Potentiometric Investigation of the Effects of Several Substituents on the Basicity of Benzilidene-o-hydroxyaniline

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Chloro-, bromo-, iodo-, nitro-, methoxy- and hydroxy-substituted benzilidene-o-hydroxyaniline were prepared in order to investigate the effects of substituents on the basicity of benzilidene-o-hydroxyaniline. For each substituent, three isomers – ortho, meta and para – were synthesised. Schiff bases were titrated potentiometrically with perchloric acid in nitrobenzene solvent at $25°$ C. All compounds gave well-shaped titration curves, from which half-neutralisation potentials were calculated. The trend in the values of half-neutralisation potentials of Schiff bases were explained in terms of the nature of the substituents. The applicability of the Hammett equation to the effect of substituents in Schiff bases in nitrobenzene solvent was discussed.

Key words: Schiff bases, nonaqueous media, substituent effect, potentiometric titration.

Introduction

It is well known that two major factors influence the basicity or acidity of molecules, namely, structural and solvent effects[1−6]. Unfortunately, in most molecules, there are two or more structural effects and it is usually difficult to decide how much each effect contributes to the acidity or basicity of similar molecules are extremely difficult to explain. Solvent effects are also very important, and the acidity or basicity of a molecule usually varies when its solvent is changed[7−8]. Potentiometric titration in non-aqueous media gives valuable information about the basicity or acidity of a compound[9−12]. In recent studies, we have investigated the effects of several electron donating and withdrawing substituents and solvents on the basicity of a number of Schiff bases[6,13,14]. In this paper, we have studied the effects of chloro, bromo, iodo, nitro, methoxy and hydroxy groups on the basicity of benzilidene-o-hydroxyanilines (Schiff base taken as the standard), when they are ortho, meta or para to the aldehyde component (benzaldehyde). Seventeen substituted benzilidene-o-hydroxyanilines were prepared and titrated potentiometrically with perchloric acid

in nitrobenzene. Whether or not the Hammett equation could be used to predict the effect of substituent on the reactivity of benzilidene-o-hydroxy aniline is discussed.

Experimental

Apparatus: An Orion Model 720 digital pH meter equipped with a combined glass electrode and a modified Ag/AgCl electrode was used for potentiometric titration. The Ag/AgCl electrode was modified by emptying its aqueous KCl solution and refilling it with a saturated solution of KCl in dry methanol. All titrations were carried out in a specially designed cell thermostated at $25 \pm 1^\circ$C under nitrogen atmosphere[15].

Materials: All Schiff bases were prepared by condensing o-hydroxyaniline with benzaldehyde and substitute benzaldehydes. The Schiff bases were purified by recrystallisation from ethanol. o-Hydroxyaniline and all substituted benzaldehydes were purchased from Merck (reagent grade) and were used as received. Nitrobenzene was purchased from Merck and purified by the method given in Ref. 16. Perchloric acid solutions used in the titrations in nitrobenzene, were prepared and standardized as previously described[16].

Results and Discussions

Seventeen substituted benzilidene-o-hydroxyanilines were prepared and titrated potentiometrically with perchloric acid in nitrobenzene. All compounds gave well-shaped titration curves (sigmoids) and those of the ortho-substituted benzilidene-o-hydroxyanilines are shown in Figure 1 as an example. From such titration curves, the half-neutralisation potentials of the compounds were found and are compiled in Table 1.
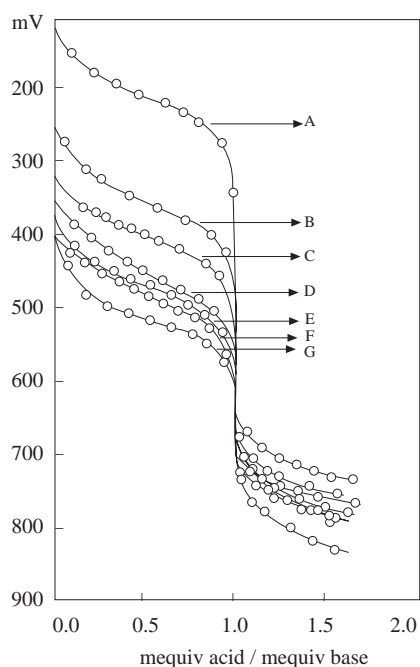
Figure 1. Potentiometric titration curves of o-substituted benzilidene-o-hydroxyanilines: (A) o-Methoxy, (B) o-Hydroxy, (C) Standard, (D) o-Chloro, (E) o-Bromo, (F) o-Iodo, (G) o-Nitro.

Table 1. Half-neutralisation potentials of substituted benzilidene-o-hydroxyanilines obtained by titration with perchloric acid in nitrobenzene at $25°$ C.

$$CH = N$$
HO
R

|	Ortho	Meta			Para		
R	hnp, mV	hnp, mV	Δ(hnp)*	σ**	hnp, mV	Δ(hnp)*	σ**
H	397	-	-	-	-	-	-
Cl	467	452	78	0.37	443	46	0.23
Br	480	455	58	0.39	440	43	0.23
I	485	458	61	0.35	440	43	0.28
NO_2	515	510	113	0.75	490	93	0.75
OCH_3	215	-	-	-	310	-87	-0.27
OH	368	393	-4	0.12	-	-	-

*Δ(hnp)=hnp-hnp$_{(standard)}$

** Hammett constants.

Using the half-neutralisation potentials obtained in this study, the effect of the substituents on the basicity of azomethine group of benzilidene-o-hydroxyaniline (standard) is discussed. Each substituent given in Table 1 varies the basicity of benzilidene-o-hydroxyaniline more or less with respect to its position. Any influence created by the substituent is reflected at least partly on the nitrogen atom of the azomethine group.

The basicity order of the hydrogen derivatives with respect to the standard is standard>p-X>m-X>o-X(X:Cl, Br, I). The lower basicity of the halogen derivatives is a result of the very strong electron-withdrawing character of halogens. The reason the ortho-derivatives are the least basic might be the strong short-range negative inductive effect of the halogen atoms. It is generally believed that the resonance effect in the para position is more greater than the inductive effect in the ortho position. However, the resonance effects of the halogens are generally very weak. If the basicities of the ortho-substituted halogen derivatives are compared with the standard, the following order is observed: standard>o-Cl>o-Br>o-I. The exact same orders are observed for the halogen derivatives of aniline and salicylideneaniline[3,17].

If R is nitro group, the basicity order of the derivatives is standard>p-NO_2 m-NO_2 >o-NO_2. The nitro group strongly attracts the negative charge of the ring and depletes it by both negative inductive and resonance effects. Therefore, nitro derivatives are less basic than benzilidene-o-hydroxyaniline itself. Another important observation is the lower basicity of the ortho-nitro derivative than of the para-nitro derivative. This can be explained by the strong short-range negative inductive effect.

Methoxy derivatives of benzilidene-o-hydroxyaniline are more basic than benzilidene-o-hydroxyaniline and the basicity order of the derivatives is o-OCH_3 >p-OCH_3 >standard. This order can be used as an indication of the extent of the contributions of the methoxy group to the basicity of azomethine nitrogen. This order is as expected in light of the electronic effect of the methoxy group. However, the higher basicity of the ortho-methoxy derivative can be explained by the formation of the intramolecular hydrogen-bonded ring when acid was added during the titration, as shown below:
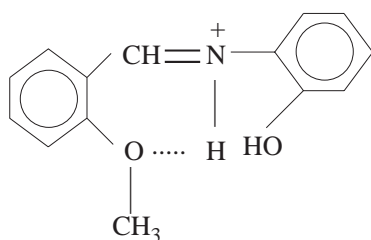
It can be assumed that hydrogen-bonded ring formation makes the substances more stabilized.

When the basicities of hydroxy derivatives with differing substitution patterns are compared, the order o-OH>m-OH>standard is found in nitrobenzene. The resonance effect of the hydroxy group overcomes its electron-withdrawing inductive effect. Thus, hydroxy derivatives are more basic than the benzilidene-o-hydroxy aniline itself. Why the ortho-derivative has the stronger basicity than the meta-derivative can be explained by the formation of the intramolecular nine-membered hydrogen-bonded ring. The comparison of half-neutralisation potential values of Schiff bases given below supports this result:

(I)	397 mV
(II)	368 mV
(III)	393 mV
(IV)	435 mV
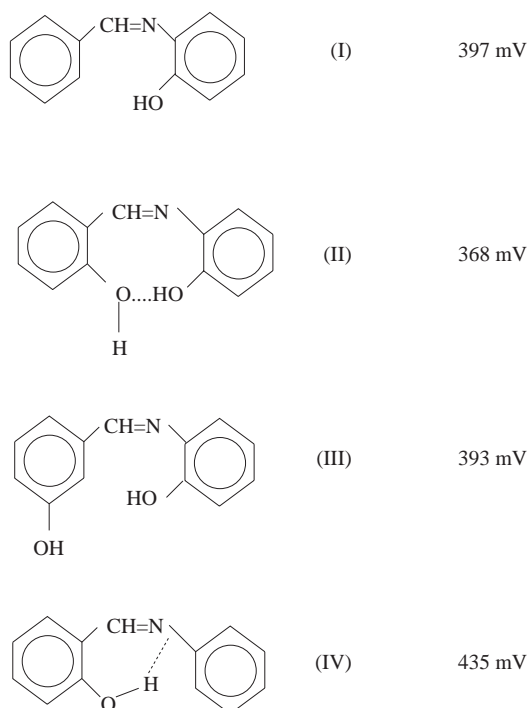
If the hydrogen bonding in Schiff base(II) had not formed, its half-neutralization potential value would not be so small.

There is no systematic discussion to date on the applicability of the Hammett equation to the behaviour of substitutents in Schiff bases in nitrobenzene solvent. For this purpose, Δ(hnp) values in Table 1 are plotted against substituent constant (σ), Figure 2. This figure show that, to a reasonable approximation, the Hammett equation equation represents the effects of substituents on the reactivity of azomethine nitrogen of Schiff bases in nitrobenzene solvent.
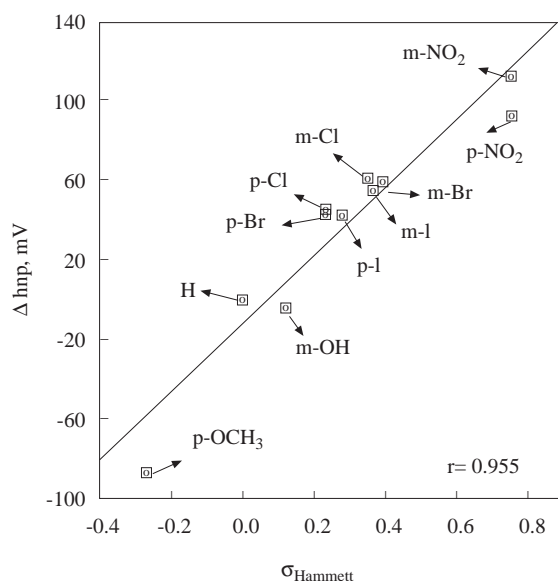
Figure 2. Plot of the Δ(hnp) of substituted benzilidene-o-hydroxyanilines against the Hammett substituted constants (σ) in nitrobenzene solvent.

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