The dihydrochloride crystallized as colorless plates decomposing and subliming over 250°.

*Anal.* Calcd. for $C_{10}H_{22}O_2N_2Cl_2$: N, 10.3; Cl, 25.9. Found: N, 10.5; Cl, 25.7.

Fraction 4 was mainly *bis*-{2-[N-(β-aminoethyl)-amino]-ethyl} ether, a light yellow oil. It was converted to the tetrahydrochloride and recrystallized three times from methanol giving small, colorless, thin plates; m. p. 185–187°.

*Anal.* Calcd. for $C_8H_{26}ON_4Cl_4$: N, 16.7; Cl, 42.2. Found: N, 16.9; Cl, 41.6.

By increasing the proportions of ethylenediamine in the reaction to 6 moles to 1, a 58% yield of 4-(β-aminoethyl)-morpholine, based on *bis*-β-chloroethyl ether, was obtained.

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## Precipitation of Barium Sulfate in the Presence of Ammonium Chloride

BY J. T. MCHENRY, G. A. AMPT AND E. HEYMANN

It has been known for a long time that the analytical errors involved in the precipitation of the sulfate radical as barium sulfate are due to the presence of foreign material in the precipitate. Several explanations for the mechanism of this inclusion of foreign material have been considered.[1]

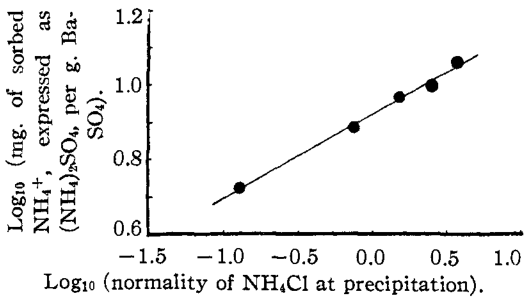

Fig. 1.

We performed a number of precipitations of barium sulfate by means of a barium chloride solution from sulfuric acid in the presence of ammonium chloride. To 200 ml. of boiling solution, containing 0.1859 equivalent of ammonium sulfate and varying amounts of ammonium chloride, 19.0 ml. of 1.96 *N* barium chloride solution was slowly added. Twenty hours after precipitation the precipitate was filtered, washed and dried in a vacuum desiccator.

The sorbed material was determined in two ways: (1) 1-g. aliquots were dissolved in 10 ml. of cold concentrated sulfuric acid, the solution poured into 200 ml. of boiling water, the liquid filtered, the precipitate washed and the filtrate made alkaline and distilled. The ammonia was collected in 0.1 *N* hydrochloric acid and the excess acid determined iodimetrically. Second extractions were carried out on the reprecipitated samples and the total extracted was regarded as the full amount of sorbed material, (2) one-gram aliquots were dissolved in 200 ml. of 50% sodium hydroxide by warming, the solution diluted to 500 ml. and then distilled. The ammonia was absorbed in 0.1 *N* hydrochloric acid. Both procedures gave results which did not differ by more than 4%.

Investigation of our precipitates, by a method first suggested by Hulett and Duschak,[2] showed that about 50% of the ammonia is present as sulfate.

Figure 1 shows that a linear relation exists between the logarithms of the amount sorbed and the ammonium chloride concentration (Freundlich's adsorption isotherm). It is, however, recognized that this empirical relation may also formally describe processes other than surface adsorption. Further it can be seen that barium sulfate, precipitated in the presence of *N* ammonium chloride contains 7.0 mg. of $NH_4$, expressed as ammonium sulfate, per 1 g. of barium sulfate.

The investigations of Kolthoff and MacNevin[3] and of Imre[4] indicate that the essential process in

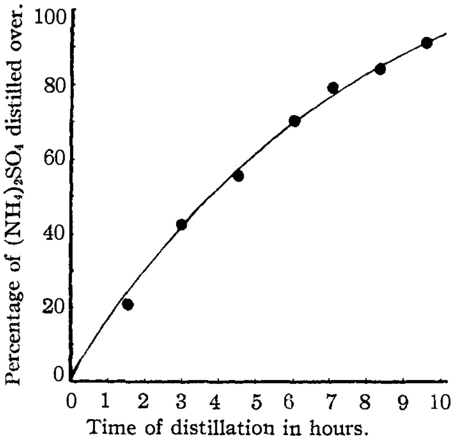

Fig. 2.

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[1] E. F. Allen and J. Johnston, THIS JOURNAL, **32**, 588 (1910); J. Johnston and L. H. Adams, *ibid.*, **33**, 829 (1911); I. M. Kolthoff, *J. Phys. Chem.*, **36**, 860 (1932); Z. Karaoglanow, *Z. anal. Chem.*, **106**, 129 (1936); *Z. physik. Chem.*, **A178**, 143 (1937); D. Balarew and co-workers, *Kolloid-Beihefte*, **30**, 249 (1929); **32**, 304 (1930); *Kolloid-Z.*, **67**, 203 (1934); **83**, 319 (1938); *Z. anal. Chem.*, **101**, 161 (1935); *Z. Krist.*, **89**, 268 (1934); *Kolloid-Beihefte*, **50**, 1 (1939).

[2] G. A. Hulett and L. A. Duschak, *Z. anorg. Chem.*, **40**, 196 (1904); cf. Treadwell and Hall, "Analytical Chemistry," Vol. II, p. 402.

[3] I. M. Kolthoff and W. M. MacNevin, THIS JOURNAL, **58**, 725 (1936).

[4] L. Imre, *Kolloid-Z.*, **87**, 12 (1939).

the inclusion of foreign material in barium sulfate precipitates is a sorption on the initially formed primary crystallites. The growth of these will be such that most of the initially sorbed material does not find its way out of the internal "mosaic" structure of the macrocrystal (*cf.* also Darwin,[5] Smekal,[6] Balarew[1]).

This point is supported by our experiments in which the precipitates were treated by prolonged boiling with dilute sodium hydroxide (0.02–0.01 *N*). In Fig. 2 the percentage of ammonium salt distilled over as ammonia is plotted against the time of distillation. It is very significant that, in this case, ammonia distils over *very slowly, ten to fifteen hours being needed to expel most of it.* This is incompatible with adsorption on the external surface of the macrocrystals only. It can only be explained on the assumption that the contaminating salt is mainly present on an internal surface of the macrocrystal. The results of the distillation experiments would, moreover, be difficult to reconcile with the existence of secondary insoluble compounds (Karaoglanow[1]) or of solid solutions.[7] It is highly improbable that, in these cases, the total ammonia could be expelled by treatment with an alkali as dilute as 0.01 *N* sodium hydroxide.

It is not quite simple to visualize a satisfactory mechanism of the formation of macrocrystals which possess a mosaic structure. Kolthoff[1] suggests that the electrolyte, adsorbed on the primary nuclei, will influence crystallization in such a way that the lattice of the eventually formed macrocrystals will contain many imperfections. Another way of visualizing the formation of a mosaic structure would be found in the assumption that the primary crystallites will grow together on certain faces to irregular macrocrystals which possess a large internal surface.

[5] C. G. Darwin, *Phil. Mag.*, **27**, 315, 675 (1914); **43**, 800 (1922).

[6] A. Smekal, *Physik. Z.*, **27**, 837 (1926); *Ann. Phys.*, **93**, 1204 (1927).

[7] G. H. Walden, Jr., and M. U. Cohen, THIS JOURNAL, **57**, 2597 (1935); P. R. Averell and G. H. Walden, Jr., *ibid.*, **59**, 907 (1937).

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## Dissociation of Carbonic Acid in Ordinary and in Heavy Water

BY G. ALEXANDER MILLS

In general, acids are considerably weaker in heavy than in ordinary water. The ratio $K^H/K^D$, where $K^H$ and $K^D$ are the dissociation constants of the acid in $H_2O$ and $D_2O$, increases with decreasing acid strength.[1] The ratio of the apparent first dissociation constants of proto- and deuterocarbonic acid has been accurately determined to be 2.68 at 25°.[2] This does not agree with the predicted value of 3.6 obtained from the function given by Rule and La Mer and recently confirmed by Martin and Butler. However, the acid strength should not be judged from the apparent dissociation constant.

In aqueous solution carbon dioxide is hydrated only to a small extent forming rather strong metacarbonic acid. The relationship between $K_1$, the hydration constant, $K_t$, the true first dissociation constant and $K_a$, the apparent first dissociation constant, is

$$\frac{(H^+)(HCO_3^-)}{(CO_2) + (H_2CO_3)} = K_a = \frac{K_tK_1}{1 + K_1}$$

If hydration of carbon dioxide is assumed to be the same in $D_2O$ as in $H_2O$ (the solubilities are very nearly identical) then $K^H{}_t/K^D{}_t = 2.68$. It has been possible to determine the total amount of carbonic acid in solution since carbon dioxide does not react immediately with water. In conjunction with conductivity data the true dissociation constant has been estimated therefore to be $4 \times 10^{-4}$.[3] From the smooth curve plot of $-\log K^H$ against[1] $K^H/K^D$ the value of 2.9 is now obtained for the ratio. This compares more favorably with 2.68 than with 3.6, the value predicted on the basis of the apparent dissociation constant.

[1] Rule and La Mer, THIS JOURNAL, **60**, 1974 (1938); Martin and Butler, *J. Chem. Soc.*, 1366 (1939).

[2] Curry and Hazelton, THIS JOURNAL, **60**, 2773 (1938).

[3] Strohecker, *Z. Nahrungsm. Untersuch. Hyg. Warenkunde*, **31**, 121 (1916); Buytendyk, Brinkman and Mook, *Biochem. J.*, **21**, 576 (1927).

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## Chlorination of 1-Hexyne in Reactive Solvents. II[1]

BY R. O. NORRIS AND G. F. HENNION

Previous papers[2,3] from this Laboratory describe the chlorination of 1-hexyne in various

[1] Paper XXXVI on the chemistry of substituted acetylenes and their derivatives; previous paper, THIS JOURNAL, **61**, 2897 (1939). Also paper 5 on halogenation in reactive solvents; *cf.*, *ibid.*, **61**, 1460 (1939).

[2] Verbanc and Hennion, *ibid.*, **60**, 1711 (1938).

[3] Norris, Vogt and Hennion, *ibid.*, **61**, 1460 (1939).