Cationic Heteroconjugation Equilibria in Systems with Heterocyclic *N*-Oxides in Non-Aqueous Media

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Abstract

The potentiometric titration method has been used to study the equilibria of cationic heteroconjugation in systems formed by substituted pyridine *N*-oxides in the polar non-aqueous solvents; nitrobenzene, acetonitrile, acetone and methanol. For comparison, the systems with trimethylamine *N*-oxide as a representative of aliphatic amine *N*-oxides and pyridine representing parent heterocyclic amines were also considered. The cationic heteroconjugation constants, i.e. the constants of conjugation reactions between free and protonated *N*-bases leading to the formation of asymmetric BHB_1^+ cations determined in experimental systems without proton transfer in media studied have been compared and discussed. Summing up: investigations of the equilibria of cationic heteroconjugation in non-aqueous media revealed that only a small range can be noted in the amphiprotic methanol, whereas in the basic aprotic solvent, acetone, the range observed is slightly greater. A full scheme of the heteroconjugation equilibria can be observed in two other aprotic protophobic solvents studied – acetonitrile and nitrobenzene.
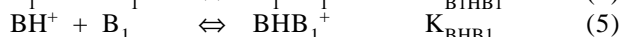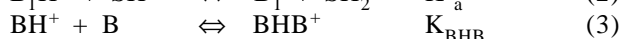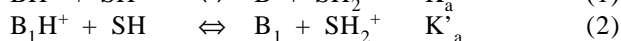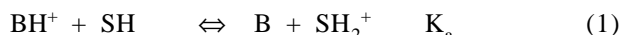
Keywords: Acid-base equilibria, heteroconjugation, non-aqueous solvents, pyridine *N*-oxides, potentiometry

Introduction

Considering the interactions between uncharged or cationic acids and bases in non-aqueous solutions, one can predict the model of acid-base equilibria established in such media [1]. However, the equilibria scheme, in aprotic solvents in particular, is very complex and dependent on the nature of the medium used. In order to obtain a complete picture of these equilibria, polar aprotic solvents are used in such studies, as they exhibit very weak, but still measurable amphiprotic properties [2]. Because of their strong differentiating properties and very weakly exhibited acidic-basic properties, these solvents are convenient

when studying such subtle properties of acid-base systems as homo- and heteroconjugation equilibria [3], in which hydrogen-bonded complexes are formed between acids and bases [4]. Studying hydrogen-bonding equilibria in apolar aprotic solvents is much more difficult because of experimental limitations and much more complex equilibrium model involving higher-order complexes [3]. Those subtle properties of solutions such as homo- and heteroconjugation are not observable in water since in this medium, due to its high polarity and capability of proton exchange, the extent of protolytic equilibria is highly limited relative to polar aprotic solvents. The former property is responsible for the high dissociation degree of the substances studied, while the latter is unfavorable for the

homo- and heteroconjugation equilibria. The cationic acids are stabilized by solvation and are thus unable to form hydrogen-bonding complexes with molecules of bases. On going from water to other amphiprotic (or polar aprotic solvents exhibiting very weak yet still measurable amphiprotic properties) solvents of decreased polarity and capability to proton exchange, the probability of establishing the conjugation equilibria increases. Therefore in polar aprotic and amphiprotic solvents of poor capability of proton exchange, for systems composed of two kinds of cationic acids (BH^+ and B_1H^+) and conjugated bases (B and B_1) it is reasonable to assume the following model of fundamental equilibria:

$$BH^+ + SH \Leftrightarrow B + SH_2^+ \qquad K_a \qquad (1)$$
$$B_1H^+ + SH \Leftrightarrow B_1 + SH_2^+ \qquad K'_a \qquad (2)$$
$$BH^+ + B \Leftrightarrow BHB^+ \qquad K_{BHB} \qquad (3)$$
$$B_1H^+ + B_1 \Leftrightarrow B_1HB_1^+ \qquad K_{B1HB1} \qquad (4)$$
$$BH^+ + B_1 \Leftrightarrow BHB_1^+ \qquad K_{BHB1} \qquad (5)$$

where Eqs. (1) and (2) define the cationic acid dissociation equilibria (with S representing the solvent molecule), Eqs. (3) and (4) define the cationic homoconjugation equilibria, and Eq. (5) defines the cationic heteroconjugation equilibrium in which BH^+ acts as a proton donor and B_1 as a proton acceptor. The last equation shows that the cationic cationic heteroconjugation (5) is a reaction in which a cationic acid BH^+ reacts with base B_1 conjugated with an acid other than BH^+ to afford a hydrogen-bonded complex cation, BHB_1^+. In these complexes B and B_1 may be both *N*-oxides and the parent amines. Consequently, depending on the nature of the species used, a variety of hydrogen bridges can be formed. The $[OHO]^+$ ones are the result of reaction of protonated *N*-oxides (BH^+) with another *N*-oxide (B_1). On the other hand, the $[OHN]^+$ bridges are formed either between the pyridinium cation and an *N*-oxide or between the protonated form of the *N*-oxide and pyridine.

It is worth mentioning that the equilibrium of cationic heteroconjugation (5) can be regarded as a particular case of the Brönsted acid-base equilibrium consisting in proton exchange between a proton donor and proton acceptor which gives rise to two co-existing conjugated acid-base pairs, HA/A$^-$ and BH^+/B:

$$B + HA \Leftrightarrow BH^+ + A^- \qquad (6)$$

This equilibrium is frequently referred to as the proton-transfer equilibrium. The formation of hydrogen bonding between acid HA and base B is crucial for the existence of the BHA complex in which the position of proton depends on the relative strength of acid and base, as well as on the nature of solvent. For a particular base, B, using proton-donor reagents of increasing strength leads to further equilibria:

$$B + HA \Leftrightarrow [B...HA] \qquad (7)$$
$$[B...HA] \Leftrightarrow BH^+...A^-] \qquad (8)$$
$$[BH^+...A^-] \Leftrightarrow BH^+ + A^- \qquad (9)$$
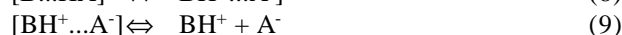
where Eq. (7) describes a weak, asymmetrical hydrogen bonding, Eq. (8) a stronger, almost symmetrical, hydrogen bond present owing to additional equilibrium of the so-called „partial proton transfer" consisting of co-existence of two tautomeric forms of the BHA complex, and Eq. (9) the formation of ion pairs in which the proton passes completely onto the base. Thus, in these systems the proton is completely transferred onto the acceptor. Consequently, the proton exchange equilibrium (6) can be described by the following equation involving equilibria (7) through (9):

$$B + HA \Leftrightarrow [B...HA] \Leftrightarrow [BH^+...A^-] \Leftrightarrow BH^+ + A^- \qquad (10).$$
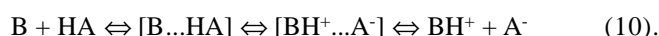
Its position depends on the relative strengths of the acid-base reactants.

Obviously, one can write down an equation equivalent to Eq. (5) defining heteroconjugation equilibrium in which B_1H^+ acts as a proton donor and B as a proton acceptor (resulting in the formation of the same heterocomplex ion B_1HB^+). Therefore, for the sake of uniqueness, it is assumed in all subsequent considerations that B is a stronger base than B_1. Bearing in mind the above considerations concerning proton-exchange equilibria, this means that the heteroconjugating „systems without proton transfer" are taken into account. Considered for the sake of comparison, the reverse B_1H^+/B ones, are called „systems with proton transfer".

The acid-base equilibria, e.g. acid dissociation and cationic homoconjugation, in systems formed by pyridine *N*-oxides have been studied in a variety of non-aqueous media, such as polar aprotic protophobic solvents — acetonitrile [5, 6], benzonitrile [7], propylene carbonate [8], nitromethane [9], acetone [10]; polar aprotic protophilic solvents - dimethyl sulfoxide [11], *N,N*-dimethylformamide [11], as well as in the amphiprotic solvent, methanol [12]. Heteroconjugation equilibria which lead to the formation of BHB_1^+ cations were studied less extensively. Moreover, the $[NHN]^+$ systems [13–17] received more attention than the $[OHO]^+$ and the $[NHO]^+$ systems [18, 19]. Therefore, the equilibria of cationic heteroconjugation in substituted pyridine *N*-oxide systems are the subjects of interest in this study and such equilibria in proton - substituted pyridine *N*-oxide systems in polar non-aqueous (both aprotic and amphiprotic) solvents were studied, using the potentiometric titration method. Consequently, measurements were carried out in acetonitrile solutions for systems containing the pairs formed by protonated tri-substituted pyridine *N*-oxide, i.e. 2,6-dimethyl-4-methoxypyridine *N*-oxide (Me$_2$MeOPyO), B, and mono-substituted pyridine *N*-oxides, B_1, with a lower basicity than B. The principal aim of this study was to compare the values of cationic heteroconjugation constants in systems studied with those ob-

tained in mono-substituted pyridine *N*-oxide *hetero* systems in acetonitrile (AN), as well as some other polar aprotic solvents: acetone (AC) and nitrobenzene (NB), and amphiprotic methanol (MeOH). To achieve this, the cationic heteroconjugation constant values for systems containing the pairs of *N*-oxides (B_1) and of cationic acids of substituted pyridine *N*-oxides (BH^+) with a higher basicity than B_1 from the following set: 4-*N'*,*N'*-dimethylamine-pyridine *N*-oxide (4NMe$_2$PyO), 4-methylpyridine *N*-oxide (4PicO), 3-methylpyridine *N*-oxide (3PicO), 2-methylpyridine *N*-oxide (2PicO), pyridine *N*-oxide (PyO), and 4-nitropyridine *N*-oxide (4NO$_2$PyO) in solvents studied were collected. For comparison, systems with pyridine, Py, as a representative of heterocyclic amines, and trimethylamine *N*-oxide, Me$_3$NO, representing aliphatic amine *N*-oxides, were also considered. Substituted pyridine *N*-oxides (mono-cyclic *N*-oxides) were chosen as model compounds in our studies since they differ sufficiently in their acidic-basic properties and exhibit a marked tendency towards conjugation. Moreover, there is a paucity of papers dealing with investigations of this class of compounds in solutions, especially in non-aqueous media.

Experimental Section

Chemicals

Compounds

Pyridine (PyO) and 4-*N'*,*N'*-dimethylamine-pyridine *N*-oxides were prepared and purified by the methods of Ochiai [20] and Katritzky [21], respectively. 4-Methoxy-2,6-dimethylpyridine *N*-oxide monohydrate was prepared from 2,6-dimethylpyridine via 4-nitro,2,6-dimethyl-pyridine *N*-oxide by standard methods. The anhydrous *N*-oxide was obtained by sublimation (at 348–353 K, 13.3 Pa), mp 373.5–374 K. 2-Picoline and 3-picoline *N*-oxides (Fluka AG), as well as pyridine were purified by vacuum distillation. 4-Picoline, 4-nitropyridine and trimethylamine *N*-oxides (Aldrich Chemical Co.) were recrystallized twice from a 3:1 mixture of acetone and methanol, methanol, and methanol, respectively.

Simple perchlorates of *N*-oxides under study were prepared by mixing together equivalent quantities of a 72% aqueous perchloric acid (Merck Co.) with *N*-oxide in methanol. The mixture was vacuum concentrated. The residue was filtered off, washed twice with chloroform and dried in vacuum over P_2O_5. Pyridine perchlorate was obtained in the same way.

Picric acid and tetraethylammonium chloride (both Fluka AG) were purified by triple crystallization from ethanol. Tetraethylammonium picrate and perchlorate were obtained by mixing together equimolar quantities of the purified picric acid or 72% aqueous $HClO_4$ solution with 25% tetraethylammonium hydroxide (Fluka AG) in ethanol. The salts were crystallized twice from ethanol.

Tetra-*n*-butylammonium picrate was obtained by mixing together equimolar quantities of the purified picric acid with 25% tetra-*n*-butylammonium hydroxide in methanol. Tetra-*n*-butylammonium perchlorate was obtained by mixing together equimolar quantities of 72% aqueous $HClO_4$ solution with 25% tetra-*n*-butylammonium hydroxide in methanol. Both salts were crystallized twice from ethanol. Tetra-*n*-butylammonium chloride (Serva Co.) was purified by triple crystallization from a 1:1 mixture acetonitrile and ethyl acetate.

2,6-Dinitrophenol (Fluka AG) was purified by triple crystallization from methanol. Tetra-*n*-butylammonium 2,6-dinitrophenolate was obtained in the same way as tetra-*n*-butylammonium picrate. The salt was crystallized twice from ethyl acetate.

Solvents

Acetonitrile (Serva Co.) was purified by the modified Coetzee method [22]. At first the solvent was dried with CaH$_2$ (10 g/dm^3) for 48 h. After decantation AN was distilled over P_2O_5 (3 g/dm^3). The distillate was dried again with CaH$_2$ and distilled after 48 h. The purified solvent had a specific conductivity of $4–10\times10^{-8}$ S cm^{-1}.

Nitrobenzene (Aldrich Chemical Co.) was initially dried for 24 h with anhydrous MgSO$_4$, and subsequently treated with activated (by heating at a temperature of 720 K for several h) Al$_2$O$_3$. NB was then distilled under reduced pressure (200 Pa), a fraction boiling at 347 K being collected. The purified solvent was stored over Al$_2$O$_3$. Under these conditions it was stable for a few weeks. The purified nitrobenzene had a specific conductivity of the order of 10^{-8} S·cm^{-1}.

Acetone (Aldrich Chemical Co.) was purified by the standard procedure: in the first stage the solvent was heated under reflux with potassium permanganate and subsequently dried with anhydrous calcium sulphate, then the solvent was redistilled with the exclusion of air humidity.

Methanol (Aldrich Chemical Co.) was purified according to a detailed procedure described by Smiataczowa [23].

Experimental procedures

The e.m.f. measurements of the cell:

indicator glass electrode	system studied	modified calomel electrode
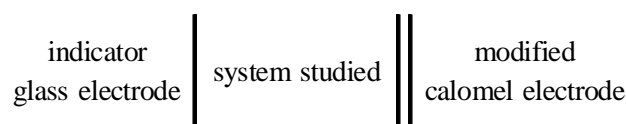
were run by an OP-208 digital potentiometer (Radelkis) with an accuracy of ±0.1 mV. An OP-7183 (Radelkis) indicator glass electrode and an OP-08303 (Radelkis) reference calomel electrode were used. The reference calomel electrode, modified by replacing the aqueous KCl solution by a 0.1 mol/dm^3 solution of tetra-*n*-butylammonium

chloride in non-aqueous solvent, was placed in a short-ened salt bridge filled with 0.01 mol/dm^3 tetra-*n*-butyl-ammonium perchlorate solution in the solvent under study. The e.m.f. measurements of the *N*-base perchlorate-*N*-base systems were run at a constant ionic strength. The solution containing base perchlorate (BHClO$_4$) at a concentration of about 10^{-3} mol/dm^3 was titrated with the solution containing the base B$_1$ at a concentration of about 10^{-2} mol/dm^3 and BHClO$_4$ (where B and B$_1$ are the *N*-oxides studied or pyridine) at the same concentration as that of the titrand (to keep the formal ionic strength constant for all titration points). The electromotive force (e.m.f.) was recorded for each titration point, after electrode relaxation (i.e. when the measured potential was stable). In the case of nitrobenzene solutions the potentiometric titration procedure employed for other solvents was supplemented with repeated rinsing of the electrodes (using methanol) following each measurement.

Each e.m.f. measurement in the system studied was preceded by the determination of the characteristic of the glass electrode. The linearity of the response of the glass electrode vs. the modified calomel electrode in acetonitrile and acetone was checked by means of the standardizing system: tetra-*n*-butylammonium picrate-picric acid (pK$_a$^{AN} = 11.0) [24], (pK$_a$^{AC} = 6.3) [25] at a constant ionic strength. 0.001 mol/dm^3 tetra-*n*-butylammonium picrate solution was titrated by the solution containing picric acid and tetra-*n*-butylammonium picrate at a concentration of 0.01 mol/dm^3 and 0.001 mol/dm^3, respectively in order to keep the formal ionic strength constant. For calibration of the glass electrode in nitrobenzene, a standardizing tetra-ethylammonium picrate-picric acid (pK$_a$^{NB} = 7.46) [26] system was used in place of the usually employed tetra-*n*-butylammonium-picric acid one due to poor solubility of tetra-*n*-butylammonium picrate in nitrobenzene. Moreover, in the case of methanol solutions, the tetra-*n*-butylammonium 2,6-dinitrophenolate-2,6-dinitrophenol standardizing system (pK$_a$ in methanol [27] is 7.8) was used. (It was found [12] that for the picric acid standardizing system that the response of indicator glass electrode is no longer linear in methanol solutions).

Solutions for potentiometric measurements were prepared on the volume basis. All potentiometric measurements were run at 298.1 ± 0.1 K.

Calculations

As already mentioned, prior to carrying out measurements in heteroconjugating systems, the reversibility of the glass electrode in the media employed was checked. In all solvents studied a linear response of the glass electrode was noted over the concentration ranges employed. The relationships E = f(log c_{HA}/c_{A^-}), where HA denotes picric acid or 2,6-dinitrophenol and A$^-$ denotes the conjugated anions

Table 1. *Heteroconjugation constant values [a] log $K_{BHB1}{}^+$ for BH$^+$/B$_1$ systems in acetonitrile at 298 K. Standard deviations in parentheses.*

BH$^+$/B$_1$ system	log $K_{BHB1}{}^+$
4NMe$_2$PyOH$^+$/4PicO	2.63 (0.11)
4NMe$_2$PyOH$^+$/3PicO	2.00 (0.20)
4NMe$_2$PyOH$^+$/2PicO	1.71 (0.26)
4NMe$_2$PyOH$^+$/PyO	– [b]
4NMe$_2$PyOH$^+$/4NO$_2$PyO	– [b]
Me$_2$MeOPyOH$^+$/4PicO	3.16 (0.02)
Me$_2$MeOPyOH$^+$/3PicO	2.77 (0.13)
Me$_2$MeOPyOH$^+$/2PicO	2.47 (0.04)
Me$_2$MeOPyOH$^+$/PyO	1.85 (0.38)
4PicOH$^+$/3PicO	3.60 (0.04)
4PicOH$^+$/2PicO	3.44 (0.03)
4PicOH$^+$/PyO	3.35 (0.03)
4PicOH$^+$/4NO$_2$PyO	– [b]
Me$_3$NOH$^+$/4NMe$_2$PyO	4.48 (0.04)
Me$_3$NOH$^+$/4PicO	1.99 (0.23)
Me$_3$NOH$^+$/3PicO	1.87 (0.15)
Me$_3$NOH$^+$/2PicO	– [b]
Me$_3$NOH$^+$/PyO	– [b]
Me$_3$NOH$^+$/4NO$_2$PyO	– [b]
PyH$^+$/4PicO	2.62 (0.25)
PyH$^+$/3PicO	2.68 (0.19)
PyH$^+$/2PicO	2.69 (0.18)
PyH$^+$/PyO	2.68 (0.17)
PyH$^+$/4NO$_2$PyO	– [b]

[a]*cationic heteroconjugation constants for all systems except those of Me$_2$MeOPyO cited from Ref. [31].*

[b]*cationic heteronjugation constants undeterminable from potentiometric measurements.*

(picrate or 2,6-dinitrophenolate) were linear in the wide range of the ratio of concentrations, as given by Eq. (11):

$$E = E^o + s \log K_{HA} + s \log c_{HA}/c_{A^-} \qquad (11)$$

The average slopes **s** were comparable with the theoretical Nernst slope being equal to 59.3, 59.6, 59.7 and 59.1 in AN, AC, NB and MeOH, respectively. Parameters **s** (slope of the response of the glass electrode) and E^o (standard e.m.f.), obtained from potentiometric titrations in stand-

Table 2. *Cationic heteroconjugation constants log K_{BHB1^+} in acetonitrile (AN), nitrobenzene (NB), acetone (AC) and methanol (MeOH) at 298 K. Standard deviations in parentheses.*

BH^+/B_1 system	log K_{BHB1^+}			
	AN [a]	NB [b]	AC [c]	MeOH [c]
$4PicOH^+/3PicO$	3.60(0.04)	3.04 [d]	2.44(0.21)	2.59(0.20)
$4PicOH^+/2PicO$	3.44(0.03)	3.05 [d]	2.23(0.18)	2.66(0.18)
$4PicOH^+/PyO$	3.35(0.03)	3.06 [d]	2.63(0.04)	2.18(0.27)
$Me_3NOH^+/4PicO$	1.99(0.23)	4.00(0.03)	2.35(0.15)	1.97(0.62)
$Me_3NOH^+/3PicO$	1.87(0.15)	3.78(0.01)	2.82(0.03)	– [e]
$Me_3NOH^+/2PicO$	– [d]	3.53(0.02)	1.97(0.36)	– [e]
$PyH^+/3PicO$	2.68(0.19)	–	– [e]	2.43(0.15)
$PyH^+/2PicO$	2.69(0.18)	–	– [e]	2.49(0.10)
PyH^+/PyO	2.68(0.17)	–	1.63 [d]	2.04(0.18)

[a] *from ref. [31]*
[b] *from ref. [33]*
[c] *from ref. [34]*
[d] *the high value of standard deviation (greater than heteroconjugation constant value determined)*
[e] *heteroconjugation constant value undeterminable from potentiometric measurements*

ardizing systems together with the results of the potentiometric titrations carried out in the systems B_1H^+/B served as a basis for the determination of the cationic heteroconjugation constants in the media under study. The constants were determined by use of the Kostrowicki and Liwo general method [28–30]. This algorithm is based on a general description of chemical equilibria in ideal solutions and uses non-linear confluence analysis to determine equilibrium parameters from physico-chemical data. The general method enables to take into account not only the errors in the e.m.f., but also those in titration volume, stock-solution preparation, electrode-calibration parameters (e.g. according to our extensive experience, the average error in a single e.m.f. measurement can be estimated at 2.0 mV and the inaccuracy in titration volume as 0.01 cm³), as well as the equilibrium constants determined from other measurements. Consequently, the acidity and homoconjugation constants of *N*-oxides and pyridine in solvents studied determined previously were not treated as unknown parameters in this study, but considered as known parameters charged with errors equal to their standard deviations. Therefore, values of the previously determined acid dissociation constants (varying within the limits of the standard error) of the protonated *N*-oxides BH^+ and B_1H^+, and

of the homoconjugation constants of these acids with conjugated bases B and B_1 in solvents studied [6, 10, 12, 31] were the basis for the determination of the equilibrium concentration of all reactants in the *hetero*systems, i.e. the heteroconjugation constants. The values of cationic heteroconjugation constants were determined based on a model accounting in the equilibrium scheme the equilibria of acid dissociation (1 and 2) of cationic acids BH^+ and B_1H^+ conjugated with *N*-oxides B and B_1, the homoconjugation equilibria (3 and 4) of the free and protonated *N*-oxides B and B_1, and the equilibrium of the cationic heteroconjugation without proton transfer (5).

Results and Discussion

The determined values of cationic heteroconjugation constants for the systems formed by protonated $Me_2MeOPyO$ and mono-substituted pyridine *N*-oxides in acetonitrile solutions are collected in Table 1 together with the constants characterizing other *hetero* systems in acetonitrile. As shown, the constants are determinable for the majority of the systems studied and the cationic heteroconjugation constant values for the $Me_2MeOPyO$ systems vary in the same way as for remaining systems formed by mono-substituted pyridine *N*-oxides.

Based on the values of determined constants, it can be stated that the cationic heteroconjugation constants in the case of $[OHO]^+$ bridges increase with increasing acceptor basicity and decrease with decreasing proton donor basicity. Furthermore, there are optimum pK_a values of both the proton donor and proton acceptor for which the heteroconjugation constants attain the highest values. Such

systems comprise an acceptor of a high enough basicity (still lower, however, than the basicity of the proton donor, as in this case a proton transfer would be realized) and a donor of a possibly low basicity (but still higher than that of the proton acceptor in order to prevent the proton transfer).

In systems with pyridine as the proton acceptor (the [OHN]$^+$ bridges), the cationic heteroconjugation constants decrease with the increasing basicity of the proton donor, similar to the case with the [OHO]$^+$ bridges, and do not depend on the basicity of proton acceptor. Thus it can be concluded that the tendency towards heteroconjugation in the systems studied is governed not only by the basicity of acceptor and donor, but first of all by the type of hydrogen bridge being formed.

In Table 2 are compared the values of cationic heteroconjugation constants for some chosen *hetero* systems studied in all polar solvents studied. On this basis, it can be concluded that the extent of cationic heteroconjugation equilibria in nitrobenzene is comparable and even larger (based on the values for the systems with protonated Me$_3$NO as a proton donor) than that in acetonitrile. On the contrary, in the most basic aprotic solvent studied, acetone, the tendency *N*-oxides towards cationic heteroconjugation is much lower than in nitrobenzene and acetonitrile, being still higher than in amphiprotic methanol. It is worth noting, however, that in the case of systems containing protonated pyridine and amine *N*-oxides , i.e. [NHO]$^+$ type bridges, a greater extent of cationic heteroconjugation equilibria (comparable with that in acetonitrile) was observed in methanol than in acetone. Nevertheless, comparison of the tendency towards cationic heteroconjugation within *N*-oxides class in the solvents studied herein shows that it declines with increasing solvent basicity in the following order:

nitrobenzene > acetonitrile > acetone > methanol.

It is worth noting that in this series the basicity increases from nitrobenzene to methanol, the donor numbers of the solvents being: 4.4, 14.9, 17.0, and 19.1, respectively [32].

Moreover, based on results in all solvents studied, it has been found that there are significant differences in the cationic heteroconjugation constant values determined in two heteroconjugating systems, i.e. systems without and with proton transfer. The proton-transfer reactions limit and even preclude the precise determination of the cationic heteroconjugation constants. On this basis it was concluded that the heteroconjugation constants should be determined in systems without proton transfer.

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