

NOTES

A Method for Separating Para-hydrogen from Oxygen and Carbon Monoxide

BY E. BERGMANN, L. FARKAS AND L. SANDLER

Para-hydrogen has often been used as a research tool for elucidating reaction mechanisms. In order to analyze the para-ortho ratio in the hydrogen, the hydrogen has to be separated from all gases taking part in, or formed by, the reaction, so that the ortho-para ratio is not changed by this process. In most cases satisfactory separation can be achieved by the use of liquid or solid air which freeze out most of the common gases. In two important cases, however, *viz.*, when oxygen or carbon monoxide is present, liquid hydrogen had to be used for the separation process. Since liquid hydrogen is not always available and its preparation is very expensive, we have tried to substitute a chemical method of separation for the physical one. For this purpose, solutions had to be found which absorb the above gases quantitatively without causing any appreciable para-ortho conversion during the absorption process.

Absorption of Oxygen.—To the quantitative absorption of oxygen a method was adapted which has been devised for the purification of nitrogen by Schlenk,¹ and which is based on the fast and complete reaction of triphenylmethylsodium solution² with gaseous oxygen. As diethyl ether as used by Schlenk and Marcus in their investigations, has a very high vapor pressure and dissolves the grease of the stopcocks, it was replaced by dibutyl ether, having a vapor pressure of a few mm. only at 20°. The solution prepared and filtered in the usual way was evaporated in a stream of pure nitrogen and dibutyl ether added gradually during this process.

The solution actually used was saturated with triphenylmethylsodium and contained an excess of this substance in solid form so as to render possible the uptake of a large amount of oxygen. The solution was kept in a shaking vessel, attached to the high vacuum apparatus by a glass spiral and remained in use for many months without renewal. The diffusion of the gas into the solution can be accelerated by cooling the solution and is completed within less than one minute.

The following two experiments characterize the above solution:

A lock system of 5 cc. capacity was connected through a very narrow capillary tube to a washing bottle containing about 20 cc. of the solution. It was found that when 130 cubic mm. (at S. T. P.) of oxygen passed through the

capillary tube no measurable amount of oxygen (less than 0.005%) could be detected by a McLeod gage on the other side of the washing bottle.

In order to test whether any appreciable ortho-para conversion takes place in presence of the triphenylmethyl sodium solution, para-hydrogen was introduced into the shaking vessel (70 cc. capacity) containing the sodium compound (30 cc.). The half-life-time of the conversion under our conditions was two and one-half hours; thus, the conversion occurring during the short period of oxygen absorption is negligible. The conversion observed is most probably due to the presence of small quantities of free (paramagnetic) triphenylmethyl.

Absorption of Carbon Monoxide.—For the absorption of carbon monoxide the common cuprous oxide-ammonia solution was used. In the same arrangement as used in the case of oxygen, 500 cubic mm. (S. T. P.) of carbon monoxide (at an actual pressure of 70 mm.) were made to pass the capillary tube and again no trace (less than 0.005%) of the gas could be detected on the other side of the washing bottle.

The following experimental arrangement was used in an actual experiment, carried out at low pressure (10^{-2} mm.).³ The gas mixture was collected in a bulb of 700 cc. to which a smaller vessel was attached, containing 40 cc. of the absorbing solution cooled, in order to accelerate the diffusion of the gas, and separated from the larger bulb by a stopcock. The gas mixture (40 cubic mm. at S. T. P.) was collected in the large bulb, the stopcock opened and the absorption vessel shaken for a few hours. A control experiment, carried out with a mixture of 20 cubic mm. of normal hydrogen and 200 cubic mm. of carbon monoxide showed that no carbon monoxide could be detected in a micro-conductivity cell after the process of absorption, indicating that the amount of carbon monoxide was reduced to at least 0.1%.

Under the conditions used, the half-life-time of the ortho-para conversion was found to be one hundred hours, although no special care had been taken to exclude from the cuprous oxide-ammonia solution divalent (paramagnetic) copper compounds which certainly are responsible for the greater part of the conversion observed. In any case the conversion during the period of absorption again is negligible.

It is obvious that the methods described may be useful in experiments with other hydrogen modifications, too, such as ortho-deuterium or mixtures of light and heavy hydrogen and hydrogen deuteride.

(3) Farkas, Hirschberg and Sandler, *THIS JOURNAL*, **61**, 3393 (1939).

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REHOVOTH, PALESTINE RECEIVED SEPTEMBER 30, 1939

Solvolytic Reactions of Organic Halides

BY MICHAEL P. BALFE AND JOSEPH KENYON

While we cannot enter into the discussion of the kinetics of these reactions, which have been de-

(1) Schlenk, Houben-Weyl's "Methoden der organischen Chemie," 1924, Vol. 4, pp. 959, 974.

(2) Schlenk and Marcus, *Ber.*, **47**, 1664 (1914).

scribed as unimolecular,¹ as bimolecular,^{2,3} as either bimolecular or termolecular,⁴ and as poly-molecular,^{5,6} the diversity of conclusions suggests, as indicated by Bartlett,⁴ that the course of these reactions is not sufficiently simple to justify the application of the kinetic method.

Our present purpose is to comment on the mode of formulation of the solvated cation which is assumed as an intermediate in these reactions by Winstein.⁶ In the hydrolysis of halides, Winstein's formulation $\text{H}_2\text{O}^+ - \text{C} \begin{array}{l} \diagup \\ \diagdown \end{array}$ leads to no difficulties, but is not generally applicable. The rearrangement of phenylmethylcarbonyl *p*-toluenesulfonate to *p*-tolyl- α -phenylethylsulfone,⁷ a reaction which involves ionization in the same sense as the solvolytic reactions mentioned above, does not occur in solution in acetonitrile, but proceeds readily in solution in formic acid. The suggestion which seems best to explain this difference in behavior is that there is a difference between the solvating properties of the two solvents.

If solvation of the cation be assumed its formulation as $\begin{array}{c} \text{H} \\ \diagup \\ \text{HO} \end{array} \text{C}=\text{O}^+ - \text{C} \begin{array}{l} \diagup \\ \diagdown \end{array}$ would, in our opinion, imply that phenylmethylcarbonyl formate should be a major product of the reaction, whereas it is in fact a minor product. The alternative explanation, that by two successive solvolytic reactions the sulfonate is converted first into the formate and then into the sulfone, is not consistent with the stereochemical observations recorded in the communication referred to.⁷

We submit, therefore, that it is undesirable to assume that in these reactions there is solvation of carbonium cations by co-valency formation between solvent and cation.

(1) Bateman, Hughes and Ingold, *THIS JOURNAL*, **60**, 3080 (1938).

(2) Olson and Halford, *ibid.*, **59**, 2644 (1937).

(3) Taylor, *J. Chem. Soc.*, 1853 (1937).

(4) Bartlett, *THIS JOURNAL*, **61**, 1630 (1939).

(5) (a) Steigmann and Hammett, *ibid.*, **59**, 2358 (1937), (b) Farinacci and Hammett, *ibid.*, **59**, 2542 (1937).

(6) Winstein, *ibid.*, **61**, 1635 (1939).

(7) Arcus, Balfe and Kenyon, *J. Chem. Soc.*, 485 (1938).

CHEMISTRY DEPARTMENT
BATTERSEA POLYTECHNIC
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Organolithium Compounds of Pyridine and Quinoline

BY HENRY GILMAN AND S. M. SPATZ

The halogen-metal interconversion reaction observed with *m*- and *p*-bromodimethylanilines,¹

(1) Gilman and Banner, *THIS JOURNAL*, **62**, 344 (1940).

mono- and dibromo- and iodocarbazoles and bromoanilines² suggested that corresponding reactions might take place with bromo- and iodopyridines and quinolines. We have found this to be the case. For example, 3-bromoquinoline and *n*-butyllithium react promptly, and carbonation of the reaction mixture gives a 52% yield of 3-quinolinecarboxylic acid. Under corresponding conditions 3-bromopyridine gives a 70% yield of nicotinic acid.

Perhaps the first evidence for the formation of Grignard reagents from 3-bromopyridine and 2-iodopyridine is to be found in a study by Harris.³ Later, Overhoff and Proost⁴ prepared 2-pyridylmagnesium bromide in quantity and obtained from it and benzaldehyde, phenyl-2-pyridylcarbinol. The formation of organolithium compounds from nitrogen heterocycles by means of other RLi compounds is of interest because it appears to be generally applicable, and because it establishes the possibility of selecting conditions to reduce the tendency of addition of an organolithium compound to the anil linkage. Under ordinary conditions, RLi compounds add promptly to the anil linkage. The reaction undoubtedly can be extended to poly-substituted nitrogen heterocycles containing functional groups in addition to bromine and iodine. For example, *o*-bromobenzoic acid and *n*-butyllithium give the lithium salt of *o*-lithiobenzoic acid, which on carbonation (followed by hydrolysis) gives a 31% yield of phthalic acid.⁵ Details on the preparation and some reactions of the organolithium compounds of various nitrogen heterocycles will be published later.

A solution of 14.6 g. (0.07 mole) of 3-bromoquinoline in 50 cc. of dry ether was added rapidly to an ether solution of a slight excess of *n*-butyllithium. The reaction was carried out at -35° for fifteen minutes, at the end of which time the transparent reddish solution was carbonated by dry-ice. On working up the reaction mixture in a customary manner, there was isolated a 52% yield of 3-quinolinecarboxylic acid. Identification was established by comparison with an authentic specimen of the acid (m. p. 270–272°); in addition, the method of mixed melting points was also used with the ethyl 3-quinolinecarboxylate (m. p., 69.5°), prepared from the 3-quinolinecarboxylic acid.

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AMES, IOWA RECEIVED DECEMBER 26, 1939

(2) Gilman, Langham and Willis, *ibid.*, **62**, 346 (1940).

(3) Harris, *Iowa State Coll. J. Sci.*, **6**, 425 (1932); [*C. A.*, **27**, 279 (1933)].

(4) Overhoff and Proost, *Rec. trav. chim.*, **57**, 179 (1938).

(5) Studies by C. E. Arntzen.

The Preparation of Ferric Mesoporphyrin Chloride

BY T. HARRISON DAVIES*

Ferric mesoporphyrin chloride is readily obtained from ferric protoporphyrin chloride by reduction of the latter with hydrogen and palladium charcoal in alkaline methyl alcohol solution. The method leads to higher yields with less labor than the procedure of Fischer and Pützer¹ and Fischer and Stängler,² in which ferric protoporphyrin chloride is first reduced to mesoporphyrin by the action of formic acid and colloidal palladium and the iron is then reintroduced in acetic acid solution. The yields are higher and the general procedure is less troublesome than the method of Fischer and Röse,³ in which ferric mesoporphyrin is obtained directly by heating ferric protoporphyrin in pyridine-methyl alcohol or pyridine-potassium methyl alcoholate solution in a bomb at 225°.

Experimental

Ferric protoporphyrin chloride (4 g.), prepared and recrystallized by the usual methods, is dissolved in 450 ml. of methyl alcohol and 50 ml. of 0.5 *N* potassium hydroxide. Palladinized charcoal (2 g. of a preparation 12% in palladium) is added. The mixture is refluxed with hydrogen bubbling until a test drop in a few ml. of 0.5 *N* sodium cyanide solution gives no evidence of the absorption bands of cyanide ferrous protoporphyrin upon reduction with a little sodium dithionite. About eight hours is ordinarily required. The solution is cooled and filtered. The catalyst, after thorough washing, drying, and shaking with air, can be used again. The filtrate is treated with 1 *N* hydrochloric acid to precipitate the metalloporphyrin. The latter is collected on a filter, washed with a little water and dried *in vacuo* over sodium hydroxide. The semi-crystalline material is dissolved in 100 ml. of chloroform containing 4 g. of quinine. The chloroform solution is added dropwise to 150 ml. of glacial acetic acid saturated with sodium chloride and held above 90° on a water-bath. During the addition, air is bubbled through the acetic acid to assist in the removal of the chloroform. The solution is allowed to cool slowly. After a few hours the crystalline ferric mesoporphyrin chloride is collected on a hardened filter, washed with 50% acetic acid, then with water, and finally dried over potassium hydroxide: yield in one preparation 2.7 g., in a second 3.2 g.

The absorption spectra of cyanide ferrous mesoporphyrin and of ethanalamine ferrous mesoporphyrin from this preparation were identical with those of a preparation of ferric mesoporphyrin chloride made by the method of Fischer and Stängler from an authentic sample of mesoporphyrin hydrochloride.

(* National Research Fellow in Medicine.

(1) Fischer and Pützer, *Z. physiol. Chem.*, **154**, 39 (1926).

(2) Fischer and Stängler, *Ann.*, **459**, 53 (1927).

(3) Fischer and Röse, *Z. physiol. Chem.*, **88**, 9 (1913).

ABSORPTION SPECTRA

Sample	In NaCN soln. + Na ₂ S ₂ O ₄	In NH ₂ CH ₂ - CH ₂ OH soln. + Na ₂ S ₂ O ₄
Ferric protoporphyrin chloride	531-541; 565-574	(525); 550-562
Ferric mesoporphyrin chloride from mesoporphyrin hydro- chloride	527-535; 555-562	(515); 542-551
Ferric mesoporphyrin chloride by this procedure	526-536; 555-562	(516); 541-550

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PASADENA, CALIFORNIA RECEIVED DECEMBER 28, 1939

Reaction of *bis*-β-Chloroethyl Ether with Ethylenediamine

BY M. E. HULTQUIST AND E. H. NORTHEY

The reaction of *bis*-β-chloroethyl ether with ammonia, aliphatic monoamines, and aromatic amines and diamines is well known.^{1,2,3,4} We sought a simpler method for the preparation of 4-(β-aminoethyl)-morpholine than the reaction of *N*-(β-bromoethyl)-phthalimide with morpholine followed by hydrolysis and found one in the action of *bis*-β-chloroethyl ether with a large excess of ethylenediamine.

To 1.875 kg. of 57.5% ethylenediamine (18 moles anhydrous) in a 5-liter flask equipped with agitator, reflux condenser and dropping funnel, 863 g. (6 moles) of *bis*-β-chloroethyl ether was added during one hour. Thirty minutes later, 505 g. of flake sodium hydroxide was added cautiously. The mixture was cooled and the precipitated salt filtered. The liquor was dried over solid sodium hydroxide and then distilled through a 60 cm. × 50 mm. packed column. After distillation of excess ethylenediamine, 370 g. (47.5% of theoretical) of 4-(β-aminoethyl)-morpholine boiling at 121-123° (68 mm.), b. p. 204.5° (768 mm.), was obtained as a water-white liquid with a refractive index of 1.4742 (25°). These values were in agreement with those of 4-(β-aminoethyl)-morpholine prepared by the phthalimide process.

Anal. Calcd. for C₆H₁₁N₂O: N, 21.55. Found: N, 21.4.

On fractionation of the residues, the following cuts were obtained: 50 g. 123° (68 mm.) to 164° (30 mm.); 69 g. 164-166° (30 mm.); 8.5 g. 166-200° (30 mm.); 7.3 g. 200-203° (30 mm.); 5.5 g. 203° (30 mm.) to 220° (4 mm.).

Fraction 2 was mainly ethylenedi-(4-morpholine). It solidified to a light yellow solid. After two recrystallizations from hexane, it was obtained as colorless, coarse prisms; m. p. 70-73°, setting point 71.3°. It was converted to the dihydrochloride by dissolving in alcohol and adding concentrated hydrochloric acid, then twice recrystallizing from dilute alcohol.

(1) Axe and Freeman, *THIS JOURNAL*, **56**, 478 (1934).

(2) A. L. Wilson to Carbide & Carbon Chemical Corp., U. S. Patent, 2,096,441, October 19, 1937.

(3) A. L. Wilson to Carbide & Carbon Chemical Corp., U. S. Patents 2,105,828, January 18, 1938.

(4) Marion C. Reed to Goodrich Tire & Rubber Co., U. S. Patent, 2,001,584, May 14, 1935.

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 $C_6H_{20}ON_4Cl_4$: 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

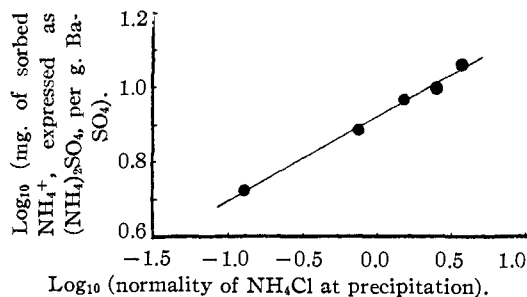


Fig. 1.

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.

(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-Beihfte*, **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-Beihfte*, **50**, 1 (1939).

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 NH₄, expressed as ammonium sulfate, per 1 g. of barium sulfate.

The investigations of Kolthoff and MacNevin³ and of Imre⁴ indicate that the essential process in

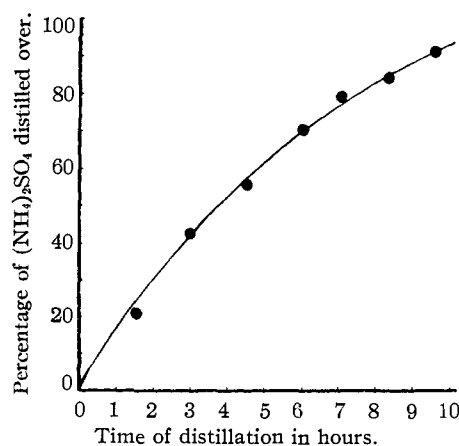


Fig. 2.

(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 Balarew¹).

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 (Karaoglanow¹) 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. Kolthoff¹ 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).

CHEMISTRY DEPARTMENT
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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 deuterio-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

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

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, $K_t^H/K_t^D = 2.68$. 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 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).

DEPARTMENT OF CHEMISTRY
DARTMOUTH COLLEGE

HANOVER, N. H.

RECEIVED NOVEMBER 7, 1939

Chlorination of 1-Hexyne in Reactive Solvents. II¹

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

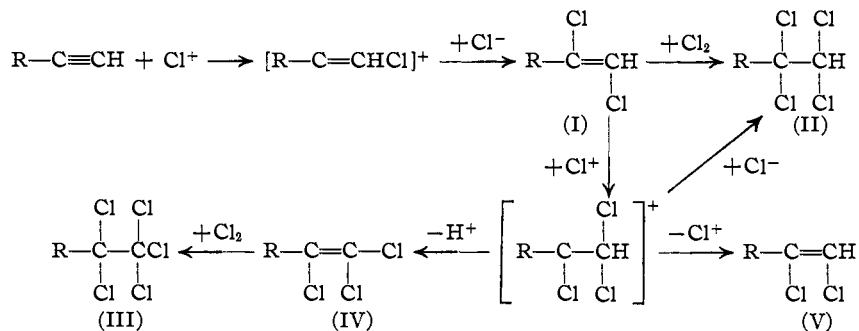
Previous papers^{2,3} from this Laboratory describe the chlorination of 1-hexyne in various

(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).

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. Fortu-



The experimental procedure and analyses and physical constants for the products have been cited previously³ and need not be repeated. However, the product having b. p. 90–93° at 10

TABLE I

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

Solvent	Reagents		Products, R is <i>n</i> -C ₅ H ₁₁				
	Vol., ml.	Cl., g.	$\text{R}-\overset{\text{Cl}}{\text{C}}=\overset{\text{Cl}}{\text{CH}}$	$\text{R}-\overset{\text{Cl}}{\text{C}}-\overset{\text{Cl}}{\text{CH}}$	$\text{R}-\overset{\text{Cl}}{\text{C}}-\overset{\text{Cl}}{\text{CH}}$	$\text{R}-\overset{\text{Cl}}{\text{C}}-\overset{\text{Cl}}{\text{CH}}$	$\text{R}-\overset{\text{Cl}}{\text{C}}-\overset{\text{Cl}}{\text{CH}}$
35% HCl-H ₂ O	300	176	23	26	25	11	14
30% H ₂ SO ₄ -H ₂ O	300	150	25	25	30	8	14
30% H ₃ PO ₄ -H ₂ O	300	115	24	30	36	10	17
22% HCl-MeOH	400	122	45	16	65	18	6

nately the individual substances boil sufficiently far apart to permit their separation by fractional distillation through an efficient column.

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 methanol² 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 formulated³ 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). Attempts⁵ 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.

(4) Concentration by volume.

(5) Unpublished work, Chas. Welsh and G. F. Hennion.

mm.; n_D^{25} 1.4760; d_4^{25} 1.225 now is reported as 1,1,2-trichloro-1-hexene rather than as 1,2,2-trichlorohexane.

CHEMICAL LABORATORY

UNIVERSITY OF NOTRE DAME

NOTRE DAME, INDIANA RECEIVED NOVEMBER 20, 1939

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's¹ 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),

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

with the identical results obtained by them. It was also applied similarly by Raudnitz, Schindler and Petru, *Ber.*, **68**, 1675 (1935), to the determination of the structure of aleuritic acid. More recently Mr. Daniel Swern of the Bureau of Agricultural Chemistry and Engineering, U. S. Department of Agriculture read a paper at the Boston meeting of the American Chemical Society on Sept. 12, 1939, entitled, "Action of Lead Tetraacetate upon Hydroxylated Oils, Fats, Fatty Acids, and Related Compounds."

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Hydrogen Fluoride as a Condensing Agent. IX.¹ Reactions of Di- and Triisobutylene with Phenol

BY J. H. SIMONS AND S. ARCHER

In connection with other work, it became necessary to determine whether or not highly branched aliphatic olefins would react with aromatic compounds to give normal or cleaved products. It is known that in the presence of large amounts of sulfuric acid, diisobutylene reacts with phenol to give cleaved products, but with small quantities of the acid the uncleaved product is obtained.² The same olefin reacts with toluene in liquid hydrogen fluoride to give mono and di-*t*-butyltoluene.³

We have found that under conditions similar to those employed by Calcott and co-workers, di- and triisobutylene both react to give *p-t*-butylphenol as the only monoalkylated phenol. However, by employing milder conditions it was possible to effect condensation without cleavage in the case of diisobutylene. By using a small amount of 70% hydrofluoric acid at 0°, *p-t*-octylphenol was isolated unaccompanied by any cleavage products. Under the same conditions dodecylphenol was not isolated when the twelve-carbon olefin was employed, although even this might be accomplished under even milder conditions.

The triisobutylene used was the so-called "lower isomer," which consists chiefly of dineopentylethylene and methylneopentyl-*t*-butylethylene. The diisobutylene was the usual commercial product, dried and redistilled, the fraction boiling at 100–103° being used.

(1) For previous paper of this series, see *THIS JOURNAL*, **61**, 1821 (1939).

(2) Ipatieff, Pines and Friedman, *ibid.*, **60**, 2495 (1938).

(3) Calcott, Tinker and Weinmayr, *ibid.*, **61**, 1010 (1939).

Experimental

Phenol and Diisobutylene

A. Large Quantities of Hydrogen Fluoride.—To 121 g. of hydrogen fluoride contained in a copper flask, was added a solution of 94 g. of phenol in 300 cc. of carbon tetrachloride. One mole of the olefin was dropped in with constant stirring, the reaction being kept at 0°. After twenty-four hours the reaction was stopped and then treated in the usual way. Distillation gave 88 g. of *t*-butylphenol, m. p. 97–98.5°, 14 g. of a fraction boiling at 165–185° (28 mm.), and a residue of 41 g. The higher boiling fraction did not solidify even after standing for some weeks.

B. Small Quantities of Hydrogen Fluoride.—A mixture of 20 g. of 70% hydrofluoric acid, 56 g. of the olefin, and 47 g. of phenol was kept at 0° for forty-eight hours. After the usual treatment, distillation gave 35 g. of *p-t*-octylphenol, m. p. 82–83°, and recovered phenol. When mixed with an authentic specimen there was no depression in melting point.

Phenol and Triisobutylene

A. Large Quantities of Hydrogen Fluoride.—One mole of phenol was dissolved in 300 cc. of carbon tetrachloride and added to 122 g. of hydrogen fluoride maintained at 0°. To this mixture one mole of the olefin was added slowly. After being stirred for twenty-four hours, the reaction was stopped. Removal of the solvent left a residue of 206 g. of which 64 g. boiled at 152–160° (38 mm.) and melted at 96–97°. This was *t*-butylphenol. The remainder of the material boiled over a wide range and probably consisted of the polybutylphenols.

B. Small Quantities of Hydrogen Fluoride.—Equimolar quantities of the olefin and the phenol were mixed and added to 20 g. of 70% hydrogen fluoride. After sixty hours the usual procedure was followed and the product treated with Claisen solution.⁴ The latter, when examined, did not give any compound that corresponded to a dodecylphenol. When 33 g. of anhydrous hydrogen fluoride was used with 105 g. of phenol and 174 g. of the olefin, for a reaction time of fourteen hours, 52 g. of *t*-butylphenol and considerable residual phenolic material were obtained.

(4) Claisen, Eisleb and Kremers, *Ann.*, **418**, 96 (1919).

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Activity Coefficients in Concentrated Aqueous Solutions of Strong Electrolytes Described by Means of a Formula Containing the Mean Ionic Diameter as Single Parameter. II. Corrected Formulation

BY PIERRE VAN RYSSELBERGHE AND SYLVAN EISENBERG

In a previous paper of the same title¹ a formula with a single parameter was set up which provided

(1) P. Van Rysselberghe and S. Eisenberg, *THIS JOURNAL*, **61**, 3030 (1939).

a good description of the behavior of activity coefficients of concentrated aqueous electrolytes. The formula was tested successfully in a large number of cases besides those reported in our previous paper and we consider it as valuable in itself as a purely empirical contribution. It has, however, no theoretical basis and we are very much indebted to Dr. H. C. Eckstrom for calling our attention to the fact that in formula (15) of this previous paper the quantity $F_{iw} = -kT \log Y$, calculated from Ursell's theory of imperfect gases should have been set equal to $N_i \Delta\mu_{iw} + N_0 \Delta\mu_{ow}$, N_0 being the number of molecules of solvent in the volume V and $\Delta\mu_{ow}$ the van der Waals contribution to the chemical potential of the solvent (other notations as in our previous paper), and not to $N_i \Delta\mu_{iw}$ alone. A complete calculation should take the solvent into account explicitly, but in our treatment it appears as the volume term. If one accepts the various other assumptions previously made, one has for the total van der Waals free energy of the solution (considered as a Gibbs free energy)

$$G_w = N_i \Delta\mu_{iw} + N_0 \Delta\mu_{ow} = kT \left[\frac{1}{2} \frac{N_i^2}{V} v + \frac{5}{64} \frac{N_i^3}{V^2} v^2 \right] \quad (1)$$

Differentiating at constant pressure, temperature and N_0 , we get the following contribution to the logarithm of the average activity coefficient of the ions:

$$\begin{aligned} \log f_{\pm w} &= \frac{\Delta\mu_{iw}}{kT} = \frac{1}{kT} \frac{\partial G_w}{\partial N_i} \\ &= \frac{N_i}{V} v + \frac{15}{64} \left(\frac{N_i}{V} \right)^2 v^2 + \frac{1}{kT} \cdot \frac{\partial G_w}{\partial V} \cdot \frac{\partial V}{\partial N_i} \\ &= \frac{N_i}{V} v + \frac{15}{64} \left(\frac{N_i}{V} \right)^2 v^2 - \\ &\quad \left[\frac{1}{2} \left(\frac{N_i}{V} \right)^2 v + \frac{10}{64} \left(\frac{N_i}{V} \right)^3 v^2 \right] \frac{\partial V}{\partial N_i} \quad (2) \end{aligned}$$

in which $\partial V/\partial N_i$ is the average partial molecular volume of the positive and negative ions. For the activity coefficient of the solvent we deduce similarly the contribution

$$\begin{aligned} \log f_{\pm ow} &= \frac{\partial G_w}{\partial V} \cdot \frac{\partial V}{\partial N_0} = \\ &= - \left[\frac{1}{2} \left(\frac{N_i}{V} \right)^2 v + \frac{10}{64} \left(\frac{N_i}{V} \right)^3 v^2 \right] \frac{\partial V}{\partial N_0} \quad (3) \end{aligned}$$

The first effect of the correction (indicated to us by Dr. Eckstrom) is that the term in C of formula (19) of our previous paper is multiplied by 2 and the term in C^2 by 3. Our first additional term in $\partial V/\partial N_i$ may significantly affect the dependence of the activity coefficient on C^2 , since v and $\partial V/\partial N_i$ are likely to be of the same order of magnitude.

In an entirely rigorous treatment one should, moreover, take into account a term containing the partial volume $\partial V/\partial N_i$ which arises from the electrostatic portion of the free energy and which is always neglected in the case of dilute solutions. The variation of dielectric constant with concentration might also be considered. We shall examine these points in the complete reinvestigation of the problem which we are planning to carry out.

Neglecting, as a provisional approximation, the terms in $\partial V/\partial N_i$ in (2), *i. e.*, using the formula

$$\log_{10} f_{\pm w} = -0.5059 \frac{\sqrt{C}}{1 + \frac{a}{3.042} \sqrt{C}} + 2.20626 \times 10^{-3} a^2 C + 2.62692 \times 10^{-5} a^3 C^2 \quad (4)$$

we have redetermined the ionic diameters for the fifteen alkali halides studied in our previous paper, in the range of concentrations 0.1 to 3 molar. We found the following average values (in parentheses we give the definite decrease observed in all cases from 0.2 to 3 molar):

LiCl:	3.82	(3.86-3.74)
LiBr:	3.93	(3.95-3.90)
LiI:	4.29	(4.43-4.20)
NaCl:	3.31	(3.43-3.15)
NaBr:	3.53	(3.58-3.41)
NaI:	3.69	(3.75-3.58)
KCl:	2.93	(3.10-2.75)
KBr:	3.02	(3.16-2.83)
KI:	3.22	(3.38-3.00)
RbCl:	2.72	(2.75-2.55)
RbBr:	2.71	(2.85-2.58)
RbI:	2.64	(2.78-2.53)
CsCl:	2.42	(2.50-2.37)
CsBr:	2.36	(2.48-2.30)
CsI:	2.17	(2.45-1.88)

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