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Electroreduction of Benzalacetone in *N,N*-dimethylformamide

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The electrochemical reduction of benzalacetone (BA) has been studied at mercury cathodes in *N,N*-dimethylformamide solutions by the techniques of cyclic voltammetry and controlled potential coulometry. The radical anion (BA⁻) forms ion pairs with tetraethylammonium cations and then disappears in oligomerization processes. A tentative structure of the dimer BA — BA⁻ ... $(C_2H_5)_4N^+$ is suggested on the basis of quantum mechanical callations.

INTRODUCTION

Electrochemical dimerization of activated olefins has been the object of particularly active mechanistic studies. Most investigations in this field have been carried out in solvents of low proton activity such as acetonitrile and *N,N*-dimethylformamide (for review cf.[1-4] and corresponding references therein). It has been observed that under these conditions the discussed compounds undergo a radical — radical dimerization,[5] visibly accelerated by addition of water.[6] Although such a mechanism seems to be a rather common pathway of electrodimerization, some evidences exist that a radical — substrate coupling is also possible, particularly in aprotic media perfectly purified from electrophilic contaminations.[7]

The present report deals with the reduction of benzalacetone (BA) at mercury cathodes in *N,N*-dimethylformamide (DMF) solutions. The result of these investigations is the evidence that under experimental conditions the mechanism of the radical decay is profoundly affected by the concentration of the reactant.

EXPERIMENTAL

Cyclic voltammetric measurements were made in a three electrode system using a Radelkis OH 105 polarograph. For higher scan rates, above 100 mV s⁻¹, voltammograms were obtained using a measuring system constructed from an EP-20A potentiostat (ELPAN, Poland) and a Hewlett-Packard 202A function generator. Cyclic voltammetric curves were recorded on a Radelkis recorder or on DT 516A oscilloscope (KABID, Poland).

The working electrode was a hanging mercury drop electrode[8] of 0.82 mm diameter; the counter electrode was constructed of cylindrical platinum gauze. An aqueous SCE was employed throughout experiments and all potentials are referred to it. Electrical contact between the SCE and the solutions investigated

was made through a two-part salt bridge with a Luggin capillary probe. One branch of this bridge was filled with saturated aqueous KCl, whereas the second one contained 0.1 M solution of tetraethylammonium perchlorate in DMF. Controlled potential electrolysis was performed at a mercury cathode with a surface area of 10 cm² using a Radelkis OH-404 apparatus.

Benzalacetone was recrystallized several times from ethanol; its melting point was in accordance with the literature data. Commercially available DMF was dried first with anhydrous K_2CO_3, later with CaH_2 and then stored over molecular sieves of 4A type. The solvent was rectified at reduced pressure under argon atmosphere. Before each experiment, the solvent was passed through a column of active alumina[9] (Woelm neutral, ICN Pharmaceuticals). Tetraethylammonium perchlorate was recrystallized from triply distilled water and dried in vacuo at 60 °C. All solutions were deaerated by argon which was passed through molecular sieves and presaturated by bubbling through the solvent. The measurements were carried out at a temperature of 23 ± 0.1 °C. Quantum chemical calculations were performed with BASF/VM computer.

RESULTS AND DISCUSSION

The cyclic voltammogram of 0.5 mM BA in DMF solution containing 0.1 M tetraethylammonium perchlorate exibits two cathodic peaks at potentials —1.66 V and —2.45 V, respectively, for sweep rate 0.1 V s⁻¹. No anodic currents complementary to these peaks were observed during reversal scan. The first peak, which is the object of our interest, is proportional to the reactant concentration within the range from 0.08 to 0.7 mM, and to the square root of the sweep rate (v), at least within the range for 0.05 to 5 V s⁻¹. The peak potential E_{pc}^I moves toward more positive values as v diminishes and the concentrations of benzalacetone (c_{BA}) and electrolyte (c_E) increase. Corresponding characteristics are collected in the Table.

TABLE

Essential Characteristics of the First Reduction Step of Benzalacetone

Parameter	Experimental value
$\Delta E_{pc}^I/\Delta \log v$	—18 ± 2 mV/log unit[a]
$\Delta E_{pc}^I/\Delta \log c_{BA}$	20 ± 3 mV/log unit[b]
$\Delta E_{pc}^I/\Delta \log c_E$	55 ± 6 mV/log unit[c]

[a] Scan rate range: 0.05 — 2.9 V s⁻¹; c_{BA} = 0.5 mM.

[b] c_{BA} range: 0.08 — 0.54 mM; sweep rate 0.1 V s⁻¹.

[c] c_E range: 0.02 — 0.15 M; c_{BA} = 0.5 mM; scan rate 3.2 V s⁻¹.

These values, together with the number of electrons transferred in electroreduction (see text below), are fully consistent with the radical — radical dimerization[10,11] influenced by the ion pairs formation between the benzalacetone radical anions and the cations of the supporting electrolyte. Analyzing the dependence of E_{pc}^I *versus* v (Figure 1), we have found the apparent rate constant of dimerization; the value of $k_{dim} = (8 ± 2) \times 10^4$ M⁻¹ s⁻¹.

Figure 1 was constructed for the solution containing 0.5 mM BA and 0.1 M $(C_2H_5)_4NClO_4$. Under these conditions, at a higher potential sweep rate (*i. e.* 2.9 V s⁻¹ and more) $\Delta E_{pc}^I/\Delta \log v = 0$ and the first reduction peak of benzalacetone becomes fully reversible. The corresponding pair of cathodic
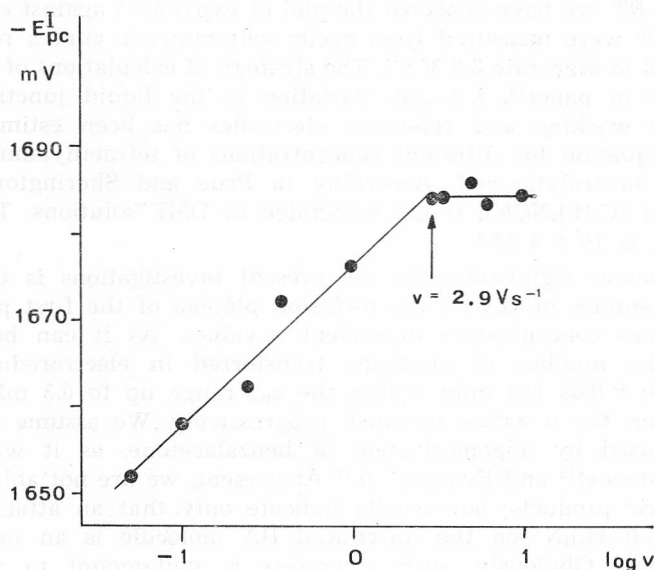
Figure 1. Variations of the first peak potential with the logarithm of the sweep rate for a 0.5 mM solution of benzalacetone in *N,N*-dimethylformamide containing 0.1 M tetraethylammonium perchlorate.

and anodic peaks is now observed with $(E_{pa}^I - E_{pc}^I) = 60 \pm 2$ mV and $i_{pa}^I/i_{pc}^I = 1.0$. Thus, it is possible to estimate the association constant value, K_{as}, proper for the equilibrium.

$$BA^{\cdot-} + (C_2H_5)_4N^+ \rightleftharpoons BA^{\cdot-} \ldots (C_2H_5)_4N^+ \qquad (1)$$

in which $BA^{\cdot-}$ and $BA^{\cdot-} \ldots (C_2H_5)_4N^+$ denote the benzalacetone radical anion and the corresponding ion pair, respectively.

It is known that the K_{as} value can be calculated on the basis of the rearranged Nernst equation[12]

$$E_o^{ip} - E_o = (RT/F) \ln (1 + K_{as} a_{M^+}) \qquad (2)$$

where E_0^{ip} and E_0 stand for the formal potentials of the electrode reaction determined in the presence and in the absence of ion association, respectively, whereas a_{M^+} marks the activity of a cation interacting with the radical anion. Large singly-charged cations, such as tetraethylammonium ions, do not generally show ion pairing with the anionic products of electrode reactions. The situation is somewhat different in the case investigated by us; therefore, we were not able to determine the value of E_o in direct experiments. Consequently, the ion pair formation constant of the $BA^{\cdot-} \ldots (C_2H_5)_4N^+$ system was estimated by the method proposed by Chauhan *et al.*[13] for solutions of varying ionic strength.

Transforming eq. (2) into exponential form

$$\exp (fE_o^{ip}) = \exp (fE_o) + \exp (fE_o) \times K_{as} \, a_{(C_2H_5)_4N^+} \qquad (3)$$

where $f = F/RT$, we have analyzed the plot of exp ($f E_o^{ip}$) against $a_{(C_2H_5)_4N^+}$. The values of E_o^{ip} were measured from cyclic voltammetric curves registered for $c_{BA} = 0.5$ mM at scan rate 3.2 V s^{-1}. The strategy of calculations of $a_{(C_2H_5)_4N^+}$was the same as in paper[13], i. e. any variation in the liquid junction potential between the working and reference electrodes has been estimated by the Henderson equation for different concentrations of tetraethylammonium perchlorate in electrolytic cell. According to Prue and Sherington[14] we have assumed that $(C_2H_5)_4NClO_4$ is not associated in DMF solutions. The resulting value of K_{as} is 10 ± 4 M^{-1}.

Of particular significance to the present investigations is the fact that coulometric studies of BA on the diffusion plateau of the first polarographic wave produces concentration dependent n-values. As it can be seen from Figure 2, the number of electrons transferred in electroreduction (n) is equal to 1.00 ± 0.05 but only within the c_{BA} range up to 0.5 mM; at higher concentrations, the n values diminish progressively. We assume that the last effect is caused by oligomerization of benzalacetone, as it was suggested earlier by Simonet[15] and Evans et al.[16] At present, we are not able to separate the oligomeric products; our results indicate only that an attack of the ion pair BA$^-$...$(C_2H_5)_4N^+$ on the unreduced BA molecule is an initial step of oligomerization. Obviously, such a process is tantamount to a radical — substrate dimerization.
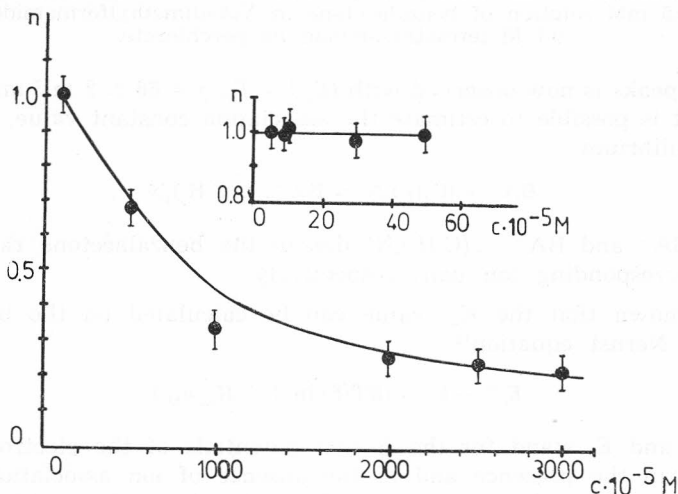

Figure 2. Plot of the number of electrons transferred during the first electro-reduction step of benzalacetone against the concentration of the reactant (0.1 M tetraethylammonium perchlorate in N,N-dimethylformamide).

What is, however, the tentative structure of the dimer BA—BA$^-$... $(C_2H_5)_4N^+$? From the formal point of view, various coupling reactions involving the formation of new C—C bonds must be taken into account. Hence, to solve the problem, we have computed the total energies of supersystems BA—BAH using the MMP2 method.[17,18] For simplicity, the radical in proto-nated form, BAH, was considered instead of the ion pair BA$^-$...$(C_2H_5)_4N^+$. According to the adopted tactics, we have taken into account the supersurface

of interaction of BA and BAH molecules, approaching the last one from various directions, turning it around benzalacetone and rotating it about the local axis so as to find the best orientation. The essential result of our calculations is presented in Figure 3. We suppose that it reflects the best orientation of the interacting molecules, at least from the energetical point of view. Other possibilities, *e. g.* an addition of BAH to the C=O group of the BA molecule, seem to be less probable.
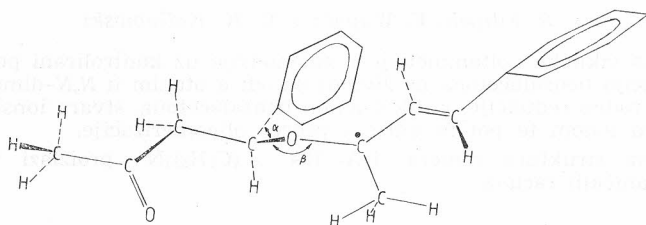

Figure 3. Structure of the dimer benzalacetone-benzalacetone radical anion computed by the MMP2 method: $\alpha = 113°$, $\beta = 115°$; the dihedral angle between the planes of the phenyl rings is $\gamma = 48°$.

Obviously, the structure proposed in Figure 3 is purely speculative and it will be verified in spectroscopic experiments. At present, it seems reasonable to suggest that the BA—BA⁻ ... $(C_2H_5)_4N^+$ radical is then capable of the BA mole, lenghthening progressively an oligomeric chain. As it follows from Figure 2, its length is dependent on the concentration of benzalacetone in solutions.

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SAŽETAK

Elektrodna redukcija benzalacetona u N,N-dimetilformamidu

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Metodama cikličke voltammetrije i kulometrije uz kontrolirani potencijal istražena je redukcija benzalacetona na živinoj katodi u otopini u N,N-dimetilformamidu. Produkt elektrodne redukcije, radikal-anion benzalacetona, stvara ionski par s tetraetilamonijevim ionom te potom ulazi u proces oligomerizacije.

Predložena struktura dimera, BA—BA⁻ . . . (C₂H₅)₄N⁺, proizlazi iz provedenih kvantno-mehaničkih računa.