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.

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[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 deutero-carbonic 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 meta-carbonic 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

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

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 4×10^{-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.

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[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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RECEIVED NOVEMBER 7, 1939

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

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[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).

oxygen-containing solvents. This work has now been continued, particularly to study the effect of high proton concentrations in the chlorination reaction. For this purpose 1-hexyne was chlorinated as an emulsion in concentrated hydrochloric acid, 30%[4] sulfuric acid and 30%[4] phosphoric acid and as a solution in methanol previously saturated with hydrogen chloride. The various experiments gave complex mixtures of hexyne chlorides as shown in Table I. Fortunately the individual substances boil sufficiently far apart to permit their separation by fractional distillation through an efficient column.

TABLE I

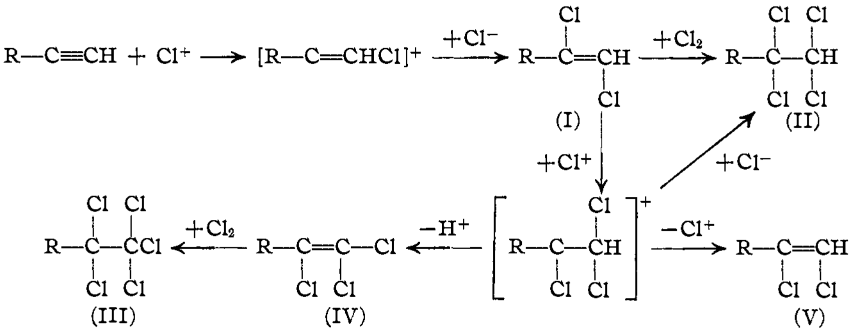
WEIGHTS OF REAGENTS AND PRODUCTS IN THE CHLORINATION OF ONE MOLE OF 1-HEXYNE AT 40–50°

Reagents			Products, R is n-C_4H_9				
Solvent	Vol., ml.	Cl_2, g.	$R\overset{Cl}{C}{=}\overset{Cl}{C}H$	$R\overset{Cl}{C}{=}\underset{Cl}{C}H$	$R\overset{Cl}{C}{=}\overset{Cl}{C}Cl$	$R\overset{Cl}{\underset{Cl}{C}}{-}\overset{Cl}{\underset{Cl}{C}}H$	$R\overset{Cl}{\underset{Cl}{C}}{-}\overset{Cl}{\underset{Cl}{C}}Cl$
35% $HCl-H_2O$	300	176	23	26	25	11	14
30% $H_2SO_4-H_2O$	300	150	25	25	30	8	14
30% $H_3PO_4-H_2O$	300	115	24	30	36	10	17
22% HCl–MeOH	400	122	45	16	65	18	6

It is noteworthy that *cis*-1,2-dichloro-1-hexene (V) was obtained in each case as well as the anticipated *trans* isomer (I) and that oxygen-containing compounds were not isolated. In methanol[2] and in water,[3] to which acid has not been added, the *trans* dichloride is obtained as well as oxygen-containing products.

The trichloride (IV) listed in Table I previously was formulated[3] as 1,2,2-trichlorohexane. It appears now that this compound actually is 1,1,2-trichloro-1-hexene and is the precursor of the pentachloride (III). Attempts[5] to prepare 1,2,2-trichlorohexane from 1-hexyne have failed. Neither *cis*- nor *trans*-1,2-dichloro-1-hexene could be made to add hydrogen chloride.

Chlorination of 2-chloro-1-hexene in carbon tetrachloride also failed to give the anticipated trichlorohexane, but yielded rather *cis*-1,2-dichloro-1-hexene (V) and 1,1,2,2-tetrachlorohexane (II). The following mechanism explains satisfactorily the various products obtained in the present investigation.



The experimental procedure and analyses and physical constants for the products have been cited previously[3] and need not be repeated. However, the product having b. p. 90–93° at 10 mm.; $n^{25}{}_D$ 1.4760; d^{25} 1.225 now is reported as 1,1,2-trichloro-1-hexene rather than as 1,2,2-trichlorohexane.

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[4] Concentration by volume.

[5] Unpublished work, Chas. Welsh and G. F. Hennion.

Remarks on "A New Method for the Cleavage of Unsaturated Fatty Acids"

BY DONALD PRICE AND RICHARD GRIFFITH

Under the above title Chi-yi Hsing and Kou-jen Chang [THIS JOURNAL, **61,** 3589 (1939)] report the application of Criegee's[1] lead tetraacetate oxidation to polyhydroxy fatty acids, which are readily obtained from the corresponding unsaturated acids by oxidation with alkaline permanganate. They describe in detail the oxidation of 9,10-dihydroxyoctadecanoic acid, the cleavage products of which were found to be pelargonic aldehyde and the hemialdehyde of azelaic acid.

These authors seem to have overlooked the fact that Criegee's method previously was applied to the same as well as other acids by Nunn and Smedley-MacLean, *Biochem. J.*, **29,** 2742 (1935),

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[1] Criegee, *Ber.*, **64,** 260 (1931); *Ann.*, **481,** 263 (1930); **507,** 159 (1933).