Thus, comparison of our data with published data shows that heterophase anion exchange, the main stage of IPC and regarded as a special catalytic phenomenon, is an extremely complex process which needs careful investigation; the observed "exchange equilibrium constants" (selectivity constants) are effective quantities which depend on the type of species involved in the exchange and on the composition and type of organic and aqueous phases.

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EXPERIMENTAL STUDY OF DIMERIZATION OF RADICAL ANIONS OF AROMATIC CARBONYL COMPOUNDS

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UDC 543.257.5:543.253:541.127:
542.953:541.515-128.2:
547.57

The rate constants of dimerization (k_1) of radical anions of acetophenone, 1-acetylnaphthalene, 9-acetylanthracene, 9-formylanthracene, and anthracene in DMF containing 0.02 M tetrabutylammonium bromide were determined by differential cyclic voltammetry. It was shown that the values of k_1 of the radical anions investigated are correlated with the values of the boundary electron density on the reaction sites, which in turn increase symbatically with an increase in the size of the aryl fragment or on incorporation of electron-acceptor functional groups in the anthracene nucleus.

According to the hypothetical theoretical model in [1, 2], the tendency of radical anions (RA) to form dimeric products according to the reaction

$$A^{\overline{\cdot}} + A^{\overline{\cdot}} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A_2^{=} \qquad (1)$$

is determined by the structure of the boundary molecular orbital (BO) of these particles. It has been shown that reaction (1) should be characteristic of aromatic compounds, and the values of $\log k_1$ should change linearly with an increase in the unpaired electron density (c^2) on the reaction site.

It was previously shown in [3] for RA of mononitro derivatives of aromatic compounds that the change in the experimentally determined k_1 and the values of c^2, which exhibit a tendency to increase as the size of the aryl fragment increases, is actually symbatic. The results of quantum chemical calculations indicate that this tendency persists in going from nitro to carbonyl compounds. To verify this conclusion, we investigated the kinetics of reactions of cathode-generated RA of aromatic carbonyl compounds: acetophenone (I), 1-acetyl-

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N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1777-1782, August, 1991. Original article submitted July 19, 1990.

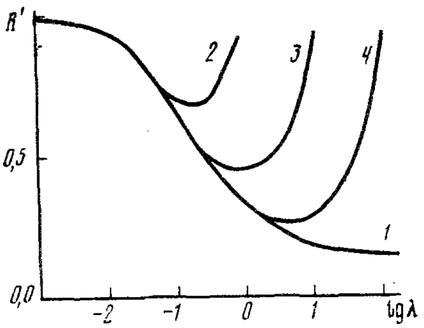


Fig. 1

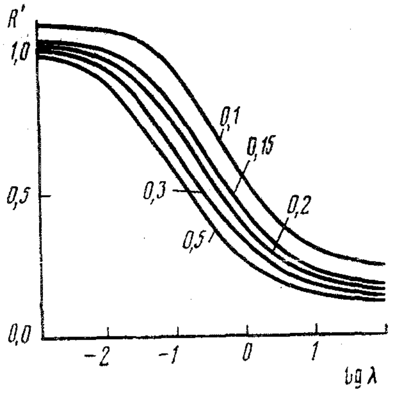


Fig. 2

Fig. 1. Theoretical curves of R' as a function of log λ ($\Delta = -0.3$ V) for different values of the equilibrium constant $K = k_{-1}/k_1$: 1) 0.0; 2) 0.1; 3) 0.01; 4) 0.001.

Fig. 2. Theoretical curves of R'—λ. The numbers above the curves correspond to the values of Δ used in the calculations of k_1.

TABLE 1. Results of Studying the First Reduction Wave of Aromatic Carbonyl Compounds (I)-(V) by Polarography, i-t Curves, and Voltammetry ($v = 0.5$ V·sec^{-1})

Compound	Polarography		i-t Curves		CVA	
	$E_{1/2}$	n	α	n	E_p, V	n
(I)	1,98	1,09			2,00	1,16
(II)	1,71	1,01			1,773	1,07
(III)	1;55	0,93	0,201±0,015	1,11	1,541	0,90
(IV)	1,14	1,00	0,202±0,004	0,96	1,141	0,97
(V)	1,92	1,07	0,199±0,012	0,95	1,934	1,01

TABLE 2. Results of Studying the Kinetics of Dimerization of Compounds (I)-(V) by DCVA

Compound	Range of change in log (v/C), V·sec^{-1}·M^{-1}·liter	Experimental values of R'	log k_1, M^{-1}·sec^{-1}
(I)	2,2–4,9	0,45–1,10	3,1±0,2
(II)	1,5–3,9	0,45–1,10	2,9±0,3
(III)	2,5–5,1	0,22–0,95	4,6±0,3
(IV)	2,3–4,7	0,22–0,60	5,3±0,2
(V)	2,2–3,4	0,68–1,06	2,8±0,4

naphthalene (II), 9-acetylanthracene (III), and 9-formylanthracene (IV). In addition, we attempted to determine k_1 for RA of anthracene (V) to evaluate the effect of incorporation of a function group in the molecule of an aromatic hydrocarbon.

DMF containing 0.02 M tetrabutylammonium bromide was selected as the base electrolyte, since this allowed us to neglect the change in the solvation energy when the reactants converted and complexation processes [1] and the proton-donor activity of the solvent [4, 5] in interpreting the experimental results.

EXPERIMENTAL

The studies were conducted with methods of cyclic voltammetry (CVA), differential cyclic voltammetry (DCVA), and classic polarography, and by analysis of the current—time functions (Table 1) with the electrolytic reduction (ER) wave limiting current potential. The instruments, electrodes, and methods used in the study are in principle similar to those described in [3].

The qualitative conclusions concerning the mechanism of electrode reactions were formed according to [6] based on the ratio of the heights of the anode (i_a) and cathode (i_k) peaks on the CVA curves (R) as a function of the rate of potential superposition (v) and depolarizer concentration (C). The ratio of the anode (i_a') and cathode (i_k') peak heights on the DCVA curves was used for the quantitative estimation of the rate constants of dimerization of RA: $R' = i_a'/i_k'$ [7]. In contrast to the traditional method of processing the experimental data [7], digital differentiation was used instead of differentiation of the analog signal with an operational amplifier. The values of R' were determined for each compound with several values of C in a relatively wide range of v, and the region of the change in the ratio v/C is shown in Table 2. The value of $\Delta = E_k - E_{1/2}$, where E_k is the potential of the change in the direction of polarization, was used as an additional variable parameter. The numerical values of k_1 were determined with the theoretical curve of $R'-\lambda$ ($\lambda = RTk_1C/Fv$), using the experimental values of R'. It should be noted that despite the differences in the method of determination, the value of k_1 obtained for (IV) is relatively close to the value determined in [8]. The DISPUT software package for solving systems of differential equations by numerical modeling created by one of us, which describes reaction schemes including stages of heterogeneous electron transfer and electrode chemical reactions, was used for calculating the theoretical curves of $R'-\lambda$. A number of service subroutines was introduced for using it in the present study.

Some of the theoretical curves of $R'-\lambda$ calculated with a constant value of $\Delta = 0.3$ V and different equilibrium constants ($K = k_1/k_{-1}$) of reaction (1) are presented in Fig. 1. Analogous curves obtained with different values of Δ for the irreversible ($k_{-1} = 0$) dimerization reaction are shown in Fig. 2.

The values of $\log\lambda$ from which k_1 were calculated were determined from the experimental values of R' (with the corresponding value of Δ) with the theoretical graphs (of the type shown in Fig. 1). Figure 1 (curve 1) shows that the theoretical R' as a function of λ for the irreversible process monotonically decrease with an increase in λ, while these functions have a minimum as in the case of the reversible process. However, the initial segments of the graphs (for higher values of R') coincide in both cases, and the presence of the reversible dissociation reaction (1) of the dimeric dianion in this region cannot affect the numerical value of k_1. The parameters of the electronic structure of the RA were calculated with the CNDO/2 method.

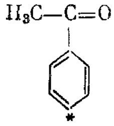
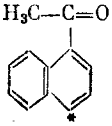
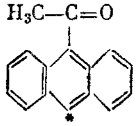
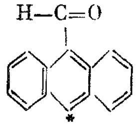
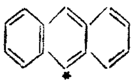
RESULTS AND DISCUSSION

The ER of compounds (I)-(V) in DMF against the background of tetrabutylammonium salts occurs in two successive stages. Since the purpose of the present study was to investigate the chemical behavior of the corresponding RA, only the data concerning the first stage of the process will subsequently be discussed. The parameters characterizing this stage for compounds (I)-(V) are reported in Table 1, which shows that the apparent number of electrons (n) participating in the electrode process, determined from the values of the limiting current (i_{lim}) of the first polarographic waves, the values of the instantaneous current for t = 1 sec on the i–t curves, and the heights of the cathode peaks on the CVA curves, is close to 1. In addition, anode peaks corresponding to oxidation of the product formed in the cathode process are observed on the anode branch of the CVA curves of (I)-(V). This suggests that transfer of an electron to the molecule of the depolarizer with the formation of the corresponding RA is the first stage of ER of all compounds studied.

The results obtained in studying ER of compounds (I)-(V) by DCVA are reported in Table 2. The R' and R experimentally determined by DCVA and CVA for low rates of potential application are lower than the theoretically predicted values [6, 7]. For example, for $\Delta = 0.3$, the experimentally determined R for compounds (I)-(V) for $v = 0.5\ V\cdot sec^{-1}$ are, respectively, 0.21 ($C = 0.35\cdot10^{-3}$ M); 0.53 ($C = 0.97\cdot10^{-3}$ M); 0.19 ($C = 1.5\cdot10^{-3}$ M); 0.20 ($C = 2.0\cdot10^{-3}$ M); 0.57 ($C = 0.60\cdot10^{-3}$ M), while the theoretical value is R = 0.755 [6]. Since the experimental values of R and R' for all compounds studied exhibit a tendency to decrease with an increase in C, we can hypothesize that the RA formed in the cathode process enter into a second-order reaction. Dimerization (1), disproportionation (2), and protonation (3) by impurities present in the solution in concentrations commensurate with the concentration of RA are possible second-order reactions in this case:

$$A^{\overline{\cdot}} + A^{\overline{\cdot}} = A^{=} + A \qquad (2)$$

TABLE 3. Values of c^2 on the Reaction Sites of Radical Anions of I-V

Compound	Maximum value	
	on the carbon of the "head" polar group	on the aromatic fragment of the "tail" molecule
 (I)	0,169	0,192
 (II)	0,070	0,194
 (III)	0,033	0,216
 (IV)	0,043	0,219
 (V)	0,188	0,188

$$A^{\overline{\cdot}} \xrightarrow{DH} AH^{\cdot}. \tag{3}$$

The last two reactions should result in the formation of electrochemically active products (depolarizer regenerated according to (2) or the easily reducible free radical $AH^{\cdot}$ [9]) and consequently values of n greater than 1, which is not observed experimentally (see Table 1).

We nevertheless believed it necessary to obtain additional data to exclude the possible competition of these processes with reaction (1). We selected the method of analysis of the shape of the current–time curves for this purpose, since the formation of electrochemically active products as a result of conversion of RA should be accompanied by a significant increase in exponent a in Eq. (1') even when n is only insignificantly greater than one [10]

$$i_{\mathrm{lim}}/i_{\mathrm{dif}} = nt^{a-a_{\mathrm{dif}}}\,{}^{\dagger} \tag{1'}$$

We only determined parameters n and a with the limiting current potentials of the first waves of (III)-(V), since their RA should exhibit a greater tendency to disproportionate than RA of (I) and (II) due to the high degree of delocalization of the electron density in the corresponding dianions $A^{=}$. In addition, RA of (V), which have a higher BMO, should exhibit the greatest basicity [11]. As Table 1 shows, the values of the parameters in Eq. (1') correspond to the theoretical value characteristic of a process not complicated by subsequent reactions resulting in the formation of electrochemically active products within the limits of the experimental error [10]. In examining the results obtained we can probably conclude that reaction (1) is the basic pathway of conversion of the RA of (I)-(V) generated on the cathode and that reactions (2) and (3) can be neglected in these conditions.

The value of R' for all compounds studied monotonically decreases with an increase in λ. The lack of a minimum on the experimental curve of R' as a function of λ indicates [12] that the rate of dissociation of dimeric dianions (even if it differs from zero) in the region of the values of C and v investigated should not affect the values of k_1 determined with the theoretical curves for irreversible reaction (1).

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†The values relating to a diffusion process are indicated by "dif" here.

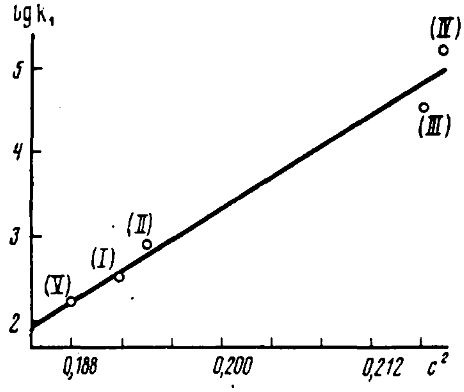

Fig. 3. Graph of the experimental values of log k_1 vs c^2.

Table 2 also shows that k_1 for RA of carbonyl derivatives of anthracene (III) and (IV) are approximately two orders of magnitude higher than for RA of (I) and (II), which have similar values of k_1, i.e., on the qualitative level, the situation is similar to the one observed in [3] for dimerization of RA of aromatic nitro compounds. At the same time, the changes in the values of c^2 and k_1 are not totally symbatic. For example, despite the fact that the density of the unpaired electron on the reaction site in RA of (II) is slightly higher (Table 3) than in RA of (I), the latter is characterized by a higher value of k_1 (see Table 2). This noncorrespondence is probably due to the fact that in contrast to (II) and (III), in the RA of (I) the values of the unpaired electron density on the C atoms of the carbonyl group and in the para position are close and consequently its reactions should take place with the participation of two reaction sites with similar rates. For this reason, a comparison of k_1 for RA of (I) with the values calculated for RA with consideration of the reaction site alone is only possible after the corresponding correction. This particularly refers to RA of (V), which have two identical reaction sites. Actually, according to the theory in [1], it is possible to obtain a linear correlation (Fig. 3) of $\log k_1 - c^2$ ($r = 0.977$) when the corrected values of k_1 are used for RA of (I) and (V). It should be noted that the standard deviation obtained (0.24) does not significantly exceed the error of the experimental determination of k_1.

The following conclusions can be drawn from the data in Table 2: 1) Incorporation of electron-acceptor functional groups in the anthracene molecule is accompanied by a sharp increase in the value of k_1, 2) the constant of dimerization of RA increases with an increase in the size of the aromatic system.

According to [1, 2], these effects should be attributed to the distribution of the electron density in the boundary orbital of the corresponding RA, and the values of $\log k_1$ should be linearly correlated with the value of c^2 on the reaction site (Table 3). The experimental values of $\log k_1$ of compounds (I)-(V) are actually a linear function of the value of c^2, calculated by the CNDO/2 method (Fig. 3). The position of the reaction site in the RA of compounds (I)-(V) determined from calculating the electronic structure of RA by the CNDO/2 method (see Table 3) is indicated by an asterisk. Note that the spin density of the RA in carbonyl derivatives do not have a maximum on the C atom of the C=O group, but on one of the C atoms in the aromatic nucleus. The formation of dimers of the "tail–tail" type should be the consequence of this. Actually, preparative reduction of (III) in DMF against the background of tetra salts will result in such a dimer with a yield of 70% [13]. In conclusion, we emphasize that our kinetic data are correlated with the theoretical data (see Fig. 3) and the results of preparative electrosynthesis.

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QUANTITATIVE EVALUATION OF THE EFFECT OF THE MEDIUM ON THE THERMODYNAMIC PARAMETERS OF CONFORMATIONAL TRANSITIONS OF SUBSTITUTED 1,3-DIOXANES IN SOLUTIONS AND GASES WITH PMR DATA

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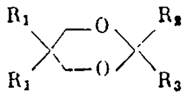
UDC 543.422.25:541.12.038:
536.7:547.841

It was shown that the reaction field model satisfactorily describes the thermodynamic parameters of conformational equilibrium of 2-acetyl-substituted 1,3-dioxanes both as a function of the properties of the solvent and the phase state of the compound studied. Quantitative agreement was obtained between the experimental and theoretical values.

The properties of the medium are one of the most important factors which determine conformational equilibrium. The theoretical and experimental aspects of considering it are discussed in detail in [1-3]. The basic difficulties which arise in interpreting the solvation effects are due to the paucity of experimental data obtained by direct methods, including the approximation of infinite dilution with the transition to the gas phase [3].

The effect of the dielectric properties of the solvent on the thermodynamic parameters of conformational equilibrium was quantitatively assessed based on PMR data with variation of the temperature in solutions and the gas phase of model compounds, substituted 1,3-dioxanes:



$R_1 = R_2 = H$, $R_3 = -C{\equiv}CH$(I); $R_1 = CH_3$, $R_2 = H$, $R_3 = -C{\equiv}CH$(II); $R_1 = R_2 = CH_3$ $R_3 = C_6H_5$(III).

These compounds were selected for the following reason. Two-component conformational chair-e ⇌chair-a equilibrium [2] with comparable fractions of the components takes place in compounds (I) and (II), and it is possible to observe both the average spectral parameters, and the spectra of the exchange components, and the physicochemical properties of compounds (I) and (II) allow conducting experiments in the gas phase. Compound (III) is used as the stereorigid spectral model.

Toluene-d_8, carbon disulfide, methylene chloride-d_2, acetone-d_6, methanol-d_4, and dimethylformamide-d_7 were used as the solvents.

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0568-5230/91/4008-1577$12.50