[CONTRIBUTION FROM THE FURMAN CHEMICAL LABORATORY OF VANDERBILT UNIVERSITY]

The Effect of Substituents on the Polarographic Half-Wave Potentials of Benzophenones and Derivatives

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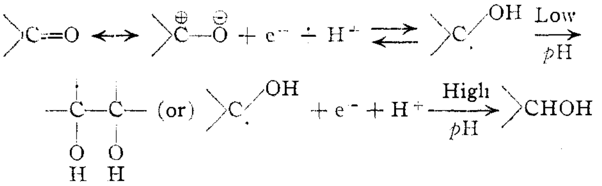
RECEIVED JANUARY 9, 1952

A plot of the half-wave potentials of substituted benzophenones in buffered acid solution *versus* Hammett's substituent constant, sigma, shows an essentially linear relationship, and the slope of the line indicates that electron-withdrawing groups favor reduction but only to a relatively small extent.

Though the literature on the polarography of carbonyl compounds is voluminous,[2] it is not possible to compare all results directly. The half-wave potential of the carbonyl group is not only dependent on the nature of the substituent but also on the pH, the buffer system, the supporting electrolyte, the ionic strength and the solvent as well as other less important factors. Shikata and Tachi[3] qualitatively conclude from a study of these data taken under variable conditions that organic carbonyl groups are more easily reduced (polarographically) as more electron-withdrawing groups are attached. It was the purpose of this study to determine polarographic reduction potentials of a number of related carbonyl groups under essentially identical conditions so that the above conclusions can be placed on a more quantitative basis.

The benzophenone series was selected for practical reasons and because of previous work[4] and knowledge available on the mechanism of reduction of benzophenone itself.[5] Pasternak[5] proposes the mechanism



Essentially, at low pH a one-electron reduction with the formation of a pinacol is involved, whereas, at high pH, a two-electron reduction takes place. Though the pinacol mechanism probably applies to the results of this investigation, Gardner[6] has indicated that both mechanisms are not sharply delineated.

Experimental

A manually operated polarograph, the "Elecdropode" (Fisher Scientific Company), was used with modifications consisting of a separate polarographic cell to facilitate temperature control, a 3.5 N calomel cell as a reference electrode, and a potentiometer (Leeds and Northrup Co., Model No. 7651) to determine the mercury pool potential to the nearest millivolt. The galvanometer was calibrated according to the method of Kolthoff and Lingane,[7] the galvanometer deflection units being converted to microamperes (1 unit = 0.018 microampere). With this apparatus, the half-wave potentials of zinc, cadmium and lead salts were determined with a precision of ±1 millivolt and in good agreement with the data in the published literature.[8] No correction was made for IR drop or junction potentials. At a mercury level of 38 cm., the capillaries were characterized as follows: Capillary A, m (mg./sec.) = 1.868; t (sec./drop) = 4.927; $m^{2/3}t^{1/6}$ = 1.979. Capillary B, m = 2.149; t = 4.057; $m^{2/3}t^{1/6}$ = 2.103.

The composition of the solutions for analysis was held constant thus fixing a number of variables. Stock solutions of 1 N sodium acetate–acetic acid, 1 N potassium chloride and of the ketones in absolute methanol were prepared. Prior to the determination, they were mixed so that the composition of the final solution was 0.1 N buffer, 0.1 N potassium chloride, 10^{-3} or 10^{-4} M ketone (depending on its solubility), 0.02 g. of gelatin per 100 ml. and 40 ml. of methanol per 100 ml. of solution. The apparent pH of the final solution was 5.20. At 40 ml. of methanol per 100 ml. of solution, variation in distance between the dropping mercury electrode and the mercury pool from 0.4 to 1.6 cm. had no effect on the half-wave potentials.

The ketones were synthesized by conventional methods (or purchased) and recrystallized from the appropriate solvent to constant (or very nearly constant) melting points (see Tables I and II). The procedure for polarographic analysis was as follows: the solution (prepared as above) was brought to 25 ± 0.1° by immersion in a thermostat and purged with a slow stream of oxygen-free and solvent-saturated nitrogen. The pool potential with respect to the reference electrode was measured, and the current–voltage relationship determined. The plot of $-E$ *vs.* i was analyzed to determine $E_{1/2}$, i_d and, in most instances, α, the apparent number of electrons transferred in the potential-determining step.[7,9] The results are given in Table I and illustrated in Fig. 1.

Discussion

It is concluded from these results that:

(1) The mechanism of Pasternak[5] is in accord with the present experimental data. At a fixed pH (5.2), the data indicate a potential-determining nucleophilic attack by the electron at the carbon atom site and that α is apparently 1.

(2) The generalization of Shikata and Tachi[3] is correct. Electron-withdrawing groups shift the half-wave potentials to less negative values. However, the substituent influence is weak (rho, the slope, is approximately +0.25 volt per Hammett unit).[10] This is usually the case for reactions dependent on hydrogen ion concentration.

(3) When more than one substituent is present in the molecule, the Hammett sigma values are

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[1] This paper was abstracted from the thesis submitted by R. W. Brockman to Vanderbilt University in 1951 in partial fulfillment of the requirements for the Ph.D. degree.

[2] Bibliography of Polarographic Literature, Leeds and Northrup Co., Philadelphia, Pa., 1950; E. H. Sargent Co., Chicago, Ill., 1946.

[3] M. Shikata and I. Tachi, *J. Chem. Soc. Japan*, **53**, 834 (1932); *Collection Czechoslov. Chem. Commun.*, **10**, 368 (1938); I. Tachi, *Mem. Coll. Agr. Kyoto Imp. Univ.*, **42**, 1 (1938).

[4] R. A. Day, Jr., and J. J. Kirkland, THIS JOURNAL, **72**, 2766 (1950).

[5] R. Pasternak, *Helv. Chim. Acta*, **31**, 753 (1948).

[6] H. J. Gardner, *Chemistry and Industry*, 819 (1951).

[7] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.

[8] I. M. Kolthoff and J. J. Lingane, *Chem. Revs.*, **24**, 1 (1939).

[9] Considerably more data and description of these determinations are available: R. W. Brockman, Ph.D. Thesis, "A Polarographic Study of Substituted Benzophenones and Derivatives," Vanderbilt University, 1951.

[10] A plot of $-E_{1/2}$ *vs.* sigma (Fig. 1) gives a negative slope. An alternate plot, $+E_{1/2}$ *vs.* sigma, provides for a comparison with Hammett's rho values and gives a line of positive slope.

TABLE I

POLAROGRAPHIC REDUCTION OF SUBSTITUTED BENZOPHENONES

Substituents	Sigma	$E_{1/2}$[b] (volts)	i_d[c]	$i_d/cm^{2/3}t^{1/6}$[f]	α[g]	Criterion of purity (m.p., °C., cor.)
4-Amino	−0.66	−1.161	5.71	2.72	1.08	123.2–124.0
4,4′-Dimethoxy	− .536[a]	−1.260	0.74[d,e]	..	..	144–145
4,4′-Dimethyl	− .340[a]	−1.187	5.01	2.53	0.68	93.5–94.2
4-Methoxy	− .268	−1.194	5.11	2.58	.90	61.0–61.5
4-*t*-Butyl	− .197	−1.166	0.60[d]	2.86	.95	B.p. 171 (3 mm.)[h] n^{22}D 1.5764[i]
4-Methyl	− .170	−1.165	5.03	2.54	.93	54–55
None	.00	−1.140	5.45	2.75	.96	48.1–48.3[4,5]
4-Chloro-4′-methyl	.057[a]	−1.102	0.81[d,e]	..	..	128.0–128.5
4-Chloro	.227	−1.093	5.19	2.62	1.00	76.0–76.1
4-Bromo	.232	−1.051	0.69[d]	3.28	1.18	81.6–82.3
3-Bromo	.391	−1.021	.66[d]	3.14	0.99	76–77
4,4′-Dichloro	.454[a]	−1.002	.48[d,e]	..	..	147–147.7[j]
3,3′-Dibromo	.782[a]	−0.913	.13[d,e]	..	..	139–140

[a] The sigma values of the two substituents are added together. [b] $E_{1/2}$ *vs.* 3.5 N calomel (average of at least three determinations); Hg pool potential *vs.* 3.5 N calomel 0.069 v. [c] 10^{-3} M ketone unless otherwise indicated. [d] 10^{-4} M ketone due to solubility considerations. [e] Some precipitation of ketone; concentration in solution not determined. [f] i_d in microamperes; c in millimoles/liter. [g] Determined from plot of $E_{d.e.}$ *vs.* log $i/i_d - i$. [h] Preparation from 4-*t*-butylbenzhydrol; m.p. 81.5–82°; E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 949 (1940). [i] Reported n^{25}D 1.5767; F. Bergmann and J. Szmuszkowicz, THIS JOURNAL, **70,** 2748 (1948). [j] Heyden Chemical Corporation.

TABLE II

POLAROGRAPHIC REDUCTION OF BENZOPHENONE DERIVATIVES

Derivative	Substituent	$E_{1/2}$[c] (volts)	i_d[d]	$i_d/cm^{2/3}t^{1/6}$[e]	α[f]	Criterion o purity (m.p., °C., cor.)
Semicarbazone[a]	None	−1.104	4.79	2.28	0.85	167–168
	α-4-Methoxy	−1.114	5.65	2.69	.84	178.5–179.5
	β-4-Methoxy	−1.117	5.62	2.60	.81	155–156
	α-4-Bromo	−1.048	5.45	2.60	.85	177–178
	β-4-Bromo	−1.050	5.23	2.49	.85	170.5–171.5
Oxime[b]	None	−0.983	9.76	4.65	..[g]	143.5–144
	α-4-Methoxy	− .973	10.02	4.77	..	147–149
	β-4-Methoxy	− .977	9.66	4.60	..	118–119
	α-4-Bromo	− .932	9.71	4.62	..	170–173
	β-4-Bromo	− .937	10.08	4.80	..	105–107.5
Hydrazone[h]	None	− .96	11.0	5.2	..	98.2–98.7

[a] Configuration of isomers determined [K. N. Carter, Ph.D. Thesis, Vanderbilt University (1951)]. [b] Configuration of isomers from the Beckmann rearrangement [J. Meisenheimer and W. Theilacker, "Stereochemie," ed. by K. Freudenberg, Vol. 3, Chap. 1, Edward Brothers, Ann Arbor, Mich., 1945]. [c] As in Table I. [d] 10^{-3} M benzophenone derivative. [e] As in Table I. [f] As in Table I. [g] α indeterminate since plot of $E_{d.e.}$ *vs.* log $i/i_d - i$ showed a variable slope and indicated an irreversible reduction. [h] Data approximate because of a maximum which was not suppressed by gelatin.

approximately additive (at least in the examples studied where few additional resonance states are brought into play). For example, sigma for the methyl group is −0.17, and sigma for 4,4′-dimethylbenzophenone was taken as −0.34.

(4) The amino group sigma value is not applicable under the conditions used. In the acid buffer, the electron-release ability of the basic amino group is undoubtedly diminished due to partial salt formation.

Several benzophenone derivatives, such as semicarbazones, oximes and hydrazones, were also included in this study. The results are given in Table II and illustrated in Fig. 1. It is concluded that the group influence is of even less importance in these series of derivatives and is certainly of no value in distinguishing *syn–anti* isomers.

Acknowledgment.—This work was made possible by a Frederick Gardner Cottrell Grant from the Research Corporation of New York to the senior author and by a U. S. Public Health Fellowship to the junior author for the year 1949–1950.

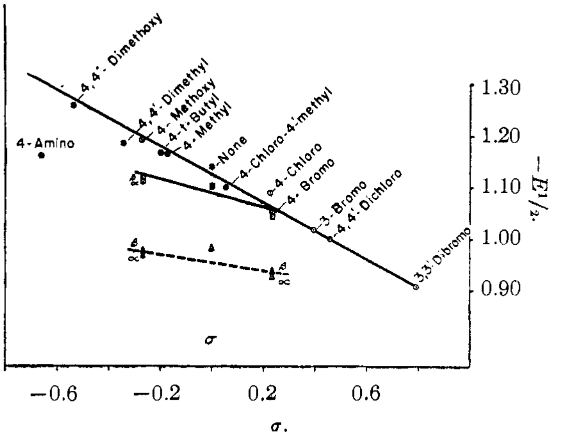

Fig. 1.—Half-wave potentials *versus* sigma: ⊙, benzophenones, substituents given; ⊡, benzophenone semicarbazones, substituents given by vertical line to benzophenone curve; △, benzophenone oximes.

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