The value of C is immaterial for the present purpose. Upon inserting this result in eq. (2) and rearranging, it follows that

$$pH + \log \frac{B}{b - B} - A\sqrt{\mu} = pK_w - pK_b - C\mu$$

The plot of the left-hand side of this expression, for various values of a and b, against μ should thus be a straight line, the intercept for zero ionic strength giving $pK_w - pK_b$. Since pK_w is known to be 14.00 at 25°, pK_b for the base can be evaluated.

The glass electrode was calibrated by means of solutions which give a good approximation to "thermodynamic" results.[3] The pK_b values obtained may thus be regarded as giving true dissociation constants. The reliability of the method was confirmed by its use to determine pK_1 for glycine; the result was 2.35 at 25°, in agreement with that obtained from cells without liquid junction.[4]

The dissociation constants found in the present work are recorded in Table I; the pK_b for ethylamine, for comparison purposes, is 3.25.

TABLE I

BASIC DISSOCIATION CONSTANTS IN AQUEOUS SOLUTION AT 25°

Base		pK_b
Monohydroxyamines		
I.	2-Amino-1-ethanol	4.55
II.	2-Amino-1-propanol	4.57
III.	2-Amino-1-butanol	4.48
IV.	2-Methyl-2-amino-1-propanol	4.28
Dihydroxyamines		
V.	2-Methyl-2-amino-1,3-propanediol	5.24
VI.	2-Ethyl-2-amino-1,3-propanediol	5.20
Trihydroxyamine		
VII.	Tris-(hydroxymethyl)-aminomethane	5.97

The results show that the introduction of an hydroxyl group into an aliphatic amine decreases the basic strength, as is to be expected from the electron attracting ($-I$) effect of this group. The first OH group increases pK_b by 1.3, the second by 1.0, and the third by about 0.75. From the pK_b values of the compounds I, II and III it is seen that the influence of the methyl group is small, although the anticipated $+I$ effect, resulting in an increase in strength of the base, is evident in IV, where both hydrogen atoms on the carbon attached to the nitrogen have been replaced by methyl groups.

Acknowledgment.—The authors wish to thank the Commercial Solvents Corporation for the gift of generous samples of six hydroxyamines.

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(3) Hitchcock and Taylor, THIS JOURNAL, **59**, 1812 (1937); **60**, 2710 (1938); MacInnes, Belcher and Shedlovsky, *ibid.*, **60**, 1094 (1938).

(4) Owen, *ibid.*, **56**, 24 (1934).

The Interaction of Hydrous Alumina with Salt Solutions

BY R. P. GRAHAM AND A. E. HORNING[1]

This note is concerned with the changes in pH of certain potassium salt solutions caused by the addition of powdered hydrous alumina. The samples of alumina used (with the exception of one of powdered bauxite) were the same as those studied in a recently-published investigation of the reactivity of hydrous alumina toward acids,[2] and the present work was carried out immediately after the study involving acids.

Experimental

The potassium salt solutions were prepared from analyzed grade reagents and distilled water freed of carbon dioxide by boiling. By reference to a Leeds and Northrup pH meter (no. 7662) standardized by the use of recrystallized analyzed grade potassium acid phthalate, the solutions were brought to a pH of 7.00 ± 0.01 using a 0.1 N solution of potassium hydroxide or of the appropriate acid. The solution under study was pipetted into a 400-ml. beaker clamped in a bath maintained at 25.0 ± 0.1°, the sample of hydrous alumina added while the solution was being agitated mechanically, and the changes in the pH of the solution followed by means of the pH meter (the stirrer was stopped momentarily when a reading was being taken). The meter was standardized immediately before each run, and the standardization checked at the conclusion of it. The pH values given in the table below are the maximum values attained (rounded to the nearest tenth of a pH unit); maximal values were reached in most cases in less than thirty minutes.

TABLE I

INCREASE IN pH OF POTASSIUM SALT SOLUTIONS UPON ADDITION OF POWDERED HYDROUS ALUMINA[a]

I. Variation in Nature of Salt Soln.			II. Variation in Concn. of Salt Soln.	
Salt	(M)	pH attained[b]	M of pot. oxalate	pH attained[b]
Fluoride	0.1	9.6	0.0005	8.0
Oxalate	.05	8.6	.0050	8.3
Sulfate	.05	8.0	.0125	8.4
Nitrate	.1	7.3	.0250	8.5
Chloride	.1	7.3	.0500	8.6
Perchlorate	.1	7.1	.250	8.7
Phosphate	.1	7.0	1.000	8.7

III. Variation in Mass of Alumina		IV. Variation in Nature of Alumina	
G. of alumina "60'	pH attained[c]	Alumina (0.5000 g.)	pH attained[c]
0.1000	7.7	"26"	8.0
.2000	8.5	"60"	8.6
.5000	8.6	"95"	8.6
1.000	8.7	Bauxite	8.1

[a] Sample of hydrous alumina added in each case to 100.0 ml. of salt solution, the pH of which had previously been adjusted to 7.00 ± 0.01. [b] Using 0.5000 g. of alumina "60." [c] Using 0.05 M potassium oxalate solution.

Discussion

The increase in the pH of neutral potassium salt solutions upon the addition of hydrous alumina

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(2) Graham and Thomas, THIS JOURNAL, **69**, 816 (1947).

may be explained by the displacement of hydroxo groups from the surface of the alumina due to the tendency of anions to bind coördinately to the aluminum in the structure. Anions vary greatly in their ability to form stable coördination compounds with aluminum, and their efficiencies in this respect[2,3] are in the same order as the *p*H effects observed (I), with the exception of the case of phosphate (which changed its *p*H by only a few hundredths of a unit). The solution of the latter (which would contain the monohydrogen phosphate ion in appreciable concentration after adjustment of the *p*H of the solution to 7.00) resisted change in *p*H because of efficient buffer action.

If the increase in the *p*H of a salt solution is due to displacement of hydroxo groups from the alumina with concomitant anion sorption, the magnitude of the effect should increase with the concentration of anion and with the mass of alumina. This was observed (II and III).

Our interpretation of the experiments in which various samples of hydrous alumina were used (IV) is that the extent of surface hydroxo groups varies with the temperature of preparation of the alumina. This interpretation would lead to the conclusion that samples "60" and "95" possess more surface hydroxo groups than does sample "26"—a conclusion, it should be noted, that was reached previously[2] on the basis of different experimental approaches.

(3) Clay and Thomas, THIS JOURNAL, **60**, 2384 (1938).

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Alkaline Degradation of Benzene Hexachloride

BY FRANCIS A. GUNTHER AND ROGER C. BLINN

Several early investigators have reported[1] that the α-form of benzene hexachloride (1,2,3,4,5,6-hexachlorocyclohexane) yielded 1,2,4-trichlorobenzene when heated with alcoholic potassium hydroxide, and Meunier[2] has reported a similar finding for the β-isomer. On the other hand, van der Linden[3] found that supposedly pure α-isomer yielded predominantly the 1,2,4-trichlorobenzene but also the 1,2,3- and 1,3,5-trichlorobenzenes. Recently, both Slade[4] and Chamlin[5] have stated that alkaline dehydrochlorination of benzene hexachloride yields a mixture of the isomers of trichlorobenzene.

In the present study, it has been shown that the pure α, β, γ, Δ and ε[6] isomers of benzene hexachloride react with 1 *N* ethanolic potassium hydroxide at reflux temperature to yield only the 1,2,4-trichlorobenzene in significant amounts.

Experimental[7]

Materials.—α-Isomer, m. p. 153–154°; β-isomer, m. p. 298–300°; γ-isomer, m. p. 112.2–113.8°; Δ-isomer, m. p. 136–137°; ε-isomer, m. p. 216–217°. The reference 1,2,4-trichlorobenzene was Eastman Kodak Company material, m. p. 15–16°, and was used without further purification.

Dehydrochlorination.—Exactly 10.00 g. (2.00 g. of the ε-isomer) of each isomer was refluxed with a 50% excess of 1 *N* ethanolic potassium hydroxide for two hours. The resulting mixture was cooled and filtered, and the filter cake of potassium chloride was washed with cold ethanol, dried and weighed. A portion of each sample of potassium chloride was analyzed for the chloride ion in the usual manner. To the combined filtrate and washings from each reaction mixture was added water until no new clouding resulted. Long centrifugation resulted in the clean separation of the oily trichlorobenzene, which was washed thoroughly, dried over calcium chloride and then distilled.

Mononitro Derivatives.[8]—Approximately 1 g. of the trichloro compound was dissolved in 5 g. of fuming nitric acid (sp. gr. 1.49), then the resulting yellow solution was poured onto crushed ice. The waxy yellow solid so obtained was washed thoroughly, then recrystallized from ethanol to a constant melting point.

Dinitro Derivatives.[8]—Approximately 1 g. of the mononitrotrichlorobenzene was redissolved in 5 g. of fuming nitric acid (sp. gr. 1.49) and 5 g. of concentrated sulfuric acid (sp. gr. 1.84) was added slowly. After refluxing for one hour, the resulting yellow solution was cooled and poured into 100 ml. of water. The pale yellow solid which separated was washed thoroughly with water, then recrystallized from ethanol to a constant melting point.

Anilino Derivatives.[8]—Approximately 1 g. of the dinitrotrichlorobenzene was mixed with 5 g. of aniline and heated for one hour on the water-bath. After cooling, the resulting red mixture was extracted several times with 6 *N* hydrochloric acid. The orange crystals were then filtered, washed with water, and recrystallized from benzene (large quantity of anilino compound) or from ethanol (small quantity of anilino compound) to a constant melting point.

Discussion

That the dehydrohalogenation treatment was, for all practical purposes, quantitative for each isomer is demonstrated by the data in Table I.

TABLE I

EXTENT OF ALKALINE DEHYDROHALOGENATION OF ISOMERIC BENZENE HEXACHLORIDES

Isomer	KCl residue, g. Expt.	Theor.	% Cl^- in residue	% Dehydrohalogenation[a]
α	7.61	7.69	93.0	92.1
β	7.64	7.69	100.0	99.4
γ	7.72	7.69	98.9	99.4
Δ	7.66	7.69	94.5	94.2
ε	1.53	1.54	95.0	94.2

[a] Washing losses traceable to the solubility of potassium chloride in iced ethanol were not considered.

Distillation of the trichlorobenzenes (obtained in 80–90% over-all yields) and their subsequent conversions into crystalline mononitro, dinitro and anilino derivatives yielded compounds possessing the melting points recorded in Table II. For purposes of comparison, a specimen of known 1,2,4-trichlorobenzene was included in the derivative series, while the corresponding comparison

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(1) Mitscherlich, *Ann. Physik*, **35**, 370 (1833); Lesimple, *Ann.*, **137**, 122 (1866); Matthews, *J. Chem. Soc.*, **59**, 170 (1891).

(2) Meunier, "Beilstein," Vol. V, p. 23.

(3) van der Linden, *Ber.*, **45**, 239 (1912).

(4) Slade, *Chem. Ind.*, **40**, 314 (1945).

(5) Chamlin, *J. Chem. Ed.*, **23**, 283 (1946).

(6) These isomers were obtained through the courtesy of Dr. E. C. Britton of the Dow Chemical Company.

(7) All melting points are corrected.

(8) Huntress and Carten, THIS JOURNAL, **62**, 511 (1940).