A STUDY OF THE ELECTROCHEMICAL REDUCTION OF CERTAIN ARYLAZO COMPOUNDS, AND THE BEHAVIOR OF THE RESULTING ANION-RADICALS, BY ESR AND POLAROGRAPHIC METHODS

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It has been shown [1] that the p-nitrophenyldiazo compounds react with nucleophilic agents, accepting electrons from the nucleophile to form paramagnetic anion-radicals (AR). We have studied the electrochemical reduction of $C_6H_4N_2X$-type diazo compounds, and the structures of the resulting AR, with a view to showing that their reduction is a one-electron process, at the same time investigating the nature and stability of the paramagnetic reduction products, and the various reactions which these products undergo.

It is known that many azo compounds undergo one-electron reduction with the formation of anion-radicals [2-4]. The structures of the anion-radicals obtained from certain of these compounds have been described in [4].

EXPERIMENTAL

The $C_6H_4N_2X$ arylazo compounds were synthesized by the methods of [5-9]. The electrochemical studies were carried out by the methods of classical and cyclic polarography, using an LP-7 polarograph (CzechSSR). Experimental methods are given in [10, 11], together with estimates of the long-term and short-term stabilities of the product anion-radicals. DMFA and, in certain cases, CH_3CN served as solvents. Each solution contained a depolarizer, the concentration of the latter ranging from $1 \cdot 10^{-3}$ to $3 \cdot 10^{-3}$ M. Electrochemical reduction for the ESR studies on the product AR was carried out in a three-electrode vacuum cell so constructed that the cathode potential could be controlled during electrolysis [11]. The ESR spectra were recorded with a Carl Zeiss ER-9 (9349 MHz) spectrometer, working at temperatures ranging from 200 to 300°K. Table 1 shows half-wave potentials ($E_{1/2}$) for reduction of the various diazo compounds, together with hyperfine structure (hfs) constants for the anion-radicals of these compounds.

DISCUSSION OF RESULTS

It can be seen from Table 1 that compounds (I)-(XIII) undergo stepwise reduction in aprotic media, the slope of the logarithmic curve [E vs log $(i/i_d - i)$, slope $\sim$0.059 V] indicating that the first of these steps is a reversible, one-electron process. On the basis of estimates of long-term AR stabilities from the cyclic polarograms, the ESR spectra obtained during electrolysis of compounds (I)-(IV) and (VI) at first-wave potentials were assigned to the primary products from the one-electron reduction process. This did not, of course, rule out the possibility that addition of the first electron might be followed by chemical reactions leading to the formation of polarographically indistinguishable products. The $E'_{1/2}$ values for compounds (I)-(IV), (XIII) varied under alteration of the Y substituent in the aromatic ring and proved to be linearly related to the substituent σ parameters (Fig. 1, curve a). The $E'_{1/2}$ values for the p-nitrophenyldiazo compounds (I), (VI), (X)-(XII) could be correlated with the $E'_{1/2}$ and $\sigma_{N=N-X}$ values (curve b).

The ESR spectra of the anion-radicals of compounds (I)-(IV) showed a number of lines which arose through unpaired electron interaction with the N and H atoms of the phenyl group. The spectrum of the anion-radical of compound (IV) suggested an appreciable F atom cleavage from the ring (Fig. 2).

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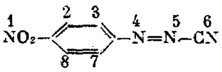
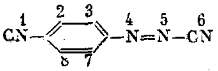
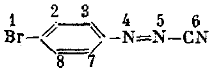
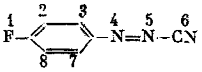
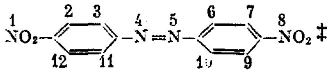
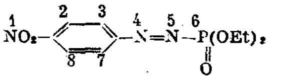
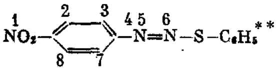
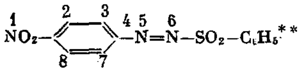
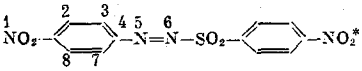
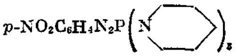
TABLE 1. Half-Wave Reduction Potentials* (V) for the $YC_6H_4 \cdot N_2X$ Diazo Compounds, and Hyperfine Structure Constants† for Their Anion-Radicals (DMFA, Bu_4NClO_4)

Compound	$E'_{1/2}$	$E''_{1/2}$	$E'''_{1/2}$	a_1	$a_{2,8}$	$a_{3,7}$	a_4	a_5	a_6
(I) 	0,12	0,73	2,17	4,9	2,1	0,7	4,2	1,4	—
(II) 	0,16	1,11		1,2	2,6	0,6	6,3	5,7	—
(III) 	0,20	1,18	—	—	1,8	0,7	5,2	2,6	—
(IV) 	0,35	1,39		11,8	2,8	1,1	8,0	4,0	—
(V)  ‡	0,43	1,73	2,05	$a_{1,8}$ 3,0	$a_{2,7\ 9,12}$ 1,5				
(VI) 	0,32	0,66	2,03	6,6	1,7	0,6	2,8	2,2	6,0
(VII)  **	0,82	1,66	—	10,2	3,2	1,0	3,8	—	—
(VIII)  **	0,31	0,70	2,18	10,2	3,2	1,0	3,8	—	—
(IX)  **	0,28	0,69	2,32	10,2	3,2	1,0	3,8	—	—
(X) $p\text{-}NO_2C_6H_4N_2CONH_2$	0,45	0,70	2,06						
(XI) $p\text{-}NO_2C_6H_4N_2N(CH_3)_2$	0,92	1,54	2,13						
(XII) 	0,20	0,60	2,36						
(XIII) $p\text{-}CH_3OC_6H_4N_2CN$	0,40	1,35	—						

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*Potential measured against the mercury pool. Precision of measurement, ±0.05 V.

†Accuracy of hfs constant determination, ±0.05 Oe.

‡Corresponds to the ESR spectrum of the 4,4'-dinitrobiphenyl anion-radical.

**Corresponds to the ESR spectrum of the nitrobenzene anion-radical.

The spectra of the anion-radicals resulting from the reduction of compound (V) at first-wave potential showed 13 lines, the constants for hyperfine splitting from the two N atoms and the four equivalent protons being those characteristic of the 4,4'-dinitrobiphenyl radical. Electron transfer to (V) obviously leads to N atom detachment with formation of a 4,4'-dinitrobiphenyl anion-radical as a secondary product. The effect here is similar to that resulting from the detachment of SO_2 in the conversion of the primary $[NO_2C_6H_4SO_2CF_3]^{\dot{-}}$ AR to the secondary $[NO_2C_6H_4CF_3]^{\dot{-}}$ [12].

It has already been pointed out that the data of cyclic polarography indicate that the first wave in the polarogram of compound (VI) arises from a reversible, one-electron reduction process. The ESR spectra showed the paramagnetic products from this reaction to be anion-radicals of the diethyl ether of p-nitrophenylazophosphoric acid, the hfs constants being those for interaction of the unpaired electron with the N atoms, the phenyl ring protons, and the P atoms. Values of these constants are shown in Table 1. The ESR spectra of secondary products, including the nitrobenzene anion-radical, appeared during the electrochemical reduction of compound (VI) at more negative potentials. The spectra of the nitrobenzene anion-radicals were also obtained during the action of alkalis on compound (VI) in DMSO solution, and this despite the fact that formation of primary anion-radicals could not be detected here. Arylazophosphoric acid ethers attack by alkalis in aqueous alcoholic solution proceeds through a homolytic mechanism with the formation of unstable aryldiimines

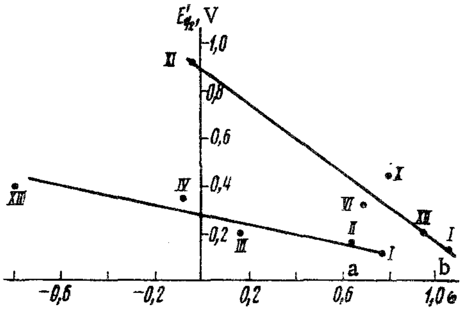

Fig. 1. Correlation between $E'_{1/2}$ values for the $YC_6H_4N_2CN$ compounds and the σ parameters for the Y substituent (a); and between the $E'_{1/2}$ values for the $NO_2C_6H_4N_2X$ diazo compounds and the $\sigma_{N=NX}$ parameters (b).

(ArN = NH) which undergo further homolytic breakdown [13]. It can be assumed that this breakdown first leads to the formation of AR of these ethers, which are then carried through the unstable aryldiimine AR to the AR of the corresponding ArH. These last were detected in the ESR spectra obtained during the interaction of compound (VI) with alkalis.

The electrochemical reduction of the sulfur-containing aryldiazo compounds (VII)-(IX) proceeds through various sequential reactions. In contrast to compound (VI), these reactions are so rapid that it was impossible to record the ESR spectra of the primary anion-radicals. The secondary products included the nitrobenzene AR, and other compounds which were difficult to identify through the ESR spectra.

The ESR spectrum of the nitrobenzene AR was also recorded in the interaction of compounds (VII) and (VIII) with alkalis in DMSO solution, and in electrochemical generation at higher reduction wave potentials. Transfer of even the first electron from the cathode to compound (IX) leads to rupture of the C—N bond with formation of the nitrobenzene anion-radical. There is nothing unusual in this behavior of the p-nitrophenyldiazothiophenyl ether, since the aryldiazo sulfides are known to be rather unstable [14]. It has been suggested that breakdown of the ArN_2SR diazo sulfides proceeds through a two-step mechanism [14], an ArN=NX compound being formed and subsequently converted to the corresponding ArH. It seems quite likely that the electrochemical reduction of compound (IX) also takes place stepwise.

The data suggest the following scheme for the electroreduction of the various compounds studied here:

$$\begin{tikzcd}
ArN{=}NX + e^- \arrow[r] & {[ArN{=}N{-}X]^{\dot{-}}} \arrow[r, "-N_2"] \arrow[d, "-X^-"'] & {[ArX]^{\dot{-}}} \\
& {[ArN{=}N]^{\cdot}} \arrow[r, "-N_2"] & Ar^{\cdot} \arrow[r] & ArH \arrow[r, "e"] & {[ArH]^{\dot{-}}}
\end{tikzcd}$$

Thus the direction of the sequential reactions, and the stability of the primary AR, both depend on the nature of the X fragment. The diazocyanides and triazene can be broken down only with difficulty, and their AR are stable. The ease of elimination of a N_2 molecule increases in going from compound (IX) to compound (VII) [14], and the AR stability falls off rapidly.

Comparison of the ESR spectra of anion-radicals generated electrochemically with the ESR spectra of the paramagnetic particles resulting from the action of nucleophiles [1] shows that chemical reaction also involves a one-electron transfer from the nucleophile, the result being that the same products are obtained from chemical transfer on the one hand, and from electrochemical transfer, on the other. Thus the ESR spectra show that the interaction of a nucleophile with compound (I) in aprotic dipolar media leads to the formation of the corresponding anion-radical, the interaction of HO^- with compound (V) in DMSO solution leads to the formation of the 4,4'-dinitrobiphenyl anion-radical, and the interaction of HO^- with compounds (VII)-(IX) in DMSO solution leads to the formation of the nitrobenzene anion-radical, all of which shows that the nucleophile is capable of reducing the product nitrobenzene through one-electron transfer.

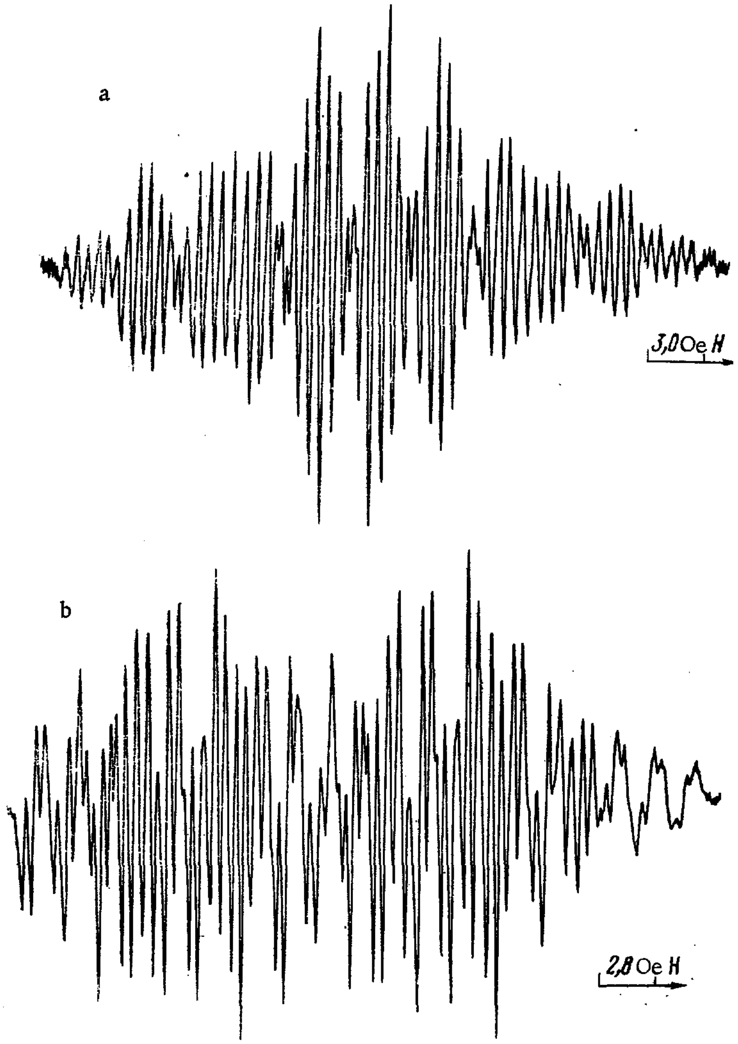

Fig. 2. ESR spectra of the anion-radical of compounds (II) (a) and (VI) (b) obtained under electrochemical generation.

Thus the data obtained here indicate that the scheme proposed for the one-electron reduction of the arylazo compounds can be extended to the reactions of the p-nitrophenyldiazo compounds with nucleophiles.

CONCLUSIONS

1. A study has been made of the electrochemical reduction of diazo compounds in aprotic media, and of chemical reactions accompanied by transfer of an electron to a molecule.

2. The formation of primary and secondary anion-radicals has been demonstrated, the structures of these radicals were determined, and a study was made of the delocalization of the unpaired electron.

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A STUDY OF THE ELECTRONIC STRUCTURES OF POLYFLUOROAROMATIC COMPOUNDS OF DIVALENT SULFUR BY X-RAY FLUORESCENCE SPECTROSCOPY

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The introduction of fluorine into the molecule frequently leads to a marked alteration in the reactivity and physical and chemical properties. An understanding of these effects requires extended study of the electronic structures of various compounds by spectral methods and by the computational methods of quantum chemistry. We have used x-ray fluorescence spectroscopy to study the structures of the 4,4'-disubstituted decafluorodiphenyl sulfides [1]. By directly following the changes in the π-electron structure of the S atom in these compounds it has been possible to obtain a better understanding of the mechanism of intramolecular interaction in the polyfluorinated diaryl sulfides.

The present work was an x-ray spectroscopic study of the electronic structure of the C_6F_5SX polyfluoroaromatic compounds of divalent sulfur, and the dependence of this structure on the X substituent at the sulfur atom. The effect of the introduction of F atoms into the benzene ring on the electronic structure of the diaryl sulfides can be seen from the SK_β-fluorescence spectra of H_2S, $(CH_3)_2S$, $(C_6H_5)_2S$, and decafluorodiphenyl sulfide shown in Fig. 1. The strong, short-wave A maxima appearing in the spectra of H_2S and $(CH_3)_2S$ arise from electron transfer from the unshared pair level to the 1 s level of the S atom, the long-wave C and D maxima in these spectra from transitions from the σ-bond levels [2, 3]. Thus the spectra of these two compounds indicate an absence of π interaction between the S atom and its environment. The A maximum is much wider and weaker in the spectrum of $(C_6H_5)_2S$. The indication here is that π conjugation is established between the 3p AO of the sulfur atom and the π system of the benzene ring, the result being that the nonbonding levels, which are almost completely filled with 3p (S) electrons in H_2S and $(CH_3)_2S$, split into a whole series of sublevels. The SK_β spectrum of $(C_6F_5)_2S$ is essentially the same as the spectrum for $(CH_3)_2S$. From this it can be concluded that the F atom exerts a saturated π-donor effect which tends to suppress conjugation of the 3p orbital of S with the π-electron system of the benzene ring.

Since the immediate and intermediate environment of the S atom remains unchanged in passing through the 4,4'-disubstituted decafluorodiphenyl sulfides, alterations in the spectra of these compounds can be assumed to arise from π-conjugation effects. In the C_6F_5SX compounds, the substituent affects the electronic structure of the S atom through the σ-level system and π conjugation. This hinders interpreting the x-ray spectral data and forces one

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