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CORRELATION OF POLAROGRAPHIC HALF-WAVE POTENTIALS WITH
NUCLEAR MAGNETIC RESONANCE "CHEMICAL SHIFTS".

PARALLEL CORRELATION WITH CHEMICAL REACTIVITY PARAMETERS

by

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Correlation of Polarographic Half-wave Potentials with
Nuclear Magnetic Resonance "Chemical Shifts".

Parallel Correlation with Chemical Reactivity Parameters

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ABSTRACT

Since nuclear magnetic resonance "chemical shifts" are considered to be good measures of electron densities in molecules, the extent to which they can be correlated with the polarographic half-wave potentials of organic compounds has been surveyed. Linear relationships were obtained, e.g., for the lower aliphatic aldehydes, for the ethyl esters of 2-bromoalkanoic acids, and for meta and para substituted benzaldehydes, iodobenzenes and nitrobenzenes; the correlation for ortho substituted nitrobenzenes is good for certain substituents but not for others; non-linear results were obtained for aliphatic nitro compounds. To extend the applicability and interpretation of the proposed correlation, parallel correlation of $E_{1/2}$ with Hammett's σ and Taft's σ^* parameters were made, since both of the latter are also regarded as indication of electronic distribution at the reactive center. The data in general support the view that changes in half-wave potential with structure are due to both electronic and steric effects, as well as perhaps to adsorption

phenomena. Significantly, NMR data obtained with one type of substituent could be correlated with $E_{\frac{1}{2}}$ data for a similar type of substituent. New NMR data for aliphatic nitro and halogen compounds are reported.

A number of qualitative and semiquantitative methods have been described for correlating the polarographic half-wave potentials of organic compounds with their structure (1-3). The purpose of the present study is to examine and to extend the correlation of irreversible polarographic processes for organic compounds with chemical reaction parameters and to consider the extent to which half-wave potentials can be correlated with nuclear magnetic resonance "chemical shifts".

In order to obtain a valid basis for examining such correlations, it is first necessary to make explicit the physical basis for the three types of data to be considered and the implications involved in attempting to formulate correlations.

Nature of the polarographic half-wave potential. - The half-wave potential, $E_{\frac{1}{2}}$, of a reversible electrode reaction is related to the free energy change of the reaction and therefore can be related to the standard electrode potential, E° (4,5). For the reversible electrode reaction,



$E_{\frac{1}{2}}$ is expressible by the equation

$$E_{\frac{1}{2}} = E^\circ - \frac{RT}{nF} \ln \left(\frac{f_R}{f_0} \right) \left(\frac{D_0}{D_R} \right)^{\frac{1}{2}} \quad (2)$$

where f_0 and f_R , and D_0 and D_R are the activity coefficients and diffusion constants of the substances O and R, respectively.

The significance of $E_{\frac{1}{2}}$ for irreversible processes was first developed by Eyring, Marker and Kwoh (6), who applied absolute rate theory to the polarographic problem. Their ideas were extended by Delahay, Koutecky, Tachi, Lai-

tinen and others (7). The fundamental concept is that the characteristics of an irreversible polarographic wave are determined by both the rate of diffusion and the rate of electrochemical reaction. For an irreversible electrode reaction of the type shown in equation 1 and involving one rate-determining step, the following equation obtains (8),

$$E_{\frac{1}{2}} = \frac{R T}{\alpha n_a F} \ln \frac{k_{f,h}^o}{\lambda_{\frac{1}{2}} D_0^{\frac{1}{2}}} + \frac{R T}{2 \alpha n_a F} \ln t$$

where $\lambda_{\frac{1}{2}}$ is a constant, α is the transfer coefficient of the forward electrode process and n_a is the number of electrons involved in the activation step, $k_{f,h}^o$ is the rate constant for the forward electrode process, and t the drop-time.

Accordingly, $E_{\frac{1}{2}}$ for an irreversible reaction depends on the factors, t , D_0 , $k_{f,h}^o$ and αn_a , which must all be considered in $E_{\frac{1}{2}}$ correlations. However, in correlating $E_{\frac{1}{2}}$ with structure for a series of compounds having the same type of reducible center and under conditions where the temperature, drop-time and diffusion coefficient are relatively constant, the variation in $E_{\frac{1}{2}}$ from one compound to another depends primarily upon variations in $k_{f,h}^o$ and αn_a . For compounds of very similar structure, αn_a is generally constant. Therefore, for an irreversible electrode reaction involving one rate-determining step, it is the value of $k_{f,h}^o$, which is significant (9).

Effect of rate constant and structure on $E_{\frac{1}{2}}$. - Polarograms for reversible and irreversible reactions are compared in Fig. 1. The "reversible" wave results when electrochemical equilibrium is achieved at the electrode. The second, more drawn-out "irreversible" wave results from a slow electron-transfer reaction at the lower part of the curve; as the potential is made more cathodic, the rate of the latter reaction increases and a greater current is observed, until, at the upper plateau of the wave, the current is diffusion controlled. Thus, the shift in $E_{\frac{1}{2}}$ is related to the rate of the electrochemical reaction, i.e., for

a series of compounds having the same reducible center, in which the rate constant mainly controls the $E_{\frac{1}{2}}$, a series of polarograms would be obtained having different half-wave potentials.

Since this rate constant (measure of the rate of electron transfer) is presumably related to the free energy of activation of the electrode reaction, reaction rates could be predicted if adequate information about the structure of the reactant, transition states, and product were available (10, 11). Unfortunately, our meager information concerning the structures and energies of these states does not readily permit such calculation.

Correlations based on electron density. - An alternative solution to the problem just indicated is based on the fact that changes in reactivity have been found to be frequently related to the electron distribution in the molecules concerned (11). Predictions of reactivities from electron densities frequently parallel predictions made from considerations of the structure or calculations of the energy of the transition state (12). Calculations of electron density changes based on molecular orbital theory have been used in correlating reactivity with structure as well as in correlating half-wave potentials (1-3).

Since changes in electron distribution induced by substituents in a given type of molecule appear to produce changes in $E_{\frac{1}{2}}$, it would be helpful to have an experimental means of readily measuring electron distribution changes. Such a method is available in measurement of nuclear magnetic resonance "chemical shifts" (13-16).

Essentially all types of polarographically electroactive molecules are amenable to NMR investigation. However, since $E_{\frac{1}{2}}$ primarily represents some measure of electron distribution about the reducible group, the NMR measurement selected must also be a measure of electron distribution at or near the reducible group. Table I lists several types of compounds applicable to scrutiny by both techniques.

Nuclear magnetic resonance. - In nuclear magnetic resonance (NMR) measurements a strong magnetic field is used to align the nuclear magnets and to induce them to precess at a characteristic frequency. A radio frequency signal is applied at right angles to the magnetic field and either the energy absorbed by the precessing nuclei or their inductive RF signal is measured as a function of the magnetic field strength. The basic precession frequency is given by

$$\omega = \gamma H \quad (4)$$

where ω is the Larmor precession frequency, γ is the gyromagnetic ratio and a constant for the nucleus, and H is the magnetic field strength. Since the electron structure of the molecule under study and the fields from neighboring molecules influence the magnetic field at the site of the nucleus, it is more nearly accurate to describe the resonance condition by the equation

$$\omega = \gamma (H_{\text{applied}} + H_{\text{local}}) \quad (5)$$

H_{local} is determined almost entirely by neighboring functional groups and the data obtained are indicative of the chemical structure of the compounds present. The difference in resonance frequency produced by differences in H_{local} are called "chemical shifts."

Displacement of the resonance lines from the same nucleus have been observed in different chemical compounds or on different atoms of the same compounds (13-15, 17-19). The explanation of this "chemical shift" is related to the electrons which circulate about the nucleus. The motion of these electrons interact with the applied magnetic field and thereby contribute a component to the net magnetic field at the nucleus.

For H^1 and F^{19} resonance, "chemical shifts" are generally considered as a measure of electron density changes (diamagnetic parameter) at a nucleus in a molecule, although a small second order paramagnetic resonance parameter does exist (17-18).

Since both $E_{\frac{1}{2}}$ and NMR shielding values are related to electron distribution

changes, it seemed highly desirable to investigate the extent of correlation of the two types of data for a variety of organic compounds.

Hammett relation. - In order to extend the examination, potential usefulness and interpretation of the proposed correlation, the Hammett σ and Taft σ^* parameters which have previously been correlated with NMR chemical shifts (15, 16, 20) and with E_{12} values (1-3) were also compared.

Hammett (21) found that within a reaction series of meta and para substituted benzene derivatives, the effect of structure on reaction rates and equilibria is nearly always determined by a single basic factor: the polar effect of the substituent. In these meta and para derivatives, substituents are rigidly held at large distances from the reaction center so that no change in steric interactions occurs between the reactant and the transition state (in the rate case) or the product state (in the equilibrium case). Generally no change in the reaction mechanism occurs within a given reaction series. The substituents thus produce free-energy changes due to one or the combination of the inductive, resonance and kinetic-energy type polar effects. Hammett's fundamental relation is

$$\log \left(\frac{k}{k_0} \text{ or } \frac{K}{K_0} \right) = \sigma \rho \quad (6)$$

where

k , K = rate or equilibrium constant for a given meta or para benzene derivative
 k_0 , K_0 = rate or equilibrium constant for the unsubstituted compound

σ = polar substituent constant, independent of the nature of the reaction
and obtained from the ionization constants of benzoic acid derivatives.

ρ = porportionality constant, dependent upon the reaction and conditions.

Taft (22) has extended the linear correlation of polar effects to aliphatic compounds and ortho benzene derivatives on the basis that, in the hydrolysis of

aliphatic esters and ortho benzoates, the transition state is the same whether the reaction is acid or base catalyzed. Thus, the steric factors incident to activation should be the same in both cases, and the ratio of hydrolysis rates in acid and in base should be a function of polar factors alone. This idea is contained in the equation

$$(\log k/k_o)_B - (\log k/k_o)_A = \sigma^* (\sigma_B - \sigma_A) \quad (7)$$

where B represents base catalyzed and A acid catalyzed hydrolysis. The values of σ^* so obtained correlate data in the expression

$$P_{\sigma^*} = \sigma^* \sigma^*$$

where P_{σ^*} is any reaction parameter having the dimensions of energy.

For the purpose of the present paper, Hammett and Taft σ and σ^* substituent values will be considered as measures of electron distribution changes in molecules, as will also be the NMR δ parameter.

Experimental Data

Table II summarizes the scope of the data considered in the present study. Polarographic half-wave potentials of both aliphatic and aromatic aldehydes, nitro compounds, and halogen compounds are compared with NMR measurements of either proton or fluorine resonance shifts, and with the Hammett and Taft reactivity equations.

The nuclear magnetic shielding parameter, δ , (as used in this paper) is defined as $10^5 (H_r - H_c)/H_r$, where H_c is the applied magnetic field for the F^{19} or H^1 resonance in the given fluorobenzene or proton-containing compound and H_r is that for the reference, fluorobenzene or water. The NMR data for the aliphatic nitro and halogen compounds (Table III) is new information obtained for the authors in the laboratory of Varian Associates; the experimental procedure has been described (13).

The formaldehyde δ value was obtained from an aqueous formalin solution (40% HCHO by weight). The protons of water and formaldehyde exchange so rapidly that there is only one resonance line; by assuming a simple exchange and no difference in the δ value of the individual molecules from what they are in the pure state (23), Gutowsky (17) calculated the formadehyde value using the δ values for water and the formalin solution and the mole fractions of each component in solution. All other NMR data are taken from the literature with the probable error for each individual δ value being about ± 0.03 δ unit (14, 15). The measurements made at Varian Associates could be duplicated to about ± 0.003 δ unit; however, bulk diamagnetic susceptibility corrections increase the uncertainty about five-fold for a given series of compounds.

The half-wave potential, defined as the potential on the polarographic wave where the current is equal to one-half its limiting value, has a probable error of approximately ± 0.005 v. A more negative $E_{\frac{1}{2}}$ value indicates more difficult reduction and a more negative δ value represents an increase in electron density.

The $E_{\frac{1}{2}}$ data, selected from published literature, were so chosen as to minimize polarizability effects of pH and background electrolyte on the electron distribution in the various types of compounds, e.g., $E_{\frac{1}{2}}$ data for the aliphatic nitro compounds are those in 0.05 M H_2SO_4 solution; data in neutral or alkaline solution would be complicated by non-reducible aci formation. $E_{\frac{1}{2}}$ data for the chloro and bromo esters are those at 0°C in acidic solution (0.5 M KCl-HCl, pH about 1.0) in order to prevent hydrolysis. The data for the aliphatic aldehydes were obtained in alkaline solution, minimizing the effect of hydrate formation which complicates interpretation of polarographic data of aldehydes in acidic solution.

The $E_{\frac{1}{2}}$ values for the substituted iodobenzenes, nitrobenzenes, and benzaldehydes were obtained in neutral solution (0.01 M tetraethylammonium bromide

in 66% alcohol) and are considered to be more representative than data in acidic or alkaline solution, where substituents such as NH_2 , OH and COOH could be ionized; the ionized substituent would have an electron distribution different than that obtained with the Hammett, Taft, or NMR data.

The σ and σ^* data were obtained from the literature (11, 21, 22) or were calculated.

Correlation of Aliphatic Organic Compounds

The correlations of $E_{\frac{1}{2}}$ for a series of aliphatic aldehydes with the NMR \int values of the proton in the aldehyde group and σ^* values (Fig. 2) are surprisingly good. (The groups indicated on the graph are the R substituents in the RCHO aldehyde, i.e., H represents formaldehyde CH_3 , acetaldehyde, etc.) In instances such as this where \int and σ^* both correlate with $E_{\frac{1}{2}}$, changes in all three parameters are probably measuring changes in electron distribution in the molecule.

Similar correlations for ethyl esters of three 2-bromoalkanoic acids (Fig. 3) are also quite good. Addition of longer alkyl substituents would probably not produce changes in electron distribution about the C-Br bond, although $E_{\frac{1}{2}}$ is known to continue to change with such variation (24). The latter $E_{\frac{1}{2}}$ changes are perhaps due to factors other than electron distribution changes.

In the case of the aliphatic nitro compounds (Fig. 4), the plots are not linear although the \int and σ^* parameters do follow the same distribution pattern, suggesting that the NMR \int function and the σ^* function are measuring related phenomena, and that the $E_{\frac{1}{2}}$ data are measuring more than only electron distribution changes.

Correlation of Aromatic Organic Compounds

The NMR \int parameter of meta substituted fluorobzenes correlates well with $E_{\frac{1}{2}}$ for similarly substituted iodobzenes, as do also the latter with σ^* value (Fig. 5). The para compounds correlate quite well with the exception of

the amino and hydroxyl substituents; possible structure changes in the latter compounds due to the polarographic background electrolyte solution may account for the noncorrelation.

The close parallelity between σ and σ values indicates that both are measuring similar functions; this supports the assumption that electron distribution changes caused by a substituent on one grouping, e.g., C-F bond, are related to the electron distribution on another similar grouping, e.g., C-I bond. More concrete support for the assumption are the good correlations obtained between $E_{\frac{1}{2}}$ and σ , and $E_{\frac{1}{2}}$ and σ for the benzaldehydes, nitrobenzenes and iodo-benzenes, and the excellent correlation between the NMR shielding parameters of meta and para substituted fluorobenzenes, and inductive and resonance parameters obtained from chemical reactivity (16).

Plots of $E_{\frac{1}{2}}$ vs. σ and σ -values of substituted benzaldehydes were almost identical to those of Fig. 5 for the iodobenzenes. In fact, the $E_{\frac{1}{2}}$ values are so similar that the two plots can be practically superposed.

Excellent correlations for both parameters are obtained with meta and para substituted nitrobenzenes (Fig. 6). Hammett σ -values for both meta and para derivatives fall on the same line while in case of the σ parameter two intersecting lines are obtained. The correlation of $E_{\frac{1}{2}}$ of ortho nitrobenzenes (obtained in acid solution) with Taft's σ^* parameter (Fig. 7) is surprisingly good for I, Br, Cl, COOH, H, and CH_3 substituents, but quite poor for NO_2 , OH, and NH_2 groups. $E_{\frac{1}{2}}$ data for neutral solution correlate better for the hydroxyl and amino groups but poorly for carboxyl and nitro groups. This variation is due in part to the effect of pH on electron distribution. In addition, NMR shifts due to ortho substituents sometimes do not follow diamagnetic parameters (electron density) alone, but are dependent also on paramagnetic effects (steric effects, bond angles, electron hybridizations, etc.) (15). $E_{\frac{1}{2}}$ for both types of solution correlate excellently with the σ^* parameter, which, as stated

before, is believed to be free of steric effects and to be only a measure of polar effects.

Conclusions

Fig. 8 is a composite of three types of data obtained in the present study for the correlation of $E_{\frac{1}{2}}$ and the NMR δ parameter: (1) excellent agreement for aliphatic aldehydes; (2) noncorrelation for chloroacetic acid and its esters (there is a sudden change in δ and $E_{\frac{1}{2}}$ in going from the acid to the methyl ester, but no change in δ upon increasing alkyl chain in the ester group, implying that little change occurs in the electron distribution about hydrogen near the C-Cl bond as a result of the substituents; these data suggest again that factors other than polar effect are influencing $E_{\frac{1}{2}}$); (3) fairly good correlation between $E_{\frac{1}{2}}$ values of iodobenzenes and the δ values of similarly substituted fluorobenzenes.

The general agreement between $E_{\frac{1}{2}}$ and δ , and between $E_{\frac{1}{2}}$ and σ and σ^* support the accepted view that the effects of substituents on reactivity are basically electronic in nature. In Fig. 4 where δ and σ^* agree but do not correlate with $E_{\frac{1}{2}}$, factors other than electronic distribution changes such as steric or adsorption effects probably cause variations in $E_{\frac{1}{2}}$. Polarizability effects of pH and background electrolyte on certain substituents could account also for non-correlation of $E_{\frac{1}{2}}$ and δ , while σ and σ^* agree.

The possibility of using NMR data obtained for one type of substituent for correlation with $E_{\frac{1}{2}}$ and reactivity data for a related substituent, e.g., Fig. 5, markedly increases the range of applicability to include certain types of organic compounds for which NMR data pertinent to the reactive center cannot be readily obtained. This feature has been recognized also for the correlation of δ and σ (16).

The application of the correlation of $E_{\frac{1}{2}}$ and δ in conjunction with Hammett's and Taft's parameters should be beneficial as a qualitative tool for predicting

relative orders of half-wave potentials and, more importantly, as a tool for elucidating mechanisms of organic electrode reactions.

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Table I. Types of Compounds Amenable to Both Polarographic and Nuclear Magnetic Shielding Studies

Type of Molecule	Reducible Group	Resonance to be Observed
RCH(Br)COOH	C-Br	-CH(Br)-
ClCH ₂ COOR	C-Cl	-CH ₂ Cl
ClCH ₂ COR	C-Cl	-CH ₂ Cl
RC ₆ H ₄ COCH ₂ F	C-F	-CH ₂ F or -CH ₂ F
RCH ₂ NO ₂	NO ₂	-CH ₂ NO ₂ , -CH ₂ NO ₂ or -CH ₂ NO ₂
R ¹ COCH ₂ R	C=O	-COCH ₂ - or -COCH ₂ -
RCHO	C=O	-CHO or -CHO ⁻
RC ₆ H ₄ CHO	C=O	-CHO or -CHO
RCH=NH	C=N	-CH=N, -CH=NH, or -CH=NH
R ¹ CH=NR	C=N	-CH=NR or -CH=NR
RCH=CH ₂	C=C	-CH=CH ₂ or -CH=CH ₂
R(R ¹)C=CH ₂	C=C	-C=CH ₂
R(R ¹)C=C(R ¹¹)H	C=C	-C=CH-
RCH=CHR ¹	C=C	-CH=CH- or -CH=CH-
CH ₃ (CH=CH) _x CHO	C=C	-CH=CH- or -CH=CH-
ROOH	-O-O-	-OOH or -OOH

^aThe resonance measurements refer to H¹, F¹⁹, N¹⁵ and O¹⁷ nuclei, as indicated for the underlined atoms.

Table II. Comparison of Half-Wave Potentials and NMR Values
for Various Substituted Compounds

<u>Type of Molecule</u>	<u>Electrode Reaction Product</u>	<u>NMR Measurement</u>
<u>Alphatic Derivatives</u>		
RCHO	RCH ₂ OH	RCHO
RCH ₂ NO ₂	RCH ₂ NHOH	RCH ₂ NO ₂
RCHBrCOOC ₂ H ₅	RCH ₂ COOC ₂ H ₅	RCHBrCOOC ₂ H ₅
ClCH ₂ COOR	CH ₃ COOR	ClCH ₂ COOR
<u>Aromatic Derivatives</u> (<u>o</u> -, <u>m</u> -, <u>p</u> -)		
RC ₆ H ₄ I	RC ₆ H ₅	RC ₆ H ₄ F
RC ₆ H ₄ CHO	RC ₆ H ₄ CH ₂ OH	RC ₆ H ₄ F
RC ₆ H ₄ NO ₂	RC ₆ H ₄ NHOH	RC ₆ H ₄ F

Table III. Comparison of Half-Wave Potentials and NMR Values for Various Substituted Compounds

Type of Molecule	Reducible group	Resonance observed	List of NMR δ values (top), substituents and $-E_{1/2}$ values (bottom)							Reference			
p-RC ₆ H ₄ I	C-I	C-F		-0.12 I 1.46	-0.23 Br 1.53	-0.24 Cl 1.54	-0.27 C ₆ H ₅ 1.585	0.00 H 1.65	-0.55 Me 1.685	-1.06 OH 1.685	-1.56 NH ₂ 1.72	15	
m-RC ₆ H ₄ I	C-I	C-F		0.26 I 1.38	0.24 Br 1.43	0.21 Cl 1.45	0.09 OH 1.62	0.00 H 1.65	-0.02 NH ₂ 1.66	-0.09 Me 1.660	15		
<u>o</u> -RC ₆ H ₄ I	C-I	C-F		1.93 I 1.235	0.55 Br 1.30	-0.27 Cl 1.34	2.50 OH 1.49	-2.31 NH ₂ 1.56 ²	0.00 H 1.65	-0.50 Me 1.683	15		
p-RC ₆ H ₄ NO ₂	NO ₂	C-F	0.69 COOH 0.390	1.08 NO ₂ 0.436	-0.12 I 0.780	-0.23 Br 0.854	-0.27 C ₆ H ₅ 0.854	-0.24 Cl 0.930	0.00 H 0.935	-0.55 Me 1.035	-1.46 NH 1.128	-1.06 OH 1.350	15
m-RC ₆ H ₄ NO ₂	NO ₂	C-F		0.05 COOH 0.440	0.33 NO ₂ 0.681	0.26 I 0.757	0.24 Br 0.816	0.21 Cl 0.830	0.00 H 0.935	-0.02 NH ₂ 0.935	-0.09 Me 0.936	0.09 OH 0.960	15
<u>o</u> -RC ₆ H ₄ NO ₂	NO ₂	C-F		0.35 COOH 0.526	-0.56 NO ₂ 0.570	1.93 I 0.816	0.55 Br 0.860	-0.27 Cl 0.866	0.00 H 0.935	-2.50 OH 0.990	-0.50 Me 1.005	-2.31 NH ₂ 1.030	15
p-RC ₆ H ₄ CHO	CHO	C-F			-0.12 I 1.400	-0.23 Br 1.410	-0.24 Cl 1.422	0.00 H 1.506	-0.55 Me 1.562	-1.46 NH ₂ 1.70 ²	-1.06 OH 1.72	15	
m-RC ₆ H ₄ CHO	CHO	C-F		0.24 Br 1.358	0.21 Cl 1.384	0.26 I 1.390	0.09 OH 1.500	0.00 H 1.506	-0.02 NH ₂ 1.52	-0.09 Me 1.526	15		

 C7
C4
C8

60

Table III (continued)

Type of Molecule	Reducible group	Resonance observed	List of NMR	δ	values	(top), substituents	and $-E_{1/2}$ values (bottom)	Reference			
<u>o-RC₆H₄CHO</u>	CHO	C-F		1.93 I 1.248	-0.27 Cl 1.331	-0.50 Me 1.493	-2.50 OH 1.504	0.00 H 1.506	15 25		
RCHO	CHO	CHO					0.04 H ^a 1.69 (1.458)	0.45 Me 1.87 (1.635)	0.50 Et 1.92 (1.678)	0.48 n-Pr 1.90 1.91	0.50 i-Pr 26 27
RCH ₂ NO ₂	NO ₂	CH ₂		-0.088 Pr 0.565	-0.095 Et 0.617	-0.097 Me 0.0663	-0.123 H 0.685		b 28		
RCHBrCOOC ₂ H ₅	C-Br	CHBr			-0.053 Et 0.34	-0.063 Me 0.35	-0.086 H 0.48		b 24,29		
ClCH ₂ COOR	C-Cl	CH ₂ Cl		-0.083 Bu 1.41	-0.083 Et 1.50	-0.070 Me 1.54	-0.160 H 1.64		b 29		

^aExtrapolated value based upon data in reference 27.

^bNew data.

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Bennett and Elving - Correlation of Polarographic Half-wave Potentials with
Nuclear Magnetic Resonance "Chemical Shifts".
Parallel Correlation with Chemical Reactivity Parameters

Figure Captions

Fig. 1. Polarograms for reversible and irreversible electrode reduction processes.

Fig. 2. Correlation of Taft σ^* and NMR δ values with $E_{\frac{1}{2}}$ values for aliphatic aldehydes.

Fig. 3. Correlation of Taft σ^* and NMR δ values with $E_{\frac{1}{2}}$ for ethyl esters of 2-bromoalkanoic acids.

Fig. 4. Trend of Taft σ^* and NMR δ values with $E_{\frac{1}{2}}$ values for aliphatic nitro compounds.

Fig. 5. Correlation of Hammett σ and NMR δ values with $E_{\frac{1}{2}}$ values for meta and para-substituted iodobenzenes.

Fig. 6. Correlation of Hammett σ and NMR δ values with $E_{\frac{1}{2}}$ values for meta and para-substituted nitrobenzenes.

Fig. 7. Correlation of Taft σ^* and NMR δ values with $E_{\frac{1}{2}}$ values for ortho-substituted nitrobenzenes. (A) $E_{\frac{1}{2}}$ values measured at pH 1.7; (B) $E_{\frac{1}{2}}$ values measured in neutral solution (0.01 M $(C_2H_5)_4NBr$ in 66% alcohol).

Fig. 8. Correlation of NMR δ values with $E_{\frac{1}{2}}$ values of aliphatic aldehydes (top), chloroacetic acid esters (middle), and meta and para-substituted iodobenzene (bottom).

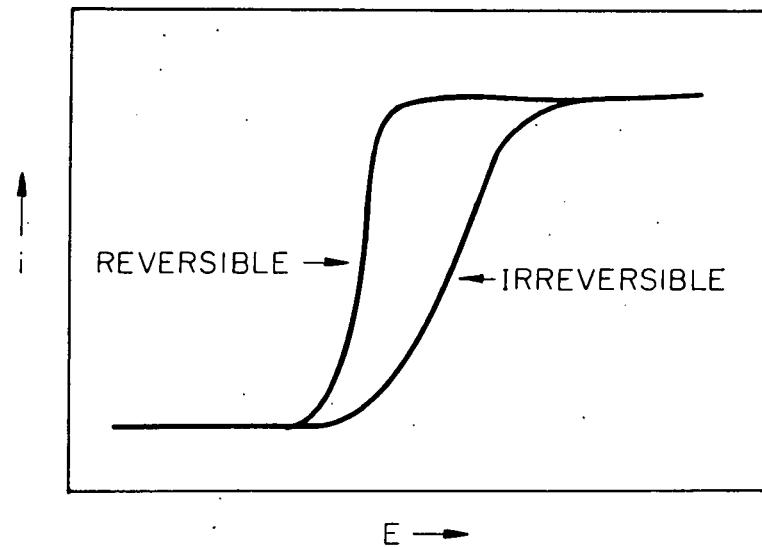


Fig. 1

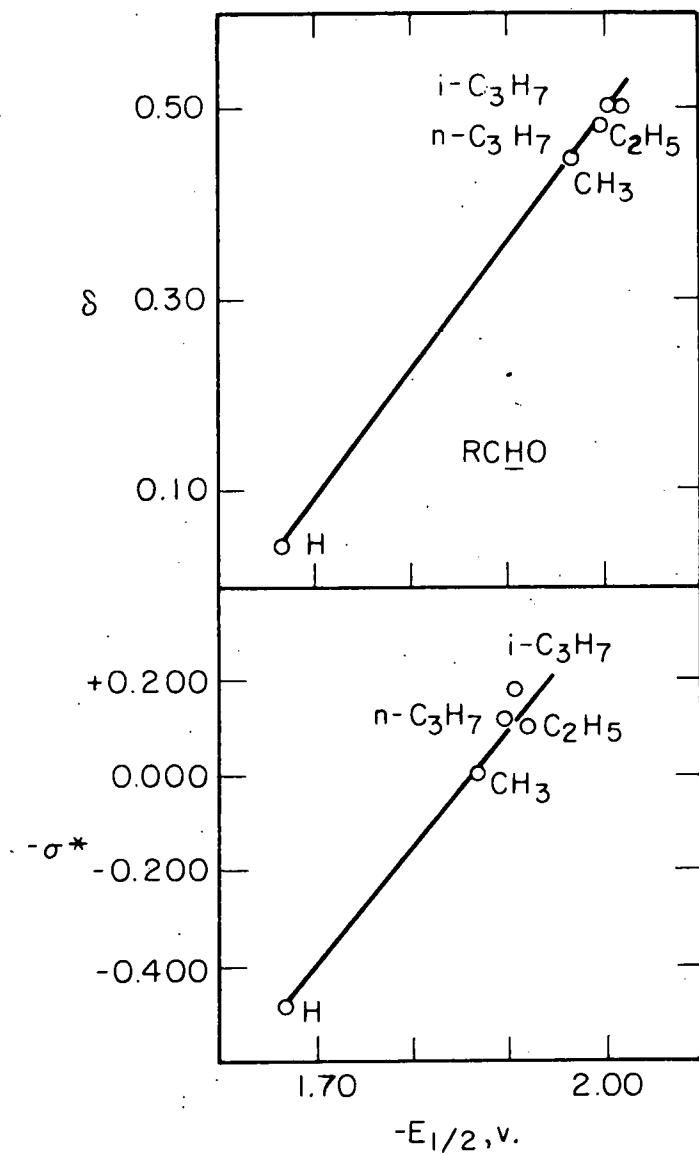


Fig. 2

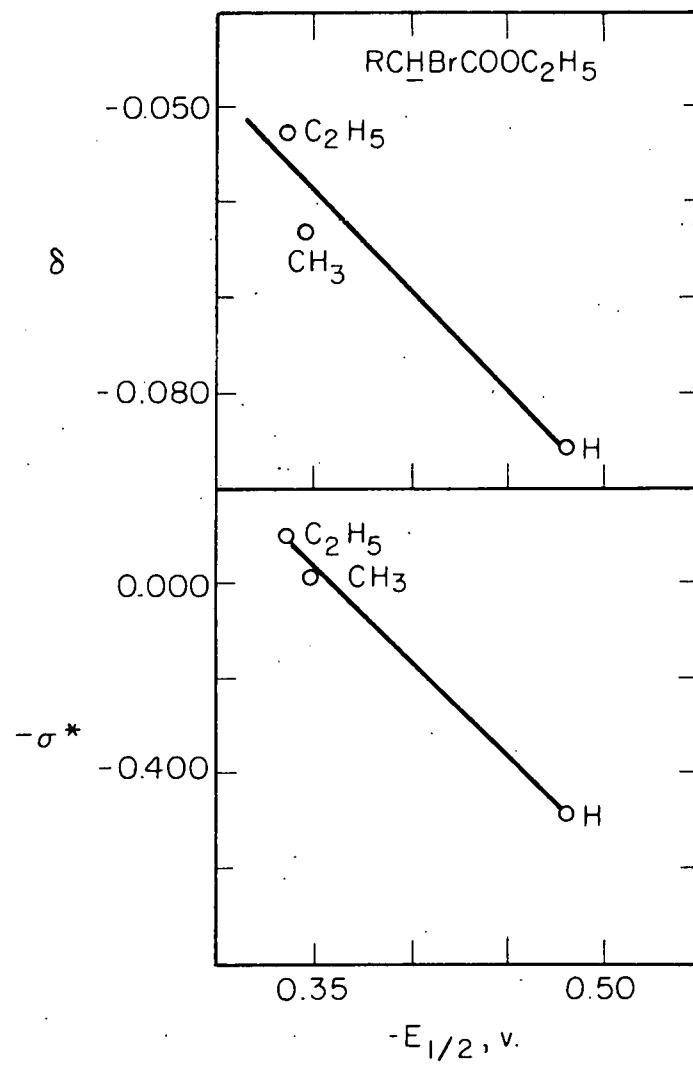


Fig. 3

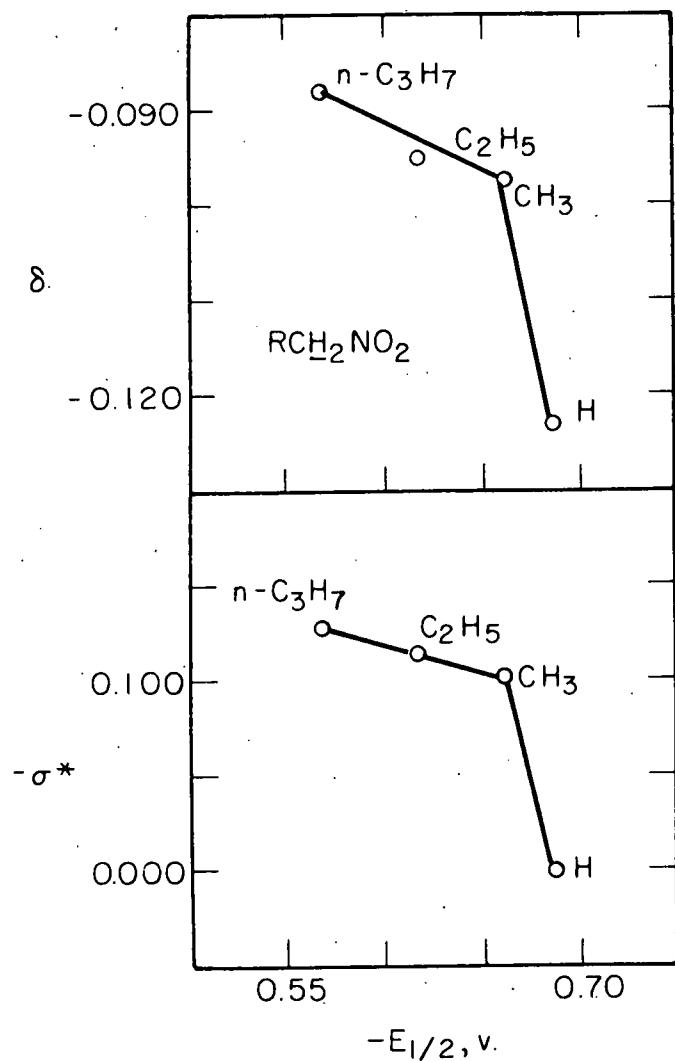
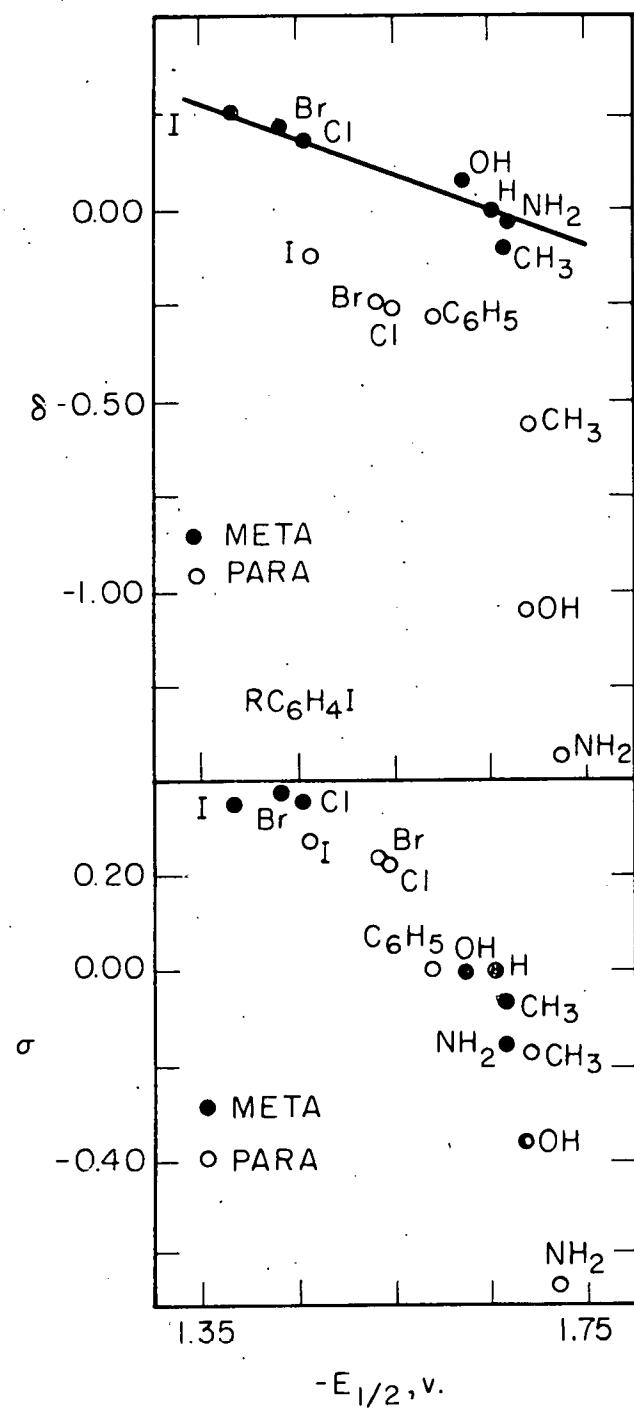


Fig 4



$-E_{1/2}, v.$

Fig. 5

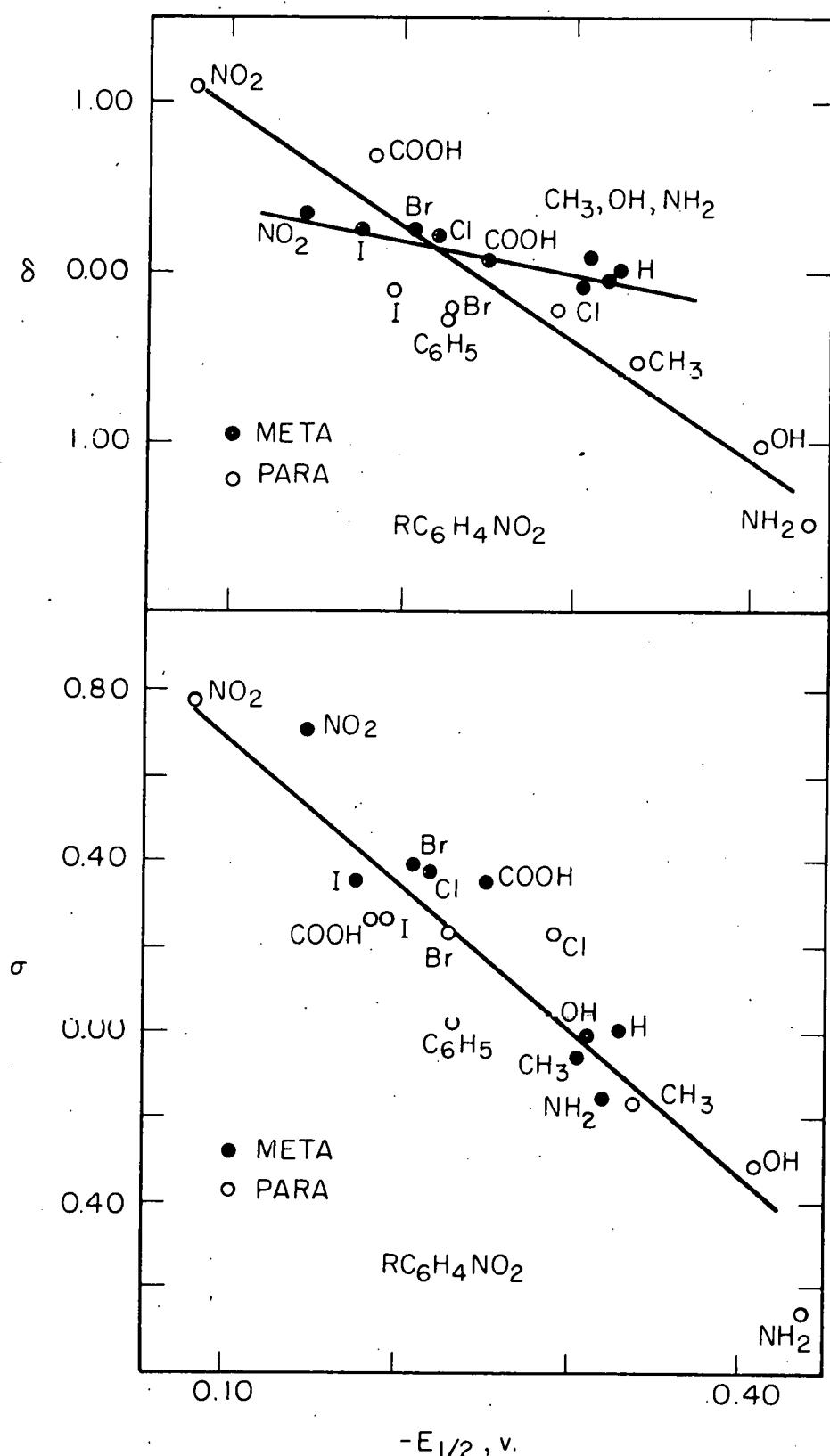


Fig. 6

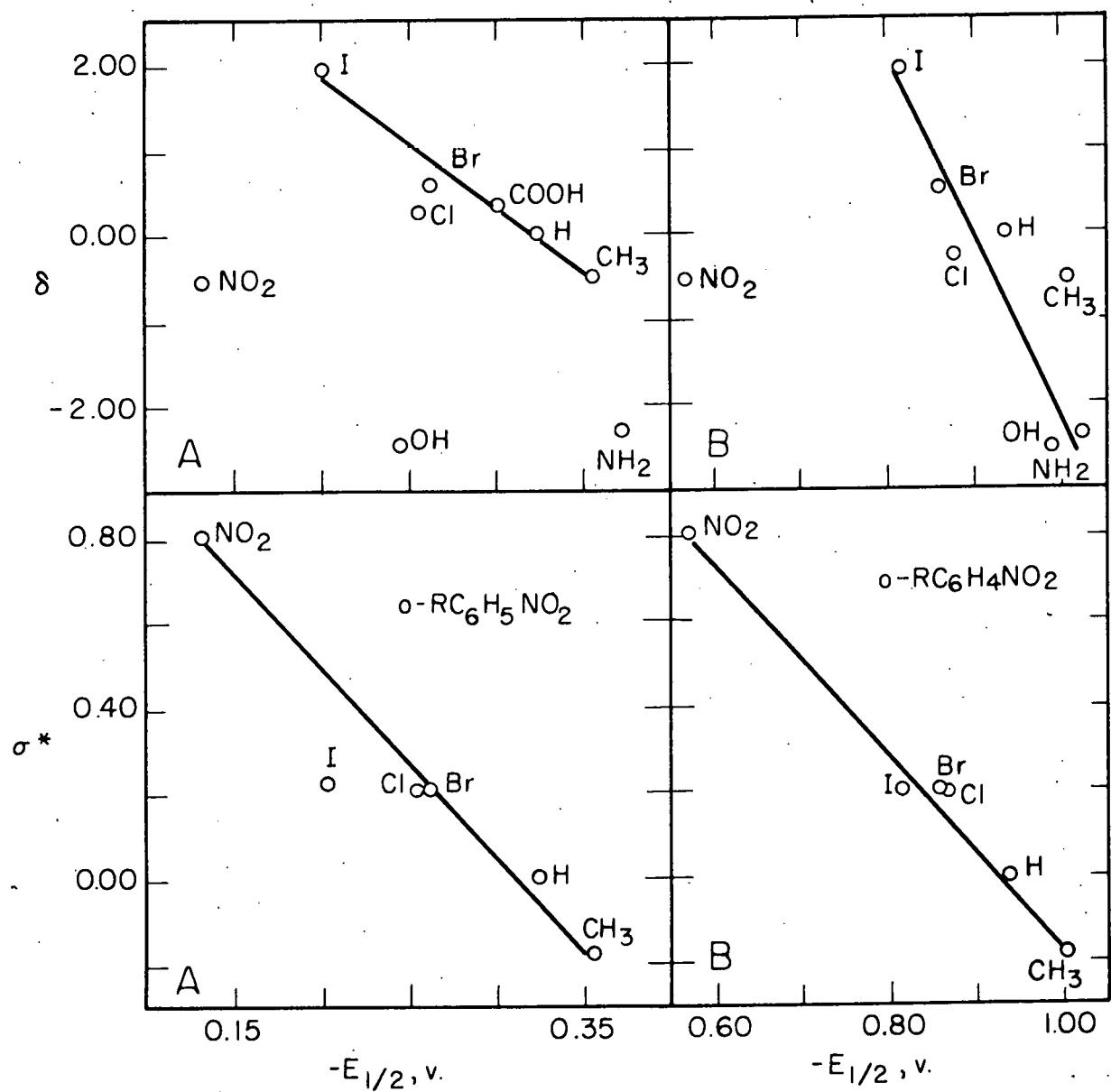


Fig. 7

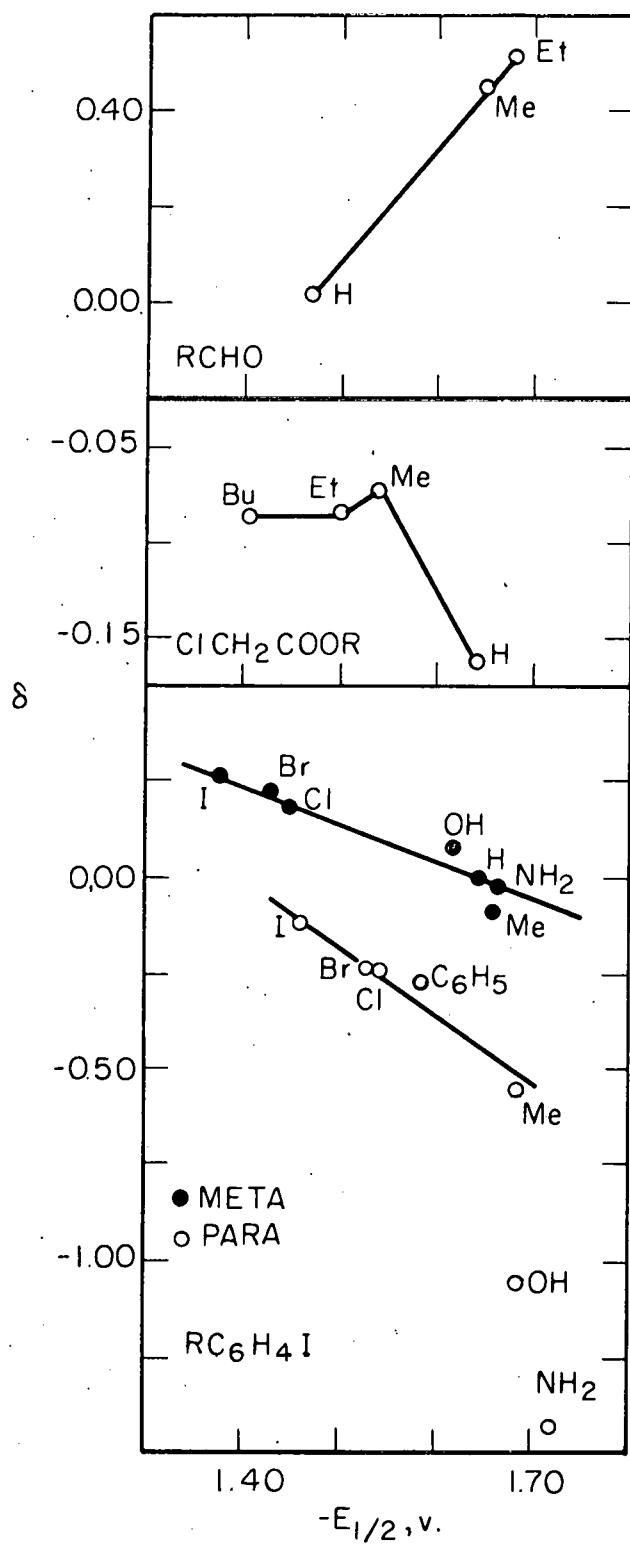


Fig. 8