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ACID STRENGTH OF PHENOXAZINE NITRODERIVATIVES

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Nowadays, the nitroderivatives of aromatic as well as pseudoaromatic compounds are drawing the attention as possible acid-base indicators[1–3]. It has been known for a long time that yellow or orange nitrophenoxazine-solutions provide in alkaline media blueviolet up to green anions[4–6]. The mononitroderivatives are very weak acids whereas polynitrophenoxazines form some stable alkaline salts[5]. In this respect the nitrophenoxazines resemble to nitroanilines or rather to some nitrodiphenylamines.

The nitroanilines, involving o-nitroaniline that has been commonly used as an indicator[7,8], as well as nitrodiphenylamines[8] have relatively little remoted positions of absorption maxima of both indicator forms in comparison with a nitrophenoxazine ones. The absorption maxima of nitrophenoxazine-anions are strongly bathochromically shifted[6,9] and their colour changes are as contrasting as in the case of sulphonphtaleins (for the colour change from yellow to blue). Their stability in the solid state as well as in the solutions is excellent and their preparation easy. That is why the nitrophenoxazines have been put to a fundamental study as indicators. They can be used only in the non-aqueous media because they are insoluble in water.

The acid strength of nitrophenoxazines has been determined through the conventional dissociation-constants gained by spectrophotometric measurements in 50 % ethanol. This determination has also been carried out by measuring half-neutralisation-points (HNP) in acetone and pyridine. In acetone and pyridine in which the nitrophenoxazines were used as indicators[10], the ranges of colour-change-potentials have been determined, too.

Experiments

The spectrophotometric measurements of dissociation-constants and HNP were performed on Beckman spectrophotometer DU Modell G 2400 in glass-cells (1,00 cm width). The temperature was 20 ± 1 °C when the dissociation-constants were measured, and 24 ± 2 °C during the measurement of HNP-values. Operational pH-values in 50 % ethanol were measured on Beckman pH-meter Modell G with Beckman glass-electrode Nr 40308 and calomel-electrode Nr 39270. The apparatus was always adjusted by means of aqueous solutions of potassium acid phthalate, Beckman buffer (pH = 6,98) and borax-buffer at 20 °C.

The HNP measurements were carried out on the pH-meter with vibration

capacitor PHK – 1 having Beckman electrodes Nr 40308 and 39970 with a bridge containing the saturated KCl solution in methanol. The measurements in pyridine were carried out by means of pH-meter Radiometer PHM-4 using the mentioned glass electrode and calomel electrode according to Marple and Fritz[11]. The cables of the electrodes were screened.

Chemicals and reagencies:

The nitrophenoxazines were prepared in the laboratory way[12]. Ammonium-buffers ($NH_4OH + NH_4Cl$) and for more alkaline region diluted KOH solutions, the ionic strength of which was kept at $\mu = 0{,}1$ with potassium chloride.

The acetone of p. a. grade was oxidated with potassium permanganate, dried with anhydrous calcium chloride, redestilled, poured through the column of a molecular sieve Calsit 5 Å (activetad at 300 °C) and redestilled once again under excluding air moisture and carbon dioxide. It contained 0,024 % of water according to C. Fischer.

Pyridine of the p. a. grade was dried with potassium hydroxide, then with anhydrous barium oxide and fractionally destilled. The water content corresponded to 0.2 %.

Methanol of the p. a. grade was purified by means of the fractional destillation.

Benzene of the p. a. grade was dried with metalic sodium, then redestilled in the presence of it.

The 0.07 M tetrabutylammoniumhydroxide was prepared in a usual way[13] and purified by pouring through the basic anex Amberlite IRA 400 in OH^- cycle[14]. Its normality was often standardized against benzoic acid potentiometrically.

The stock solutions of indicators were prepared in ethanol as 2×10^{-4} or 1×10^{-4} M respectivelly, in acetone and pyridine as 4×10^{-5} or 2×10^{-5} M resp. (more concentrated in the case of mononitroderivatives, more diluted in the case of polynitroderivatives).

Dissociation-constants in 50 % ethanol:

The samples for the measurements were prepared by the appropriate mixing of stock-solutions of nitrophenoxazines with ethanol and buffers. They contained 50 % vol. of ethanol and the indicator in the concentration 4×10^{-5} or 2×10^{-5} M resp. The ionic strength was kept at 0.05. When using these solutions several absorption curves at different operational pH-values were obtained for each compound in a visible region and in that way the positions of absorption maxima as well as the molar absorptivities of both forms of indicators were determined. On the basis of the absorption curves thus obtained, four wavelenghts for each indicator were selected in order to gain pH-extinction curves. In the colour change region of an indicator 6 to 8 absorbance values for each of four chosen wavelengths were gained. For the calculations of pK_I—values the following equation was used

$$pK_I = pH + \log \frac{|A - A_2|}{|A_1 - A|} \qquad (1), \text{ where}$$

pH denotes "operational pH" (the system of electrodes was adjusted by using aqueous buffer-solutions), A_1 denotes the absorbance of a pure acid indicator form, A the absorbance of a measured mixture of both indicator forms at a given pH-value and A_2 the absorbance of a pure basic form of the indicator — all that at the same wavelength and under the same total analytical concentration of the indicator.

In the case of very weak acid indicators where it was impossible to gain the appropriate linear part of the alkaline branch of pH-extinction curve in solution with ionic strength $\mu = 0.05$, the value of A_2 was calculated from the points of the steep part of the curve.

The mean value of pK_I for each indicator was obtained from 25—30 values by statistical method (excluding extreme results and calculation of the confidence interval).

HNP of indicators in acetone and pyridine:

70 ml 4×10^{-5} M or 2×10^{-5} M solution of an acid indicator form in acetone or pyridine were put into the titration vessel and their potential was measured. 5 ml of that solution were taken into a spectrophotometric cell and their absorption measured at the selected wavelengths. Then 0.07 M tetrabutylammonium-hydroxide solution was gradually added and after each addition (0.01 ml) the potential as well as the absorbance were measured. The transfer of the sample from the titration vessel was performed under the inert atmosphere (N_2) and the spectrophotometric measurement was carried out in the stoppered cells. When the absorbance under addition of base had practically stopped to change, such a quantity of the base solution was still added, that its total volume corresponded to 0.20 ml, and the potential and absorbance were measured once more. The wavelengths within which the measurement was performed, were selected according to the course of the spectra of both indicator forms in acetone and in pyridine. The solution of a basic form was prepared through adding 0.2 ml 0.07 M solution of quarternary base to 50 ml of the solution of an indicator. The volumetric change was neclected. The HNP was determined by means of numerical or graphical interpolation as a potential of the point, in which the concentration of an acid (c_A) as well as of a basic form (c_B) of indicator were the same.

HNP determined in pyridine are somewhat less reliable than in acetone. The measurements performed in pyridine are undergoing some strong electrostatical neighbouring influences and therefore they require a high input-resistance instrument. The Radiometer PHM —4 having the input-resistance of 10^{12} Ohms is sufficient for the potential jump not to be influenced by the apparatus itself when titration in pyridine is being carried out, but it is affected by an induction of electrostatical charges from the glass parts of the apparatus. That is why the whole apparatus was placed in the large Faraday cage during the measurement of HNP in pyridine.

Results

The table 1 shows the obtained values of dissociation constants and half neutralisation points.

As it was expected 1-nitrophenoxazine is the weakest and 1, 3, 7, 9-tetranitrophenoxazine the strongest acid in all mentioned solvents. The latter derivative appears in acetone as well as in pyridine as a comparatively strong acid with 2,4-dinitrophenol and with the hydrochloric acid as well.

Concerning the group of investigated compounds the multiple relations appeared among the values found in the individual solvents and even the order of acid strength in the certain solvent is in some cases unexpected. In all the solvents the 1-nitrophenoxazine is a substantially weaker acid in comparison with 3-nitrophenoxazine although in respect to the induction and mesomeric effect of the nitrogroup, the strength of both of these substances ought to be

Tab. 1.: pKj and HNP values of nitrophenoxazine indicators.

Substituted phenoxazine	pK_I – 50% EtOH[a]	HNP – acetone mV	HNP – pyridine mV
1-NO_2	14.7 ± 0.5[b]	−478	−743[c]
3-NO_2	12.27 ± 0.02	−262	−480
1-CH_3, 3-NO_2	12.46 ± 0.02	−270	−482
9-CH_3, 3-NO_2	12.50 ± 0.03	−245	−473
1,7-CH_3, 3-NO_2	12.16 ± 0.01	−241	−485
1,9-CH_3, 3-NO_2	12.06 ± 0.03	−231	−457
7,9-CH_3, 3-NO_2	12.31 ± 0.03	—	—
1,3-NO_2	11.17 ± 0.02	−79	−289
3,7-NO_2	11.26 ± 0.02	−70	−322
1,3,9-NO_2	11.82 ± 0.03	−63	−255
1,3,7-NO_2	9.60 ± 0.01	87	−218
1,3,7,9-NO_2	9.38 ± 0.02	159[c]	−127

a . . . The results are given in the form $pK_I \pm 2s_{\bar{x}}$

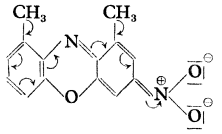
b . . . The value was calculated from several points on the steep part of the pH-extinction curve

c . . . Little reliable values. Tetranitrophenoxazine obviously reacts with the solvent in the sense of Zimmermann reaction[17] as the meta-polynitroderivative. In the case of 1-nitrophenoxazine it is impossible to remove small changes of colour by manipulation. Measured potential is probably more negative than right HNP value.

roughly the same. It is obvious that with the 1-nitroderivative the acid form is stabilized by a hydrogen bond, whereas the basic form (anion) shows a sterical hindrance of solvation. Both mentioned effect cause the weakening of the acid. Furthermore, in the case of 1-nitrophenoxazine, a certain disturbance of molecular planarity may take place. It can be seen as a steric hindrance of the conjugation. In accordance with this fact even the 1, 3, 7-trinitrophenoxazine appears to be in all the solvents stronger in comparison with 1, 3, 9-trinitroderivative.

According to these facts would be possible to give the opinion that the nitrogroup in „para-position" to the reaction centre (to the NH-group) strengthens the acidity more than the nitrogroup in „ortho-position". The first discrepancy can be found already in the comparison of both the dinitrophenoxazines. The 3,7-dinitroderivative is in the medium of 50 % ethanol as well as in pyridine a weaker acid than 1, 3-dinitroderivative, and the 1, 3, 9-trinitrophenoxazine is in 50 % ethanol even weaker as both the dinitroderivatives. It seems, however, that we must take into account even the symmetry of the substitution around the reaction centre. When substituting various nuclei the induction effects of the nitrogroups are directed in oposite direction and through the conductive connection of a pseudoaromatic system they are essentially mutually eliminated. A certain relation is offered even in comparison with the absorption spectra. A perfect symmetry of a 3, 7-dinitrophenoxazine-anion is the cause of the fact that this particle is absorbing at the longest wavelength from all the basic forms of nitrophenoxazines. The bathochromic shift is 215 nm due to the dissociation[9]. Making an incompetent simplification by presumption that the change of the position of the absorption maxima is influenced only by the energy change of molecular orbitals in the ground, but not in the excited state, we can say that the anion of 3, 7-dinitroderivative has a very high energy and that is why it is only little stabile. At acidobasic equilibrium the low stability of the conjugated base, which first of all is due to symmetry of molecule, comes to be evident in this case through the weakening effect of an acid.

Similar aspects may be taken into consideration even in the series of methyl-substituated 3-nitrophenoxazine derivatives in 50 % ethanol and acetone (in pyridine it is necessary to take those delicate differences in the HNP-values with great precautions). According to the expected positive induction effect of a methyl group both the monomethylderivatives are weaker acids (in 50 % ethanol) than 3-nitrophenoxazine. However, the dimethylderivatives, here investigated, are stronger acids than monomethylderivatives. When substituted by two methyl-groups, the hyperconjugative influence of the methylgroups evidently predominates and it stabilizes the anion and in this way strengthens the acid. The situation can be expressed for example with the following formula:



In accordance with this fact (considering again the ground state only) the hypsochromic shift (anion stabilization) with an increasing number of methylgroups can be given[9]. The similar influence of the methylgroups causing the increase

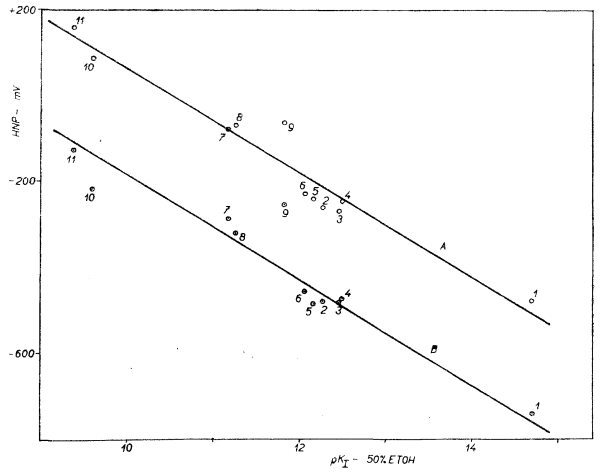


Fig. 1
Correlation between the pK_I and HNP values.
A . . . relationship between pK_I and HNP in acetone;
B . . . relationship between pK_I and HNP in pyridine

of thermodynamic stability of an anion in comparison to the neutral molecule of the nitroform has been found for nitroalkanes[15]. From the dimethylderivatives, here investigated, the 7, 9-dimethyl-3-nitrophenoxazine seems to be the weakest acid; the induction effect of its methylgroups are directed conformly towards the reaction centre and the hyperconjugative anion-stabilization does not predominante in such an expressive way. The more expressive elimination of the opposite induction effects of methylgroups is the result by the two other remaining dimethylderivatives, the hyperconjugation fully predominates and that is why both the dimethylderivatives represent even stronger acids when compared with the 3-nitrophenoxazine itself.

There is an interesting problem, to what extent we can put into the correlation the HNP-values measured in acetone and pyridine one to other and to the pK_I--values. Although the whole group may be regarded as the substances of the same structural type, it can be said already in advance, that with the investigated group of substances in given solvents no linear correlation can be expected. The main reason appears to be the change of the solvation energy within the region of the specific solvation effects. As far as the solvents are concerned, it should be emphasized they are solvents of basicly different charackter. From among the speci ic solvation effects the steric effects and the influence of hydrogen bonds make themselves felt. In short one cannot expect in this scase the linear correlation for the same reasons, for which one cannot put into correlation the pK_a values of the m- and p-substituted benzoic acids with the values of the o-substituted acids. Figs. 1. and 2. show the above-mentioned relations.

The lines were interposed empirically, not in the numerical way, because the relationships are not taken for linearly correlable ones. Nevertheless, there is some relationship but apparently it is not linear. In some cases with the change of a solvent the order of indicator acidity is changed, too. With 1, 3, 9—trinitrophenoxazine the largest deviation from a possible straight line is given. That is why it was not taken into consideration in drawing the straight line. The position of values given for 1-nitrophenoxazine (with respect to the little accuracy in determining the corresponding values) is uncertain, too. Obviously, as the best appears to be the relation existing between the values measured in both aprotic solvents.

Besides HNP-values given in acetone and pyridine, the potential region of a colour change of individual indicators was determined. From measured absorbancies the content of the base- and acid- indicator forms was determined (in percents) according to the relations:

$$c_A = \frac{|A - A_2| \times 100}{|A_1 - A_2|} \quad \text{and} \quad c_B = 100 - c_A \qquad (2)$$

The colour change is not symmetrical around HNP because the molar absorptivity of maxima of the basic form has approximately twice as high value as that of the acid form. The majority of indicators show the colour change from yellow through green to blue and the solution appears to be "visually blue" when concentration $c_B = 60$ % is reached. So as the region of colour change (to be observed visually) is taken a potential interval corresponding to the values 10 to 60 % c_B in the equilibrium mixture. The greatest visual change appears from 20 to 30 % c_B.

In the table 2 the measured and evaluated regions of colour change of individual indicators are summarized. The limit values have been calculated as follows:

$$E_{10\%} = HNP + 0.059 \log 9 \quad \text{and} \quad E_{60\%} = HNP + 0.059 \log \frac{2}{3} \quad (3)$$

The concordance between the calculated and the measured values appears as relatively good one. In acetone the region measured with the strongest acids appears to be a little narrower, and with the weaker acids broader than the calculated one. The second effect might come to be true if with these acids in acetone some homoconjugation appeared between them and their anions[16]. The homo-

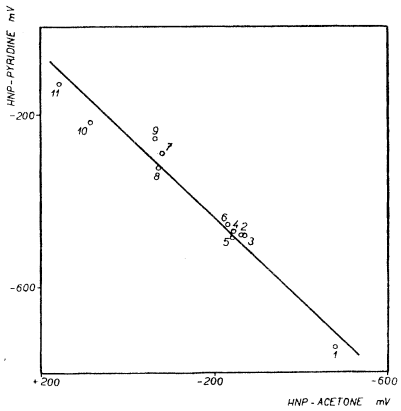


Fig. 2
Correlation between the HNP values in acetone and pyridine.
1 . . . 1-nitro-; 2 . . . 3-nitro-; 3 . . . 1-methyl-3-nitro-; 4 . . . 9-methyl-3-nitro-; 5 . . . 1,7-dimethyl-3-nitro-; 6 . . . 1,9-dimethyl-3-nitro;- 7 . . . 1,3-dinitro-; 8 . . . 3,7-dinitro-; 9 . . . 1,3,9--trinitro-; 10 . . . 1,3,7-trinitro-; and 11 . . . 1,3,7,9-tetranitrophenoxazine.

conjugation was not observed by means of spectrophotometry and furthermore, it appeared to be very improbable with compounds having such structure. Especially, with 1, 9-dimethyl-3-nitrophenoxazine this homoconjugation effect must be ruled out. The invalidity of equations (3) might be given for some other reasons in consequence of some more complicated equilibrium-states brought about by the solvolysis. The greatest discrepancy between the calculated range of potential colour change and the observed one comes out with the weakest acid- 1-nitrophenoxazine. The discrepancy may be due to some experimental faults because we worked in an unbuffered media to avoid the influence of heteroconjugation and other equilibrium states combined with some buffer components.

Tab. 2. Region of colour change of nitrophenoxazines in acetone and pyridine

Substituted phenoxazine	Colour change	in acetone		in pyridine	
		ΔE_{calc} mV	ΔE_{meas} mV	ΔE_{calc} mV	ΔE_{meas} mV
1-NO_2	orange-blue	−422 to −488	−392 to −495	−687 to −753	—
3-NO_2	yellow-blue	−206 to −272	−190 to −275	−424 to −490	−425 to −487
1-CH_3, 3-NO_2	yellow-blue	−214 to −280	−202 to −281	−426 to −492	−414 to −493
9-CH_3, 3-NO_2	yellow-blue	−189 to −255	−185 to −256	−417 to −483	−412 to −484
1,7-CH_3, 3-NO_2	yellow-violetblue	−185 to −251	−167 to −257	−429 to −495	−436 to −488
1,9-CH_3, 3-NO_2	yellow-violetblue	−175 to −241	−164 to −257	−401 to −467	−420 to −460
1,3-NO_2	yellow-violet	−23 to −89	−23 to −88	−233 to −299	−232 to −297
3,7-NO_2	yellow-bluegreen	−14 to −80	−30 to −76	−256 to −332	−266 to −330
1,3,9-NO_2	yellow-violet	−7 to −73	−19 to −70	−199 to −265	−205 to −259
1,3,7-NO_2	yellow-violet	+143 to +77	+147 to +74	−162 to −228	−165 to −224
1,3,7,9-NO_2	orange-greenblue	+215 to +149	+221 to +148	−71 to −137	−63 to −144

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SHRNUTÍ

SÍLA NITROFENOXAZINŮ JAKO KYSELIN

ZDENĚK STRÁNSKÝ

Nitrofenoxaziny se osvědčují jako indikátory pro stanovení slabých kyselin v nevodných prostředích. Byly proto zjištěny konvenční disociační konstanty v 50 %ním ethanolu a hodnoty potenciálů poloviční neutralizace v acetonu a v pyridinu. V acetonu a v pyridinu byly též změřeny oblasti potenciálů barevného přechodu. Je diskutován vliv struktury nitrofenoxazinů a vliv prostředí na naměřené hodnoty.

ZUSAMMENFASSUNG

AZIDITÄT VON NITROPHENOXAZINEN

ZDENĚK STRÁNSKÝ

Nitrophenoxazine bewährte sich sehr gut als Indikatoren für die Bestimmung von schwachen Säuren in nichtwässerigen Medien. Es wurden deswegen die konventionellen Dissoziationskonstanten in 50proz. Äthanol und Werte des Halbneutralisationspotentials in Aceton und Pyridin ermittelt. In den letzgenannten zwei Lösungsmitteln wurden auch Bereiche des Farbumschlagspotentials festgestellt. In der Arbeit wird auch der Einfluß der Nitrophenoxazinstruktur und des Mediums auf die abgemessenen Werte diskutiert.