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ELECTRON TRANSFER AS THE INITIATING STAGE OF DEHYDROGENATION OF BENZIMIDAZOLINES BY THE TRIPHENYLMETHYL CATION

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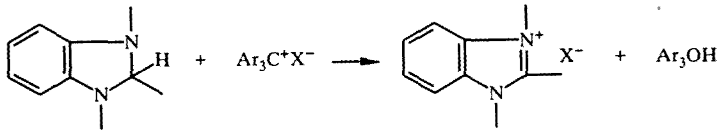
We consider a radical-ion mechanism for dehydroaromatization of benzimidazolines by triarylmethyl cations, including as the initial step electron transfer from the hydroheteroaromatic compound to the electrophilic reagent. We draw the conclusion that there is significant weakening of the $C_{(2)}-H$ *bond in the benzimidazoline radical cation formed in this stage.*

We know that benzimidazolines (2,3-dihydrobenzimidazoles) with a hydrogen atom in the 2 position react readily with triacrylmethyl cations according to a dehydrogenation–hydrogenation scheme with formation of benzimidazolium salts and triacrylmethanes [1, 2]:



I

(1)

This reaction, like many other similar conversions with migration of a hydrogen, may be classified as electrophilic substitution at the hydrogen atom [3]. The use of the term "hydride transfer" for such processes seems less fortuitous. First of all, participation of the H^- ion is a very low probability due to the fact that its abstraction from organic compounds is not energetically favorable, even from such compounds as benzimidazolines, which due to low ionization potentials and high stability of benzimidazolium cations should lose an H^- ion much more easily than most other organic substrates. Secondly, the indicated term creates the impression of a necessarily nonradical character of the reaction and does not formally encompass the one-electron channel of dehydrogenation (widely discussed in recent years) in which migration of the hydrogen precedes electron transfer and formation of a "donor hydride ion" radical cation (see, for example, [4]).

For reaction (1), the one-electron mechanism is especially probable due to the pronounced tendency of benzimidazolines to donate an electron to electrophilic reagents [5-7] and the strong electron–acceptor properties of triarylmethyl cations. The effect of these factors leads to the fact that electron transfer from simple benzimidazolines to the triphenylmethyl cation should be approximately energy-neutral ($\Delta G^0 \sim 0$).† According to the accepted kinetic scheme in [11, 12], the given process should occur in a short-lived collision complex of the reagent and the substrate:

$$\mathrm{I} + \mathrm{Ph_3C^+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{I...Ph_3C^+} \longrightarrow \mathrm{I^{+\cdot}} + \mathrm{Ph_3C^{\cdot}} \qquad (2)$$

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[*] Deceased.

[†] This follows from the approximate calculation of ΔG^0 according to the formula $\Delta G^0 = (E_{red}{}^0 - E_{ox}{}^0)F$ [8], where $E_{red}{}^0$ and $E_{ox}{}^0$ are the standard oxidation-reduction potentials characterizing the process of reduction of the oxidizing agent and oxidation of the reducing agent. For benzimidazolines not containing strong electron-acceptor (donor) substituents, $E_{ox}{}^0 \sim E_{ox}{}^p \sim 0.3$ V rel. to SCE [9], and for the Ph_3C^+ cation $E_{red}{}^0 \sim E_{red}{}^p \sim 0.3$ V rel. to SCE [10].

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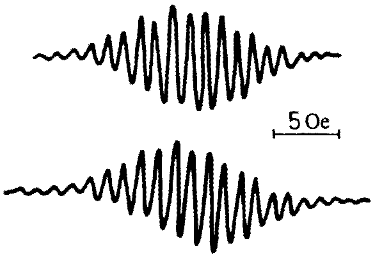


Fig. 1. EPR spectrum of the triphenyl methyl free radical, formed in the reaction of benzimidazoline IIb with triphenylchloromethane in benzene (upper spectrum) and its reconstruction (lower spectrum), obtained for hfs constants $a_0 = 2.55$, $a_m = 1.11$, $a_p = 2.77$ Oe and $\Delta H = 0.38$ Oe.

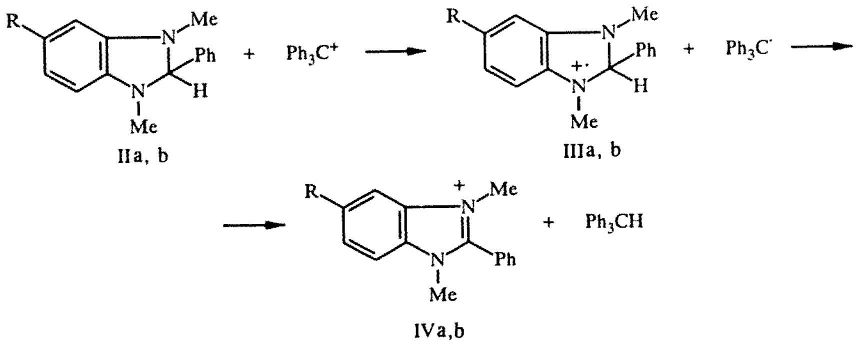
The effective rate constant for electron transfer is determined first of all by its free energy ΔG^0 and the total reorganization energy λ [12]. The latter quantity is approximated as half the sum of the total reorganization energies of the two degenerate electron exchange reactions: between the benzimidazoline system and its radical cation and between the benzimidazoline system and its radical cation and between the triphenylmethyl cation and the triphenylmethyl radical. For the first of these reactions, $\lambda \sim 80$ kJ/mole [13]; for the second, the indicated quantity is about 66 kJ/mole (determined based on the reaction rate constant $1.3 \cdot 10^8$ liters/(moles·sec) [14] from the relation presented in [12]). Consequently, for process (2), $\lambda \sim 77$ kJ/mole. The rate constants for the formation and reversible dissociation of the collision complex k_1, k_{-1} and the pre-exponential factor Z for transition of the complex to the electron transfer products for the typical outer-sphere mechanism for electron transfer are about $2 \cdot 10^{10}$ liters/(moles·sec), $6 \cdot 10^{10}$ and 10^{13} sec^{-1} respectively [11]. Using the formula

$$k_{\mathrm{eff}} \approx k_1 \left\{ 1 + k_{-1} z^{-1} \exp \left[0{,}25\lambda \left(1 + \Delta G^0 \lambda^{-1} \right)^2 R^{-1} T^{-1} \right] \right\}^{-1},$$

used for electron transfer processes in [11, 12], it is easy to show that in the case of conversions of type (2), the effective rate constant should be about 10^9 liters/(moles·sec). This result suggests greater probability of electron transfer from benzimidazolines to the triphenylmethyl cation.

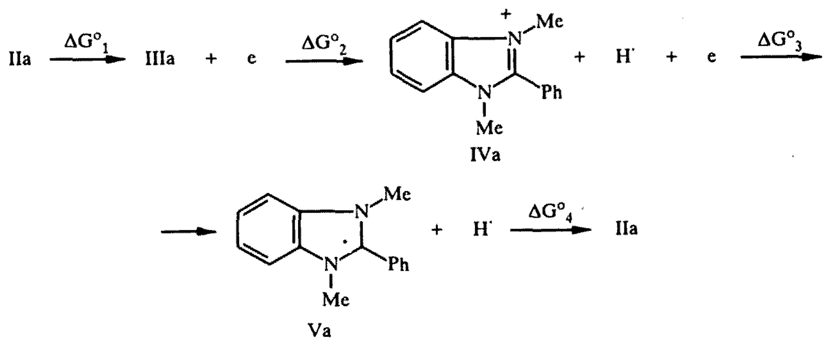
For the example of reactions of 1,3-dimethyl-2-phenyl-(IIa) and 1,3-dimethyl-2-phenyl-5-triphenyl-methylbenzimidazoline (IIb) with triphenylmethyl chloride, we were able to obtain experimental proof that electron transfer occurs. When carrying out the given reactions in benzene at room temperature under vacuum, using EPR we registered formation of the triphenylmethyl radical. The EPR spectrum of this radical (see Fig. 1) is a multiplet of equidistant lines and is practically identical to the spectrum modeled using known hfs constants [15].

EPR spectra are not observed for radical cations of substrates IIa, b, which is explained by their low stability and rapid consumption in subsequent conversions, leading to formation of benzimidazolium salts. These conversions may include spontaneous decomposition of the radical cation with cleavage of a proton or atomic (molecular) hydrogen [9], and also abstraction of a hydrogen atom from the radical cation by the triphenylmethyl radical with formation of



II—IV a R = H, b R = Ph$_3$C

Since triarylmethyl radicals have relatively low reactivity, insufficient for abstraction of a hydrogen atom from typical organic substrates, we can hypothesize that the migrating hydrogen atom is bound in radical cations of benzimidazolines via an anomalously labile bond. This property should be characteristic specifically for the radical-cation form but not for the diamagnetic form. This follows from consideration of the cycle presented below for conversions of benzimidazoline IIa:



Due to the properties of the cycle,

$$\Delta G_1^0 + \Delta G_3^0 = -(\Delta G_2^0 + \Delta G_4^0),$$

and the quantity $-(\Delta G_2^0 + \Delta G_4^0)$ is equal to the change in free energy of the $C_{(2)}-H$ bond upon going from benzimidazoline IIa to its radical cation (IIIa). The first and third processes of the cycle represent removal and addition of an electron. Consequently,

$$\Delta G_1^0 + \Delta G_3^0 = E_{IVa}^0 - E_{IIa}^0,$$

where E_{IVa}^0 and E_{IIa}^0 are the standard oxidation–reduction potentials of the couples Va/IVa and IIa/IIIa. The exact values of these potentials are not known, but to a first approximation they may be assumed to be equal to electrochemical potentials E^p for oxidation of the compound IIa and reduction of the cation IVa, which are about 0.3 and −1.6 V relative to the saturated calomel electrode [9]. Hence $\Delta G_1^0 + \Delta G_3^0 \sim 1.9$ eV (180 kJ/mole). Thus the $C_{(2)}-H$ bond in the radical cation IIIa is about 180 kJ/mole weaker than in the diamagnetic form IIa.

The conclusion that a labile C−H bond is present in the radical IIIa is supported also by the formation of molecular hydrogen upon reaction of compound IIa with one-electron oxidizing agents [9].

We may assume that loosening of the bond with participation of the hydrogen atom upon one-electron oxidation is a general property of compounds tending toward hydrogenation of electrophilic agents. This is supported by data on separation of hydrogen in reactions of derivatives of 1,2-dihydropyrimidine [9] and trisubstituted silanes [16-18] with one-electron oxidizing agents, and also the facile abstraction of low-reactivity free radicals of hydrogen atoms from the stable 1,6-diaza[4.4.4]bicyclododecane radical cation [19].

EXPERIMENTAL

The EPR spectra were taken on the Radipan SE-2543 instrument. Reconstruction of the EPR spectrum of the triphenylmethyl radical was done using the program ESR-1 in BASIC [20]. The PMR spectrum was recorded on the Tesla BS-487C spectrometer (80 MHz).

The elemental analysis data for the described compounds for C, H, and N correspond to the calculated values.

N,N′-Dimethyl-4-triphenylmethyl-o-phenylenediamine. 6 g (18 mmoles) triphenylmethylperchlorate was added with stirring and water-cooling to a solution of 2.4 g (18 mmoles) N,N′-dimethyl-o-phenylenediamine in 15 ml acetonitrile. After 5 min, the reaction mixture was poured into 50 ml of dilute hydrochloric acid (1:1), the precipitate was filtered, washed with water, and dried. Yield of the diamine: 2.8 g (42%). T_{mp} 191-192°C (from propanol). PMR spectrum (C_6D_6): 2.11 (3H, s, N-Me), 2.28 (3H, s, N-Me), 6.41 (1H, d, 6-H, $J_{5,6}$ = 7.5 Hz), 6.53 (1H, d, $J_{3,5}$ = 2.0 Hz), 6.81 (1H, doublet of doublets, 5-H), 6.83-8.00 ppm (15H, m, phenyl protons).

1,3-Dimethyl-2-phenyl-5-triphenylamethylbenzimidazoline (IIb). 0.5 ml acetic acid and 1.0 g (9.5 mmoles) benzaldehyde were added to a suspension of 3.2 g (8.5 mmoles) N,N′-dimethyl-4-triphenylmethyl-o-phenylenediamine in

30 ml n-butanol. The mixture was heated to boiling, boiled for 5 min, and cooled. The precipitate of benzimidazoline was filtered off and dried. Yield: 2.2 g (69%). T_{mp} 213-214°C (under vacuum at 2 mm Hg).

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