DEPROTONATION OF SHORT-LIVING RADICAL CATIONS OF PYRROLYLBENZENES*

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The deprotonation reaction of radical cations of 1-(2-pyrrolyl)-4-(1-vinyl-2-pyrrolyl)benzene has been studied by nanosecond laser photolysis. Bimolecular rate constants have been determined for the transfer of proton to the heterocyclic base. Analysis of the yields has been carried out of the final products of the radical-cation reaction of 1-(2-pyrrolyl)-4-(1-vinyl-2-pyrrolyl)benzene in the presence and absence of bases. Comparison of the results of impulse and stationary photolysis showed that inhibition of the radical cation reaction occurs at the stage of forming the radical cations.

Keywords: 1-(2-pyrrolyl)-4-(1-vinyl-2-pyrrolyl)benzene, radical-cation, deprotonation, nanosecond laser photolysis.

It is recorded in the literature that on electropolymerization of pyrroles in the presence of small quantities of water or bases the polymers have higher conductivity than those obtained in dry acetonitrile. The reason for this phenomenon is linked with an increase in the acidity of the medium at the stage of aromatizing dihydrodimers of dications formed as a result of pairing radical cations (RC). Under acidic conditions pyrrole is protonated and then may react with the initial monomer at positions 2 or 3, giving defects in the form of unconjugated oligomers. To prevent the formation of such defects it is necessary to deprotonate the dications as rapidly as possible and to remove the resulting protons [1, 2]. In addition the introduction of bases may completely inhibit the polymerization process by deprotonating the initial radical cations. Similar problems may also arise in the process of forming polyconjugated systems based on dipyrrolylbenzenes on chemical, electrochemical, or photochemical oxidation of them.



* Dedicated to Academician B. A. Trofimov on his 70th jubilee.

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In the present work, the deprotonation of a molecule $1 \text{ RC} (1^+)$ with a series of heterocyclic bases (**B**) in acetonitrile has been studied by nanosecond laser photolysis (NLP) using 1-(2-pyrrolyl)-4-(1-vinyl-2-pyrrolyl)-benzene (1) as the example.

Chloroform was used as oxidizing agent. Azoles **B** were used as bases (values of pK_{BH}^+ from [3] are given in parentheses): 4-bromopyrazole (6.3), indazole (7.1), pyrazole (8.8), 3-methylpyrazole (9.8), 3,5-dimethylpyrazole (10.9), benzimidazole (12.7), 2-methylbenzimidazole (13.6), imidazole (14.6), and 2-methylimidazole (15.8). Reactions were carried out in MeCN.

RC 1 was obtained photochemically by NLP according to Scheme 1.

Scheme 1

absorption of light. I_{abs}	1.1
internal conversion, k_{ic}	1.2
fluorescence, $k_{\rm rad}$	1.3
intercombinational	1.4
conversion, $k_{\rm isc}$	
transfer of electron, k_q	1.5
transfer of proton, $k_{\rm r}$	1.6
other reactions, $k_{\rm p}$	1.7
	absorption of light, I_{abs} internal conversion, k_{ic} fluorescence, k_{rad} intercombinational conversion, k_{isc} transfer of electron, k_q transfer of proton, k_r other reactions, k_p

The choice of bases is dictated:

1. By the fairly wide range of pK_{BH}^{+} values in a relatively uniform heterocyclic series;

2. By the absence of absorption at the wavelength of the laser ($\lambda_{ex} = 337.1$ nm), which made possible excitation of only the substance being investigated;

3. By the higher energy levels of the lowest excited singlet and triplet states of bases **B** relative to the energy levels of the corresponding states of compound 1. Such a relative disposition of energy levels makes quenching of the electron-activated state of compound 1 by an energy transfer mechanism scarcely probable;

4. By the higher values, compared to compound 1, of the ionization potentials of molecules **B**. In this connection, the transfer of an electron from the heterocyclic bases being used to RC 1, i.e. $1^+ + B \rightarrow 1 + BH^+$, is not beneficial thermodynamically.

The formal kinetic analysis of Scheme 1 for the case of nonstationary excitation, under the experimental conditions $k_{\Sigma} > k_L$ and assuming that the concentration of compound **1** is not changed and the radical cations are consumed only in reaction 1.6, leads to the following expression for the dependence of radical-cation concentration on time.

$$[\mathbf{1}^{+}](t) = \frac{\alpha k_q [\mathrm{R-Cl}]}{k_{\Sigma} k_L} \cdot [\mathbf{1}](o) [\exp(-k_r t) - \exp(-k_L t)],$$

where, $k_{\Sigma} = k_0 + k_q$ [R-Cl], sec⁻¹; $k_L = 10^8$ sec⁻¹, the reciprocal value of the duration of the laser impulse on height 1/e; $k_r = k_p + k_H^+$ [**B**]; α is a constant characterizing the absorbing ability of the substance, the geometry of sample irradiation, and the power of the laser, sec⁻¹.

The analysis carried out shows that the time of introducing radical cations into reaction is described by the growing portion of the kinetic curve and is determined by the duration of the laser impulse, i.e. it may be considered as "instantaneous". The decrease in the kinetic curve determines the observed pseudounimolecular rate constant for the transfer of proton k_r (1.6).

The example of "quenching" RC 1 by imidazole in reaction 1.6 is represented in Fig. 1. The values of k_r for all the bases were determined from the kinetics of the attenuation of the optical density at the absorption maximum of RC 1 at several concentrations of base (Fig. 1). For this, in order to guarantee the pseudouni-molecular character of the reaction, the minimum concentration of base was chosen at not less than an eightfold

excess over the concentration formed on photolysis of RC 1. The bimolecular rate constants $k_{\rm H}^+$ were determined for each base from the tangents of the angle of the linear dependence of k_r on concentration of base **B**.



Fig. 1. Laser photolysis of the system compound 1 + imidazole in a medium of MeCN + CHCl₃ (10 vol.%): a - change of optical density at the absorption maximum of RC 1^+ with time at concentrations of imidazole of 1 - 0; $2 - 8 \cdot 10^{-4}$; $3 - 3 \cdot 10^{-3}$; $4 - 10^{-2}$ M; b - absorption spectrum obtained 1 - directly after excitation (RC 1); 2 - 2.5 msec later (neutral radical 1). Concentration of imidazole was 1.5×10^{-3} M.

A linear relationship was observed between log $k_{\rm H}^+$ and $pK_{\rm BH}^+$ of bases (Fig. 2). At $pK_{\rm BH}^+ = 15.8$ (2-methylimidazole) the value of $k_{\rm H}^+$ remained close to the diffusion limit, which, in agreement with [3], enables pK^{1+} in MeCN to be estimated as ≥ 16 .

We discovered previously [4] that on stationary photolysis of dipyrrolylbenzenes in the presence of chloromethanes colored products of an oligomeric nature are observed with $\lambda_{max} \sim 610$ nm (subsequently product **P600**), genetically linked with radical cations (Scheme 1, 1.7). In [4] the nature of the oligomers was not specially studied. We note that the dication of 2,2'5'2":5",2"'-quaterpyrrole has a very similar shaped absorption band in the visible region ($\lambda_{max} = 680$ nm). The quaterpyrrole was obtained as a result of pairing at the α -position of two radical cations of 2,2'-bipyrrole (RC–RC echanism) on electrochemical and photochemical (in the presence of CCl₄) oxidation of 2,2'-bipyrrole in MeCN [2]. On photochemical polymerization of 2,2'-bithiophene and 2,2'5'2"'-terthiophene in a medium of MeCN in the presence of CCl₄ as electron acceptor the formation of colored reaction products was also recorded, which in accordance with NMR investigations were considered as nanodimensional α -linked oligomers, partially protonated at the α -position [5].



Fig. 2. Dependence of the bimolecular rate constant for the transfer of proton in the reaction $\mathbf{1}^{+} + \mathbf{B}$ in MeCN on the p K_{BH} + of bases: l – pyrazole; 2 – 3-methylpyrazole, 3 – 3,5-dimethylpyrazole, 4 – benzimidazole; 5 – 2-methylbenzimidazole, 6 – imidazole, 7 – 2-methylimidazole. y = 0.6443x - 0.6916; $R^2 = 0.9873$.

The related character of the discussed heterocyclic compounds and the close photochemical conditions of the experiments enable us with a high degree of probability to propose that product P600 has the structure of the dication of the dihydrodimer of 1-(2-pyrrolyl)-4-(1-vinyl-2-pyrrolyl)benzene (2^{2+}).



The possibility of forming dihydrodimer 2^{2+} according to a RC–RC mechanism was confirmed by the high values of the calculated spin densities on the α -carbon atoms of the pyrrole rings (0.237 for an unsubstituted pyrrole ring and 0.234 for a pyrrole ring with an N-vinyl substituent) (Fig. 3).



Fig. 3. Optimized geometry [UB3LYP/6-31 + G(d)] and spin density distribution (isospin 0.005) of RC 1.

Experiments which, on the one hand, confirm the connection of radical cations with product **P600**, and on the other demonstrate the inhibition of cation-radical reactions of compound **1** with bases are demonstrated in Fig. 4.

In the first experiment the stationary photochemical oxidation of 1 by $CHCl_3$ was carried out in the absence of base. Titration of the solution obtained after the end of photolysis with base leads to complete disappearance of the absorption band of product **P600** and the appearance of a new absorption band with a maximum at 525 nm (**P500**, Fig. 4*a*).

In the second experiment the base was introduced directly before photolysis. The presence of base in the solution being photolyzed practically completely eliminates the formation of product **P600**, as in the first case, however product **P500** is formed in only trace amounts (Fig. 4*b*).



Fig. 4. Dependence of the absorption spectrum of the system of compound 1 ($5 \cdot 10^{-3}$ M) and CHCl₃ (10 vol%) in MeCN on time of irradiation: a – in the absence of imidazole (base was added after the end of photolysis); b – imidazole ($3 \cdot 10^{-3}$) was introduced directly before photolysis. Time of irradiating solutions was 115 sec.

In both cases solutions had the same concentrations and were irradiated for the same time. The ratio of yields of product **P500** in experiments A and B and the results of NLP on deprotonation demonstrate inhibition of the cation-radical reaction at the stage of forming radical cation 1^+ .

The information obtained shows the need for a delicate approach on selecting the strength and concentration of bases on carrying out radical-cation syntheses of polyconjugated polymers and may be useful when considering other pyrrole-containing monomers.

EXPERIMENTAL

Synthesis of compound 1 by the Trofimov reaction was described in [4]. MeCN and CHCl₃ from Merck Uvasol (99.9%) were used without further purification. Electronic absorption spectra were obtained on a Perkin-Elmer Lambda 35 spectrophotometer. Spectral-kinetic properties of the short-living products were investigated on a laser photolysis (NLP) device [6]. Excitation of samples was carried out in a quartz cuvette 1×1 cm² N2-laser AIL-3 (energy of impulse was 10^{-3} J, duration of radiation impulse at half-height was 7 nsec). Directly before the experiment samples were freed from oxygen of the air by passing argon for 20 min. A DRSh-500 mercury lamp was used as the source of stationary excitation with a color filter separating light with λ_{max} 313 nm.

Calculation of the equilibrium structure and the spin density of RC-1 was carried out by the DFT B3LYP//6-31 + G(d) method, with the GAUSSIAN 2003 set of programs.

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