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TETRAZOLES.

15.* ELECTRICAL CONDUCTIVITY OF 5-PHENYLTETRAZOLE AND ITS SALTS IN WATER AND ORGANIC SOLVENTS

V. M. Tsentovskii, V. E. Bashkirtseva, M. I. Evgen'ev,
Z. P. Ivanova, V. S. Poplavskii, V. A. Ostrovskii,
and G. I. Koldobskii

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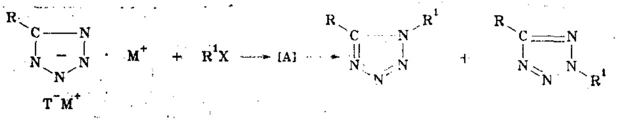
The electrical conductivity of 5-phenyltetrazole and its potassium, cesium, and ammonium salts in water, acetone, acetonitrile, nitromethane, and dimethyl sulfoxide has been studied. 5-Phenyltetrazole and its ammonium salt exists in an associated state in organic solvents. The potassium and cesium salts of 5-phenyltetrazole are practically completely dissociated in water, acetonitrile, nitromethane, and dimethyl sulfoxide when the concentration is less than 10^{-3} M.

One of the widely used methods for obtaining 1,5- and 2,5-disubstituted tetrazoles is the alkylation of salts of 5-substituted tetrazoles (T^-M^+) [1]. On the basis of a study of the kinetics of this reaction it has been shown that the alkylation takes place according to a two-step mechanism [2, 3]:



[A] — an unstable intermediate.

However, the absence of quantitative information on the state of the salts of the 5-substituted tetrazoles in the solvents used for alkylation prevents the further development of investigations in this area. For this reason we studied the electrical conductivity of 5-phenyltetrazole and its potassium, cesium, and ammonium salts in water, acetone, acetonitrile, nitromethane, and dimethyl sulfoxide. The experimental data from the conductometric measurements were treated according to the method in [4]. The values of the dissociation constants of 5-phenyltetrazole and its salts were calculated with the aid of the Bray—Kraus, Shedlovsky, and Ostwald equations. The thermodynamic values of the dissociation constants (K_d) were found according to the Debye—Hückel equation. The parameters obtained for the electrical conductivity are presented in Table 1.

The salts of the 5-substituted tetrazoles in organic solvents can be found in the form of various ionic species, viz., free ions, solvent-separated ion pairs, and contact ion pairs, as well as more complex agglomerates:

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*For Report 14, see [3].

S. M. Korov Kazan' Chemical Technology Institute, Kazan' 420015. Lensovet Leningrad Technological Institute, Leningrad 198013. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1556-1558, November, 1983. Original article submitted January 4, 1983.

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$$T^-M^+ \rightleftarrows T^- \| M^+ \rightleftarrows T \quad + \quad M^+ \qquad (1)$$

The reactivity and selectivity of such particles differ significantly. This circumstance must be taken into account in the study of the mechanism of alkylation. The state of equilibrium (1) depends on the nature of the solvent and the counterion, the concentration of the salt, and the temperature. The dissociation constant of 5-phenyltetrazole in water obtained conductometrically (Table 1), is in good agreement with the value calculated according to the equation $pK_\alpha = 1.27\sigma + 4.40$ [5] ($2.93 \cdot 10^{-5}$ and $3.16 \cdot 10^{-5}$, respectively). The dissociation constant of 5-phenyltetrazole decreases upon the transition from water to solvents with a lower dielectric constant. In water it is approximately 10^3 times greater than in acetone. It is also significant that the dissociation constants of 5-phenyltetrazole in dimethyl sulfoxide and 75% aqueous dimethyl sulfoxide [6] are in agreement with one another. Regardless of the nature of the solvent, the temperature has only a slight influence on the dissociation constant of 5-phenyltetrazole in the 20-45°C range.

The influence of the dielectric constant of the solvent, the nature of the cation, and the concentration of the electrolyte on the state of equilibrium (1) is also clearly traced in the example of the salts of 5-phenyltetrazole. At concentrations above 10^{-3} M all the salts exist in an associated state, regardless of the dielectric constant of the solvent and the nature of the cation. This is evinced by the values of the slopes of the conductivity isotherms found experimentally (s_{exp}) and calculated from the Onsager equation (s_{theor}) [7]. In all cases, $s_{exp} > s_{theor}$ (Table 1). In the case of the potassium and cesium salts at concentrations less than 10^{-3} M, equilibrium (1) is shifted to the right in such solvents as acetonitrile, nitromethane, and dimethyl sulfoxide. In fact, the degree of dissociation of these salts in concentrations from 10^{-3} to 10^{-5} M, calculated from the Ostwald equation are practically equal to unity. It is also noteworthy that similar results were obtained in the study of the UV spectra of potassium and cesium salts in acetonitrile [8, 9]. The influence of the nature of the cation is manifested especially clearly in the case of the ammonium salt of 5-phenyltetrazole. Even when the concentration is less than 10^{-3} M, the ammonium salt exists in the associated state in all the solvents studied.

Precisely as in the case of 5-phenyltetrazole, the dissociation constants of all the salts studied are only slightly dependent on the temperature. For example, the dissociation constants of the potassium salts of 5-phenyltetrazole in acetonitrile at 20 and 45°C are equal to $2.82 \cdot 10^{-2}$ and $1.40 \cdot 10^{-2}$, respectively. It is interesting that the values of K_d obtained in nitromethane deviate somewhat from the general dependence of the dissociation constants of 5-phenyltetrazole and its salts on the dielectric constant of the solvent. This is clearly attributable to the specific solvation of the tetrazolate anion by the solvent due to the formation of a hydrogen bond.

TABLE 1. Parameters of the Electrical Conductivity of 5-Phenyltetrazole and its Salts (T^-M^+) in Water and Organic Solvents, 25°C

M^+	Solvent	λ_0, $cm^2 \cdot \Omega^{-1} \cdot mole^{-1}$	s_{theor}	s_{exp}	K_d
H^+	Water	378,9	89,15	1746	$2,93 \cdot 10^{-5}$
	Acetone	150,0	—	—	$3,60 \cdot 10^{-8}$
	Acetonitrile	144,2	—	—	$9,00 \cdot 10^{-8}$
	Nitromethane	51,99	—	—	$2,59 \cdot 10^{-7}$
	DMSO	76,08	—	—	$1,37 \cdot 10^{-7}$
K^+	Water	102,6	84,2	190,2	$6,77 \cdot 10^{-2}$
	Acetone	144,0	571,7	2121	$1,27 \cdot 10^{-3}$
	Acetonitrile	142,4	330,8	448,5	$2,69 \cdot 10^{-2}$
	Nitromethane	100,1	196,5	1136	$1,50 \cdot 10^{-2}$
	DMSO	27,98	—	—	$3,20 \cdot 10^{-2}$
Cs^+	Water	118,6	104,6	332,5	$6,79 \cdot 10^{-2}$
	Acetone	214,6	554,9	884,1	$4,75 \cdot 10^{-4}$
	Acetonitrile	196,9	353,7	961,1	$2,64 \cdot 10^{-3}$
	Nitromethane	110,1	199,9	475,8	$6,20 \cdot 10^{-3}$
	DMSO	45,59	57,81	102,8	$4,79 \cdot 10^{-3}$
NH_4^+	Water	141,5	93,19	3019	$5,40 \cdot 10^{-4}$
	Acetone	156,9	360,2	451,9	$1,13 \cdot 10^{-6}$
	Acetonitrile	147,1	252,9	519,2	$6,92 \cdot 10^{-6}$
	Nitromethane	61,59	147,5	827,9	$2,70 \cdot 10^{-5}$
	DMSO	82,98	—		$2,87 \cdot 10^{-5}$

Thus, in choosing a solvent for the alkylation of the alkali metal salts of 5-substituted tetrazoles, primary consideration should be given to its dielectric constant and ability to specifically solvate tetrazolate anions.

EXPERIMENTAL

The electrical conductivity of 5-phenyltetrazole and its salts was measured on LM-301 and Impul's KL 1-2 conductometers in closed thermostated (±0.05°C) 10-cm^3 cells with a vertical orientation of the electrodes, which were made from unblackened platinum and had an area equal to 1 cm^2. The constant of the cells determined with respect to aqueous solutions of KCl are equal to 0.345 and 0.206 (25 ± 0.05°C). respectively. The conductometric measurements were carried out with an accuracy of ±0.25 rel. %. The experimental data were treated with the use of the algorithm and the block diagram presented in [4, 10].

5-Phenyltetrazole and its salts were obtained by known methods. All the compounds had characteristics which correspond to the literature data [9, 11, 12]. The solvents were purified as described in [13, 14]. The degree of purity of the solvents was monitored by GLC and according to the value of the specific conductance.

solvent	water	acetone	acetonitrile	nitromethane	DMSO
$\varkappa \cdot 10^7$, $\Omega^{-1}cm^{-1}$	6.25	1.35	1.50	1.50	5.25

Freshly distilled solvents were used for the measurements.

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