-point.

Discussion of Theory

In the method mentioned above the sample is treated with a given volume of a solution of lithium aluminum hydride. The excess hydride is determined by back titration with a standardized solution of one of the lower primary alcohols in benzene. The end-point reaction then can be loosely pictured as neutralization of a strong base, lithium aluminum hydride, by a weak acid, alcohol.

$$\underset{\text{acid}}{ROH} + \underset{\text{base}}{{}^1/_4LiAlH_4} \longrightarrow \underset{\text{salt}}{{}^1/_4LiAl(OR)_4} + H_2$$

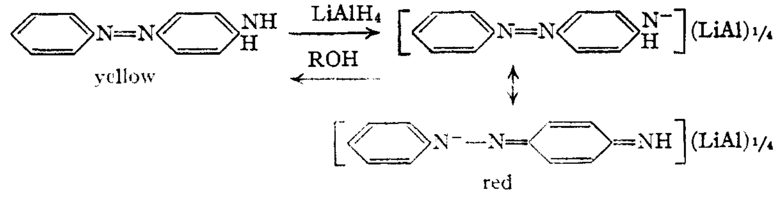
It is evident, however, that any suitable chemical indicator for such a system must necessarily be a very weak acid.

Since the pK_a values of alcohols which are used as the acid in the system are estimated to be of the order of 16–17, the hypothetical pK_I of suitable indicators must be 20 or greater. This requirement leaves for consideration, in main, substances having acidic hydrogen attached to either carbon or nitrogen atoms.

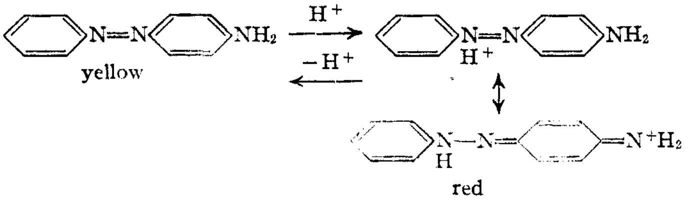
A number of hydrocarbons containing acidic hydrogen including triphenylmethane, tridiphenylmethane, phenylacetylene, fluorene and phenylfluorene were investigated as possible indicators. Although several in this group showed some promise, none proved entirely satisfactory.

In the present investigation greater attention was paid to the possible application of N–H acidic hydrogens to the indicator problem, mainly because of ready availability or ease of synthesis of promising compounds having this group. It is evident that the amino group in any suitable indicator must be conjugated to the chromophoric grouping. This fact plus the observation that azo linkages are not attacked by lithium aluminum hydride would indicate that compounds such as, for example, p-aminoazobenzene may be suitable indicators.

At least on paper, the latter compound can be expected to undergo the changes



The electronic configuration of the postulated resonating salt form is very similar to that generally accepted for the same compound in strongly acidic solutions. That is



This postulated similarity in the electronic configurations of p-aminoazobenzene under strongly basic and strongly acidic conditions is actually manifested by many common indicators. Phenolphthalein, for example, exists in red quinoid forms both in alkaline and strongly acid solutions.

p-Aminoazobenzene itself is not totally satisfactory as an indicator for investigational purposes as it possesses two replaceable hydrogens with

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[1] This paper is in part based on a Master's dissertation submitted to the Graduate School of the University of Wisconsin by Mr. D. A. Zuck in partial fulfillment of the requirements of the M. S. degree.

[2] Fellow of American Foundation for Pharmaceutical Education.

[3] T. Higuchi, C. Lintner and R. H. Schleif, *Science*, **111**, 63 (1950).

[4] C. Lintner, R. H. Schleif and T. Higuchi, *Anal. Chem.*, **22**, 534 (1950).

[5] C. Lintner, D. Zuck and T. Higuchi, *J. Am. Ph. A., Sc. Ed.*, **39**, 418 (1950).

[6] T. Higuchi, *Anal. Chem.*, **22**, 955 (1950).