

CHARGE-TRANSFER INTERACTION IN COMPLEXES BETWEEN ACIDS AND THEIR ANIONS

M. HEYROVSKÝ^a, S. VAVŘIČKA^b and O. EXNER^a

^a *J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, Prague 1 and*

^b *Department of Physical Chemistry,
Charles University, Prague 2*

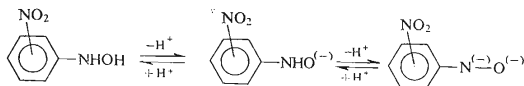
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The study of absorption spectra of 4-nitrophenylhydroxylamine in solution has shown that in the pH-region around pK_A 10.0 a complex between the molecule and its anion is formed giving a charge-transfer absorption. Preliminary experiments with similar compounds indicate that the charge-transfer interaction between a molecule and its anion is probably a more general effect.

The charge-transfer spectra have mostly been studied in complexes between two types of molecules one of which has the character of a donor and the other of an acceptor of electron¹. The possibility of electron donor-acceptor interaction between molecules of the same kind has also been discussed in the literature^{1,2}. In the gas phase the formation of charge-transfer complexes between aromatic molecules and their positively charged ions was observed³. However, to our knowledge, the charge-transfer interaction has not yet been observed between two forms of the same molecule differing only by protonation. In such a case the anion would behave like an electron donor and the corresponding acid as the acceptor; it is essential that the molecule should bear functional groups which give the molecule the donor and acceptor character. The complexes of organic acids and their anions, referred to inappropriately as homoconjugates, are well known and are remarkably stable in crystalline state⁴, in polar aprotic solvents⁵ and even in water⁶.

In the present paper we describe the electron absorption spectrum of weakly alkaline aqueous solutions of 4-nitrophenylhydroxylamine which we interpret by the charge transfer in a complex between the molecule and its anion. On the basis of our experiments with some different compounds we suppose that this effect is of a more general nature.

The conspicuous changes of colour of the solutions of 4-nitrophenylhydroxylamine and of its 2-isomer with the change of pH were already observed when they were prepared for the first time by Kuhn and Weygand⁷. The light greenish-yellow acidic aqueous alcoholic solutions of 4-nitrophenylhydroxylamine turn into scarlet red in weakly alkaline and into deep yellow in strongly alkaline solutions. In the case of 2-nitrophenylhydroxylamine the corresponding sequence of colours is yellow, bright blue-violet and dark red. Kuhn and Weygand⁷ attributed the colour changes to the formation of differently coloured mono- and divalent anions by dissociation of protons from the hydroxylamino group:



Holleck and Schmidt⁸ observed three maxima in the absorption spectra of both 2- and 4-nitrophenylhydroxylamines which, they supposed, were due to the above three species.

However, the existence of a divalent anion is *a priori* improbable, as it requires the presence of two equal charges on two neighbouring atoms of which only one can be partly delocalized by the mesomeric effect of the conjugated nitro group. Stable ions of such species in aqueous solutions are not known. Also our experimental results confirmed that the colour changes cannot be explained by a mere double dissociation.

EXPERIMENTAL

4-Nitrophenylhydroxylamine was prepared according to Kuhn and Weygand⁷. For the preparation an apparatus for working in inert atmosphere was used in connection with an oil vacuum pump and an argon cylinder. The yellow crystals recrystallized from a benzene-cyclohexane mixture began to melt at 102°C with simultaneous decomposition which is in fair agreement with the result of Kuhn and Weygand (107°C under decomposition).

The crystalline adduct of 4-nitrophenol with sodium 4-nitrophenolate was prepared from analytical grade chemicals by the method of Hadži and coworkers⁴. Sodium 4-nitrophenolate was precipitated from an aqueous-methanolic solution of 4-nitrophenol by an excess of concentrated NaOH solution and purified by recrystallization from dilute NaOH. All other chemicals were of analytical grade. The spectra of 4-nitrophenylhydroxylamine and 4-nitrophenylhydrazine in solutions saturated with argon were recorded in a spectrophotometer Unicam SP 800. The reflection spectra were recorded in the same spectrophotometer by using the adapter for diffuse reflectance SP 890. The measurements of pH were made with the compensation pH-meter Radiometer PHM 4 with a glass electrode.

RESULTS AND DISCUSSION

Absorption spectra of solutions of 4-nitrophenylhydroxylamine at three different pH-values corresponding to the three characteristic colours are shown in Fig. 1. The red colour appearing in slightly alkaline solutions and ascribed⁷ to the monovalent anion is due to the broad absorption maximum at wavelengths longer than those of the absorption maxima assigned^{7,8} to the molecule and the divalent anion. The pH-dependence of extinction at λ 530 nm in this absorption curve is given by the points in Fig. 2. This wavelength was chosen since the acidic and the strongly alkaline solutions have negligible absorption there. If the assumption of Kuhn and Weygand were correct then the two inflexion points on the curve in Fig. 2 at the pH-values 8.8 and 11.2 should represent the pK_A values of dissociation of 4-nitrophenylhydroxylamine into its mono- and divalent anions. These values are too close to each other for the dissociation of two protons from a molecule leading to the formation of an ion bearing two negative charges on neighbouring atoms. For a double dissociation of similar compounds there are not many experimental data at hand; for the doubly protonated cation of 4-nitrophenylhydrazine, for example, the constants pK_{A_1} 3.70 and pK_{A_2} — 9.2 were found⁹.

If the three maxima in Fig. 1 were characteristic of the three species proposed by Kuhn and Weygand, then the dependence of extinction in any of them on the

total concentration of 4-nitrophenylhydroxylamine would be a straight line passing through the origin. The points in Fig. 3 stand for the concentration dependence of extinction at λ 530 nm of the absorption spectrum of the red coloured solutions. It can be seen that although the dependence is approximately linear, it does not pass through the origin, but makes an intercept on the concentration axis. This is a further argument against the interpretation of the colour changes by a double dissociation of 4-nitrophenylhydroxylamine. In order to account better for the experimental facts we propose a different explanation for the colour changes. Nitrophenols are known to form complexes between the molecules and their anions through hydrogen bonds^{4,5}. We assume that a similar complex is formed also in solutions of 4-nitrophenylhydroxylamine. The position at long wavelengths and the broad shape of the absorption maximum of the red solution with its peak at 470 nm (curve 2, Fig. 1) suggest that the spectrum is due to charge transfer in the complex between the anion as electron donor and the molecule as acceptor. Since the extinction in the region of the inflexion at 560 nm changes proportionally with the whole absorption curve when the pH and the concentration of 4-nitrophenylhydroxylamine are changed, it appears that in the solution prevails only one complex showing the charge-transfer absorption and that this absorption is characterized by a double maximum. If we suppose that the absorption of light by the complex molecule-anion in our experimental

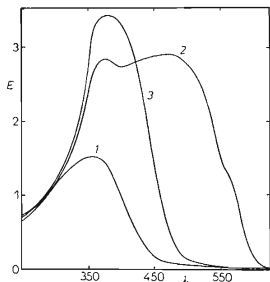


FIG. 1

Absorption Spectra of $3 \cdot 10^{-4}$ M Aqueous Solution of 4-Nitrophenylhydroxylamine in $1\text{M-H}_2\text{SO}_4$ (1), in Borate Buffer pH 10.0 (2) and in 1M-NaOH (3)

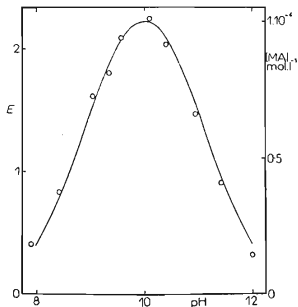


FIG. 2

pH-Dependence of Extinction at λ 530 nm of $3 \cdot 10^{-4}$ M Solution of 4-Nitrophenylhydroxylamine (Points) Compared with the pH-Dependence of the Concentration of the Complex Molecule-Anion Calculated from Eq. (4) (Line)

conditions followed the Lambert-Beer's law, then the points in Fig. 2 express the dependence of the concentration of the complex on pH and the position of the maximum of the curve at pH 10.0 corresponds to the first pK_A value of 4-nitrophenylhydroxylamine.

For the equilibrium state between the molecule M, anion A, complex MA and hydrogen ions in the solution following relations hold:

a) dissociation of the molecule $M \rightleftharpoons A + H^+$ with the apparent dissociation constant $K_A = \frac{[A][H^+]}{[M]}$ (1), b) complex formation $M + A \rightleftharpoons MA$ with the apparent complexity constant $K_C = \frac{[MA]}{[M][A]}$ (2), c) the total analytical concentration of 4-nitrophenylhydroxylamine

$$[N] = [M] + [A] + 2[MA] \quad (3)$$

From Eqs (1-3) one can obtain for the concentration of the complex

$$\sqrt{[MA]} = -\frac{[H^+] + K_A}{\sqrt{16K_A K_C [H^+]}} \pm \sqrt{\left(\frac{([H^+] + K_A)^2}{16K_A K_C [H^+]} + \frac{[N]}{2}\right)} \quad (4)$$

The negative sign before the second term on the right side of Eq. (4) leads to values with no physical meaning. The form of the $[MA]$ vs. pH curve depends on the value of the complexity constant K_C . By the method of successive approximation various values of K_C were substituted in Eq. (4), until the calculated $[MA]$ - pH curves coincided with the experimentally found dependence of extinction on pH (Fig. 2, points). The best agreement was obtained for $K_C = 2 \cdot 10^4$ (Fig. 2, line).

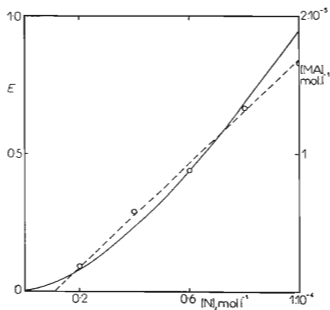


Fig. 3

Dependence of Extinction at λ 530 nm of the Solution of 4-Nitrophenylhydroxylamine at pH 10 on the Total Concentration (Points) Compared with the Dependence of the Concentration of the Complex Molecule-Anion Calculated from Eq. (4) (Full Line)

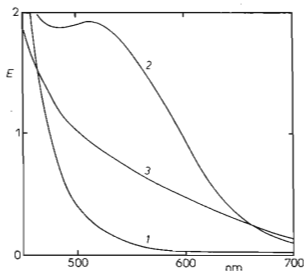


FIG. 4

Absorption Spectra of $9.5 \cdot 10^{-4}$ M Aqueous Solution of 4-Nitrophenylhydrazine at pH 10.4 (1), 12.9 (2) and 13.7 (3)

For the experimental conditions at which the spectrum 2 in Fig. 1 was recorded ($[N] = 3 \cdot 10^{-4}M$, pH 10.0) it follows from Eq. (4) with the use of $K_C 2 \cdot 10^4$ that about 57% of 4-nitrophenylhydroxylamine in the solution is in the form of complex in equilibrium with the anion and the undissociated molecule. The relatively high value of the constant K_C as compared with the constants of charge-transfer complexes¹ can be ascribed to the hydrogen bond which represents an additional bond to the CT interaction between the donor and acceptor. For the complexity constant of a hydrogen-bonded adduct of 4-nitrophenol and its anion the value of about $3 \cdot 10^3$ was found⁵ in acetonitrile (in water this adduct is insoluble⁴).

The dependence of the concentration of the complex molecule-anion on the total analytical concentration of 4-nitrophenylhydroxylamine calculated from Eq. (4) with $K_C 2 \cdot 10^4$ is represented in Fig. 3 by the full line. The agreement with the experimental points is satisfactory considering the simplified picture of the system leading to Eq. (4). When the value $K_C 2 \cdot 10^4$ is used, the extinction coefficient at the peak of the CT absorption maximum, λ 470 nm, is obtained from the experimental data as $\epsilon_{\max} 3 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. With this value the complex molecule-anion of 4-nitrophenylhydroxylamine ranks with the most strongly absorbing CT complexes¹.

From the analogy in colour changes of 2- and 4-nitrophenylhydroxylamine it appears that the bearer of the prominent colour of 2-nitrophenylhydroxylamine in weakly alkaline medium is also a complex between the molecule and anion showing charge-transfer interaction. From the spectra published in the paper by Holleck and Schmidt⁸ the pK_A value of 2-nitrophenylhydroxylamine can be estimated as 11.9. A picture similar to that of the nitrophenylhydroxylamines can be obtained with 4-nitrophenylhydrazine (Fig. 4): in alkaline solutions an absorption maximum at wavelengths longer than 450 nm appears which decreases when pH is further increased. The formation of a divalent anion at the values of pH reached is especially

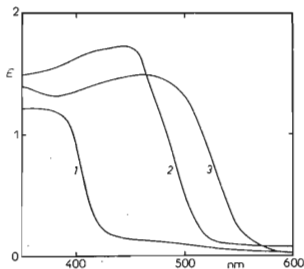


FIG. 5
Reflection Spectra of 4-Nitrophenol (1),
Sodium 4-Nitrophenolate (2), Adduct 4-Ni-
trophenol-Sodium 4-nitrophenolate (3)

Powdered crystals, spectra recorded with
reference to MgO.

improbable with this compound. An exact estimation of the pK_A value from the maximum of extinction in the long wavelength region, however, is difficult due to the decomposition of 4-nitrophenylhydrazine which takes place in strongly alkaline media even in the absence of oxygen.

Judging from the results of Kross and Fassel¹⁰, it could be expected that between the molecule and the anion of 2- and 4-nitrophenylhydroxylamine and of 4-nitrophenylhydrazine in addition to the charge-transfer interaction of the π -orbitals a localized interaction of the donor groups (nitrogen atoms) with the acceptor groups (nitro groups) takes place. This might account for the split of the C—T absorption band¹ (Fig. 1). The orientation of the partners in the complex, in that case, would be head-to-tail, with hydrogen bonds supporting the overall electron donor-acceptor interaction.

According to the colour changes observed during gradual alkalization of aqueous solutions of 4-nitrophenol it seems that in the crystalline adduct molecule-anion which precipitates in weakly alkaline solutions⁴ there is also a charge-transfer interaction taking place. In favour of this conclusion speak the reflection spectra of crystalline substances shown in Fig. 5. The absorption of light by crystals of the adduct extends to longer wavelengths than the absorption by the crystals of both 4-nitrophenol and sodium 4-nitrophenolate. The fact that when formed in acetonitrile the adduct does not show similar absorption⁵ suggests that in the crystal lattice the mutual position of the molecule and its anion is particularly favourable for the charge-transfer interaction. From aqueous solutions the adduct crystallizes in the form of a dihydrate and it is possible that the water molecules contribute to the favourable structure.

REFERENCES

1. Briegleb G.: *Elektronen-Donator-Acceptor-Komplexe*. Springer, Berlin 1961.
2. Foster R.: *Organic Charge-Transfer Complexes*. Academic Press, London 1969.
3. Job B. E., Patterson W. R.: Symposium *Newer Methods in Structural Chemistry*, Oxford 1966; United Trade Press, London 1967.
4. Hadži D., Novak A., Gordon J. E.: *J. Phys. Chem.* 67, 1118 (1963).
5. Kolthoff I. M., Chantooni M. K., jr, Bhowmik S.: *J. Am. Chem. Soc.* 88, 5430 (1966).
6. Farrer H.N., Rossotti F. J. C.: *Acta Chem. Scand.* 17, 1824 (1963).
7. Kuhn R., Weygand F.: *Ber.* 69, 1969 (1936).
8. Holleck L., Schmidt H.: *Ber. Bunsenges.* 59, 56 (1955).
9. Brignell P. J., Johnson C. D., Katritzky A. R., Shakir N., Tarhan H. O., Walker G.: *J. Chem. Soc. (B)* 1967, 1233.
10. Kross R. D., Fassel V. A.: *J. Am. Chem. Soc.* 79, 38 (1957).

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