INVESTIGATION OF THE DIMERIZATION OF ACRIDINE RADICAL ANIONS BY ELECTROCHEMICAL METHODS

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The electrochemical reduction of acridine (dimethylformamide (DMF) and Bu_4NClO_4) was investigated by differential cyclic voltammetry and controlled-potential electrolysis. The experimental data (dimerization rate constant and yield of the 9,9' dimer) agreed with the theoretically calculated ones.

The results of theoretical and experimental investigations [1-7] show that in aprotic media the most characteristic reaction of radical anions of aromatic compounds is dimerization with the formation of dimeric dianions ($A_2{}^{2-}$), the subsequent reaction of which with proton donors (DN) affords the corresponding tetrahydro derivatives

$$2A^{\dot{-}} \xrightarrow{k} A_2{}^{2-} \xrightarrow{DN} A_2H_2 \qquad (1)$$

The tetrahydro dimers A_2H_2 were obtained in the electrochemical reduction of 9-nitro [4], 9-acetyl [6], and 9-cyano derivatives [7] of anthracene.

According to the theory of [1-3], the high rate and selectivity of the dimerization of these compounds are due to the essential localization of an unpaired electron on the C^{10} atom of the aromatic ring. Because the theoretical model of [1-3] was not used previously for description of the reactivity of radical anions of heteroaromatic compounds, it seemed of interest to verify experimentally the correctness of the predictions, made on its basis, of the rate and selectivity of dimerization involving radical anions of acridine (I). The results of a calculation that we carried out by the method of complete neglect of differential overlap (CNDO/2) showed that the value of the square of the amplitude of the wave function (c^2) of the boundary molecular orbital on the C^{10} atom in radical anions of 9-substituted anthracenes fluctuates in the range from 0.2 to 0.22. In radical anions of (I), the value of c^2 corresponding to the C^9 atom is also rather great and is equal to 0.208. Using the approach described in [1-3] and the parameters of the electronic structure of (I) obtained as a result of the calculation, we evaluated the theoretical values of the dimerization rate constant (log k = 3.1) and the yield of the 9,9' dimer (∿80%). To compare the calculated and experimental data, we used differential cyclic voltammetry (DCVA) and controlled-potential electrolysis (CPE) to investigate the electrochemical reduction of (I) in DMF solutions containing 0.1 M Bu_4NClO_4 as a supporting electrolyte at the radical-anion generation potential.

RESULTS AND DISCUSSION

The DCVA curves of (I) in DMF solutions contained anodic and cathodic peaks, whose correlation R' depended on the concentration of the depolarizer C and the potential-scanning rate v. The value of R' increased monotonically with increasing parameter $\chi = CRT/Fv$. The ranges of the values of C and v that were used in the present paper corresponded to the change of log χ from 1.9 to 4.0 $V \cdot sec^{-1} \cdot liter \cdot mole^{-1}$, and the recorded values of R' were in the range 0.5-1.05. An additional variable parameter was the potential of change of direction of the electrode polarization. The absence of minimums characteristic of reversible radical-anion dimerization processes on the curve of the relation of R' to log χ (see review [8]) makes it possible to ignore the dissociation of the dimeric dianion. Therefore, we carried out the calculation of the rate constants of dimerization according to the experimental values of R' using the theoretical curves of processes with an irreversible second-order reaction following the charge-transfer stage. The obtained experimental value of

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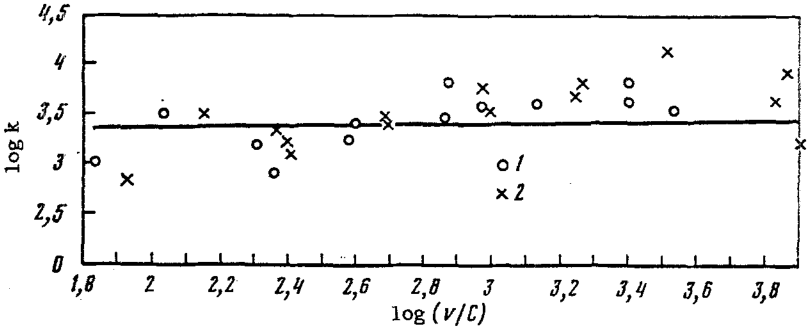

Fig. 1. Experimental values of rate constant of dimerization of acridine radical anions in DMF containing 0.1 M Bu_4NClO_4 determined according to ratio of anodic and cathodic peaks on DCVA curves for different values of potential-scanning rate (v) and depolarizer concentration (C): 1) 3.8 mmoles/liter; 2) 1.8 mmoles/liter.

log k = 3.3 ± 0.4 (liters·mole^{-1}·sec^{-1}) is rather close to the theoretical value given above. This result can be considered as an argument in favor of the applicability of the theoretical model proposed in [1-3] not only to unsaturated and aromatic systems, but also to radical anions of heteroaromatic compounds.

It is known that the addition of small amounts of water to an aprotic solvent is accompanied by an increase of the dimerization rate of radical anions of olefins and aromatic compounds (see, e.g., the bibliography in [9]). We also observed an analogous phenomenon for (I). In particular, the addition of 10 vol. % of water to the solution led to an approximately 1.5-2.0-fold decrease of R' at v = 1-4 V·sec^{-1} (log k = 4.0 ± 0.1). This effect cannot be explained by protonation of radical anions (an electrochemical-cell-type process) because in this case one would expect an increase of the total number of electrons transferred to the molecule of (I) during electrochemical reduction. However, the value of the limiting current in the polarograms of acridine practically did not depend (taking into account the viscosity change of the solution) on the water concentration to 0.35 M. Nevertheless, direct proof of the absence of protonation of radical anions of (I) by water in this case can be obtained only as a result of carrying out preparative CPE. In addition, recovery of the corresponding products would serve as proof of the correctness of assigning the measured rate constants to the formation of 9,9' dimers.

In the beginning of the CPE, the current of the electrochemical reduction of (I) changed only little with time, but by the end of the electrolysis it decreased, with practically complete exhaustion of the depolarizer occurring after passage of 1 F/mole according to the polarographic monitoring. Water was added to the catholyte after termination of electrolysis without oxygen access, and the whole was extracted with ether. Chromatography of the extract on SiO_2 resulted in the recovery of (I) (10-15%) and dihydroacridine (II) (50-60%), and the spectral characteristics of the latter corresponded to those described in [10]. The recovery of a significant amount of (I) with its complete exhaustion during electrolysis suggested that the dimeric intermediates decomposed during treatment of the solutions after electrolysis. An analysis of the PMR spectra of the extracts showed that the ratio of (II) to (I) fluctuated in various runs from 3 to 1, and it should be noted that in the presence of oxygen in solution (II) was oxidized to (I).

The electrochemical reduction of (I) in DMF containing 7-10% of water was accompanied by the formation of a precipitate during electrolysis. The filtered precipitate (60-70%) dissolved only in CF_3COOH. An analysis of the PMR, IR, and mass spectra and the agreement of these data with those of [10] made it possible to assign it the structure of the dimer 9,9'-10,10'-tetrahydro-9,9'-biacridyl. After separation of the precipitate, the filtrate contained (II) and (I) (1:1). Because in alkaline solutions the tetrahydro dimer was oxidized in the presence of oxygen of air to (I), its actual yield during electrolysis was probably higher than 70%. When CPE was carried out in DMF without water additions, the yield of the dimer did not exceed 10%.

Thus, the results of CPE showed that C^9 atoms acted as reaction centers in the dimerization of radical anions of (I) and, therefore, the closeness of the experimental value of k to the theoretically calculated one using values of the spin density on these atoms was not random.

EXPERIMENTAL

Current—voltage measurements were carried out using a PO-512 oscillographic polarograph with a three-electrode circuit. The freely dropping mercury electrode had the characteristics $m = 0.218\ \mathrm{mg \cdot sec^{-1}}$ and $t = 15$ sec. The setup for automated recording and treatment of the current—voltage curves also contained an F-4222 analog-to-digital converter, a device for communication with the components, and an Élektronika DZ/28 computer with standard peripheral equipment. A TsAP-200-001 digital-to-analog converter, an S1-48B oscillograph, and an N-306 graph plotter were used for imaging of the graphic data.

All measurements were carried out in a "first-drop" regime. The value of the uncompensated resistance of the solution, determined according to the slope of the curve of the relation of the peak potential on the current—voltage patterns of $KClO_4$ to the value of the current at this potential was used for numerical correction of the shape of the DCVA curves. In some cases (low values of v), corrections were introduced into the growth of the mercury drop. Numerical differentiation was carried out according to a five-point equation.

The calculation of the theoretical curves of the relation of R' to the dimensionless parameter $\chi = \log(CRTk/Fv)$ was carried out according to an explicit finite-difference scheme. As an example, Fig. 1 shows the values of k obtained for various values of v in solutions containing 1.8 and 3.8 mmoles of acridine.

The electronic-structure parameters of (I) were calculated by the CNDO/2 method in a variant of the unrestricted Hartree—Fock method, with (I) being obtained from acridine hydrochloride by the method of [11]. The purification of DMF and the supporting-electrolyte salt and also the conditions for preparative electrolysis are given in [6]. After termination of electrolysis (P-5848 potentiostat, Hg cathode ($\sim$20 cm^2), Pt-gauze anode, saturated calomel reference electrode, and $E = -1.9$ V) and separation of the anolyte, neutral or weakly acidified water was added to the catholyte, the precipitate was filtered after 2 h, the filtrate was extracted with ether and dried over $MgSO_4$, and the solvent was removed. Column chromatography was carried out on SiO_2 with a mixture of hexane and $CHCl_3$ (from 20 to 50% $CHCl_3$).

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