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INVESTIGATION OF THE PROTOLYTIC EQUILIBRIA OF NITRAMINOTETRAZOLES IN AQUEOUS MEDIA

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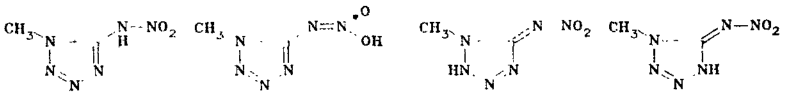
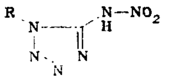
The UV and Raman spectra of a number of nitraminotetrazoles were recorded in aqueous media. The dependence of the spectral characteristics on the pH and H_0 was studied, and the dissociation constants of neutral and protonated molecules were determined. It was established that 5-nitramino- and 1-methyl-5-nitraminotetrazole exist in the nitrimine form in aqueous solutions.

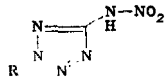
Up to the present time, the dissociation and protonation of nitraminotetrazoles had not been systematically studied; there were only data on the dissociation constants of individual compounds of this series [1]. The question of the tautomeric form of nitraminotetrazoles, for which nitramine, isonitramine, and nitrimine structures have been proposed [1], also remained in dispute; thus, for 1-methyl-5-nitroaminotetrazole, respectively:



The purpose of this work was to determine the dissociation constants of the neutral molecules (pK_a), their protonated forms (pK_{BH^+}), and to interpret the data from the standpoint of the possibility of existence of tautomeric forms of nitraminotetrazoles I-V.



I-III



IV,V

I R=H; II, IV R=CH_3; III, V R=C_2H_5

The values of pK_a and pK_{BH^+} of compounds I-V (Tables 1 and 2) were determined by methods of spectroscopy (UV, Raman) and potentiometric titration. Monotypic dependences of the UV and Raman spectra on the acidity of the medium are observed for I, II and IV, V, while differences of the UV spectra are observed for III.

The results obtained permit a sufficiently reliable interpretation of the structure only of compounds I and II. The low acidity of II ($pK_a \sim 6$) excludes the possibility of existence of this compound in nitramine or isonitramine tautomeric forms, which should be strong acids.

Evidence against an isonitramine tautomeric form was obtained in a study of the Raman spectra of compound II. It was found that the Raman spectra are unchanged when the nitrogen

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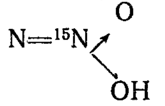
TABLE 1. Acidity and Basicity of I-V

Compound	UV spectroscopy	Raman spectroscopy	Potentiometric titration
I	pK_{a_2} 5,93±0,06 pK_{BH^+} 0,61±0,06 −5,64±0,03	pK_{a_2} 5,83	pK_{a_1} ~1,0* pK_{a_2} 6,16±0,03
II	pK_a 5,87±0,05 pK_{BH^+} 0,79±0,05 −5,83±0,05	pK_a 5,57	pK_a 6,04±0,03
III	pK_a 1,45±0,07 pK_{BH^+} −6,17±0,1	—	pK_a ~1,3*
IV	pK_a 1,48±0,06 pK_{BH^+} −4,73±0,07	—	pK_a ~1,7*
V	pK_a 1,49±0,03 pK_{BH^+} −4,93±0,06	—	

*In this pH region the precise value of pK_a cannot be determined by potentiometric titration [2]. A 0.2 M aqueous solution of the compound was titrated with 2 M NaOH.

TABLE 2. . Main Lines of the Raman Spectra of Aqueous Solutions of the Investigate Substances

Compound	pH≤4,5		pH 5,2–5,7		pH≥7,0
I	1526 s — 1318 m (1322 for ^{15}N) — 1002 m		1526 s (ρ=0,4) 1446 s (ρ=0,4) 1318 m (1322 m for ^{15}N) 1015 m 1002 m		— 1446 s — 1015 m —
II	**H_2O** 1526 s — 1318 m (1322 m for ^{15}N) — 1002 m	**D_2O** 1503 s — 1280 m — 996 m	**H_2O** 1526 s 1446 s 1318 m (1322 m for ^{15}N) 1015 m 1000 m	**D_2O** 1503 s 1446 s 1280 m 1013 m 996 m	**H_2O and D_2O** — 1446 s — 1015 m · 1013 m —
IV	1478 s 1015 s	—	—	—	1478 s 1015 s
V	1478 s 1015 s	—	—	—	1478 s 1015 s

^{14}N in the NO_2 group in compound II is replaced by ^{15}N (Table 2). These results contradict the isonitramine form, where the fragment  $N{=}^{15}N(O)OH$ should change the Raman spectrum with a very large degree of probability, on account of the change in the mass of the nitrogen atom at the double bond. At the same time, deuteration of II appreciably changes the Raman spectrum (Table 2, shift of the absorption band from 1526 to 1503 cm^{-1}), which may be a consequence of the addition of deuterium to the nitrimine structure.

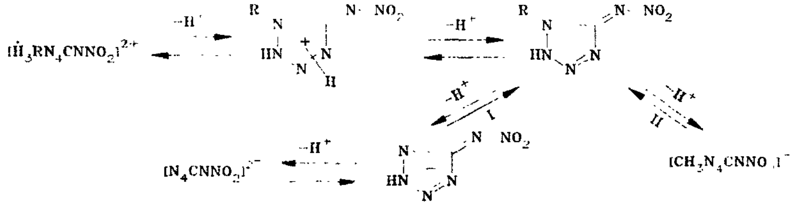
The results of Raman spectroscopy for I suggest that I, like II, exists in a nitrimine tautomeric form. Actually, the Raman spectra of the monoanion of I are analogous to the Raman spectra of II; moreover, replacement of the nitrogen ^{14}N in the NO_2 group by ^{15}N for compound I does not change the Raman spectrum, while deuteration of I shifts the absorption band from 1526 to 1503 cm^{-1} (Table 2).

Additional evidence against a nitramine tautomeric form was obtained in a study of the protonation of I and II. The values of pK_{BH^+}, 0.61 (I) and 0.79 (II), can belong only to rather highly basic compounds. The tetrazole, however, is a weak base (pK_{BH^+} — 3) [3], while the introduction of a weak electron acceptor substituent $NHNO_2$ into the 5-position should not increase the basicity of the tetrazole fragment. Therefore protonation of the nitramine form of compounds I and II at the tetrazole ring is excluded in the region of pH 0-2.

At the same time, protonation of the nitramine form of I and II at the $NHNO_2$ group is also excluded, since the addition of a proton should cause it to decompose [4]. However, within the investigated range of acidity, compounds I and II do not break down. Consequently, the values found for pK_{BH^+} cannot correspond to protonation of the nitramine tautomeric form. On the other hand, it is known that iminotetrazoles are strong bases (for 1,4-dimethyl-5-iminotetrazole, pK_{BH^+} 8.93, for 1,3-dimethyl-5-iminotetrazole pK_{BH^+} 11.75 [5, 6]). The possibility remains that the nitriminotetrazoles corresponding to them are also highly basic and can be protonated at pH 0-2.

The second protonation constants of I and II (pK_{BH^+} −5.64 and −5.83) should evidently correspond to the formation of dications.

As a result of the investigations, the following scheme of the dissociation and protonation of I and II is proposed (for one of the possible nitrimine forms):



In the dissociation of I, the value of pK_{a1} ∿ 1.0 should correspond to the elimination of a proton from the N_1 atom and not the N_2 atoms, since the value of pK_{a1} for I differs significantly from the value of pK_a for II (∿6).

In a consideration of the spectroscopic properties of compounds III-V, we cannot draw an unambiguous conclusion about their structure, since the values of pK_a and pK_{BH^+} may correspond to different tautomeric forms.

EXPERIMENTAL

The UV spectra were recorded in buffer solutions and in H_2SO_4 on a Spektromom-203 spectrophotometer. The values of pK_a were calculated according to [2], the values of pK_{BH^+} according to the Stewart-Granger method [7]. The Raman spectra were recorded H_2SO_4 and NaOH on a DFS-12 spectrometer with He-Ne as the source of excitation. The values of pK_a for I and II were determined according to the intensity ratio of the absorption bands at 1446 and 1526 cm^{-1}.

Potentiometric titration was performed on a pH-121 pH meter with glass electrode at 25 ± 0.5°C. The values of pK_a were calculated according to [2].

The initial I-III were produced according to the method of [1, 8].

2-Methyl(ethyl)-5-nitraminotetrazoles (IV, V) were produced according to a procedure analogous to [1]. To 15 g of 40% HNO_3 (0.015 M) at 95°C we added 0.07 mole of 2-methyl-5-aminotetrazole or 2-ethyl-5-aminotetrazole and evaporated the solution obtained to dryness. The nitrate remaining was added at 0°C to 80 ml of H_2SO_4 (d 1.836); the reaction mass was exposed for 1 h without cooling, poured out onto 250 g of ice, and extracted with ether. The ether extract was treated with anhydrous Na_2SO_4 and activated charcoal. After removal of the ether, IV and V were obtained. For IV found: N 58.2%, acid number 275.0 mg NaOH/g, $C_2H_4N_6O_2$. Calculated: N 58.3%; acid number 277.7 mg NaOH/g. For V found: N 53.0%; acid number 251.9 mg NaOH/g. $C_3H_6N_6O_2$. Calculated: N 53.2%; acid number 253.2 mg NaOH/g.

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