B) A solution of 5 mmole of 1-heptyl-4,5-dihydroxymethyl-1,2,3-triazole in 5 ml of dioxane containing 0.01 g of sodium was added to a solution of 1.3 g (0.01 mole) of benzoylacetylene in 5 ml of dioxane, and the mixture was heated with stirring for 1 h. It was then worked up as in method A to give 1.22 g (68%) of acetal VIII with mp 68-69°C.

C) A solution of 1.3 g (0.01 mole) of benzoylacetylene, 0.9 g (0.01 mole) of 2-hydroxymethyl-1,2,3-triazole (IVa), and one to two drops of triethylamine in 5 ml of dioxane was heated for 3 h, after which the solution was concentrated, and the precipitated crystals of triazolyl vinyl ketone VIIIa were removed by filtration to give 0.6 g (30%) of a product with mp 130-131°C [1]. The evaporated mother liquor was chromatographed with a column filled with aluminum oxide, and the eluent was removed to give 0.2 g (10%) of VIIIa and 0.4 g (20%) of VIIIb with mp 92-93°C. The PMR spectra of triazolyl vinyl ketones VIIIa,b contain signals of protons of the triazole ring (8.81 and 8.04 for VIIIa and 8.07 ppm for VIIb) and of protons of a double bond (7.80, 8.45, 7.90, and 8.40 ppm). The IR spectra contain a band at 1680 cm^{-1}, which is characteristic for a carbonyl group, and a band at 1620 cm^{-1}, which is characteristic for a conjugated double bond. The principal constants of the compounds obtained are presented in Table 1.

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TETRAZOLES.

13.* PROTONATION OF TETRAZOLYLACETIC ACIDS

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The protonation of isomeric 1H-, 2H-, and 5H-tetrazolylacetic acids, as well as a series of 5-aryl-1H- and 5-aryl-2H-tetrazolylacetic acids, in aqueous sulfuric acid solutions was studied by IR, UV, and PMR spectroscopy. It is shown that all of the investigated tetrazolylacetic acids are protonated in the tetrazole ring at sulfuric acid concentrations up to 96%; the proton adds to the nitrogen atom in the 4 position.

The acid–base properties of tetrazolylacetic acids have not been adequately studied [2]. It is known that these compounds are stronger acids than acetic acid [3]. No information regarding the basicities of tetrazolylacetic acids is available. At the same time, such data are necessary in the investigation of the kinetics and mechanism of acid-catalyzed reactions of these compounds. In this connection we studied the protonation of isomeric 1H-,

*See [1] for communication 12.

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TABLE 1. Chemical Shifts of the Methylene Protons and Frequencies of the Stretching Vibrations of the Carbonyl Group of Tetrazolylacetic Acids in Aqueous H_2SO_4 Solutions at 25°C

Compound	H_2SO_4 concn., %				
	30,2	76,4	96,5	83,5	96,5
	δCH_2, ppm			$\nu C{=}O$, cm^{-1}	
Ia	5,55	5,82	5,82	1730	1740
IIa	5,78	6,10	6,10	1735	1740
III	4,30	4,75	4,75	1730	1740

TABLE 2. Protonation of Tetrazolylacetic Acids in Aqueous H_2SO_4 Solutions at 25°C

Compound	$\lg I = -mH_0 + pK'_{BH^+}$					
	m	$-pK'_{BH^+}$	$-pK_{BH^+}$	r	n	s
Ia	1,02±0,01	3,72±0,07	3,65; 3,65*	0,98	9	0,21
IIa	0,90±0,05	4,08±0,21	4,53; 4,32*	0,99	8	0,08
III	0,91±0,04	2,72±0,11	2,99; 2,92*	0,99	9	0,07

*Calculated from Eq. (2)

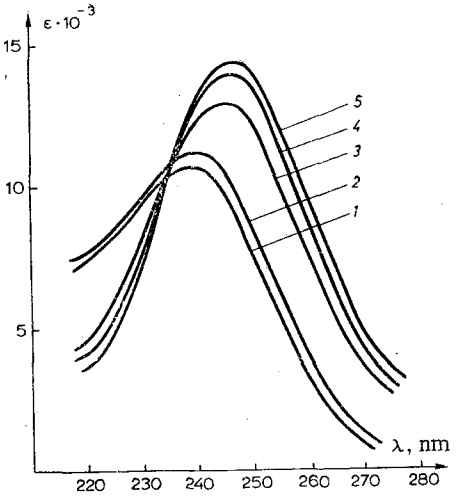
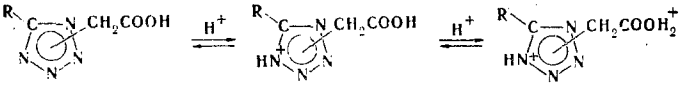


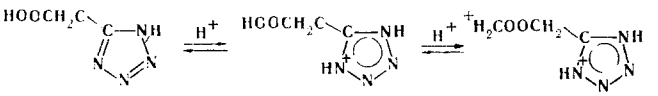
Fig. 1. UV spectra of 5-(m-methylphenyl)-2H-tetrazolylacetic acid in aqueous sulfuric acid solutions, %: 1) 39.0; 2) 45.0; 3) 60.8; 4) 65.4; 5) 69.9.

2H-, and 5H-tetrazolylacetic acids (Ia, IIa, and III), as well as two series of 5-aryl-1H- and 5-aryl-2H-tetrazolylacetic acids (Ib-i, IIb-i), in aqueous sulfuric acid solutions by IR, UV, and PMR spectroscopy.

On the basis of the available information on the basicities of substituted tetrazoles [4] and carboxylic acids [5] it may be assumed that in aqueous sulfuric acid solutions with moderate concentrations tetrazolylacetic acids are protonated in the tetrazole ring; protonation at the carboxy group is also possible when the sulfuric acid concentration is increased.



I, IIa-i



III

a R=H; b *p*-$CH_3C_6H_4$; c *m*-$CH_3C_6H_4$; d C_6H_5; e *p*-ClC_6H_4; f *p*-BrC_6H_4; g *m*-ClC_6H_4; h *m*-$NO_2C_6H_4$; i *p*-$NO_2C_6H_4$

This fact must be taken into account in the quantitative evaluation of the basicities of tetrazolylacetic acids.

TABLE 3. Protonation of 5-Aryl-1H- and 5-Aryl-2H-tetrazolyl-acetic Acids (Ib-i, IIb-i) in Aqueous H_2SO_4 Solutions at 25°C

Compound	λ_{anal}, nm	$\lg I = -mH_0 + pK'_{BH^+}$				
		m	$-pK'_{BH^+}$	$-pK^*_{BH^+}$	r†	s
Ib	235	1,07±0,09	3,14±0,25	2,95	0,98	0,14
	240	1,09±0,09	3,30±0,25		0,98	0,14
	265	1,04±0,07	2,99±0,20		0,99	0,11
	270	1,08±0,08	3,20±0,23		0,98	0,13
Ic	230	0,86±0,05	2,61±0,17	3,03	0,99	0,08
	250	1,06±0,08	3,17±0,24		0,98	0,15
	255	0,92±0,05	2,83±0,16		0,99	0,09
Id	245	0,91±0,03	3,02±0,11	3,44	0,99	0,05
	250	0,97±0,02	3,34±0,08		0,99	0,06
	255	0,97±0,02	3,44±0,09		0,99	0,05
Ie	230	0,88±0,03	3,25±0,12	3,73	0,99	0,05
	235	1,04±0,08	3,88±0,38		0,98	0,09
	240	1,10±0,05	4,14±0,16		0,99	0,07
If	235	1,05±0,06	3,81±0,20	3,63	0,99	0,11
	240	1,04±0,08	3,79±0,30		0,98	0,17
	275	1,05±0,06	3,79±0,30		0,99	0,14
Ig	245	1,05±0,04	3,90±0,15		0,99	0,05
	250	0,90±0,04	3,33±0,15		0,99	0,06
Ih	220	0,90±0,02	3,83±0,07	4,40	0,99	0,04
	225	0,88±0,04	4,12±0,16		0,99	0,07
	245	1,00±0,02	4,26±0,09		0,99	0,05
Ii	250	0,85±0,06	3,76±0,24	4,41	0,98	0,07
	255	0,89±0,06	3,91±0,27		0,98	0,10
IIb	260	1,08±0,08	4,07±0,31	3,74	0,98	0,10
	265	0,99±0,05	3,68±0,22		0,99	0,06
IIc	245	0,93±0,03	3,64±0,12	4,05	0,99	0,05
	250	0,96±0,03	3,86±0,11		0,99	0,05
	255	0,91±0,03	3,86±0,13		0,99	0,06
IId	250	0,91±0,06	3,74±0,22	4,13	0,99	0,09
	255	0,97±0,06	4,02±0,23		0,99	0,09
IIe	260	1,00±0,05	4,51±0,24	4,50	0,99	0,11
	265	1,09±0,05	4,88±0,24		0,99	0,10
	270	1,08±0,05	4,87±0,22		0,99	0,10
IIf	265	0,87±0,05	3,90±0,20	4,54	0,99	0,09
	270	1,00±0,07	4,59±0,34		0,98	0,15
IIg	245	0,95±0,04	4,59±0,18	4,97	0,99	0,07
	250	0,95±0,04	4,80±0,19		0,99	0,07
	255	0,95±0,04	4,87±0,21		0,99	0,07
IIh	240	1,00±0,04	5,20±0,18	5,19	0,99	0,06
	250	1,00±0,03	5,20±0,14		0,99	0,05
	255	1,02±0,04	5,27±0,19		0,99	0,06
IIi	265	0,94±0,03	4,87±0,15	5,22	0,99	0,04
	270	0,92±0,03	4,84±0,16		0,99	0,05

*The pK_{BH^+} values presented are averages of the values obtained at various wavelengths.

†For all of the compounds the number of points was no less than eight in the calculation of the regression lines.

Signals of protons of a methylene group are observed in the PMR spectra of 1H-, 2H-, and 5H-tetrazolylacetic acids in 30% H_2SO_4 at 4.30-6.10 ppm. For all of the compounds the signal of the methylene protons is shifted to weak field as the sulfuric acid concentration is increased to ∿76%; this is associated with protonation of the investigated tetrazolylacetic acids in the tetrazole ring. No substantial changes in the PMR spectra are observed at sulfuric acid concentrations from 77% to 96% (Table 1). This evidently means that tetrazolylacetic acids exist in the monoprotonated form over the investigated range of H_2SO_4 concentrations. In order to convince ourselves of the validity of this assumption we studied the IR spectra

of 1H-, 2H-, and 5H-tetrazolylacetic acids in sulfuric acid. It is known that the addition of a proton to the carboxy group leads to a decrease in the intensity and to a shift of the νC=O vibrations to the lower-frequency region [6]. However, an analysis of the IR spectra of tetrazolylacetic acids in 83-96% H_2SO_4 solutions provides evidence that there are no substantial changes in the character of the band of the stretching vibrations of the carboxy group (νC=O) (Table 1). Thus protonation of isomeric tetrazolylacetic acids in the tetrazole ring is realized over the range of 30-77% H_2SO_4 concentrations. At higher concentrations (up to 96% H_2SO_4) they exist in the monoprotonated form.

For the determination of the basicity constants of the isomeric tetrazolylacetic acids in the tetrazole ring the experimental data were treated by the method in [7]. The pK_{BH^+} values were calculated from the expression

$$\lg I = -mH_0 + pK_{BH^+}, \quad (1)$$

where $I = [TH^+]/[T]$. The criterion that determines the applicability of one or another acidity function for the description of the protonation of weak organic bases is the magnitude of slope m of Eq. (1) [8]. It is generally accepted that if $m = 1 \pm 0.1$, the investigated compounds are Hammett bases. At greater deviations of the slope from unity, one must use a different (from H_0) acidity function [8]. As a result of this, a situation arises in which the pK_{BH^+} values calculated by means of various acidity functions cannot be compared directly with one another [8]. In a number of cases this creates insurmountable difficulties in the interpretation of the data from kinetic studies of acid-catalyzed reactions. Some authors see the solution of this problem in the creation of a unified acidity function [9, 10]. Thus Cox and Yates [10] have proposed a new acidity function X (excess acidity) and an equation for the calculation of the pK_{BH^+} values of weak organic bases:

$$\lg I - \lg C_{H^+} = m^*X + pK_{BH^+}, \quad (2)$$

where C_{H^+} is the concentration of the hydrated protons in solution. Without analyzing Eq. (2) in detail, let us note that the ionization ratios I, necessary for the construction of an X scale, are determined by the same method as in the classical Hammett method. This fact to a certain degree reduces the fruitfulness of this approach. At the same time, the application of the X scale for the determination of the pK_{BH^+} values may make it possible to reduce to a unified system the available enormous amount of experimental data on the basicities of weak organic bases.

Considering this fact, the pK_{BH^+} values for 1H-, 2H-, and 5H-tetrazolylacetic acids were calculated from both Eq. (1) and Eq. (2); in all cases we obtained virtually coincident values (Table 2). The isomeric tetrazolylacetic acids, like other substituted tetrazoles [4], are protonated in the same way as Hammett bases. One's attention is drawn to the fact that isomerism has an appreciable effect on the basicities of tetrazolylacetic acids. The pK_{BH^+} value changes by 1.5 orders of magnitude on passing from 2H- to 5H-tetrazolylacetic acid.

In the next stage of the research we studied the protonation of two series of 5-aryl-1H- and 5-aryl-2H-tetrazolylacetic acids in aqueous solutions of sulfuric acid by UV spectroscopy.

The UV spectra of acids Ib-i and IIb-i in sulfuric acid depend substantially on the H_2SO_4 concentration (Fig. 1). This makes it possible without difficulty to select the analytical wavelength for the calculation of ionization ratios I. The I values were calculated from the experimental data obtained at various wavelengths; the interval of the measurements was 5-35 nm. The basicity constants (Table 3) were calculated from Eq. (1).

In all cases 2H-tetrazolylacetic acids are weaker bases than the isomeric 1H derivatives. The thermodynamic pK_{BH^+} values of 5-aryl-1H- and 5-aryl-2H-tetrazolylacetic acids correlate with the σ substituent constants:

$$pK_{BH^+} = -(1.53 \pm 0.13)\sigma - (3.26 \pm 0.05),$$
$$r = 0.98,\ n = 8,\ s = 0.12,$$

$$pK_{BH^+} = -(1.50 \pm 0.12)\sigma - (4.16 \pm 0.05),$$
$$r = 0.98,\ n = 8,\ s = 0.13.$$

Similar correlations are observed for 1-methyl-5-aryl- and 2-methyl-5-aryl-tetrazoles [11]; the ρ reaction constants virtually coincide with the ρ values found for isomeric tetrazolylacetic acids. Since the protonation center in 1,5- and 2,5-disubstituted tetrazoles is the nitrogen atom in the 4 position of the ring, on the basis of the correlations found above it may be assumed that the addition of a proton in isomeric tetrazolylacetic acids takes place at the nitrogen atom in the same position.

Thus it is evident that the reactions of tetrazolylacetic acids in which the first step is protonation of the carboxy group can take place successfully only in media with high acidities.

EXPERIMENTAL

The PMR spectra of $\sim 5 \cdot 10^{2}$ mole/liter solutions of the compounds were recorded with a Perkin-Elmer R-12 spectrometer (60 MHz) with tetramethylammonium bromide as the internal standard. The IR spectra were recorded with a Perkin-Elmer 457 spectrometer in germanium cuvettes The UV spectra of $\sim 1 \cdot 10^{-5}$ mole/liter solutions of the tetrazolylacetic acids were recorded with an SF-26 spectrophotometer with a thermostated block (25 ± 0.1°C).

The tetrazolylacetic acids were obtained by known methods. All of the compounds had characteristics that were in agreement with the literature data [3, 12-14]. The sulfuric acid solutions were prepared by dilution of 96% H_2SO_4 (chemically pure) with twice-distilled water. The concentration was determined by potentiometric titration with 0.1 N NaOH solution with an accuracy of ±0.1%. The values of the acidity function were taken from [15].

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