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PROTON EXCHANGE IN 1-VINYL-1,2,4-TRIAZOLE AND ITS DERIVATIVES

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Proton exchange at C(5) of the triazole ring has been studied in 1-vinyl-1,2,4-triazole, 1-ethyl-1,2,4-triazole, poly-1-vinyl-1,2,4-triazole, and their quaternary salts. The rate of exchange is catalyzed by bases and inhibited by acids.

Proton exchange in 1,2,4-triazoles has received little attention [1, 2]. Rapid hydrogen exchange between a protic solvent and the macromolecule has been reported [1] in studies of the PMR spectra of quaternary salts of poly-1-vinyl-1,2,4-triazole. We have now examined proton exchange in 1-vinyl-1,2,4-triazole (I), its saturated analog 1-ethyl-1,2,4-triazole (II), poly-1-vinyl-1,2,4-triazole (III), and their quaternary salts (IV-VI). The results obtained are shown in Table 1.

PMR spectroscopy showed that on heating (I) and (II) in D₂O, exchange took place involving the proton at C(5) of the triazole ring (Figs. 1 and 2). From the kinetic data for proton exchange in unsubstituted 1,2,4-triazole [2], the following reaction sequence is proposed:

TABLE 1. Half-Exchange Times $\tau_{1/2}$ for 1-Vinyl-1,2,4-triazole and Its Derivatives

Compound	T _{react}	Solvent	$\tau_{1/2}$, min	Compound	T _{react}	Solvent	$\tau_{1/2}$, min
I	60	D ₂ O	70	IV	53	D ₂ O+DCI	30
II	60	D ₂ O	90	V	53	D ₂ O+DCI	5
III	90	D ₂ O	360	VI	53	D ₂ O+DCI	600

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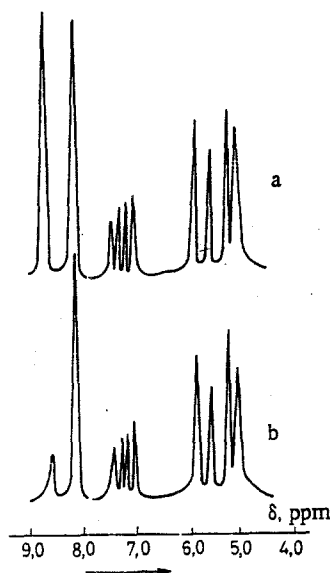


Fig. 1

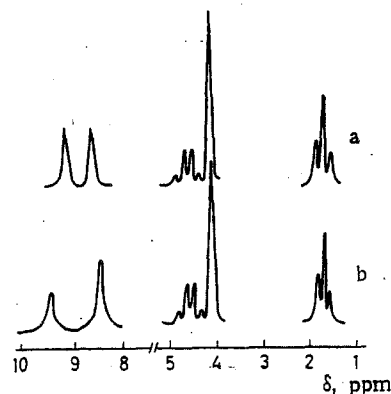
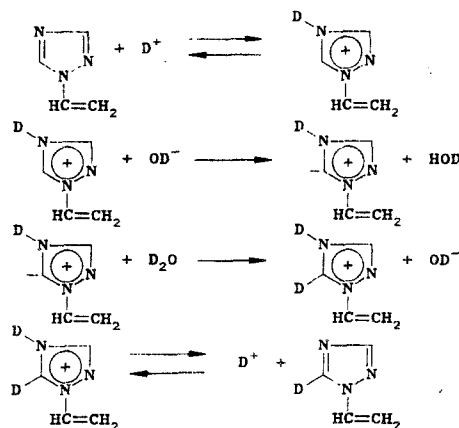


Fig. 2

Fig. 1. PMR spectra of 1-vinyl-1,2,4-triazole in D_2O (1 M): a) at the instant of mixing, b) after 240 min. Reaction temperature $60^\circ C$, external standard HMDS.

Fig. 2. PMR spectra of 1-ethyl-1,2,4-triazole in D_2O (1 M): a) at the instant of mixing, b) after 180 min. Reaction temperature $60^\circ C$, external standard HMDS.



In order to confirm this mechanism, the basicities of (I) and (II) in water were found. As expected, the introduction of the vinyl group reduces the basicity of the triazole ring (pK_{BH^+} of (I) 2.68, of (II) 3.08, and 1,2,4-triazole 2.27 [3]). The pK_{BH^+} values were used to calculate the concentrations of 1-vinyl-1,2,4-triazolium and 1-ethyl-1,2,4-triazolium cations in D_2O at pH 6 (the conditions under which proton exchange was studied). These concentrations were found to be 0.05 and 0.12%, respectively.

It has thus been found that the cations are present in aqueous solutions in kinetically significant amounts. It is to be expected that in the cations of (I), and even more so in its quaternary salts, exchange will take place much more rapidly. As expected, proton exchange in the quaternary salt (IV) takes place much more rapidly than in the starting compound (I) (Fig. 3). For comparison, Fig. 3a shows the PMR spectrum of (IV) in $DMSO-D_6$, in which no exchange occurs.

Exchange occurs in D_2O and CD_3OD at such a rate that it is not possible to observe it by PMR (Fig. 3b). To reduce the rate of exchange, measurements were carried out in the presence of DCl (Fig. 3c). Figure 4 shows the PMR spectrum of (VI). The retardation of exchange in the case of (VI) is due to the electron-donor properties of the ethyl group.

Bearing in mind the proton exchange in (I) found by us, similar exchange would be expected to occur also in (III). We have shown by PMR that on heating in D_2O , (III) also

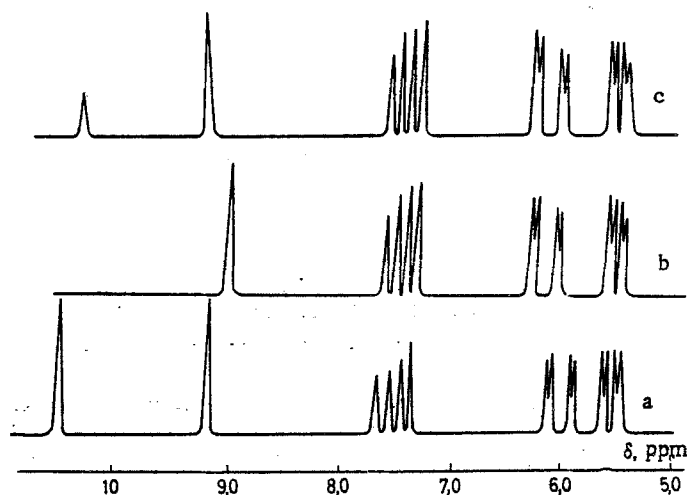


Fig. 3

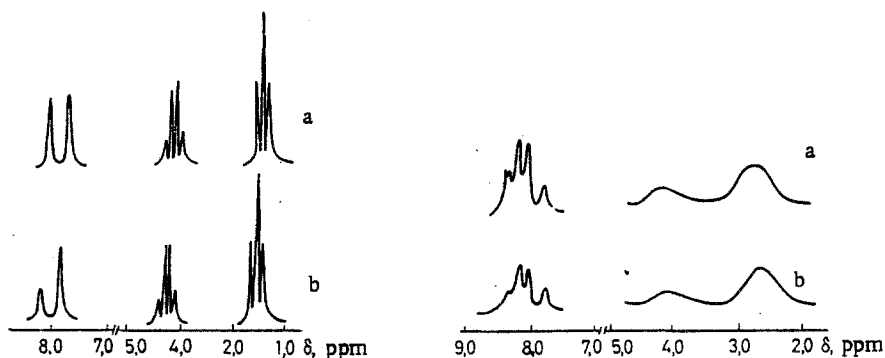


Fig. 4

Fig. 5

Fig. 3. PMR spectra of 4-methyl-1-vinyl-1,2,4-triazolium iodide: a) in DMSO- D_6 , b) in CD_3OD at the instant of mixing (0.1 M), c) in 0.06 N DCl in D_2O after 30 min. Reaction temperature 53°C, external standard HMDS.

Fig. 4. PMR spectra of 4-methyl-1-ethyl-1,2,4-triazolium iodide in 0.06 N DCl in D_2O (0.2 M): a) at the instant of mixing, b) after 600 min. Reaction temperature 53°C, external standard HMDS.

Fig. 5. PMR spectra of poly-1-vinyl-1,2,4-triazole in D_2O (1 M): a) at the instant of mixing, b) after 360 min. Reaction temperature 90°C, external standard HMDS.

undergoes proton exchange (Fig. 5), but at a much slower rate (Table 1) than in the monomer. This is due to reduced basicity and steric hindrance in the polymer, as compared with the monomer. Examination of (V) [1] (Fig. 6) shows that exchange takes place more rapidly in the polymeric salts than in the original monomer (I) or its saturated analog (VI). Proton exchange in polymeric quaternary salts, as in the monomeric azolium cations, is catalyzed by bases and inhibited by acids.

The increased kinetic acidity of the C-H bond in (V) as compared with that of (VI) is due to the effect of the adjacent electronegative substituents transmitted along the polymer chain, and the electrostatic effects of the total charge on the polycation.

EXPERIMENTAL

PMR spectra were obtained on a Tesla BS-487C spectrometer (80 MHz), external standard HMDS. A sealed ampul containing the solution of the test compound was placed in the resonator of the spectrometer, and maintained at the required temperature. The rate of exchange

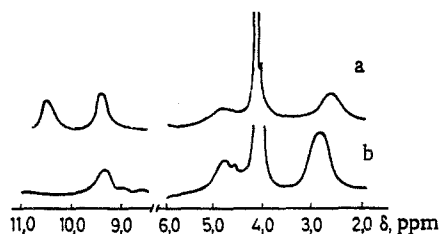


Fig. 6. PMR spectra of poly-4-methyl-1-vinyl-1,2,4-triazolium iodide: a) in DMSO-D₆ (0.2 M), b) in 0.06 N DCl in D₂O 20 min after mixing. Reaction temperature 53°C, external standard HMDS.

was found from the changes in the spectrometer signals with time. The PMR spectra of (I)-(III) were obtained in D₂O solution (1 M), at 60 and 90°C, respectively, of (IV) in solution in 0.06 N DCl in CD₃OD (0.1 M) at 53°C, and of (V) in solution in DMSO-D₆ (0.2 M) and in solution in 0.06 N DCl in D₂O at 53°C.

The pK_{BH^+} values of (I) and (II) were found by spectrophotometry, as described in [4].

Compound (I) was obtained as described in [5], (II) as in [6], (III) as in [7], and (IV)-(VI) as in [8].

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