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STRUCTURE AND CHARACTERISTICS OF THE IONIC FORMS OF HETEROARENIUM SALTS IN ORGANIC SOLVENTS (REVIEW)

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The results of investigations into the formation of the various ionic forms of heteroarenium salts, their characteristics, and their reactivity are summarized. Salts containing (4n+2)π-electron aromatic cations (n = 0-3), including chalcogenopyrylium (O, S, Se), azinium, benzo- and dibenzoazinium, and chalcogenoazolium (O, S, Se, NR) ions are examined. In this system of compounds the relationships between the structure and the macroscopic characteristics of the heteroarenium salts (ionization constants, association/dissociation constants, distances of closest interionic approach) and the effect of the nature of the ionic forms in the solutions on their reactivity in heterolytic reactions are analyzed.

Keywords: azinium, azolium, benzo-annelated azinium, heteroarenium, chalcogenopyrylium salts, association constants, ionization constants, ionic forms, reactivity.

Salt forms and in particular heteroarenium salts occupy an extremely important position in the chemistry of heterocyclic compounds, being of interest both in structural respects and in their high reactivity in nucleophilic reactions, recyclization reactions [1-3], and more recently at the applied level as ionic liquids [4]. It is on the basis of heteroarenium salts that the modern chemistry of stable carbenes – the organic chemistry of the divalent carbon atom – has developed [5-9].

In spite of numerous investigations into the structure of the salts, carried out by various physicochemical methods (spectral, polarographic, X-ray crystallographic, etc.) direct information about their properties as salts, i.e., their capacity for dissociation/association and the formation of various ionic forms (free ions, various ionic associates – ion pairs and ion triplets), has remained almost in the dark. Among the characteristics directly describing the state of heteroarenium salts in solutions the most important are clearly the thermodynamic characteristics (which can be regarded as macroscopic in contrast to the microscopic characteristics relating, for example, to the spectral characteristics) – the ionic association (K_a)/dissociation (K_d) constants, the distance of closest approach of the ions, and theories about the dependence of these quantities on the structure of the salts. Information on the ionic association of heteroarenium salts is of considerable interest for assessing their reactivity. It is also important for understanding the processes that give rise to the effectiveness of organic electrolytes containing heteroaromatic cations in physical systems (e.g., as luminophores [10]).

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The aim of this review is to provide up-to-date information on the above-mentioned macroscopic characteristics of heteroarenium salts. Of undoubted interest to the chemist here are the theories about the effect of the chemical structure of a series of key classes of hetarenium salts on their ionic association constants in the nonaqueous solvents most often used in synthesis. Also worthy of consideration are data on the degree of difference in the reactivity of the various ionic forms: the free ions and undissociated ionic associates (ion pairs, triplets) of heteroarenium salts.

Methods of Investigation and Treatment of Data. Most of the experimental data on determination of the thermodynamic association constants K_a of heteroarenium salts were obtained by the conductometric method as the most direct method for their determination. Spectral methods (^{1}H NMR, UV spectroscopy) have also been used.

Methods for the treatment of conductometric data, including the classical Kraus–Bray [11], Fuoss–Kraus [12], Fuoss–Onsager–Skinner [13], Shidlovskii [14], Ebeling [15] and other [16] models, were developed for simple inorganic salts (where the counterions were taken as point charges or spheres) and were extended to various ammonium salts [17, 18] and in particular to pyridinium salts with delocalized positive charge, the structure of which was first treated as "a counterion above the plane of a pyridinium cation" by means of quantum-chemical apparatus [19] and later by molecular mechanics (e.g., [20, 21]).

Within the framework of these approaches the existence of the following equilibria was proposed:

$$\mathrm{Htar^+Y^-} \overset{K_1}{\rightleftarrows} \mathrm{Htar^+\|Y^-} \overset{K_2}{\rightleftarrows} \mathrm{Htar^+ + Y^-}\,;$$

$$K_d = K_1K_2/(1 + K_1);\ K_a = K_d^{-1} \qquad (1)$$

In the region of large concentrations, where the reverse behavior of the electric conductivity is observed (i.e., increase of the conductivity with concentration) it becomes possible to use the Fuoss model [14, 22], which assumes the existence of equilibria involving the participation of ion triplets, defined by the constant K_3:

$$\mathrm{Htar^+\|Y^- + Y^-} \rightleftarrows \mathrm{Y^-\,Htar^+\,Y^-}\,;$$

$$\mathrm{Htar^+\|Y^- + Htar^+} \rightleftarrows \mathrm{Htar^+Y^-Htar^+} \qquad (2)$$

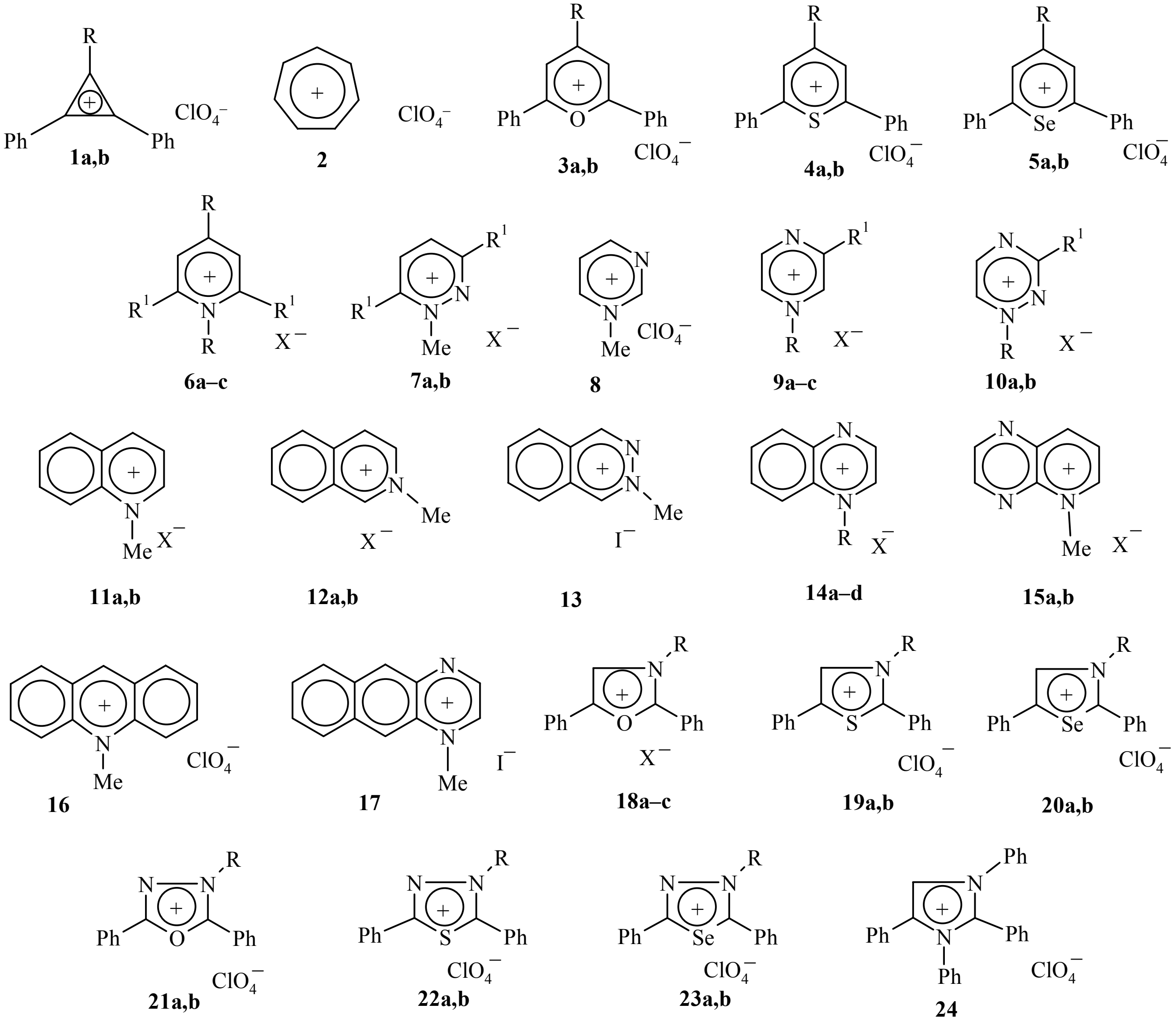
Features of the conductometric behavior of heteroarenium salts in organic solvents were also examined in [23-26].

A method for the determination of the ionic dissociation constants by ^{1}H NMR spectroscopy was proposed by Buckson and Smith [27] for strong electrolytes (K_d = ~10^{-2} mol/l), although even in this case, according to the authors, the determined dissociation constants differ from the conductometric values by approximately two times. The method starts out with the establishment of a relationship between the chemical shifts $\delta = f(c)$ and the concentration, from which by extrapolation to zero concentration the value of the chemical shift for the free cations δ_i can be obtained from the intercept on the ordinate axis. Use of the latter in a simple calculation leads to the K_d value of the salt. The success in the determination of the constant K_d in this method comes down to the reliability of the extraction of δ_i, i.e., to validation of the extrapolation of the $\delta = f(c)$ relation to the ordinate axis, which with the employed concentrations in the ^{1}H NMR method would reflect the characteristics of the free ions and not the various ionic associates, and this can be problematical in the case of weak electrolytes.

1. Association Constants of Heteroarenium Salts

It is convenient to arrange the existing published material on the association constants of heteroarenium salts K_a according to the chemical classes of the heteroaromatic cations. We then arrive at a system containing a successive Hückel series of $(4n+2)\pi$-electron aromatic/heteroaromatic cations (Scheme).

Scheme



1a, **3a–5a** R = H; **6a,c**, **9a,c**, **10a**, **14a,b**, **18a,c**, **19a–23a** R = Me; **3b–6b**, **18b–23b** R = Ph;
1b R = CH_2COPh; **9b**, **10b**, **14c,d** R = Et; **6c**, **7a**, **9a,b** R^1 = H; **6a,b**, **7b** R^1 = Ph; **9c** R^1 = $CONH_2$;
10a R^1 = N-morpholinyl; **1a,b**, **3a,b–6a,b**, **7a**, **9a**, **11a**, **12a**, **14a**, **15a**, **18a,b** X = ClO_4^-;
6c, **7b**, **9c**, **10a**, **11b**, **12b**, **14b,d**, **15b** X = I; **9b**, **10b**, **14c** X = BF_4; **18c** X = TsO

To date there are data for *n* = 0-3, among which the aromatic cations characterized by total equivalence of all the bonds and charge distribution in the ring can be regarded as starting points during comparison of results in the given system. In this respect some arenium salts, chalcogenopyrylium (O, S, Se), azinium, a series of benzo- and dibenzoazinium, and chalcogenoazolium salts (O, S, Se, NR) were then characterized. In such a series of compounds it is possible to trace certain dependences on the structure of a series of macroscopic characteristics of the heteroarenium salts (ionization, association/dissociation constants, limiting molar electric conductivities, distances of closest interionic approach). As a result we obtain some general picture as to how the heteroarenium salts of various types stand in terms of the given macroscopic characteristics at least in some organic solvents popular in organic synthesis.

TABLE 1. The Ionic Association Constants (K_a*) of the Arenium Salts at 25.00 ± 0.01°C in Ethanol ($\kappa = 2.1 \cdot 10^{-8}\ \Omega^{-1} \cdot cm^{-1}$) and in Acetonitrile ($\kappa = 1.0 \cdot 10^{-7}\ \Omega^{-1} \cdot cm^{-1}$)

Salt	$K_a \cdot 10^{-2}$ l·mol^{-1}		Salt	$K_a \cdot 10^{-2}$ l·mol^{-1}	
	in EtOH	in MeCN		in EtOH	in MeCN
1a	361.0	123.2	**1b**	392.0	135.1
2	0.86	0.11			
3a	13.40	1.87	**3b**	19.75	2.57
4a	17.67	1.95	**4b**	25.64	3.06
5a	20.48	2.57	**5b**	32.10	4.02
6a	19.12	3.16	**6b**	29.74	4.78
6c	17.45				
7a	14.80	2.60	**7b**	12.25	
8	10.27	1.24			
9a	5.20	1.00	**9b**	6.67	
9c	3.86				
10a	13.15		**10b**	15.74	
11a	21.10	4.60	**11b**	19.44	
12a	33.62	5.95	**12b**	28.45	
13	18.31				
14a	30.20		**14c**	31.50	
14b	26.30		**14d**	16.80	
15a	29.24		**15b**	25.72	
16	36.90	6.86			
17	27.46				
18a	250	55.80	**18c**	408	93.75
18b	293	66.10			
19a	332	66.30	**19b**	385	77.85
20a	393	91.12	**20b**	457	101.50
21a	128	15.92	**21b**	152	24.48
22a	165	18.80	**22b**	185	27.90
23a	202	25.28	**23b**	225	37.62
24	129.1	19.71			

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*Data from [28], obtained by Ebeling's method in the range of salt concentrations 10^{-4}-10^{-6} M. The standard deviations of the K_a values are in the range of 0.01-0.04 l/mol.

Salts Containing Aromatic Cations (without Heteroatoms in the Ring). The cyclopropenylium **1a**,**b** and tropylium **2** salts were investigated (Scheme, Table 1) [28]. In ethanol they differ greatly (by almost three orders of magnitude) from each other in the K_a value. In the transition to acetonitrile, a solvent with a higher dielectric constant, where the association is weaker, the effect is felt more strongly in the seven-membered than in the three-membered systems (K_a decreases by eight and three times respectively). Replacement of the H substituents in the cyclopropenylium ring by CH_2COPh (**1b**) has very little effect on the K_a value (by only ~1.1 times). In dichloromethane ($\varepsilon = 9.7$) high values of K_a ($4.9 \cdot 10^4$-$1.3 \cdot 10^5$ l/mol) were obtained for the series of tropylium salts [10] $C_7H_7^+BF_4^-$, C_7H_6–$C_6H_4CH_3^+X^-$ (X = BF_4, ClO_4, Cl, Br, I) (in the range of concentrations 10^{-3}-10^{-6} M at 18°C), which is substantially larger than in ethanol and acetonitrile – solvents with higher ε values (ε 24.3 and 37.5 respectively [29]).

Chalcogenopyrylium and Azinium Salts. The transition from tropylium salts to salts of the pyrylium and pyridinium series can be regarded as replacement of the formal ethylene unit in the tropylium cation by a heteroatom, which gives up a free electron pair to the aromatic sextet. The pyrylium **3a**,**b**, thiapyrylium (**4a**,**b**), and selenapyrylium **5a**,**b** salts, the azinium salts (pyridinium **6a-c** [23, 28], pyridazinium **7a**,**b**, pyrimidinium **8**, pyrazinium **9a-c**, triazinium **10a**,**b**) and their benzocondensed derivatives (quinolinium **11a**,**b**, isoquinolinium **12a**,**b**, phthalazinium **13**, quinoxalinium **14a-d**, pyridinio[2,3-*b*]pyrazine **15a**,**b**, acridinium **16**, and benzo[*h*]quinoxalinium **17** [30] salts] have been investigated most systematically in ethanol and acetonitrile (Scheme, Table 1).

In spite of the fact that the investigated salts cover a wide range of aromatic π-systems (from 6π to 14π electron) their cations in fact comprise a single 6π isoelectronic series of aromatic electrolytes since the positive π-charge in them is concentrated predominantly in the heterocore [31]. The association constants K_a for the wide range of such salts containing heteroaromatic six-membered cations with fairly wide variations in chemical structure vary in the range of $(4\text{-}37)\cdot10^2$ l/mol in ethanol and $(1\text{-}7)\cdot10^2$ l/mol in acetonitrile. Within these comparatively narrow limits the nature of the heteroatom of the cation has the greatest significance. Replacement of the heteroatoms in the heteroaromatic cation within the limits of group 16 of the periodic system (from O to Se, salts **3a**,**b**-**5a**,**b**) leads to an increase of the association by approximately 1.5 times, and it increases by almost two times in the transition to the pyridinium system (**6a-c**). Replacement of the trigonal nitrogen atom in the cationoid ring by a pyridine nitrogen atom (salts **7a**,**b**-**10a**,**b**) leads to less associated systems, where an extremely substantial role is played by the position of substitution in the series $\alpha > \beta \gg \gamma$ [30]. Another appreciable factor is benzoannelation (salts **11-17**), which leads to increased association [30]. At the same time it is necessary to note the leveling effect of benzoannelation on the association of the azinium cations. Thus, during the benzoannelation of pyridinium and pyrazinium cations, which themselves differ appreciably in K_a values, we arrive at the condensed systems **14a**,**b**, **15a**,**b**, and **17** close in K_a values if the identical orientation of the annelated ring in relation to the pyrrole nitrogen atom survives in the cyclic cation. Replacement of the sp^2-carbon atom in the non-cationoid ring (**11a**,**b**) by a nitrogen atom (**15a**,**b**) [30], which increases the electron-accepting power of the annelated ring, is accompanied by increased ionic association. The effect of replacement of the counterion is fairly constant: the decrease of the association constant in the transition from the perchlorate ion to iodide in the azinium salts can be expressed in terms of the following equation:

$$\Phi_c = K_a(\mathrm{Ht^+ClO_4^-})/K_a(\mathrm{Ht^+I^-}) = 1.2.$$

In acetonitrile, the dielectric constant of which is significantly higher than that of ethanol, the K_a values decrease by a factor of approximately five, but the structural effects vary in the same order.

The bispyridinium salts **25a-s** were investigated in ethanol [31].

$$\mathrm{R{-}N^+C_5H_4{-}C_5H_4N^+{-}R\cdot 2X^-}$$

25a–s

a, **b** R = Me; **c–e** R = Ph; **f–i** R = 4-NCC_6H_4; **j**, **k** R = C_7H_{15}; **l** R = $C_{11}H_{23}$; **m** R = $C_{16}H_{33}$;
n R = CH_2CO_2Et; **o** R = 4-$MeCO_2C_6H_4$; **p** R = 4-HOC_6H_4; **q** R = C_2H_4OH; **r, s** R = CH_2CO_2H;
a, **d**, **g**, **j** X = I; **b**, **e**, **h**, **k** X = ClO_4; **c**, **f**, **l–p**, **r** X = Br; **i** X = BF_4; **q**, **s** X = Cl [32]

In the range of concentrations where a linear dependence of the electric conductivity on concentration $\Lambda = f(c)$ in the adopted methods is fulfilled a one-step dissociation of the salts is assumed. In comparison with the pyridinium salts the bispyridinium salts are more strongly associated (K_a for this series increases by approximately twice), and this can be explained by the electron-accepting interaction of the pyridinium nuclei with each other, which substantially affects the distribution of positive charge in the heteronuclei. Their association constants K_a in ethanol vary in the range of (5-65)·10^2 l/mol. The weakening of the interionic association with elongation of the alkyl substituent at the cyclic nitrogen atom (**25l,m**) is interesting and may be due to screening of the charge of the heteronucleus. The K_a value changes by 1.2-1.6 times with change in the nature of the anion.

For some salts of N-acetyl-4-dimethylaminopyridinium with various anions (Cl^-, Br^-, ClO_4^-, BPh_4^-) in acetonitrile (T = 298K) [33-36] K_a values in the range of (0.31-0.43)·10^2 l/mol were obtained; however, the ambiguity of the data in these publications, analyzed in [23, 27], should be noted. The results presented in [38] probably provide qualitative information on the dissociation of the series of N-acylpyridinium and N-hydroxyacylpyridinium salts in acetonitrile ($K_d \approx 10^{-2}$ mol/l, 298K).

For the 1-acetoxypyridinium salts $4\text{-R–}C_5H_4N^+\text{–OCOMe·}X^-$ (R = H, NMe_2, OMe, X = Cl, Br, ClO_4, BPh_4) [39, 40], as also for the phenylacetyl analogs $4\text{-R–}C_5H_4N^+\text{–OCOCH}_2\text{Ph·ClO}_4^-$ (R = NMe_2, OMe, H), the dissociation constants in acetonitrile (T = 298K) in the range of K_d = (0.5-4.2)·10^{-2} mol/l (calculated by the Shidlovskii method) were obtained [41], but the value of K_d = 12.0·10^{-2} mol/l in the last series with R = H falls outside the general series for no obvious reason.

In methylene chloride the dissociation of the salts $4\text{-R–}C_5H_4N^+\text{–OCOMe}X^-$ is very small, and with R = NMe_2 and X = Cl, Br, BPh_4 K_d = (3.49, 4.78, 57.6)·10^{-6} mol/l (according to Walden and Izmailov) [39]; the authors assume that the dependence of the dissociation constants on the nature of the substituents may be due to their effect on the distribution of charge in the cation of the ion pair.

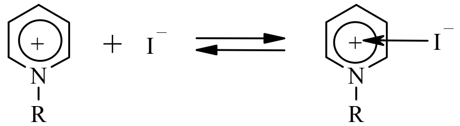
In [42, 43] the dissociation constants of a series of 1-aryl-4-dimethylaminopyridinium salts were determined by the conductometric method according to Kraus and Bray in acetonitrile at 298K:

$$1\text{-}(2\text{-}R^1\text{-}4\text{-}R^1\text{-}5\text{-}R^2\text{–}C_6H_2)\text{-}4\text{-}Me_2N\text{–}C_5H_4N^+\,X^-$$

$R^1 = NO_2$, $R^2 = H$, X = F, Cl, I, OSO_2Ph; $R^1 = R^2 = NO_2$, X = Cl; $R^1 = CF_3SO_2$, $R^2 = H$,
X = Cl and $1\text{-Et-}2\text{-}[2,4\text{-}(O_2N)_2C_6H_3O]\text{–}C_5H_4N^+\,BPh_4^-$

It was found that the K_d values lie in the range of (4-9)·10^{-3} mol/l. It was concluded that they are not very sensitive to the nature of substituents both in the pyridine and in the phenyl rings and, in contrast to the imidazolium salts, to the nature of the anion.

In aqueous solutions (ε = 80.4) 1-methylpyridinium iodide is a charge-transfer complex, and its K_a value is 2.3 ± 0.3 l/mol. The three additional methyl groups in the 1,2,4,6-tetramethylpyridinium ion reduce the K_a value to 1.83 ± 0.3 l/mol, and in ethanol significant association to ion pairs is observed [44].



The dissociation constants K_d for the salts $4\text{-NC–}C_5H_4N^+\text{–Et·}I^-$ were obtained in nine solvents with different polarity, mol/l: in $CHCl_3$, CH_2Cl_2, HCO_2Me, *t*-AmOH, and 2-PrOH $K_d \approx 0$; in EtOH and Me_2CO, $K_d \approx 0.2·10^{-2}$; in MeCN, $K_d = 1.04·10^{-2}$; in DMF, $K_d = 3.96·10^{-2}$ [45].

The ionic association and the reaction of the ions with the solvent in water–ethanol mixtures were investigated for N-ethyl-4-cyanopyridinium iodide [46] as a function of the concentration of the dissolved salt, and the data were analyzed with regard to the existence of solvent-separated ion pairs. The temperature variations of the association constants were established.

In [46] the dependence of the limiting solubility and the dissociation constants of bolaform electrolytes (a type of electrolyte in which the charges are separated by the chain of atoms in a polyion) was discussed: 1,2-ethane-, 1,4-butane-, and 1,10-decane-N,N′-bispyridinium dibromides, and also the diethyl ether of bis-β-pyridinium dichloride.

In compounds of the tricationic calixarene type – pyridinium salts based on cyclodextrin – there is high affinity to strongly basic anions (phosphate, pyrophosphate) in pH ranges close to neutral, with K_a = 7000-9000 l/mol [21] but weak bonding with weakly basic anions such as I^-, ClO_4^-, SCN^-, and even SO_4^{2-}. The stability of the salt may be due both to electrostatic and to van der Waals interactions.

The association constants were determined for pseudorotaxane assemblies with positively charged pyridinium, pyridinionicotinamide, imidazolium, benzimidazolium, and guanidinium ions and macrocyclic isophthalimide polyester ligands, and the lowest association constants were obtained for those paired with chloride ions [48].

The pyridinium salts were also investigated as polymeric electrolytes [49].

Azolium Salts. The salts of oxa- (**18a-c**), thia- (**19a**,**b**), selenazolium **20a**,**b** derivatives, and 1,3,4-oxa- (**21a**,**b**), 1,3,4-thia- (**22a**,**b**), 1,3,4-selenadiazolium (**23a**,**b**) derivatives, and imidazolium derivative **24** in ethanol and acetonitrile were studied most comprehensively (Scheme, Table 1) [28].

In spite of the substantial difference in the structure of the azoles, which is determined by the nature of the heteroatoms participating in the formation of the 6-π-heteroaromatic system and belonging to various groups and periods of the periodic system of elements, and also the differences in the sizes and electronic effects of the N-substituents in the azoles, their association constants K_a vary in the ranges of $(130\text{-}458)\cdot10^2$ l/mol in ethanol and $(16\text{-}102)\cdot10^2$ l/mol in acetonitrile. With increase of the atomic number of the heteroatom of group 16 of the periodic system the interionic association of the azoliums increases from O to Se (cf. salts **18a**,**b-20a**,**b**), and **21a**,**b-23a**,**b**) (K_a increases by approximately 1.5 times), while in the transition to group 15 (salt **24**) the K_a value decreases by approximately half (cf. **18b**), such salts are appreciably more dissociated. Replacement of the methyl group by phenyl at the nitrogen atom leads only to a small increase of K_a (by 1.1-1.2 times). The nature of the anion has a more appreciable effect (cf. salts **18a** and **18c**). In the transition from ethanol to acetonitrile K_a decreases by almost half an order of magnitude for the whole series.

In [33-36] K_a values in the range of $(0.91\text{-}5.30)\cdot10^2$ l/mol were obtained in acetonitrile for some 1-methyl-2-acetylimidazolium salts with various anions. The results were analyzed in [37].

Dissociation constants K_d in the range of $(1.05\text{-}98.9)\cdot10^{-2}$ mol/l were obtained for some imidazolium salts 1-Me-3-(RCO)-Im^+X^- (R = Me, Me_2N; X = Cl, ClO_4, BPh_4) in acetonitrile by ^1H NMR spectroscopy using the method of Buxton and Smith [43], and for both R series of salts the K_d values varied in relation to the anion in the following order: Cl < ClO_4 < BPh_4. However, the results differ from the conductometric values by almost an order of magnitude.

In the last decade, particularly in connection with the development of green chemistry [57, 58], the so-called ionic liquids – aromatic salts that exist in the liquid state under normal (working) conditions (10-50°C) – have attracted great attention [4]. Particularly effective at the applied level their range mostly includes dialkyl-substituted imidazolium salts, which are also marked by sufficient chemical and thermodynamic stability. The electrophilic characteristics of such salts under various conditions and some of the directions in these investigations are discussed below.

It was established that organic solvents increase the interionic association of ionic liquids with identical viscosity (1-*n*-butyl-3-methylimidazolium hexafluorophosphate, tetrafluoroborate, and trifluoroacetate at 298.15K) [59], and the effect depends of the dielectric constant of the solvent. Water promotes dissociation appreciably on account of the high dielectric constant and the ability to form strong hydrogen bonds with the anions of the ionic liquid.

The ionic conductivity of 1-butyl-3-methylimidazolium bromide (BMIBr) was investigated at 45°C and also in the presence of SO_2, with which the complex BMIBr–SO_2 is formed. Measurement of the ionic conductivity and the diffusion coefficient indicates a high degree of association in the BMIBr–SO_2 system. Although molecular dynamics shows that the cation–anion distances remain in a narrow range variations are observed in the interionic distances in the second layer, leading to a smaller degree of organization of the structure at long distances [60].

With the dibromides of N,N'-disubstituted methylenediimidazolium salts it is possible to obtain mobile pseudorotaxanes with macrocycles (β-cyclodextrin, tetrapropoxycalix[4]arene, dibenzo-24-crown-8 ether). The association constants of such complexes were determined, and they lie in the range of $(2.1\text{-}4.2)\cdot10^3$ l/mol [61].

The ionic association constants of salts containing the anthraquinonide anion and imidazolium cation – from 1-alkyl-3-methylimidazolium base ionic liquids – were investigated [62].

Considerable attention has been paid to polymeric ionic liquids [63, 64] (mostly based on imidazolium salts). Series of polymerized ionic liquids were synthesized and investigated in order to produce polymeric electrolytes. The polyionic liquid 1-ethyl-3-(2-methacryloyloxyethyl)imidazolium iodide was synthesized and investigated as a single-ion conductor. If the plasticizer polyacrylonitrile is added a gel-polymer electrolyte, for which the ionic conductivity at room temperature amounts to $1\cdot10^{-3}$ $S\cdot cm^{-1}$, is obtained [65].

Determination of the Dependence of the Relative Changes in the Ionic Association Constants of Heteroarenium Salts on their Structure. The Effect of an Isoelectronic Unit in Aromatic Cations. On the basis of classified data on the ionic association constants of heteroarenium salts it is possible to reach certain conclusions about the relationships between the associative properties and the structure. According to the ionic association constants of $(1\text{-}460)\cdot10^2$ l/mol in absolute ethanol and $(0.1\text{-}135)\cdot10^2$ l/mol in acetonitrile in the range of concentrations of $2\cdot10^{-6}$-$1\cdot10^{-4}$ M the heteroarenium salts can be assigned to weak electrolytes. To analyze the character of the changes of the ionic association constants with structure it is advisable to use their relative values (the structural factors Φ_s), which correspond to the sensitivity of ionic association to structural changes and is expressed by the ratio of the given K_{av} value of the salt, where there is a specific structural change, to the K_{as} value of a reference salt (for example, an isoelectronic analog differing in the structural unit that changes) $\Phi_s = K_{av}/K_{as}$.

As seen from Table 2, the same structural changes in the various classes of arenium salts are characterized by fairly constant values of Φ_s in various solvent differing appreciably in dielectric constant ε (ethanol, acetonitrile).

First, there is the deciding effect of replacement of a formal ethylene unit in an aromatic cation by a *p*-isoelectronic heteroatom on the K_a value (Φ_s = 12-22 in ethanol, 22-40 in acetonitrile). The same effect is observed during variation of the dissociation constants K_2 (Table 3) and the smallest interionic distances *a* (Table 4) of the heteroarenium salts. The isoelectronic unit has a common effect in the aromatic cations, and this appears in all cases where the value of K_a is significant.

TABLE 2. The Values of the Structural Factors Φ_s (the Sensitivity of the K_a constants of the Arenium Salts to structural Changes)

Change of unit in cyclic cation	Φ_s	
	EtOH	MeCN
CH=CH by NMe		
K_a(**18a**) / K_a(**3a**)	19	34
K_a(**19a**) / K_a(**4a**)	19	34
K_a(**20a**) / K_a(**5a**)	19	34
CH=CH by NPh		
K_a(**18b**) / K_a(**3a**)	22	40
K_a(**19b**) / K_a(**4a**)	22	40
K_a(**20b**) / K_a(**5a**)	22	40
CH=CPh by NMe		
K_a (**18a**) / K_a(**3b**)	13	22
K_a(**19a**) / K_a(**4b**)	13	22
K_a(**20a**) / K_a(**5b**)	12	23
Replacement of CH by N		
K_a(**21a**) / K_a **18a**)	0.5	0.3
K_a(**22a**) / K_a(**19a**)	0.5	0.3
K_a(**23a**) / K_a(**20a**)	0.5	0.3

TABLE 3. The Constants of the Ionic Equilibria (K_1* and K_2) of Heteroarenium salts in Ethanol at 25.1 ± 0.1°C and the Distances of Closest Approach of the Ions (a)

Salt	$K_1 \cdot 10^2$	$K_2 \cdot 10^3$ mol•l^{-1}	a, pm	Salt	$K_1 \cdot 10^2$	$K_2 \cdot 10^3$ mol•l^{-1}	a, pm
3a	8.3	9.7	326	**12a**	3.1	10.0	329
4a	5.9	10.1	329	**16**	2.9	9.6	326
5a	4.6	11.0	337	**18a**	3.2	1.3	227
6a	5.3	10.5	339	**19a**	2.4	1.3	227
7a	6.7	10.8	336	**20a**	2.2	1.2	224
8	9.8	10.9	336	**21a**	7.0	1.2	224
9a	9.9	12.0	345	**22a**	4.9	1.3	227
11a	5.0	10.0	329	**24**	7.6	1.1	222

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*K_1 is dimensionless. Data from [23, 28].

Second, other structural changes have a small effect compared with the indicated effect in a range of approximately one order of magnitude in the K_a values, although the forms in which they appear are not equally significant.

Thus, during replacement of the *p*-isoelectronic atoms (O, S, Se, NR) in the aromatic ring of azoliums and aziniums the factor Φ_s remains almost unchanged, and during replacement of the trigonal carbon atom by a pyridinium nitrogen atom $\Phi_s \approx 0.5$ (in ethanol) and 0.3 (in acetonitrile) since less associated systems are produced. Analysis of the investigated K_a constants of bispyridinium and imidazolium salts with various N-functional groups shows that the effect of the electronic nature of the substituent too, like the effect of its size, varies within the range of one order of magnitude in the K_a values. Depending on the nature of the anion, the K_a value for the heteroarenium salts increases within the same range in the following order:

$$BF_4^- < ClO_4^- \lesseqgtr I^- < Br^- < Cl^- < TsO^-.$$

We note that cyclopropenylium salts, which do not belong to the 6π-isoelectronic series of aromatic cations, apparently lie outside the noted relationship. In actual fact they differ strongly from six-membered ($\Phi_s \sim 10$-30 in ethanol, ~ 30-70 in acetonitrile) and especially from seven-membered systems ($\Phi_s \sim 400$ in ethanol, ~ 1000 in acetonitrile). At the same time their K_a values in these solvents are close to the corresponding K_a values of the azolium salts ($\Phi_s \sim 1$). This may be due to dispersal of the positive charge caused by displacement of the π-cloud in the rings: mostly a triad in the mentioned cationic systems but by four atoms in the six-membered and by seven atoms in the seven-membered cations.

2. The Ionization Constants of Intimate Ion Pairs and the Dissociation Constants of Loose Ion Pairs of Heteroarenium Salts

The association constants K_a of a series of heteroarenium salts were determined by the method of Vierordt [66] using UV spectroscopy, and they were found to be close to those determined by a conductometric experiment [23, 28]. The latter are clearly more accurate since it is difficult to achieve complete separation of the absorption bands for each of the ionic forms in the spectral experiment. In the spectral experiment, however, it proved very useful that the constants of the intimate ⇄ loose ion pair equilibrium (K_1) and the dissociation constants of the loose ionic form (K_2) can be determined separately by this method (Eq. (1), Table 3, data taken from [23, 28]). As follows from the table, it can be considered that the free energies of the transition (the symbatic constants K_1 or K_2) from the intimate ion pairs to the loose ion pairs for arenium salts are lower than the free energies of the dissociation stage. However, attention is drawn particularly to the fact that the ionization constants K_1 are less sensitive to structural changes than the dissociation constants K_2, where the effect of the isoelectronic unit shows up quite clearly. It is clear that the effect of the structure on the ionic association of the heteroarenium salts is most significant at the stage of dissociation of the loose ion pairs/association of the free ions to loose ion pairs.

3. The Distances of Closest Approach of the Ions in the Loose Ion Pairs of Heteroarenium Salts

The distances of closest approach of the ions (a) in loose ion pairs are determined by the Fuoss–Eigen method [67] through the association constants K_a.

However, for heteroarenium salts use of the general constant K_a in the calculations leads to impossibly low values for the distances as a result of a substantial contribution from the charge separation process in the intimate ion pairs (i.e., their ionization) to the general constant K_a. Exclusion of this process by working with the pure dissociation constants of the loose ion pairs K_2 gives extremely good results (Table 3, selective data from [23, 28]) comparable with existing data for certain salts (in particular pyridinium and pyrylium [68, 69]) from their X-ray crystallographic investigations, although in this case the various states of aggregation of the samples must be taken into account. As follows from Table 3, in the series of heteroarenium salts the distances a, which depend on the constant K_a, decrease sharply if the formal ethylene bond in the aromatic ring of the cation is replaced by a *p*-isoelectronic atom, i.e., the effect of the isoelectronic unit is observed.

Generally, when the Fuoss–Eigen equation is used it is important to take account of the fact that it can be applied not only to solvate-separated ion pairs but also to any ionic associates but on the condition that all the interionic distances in the formed associates are identical, i.e., that such associates are the only paired particles in the solution. Such clear evidence is not always available, and in these cases the determination of the parameter a becomes ambiguous (e.g., in [34]).

4. Ion Triplets in Heteroarenium Salts

In conductometric investigations at higher concentrations there is a change in the form of the conductivity isotherm of heteroarenium salts; the conductivity increases with the concentration, indicating that ion triplets are formed at such concentrations (see Eq. (2)) [14, 22]. It should be noted that the region of ion triplets for heteroarenium salts [23, 28] in the investigated organic solvents is shifted significantly toward lower concentrations (~10^{-4} M) compared with inorganic salts (usually ~10^{-2} M, e.g., [70]).

TABLE 4. The Ionization Constants (K_3*) of Heteroarenium Salts to Ion Triplets in Ethanol ($\kappa = 2.1\cdot10^{-8}\ \Omega^{-1}\cdot\mathrm{cm}^{-1}$) at 25.00 ± 0.01°C

Salt	K_3•10^{-4} l•mol^{-1}	Salt	K_3•10^{-4} l•mol^{-1}	Salt	K_3•10^{-4} l•mol^{-1}
3a	1.11	**9a**	1.41	**20a**	8.20
4a	1.50	**11a**	4.36	**21a**	5.70
5a	2.00	**12a**	5.32	**22a**	6.10
6a	2.40	**16**	7.00	**23a**	8.10
7a	4.10	**18a**	7.80	**24**	2.70
8	2.60	**19a**	7.15		

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* The presented values relate to the range of salt concentrations (0.5-2.0)·10^{-4} M. The standard deviations of these values lie in the range of 0.01-0.04 l/mol. Data from [23].

The effect of the structure of the salts on the association constants of the triplets K_3 varies directly with the effect on the K_a constant, but in a number of cases it is noticeably smoothened particularly during benzannelation, where the effect of the isoelectronic unit is also less clearly defined (K_3 only changes by approximately three times). A characteristic feature of ionic association in the region of the triplets of heteroarenium salts is lower sensitivity to the structure of the cations (Table 4).

It was noticed in [39] that the conductivity isotherms of the salts

$$R–C_5H_4N^+–OAc\ X^-$$

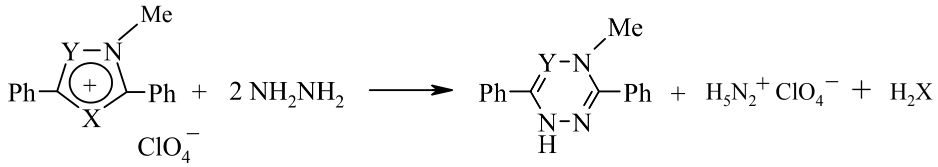
also indicate the presence of ion triplets with $K_3 = (2.6\text{-}6.7)\cdot 10^{-3}$ mol/l in solutions in CH_2Cl_2.

5. The Reactivity of the Ions and Ionic Associates of Heteroarenium Salts

Apparently reactions with nucleophiles are the most characteristic of heteroarenium salts. In particular, the reaction of azolium salts with such two-center nucleophiles as hydrazine and methylhydrazine leads to cyclic dihydroazines. They are important and extremely common reactions for the recyclization of azolium salts [71-74]. The kinetics of such reactions was investigated (by UV spectroscopy) for examples of the reactions of chalcogenoazolium salts (the perchlorates of oxazolium **18a**, thiazolium **19a**, and 1,3,4-thiadiazolium **22a** [75] derivatives), in which the number and nature of the heteroatoms in the rings were varied, with hydrazine in absolute ethanol. The stoichiometric equations of these recyclization reactions correspond to the reaction of the azolium perchlorate molecule with two molecules of hydrazine, one of which substitutes the bridging heteroatom (X = O or S) in the ring while the other combines with the released perchloric acid in the fast stage to form hydrazine perchlorate. These transformations take place with almost quantitative yields. In all cases first order of the reaction of the hydrazine and the absence of catalysis by another molecule of hydrazine were established in all cases. The reaction can be interpreted in terms of the extended ANRORC mechanism [76]. If the low values of the equilibrium constants K_1 of the ionization stage for the salts (see section 2) are taken into account, the intimate ion pairs and free ions are mostly significant in these reactions, and this determines the two paths for the transformation of the salt. According to the modernized version of Acree's equation $k_2 = k_{ip} + (k_i - k_{ip})\alpha$, where instead of the total constant of the ion pairs it was possible to use the separate rate constants k_{ip} and k_i with participation of the intimate ion pairs and the free ions [75], the corresponding equations for the salts were obtained (for $N = 8$, $S_0 = 0.01$):

oxazolium $k_2 = (1.26\pm0.01) + (-12545\pm810)\ [c]$, $R = 0.987$;
thiazolium $k_2 = (0.77\pm0.01) + (-7897\pm350)\ [c]$, $R = 0.994$;
thiadiazolium $k_2 = (1.92\pm0.01) + (-14504\pm600)\ [c]$, $R = 0.994$.

It follows from these equations that the cationic form of the azoliums is appreciably more reactive, by about 10 times, than the intimate ion pair form, and the rate constants vary with the structure in the following order: 1,3,4-thiadiazolium > oxazolium > thiazolium. The reactivity in this series is increased 2.4 times if the C-4 atom in the ring is replaced by a pyridinium N atom and by only 1.6 times if the O heteroatom is replaced by S.



18a, **19a**, **22a**

18a X = O, Y = CH; **19a** X = S, Y = CH; **22a** X = S, Y = N

Exchange (group transfer) reactions in heterocyclic salts have been widely investigated.

The kinetics of anion exchange in 1-alkylpyridinium iodides with methyl tosylate, which takes place as nucleophilic substitution, was studied in a series of solvents ($CHCl_3$, CH_2Cl_2, HCO_2Me, *t*-AmOH, 2-PrOH, EtOH, Me_2CO, MeCN) [45]:

$$X–C_5H_4N^+–R\ I^- + TsOMe \rightarrow X–C_5H_4N^+–R\ TsO^- + MeI$$

X = 4-, 3- or 2-CN, 2-CO_2Et, R = Me, Et

Investigation of the reactivity of the ionic forms of these salts in exchange in the indicated solvents showed that the rate constants of the free ions k_f are larger than those of the ion pairs k_p: $k_f > k_p$, and the effect of the substituents due to the distribution of the charges in the cyclic cation indicates that the reaction can be used for synthetic purposes [45].

Acyl exchange in pyridinium salts is of considerable interest in nucleophilic catalysis [77, 78]. Symmetrical acyl exchange reactions in 1-acyloxypyridinium salts and pyridine N-oxides in solutions in methylene chloride were studied [39]:

$$RC_5H_4N^+OAc\ X^- + R–C_5H_4N^*\rightarrow O \rightleftarrows RC_5H_4N\rightarrow O + RC_5H_4N^*OAc\ X^-$$

They take place by a mechanism of bimolecular nucleophilic substitution, and their rate is determined by the ionic forms of the reacting heterocyclic particles in the solution [39]. In methylene chloride solutions the salts are present mostly in the form of intimate ion pairs, the dissociation of which into ions is insignificant, and the kinetic parameters mainly characterize the reactivity of these particles, while the other particles do not have an effect. In acetonitrile, however, the observed rate constants vary with the concentration, and this is due to the simultaneous existence of ions and ion pairs in the reaction mixture, where the reactivity of the ion pairs is substantially lower than that of the free solvated cations.

In a series of kinetic investigations of the reactions of pyridinium salts under the influence of arylamines only the order of the dissociation constants was used; the range of the constants made it possible to consider that the salts were almost completely dissociated under the conditions of the kinetic experiment [43, 78-83]; however, their values were not used in the kinetic calculations in all cases, and the role of the other ionic associates under the working conditions was disregarded.

In [79-85] the transfer of acyl groups (the rate and equilibrium constants) from the respective N- and O-acylonium salts to the N-oxides of pyridines, highly basic pyridines, and N-methylimidazole in acetonitrile solutions (298 K) was studied:

$$AcNu_i^+{\cdot}BPh_4^- + Nu_j \rightleftarrows AcNu_j^+{\cdot}BPh_4^- + Nu_i$$

Ac = MeOCO, MeCO, Me_2NCO, Nu = 4-RC_5H_4N (R = H, Me, MeO, Me_2N, PhCH=CH, $Me_2NC_6H_4CH$=CH)

$$4\text{-}RC_5H_4N \rightarrow O$$

(R = H, Cl, Me, Et, MeO, Me_2N, PhCH=CH, $Me_2NC_6H_4CH$=CH; 1-MeIm)

At low concentrations no higher than $5{\cdot}10^{-3}$ M and with the corresponding dissociation constants (in the order of 10^{-2} mol/l) it was assumed that the degree of dissociation is $\alpha \geq 0.7$ and that only solvated cations of the pyridinium derivatives take part in the processes. Under such conditions the reaction takes place in one stage by a concerted S_N2 mechanism [80, 81, 83].

Thus, a substantial difference in the reactivity of the ionic forms can be clearly traced in the heterolytic reactions of heterocyclic salts. In solvents with low dielectric constants and also even in such solvents as acetonitrile at elevated concentrations of the salts the almost completely associated forms of the salts right up to ion triplets, the reactivity of which is significantly lower in heterolytic reactions than that of free/solvated ions, become really significant.

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