On the basicity of hydroxylamine and its derivatives

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The pK_a values of hydroxylamine and its derivatives were determined
titrimetrically in water and water—ethanol mixtures. The obtained pK_a
values of the O-alkylhydroxylamines were correlated with the half-wave
potentials of the polarographic reduction waves. A surprisingly high pK_a
value of hydroxylamine was explained on the basis of the formation of
hydrogen bonds with solvent proved by means of infrared spectra.

The positive induction effect of alkyl causes a higher basicity of aliphatic amines
with respect to ammonia [1—3] but the alkylation of hydroxylamine brings about
a decrease in the pK_a values of alkylhydroxylamines in comparison with hydroxyl-
amine. This effect has been described in literature earlier but remained without
explanation [4]. The present communication is devoted to the interpretation of
this effect.

Experimental

Hydroxylammonium chloride, methylammonium chloride, dibutylamine, and piperi-
dine were of anal. grade (Lachema, Brno). O-Methyl- and O-ethylhydroxylammonium
chlorides were prepared according to [5] by alkylating potassium hydroxylaminedisulfo-
nate with dialkyl sulfate. O-Benzylhydroxylammonium chloride was obtained by hydro-
lyzing O-benzylacetoxime according to *Janny* [6]. N-Methylhydroxylammonium chloride
was prepared by reduction of nitromethane with zinc [7]. N-Dibutyl- and N-dibenzyl-
hydroxylamines were prepared by alkylation of hydroxylamine with butyl bromide [8]
or benzyl chloride [9]. N-Oxypiperidine was obtained by oxidation of piperidine with
hydrogen peroxide [10]. The purity of preparations was checked by melting points and
the content of nitrogen or chlorine.

The pK_a values were determined titrimetrically on a Radelkis OP 205 pH-meter with
a glass electrode and a separated 0.1 N silver chloride electrode filled with the same solvent
as that of titrated solution. Before titration the glass electrode was soaked for 24 hrs in
a given solvent as recommended in literature [11]. The electrodes were calibrated with
citrate buffer solutions according to [12]. Titrations were performed with 0.01 M solutions
(in the case of N-dibenzylhydroxylamine with 0.005 M solution) in water, 10, 30, and 50%
(weight) ethanol while the ionic strength was adjusted to $\mu = 0.1$ with sodium perchlo-
rate (anal. grade, Lachema, Brno). The solutions were titrated with 0.1 M solution of
NaOH (anal. grade, Lachema, Brno) or 0.1 M solution of perchloric acid (anal. grade,
Jenapharm) in the same solvent.

The dissociation constant is defined by equation

$$K_a = \frac{a_{H^+}\, a_B}{a_{BH^+}}.$$

Here it is possible without any significant error to replace the activity of base by its concentration because it is known that the activity coefficients of non-electrolytes are close to unit value in 0.01 M solutions. The activity of protonized form may be expressed by its concentration and activity coefficient. Therefore the above equation may be written in the form

$$pK_a = pa_{H^+} + \log \frac{c_{BH^+}}{c_B} + \log f_{BH^+}.$$

The activity coefficients were calculated from equation

$$-\log f_{\pm} = \frac{A\, z_i^2\, \sqrt{\mu}}{1 + B\, r\sqrt{\mu}}.$$

The values calculated by adding the interatomic distances [13] were inserted for r. However, these values were corrected for a possible rotation about single bonds in the case of longer alkyls. The values of dielectric constants (D) of the solvents were taken from literature [14]. The reproducibility of thus obtained values was ± 0.01 pK_a, the accuracy of measurements with respect to [11] being only ± 0.02 pK_a.

For polarographic experiments aqueous 1×10^{-3} M solutions of the substances were prepared. These solutions were mixed with equal volume of the buffer solutions and used for polarographic investigations after stirring and removing oxygen with nitrogen. These investigations were carried out with a polarograph LP 7 (Laboratorní přístroje, Prague), a Kalousek vessel with separated saturated calomel electrode and a dropping mercury electrode (drop time $t = 2.9$ s, outflow rate $m = 3.41$ mgHg s^{-1}, potential applied to the drop 0.00 V). The i.r. spectra were taken on a UR-20 (Zeiss, Jena) spectrophotometer in a 1.4-cm cell.

Results and discussion

The pK_a values of the investigated substances found titrimetrically in water and in mixed solvents water—ethanol are summarized in Table 1 and the relationship between pK_a and $1/D$ is presented in Fig. 1. Because of the low solubility of N-dibenzylhydroxylamine and N-dibutylhydroxylamine the pK_a values of these substances were measured only in solutions with higher concentrations of alcohol. It is obvious from Table 1 that the pK_a values of O-alkylhydroxylamines obey the Taft equation except for hydroxylamine, the pK_a value of which is approximately by 1.5 unit higher than the value corresponding to the Taft equation. The high reproducibility of the pK_a values excludes dimerization of the titrated substances in a given medium and the dependence of pK_a on $1/D$ is practically identical in the whole series studied. It follows from this fact that the potentiometric measurements alone are not sufficient for the interpretation of the above-mentioned anomalies and therefore the spectral method had to be used.

For the study of infrared spectra N-dibenzylhydroxylamine was used because of its good solubility in all solvents investigated. This substance in 10^{-2} M solution

Table 1

The pK_a values of hydroxylamines in water and in mixed solvents water—ethanol at 20°C

Substance	Ionic radius in A (chosen)	Weight % of ethanol in the medium			
		0	10	30	50
N-Dibenzylhydroxylamine	10	—	—	—	3.21
N-Dibutylhydroxylamine	6	—	—	5.38	5.00
N-Oxypiperidine	6	5.39	5.34	5.25	5.14
N-Methylhydroxylamine	4	5.80	5.76	5.70	5.59
Hydroxylamine	4	5.93	5.825	5.69	5.44
O-Methylhydroxylamine	4	4.58	4.52	4.20	3.85
O-Ethylhydroxylamine	5	4.65	4.61	4.26	3.96
O-Benzylhydroxylamine	8	4.23	4.21	3.86	3.53

of carbon tetrachloride shows a band at about 3600 cm^{-1} which corresponds to the stretching vibrations of the free OH groups. In the case of mixed solvents carbon tetrachloride—dioxan and carbon tetrachloride—benzonitrile it was possible to observe at lower wavelengths (approximately 3480 cm^{-1}) a broad vibration band ν(OH) corresponding to the OH groups bound by hydrogen bond. The formation of hydrogen bonds between the OH groups of hydroxylamine and the molecules of solvent bringing about an increase in the electron density on the nitrogen atom of hydroxylamine accounts for a high basicity of those derivatives which have an OH group in the molecule because the induction effect of the electron pair of solvent taking part in the formation of hydrogen bond is greater than the induction effect of alkyl.

Earlier, other authors [15, 16] studied polarographically hydroxylamine and its derivatives. They revealed a two-electron diffusion wave corresponding to the re-
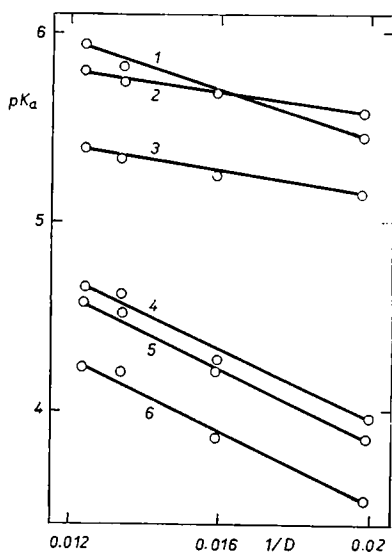

Fig. 1. The pK_a value of hydroxylamine and its derivatives as a function of the reciprocal value of the dielectric constant of solvent at 20°C.
1. Hydroxylamine; *2.* N-methylhydroxylamine; *3.* N-oxypiperidine; *4.* O-ethylhydroxylamine; *5.* O-methylhydroxylamine; *6.* O-benzylhydroxylamine.

duction of hydroxylammonium salt to the respective amine. Our results are in excellent agreement with the quoted authors. In the region $pa_{H}^{+} < pK_a$ the half-wave potential is only little dependent on pa_{H}^{+}. This fact has been used in the confrontation of the half-wave potentials of hydroxylamine with those of its O-alkyl derivatives. The half-wave potentials of these substances in aqueous buffer solutions are listed in Table 2. The comparison of the half-wave potentials at $pa_{H}^{+} = 4.10$ with the pK_a values given in Table 1 shows in conformity with spectral measurements that the hydrogen bond between the OH group of hydroxylamine and the oxygen atom of water molecule is preserved even in the proximity of the drop and causes a reduction of hydroxylamine at more negative potentials when compared with its O-alkyl derivatives.

The comparison of the values from Table 1 with those in Table 3 (which contains the obtained pK_a values of amine in 50 wt % ethanol) was employed in studying the effect of alkylation at nitrogen upon the pK_a values of N-alkylhydroxylamines. This comparison shows clearly that the alkylation of ammonia shifts the pK_a values markedly into more alkaline region and the alkylation of hydroxylamine on nitrogen atom by one methyl group does not practically change the pK_a value while the substitution of both hydrogen atoms on nitrogen atom of hydroxylamine shifts the pK_a values unambiguously into more acid region.

The possible effect of hydrogen bonds on the pK_a values of these substances was investigated by measuring the infrared spectra of O-benzylhydroxylamine in carbon tetrachloride and in the mixed solvent carbon tetrachloride—dioxan. The symmetric and asymmetric N—H stretching vibrations at 3240 and 3325 cm^{-1} were found in both solvents. These values are in agreement with the literary data on the infrared

Table 2

Half-wave potentials of the polarographic reduction of O-alkylhydroxylamines in acetate buffer solution at $pa_{H}^{+} = 4.10$

Substance	$-E_{1/2}$ [V]
Hydroxylamine	1.48
O-Methylhydroxylamine	1.38
O-Ethylhydroxylamine	1.33
O-Benzylhydroxylamine	1.20

Table 3

The pK_a values of amines in 50% ethanol (by weight) at 20°C

Substance	Ionic radius in A (chosen)	pK_a
Ammonia	4	8.51
Methylamine	4	9.85
Dibutylamine	6	9.65
Piperidine	6	9.97

spectra of O-alkylhydroxylamines [17]. If the solvent is replaced, these bands remain unchanged. In contrast to these experiments it is known from literature [18] that owing to the intermolecular hydrogen bonds hydroxylammonium chloride shows some bands corresponding to vibrations of the bonded $-NH_3^+$ groups. These hydrogen bonds were also revealed in the solid state by means of structural analysis [19—21]. Therefore it may be concluded that only the protonized form of substances forms the hydrogen bonds with solvent. The induction effect of the electron pair of solvent participating in the formation of hydrogen bond is thus greater than that of alkyl which results in an abnormal change in the pK_a values of N-alkylhydroxylamines. It is worth noticing that the hydrogen bonds $N-H$ O may be considerably weaker than the hydrogen bonds $O-H$ O because their influence on the electron density of nitrogen atom is more immediate.

An increase in the electron density at nitrogen atom brings about the increase in the basicity of the substance. Therefore hydroxylamine is the most basic substance in the series studied because it is able to form the hydrogen bonds with solvent by its $-OH$ as well as $-NH_3^+$ groups. N-Alkylhydroxylamines which form the hydrogen bonds with solvent by their free $-OH$ group are less basic while the lowest basicity is exhibited by O-alkylhydroxylamines forming only weak hydrogen bonds by their $-NH_3^+$ groups.

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