2. *From 2,4'-diacetamidobiphenyl.* Ten g. of 2,4'-diacetamidobiphenyl was dissolved in 150 ml. of glacial acetic acid and 75 ml. of acetic anhydride. Ten g. of anhydrous potassium acetate and 1 g. of phosphorus pentoxide were added, and the solution was cooled to −5°. The solution was stirred and a solution of 5.5 g. of redistilled nitrosyl chloride in 10 ml. of acetic anhydride was added at −20°. Stirring was continued for 15 min., the mixture was poured onto 500 g. of ice and water and the solution was extracted twice with 200 ml. of benzene. The benzene extract was washed twice with 50 ml. of ice water and dried over anhydrous sodium sulfate. The solution was warmed to 35–40° until no more nitrogen was evolved (1 hr.), filtered, and the benzene removed by distillation to leave 10 g. of a black tar. The black tar was chromatographed on acid alumina (Woelm, Grade I), using benzene as eluant. The eluate coming through the column before the colored material was evaporated to dryness to give 0.3 g. (3%) of 2,4'-diphenylbiphenyl, m.p. 209–210° from benzene or toluene. Ultraviolet absorption: λ_{max} 257 mμ (log ϵ, 4.55); 274 mμ (log ϵ, 4.55) in methanol (Beckman DK-2 spectrophotometer). Infrared absorption: 1605(w), 1529(w), 1484(m), 1456(w), 1403(w), 1350(w), 1170(w), 1076(w), 1005(m), 908(w), 839(s), 748(v.s.), 686(s) cm.$^{-1}$ All bands attributable to *o*-, *p*- or monosubstituted benzenes. (KBr pellet; Baird recording double-beam spectrometer).

Anal.[18] Calcd. for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 93.90; H, 6.20.

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[18] Analysis by Micro Tech Laboratories, Skokie, Ill.

Application of the Equilibrium Theory of Solvent Isotope Effects to Deoxymercuration

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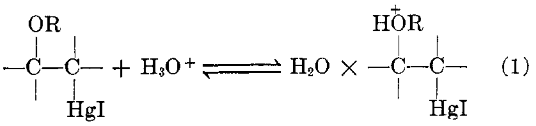
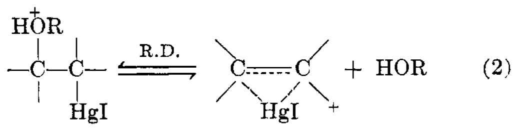
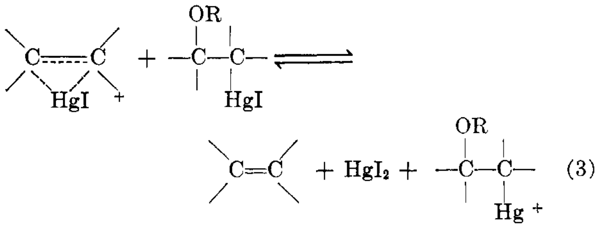
In previous papers[1,2] the mechanism of deoxymercuration induced by nonhalogen acids has been discussed, and evidence favoring a prototropic equilibrium followed by a rate-determining reaction of the protonated substrate was presented. The suggested mechanism is shown in Equations 1–3.



$$-\overset{\text{OR}}{\text{C}}-\underset{\text{HgI}}{\text{C}}- + \text{H}_3\text{O}^+ \rightleftharpoons \text{H}_2\text{O} \times -\overset{\text{H}\overset{+}{\text{O}}\text{R}}{\text{C}}-\underset{\text{HgI}}{\text{C}}- \quad (1)$$



$$-\overset{\text{H}\overset{+}{\text{O}}\text{R}}{\text{C}}-\underset{\text{HgI}}{\text{C}}- \xrightleftharpoons{\text{R.D.}} \underset{\text{HgI}^{+}}{>\text{C}\cdots\text{C}<} + \text{HOR} \quad (2)$$



$$\underset{\text{HgI}^{+}}{>\text{C}\cdots\text{C}<} + -\overset{\text{OR}}{\text{C}}-\underset{\text{HgI}}{\text{C}}- \rightleftharpoons >\text{C}=\text{C}< + \text{HgI}_2 + -\overset{\text{OR}}{\text{C}}-\underset{\text{Hg}^{+}}{\text{C}}- \quad (3)$$

For such a mechanism it would be expected that the equilibrium theory of solvent isotope effects[3] would successfully predict the dependence of rate on solvent deuterium content in partially deuterated water when R is an alkyl group. Although the precision was inadequate for a definite conclusion, the work on 2-methoxy-1-iodomercuripropane (I) suggested that there were systematic differences between observed and predicted rates.[1]

The reason for the lack of precision in the earlier work was that I is deoxymercurated at an inconveniently high rate. The dependence of rate on solvent deuterium content has now been examined for 2-methoxy-1-iodomercuriethane (II). Deoxymercuration of II is slower than deoxymercuration of I by a factor of about 10, so that considerably better precision could be obtained. The present results are in accord with the predictions of the equilibrium theory of solvent isotope effects.[3]

Rates were obtained spectrophotometrically at 25° by following the build-up of the mercuric iodide absorption at 2800 Å. The initial substrate concentration was 3 × 10^{-5} and the acid was always in large excess. Reactions were followed to 50–80% of completion. With a large excess of acid the mechanism shown in Equations 1–3 leads to the rate law shown in Equation 4,

$$k_1 = \frac{2.303}{2(t - t_0)} \log \frac{(\text{D}_\infty - \text{D}_0)}{(\text{D}_\infty - \text{D}_t)} \quad (4)$$

where k_1 is the pseudo first-order rate constant and D_t is the optical density at time t.[1] The quantity log $[(D_\infty - D_0)/(D_\infty - D_t)]$ was evaluated from semilogarithmic plots of $(D_\infty - D_t)$ *vs.* t. A typical example of such a plot is shown in Fig. 1. None of the present plots showed the negative curvature mentioned previously,[1] but such curvature was not specifically sought.

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[1] M. M. Kreevoy, *J. Am. Chem. Soc.*, **81**, 1099 (1959).

[2] M. M. Kreevoy and Frances R. Kowitt, *J. Am. Chem. Soc.*, in press.

[3] E. L. Purlee, *J. Am. Chem. Soc.*, **81**, 263 (1959); this paper gives earlier references.

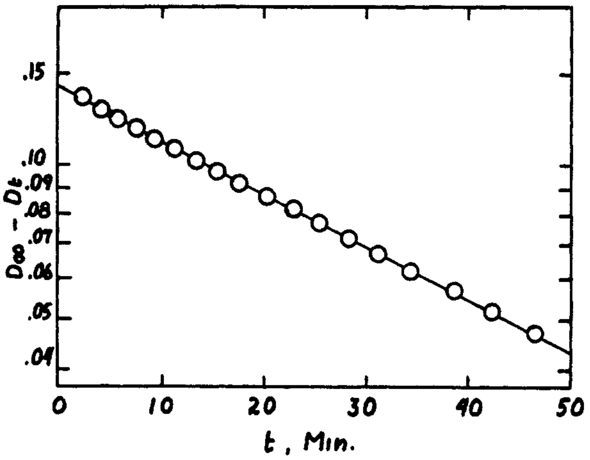

Fig. 1. Typical semilogarithmic plot of $(D_\infty - D_t)$ *vs.* t. The circles are not error circles; they merely identify the points

In undeuterated water, 9 values of k_1 were obtained at acid concentrations ranging from 1.21×10^{-1} to 8.47×10^{-3}. The mean value of $k_2^{H_2O}$ ($k_2 = k_1/(H^+)$) was 3.31×10^{-2}, the average deviation from the mean was 0.07×10^{-2} and the probable error of the mean was 0.02×10^{-2}.[4] No systematic variations in k_2 with acid concentration could be observed. Fourteen determinations of k_2 were made in partially deuterated solutions, the deuterium content ranging up to 98.0 atom %.

Purlee[3] has recently reworked the equilibrium theory of solvent isotope effects, introducing modern values for the various parameters. From his work the rate constant, k_2^n, in a solvent containing 100 n atom % deuterium, is given by Equation 5.

$$\frac{k_2^n}{k_2^{H_2O}} = \frac{1}{Q'(n)}\left[1 - n\left(\frac{k_2^{D_2O}}{3.32k_2^{H_2O}} - 1\right)\right] \quad (5)$$

In Equation 5, $Q'(n)$ is an empirically determined function of n, tabulated by Purlee,[3] and $k_2^{D_2O}$ is the rate constant in pure D_2O. It has been customary[3] to plot calculated and observed values of $k_2^n/k_2^{H_2O}$ against n. This procedure has two disadvantages: (1) $k_2^{D_2O}$ is not usually available from direct measurements and must be obtained by a short extrapolation; (2) the resulting plots are nonlinear. In the present work it seems desirable to rearrange Equation 5 to get Equation 6, which gives the quantity $Q'(n)k^n$ as a linear function

$$Q'(n)k_2^n = k_2^{H_2O} + n\left(\frac{3.32k_2^{H_2O} - k_2^{D_2O}}{3.32}\right) \quad (6)$$

of n with intercept k^{H_2O} and slope $(3.32\ k_2^{H_2O} - k_2^{D_2O})/3.32$.[5] Fig. 2 shows the plot of $Q'(n)k_2^n$ *vs.* n obtained from the present data.

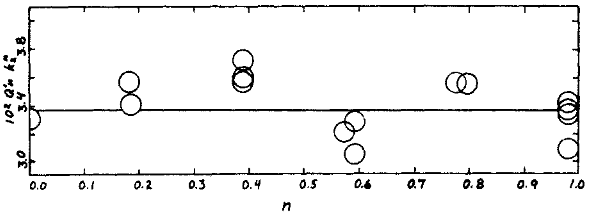

Fig. 2. A plot of $Q'(n)k_2$ *vs.* n. The circles show the error that would be introduced into $Q'(n)k_2^n$ by an uncertainty of ~2% in k_2^n. The latter is the average deviation from the mean for rate constants in H_2O. The point for $n = 0$ is the mean of nine determinations. The line is the least-squares slope

The best straight line, obtained by the method of least squares from all 23 pieces of data, has a slope of 0.000 (apparently accidental) and an intercept, $k_2^{H_2O}$, of 3.37×10^{-2} l. mole^{-1} sec.$^{-1}$ From the zero slope and the least-squares value of $k_2^{H_2O}$, $k_2^{D_2O}$ has a value of 11.2×10^{-2} l. mole^{-1} sec.$^{-1}$, and $k_2^{D_2O}/k_2^{H_2O}$ is 3.32. This value is similar to and more accurate than solvent isotope effects previously reported for closely related reactions.[1,2]

The average deviation of the points from the line corresponds to a 5% uncertainty in the quantity $Q'(n)k_2^n$. This is somewhat larger than the average deviation from the mean value of the rate constants in H_2O, but the deviations are not systematic and the fraction D is involved here as an additional variable, because $Q'(n)$ is a function of n. This result is in accord with the expectations following from the suggested mechanism and gives further support to that mechanism.

EXPERIMENTAL

2-Methoxy-1-iodomercuriethane was prepared by the method of Schroeller, Schrauth, and Essers,[6,7] and had a m.p. of 42.5° (uncorr.). Its m.p. has previously been reported to be 42°.[7] Its infrared spectrum was about what one would expect of an aliphatic ether.

Deuterium oxide was obtained from Stuart Oxygen Co. and was certified to be >99.5% D. Three determinations of its deuterium content were made during the course of the kinetic measurements, by determining its density.[8] The results indicated 98.3, 97.5, and 99.7 atom % D, and the D_2O used was all assumed to be 98.5 atom % D, the average of the three.

Methods of making up standard acids and solvents, and the technique of measuring rates have been described previously.[1] The substrate, II, was handled as a stock solution in methanol, with the result that all solutions in which rates were measured contained 2% of methanol by volume. It has been shown, however, that small quantities of methanol have little or no effect on the rate of reactions of this type.[1]

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(4) R. Livingston, *Physico Chemical Experiments,* The Macmillan Co., New York, 1957, Chap. I.

(5) Equation 6 is similar to equations used by N. C. Deno and W. L. Evans, *J. Am. Chem. Soc.,* **78,** 582 (1956) to analyze solvent isotope data.

(6) W. Schroeller, W. Schrauth, and W. Essers, *Ber.,* **46,** 2867 (1913).

(7) F. A. Cotton and J. R. Leto, *J. Am. Chem. Soc.,* **80,** 4823 (1958).

(8) I. Kirshenbaum, *Physical Properties and Analysis of Heavy Water,* McGraw-Hill Book Co., Inc., New York, 1951, p. 16

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The Kolbe Electrolysis in Dimethylformamide

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Previous reports[1] from this laboratory have indicated the efficacy of *N*,*N*-dialkylamides in encouraging the dimerization of cathodically generated organic free radicals. This note describes an extension of the principle to anodic syntheses and presents the results of attempts to improve the yield of dimer in the Kolbe electrolysis[2] of two organic acids.

The most commonly used solvents for the Kolbe electrosynthesis are methanol and water. To a varying degree the Kolbe dimer is accompanied by ethers, alcohols, esters, and monomeric paraffins and olefins.[3] The failure to isolate higher yields of dimer in many of the reactions can be ascribed in part to diversion of the intermediate by reaction with the solvent. To obviate this difficulty a nonreacting, highly polar solvent, dimethylformamide, was used as the electrolysis medium.

The electrolysis of diphenylacetic acid in methanol has been studied previously by Riccobini[4] and by v. d. Hoek and Nauta.[5] In methanol-pyridine mixtures, these workers obtained 6% and 8.9% respectively of tetraphenylethane. Among other products, the latter workers obtained 42.6% of methyl benzhydryl ether. In our hands the electrolysis of diphenylacetic acid in methanol with triethylamine added as the base afforded an 80% yield of methyl benzhydryl ether identified by infrared comparison with authentic material. No tetraphenylethane could be isolated. Likewise, Linstead, Shephard, and Weedon[6] obtained a 73% yield of benzhydrol on saponification of the acetate formed from the electrolysis of diphenylacetic acid in acetic acid.

When the electrolysis medium was changed to dimethylformamide, a 24% yield of tetraphenylethane was obtained. This experiment was conducted for the isolation of only the Kolbe dimer and no attempt was made to find other products.

No description of the Kolbe electrolysis of hydratropic acid could be found in the literature and it was studied in somewhat more detail. Triethylamine again served as the base and the electrolysis was performed in methanol and in dimethylformamide.

In methanol the products obtained in minor amounts included styrene, α-phenethyl alcohol and acetophenone. The major products were 21% of 2,3-diphenylbutane (*meso* and *dl*) and 20% of methyl α-phenethyl ether. The products were analyzed and identified through infrared spectroscopy, vapor phase chromatography and formation of derivatives.

All of the products can be readily explained by the intermediate formation of an α-methylbenzyl radical which can dimerize, react with the solvent or with radicals generated from the solvent, be oxidized, or lose a hydrogen atom.

In dimethylformamide as the solvent the amount of dimer was doubled. 2,3-Diphenylbutane (*meso* and *dl*) was isolated in 41% yield and α-phenethyl alcohol was obtained in 8.2% yield. The latter product could arise from the reaction of the intermediary radical with water present in the dimethylformamide.

It thus appears that dimethylformamide is a good solvent in which to perform the Kolbe electrosynthesis to the relative exclusion of the common side products.

EXPERIMENTAL

All melting points and boiling points are uncorrected. A Perkin-Elmer *154B* vapor fractometer with a "K" column and helium as the carrier gas was used for analysis.

Electrolysis procedure. The electrolysis cell consisted of a 150 ml. tall-form beaker containing the appropriate solution. The cell was cooled with an ice water bath and the cell contents were mixed with a magnetic stirrer. The electrodes were pieces of smooth platinum, 2 cm. × 3 cm., 1 cm. apart and totally immersed in the solution. Current was supplied by a voltage regulated D.C. power supply. An ammeter was connected in series. The initial and final applied voltages for each experiment are indicated. The current was 0.4 amp. and did not vary more than 10% during any of the electrolyses. In each case a solution of 0.1 mol. of the acid, 3 ml. of triethylamine, and 100 ml. of the solvent was used.

Electrolyses. Diphenylacetic acid in methanol. The solution was electrolyzed for 20 hr. and the voltage was increased from 95 volts to 135 volts during the electrolysis. The methanol was partially evaporated at room temperature and the dark residue was poured into a liter of salt water and extracted four times with chloroform. The extract was washed twice with saturated sodium bicarbonate solution and several times with water. It was dried over magnesium sulfate and the chloroform was distilled, leaving a dark tar which would not crystallize. Distillation at 3 mm. gave 16 g. (80%) of methyl benzhydryl ether. Redistillation afforded 15 g., b.p. 86–90° at 0.3 mm., n_D^{28} 1.5623 (reported[7]

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[2] B. C. L. Weedon, *Quart. Revs. (London)*, **6**, 380 (1952).

[3] C. Walling, *Free Radicals in Solution*, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 580.

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[5] A. J. v. d. Hoek and W. T. Nauta, *Rec. trav. chim.*, **61**, 845 (1942).

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[7] C. C. Price and G. Berti, *J. Am. Chem. Soc.*, **76**, 1207 (1954).