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Abstract

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ON THE QUESTION OF A QUANTITATIVE ASSESSMENT OF THE INFLUENCE OF SUBSTITUENTS ON THE POLAROGRAPHIC REDUCTION OF CERTAIN AZOMETHINE COMPOUNDS

One of the most urgent problems of modern chemistry is the establishment of a quantitative interrelation between the structure of organic compounds and their reactivity. In the general case this problem still remains very complex; however, particular regularities described by empirical or semiempirical equations are quite accessible and make it possible to express numerically the influence of molecular structure on the reactivity of a compound. This applies above all to the well-known Hammett rule, which encompasses the rate constants and equilibrium constants of nucleophilic substitution reactions of aromatic derivatives with substituents in the *n*- or *m*-position ($^{1-3}$). Since the polarographic reduction of a functional group may be represented as a nucleophilic substitution reaction, then, as has been shown by a number of authors ($^{4-7}$), the Hammett equation for an electrochemical reaction takes the following form: $E_{1/2} - E^0_{1/2} = \rho'\sigma$, where $E^0_{1/2}$ and $E_{1/2}$ are the half-wave potentials, respectively, of the unsubstituted and substituted derivative; ρ' is a constant of the electrochemical reaction, characterizing the degree of susceptibility of the reaction center (the group being reduced) to the influence of substituents; σ is a constant characterizing the degree of influence of the given substituent in the benzene ring on the ability to undergo reduction. The validity of the Hammett equation for irreversible reactions, in particular for irreversible polarographic reduction, is observed only when data for a series of derivatives are obtained under completely identical conditions.

The Hammett rule in polarography has proved valid not only for aromatic compounds (tropolones, benzaldehydes, acetophenones, benzophenones, nitro compounds, azobenzenes, phthalimides) (^{4,8}), but also for heterocyclic (^{9,10}) (thiophene, selenophene, pyrrole, furan, pyridine, thiazole, tetrazolium salts), quinoid (^{7}), and pseudoaromatic (^{11}) (azulenes, sydnones) compounds. The possibilities for applying the Hammett rule in the polarography of organic compounds are very diverse. First, it makes it possible to predict the polarographic behavior of some derivatives from values determined for others; second, it may be used for identifying compounds in mixtures, including isomers, for determining the equilibrium constant at known ρ' (^{12}), and for quantitatively assessing the influence of substituents on the electrode process.

With the aim of quantitatively assessing the influence of substituents on the reduction of compounds containing an azomethine grouping, we applied the Hammett equation to the polarographic reduction of phenylhydrazones, semicarbazones, and thiosemicarbazones of certain aromatic aldehydes. Derivatives of benzoic, cuminic, *n*-dimethylaminobenzoic, *n*- and *m*-nitrobenzoic aldehydes, as well as acetophenone and *n*-chloroacetophenone, were studied. The polarographic study of the indicated compounds was carried out in 20% methanol-water solutions with a concentration of 10^{-4} mole/l against a phosphate- of a borate buffer with pH 6.0 at 25°. Table 1 gives the results of microcoulometric and polarographic investigation of some of the above-mentioned azomethine derivatives, which show that both phenylhydrazones and semi- and thiosemicarbazones are reduced by one and the same mechanism.

Table 1

No.	Azomethine derivative	Number of electrons participating in reduction	tan of the slope angle of the straight line $E = f\left(\lg \frac{i}{id-i}\right)$	$\frac{dE_{1/2}}{d\text{pH}}$
1	Phenylhydrazone of benzaldehyde	1.80	0.048	0.050
2	Phenylhydrazone of acetophenone	1.94	0.062	0.038
3	Semicarbazone of acetophenone	1.90	0.070	0.043
4	Thiosemicarbazone of benzaldehyde	1.97	0.056	0.055
5	Thiosemicarbazone of acetophenone	2.09	0.060	0.033

It was also found that the number of electrons going into the reduction of the nitro group in derivatives of *n*- and *m*-nitrobenzaldehydes is equal to four, i.e., the nitro groups in them are reduced to hydroxylamine. Therefore we examined the influence on the polarographic reduction of the

Fig. 1. 1 —phenylhydrazones, 2 —thiosemicarbazones, 3 —semicarbazones

Figure 1: Fig. 1. 1 —phenylhydrazones, 2 —thiosemicarbazones, 3 —semicarbazones

$$> C = N-$$

bond in nitrobenzaldehyde derivatives not of the nitro group, but of the hydroxylamine group.

Fig. 1. 1 —phenylhydrazones, 2 —thiosemicarbazones, 3 —semicarbazones.

On the basis of the obtained values of the half-wave potentials, given in Table 2, plots were constructed in the coordinates $E_{1/2}$ and σ (in Hammett units) (^{2}). As is seen from Fig. 1, in these cases as well a satisfactory linear dependence is observed between the half-wave potentials and the σ values of the substituents. From the slope of the straight lines obtained, the values of ρ', given in Table 3, were determined. The value of ρ' for semicarbazones of aromatic aldehydes is close to the value 0.12-0.13 found by Pearson for semicarbazones of certain benzophenones (^{4}). The values of ρ' obtained by us are relatively small, i.e., the influence of the substituent on the reduction of the azomethine groups in the compounds studied is comparatively insignificant, and the degree of this influence, depending on the features

Table 2

No.	Carbonyl compound	Phenylhydrazone	Thiosemicarbazone	Semicarbazone
1	Benzaldehyde	−1.065	−1.110	−1.122
2	*n*-Isopropylbenzaldehyde	−1.068	−1.123	−1.138
3	*n*-Dimethylaminobenzaldehyde	−1.070	−1.150	−1.190
4	*n*-Nitrobenzaldehyde	−1.070	−1.144	−1.174
5	*m*-Nitrobenzaldehyde	−1.068	−1.115	−1.130
6	Acetophenone	−1.170	−1.210	−1.276
7	*n*-Chloroacetophenone	−1.154	−1.162	−1.220

of the conducting system of bonds in the molecule increases in the series phenylhydrazones—thiosemicarbazones—semicarbazones.

The electronic structure of all the compounds studied is characterized by $p\pi$-conjugation and by a relatively high mobility of the delocalized electron cloud of their molecules, the density of which is most evenly distributed in the case of phenylhydrazones

$$\mathrm{X{-}C_6H_4{-}CH{=}N{-}NH{-}C_6H_5}$$

This is connected with the presence of a second phenyl radical at the end of the conjugated chain. Since the reducible azomethine bond is not at the end of the conjugation chain, but is only one of the transmitting links of this chain, under the influence of one or another substituent in the phenyl ring of the starting aldehyde its electron density changes only slightly; this explains the rather close values of the half-wave potentials of derivatives of substituted and unsubstituted carbonyl compounds.

Table 3

No.	Carbonyl compound	ρ'-constant of the reduction reaction of the $> C{=}N'$ bond: phenylhydrazones	ρ'-constant of the reduction reaction of the $> C{=}N'$ bond: thiosemicarbazones	ρ'-constant of the reduction reaction of the $> C{=}N'$ bond: semicarbazones
1	Aromatic aldehydes	0.004	0.094	0.132
2	Acetophenones	0.070	0.208	0.244

Semi- and thiosemicarbazones, in contrast to phenylhydrazones, have at the end of the conjugation chain electronegative oxygen and sulfur atoms, the direction of whose action on the molecule is consistent with the direction of polarization of the $> C = N-$ bond and with the influence of electron-donor substituents in the phenyl nucleus, and causes a shift of the delocalized electron cloud toward them.

$$\mathrm{X{-}C_6H_4{-}CH{=}N{-}NH{-}C({=}\,O,S){-}NH_2}$$

This shift is more significant in semicarbazones, since the oxygen atom, being more electronegative than sulfur, causes a greater asymmetry of the electron cloud of the conjugated bonds of the molecule and more strongly affects the electron density of the azomethine group.

Thus, the influence of the substituent is manifested to a greater extent for semicarbazones than for thiosemicarbazones and phenylhydrazones of carbonyl compounds.

A certain increase in the values of ρ' for the azomethine derivatives of acetophenones can be explained by the influence of the methyl radical, which disturbs the relatively even density of the electron cloud of the system of conjugated bonds and increases the electron density of the azomethine group.

$$X{-}C_6H_4{-}C(CH_3){=}N{-}NH{-}C_6H_5$$

Therefore the electron density of $> C = N-$ bonds can readily change under the influence of a substituent in the phenyl nucleus. In the case of derivatives of *p*-chloroacetophenone, the electronegative chlorine atom acts in the direc-

···field, opposite to the direction of polarization of the azomethine bond, and leads to a decrease in its electron density, i.e., facilitates polarographic reduction.

The studied azomethine derivatives of nitrobenzaldehydes may also be regarded as substituted aromatic nitro compounds. Therefore, the data we have obtained make it possible to solve the inverse problem as well—to calculate the values of σ for phenylhydrazone, semicarbazone, and thiosemicarbazone substituents from the electrochemical reduction reaction of the nitro group. Table 4 gives the values of σ for these substituents, calculated from the difference between the half-wave potentials of substituted and unsubstituted nitrobenzenes, under the condition that $\rho' = 0.16$ ([5],[8]).

Table 4

No.	Substituent	$-E_{1/2}$, V para-	$-E_{1/2}$, V meta-	σ para-	σ meta-
1	–	−0.480		0	
2	$-C(=N{-}NH{-}C_6H_5)H$	0.340	0.356	+0.88	+0.78
3	$-C(=N{-}NH{-}C(=O){-}NH_2)H$	0.350	0.378	+0.81	+0.64
4	$-C(=N{-}NH{-}C(=S){-}NH_2)H$	0.350	0.373	+0.81	+0.67

The values of σ thus found for various substituents containing an azomethine grouping proved to be very close in magnitude; i.e., they exert practically the same influence on the reduction of the nitro group, transmitted through the π-bond system of the benzene ring. This also testifies to the similarity of the electronic structures of these substituents with a $\pi p \pi$-conjugated bond system, possessing relatively great mobility of the delocalized electron cloud.

In conclusion it should be noted that the values of ρ' and σ presented in this work are tentative, since they were obtained in the study of a small number of compounds and undoubtedly require refinement.

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Note: Figure translations are in progress. See original paper for figures.