molecules of olefin oxide added are in fact immediately adjacent to each other and not non-adjacent, as in $\mathrm{RCH(O\overset{|}{\underset{|}{C}}—\overset{|}{\underset{|}{C}}OR')_2}$, for example, was proved by identification of hydrolysis products. As would be expected, the 1:1 addition was favored by maintaining a considerable excess of the acetal during reaction. All the products were liquids miscible with water and common alcohols, ethers, esters and hydrocarbons.

Experimental

Methylal and Ethylene Oxide.—A solution of 12 g. of boron trifluoride in 500 g. (6.6 moles) of methylal was prepared at 0° with stirring. An ice-cooled condenser was attached and 200 g. (4.5 moles) of liquid ethylene oxide was gradually introduced under the same conditions. The mixture was added to an aqueous slurry of potassium carbonate and allowed to stand for separation of layers. The lower layer upon brief steam distillation and saturation of the distillate with potassium carbonate gave 6 g. of an organic liquid identified as *p*-dioxane by its boiling point (101°) and its formation of an insoluble complex with mercuric chloride.[2] The upper layer was rapidly distilled at atmospheric pressure up to 140°, where noticeable decomposition began, and thereafter under reduced pressure. Refractionation in a Todd column gave considerable unreacted methylal, b.p. 40–55°, *p*-dioxane (3 g.), and the following other products.

1-Methoxymethoxy-2-methoxyethane (I), b.p. 130–131.5° (750 mm.), 97 g. (18%). This compound had $n^{25}{}_{\mathrm{D}}$ 1.3913 and $d^{25}{}_4$ 0.9465.

Anal. Calcd. for $C_5H_{12}O_3$: C, 49.98; H, 10.07; mol. wt., 120; *MR*, 30.07. Found: C, 49.56; H, 9.87; mol. wt.,[3] 119, 121; *MR*, 30.12.

I was characterized by its non-reaction with metallic sodium and by hydrolysis in 5% aqueous hydrochloric acid to (a) methanol, characterized as the 3,5-dinitrobenzoate (b) 2-methoxyethanol, characterized as the *p*-nitrobenzoate, m.p. 49°, and (c) formaldehyde, identified as the 2,4-dinitrophenylhydrazone. As might be surmised from its structure, this new acetal is a solvent in which the addition of sodium to naphthalene[4] can be effected.

1-(2-Methoxyethoxy)-2-methoxymethoxyethane (II), b.p. 185° (748 mm.) or 139–140.5° (98 mm.), was obtained in 14% yield (47 g.). It has $n^{27}{}_{\mathrm{D}}$ 1.4089 and $d^{27}{}_4$ 0.9896.

Anal. Calcd. for $C_7H_{16}O_4$: C, 51.20; H, 9.82; mol. wt., 164; *MR*, 41.10. Found: C, 51.20; H, 9.74; mol. wt.,[3] 166, 167; *MR*, 41.16.

Hydrolysis gave methanol, formaldehyde and a liquid boiling at 190–193°, but no 2-methoxyethanol. Since 2-(2-methoxyethoxy)-ethanol boils at 194°, the parent structure must have been that of II rather than the isomeric bis-(2-methoxyethoxy)-methane.

A series of fractions boiling higher than II was obtained, but there was no distinct plateau on the boiling point curve to signify isolation of a higher analog of I and II.

A preparative run in which the molar ratio of methylal to ethylene oxide was 3:1 gave a 53% yield of I and only 5% of II.

Anhydrous aluminum chloride, zinc chloride, calcium chloride and mercuric chloride were all insoluble in methylal and failed to catalyze its reaction with ethylene oxide. Methylal and ethylene oxide also yielded no adduct upon being heated overnight in sealed tubes at temperatures up to 200°.

Methylal and Propylene Oxide.—Methylal (912 g., 12 moles), boron trifluoride (17 g.) and propylene oxide (232 g., 4 moles) were caused to react as before. The major products comprised about 20 g. of material which was assumed to be dimethyldioxanes, a large fraction (III) boiling at 135–143° (744 mm.), and 195 g. of residue boiling above 195°. III, obtained in 330-g. (61%) yield, $n^{32}{}_{\mathrm{D}}$ 1.3902, $d^{32}{}_4$ 0.9182, was considered to be the expected mixture of 1-methoxymethoxy-2-methoxypropane and 1-methoxy-2-methoxymethoxypropane. No attempt was made to separate the isomers.

Anal. Calcd. for $C_6H_{14}O_3$: C, 53.71; H, 10.52; mol. wt., 134; *MR*, 34.84. Found: C, 53.73; H, 10.45; mol. wt.,[3] 131, 132; *MR*, 34.64.

Ethylal and Ethylene Oxide.—By the same method, 1560 g. (15 moles) of ethylal, 15 g. of boron trifluoride and 220 g. (5 moles) of ethylene oxide gave 364 g. (49%) of 1-(ethoxymethoxy)-2-ethoxyethane, b.p. 163–164° (746 mm.), $n^{32}{}_{\mathrm{D}}$ 1.3940, $d^{32}{}_4$ 0.8974.

Anal. Calcd. for $C_7H_{16}O_3$: C, 56.73; H, 10.88; mol. wt., 148; *MR*, 39.46. Found: C, 56.80; H, 10.78; mol. wt.,[3] 149, 150; *MR*, 39.37.

Dimethyl Acetal and Ethylene Oxide.—Dimethyl acetal (900 g., 10 moles), boron trifluoride (20 g.) and ethylene oxide (88 g., 2 moles) did not react so smoothly as usual, and the crude product fractions all contained hydroxyl compounds, presumably from hydrolysis. Treatment of the 130–155° fraction with excess metallic sodium and refractionation gave 69 g. (22%) of 1-(1-methoxyethoxy)-2-methoxyethane, b.p. 141° (746 mm.), $n^{32}{}_{\mathrm{D}}$ 1.3930, $d^{32}{}_4$ 0.9218.

Anal. Calcd. for $C_6H_{14}O_3$: C, 53.73; H, 10.52; mol. wt., 134; *MR*, 34.84. Found: C, 53.70; H, 10.41; mol. wt.,[3] 135, 136; *MR*, 34.75.

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[2] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3d ed., John Wiley and Sons, Inc., New York, N. Y., 1948.

[3] J. J. Hawkins and P. Arthur, *Anal. Chem.*, **23**, 533 (1951).

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Effect of Structure on the Polarographic Reduction of Iodo Compounds

BY EUGENE L. COLICHMAN[1] AND SHIH KUNG LIU[2]

RECEIVED SEPTEMBER 19, 1953

The presently reported investigation deals with the polarographic properties of twenty-nine different iodo compounds. Polarographic data have not appeared in the literature[3] on the majority of these compounds. Results are considered in terms of Hammett's[4] linear free-energy relationship between structure and reactivity. The abnormal and unique polarographic properties noted in some cases are appraised and compared with normal behavior. The criterion of normalcy is the quantitative relationship found between structure and susceptibility to polarographic reduction. Hammett's rho–sigma function[4] serves well in establishing this quantitative relationship.

Results and Discussion

Ortho or Proximity Effect.—It is apparent (Table I) that most substituents in the ortho position to the iodo group lead to abnormal half-wave potentials. The *proximity* phenomenon seems to facilitate the polarographic reduction of the iodo group whether the ortho substituent is *electropositive* or *electronegative*. *Ortho* or *proximity* effects are well known[4] in

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[1] North American Aviation, Inc., Atomic Energy Research Department, Downey, California.

[2] In partial fulfillment of the requirements for the Degree of Master of Science from the University of Portland.

[3] E. Gergely and T. Iredale, *J. Chem. Soc.*, **13**, 3502 (1951), have reported half-wave potential values for some of the iodo compounds under conditions different from those here.

[4] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1940, 1st Ed., Chap. VII, pp. 184–228.

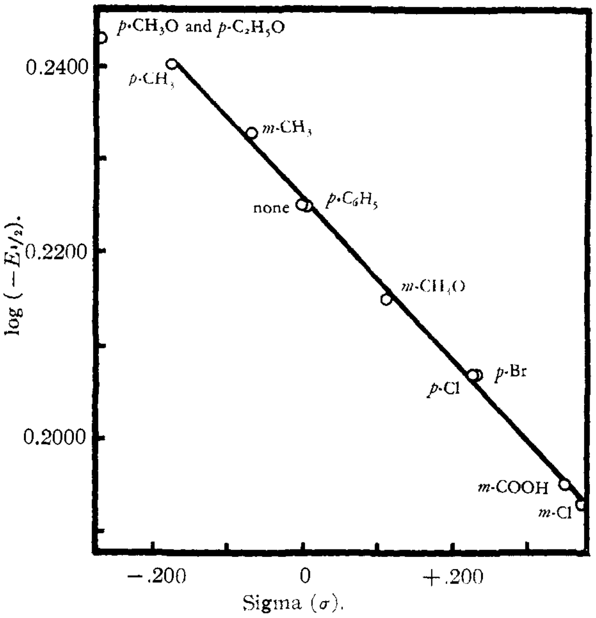

Fig. 1.—Linear relationship between half-wave potentials and Hammett's sigma substituent constants.

ordinary organic reaction kinetics involving covalent bonds. A previous conductance study[5] on substituted phenyl quaternary ammonium salts indicated a pronounced *ortho* or *proximity* effect for ion-pair formation (electrostatic bonding) in nonaqueous solutions. It is interesting to notice that these results[5] involving *coulombic* forces showed a negligible or small *ortho* effect for weakly polar groups such as methyl. An exactly analogous situation is found for the *o*-methyl group in the present polarographic reduction which undoubtedly involves *covalent* forces.

TABLE I

HALF-WAVE POTENTIALS OF THE VARIOUS IODO COMPOUNDS AT 0.001 *M* *vs.* S.C.E.

Iodo compound	$-E_{1/2}$	Iodo compound	$-E_{1/2}$
Iodobenzene	1.68	*o*-Iodobenzoic acid	1.47
o-Chloroiodobenzene	1.48	*m*-Iodobenzoic acid	1.57
m-Chloroiodobenzene	1.56	*p*-Iodobenzoic acid	1.57
p-Chloroiodobenzene	1.61	*o*-Iodobiphenyl	1.61
o-Bromoiodobenzene	1.50	*p*-Iodobiphenyl	1.68
p-Bromoiodobenzene	1.61	2-Iodo-1,3-dimethyl-	
o-Iodotoluene	1.70	benzene	1.75
m-Iodotoluene	1.71	2-Iodo-1,4-dimethyl-	
p-Iodotoluene	1.74	benzene	1.74
o-Iodoanisole	1.60	4-Iodo-1,3-dimethyl-	
m-Iodoanisole	1.64	benzene	1.74
p-Iodoanisole	1.75	*p*-Fluoroiodobenzene	0.72
o-Iodophenetole	1.64		1.66
p-Iodophenetole	1.75	α-Iodonaphthalene	1.62
o-Iodophenol	1.55	Iodocyclohexane	1.47
p-Iodoaniline	1.76	7-Iodo-8-hydroxy-	1.23[a]
p-Iodoacetanilide	1.66	quinoline-5-sulfonic	1.42
		acid	

[a] *First* wave apparently corresponds to quinoline linkage polarography since it shows much the same properties reported by P. C. Tompkins and C. L. A. Schmidt, *J. Biol. Chem.*, **143**, 643 (1942), for pyridine derivatives, namely: half-wave does not vary with concentration and slope analysis yields value near 0.059 corresponding to a *one* electron reversible reduction.

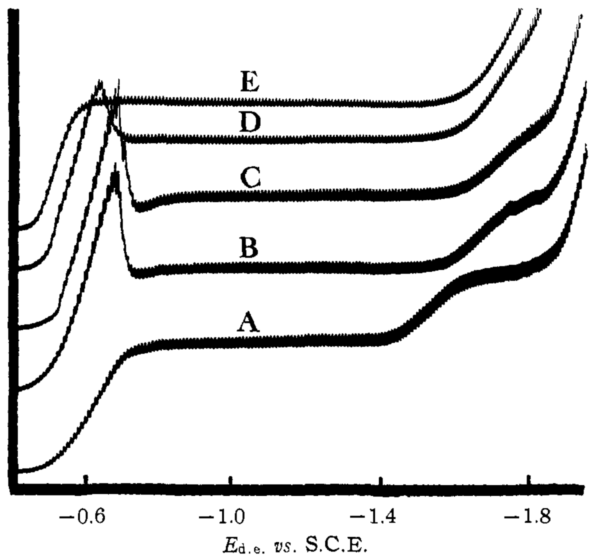

Fig. 2.—0.001 *M* nitroiodobenzenes in 50% alcohol buffer, *p*H 7.0 (0.05 *M* potassium dihydrogen phosphate and 0.006 *M* sodium hydroxide): A, *o*-NO$_2$; B, *m*-NO$_2$; C, *p*-NO$_2$; D, *p*-NO$_2$ with gelatin at 0.01%; E, *p*-NO$_2$ with gelatin at 0.03%.

Hammett Function.—It is seen (Fig. 1) that Hammett's rho–sigma function[4] $\log k - \log k^0 = \rho\sigma$ assumes the form $\log(-E_{1/2}) - \log(-E_{1/2}{}^0) = \rho\sigma$ in quantitatively describing the effect of structure on the polarographic reduction of various iodobenzenes. It does not follow by mathematical deduction that half-wave potential $(-E_{1/2})$ can be directly substituted for equilibrium or rate constant (k).

Hammett[4] previously cited two experimental studies showing that linear free-energy relationships can be found among ordinary reversible oxidation–reduction reactions.

Polarography of *p*-Fluoroiodobenzene.—Two approximately equal reduction waves were found (Table I) for *p*-fluoroiodobenzene. I_d/C values for waves *one* and *two* were: 4.80 and 4.50 μa./m*M*. A comparison of these similar diffusion current data with those found for the reduction of the iodo group in the other substituted iodobenzenes indicates that the stepwise reduction of *p*-fluoroiodobenzene occurs in *two* successive 2-electron processes. It was shown that fluorobenzene was not reducible at all under similar conditions. Apparently the fluoro group in *p*-fluoroiodobenzene exhibits unique behavior at the dropping mercury electrode. The I_d/C polarographic data cited above and the similarity of the second half-wave potential of *p*-fluoroiodobenzene with that of iodobenzene suggest[6] the following reduction mechanism

$$FC_6H_4I + 2H^+ + 2e = C_6H_5I + HF, (E_{1/2})_{0.001M} = -0.72 \text{ v.}$$

$$C_6H_5I + 2H^+ + 2e = C_6H_6 + HI, (E_{1/2})_{0.001M} = -1.66 \text{ v.}$$

The iodo group seemingly increases the reactivity

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[5] J. B. Ramsey and E. L. Colichman, THIS JOURNAL, **69**, 3041 (1947).

[6] Thanks are due Dr. S. Wawzonek for suggesting this explanation.

of fluorine so that this ordinarily non-reducible group becomes labile.

Anomalous Maximum Suppression.—Another manifestation of the ortho effect is seen in the different tendency toward maxima exhibited by *o*-nitroiodobenzene as compared to the corresponding meta and para isomers. As shown by the polarograms given in Fig. 2, both the meta and para derivatives yield large maxima while the ortho isomer shows no maximum at the same concentration.

Suppression of the polarographic maximum in the case of *p*-nitroiodobenzene (Fig. 2) yields a *smaller* negative half-wave potential than that obtained from the unsuppressed curve. Behavior in this case appears to be unique by comparison with the more negative half-wave potentials that are usually found[7,8] as a result of maxima suppression.

Experimental

The apparatus, accessories and polarographic characteristics were the same as described in previous communications from this Laboratory.[7,9] All measurements were made at 25.00 ± 0.05° and at a drop-time of 3.00 seconds.

All the iodo compounds investigated polarographically were Eastman Kodak Co. White Label grade with the exception of *m*-iodo- and *p*-iodoanisoles. *m*-Iodoanisole was synthesized by accepted procedure[10,11] from *m*-aminophenol (Eastman Kodak Co. Yellow Label grade). It boiled at 117° at 13 mm., b.p. reported[11] is 123° at 14 mm. *p*-Iodoanisole was prepared by the iodination[12] of anisole. The yield after recrystallization from ethanol was 57.5%, m.p. 50–51°. The reported m.p.[12] is 51–52°.

All iodo compounds were investigated polarographically in a 90% alcohol *p*H 7.00 buffer solution[13] containing 0.060 *M* lithium chloride, 0.024 *M* potassium acetate and 0.013 *M* acetic acid.

Methyl cellulose (1500 cps. viscosity) from Dow Chemical Co. was used as a suppressor and was maintained at a constant ratio of maximum suppressor to iodo compound equal to 5% per molarity. A recent investigation[7] showed the desirability of using a constant ratio of suppressor to reduction material in alcohol–water mixtures.

Acknowledgment.—The authors are indebted to the Research Corporation for supporting this work.

(7) E. L. Colichman, THIS JOURNAL, **74**, 722 (1952).

(8) E. L. Colichman, *ibid.*, **72**, 4036 (1950).

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(10) F. Reverdin and A. de Luc, *Ber.*, **47**, 1537 (1914).

(11) E. Votocek and J. Matejka, *ibid.*, **46**, 1755 (1913).

(12) F. F. Blicke and F. D. Smith, THIS JOURNAL, **50**, 1229 (1928).

(13) Measured with an ordinary Beckman *p*H meter, employing usual aqueous reference cell, thus is an effective *p*H value.

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Freezing Points of the System Water–Trifluoroacetic Acid

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Although trifluoroacetic acid is known to be miscible with water in all proportions and to behave as a strong acid, no report has been made of a systematic study of the system water–trifluoroacetic acid. The purpose of this note is to give the information about freezing points which is summarized in Fig. 1. Numerical data for the points indicated by letters in the figure are listed in Table I. The value observed for the melting point of the pure acid is a little lower than −15.25°, the temperature reported by Swarts.[1]

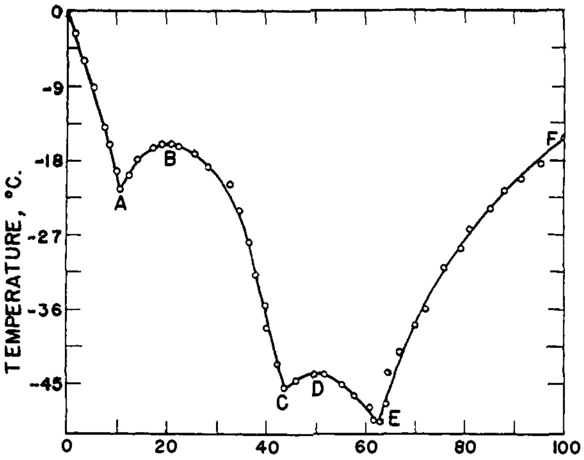

Fig. 1.—System CF_3COOH–H_2O.

TABLE I

Point	Nature of the point	Temp., °C.	Acid, mole %
A	Eutectic	−21.55	10.59
B	M.p. of $CF_3COOH \cdot 4H_2O$	−16.06	20.00
C	Eutectic	−45.51	43.9
D	M.p. of $CF_3COOH \cdot H_2O$	−43.73	50.0
E	Eutectic	−49.56	62.5
F	M.p. of CF_3COOH	−15.36	100.0

Data for the part of the system in which ice is the solid phase are given in Table II. Concentrations are in moles per 1000 g. of water.

TABLE II

m	Freezing temp., °C.	*m*	Freezing temp., °C.	*m*	Freezing temp., °C.
0.0878	−0.34	1.134	−3.75	3.949	−12.52
.1397	−0.50	1.603	−5.12	4.146	−13.20
.1832	−0.68	1.884	−6.00	4.381	−13.92
.2955	−1.03	2.300	−7.32	5.098	−16.10
.7206	−2.36	2.571	−8.20	5.997	−19.38
.8164	−2.70	2.929	−9.22	6.541	−21.53

Materials.—Trifluoroacetic acid was obtained from the Minnesota Mining and Manufacturing Co. Although the acid behaved as a material of high purity as obtained from the manufacturer, it was further purified by distillation. The center cut of the distillate was then frozen, and later as it slowly melted the liquid was drained away from the crystals. After about one third of the acid had been removed in this manner, the remaining solid was allowed to melt and subsequently was used for preparing solutions. The other component was distilled water. In this study no attempt was made to exclude atmospheric gases; therefore, the solutions must have been saturated with air.

Procedure.—Temperatures were measured with a precision of 0.01° using a copper–constantan thermocouple which was found to agree with the standard temperature scale for such a couple to within 0.05° at the sublimation temperature of carbon dioxide, the melting point of carbon tetrachloride, the melting point of ice and the boiling point of water.

Approximately 100 ml. of the solution to be frozen was placed in a 500-ml. wide mouth Dewar flask. As the liquid was stirred, it was partially frozen using as the refrigerant either liquid nitrogen or liquid oxygen held in a test-tube partially immersed in the solution. After all of the refriger-

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(1) F. Swarts, *Bull. soc. chim. Belg.*, **43**, 471 (1934).