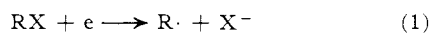# Acidity of Hydrocarbons. XIV. Polarographic Reduction of Substituted Benzyl Chlorides and Polycyclic Arylmethyl Chlorides[1]

BY ANDREW STREITWIESER, JR. AND CHARLES PERRIN[2]

Half-wave potentials for polarographic reduction of substituted benzyl chlorides and polycyclic arylmethyl chlorides in dimethylformamide are compared with the half-wave potential for benzyl chloride. A satisfactory Hammett σ–ρ plot is not obtained and the deviations are discussed in terms of radical-stabilizing effects of substituents. The results are compared with kinetic acidities of hydrocarbons with the help of molecular orbital theory. Polarographic reductions of halides are found to have only limited application as measures of carbanion stabilities.

Polarographic reduction of organic halides is usually considered in terms of the reactions[3]

$$RX + e \longrightarrow R\cdot + X^- \qquad (1)$$
$$R + e \longrightarrow R^- \qquad (2)$$
$$R^- + solvent \longrightarrow RH, or \qquad (3)$$
$$RX + 2e \longrightarrow R^- + X^- \qquad (4)$$

The reduction is irreversible; hence, the experimental half-wave potential does not have simple thermodynamic significance but involves the rate constant for some reaction proceeding at the electrode surface. This reaction has been likened to an SN2 displacement reaction at the rear of the carbon–halogen bond by the electron-rich mercury surface.[3,4] In the case of benzyl halides, evidence is at hand from controlled potential electrolyses for the involvement as intermediates of both radicals and anions: carbonation of the electrolysis solution of benzyl chloride produced a small yield of phenylacetic acid,[5] whereas 4,4'-dinitrobibenzyl has been isolated from the electrolysis of p-nitrobenzyl bromide.[6] In any event, the transition state for polarographic reduction may involve an electron-rich carbon and suggests the possibility that the half-wave potentials of a series of related benzyl halides may provide a simple measure of the relative stabilities of the related carbanions. Alternatively, bond-breaking or radical character may be a dominating influence at the transition state. We investigated these concepts by a study of the half-wave potentials of substituted benzyl chlorides and of polycyclic arylmethyl chlorides. The experimental changes in half-wave potential as a function of structure may be compared with Hammett σ-values; in addition, relative rates are available for hydrogen isotope exchange of substituted toluene-α-t's[7] and of polycyclic methylarene-α-d's[8] with lithium cyclohexylamide, reactions in which relative carbanion stabilities are involved.

All polarograms were run in dimethylformamide (DMF) containing 0.100 M tetraethylammonium

chloride as supporting electrolyte, a solvent system in which all substrates are sufficiently soluble. This solvent system does not produce the dip in the current voltage curve found for benzyl chloride in aqueous solution by Marple, Hummelstedt, and Rogers.[9] Arylmethyl chlorides were chosen to avoid the formation of organomercury compounds which complicate the polarography of benzyl iodide[5,10] and to reduce the possibility of solvolysis; no evidence of solvolysis was found. The use of chloride ion in the supporting electrolyte with an alkyl chloride also prevents the complication of halide displacement.[5]

Experimental

Instrumentation.—Current–potential curves were recorded with a Sargent Model XV polarograph. All potentials were measured with reference to a silver–silver chloride anode in 0.100 M tetraethylammonium chloride in DMF, separated from the cathode compartment by a sintered glass disk in an H-cell. The potential of the reference electrode was −0.360 v. vs. s.c.e., as measured with a Beckman Model G pH meter. The resistance of the cell was 2800 ± 100 ohms, as measured with an ESI impedance bridge; capillary characteristics: $h = 60.0$ cm., t_{max} 5.5 sec. (open circuit), $m = 1.31$ mg. mercury/sec.

Materials.—Dimethylformamide was technical grade, purified according to Leader and Gormley[11]: b.p. 151–152°. Tetraethylammonium chloride was Eastman White Label, recrystallized from ethanol–water and stored in vacuum desiccator until use. The residual current of solvent plus 0.1 M supporting electrolyte was sufficiently negligible compared to the substrate waves; reduction of the supporting electrolyte does not occur until potentials considerably more negative than those at which the substrates are reducible. House nitrogen, without further purification, was found adequate for deoxygenating the solutions.

Chloromethyl aromatics were either commercially available materials or compounds prepared previously in these laboratories.[8] Substituted benzyl chlorides were commercially available materials, purified when necessary, with the following exceptions: p-chloro, m-chloro, m-bromo, and m-methoxy were prepared from the corresponding acids by Mr. Steven Pulver. For each polarographic run, a fresh sample of p-methoxybenzyl chloride was prepared from anisyl alcohol (Eastman) by the method of Streitwieser and Langworthy[8] using thionyl chloride purified according to the method described by Fieser.[12] p-Methylthiobenzyl chloride was prepared in very poor yield by the Vilsmeier reaction[13] applied to thioanisole (Aldrich) followed by purification of the aldehyde as its bisulfite addition product, reduction[14] with lithium aluminum hydride, and conversion to the chloride with thionyl chloride.[8,12] p-Trifluoromethylbenzyl alcohol[15] was prepared from p-trifluoromethylbenzoyl chloride (Pierce Chemical

(1) This research was supported in part by a grant from the Petroleum Research Fund of the American Chemical Society and acknowledgment is made to the donors of this fund. Paper XIII: A. Streitwieser, Jr., W. M. Padgett, and I. Schwager, *J. Phys. Chem.*, **68**, 2922 (1964).

(2) National Science Foundation Postdoctoral Fellow, 1963.

(3) For example, see P. J. Elving, *Record Chem. Progr.*, **14**, 99 (1953), P. J. Elving and B. Pullman, "Advances in Chemical Physics," Vol. III, I. Prigogine, Ed., Interscience Publishers, Inc., New York, N. Y., 1961, p. 1.

(4) F. L. Lambert and K. Kobayashi, *J. Am. Chem. Soc.*, **82**, 5324 (1960).

(5) S. Wawzonek, R. C. Duty, and J. H. Wagen Knecht, *J. Electrochem. Soc.*, **111**, 74 (1964).

(6) G. Klopman, *Helv. Chim. Acta*, **44**, 1908 (1961).

(7) A. Streitwieser, Jr., and H. F. Koch, *J. Am. Chem. Soc.*, **86**, 404 (1964).

(8) A. Streitwieser, Jr., and W. C. Langworthy, *ibid.*, **85**, 1757 (1963).

(9) L. W. Marple, L. E. I. Hummelstedt, and L. B. Rogers, *J. Electrochem. Soc.*, **107**, 437 (1960).

(10) N. S. Hush and K. B. Oldham, *J. Electroanal. Chem.*, **6**, 34 (1963).

(11) G. R. Leader and J. F. Gormley, *J. Am. Chem. Soc.*, **73**, 5731 (1951).

(12) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., 1955, p. 345.

(13) M.-R. de Maheas, *Bull. soc. chim. France*, [5] 1989 (1962).

(14) E. L. Anderson and H. E. Reiff, U. S. Patent 2,989,539; *Chem. Abstr.*, **56**, 4773g (1962).

(15) H. B. Hass and M. L. Bender, *J. Am. Chem. Soc.*, **71**, 1767 (1949).
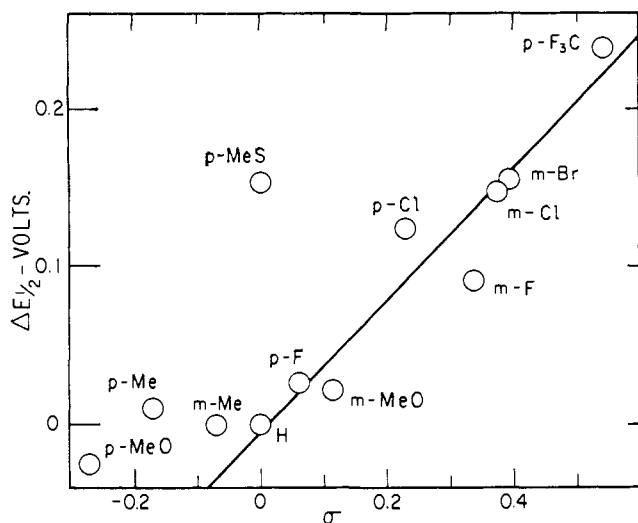
Fig. 1.—Comparison of the effect of substituents on the polarographic half-wave potential for reduction of benzyl chloride with Hammett σ-constants.

Co.) and excess $LiAlH_4$: b.p. 86° (8 mm.), m.p. 22–23.5°. This material was treated[8] with thionyl chloride to produce p-trifluoromethylbenzyl chloride: b.p. 61° (8 mm.), f.p. 19°, having satisfactory infrared and n.m.r. spectra.

Anal.[16] Calcd. for $C_8H_6ClF_3$: Cl, 18.2. Found: Cl, 17.85.

Experimental Procedure.—The half-wave potential of benzyl chloride was found to vary slightly with concentration, with a smaller variation at higher concentrations. Maxima were observed at concentrations greater than *ca.* 2 mM. Therefore, two solutions of each chloromethyl compound were prepared at concentrations bracketing 1 mM, and the value of $E_{1/2}$ at 1.00 mM was obtained by linear interpolation. All half-wave potentials of chloromethyl compounds are reported as the value at this somewhat arbitrary concentration. No surface-active agents were used. All measurements were made at 24 ± 1°.

The solution resistance of 2800 ohms causes, at substrate concentration of 1 mM, an IR drop of *ca.* 10 mv., a small correction which was applied to all half-wave potentials.

From replicate runs, the reproducibility in the differences of half-wave potentials of substituted halide and parent halide was not worse than ±10 mv., except for p-methyl, which varied by more than 20 mv. This value is taken as the limit of error of the results presented here. The half-wave potential of benzyl chloride was found to be −1.54 v. (*vs.* Ag–AgCl reference), although the variation from day to day was slightly greater than 10 mv. No maxima were observed for the compounds reported here, at the concentrations under consideration.

In preliminary work in this laboratory, Pulver had observed both no effect of benzyl chloride upon the electrocapillary curve of mercury in DMF and a half-order dependence of current on column height, results suggesting kinetic and diffusion control of half-wave potentials, rather than any adsorption effect.

Results

The value of αn_a, the product of the transfer coefficient and the number of electrons transferred in the rate-limiting electrode process (here one[3]), was found to be 0.22 from current–voltage curves of benzyl chloride, p-methoxybenzyl chloride, and p-methylthiobenzyl chloride, analyzed according to the method of Delahay.[17] However, the current–voltage curves were noticeably asymmetric, and, as a result, the plots of log $\lambda/t^{1/2}$ (Delahay's[17] parameter, λ; t = drop time) were not strictly linear. Thus, the value of αn_a, determined as the slope of this curve, should be considered as only approximate, especially so inasmuch as values of α are generally in the range from 0.3 to 0.7.

(16) Analysis by the Microanalytical Laboratory, University of California, Berkeley.

(17) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, p. 74ff.
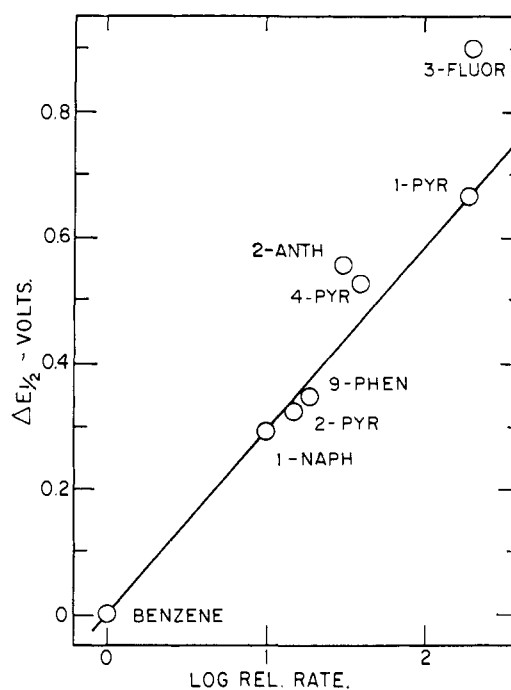

Fig. 2.—Comparison of relative half-wave potentials for reduction of polycyclic arylmethyl chlorides with relative exchange rates of the corresponding deuteriomethylarenes with lithium cyclohexylamide.

The polarographic half-wave potentials of substituted benzyl chlorides and chloromethylarenes are listed in Tables I and II, respectively. In the column headed $\Delta E_{1/2}$ are listed values of $E_{1/2}$ (substituted) − $E_{1/2}$ (benzyl chloride) For reference purposes relative rates[7,8] of deuterium or tritium exchange in the corresponding hydrogen compound are included. Figure 1 shows a plot of $\Delta E_{1/2}$ for substituted benzyl chlorides *vs.* Hammett σ-values; Fig. 2 shows a plot of $\Delta E_{1/2}$ for chloromethylarenes *vs.* the logarithm of the relative rate constant for hydrogen exchange in the corresponding methylarene.[8]

TABLE I

POLAROGRAPHIC REDUCTION OF SUBSTITUTED BENZYL CHLORIDES

Substituent	$\Delta E_{1/2}$,[a] v.	log k/k_0[b]
H	0.00	0.00
m-Br	.155	
m-Cl	.148	
p-Cl	.124	
m-F	.091	1.34
p-F	.026	−0.14
m-MeO	.021	0.32
p-MeO	− .025	−1.04
m-Me	− .001	−0.22
p-Me	.01	−0.51
p-MeS	.153	
p-F$_3$C	.238	2.25

[a] Similar results were obtained by Mr. S. Pulver in DMF with 0.1 M tetraethylammonium perchlorate as supporting electrolyte. [b] Relative rate of exchange of the toluene-α-t with lithium cyclohexylamide in cyclohexylamine at 50° (ref. 7).

Several compounds, including p-nitrobenzyl chloride, 8-chloromethylfluoranthene, and 3-chloromethylphenanthrene, produced double waves, with oddly shaped maxima, even at concentrations below 1 mM, and no half-wave potential is reported here for such compounds. Some other process, perhaps involving the

TABLE II

POLAROGRAPHIC REDUCTION OF CHLOROMETHYLARENES

Arene	Position	$\Delta E^{1}/_{2}$, v.	$\log k/k_0{}^a$
Benzene		0.00	0.00
Naphthalene	1	.292	1.01
Anthracene	2	.556	1.49
Phenanthrene	2	.250	
Phenanthrene	9	.348	1.28
Pyrene	1	.665	2.28
Pyrene	2	.324	1.18
Pyrene	4	.527	1.60
Fluoranthene	3	.90	(2.3)

^{a} Relative rate of exchange of the deuteriomethylarene with lithium cyclohexylamide in cyclohexylamine at 50° (ref. 8).

remainder of the aromatic system, may be occurring at the electrode.

Discussion

Substituted Benzyl Chlorides.—It is clear from Fig. 1 that the polarographic half-wave potentials for substituted benzyl chlorides do not give a satisfactory Hammett $\sigma-\rho$ correlation. Zuman[18] has made an extensive study of the application of the Hammett equation to polarographic half-wave potentials. In contrast to the present work, he found in the reductions of carbonyl compounds, iodobenzenes, nitrobenzenes, and azobenzenes, that the half-wave potentials give good Hammett correlations with positive reaction constants, ρ. He has attributed this behavior to the nucleophilic character of the electrode, whereby electron-withdrawing substituents facilitate reduction.
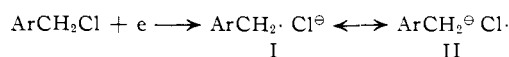
Previously, Klopman[6] investigated the polarographic reduction of several substituted benzyl bromides: p-methoxy, p-methyl, p-bromo, p-carbomethoxy, and p-nitro. He found that all of the substituents he studied shift the half-wave potentials to more positive values; that is, the Hammett $\sigma-\rho$ relationship is not followed, but all his substituents facilitate reduction of benzyl bromide at a dropping mercury electrode. Except for the effect of p-methoxy, our results with benzyl chloride are in qualitative agreement with his. From those substituents with a positive σ, it is possible to estimate a crude value of 1.45 for ρ in our case. This value has been calculated from the least-squares slope of $E_{1/2}$ vs. σ (drawn in Fig. 1), with a differential

$$\rho = \frac{d \log k_{h,f}}{d\sigma} = 2.303 \frac{\alpha n_a F}{RT} \frac{dE_{1/2}}{d\sigma} - \frac{d \log t^{1/2}}{d\sigma} \quad (5)$$

form of the equation recommended by Delahay[17] for relating half-wave potentials to electrode surface rate constants, subject to the assumption that all of the substrates have the same diffusion coefficient. Since the value for αn_a of 0.22 is only approximate, and perhaps but a lower bound, the magnitude of ρ is also subject to uncertainty, but its sign is undoubtedly positive.

Notice that this is expressed in the usual dimensionless form for ρ, rather than with the dimensions of volts, as reported by Zuman[18]. This value still reflects the facilitating effect of electron-attracting substituents, undoubtedly largely attributed to the nucleophilic character of the cathode, as pointed out by Zuman.[18] However, part of the polar effect may also arise from destabilization of the reactant as a

result of the electrostatic interaction of the substituent with the C–Cl bond dipole. However, the serious deviations in Fig. 1 emphasize that this picture is oversimplified. We propose, following eq. 1, that the transition state has free-radical character and that the stabilization of an odd electron by a substituent must be taken into account. In this view, it is useful to consider the transition state in terms of the resonance structures I and II

$$\text{ArCH}_2\text{Cl} + \text{e} \longrightarrow \text{ArCH}_2\cdot \text{ Cl}^{\ominus} \longleftrightarrow \text{ArCH}_2{}^{\ominus} \text{ Cl}\cdot$$
$$\text{I} \qquad\qquad\qquad \text{II}$$

The polar effect, as measured by σ, operates on II, but radical stabilization effects, which are not at all measured by σ, operate on I; that is, a substituent of modest polarity which can stabilize an odd electron can facilitate reduction by its stabilization of I. The methylthio group is a prime example and, indeed, was chosen in order to test this point. The σ-value of the p-CH$_3$S group is 0.00, but the radical-stabilizing effect of sulfide is well known.[19] Figure 1 shows the extreme deviation of this group from the $\sigma\rho$-correlation line. This greater ease of reduction is undoubtedly attributed to the significant contribution to I of structures such as III.

III	IV	V
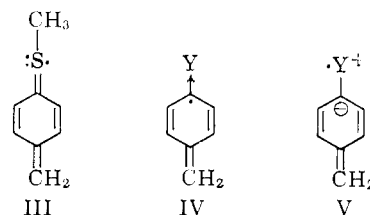
Although the radical character is shown clearly by the powerful effect of the thioether substituent, it should be noted that the same effect should exist to some extent with virtually all substituents relative to hydrogen; that is, all groups appear to stabilize a radical more than hydrogen[20] by resonance structures analogous to III or by IV and V.

We should, perhaps, use a modified form of the Hammett equation involving a more complex term, $\rho(\sigma + \lambda \sigma\cdot)$ in which $\sigma\cdot$ measures radical-stabilizing ability. A similar combination of $\sigma + \sigma^+$ is known to be very effective in handling resonance stabilization in reactions with carbonium ion character.[21] Unfortunately, suitable values for $\sigma\cdot$ are nonexistent. This approach, however, suggests that the slope for the polar effect in Fig. 1 may actually be more shallow. A slope defined by H, m-F, and m-OCH$_3$ does give $\rho \cong 0.8$.

More quantitative information on radical-stabilizing effects would be highly desirable. Many radical reactions such as radical abstractions have well recognized polar components which are difficult to dissect from the nonpolar radical contribution (vide infra). Radical-stabilizing effects should be reflected in bond strengths of substituted benzyl halides or toluenes. The available values for C–Br bond strengths in benzyl bromides indicate that all substituents facilitate

(18) P. Zuman, Collection Czech. Chem. Commun., 25, 3225 (1960).

(19) W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw–Hill Book Co., Inc., New York, N. Y., 1962, p. 37.
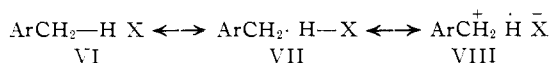
(20) We need only recall, for example, the relative ease of free-radical polymerization of vinyl esters, vinyl halides, and vinyl ethers compared to ethylene, the relative stabilities of methyl, ethyl, isopropyl, t-butyl radicals, etc.

(21) Y. Yukawa and Y. Tsuno, Bull. Chem. Soc., Japan, 32, 971 (1959).

homolytic bond breaking, but the magnitude of the effect is comparable to the experimental errors.[22] Moreover, these data do not reflect only radical stabilities, but also involve the electrostatic interaction of the substituent with the C–Br bond dipole. A possible approach is the elimination of the polar effect by a study of substituent effects on anodic polarography, in a fashion similar to that of Taft[23] for the separation of polar effects. Anodic polarography of a suitable set of substituted benzyl compounds, in which there is a cationic leaving group (substituted benzylmercuric acetates or benzylboronic acids may be suggested), should afford a negative value of ρ.[24] The extent to which a substituent lies above both σ–ρ plots would then represent the radical-stabilizing power of a substituent, with the polar effect eliminated.

Finally, these results raise the question of radical stabilization in substituent effects on rates of radical abstraction reactions from substituted toluenes and phenols. Such results have been collected recently by Howard and Ingold.[25] All of their examples follow a Hammett-type equation with negative ρ. However, they find that many of the reactions are better correlated with σ^+, and explain this behavior on the basis of a significant contribution of the polar structure VIII to the transition state, induced by the high electronegativity of the attacking radical, X·

$$\text{ArCH}_2\text{--H} \; X \longleftrightarrow \text{ArCH}_2\cdot \; H\text{--}X \longleftrightarrow \text{Ar}\overset{+}{\text{C}}\text{H}_2 \; H \; \overset{-}{X}$$
$$\text{VI} \qquad\qquad \text{VII} \qquad\qquad \text{VIII}$$

The contribution of VIII may well be significant in many cases, but the variability of the correlation, being better sometimes with σ and other times with σ^+, suggests the contribution of VIII is not so important as a correlation with σ^+ may suggest but that VII also plays a significant role. Usually, a correlation with σ^+ appears better because the p-methoxy and p-methyl substituents exert a more marked accelerating effect (on reactions with negative ρ) than would be expected on the basis of their σ-values. Yet, on the basis of radical-stabilizing ability alone, p-methoxy and p-methyl could accelerate the reaction via a contribution by VII. The unique aspect of our polarographic system is that it proceeds with a *positive* ρ, and permits us to recognize the radical-stabilizing effect of p-methoxy and p-methyl without the possibility of attributing the effect to a σ^+ correlation. In a similar example, substituent effects in the concerted decomposition of t-butyl phenylperacetates have been correlated with σ^+,[26] but the point for the p-nitro group lies above the correlation line. Bartlett and Rüchardt have suggested that the p-nitro group has an additional resonance effect, stabilizing a benzyl radical, even though this effect is insufficient to overcome the polar effect. But this radical-stabilizing effect should not be limited to p-nitro, but should be exerted by all substituents, although to a lesser extent. There is unquestionably a polar effect operative, but it is not obvious that σ^+ is the appropriate measure of that

effect, inasmuch as there must also be radical-stabilizing effects which are related to σ or σ^+ in a more complicated fashion. It would seem that previous workers have tried to fit rates of radical reactions to either σ or σ^+, without regard to the nature of the effect of a substituent on benzyl radical stabilities, independent of the polar effect. The present results suggest, for example, the prediction that t-butyl p-methylthiophenylperacetate should decompose more rapidly than t-butyl p-methoxyphenylperacetate, although adherence to σ^+ requires the reverse prediction.

Chloromethylarenes.—In the above discussion, a poor correlation of half-wave potentials with σ was attributed to the special requirements of a transition state which strikes a balance between radical and anion character. In contrast, the kinetic acidities of substituted toluenes correlate well with σ-values.[7] We conclude that the polarographic method has but limited application to the experimental evaluation of carbanion stabilities. It is noteworthy, therefore, that the polarographic half-wave potentials of chloromethylarenes correlate reasonably well with the kinetic acidities of the corresponding methylarenes, with the exception of the nonalternant fluoranthene system, and, to a lesser extent, the anthracene system. This correlation, however, is less surprising when we recall that the exchange rates of the hydrocarbons correlate satisfactorily with Hückel MO calculations in which the corresponding arylmethyl anions are taken as models of the exchange transition states.[27] The transition state of the exchange reaction is taken as an odd alternant anion, whereas the transition state for the polarographic reduction of the corresponding arylmethyl chloride is similar to an odd alternant radical. These models differ by only a single electron in a nonbonding molecular orbital and correspond, in the Hückel approximation, to the same energy change. Hence, in HMO theory, energy differences in the two series should parallel each other and a correlation as in Fig. 2 should result. The nonalternant fluoranthene system should not be expected to fit this correlation, since the distinguishing electron is now in a bonding orbital. It should be mentioned, however, that the exchange rate for 3-methylfluoranthene-α-d is subject to substantial uncertainty.[8]

A surprising feature of the correlation is that benzyl and α-naphthyl functions fit the same correlation in Fig. 2. The dispersion of the kinetic acidities into two lines characteristic of these steric types in the correlation with HMO calculations[27] implies a like dispersion for plots of $\Delta E_{1/2}$ vs. HMO calculations. This result may mean that the steric requirements of the two processes are similar. It is also unusual that the polarographic reduction should reproduce the reactivity of 2-pyrenylmethyl systems, enhanced over what would be predicted by HMO calculations. To the extent that the transition state for polarographic reduction is an arylmethyl radical, the ω-technique cannot improve the correlation of polarographic half-wave potentials with HMO calculations, so another explanation must be sought.[27]

Acknowledgment.—We are indebted to Mr. Steven Pulver and Dr. Irving Schwager for important preliminary experiments.

(22) M. Szwarc, C. H. Leigh, and A. H. Sehon, *J. Chem. Phys.*, **19**, 657 (1951).

(23) R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 556.

(24) The positive values of α found by Zuman[18] for anodic polarography may be attributed to the superposition of protonation effects.

(25) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744 (1963).

(26) P. D. Bartlett and C. Rüchardt, *J. Am. Chem. Soc.*, **82**, 1756 (1960).

(27) A. Streitwieser, Jr., W. C. Langworthy, and J. I. Brauman, *J. Am. Chem. Soc.*, **85**, 1761 (1963).

Appendix

The radical-stabilizing ability of all substituents may be understood in terms of a crude Hückel MO model. The substituted benzyl radical will be approximated by $\ddot{X}$-$CH_2\cdot$ or Y-$CH_2\cdot$. More realistic models, a benzyl radical with either a changed Coulomb integral for the *para* carbon or a *para* substituent which contributes an extra π-orbital to the system, treated by second-order perturbation methods, lead to similar results. The parameters for an electron-donating substituent, X, are $\alpha_X = \alpha_0 + h\beta_0$, $\beta_{CX} = k\beta_0$, with the substituent contributing two π-electrons. The parameters for an electron-withdrawing substituent, Y, are $\alpha_Y = \alpha_0 - h\beta_0$, $\beta_{CY} = k\beta_0$, with the substituent contributing a vacant p-orbital. As defined here, $h \geqslant 0$ and $k > 0$. In Table III, we compare the change in π-energy (D.E.) for the bonding of both types of substituents with a carbonium ion, radical, and carbanion carbon. For parameters as defined, the electron-donating substituent always stabilizes a carbonium ion and the electron-withdrawing group stabilizes an anion, but both types of groups stabilize a radical by an amount $(-h + [h^2 + 4k^2]^{1/2})/2$. Of course, this model does not allow for electron-repulsion effects nor does it allow for the use of an empty d-orbital of an electron-donating substituent in addition to its filled p-orbital, a factor which is undoubtedly responsible for placing the methylthio group so far off a correlation diagram which considers only polar effects. This crude model should not be pushed so far as to require a V-shaped or parabolic σ–ρ plot for radical reactions (although Klopman's[6] is quite close to parabolic, and the relative reactivities[28] of substituted styrenes in copolymerization, to produce a substituted benzyl radical, correlate with σ to exhibit a slight, but noticeable, upward curvature), but is intended to suggest that an apparent correlation with σ^+ may result, not necessarily only because of a resemblance of the transition state to a benzyl cation, but also because of the special nature of substituent effects on benzyl radical stabilities.

TABLE III

SUBSTITUENT EFFECTS ON HMO DELOCALIZATION ENERGIES

	Electron-donating			Electron-withdrawing	
n_π	System	D.E./β	n_π	System	D.E./β
2	Cation	$-h + \sqrt{h^2 + 4k^2}$	0	Cation	0
3	Radical	$(-h + \sqrt{h^2 + 4k^2})/2$	1	Radical	$(-h + \sqrt{h^2 + 4k^2})/2$
4	Anion	0	2	Anion	$-h + \sqrt{h^2 + 4k^2}$

(28) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Fig. 4.9, p. 137.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF TEXAS A&M UNIVERSITY, COLLEGE STATION, TEXAS]

The Correlation of the Electronic Spectra and Acidity of 5-Substituted 2-Nitrophenols with Structure

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The electronic spectra and pK_A's of a series of 5-substituted 2-nitrophenols (I) have been measured and compared with corresponding data previously reported (ref. 6) for a series of 4-substituted 2-nitrophenols (II). For each series, there is a good correlation between pK_A and Hammett's σ; however, the ρ-value of -3.01 for I is much more negative than that of -2.16 for II. Whereas, for II, satisfactory correlations were found for $\Delta\nu$ vs. pK_A, ν_B vs. σ_p^+, and ν_A vs. σ_p^+, the corresponding correlations for I are unsatisfactory [$\nu_B = (1/\lambda_{max}^{NaOH}) \times 10^7$, $\nu_A = (1/\lambda_{max}^{HCl}) \times 10^7$, $\Delta\nu = \nu_B - \nu_A$]. For both series, there are good correlations between ν_B and ν_A. A good correlation between $\Delta\nu$ and σ_p^+ exists for II, but no satisfactory linear relationship for I could be found between $\Delta\nu$ and any pertinent set of substituent constants. However, good correlations exist between $\Delta\nu_A^*$ and $(\sigma_p^\pm - \sigma_m)$ and between $\Delta\nu_B^*$ and $(\sigma_p^\pm - \sigma_m)$, where $\Delta\nu_A^*$ is ν_A for a I minus ν_A for the corresponding II, $\Delta\nu_B^*$ is ν_B for a I minus ν_B for the corresponding II, and $\sigma_p^\pm$ is the applicable σ_p^+ or σ_p^- value. It is proposed that the quantity $(\sigma_p^= - \sigma_m)$ is an approximate measure of the maximum resonance contribution that a substituent may make in either a 4- or a 5-substituted 2-nitrophenol. All of the above relationships are discussed.

Introduction

Recently, it has been shown[2,3] for the 2,4-dinitrophenylhydrazones of carbonyl compounds that $\Delta\nu$, the wave number shift in basic solution, can be correlated with the substituent constants of Hammett[4a] or Taft.[5] Also, it has been shown[6] that certain aspects of the electronic spectra of 4-substituted 2-nitrophenols conform to Hammett[7] relationships. These observations indicate that the effects of substituents on chemical reactivity and on electronic spectra are similar.

The purpose of the present article is to report and comment upon the results produced by moving the variable substituent from the 4-position of 4-substituted 2-nitrophenols to the 5-position of 5-substituted 2-nitrophenols, while maintaining all other conditions as similar as possible to those for the former series. These two series of substituted 2-nitrophenols are appropriate for this study since the nitro group: (1) ensures that the pertinent electronic spectra will appear in the visible or near-ultraviolet region; (2) chelates with the hydroxy group, thereby suppressing molecular association; and (3) is sufficiently removed from the 4- or 5-substituent that no steric interaction occurs.

Results and Discussion

The pK_A's and absorption spectra of a series of 5-substituted 2-nitrophenols have been measured and the re-

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