ELECTROCHEMICALLY INITIATED FRAGMENTATION REACTION

OF 9,9'-DINITRO-9,9',10,10'-TETRAHYDRO-10,10'-BIANTHRYL

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A mechanism for the electroreduction of 9,9'-dinitro-9,9',10,10'tetrahydro-10,10'bianthryl in DMF, which results in the formation of anthracene and 9-nitroanthracene has been proposed on the basis of data from polarography, cyclic voltammetry, and electrolysis at a controlled potential.

It is known [1] that the central C-C bond in hexaphenylethane and tetraphenylethane is exceptionally weak and readily undergoes photolysis and thermolysis. 9,9'-Dinitro-9,9',10, 10'-tetrahydro-10,10'-bianthryl (I), whose electrolysis was previously described by us in [2], contains a structural fragment similar to tetraphenylethane. For this reason, the $C_{10}-C_{10}'$, bond should apparently be expected to display an increased tendency to undergo dissociation.

It was found that the moderate heating of I in DMF is accompanied by its decomposition and the formation of anthracene (II) and 9-nitroanthracene (III). For this reason, it would be of interest to ascertain whether the presence of an extra electron in the lowest antibonding molecular orbital of I would also initiate cleavage of the $C_{10}-C_{10}$ ' bond. Therefore, we investigated the electroreduction of I in DMF containing a tetrabutylammonium salt as the supporting electrolyte.

EXPERIMENTAL

The polarographic investigations were carried out on a GWP-673 polarograph (East Germany). The polarograms were recorded with the use of a dropping mercury electrode (d.m.e.) with a scraper for the forced detachment of the drops (the flow rate of mercury was $m = 0.712 \text{ mg} \cdot \text{sec}^{-1}$, and the dropping period was t = 0.34 sec). The potentials were measured with the aid of a three-electrode system relative to a saturated aqueous calomel electrode (s.c.e.). The latter was connected to the solution through a bridge with a porous ceramic membrane filled with the supporting electrode.

The cyclic voltammograms were recorded on a PO-3 oscillograph polarograph with the use of a slow dropping mercury (m = $0.23 \text{ mg} \cdot \text{sec}^{-1}$, t = 14 sec) and a glassy carbon electrode with a total surface s = $2.27 \cdot 10^{-2} \text{ cm}^2$. The curves were recorded with the aid of a loop oscillograph.

The investigation was carried out in solutions of DMF in the presence of tetrabutylammonium salts at $25 \pm 0.1^{\circ}$ C. The solutions were deaerated by argon. The DMF used was purified as described in [3]. The water content in the purified solvent (0.05-0.06%) was determined by a titration with the use of the Fischer reagent. Bu₄NBr was recrystallized from an acetone-ether mixture and dried at 80°C and a reduced pressure (3-4 mm Hg).

The electrolysis was carried out under potentiostatic conditions at a potential of -1.5 V relative to an s.c.e. The mercury pool (11 cm²) served as the cathode, and a platinum grid served as the anode. The anodic compartment of the cell was separated from the cathodic compartment by a ceramic membrane. A solution of 20 mg of I in 20 ml of DMF containing 0.05 M Bu₄NBr was prepared. The changes in the concentration of the depolarizer during the electrolysis process were monitored polarographically. After the exhaustive electroreduction of I, 10 ml of the catholyte was mixed in an argon atmosphere with an aqueous solution of acetic acid (1%). The weight of the precipitate formed was 6.5 mg (65%) after filtration and drying The composition of the electrolysis products was established on the basis of a comparison of the

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Fig. 1. Polarograms of II (1), I (2), and III (3) in DMF on a background of 0.02 M Bu_4NBr . The concentration of the depolarizer was 10^{-3} M.

Fig. 2. Cyclic voltammograms of I (2.2 mmoles/liter, a) and III (0.3 mmoles/liter, b) on a d.m.e. in DMF containing 0.02 M Bu_4NC10_4 for a rate of scanning of the potential equal to 1 V·sec⁻¹.

PMR spectrum of the mixture with the spectra of known samples of the compounds. Adamantane served as a standard for calculating the yield of the products on the basis of the PMR spectrum. Nitroanthracene (39%), anthracene (32%), anthraquinone (9%), and I (20%) were discovered in the mixture after the electroreduction of I.

The thermal stability of I was determined by heating a DMF solution of this compound in a water bath. The mixture was analyzed by TLC on Silufol UV-254; the eluents were ether and hexane. Compounds II and III were discovered in the mixture after the solution of I was heated.

RESULTS AND DISCUSSION

The polarogram of I (Fig. 1) displays two waves (the values of $E_1/_2$ are equal to -1.36 and -1.96 V, respectively), which correspond to the two cathode peaks (Fig. 2) on the cyclic voltammograms. It is noteworthy that, as is seen from Fig. 1, the value of $E_1/_2$ for the second wave recorded during the electroreduction of I is close to the value of $E_1/_2$ of the first wave observed for II (-1.95 V). The potentials of the cathodic (C-2) and anodic (A-1) peaks on the cyclic voltammograms of I (Fig. 2a) also practically coincide with the potentials of the peaks corresponding to the reduction of II to its radical anion and the oxidation of the latter (Fig. 2b). The fit just indicated allows us to postulate that one of the products of the first step of the electroreduction of I is II.

One special feature of the polarographic behavior of I is the fact that the current begins to decrease when a potential on the order of -2.5 V is achieved (see Fig. 1). This phenomenon cannot be caused by the shortening of the dropping period of the dropping mercury electrode, since the polarograms of II and III obtained under similar conditions do not have any anomalies in this range of potentials. The available data are insufficient for drawing a final conclusion regarding the factors causing the drop in the current as the cathodic potential is increased. However, it is interesting that the drop just indicated occurs in the range of the potential corresponding to the ascent on the polarographic wave of II, i.e., under conditions corresponding to the generation of the dianions of this compound. In view of the high basicity of the dianion of II [4], it should be expected that it will be postulated by I as it diffuses to the electrode. The proton-donor properties of I are caused by the presence of the H_9 and $H_{9'}$ atoms, which are activated of the electron-acceptor substituents, in the molecule. The acid character of these atoms is confirmed by the fact that, according to the data from UV spectroscopy, the introduction of bases into a solution of I results in the formation of the corresponding anion [5]. Since the products of the acid-base reaction under consideration are electrochemically inactive, the resultant decrease in the concentration of I in the region next to the electrode should cause a decrease in the current as the number of dianions of II formed on the electrode increases, i.e., as the absolute value of the potential increases,

Thus, the data from polarography and cyclic voltammetry attest to the formation of II at potentials corresponding to the first step in the reduction of I.

The most probable path for the formation of II (in analogy to the behavior of σ complexes [6]) is the elimination of a nitrite ion from anion IV [Eq. (1)],



which, in turn is one of the possible products of the dissociation of the radical anion of I (reaction 2)

The extremely low stability of the radical anion of II is evidenced by the fact that the cyclic voltammograms of I (see Fig. 2a) do not contain an anodic peak corresponding to the oxidation of this radical anion over the entire range of scanning rates of the potential investigated (up to $20 \text{ V} \cdot \text{sec}^{-1}$). The formation of IV as a result of reduction of the π radical V at the potentials of the first polarographic wave of I [reaction (3)] likewise cannot be ruled out:

$$(V) \stackrel{+c}{-} (IV) \tag{3}$$

However, the foregoing statements do not allow us to conclude that the only product of the electrochemical decomposition of I is II. In particular, a reaction scheme including steps 1-3 presupposes that the overall process taking place at potentials corresponding to the limiting current of the first wave of the reduction of I should be described by Eq. (4).

$$(I) \xrightarrow{+2\vec{o}}_{-2NO_{2}^{-}} 2(II)$$

$$(4)$$

In this case the effective number of electrons participating in the reduction process at the potentials of the first (n_1) and second (n_2) polarographic waves of I should coincide and should be equal to 2. The latter statement is apparently valid under the conditions of the cyclic voltammetry of I, where the heights of the first and second cathodic peaks are close (see Fig. 2a). The slightly lower height of the first cathodic peak $(n_1 = 1.73)$ in comparison to the height of the second cathodic peak $(n_2 = 2.04)$ is probably due to the fact that values of n were calculated under the assumption that the diffusion coefficients of I and II were assumed to be equal to $10^{-5} \text{ m}^2 \cdot \text{sec}^{-1}$, although the value for I should be appreciably lower due to the large geometric dimensions of this compound. At the same time, as is seen from Fig. 1, the limiting current (ilim) of the first polarographic wave of I is approximately 1.4 times higher than that of the second wave. In addition, the semilogarithmic plot of the dependence of log i/(ilim - i) on E for this wave has a clearly nonlinear character, which indicates that the current recorded at these potentials is the sum of the currents of two polarographic waves with similar values of $E_1/_2$. Therefore, a secondary reaction, which competes with the formation of II and produces products capable of being reduced at potentials corresponding to the first wave of I, begins to be manifested in a time interval corresponding to the polarographic method. Taking into account the formation of III upon the thermolysis of I and the closeness of the values of $E_1/2$ for the first wave of I and the second wave of III, we may postulate that under the conditions of polarography the decomposition of the radical anion of I results in the formation of a certain quantity of III along with II. The most probable reaction resulting in the formation of III is aromatization of radical V [Eq. (5)]

$$(V) \xrightarrow{-H} (III)$$
(5)

which competes with rection (3). A theoretical analysis of a reaction scheme which includes the competition between the electroreduction of the conversion product of the radical anion and the first-order bulk reaction [7] involving this product shows that the contribution of this reaction to the overall mechanism of the process does, in fact, increase as the time of electrolysis on the d.m.e. increases. Thus, the available experimental data allow us to describe the mechanism of the process at the positions of the first wave corresponding to the reduction of I as a set of steps resulting in the formation of the radical anion and reactions (1)-(3) and (5).

In order to directly prove the structure of the decomposition products of the radical anion of I, we carried out the preparative electroreduction of I at a controlled potential equal to -1.5 V. The content of anthracene in the catholyte determined after electrolysis on the basis of the polarographic data corresponds to the yield determined on the basis of the PMR spectrum, and this value is significantly lower than the value which might have been expected on the basis of reaction (4). The quantity of electricity utilized for the reduction of I corresponds to 1.82 electrons per molecule of the depolarizer, which is consistent with the reaction scheme proposed above. The catholyte obtained after acidification contains approximately equal quantities of II and III. The formation of these compounds should be regarded as a weighty argument in favor of the occurrence of reactions (1), (2), and (5). The appearance of I as a result of acidification of the catholyte is attributed to the fact that the catholyte contained its dianion, which, as was previously shown in [2], forms with a high yield upon the electroreduction of III.

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