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STUDY OF THE MECHANISM OF THE INTERACTION OF CERTAIN AROMATIC DINITRO DERIVATIVES WITH ALKALI BY THE E.P.R. METHOD

It is known that the nitro group, like the carbonyl group, activates the neighboring methylene group, as a result of which a labile C—H bond is obtained, which is cleaved in addition reactions. At the same time, migration of the double bond is observed, as in keto-enol tautomerism. Hantzsch ([1]) established that phenylnitromethane can exist in nitro and isonitro forms, the equilibrium between which in an alkaline medium is shifted toward the latter

$$C_6H_5-CH_2-N\begin{matrix}\nearrow O\\ \searrow O\end{matrix} \underset{\text{acid}}{\overset{\text{alkali}}{\rightleftarrows}} C_6H_5-CH=N\begin{matrix}\nearrow O\\ \searrow OH\end{matrix}.$$

Subsequent studies of this equilibrium, including polarographic studies ([2]), showed that the transition of the nitro form into the isonitro form occurs through the stage of formation of an anion arising from the nitro compound upon abstraction of a methylene proton. The acidic character of the methyl protons in para-nitrotoluene was also confirmed in works ([3,4]) by analysis of e.p.r. spectra and absorption spectra of colored solutions containing C_4H_9OK. It is natural to suppose that the bridge protons of 4,4′-dinitrodiphenylmethane and 4,4′-dinitrodibenzyl should possess considerable mobility, owing to the fact that transition into the isonitro form leads to an increase in conjugation encompassing both phenyl rings. In order to test the acidic character of the bridge protons and to elucidate the possibility of formation of ion-radicals under the action of alkali, in the present work the e.p.r. method was used to study the interaction of a solution of tetra-*n*-butylammonium hydroxide $(C_4H_9)_4NOH$ in N,N-dimethylformamide and acetonitrile with 4,4′-dinitrodiphenylmethane, 4,4′-dinitrodibenzyl, and trans-4,4′-dinitrostilbene. It seemed interesting to us to investigate these systems in connection with the fact that we had previously obtained the e.p.r. spectra of the anion-radicals arising during electrochemical reduction of the above-mentioned dinitro derivatives ([5]).

Experimental Part

For investigation by the e.p.r. method of the action of alkali on aromatic dinitro derivatives, 10^{-3} M solutions of the substances were used as a rule, although in the case of a solution of 4,4′-dinitrodiphenylmethane in acetonitrile the spectrum was obtained at a substantially higher concentration of the substance

($4 \cdot 10^{-3}$ M). The concentration of alkali was varied within the range from $5 \cdot 10^{-3}$ to 10^{-2} N. The solutions of the substances were first deoxygenated by repeated freezing in liquid nitrogen, evacuation to 10^{-3} mm Hg, and thawing directly in ampoules with a side pocket containing the corresponding weighed portion of alkali. The subsequent reaction of the substance with the alkali was carried out at room temperature. For electrochemical generation of radicals in the resonator, a cell described previously ([5]), with a side pocket for $(C_4H_9)_4NOH$, was used.

The e.p.r. spectra were recorded on a standard RE-1301 radiospectrometer at room temperature.

The characteristics of the reagents used in the work are given in another article (5). The alkali $(C_4H_9)_4NOH$ was used as a commercial reagent of "chemically pure" grade and contained water of crystallization. Table 1 summarizes the splitting constants of the EPR spectra. The experimental spectra are shown in Figs. 1 and 2.

Discussion of results

For all the compounds studied, the action of the alkali $(C_4H_9)_4NOH$ produces an intense blue coloration, sensitive to atmospheric oxygen. Under certain conditions all the colored solutions give an EPR signal.

Table 1

No.	Compound	Solvent	a_N (oersted)	a_1 ortho (oersted)	a_2 meta (oersted)	a_3 bridge (oersted)
1	4,4′-dinitrodiphenylmethane	DMF	4.4	2.2	1.1	
1	4,4′-dinitrodiphenylmethane	Ac	6.0	1.2	1.2	1.2
2	4,4′-dinitrobibenzyl	DMF	2.4	1.2		3.6
2	4,4′-dinitrobibenzyl	Ac	3.5	1.4		3.5
3	trans-4,4′-dinitrostilbene	DMF	2.4	1.2		3.6
3	trans-4,4′-dinitrostilbene	Ac	3.5	1.4		3.5

The EPR spectrum of the radical formed upon interaction of a 10^{-3} M solution of 4,4′-dinitrodiphenylmethane in dimethylformamide with a 10^{-2} N solution of $(C_4H_9)_4NOH$ consists of 29 components of hyperfine structure (h.f.s.). The

intensity ratio of the components corresponds to interaction of the unpaired electron with 2 equivalent nitrogen nuclei and two groups of protons, each containing 4 equivalent nuclei. Thus, the anion-radical formed in this case has the same structure as in the electrochemical reduction of 4,4′-dinitrodiphenylmethane in dimethylformamide (5). When dimethylformamide is replaced by acetonitrile (CH_3CN), the deeply colored product of the interaction gives no EPR signal. Increasing the concentration of the substance to $4 \cdot 10^{-3}\,M$ leads to the formation of a radical whose spectrum, differing in character from the spectrum in dimethylformamide, can be interpreted as a quintet from 2 equivalent nitrogens, split into 10 lines by 9 protons.

It should be noted that in all cases the appearance of color precedes in time the appearance of the EPR signal, and, for the solution of 4,4′-dinitrodiphenylmethane in CH_3CN, not all colored solutions give a signal. This makes it possible to propose the following mechanism for formation of the anion-radical from 4,4′-dinitrodiphenylmethane:

$$NO_2{-}C_6H_4{-}CH_2{-}C_6H_4{-}NO_2 + OH^- \rightleftharpoons^- O{-}N^+(=O){-}C_6H_4{=}CH{-}C_6H_4{-}NO_2 + H_2O; \tag{1}$$

$$^-O{-}N^+(=O){-}C_6H_4{=}CH{-}C_6H_4{-}NO_2 \overset{+e}{\rightleftharpoons} {}^-O{-}N^+(=O){-}C_6H_4{=}CH{-}C_6H_4{-}N^\bullet(O^-)_2. \tag{2}$$

Apparently, a colored diamagnetic anion is first formed, which, by adding one more electron, is converted into an anion-radical.

To confirm the proposed mechanism of anion-radical formation, alkaline solutions of 4,4′-dinitrodiphenylmethane in dimethylformamide and acetonitrile were subjected to electrolysis at the cathode (5). In this case the voltage applied to the electrodes ($\Delta U = 0.4$ V) was deliberately smaller than the potential difference required to generate anion-radicals in nonalkaline solutions ($\Delta U = 1.5$ V). The EPR signal for 4,4′-dinitrodiphenylmethane in dimethylformamide (Fig. 1a) then increases strongly in intensity without any change in the character of the spectrum. Electrolysis

the same diamagnetic colored solution of $NO_2C_6H_4CH_2C_6H_4NO_2$ in acetonitrile leads to the appearance of an anion-radical, whose EPR spectrum (Fig. 1b) is identical with the spectrum of the radical formed without electrolysis, but at a high concentration of the substance. Thus, the formation of the radical at the cathode at a comparatively low potential confirms the proposed mechanism of anion-radical formation in stage 2, which is probably hindered in acetonitrile.

Fig. 1. EPR spectra of anion-radicals formed in the interaction of 4,4′-dinitrodiphenylmethane with $(C_4H_9)_4NOH$ and $\Delta U = 0.4$ V: in dimethylformamide (top) and in acetonitrile (bottom)

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Figure 1: Fig. 1. EPR spectra of anion-radicals formed in the interaction of 4,4′-dinitrodiphenylmethane with $(C_4H_9)_4NOH$ and $\Delta U = 0.4$ V: in dimethylformamide (top) and in acetonitrile (bottom)

Fig. 2. EPR spectrum of the anion-radical formed in the interaction of $(C_4H_9)_4NOH$ with trans-4,4′-dinitrostilbene in acetonitrile

Figure 2: Fig. 2. EPR spectrum of the anion-radical formed in the interaction of $(C_4H_9)_4NOH$ with trans-4,4′-dinitrostilbene in acetonitrile

Apparently, during the electrochemical reduction of 4,4′-dinitrodiphenylmethane in non-alkaline solutions [5], the anion-radical formed also eliminates a proton from the methylene bridge, as a result of which a through-conjugated π-bond system arises, ensuring delocalization of the unpaired electron over the whole molecule:

$$NO_2\text{–}CH_2\text{–}NO_2 \underset{\leftarrow}{\overset{+\bar{e}}{\rightleftarrows}} [NO_2\text{–}CH_2\text{–}NO_2]^{-\cdot} \tag{3}$$

$$[NO_2\text{–}CH_2\text{–}NO_2]^- \rightleftarrows {}^-O\text{–}\overset{+}{N}\left(=\!\!\rangle\!\!=CH\text{–}\rangle\!\!=\overset{+}{N}\!/O^-\right) + H^+. \tag{4}$$

In this case, reaction (4) should be promoted by the basic character of polar dimethylformamide.

Fig. 2. EPR spectrum of the anion-radical formed in the interaction of $(C_4H_9)_4NOH$ with trans-4,4′-dinitrostilbene in acetonitrile

The radical arising upon interaction of a 10^{-3} M solution of 4,4′-dinitrodibenzyl in dimethylformamide with $5 \cdot 10^{-3}$ N concentration of $(C_4H_9)_4NOH$ gives the same EPR spectrum as 4,4′-dinitrostilbene upon electrochemical reduction (5). Increasing the concentration of OH^- ions to 10^{-2} does not cause a sharp decrease in the signal. The formation of the anion-radical of 4,4′-dinitrostilbene from 4,4′-dinitrodibenzyl undoubtedly indicates that the reaction proceeds through the stage of abstraction of methylene protons:

$$\begin{gathered} NO_2\text{–}C_6H_4\text{–}CH_2CH_2\text{–}C_6H_4\text{–}NO_2 + 2OH^- \rightleftharpoons \\ {}^-O\text{–}\overset{+}{N}(=O)\text{–}C_6H_4{=}CH{-}CH{=}C_6H_4\text{–}\overset{+}{N}(=O)\text{–}O^- + 2H_2O; \end{gathered} \tag{5}$$

$$^{-}O-\overset{+}{N}(=O)-C_6H_4=CH-CH=C_6H_4-\overset{+}{N}(=O)-O^{-} \underset{\leftarrow}{\overset{+e}{\rightleftarrows}} {}^{-}O-\overset{+}{N}(=O)-C_6H_4=CH-\dot{C}H-C_6H_4-NO_2. \quad (6)$$

Thus, in order to obtain an anion-radical from the dianion, the latter must give up one electron (reaction (6)). This was experimentally confirmed by us during electrolysis of the diamagnetically colored dianion (concentration of $(C_4H_9)_4NOH = 10^{-2}$ N) at the anode at $\Delta U = 0.4$ V. The EPR spectra of the anion-radicals obtained in this case proved to be identical with the spectra of the anion-radicals formed under the action of alkali (concentration of $(C_4H_9)_4NOH < 10^{-2}$ N). Thus, the HFS of the spectrum of the anion-radical arising in an alkaline solution of 4,4′-dinitrodibenzyl in dimethylformamide (Fig. 2) may be represented as a main triplet from the bridge protons, followed by splitting into two quintets from 2 nitrogen nuclei and 4 protons. For the solution in CH_3CN, the good agreement between the experimental and theoretical spectra indicates equal interaction of the unpaired electron with 2 equivalent protons and two nitrogen nuclei. It should be noted that, in the case of an OH^{-}-ion concentration greater than 10^{-2} N, reaction (6) is probably hindered, since all the starting substance can pass into the form of the dianion, and only the application of a positive potential shifts the equilibrium of reaction (6) to the right.

The proposed mechanism is confirmed by the EPR spectra obtained under the action of alkali on solutions of 4,4′-dinitrostilbene, which are identical to the spectra of the anion-radicals arising in alkaline solutions of 4,4′-dinitrodibenzyl. However, in the case of 4,4′-dinitrostilbene the appearance of the color and of the radical proceeds more slowly than for 4,4′-dinitrodibenzyl, possibly because reaction (5) does not occur, and the formation of the anion-radical is effected owing to the electron-donor properties of the OH^{-} ion (6):

$$NO_2-C_6H_4-CH=CH-C_6H_4-NO_2 \underset{\leftarrow}{\overset{+e}{\rightleftarrows}} {}^{-}O-\overset{+}{N}(=O)-C_6H_4=CH-\dot{C}H-C_6H_4-NO_2. \quad (7)$$

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Note: Figure translations are in progress. See original paper for figures.