The Electrolytic Formation and Cleavage of N-Methyl-N-(triphenylacetoxymethyl)formamide

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The electrolysis of triphenylacetic acid in dimethylformamide afforded a high yield of N-methyl-N-(triphenylacetoxymethyl)formamide. After further electrolysis, the isolation of triphenylmethane and evidence of carbon monoxide formation indicated an acyl–oxygen cleavage of the ester at the cathode.

It is generally accepted that the Kolbe synthesis of hydrocarbons follows a free-radical sequence initiated by the anodic oxidation of a carboxylate ion.[1] In

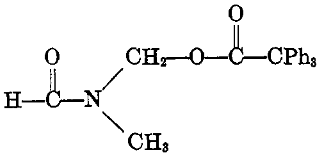
$$R{-}COO^- \xrightarrow{-e} R{-}COO\cdot \longrightarrow CO_2 + R\cdot \xrightarrow{R\cdot} R{-}R$$

many cases, however, other products in addition to or to the exclusion of the hydrocarbon are obtained. In the latter instances, there is evidence to suggest that some of these products are a consequence of the formation of carbonium ion intermediates from a two-electron transfer.[2]

$$R\cdot \xrightarrow{-e} R^+$$

In this report, the products obtained from the electrolysis of triphenylacetic acid in dimethylformamide indicate that radical cleavage of an ester may occur subsequent to its formation, thereby leading to additional products.

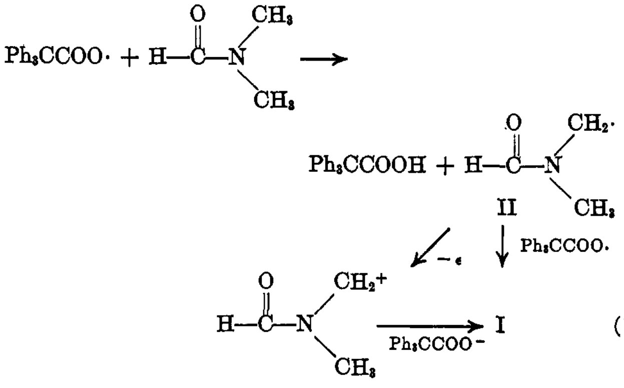
The electrolysis of triphenylacetic acid in methanol or in acetic acid affords[3] methyl triphenyl ether and triphenylmethyl acetate, respectively, but no hexaphenylethane. In dimethylformamide, we realized a yield of 65% N-methyl-N-(triphenylacetoxymethyl)-formamide (I), 3% triphenylmethane, and 5.5%



I

carbon dioxide. The formation of I is analogous to the acetoxylated product isolated by Ross and his coworkers[4] from the electrolysis of acetic acid in dimethylformamide, and probably results *via* one of the paths suggested by them.

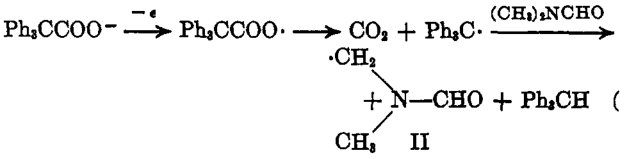
The low yield of carbon dioxide in this reaction, particularly evident when compared with other acids[5] which yield benzylic radicals upon electrolysis,



(1)

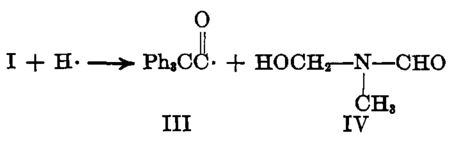
prompted further examination of the triphenylacetic acid electrolysis.

Under similar conditions but after almost doubling the electrolysis time, no ester I was found, but 79% triphenylmethane was isolated. However, only 33% of the theoretical amount of carbon dioxide was produced. This discrepancy between the yield of triphenylmethane and carbon dioxide indicated that all of the triphenylacetoxyl radical did not decarboxylate in the expected manner, and that part of the yield of triphenylmethane must have arisen by a different sequence. Thus, the triphenylmethane corresponding to the evolution of carbon dioxide probably arises from the sequence

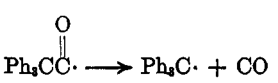


(2)

which also supplies the radical II in eq. 1. The formation of the remainder of the triphenylmethane without a concomitant evolution of carbon dioxide can be explained by a displacement reaction effected by atomic hydrogen at the cathode. The triphenylacyl radical



(III) would be expected to decarbonylate,[6] and carbon monoxide was qualitatively shown to be evolved by a



$$Ph_3C\overset{O}{\overset{\|}{C}}\cdot \longrightarrow Ph_3C\cdot + CO$$

positive reaction with palladium chloride.[7] Furthermore, by using a cell with divided electrode compart-

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[1] Several reviews of this reaction are (a) B. C. L. Weedon, *Quart. Rev.* (London), **6**, 380 (1952); (b) B. C. L. Weedon *Advan. Org. Chem.*, **1**, 1 (1960); (c) M. J. Allen, "Organic Electrode Processes," Reinhold Publishing Corp., New York, N. Y., 1958, pp. 95–115; (d) A. P. Tomilov and M. Ya Fioshin, *Russ Chem. Rev.* (Engl. Transl.), **32**, 30 (1963).

[2] (a) W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **86**, 4686 (1964); (b) W. A. Bonner and F. D. Mango, *J. Org. Chem.*, **29**, 430 (1964); (c) E. J. Dorey, N. L. Bauld, R. T. LaLonde, and J. Casanova, Jr., *J. Am. Chem. Soc.*, **82**, 2645 (1960); (d) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 581; (e) L. Eberson, *Acta Chem. Scand.*, **17**, 1196, 2004 (1963).

[3] (a) R. P. Linstead, B. R. Shephard, and B. C. L. Weedon, *J. Chem. Soc.*, 3641 (1952); (b) A. J. v. d. Hoek and W. T. Nauta, *Rev. trav. chim.*, **61**, 845 (1942).

[4] S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Am. Chem. Soc.*, **86**, 2745 (1964).

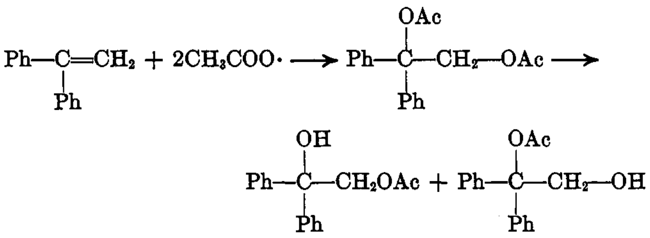
[5] Unpublished results.

[6] See ref. 2d, p. 279.

[7] R. Nowicki, *Chem. Zentr.*, **85**, 1120 (1911); H. Gilman and C. W. Gerow, *J. Am. Chem. Soc.*, **77**, 4675 (1955).

ments, it was similarly shown that the carbon monoxide was produced in the cathode section. Attempts to isolate IV were unsuccessful.

Although the electrolysis of esters[8] does not always result in an acyl–oxygen displacement, evidence for such reactions may be inferred from some of the products reported by Bonner and Mango.[2b] These were isolated after the electrolysis of sodium acetate–acetic acid in the presence of 1,1-diphenylethane.



$$\underset{\textstyle Ph}{Ph{-}C}{=}CH_2 + 2CH_3COO\cdot \longrightarrow Ph{-}\overset{\textstyle OAc}{\underset{\textstyle Ph}{C}}{-}CH_2{-}OAc \longrightarrow Ph{-}\overset{\textstyle OH}{\underset{\textstyle Ph}{C}}{-}CH_2OAc + Ph{-}\overset{\textstyle OAc}{\underset{\textstyle Ph}{C}}{-}CH_2{-}OH$$

Experimental

Electrolysis of Triphenylacetic Acid in Dimethylformamide.—The electrodes consisted of two pieces of smooth platinum foil (2 × 3 cm.) attached to short lengths of platinum wire. These were sealed into glass tubing which extended down from a ₸ 45/50 (male) glass head, which also held a 24/40 joint for a condenser. The glass tubes were filled with mercury to make power connections, and the electrodes were spaced 0.5 in. apart. The cell compartment (160 ml.) was fitted to receive the electrode unit and was equipped with a nitrogen gas inlet, a thermometer well, a water jacket for cooling, and a magnetic stirring bar. A refrigerated, circulating bath was used to maintain the solution temperature at 25–30°. The d.c. power supply had an output of 150 v., 15 amp.

The CO_2 was determined by using an Ascarite-filled absorption bulb connected to the condenser through a cold finger trap.

The cell was charged with a solution of 5.76 g. (0.02 mole) of triphenylacetic acid[9] and 0.6 ml. of triethylamine in 60 ml. of purified dimethylformamide. Electrolysis was continued for 2 hr. and 50 min., at a current density of 16.7 ma./cm.^{2} (100–150 v.). A total of 48.1 mg. (5.5%) of CO_2 was collected. The evolution of CO was detected by the darkening of a strip of absorbent paper soaked with a $PdCl_2$ solution.

The resulting solution was diluted with water to precipitate most of the products. Separation was accomplished by chromatography on alumina. Elution with *n*-hexane afforded 110 mg. (3%) of triphenylmethane, m.p. 93° (lit.[10] m.p. 92°). Further elution with benzene gave 3.6 g. of I, m.p. 175–177°, $\gamma_{C=O}$ 5.75, 5.90 μ.

Anal. Calcd. for $C_{23}H_{21}NO_3$: C, 76.86; H, 5.84; N, 3.90. Found: C, 76.89; H, 5.90; N, 3.83.

In a similar manner, 5.76 g. (0.02 mole) of triphenylacetic acid and 0.6 ml. of triethylamine in 60 ml. of purified dimethylformamide was electrolyzed for 5 hr. during which time the current density dropped from 16.7 to 4.6 ma./cm.^{2} (100–150 v.). A total of 289 mg. (33%) of CO_2 was collected, and CO was qualitatively detected. Chromatography gave 3.87 g. (81%) of triphenylmethane which was the only product which could be isolated.

A modified H-tube, equipped with a medium glass frit to allow separated electrode compartments, was fitted with circular smooth platinum disk electrodes. A condenser, cold trap, and gas absorption bulb were connected to each compartment. Provisions to detect CO from each electrode were also made.

Into each compartment was placed a solution containing 2.88 g. (0.01 mole) of triphenylacetic acid, 0.8 ml. of triethylamine, 0.72 g. (0.002 mole) of ester I, and 30 ml. of dimethylformamide. The electrolysis was carried out for 13 hr. at a current density of 1.4–0.5 ma./cm.^{2}. The solution in the anode compartment became darker in color than that in the cathode compartment, and continuous gassing was observed at the cathode. The evolution of CO was evident only at the cathode. After removing the solvent under reduced pressure, the residue from each compartment was dissolved in ether and extracted with Na_2CO_3 solution. No acid was found. The residue from the anode was 4.33 g., while 2.45 g. was obtained from the cathode compartment. Thin layer chromatography of the residues showed that triphenylmethane was present in both compartments, although some migration between them appears to have occurred. An electroosmotic effect resulted in an increase of solution volume in the cathode compartment during the electrolysis.

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(8) (a) T. Okubo and S. Tsutsumi, *Tech. Rept. Osaka Univ.*, **13**, 495 (1963); (b) T. Okubo and S. Tsutsumi, *Bull. Chem. Soc. Japan*, **37**, 1794 (1964).

(9) J. Schmidlin, *Ber.*, **39**, 634 (1906).

(10) J. F. Norris, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 548.

Reactions of Nitro Alcohols. II.[1] The Kinetics of Dissociation of 2,2-Dinitropropanol in Aqueous Buffers

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The rates of dissociation of 2,2-dinitropropanol to formaldehyde and the carbanion of 1,1-dinitroethane were measured in aqueous buffers at precisely controlled temperatures near 10, 25, and 40°. The kinetic data are consistent with the following dissociation mechanism: rapid ionization of the carbinol to $CH_3C(NO_2)_2CH_2O^-$, followed by slow dissociation, by a reversible reaction, to the products. The bimolecular rate constant for the reaction of formaldehyde and the carbanion of 1,1-dinitroethane was evaluated at each temperature; E_a, ΔH^*, and ΔS^* for the reaction of these species were found to be 18.8 kcal. mole^{-1}, 18.2 kcal. mole^{-1}, and +1.5 e.u., respectively.

The dissociation of 2,2-dinitropropanol (A) and of four other polynitromethylcarbinols has been shown to be a pH-dependent equilibrium of the form represented by eq. 1.[1] The equilibrium constant, K, for

$$\underset{\textstyle A}{CH_3C(NO_2)_2CH_2OH} + OH^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{\textstyle B}{CH_3C(NO_2)_2^-} + \underset{\textstyle C}{CH_2(OH)_2} \quad (1)$$

(1) was determined for aqueous phosphate buffers of ionic strength 0.1. It was noticed that the steady-state concentrations were attained rather slowly. The purpose of this study is to measure and interpret these equilibration rates.

Experimental

Apparatus and Chemicals.—2,2-Dinitropropanol was made by the reaction of formaldehyde with 1,1-dinitroethane, which, in turn, was made from 1-chloro-1-nitroethane by the ter Meer

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(1) Paper I: T. N. Hall, *J. Org. Chem.*, **29**, 3587 (1964).