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LINEAR FREE ENERGY CORRELATION OF THE HALF-WAVE POTENTIALS OF SOME SUBSTITUTED N-AROYL-N'-PHENYL DIIMIDES AND N-BENZOYL-N'-ARYL DIIMIDES

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Sir:

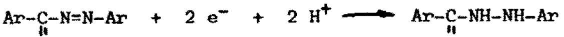
We wish to report the polarographic study of two series of disubstituted diimides in 70% AQUEOUS ETHANOL WITH 0.1N potassium chloride as supporting electrolyte at 30.0°C(2). See Table I.

TABLE I

Series A N-Aroyl-N'-Phenyl Diimide	(8) $E_{1/2}$ Volts	Series B N-Benzoyl-N'-Aryl Diimides(7)	(8) $E_{1/2}$ Volts
H	0.355 ± .003	H	0.355 ± .003
p-CH_3	0.371 ± .003	p-CH_3	0.380 ± .004
m-CH_3	0.362 ± .003	m-CH_3	0.370 ± .002
p-Cl	0.342 ± .003	p-Cl	0.337 ± .005
m-Cl	0.331 ± .004	p-NO_2	0.210 ± .002
p-NO_2	0.310 ± .004	m-NO_2	0.275 ± .003
p-CH_3O	0.380 ± .003		

Whereas hydrazides,(3) azobenzenes,(4) aromatic ketones,(5) and chalcones(6) have been extensively studied polarographically, these azo compounds have not.

Both series A and B undergo a single two electron reduction.(9) The general equation of the reaction in 70% aqueous ethanol is most probably as follows:



$$Ar-\underset{\overset{\|}{O}}{C}-N=N-Ar + 2\,e^- + 2\,H^+ \longrightarrow Ar-\underset{\overset{\|}{O}}{C}-NH-NH-Ar \qquad \text{eq. I}$$

Plots of $E_{1/2}^{X} - E_{1/2}^{o}$ versus standard Hammett sigma constants afforded linear relationships for both series of compounds.(10) The rho values, ρ_{π} for series A and B were +0.07 and +0.14 volts, respectively, $E_{1/2}^{X}$ and $E_{1/2}^{o}$ are the half-wave potentials of substituted and standard compounds, respectively, ρ_{π} is a polarographic reaction constant. The positive values of ρ_{π} means that the substrate with an electron-withdrawing substituent is reduced at less negative potentials than is the standard substrate. When dealing with Hammett relationships in polarographic studies the reaction constants ρ_{π} are almost uniformly positive thus corroborating the fact that the electron is a nucleophilic reagent. However, we feel that the magnitude of the ρ_{π} for series B, being two times that of A, strongly suggests that the -N=N- moiety is undergoing reduction as opposed to that of the carbonyl group, since the substituents in series B are closer to and in direct conjugation with the azo linkage. When we tried to carry out constant potential electrolysis on these compounds, so as to be able to isolate some of the hydrazides, we found that the diimides were undergoing solvolysis.(11) We are actively investigating this apparent solvolysis, since it is known that these diimides lead to free radicals upon alcoholysis,(12) however there is still some question as to whether or not the initial reaction is truly a solvolysis or a radical decomposition.

Zuman(13) has demonstrated that there exists a linear relationship between the values of reaction constants, $\rho_{\pi}R$, with values of half-wave potentials of the unsubstituted reference compound bearing the same electroactive group R, $(E_{1/2})_{H}^{R}$ and characterizing the reactivity of the group R towards nucleophilic attack by an electron. The half-wave potential of N-Benzoyl-N'-Phenyl Diimide, (I), and the reaction constant for series B fit very well on Zuman's plot. This plot indicates that the $-N{=}N{-}\underset{\underset{O}{\|}}{C}-$ moiety is more electroactive toward reduction than either the azo or carbonyl moiety.

These diimides, which may be thought of as nitrogen analogs of chalcones, behave somewhat differently from this class of unsaturated ketones conjugated with an aromatic ring. Whereas chalcone undergoes an one-electron reduction in acid followed by dimerization of the radicals at the β position. In basic solution, two-electron reduction hydrogenating the double bond; while in nearly neutral solution both one-electron and two-electron processes occur.(14) Both reduction products of chalcone are electroactive and a further reduction wave is observed near the $E_{1/2}$ of acetophenone. Compound (I) in both acidic and basic solutions undergo a very rapid heterolysis.(12) In nearly neutral solution, one clean two-electron reduction is observed, which most probably froms the non electroactive, N-Benzoyl-N'-phenyl hydrazide.

In DMF the reduction of chalcone is complicated since it is presumded that the radical anion initially formed polymerizes, and these polymers are electroactive. Compound (I) gives two one-electron reductions in DMF, thus indicating that the initial radical anion is quite lone-lived, and we are currently investigating this radical ion.

NOTES

(1) We are pleased to acknowledge the generous support of this work in part by the Petroleum Research Foundation Grant 894-G1-RPG-1239.

(2) The polarographic reductions were carried out on a Sargent Recording Polarograph Model XXI equipped with a thermostated H cell. Caromel electrode was used as the reference, and the dropping mercury electrode was the working electrode.

(3) Miller, D.M., Can. J. Chem., 33, 1806 (1955); Lund, H., Acta. Chem. Scand., 17, 1077 (1963); Schlitt, L., M. Rink, and M. Stackelberg, J. Electroanal. Chem., 13, 10(1967).

(4) Wawzonek, S. and J.D. Frederickson, J. Am. Chem. Soc., 77, 3985 (1955).

(5) Gardner, H.J., Chem. Ind. (London), 1951, 319.

(6) Pasternak, R., Helv. Chim. Acta., 31 753 (1948).

(7) The elemental analyses of new compounds agreed well with calculations, and their infrared and ultra-violet spectra are consistent with the assigned structures.

(8) The half-wave potentials are an average of three determinations, relative to the Calomel Electrode.

(9) Plots of log $\left(\frac{i}{id-i}\right)$ vs E were non linear for series A and B.

(10) For a review of the effect of substitutents on polarographic half-wave potentials, see Zuman, P., Collection Czech. Chem. Commun., 19, 599 (1954); 25, 3225 (1960); 27, 2035 (1962); Advan. Polarog., 3, 812 (1960).

(11) Under conditions of the polarographic study, both in the presence and absence of a potential, 10^{-3}M of azo compound in 70% aqueous ethanol with 0.1M potassium chloride as supporting electrolyte at 30.0°C under argon, high yields of ethyl benzoates> 90% are formed as determined via vapor phase chromatography using a five foot, ¼ inch 10% SE-30 chromosorb W column at 90.0°C.

(12) Cohen, S.G. and J. Nicholson, J. Am. Chem. Soc., 86, 3892 (1964); J. Org. Chem., 30, 1162 (1965).

(13) Zuman, P., in Progress in Physical Organic Chemistry, Vol. 5, A Streitwieser and R.W. Taft, Eds. Interscience, New York, 1967, p. 81.

(14) Perrin, C.L. in Progress in Physical Organic Chemistry, Vol. 3, S.G. Cohen, A. Streitwieser and R.W. Taft, Eds. Interscience, New York, 1965, p. 165.