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A Voltammetric Study of the Reduction of Triptindanones in *N,N*-Dimethylformamide*

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The mechanism of electroreduction of 9-triptindanone (**1**), 9,10-triptindanedione (**2**), and 9,10,11-triptindanetrione (**3**) was studied by use of the cyclic voltammetric method. All carbonyl groups were reduced giving one, two, and three one-electron cathodic peaks for **1**, **2**, and **3**, respectively and the corresponding oxidation peaks. The first electron transfer is reversible and the radical anions formed are stable. Additional small peaks for **2** and **3** were discussed in terms of an adsorption of reactants and intermediates and their reactions with the participation of supporting electrolyte cations as well as the residual water.

Key words: triptindanones, electroreduction, radical anions, 1,3-diketones, propellanes

Electroreduction of a number of carbonyl compounds, including 1,2,3-indanetrione and its hydrate ninhydrin [1–3], was already studied many years ago. Radical anions formed in the first one-electron step in formally aprotic solvents like *N,N*-dimethylformamide (DMF) in the presence of Na^+, K^+ and tetraethylammonium cations of the supporting electrolyte as well as their ion pairs formed with Li^+ and Ba^{2+} cations are relatively stable [2,3]. On the other hand, electrochemical properties of 9-triptindanone (**1**), 9,10-triptindanedione (**2**), and 9,10,11-triptindanetrione (**3**), a new class of ketones (Scheme 1) developed recently [4,5], have not been investigated yet. They are very interesting as starting reactants for the synthesis of triptindanes bearing functional groups at the "top" of the carbon framework, *i.e.*, in positions 9, 10, and 11 [4] as well as other members of centropolyindanes, a new group of polycyclic aromatic hydrocarbons. In particular, triketone **3** with formal C_{3v} molecular symmetry was successfully used for a synthesis of centrohexaindane [6], which represents the rare class of topologically (or graph theoretically) nonplanar molecules [7] characterized by a maximum number of rings fused with each other in three dimensions.

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* Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.
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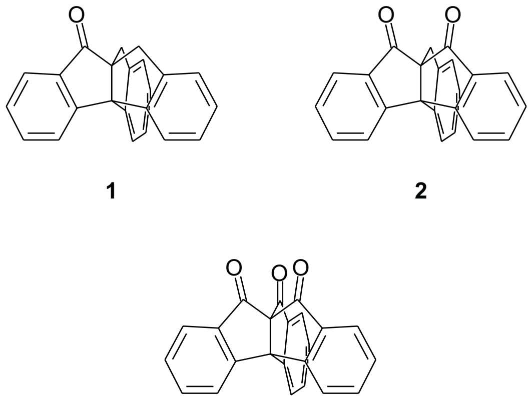
Scheme 1



1 2 3

From the electrochemical point of view a comparison of the properties of anions produced during the reduction of planar 1,2,3-indanetrione with that of spatial triketone **3** may be of particular interest, chiefly because of the different stability of anions formed successively by the reduction of consecutive carbonyl groups, and a possibility of differences in solvation and association with supporting electrolyte cations. The present paper describes a preliminary mechanistic study of the electroreduction of three triptindanones **1**, **2**, and **3** in DMF in the presence of tetrabutylammonium perchlorate (TBAP) by means of cyclic voltammetric method. The technique used has been found to be particularly useful in investigations of the mechanisms in organic electrochemistry, and at an early stage of such applications the contribution of Galus *et al.* [8] should be mentioned.

EXPERIMENTAL

The syntheses of **1**, **2**, and, **3** were described in original papers [4,5]. Anhydrous DMF (99.8%) from Aldrich was used as received. TBAP (electrochemical grade, Fluka) was dried under reduced pressure. Concentrations of TBAP were usually 0.1 M and concentrations of reactants were usually 0.5 mM but for **3** they were also changed in the range from 0.1 to 1 mM.

For voltammetric measurements a three-electrode cell was used consisting of a static mercury drop electrode (SMDE, Laboratorni Pristroje, Prague), a Pt counter electrode and Ag/0.1 M Ag^+ couple in acetonitrile as the reference electrode. All potentials are expressed against that reference electrode, unless otherwise indicated. A gold disc electrode (1.5 mm diameter) was also used as the working electrode in order to observe adsorption phenomena. Cyclic voltammetric curves at 24–25°C were recorded with a PAR 273A potentiostat controlled by an IBM PC computer by means of the software M270 from PAR. Argon gas was bubbled through the solution before each experiment and blown above the solution surface during the measurements.

RESULTS AND DISCUSSION

Cyclic voltammograms of the three reactants under investigation recorded at the scan rate $v = 1\ \mathrm{V\ s^{-1}}$ are shown in Fig. 1. Obviously, the number of cathodic and anodic peaks increases with the number of carbonyl groups in the molecules. For the monoketone **1** the reversible reduction-oxidation process I is observed with the cathodic peak potential $E_{pc} = -2.398$ V, whereas a small irreversible reduction process can be observed at –3.0 V. Near the reduction limit at –3.3 V a second irreversible reduction peak IC is observed. The process I corresponds to the reversible one-electron exchange as indicated by the cathodic peak width $E_{pc} - E_{pc/2} = 62$ mV, the anodic to cathodic peak ratio $i_{pa}/i_{pc} = 0.9$ and the fact that E_{pc} is independent of the scan rate (in the range 0.1 to 1.0 $\mathrm{V\ s^{-1}}$); the difference in cathodic and anodic peak potentials $\Delta E_p = E_{pc} - E_{pa} = 72$ mV is a little higher than expected theoretically but the characteristics of the anodic peak are obtained with less accuracy. The peak current i_{pc} depends linearly on $v^{1/2}$ indicating its diffusional limitation. All characteristics found confirm that a stable radical anion is formed in process I. The formal potential of this step (calculated as a mean value between the anodic and cathodic peaks) is equal to $E^o = -2.87$ V *vs*. SCE. The ratio of peak currents i_{pc} for processes I and IC is equal to 1:0.88 indicating the same number of exchanged electrons. Thus, it is reasonable to describe the process IC as the second reduction step resulting in the formation of a carbinol dianion from a radical anion; however, this process should be reversible and thus it must be followed by a fast decay of dianions.

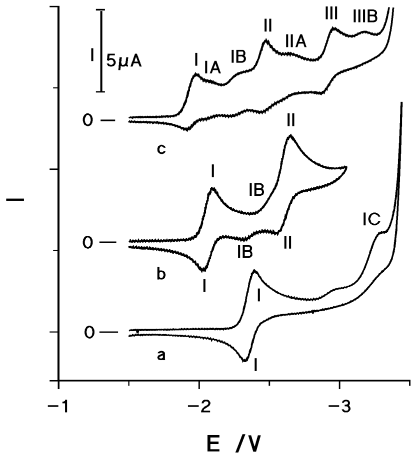


Figure 1. Cyclic voltammetric curves of 0.5 mM solutions of (a) 9-triptindanone (**1**), (b) 9,10-triptindanedione (**2**), and (c) 9,10,11-triptindanetrione (**3**) in DMF, 0.1 M TBAP; scan rate 1 $\mathrm{V\ s^{-1}}$.

For diketone **2** two pairs of peaks for two redox processes (denoted I and II) are observed as well as an additional irreversible process IB at the foot of the reduction current of peak II. The oxidation peak corresponding to the reduction IB is evident only if the potential scan is reversed just after the peak II and it is shifted to more positive potentials as shown in Fig. 1. If the scan rate is reversed near the potential limit of the supporting electrolyte the oxidation peak IB disappears. A similar process IB was observed also for triketone **3** and will be discussed below. A small hump is also present in the curve of the reduction current of **2** at –3.09 V, but is not shown in Fig. 1. The first reduction process I with $E_{pc} = -2.097$ V is characterized by $E_{pc} - E_{pc/2} = 59$ mV, $i_{pa}/i_{pc} = 0.9$, $\Delta E_p = E_{pc} - E_{pa} = 62$ mV, and E_{pc} is independent of the scan rate (for $v = 0.05–1.0$ V s^{-1}); thus, it corresponds to the reversible one-electron processes of radical anions formation and their re-oxidation. The characteristics of the second redox process II is less accurate because of an interference of the reduction process IB. Nevertheless, taking into account only the higher part of the reduction peak it is evident that process II is not fully reversible: $\Delta E_p = E_{pc} - E_{pa} = 78$ mV for $v = 0.05$ V s^{-1}, increasing to 93 mV for $v = 1$ V s^{-1}; $i_{pa}/i_{pc} = 0.8$, but $E_{pc} - E_{pc/2} = 60$ mV. Moreover, E_{pc} depends on the scan rate giving $\partial E_{pc}/\partial \log v = -46$ mV and i_{pc} increases with the scan rate but is not proportional to $v^{1/2}$. This means that this process has the quasi-reversible nature [9]. It corresponds to the one-electron reduction of the second carbonyl group as concluded from a comparison with the behavior of other reactants under investigation. The dianion formed has most probably a biradical structure because the formation of the endiol dianion, as considered for ninhydrin [2], is impossible for the three fused rings in triptindanones.

For triketone **3** three pairs of reduction and oxidation peaks (denoted I, II and III in Fig. 1) are observed as well as two additional small reduction humps (IA and IIA) and peaks of different nature denoted IB and IIIB. Process I at $E_{pc} = -1.978$ V corresponds to the reversible formation of the radical anion and its characteristics are similar to those of the process I found for **1** and **2**. In fact, E_{pc} is independent of v, $E_{pc} - E_{pc/2} = 62$ mV, $i_{pa}/i_{pc} = 0.8$ and $\Delta E_p = E_{pc} - E_{pa} = 68$ mV. The analysis of the reduction peak II is less accurate due to an interference of nearby processes IB and IIA. Nevertheless, its characteristics are similar to those of the quasi-reversible electron transfer to the second carbonyl group found for **2** (process II): $E_{pc} - E_{pc/2} = 62$ mV (measured for higher concentrations of triketone [**3**] = 0.75 and 1 mM), E_{pc} depends on the scan rate (with the same slope as for **2** in solutions of the same concentrations) and i_{pc} increases with $v^{1/2}$, but not linearly. A comparison with the behavior of other reactants allows one to suggest that peak II also corresponds to the reduction of the second carbonyl group of **3** yielding the biradical dianion.

The humps denoted IA and IIA were identified as adsorption peaks corresponding to the relatively strong adsorption of the reactant of processes I and II, respectively [10]. For IIA this was confirmed by measurements on the gold electrode. The voltammetric curves recorded at the fresh surface of electrode showed a very high and sharp tensammetric peak just after the reduction peak II. However, after recording a number of curves the height of this peak decreases, finally resulting in a hump similar to the one observed on the mercury electrode (Fig. 1).

The cathodic current coresponding to step IB was found to decrease with an increase in the reactant concentration as shown in Fig. 2. For the lowest concentration of the triketone (0.1 mM) the peak current for IB is only 65% lower than that for peak I (curve *a* in Fig. 2), whereas at the highest concentration of 1 mM (curve *b*) it disappears completely. It should be added that the ratio of peak currents for processes II and I is independent of the reactant concentration. Moreover, in voltammograms with the well shaped peak IB the sum of i_{pc} for peaks I and IB is approximately equal to the height of the peak II.

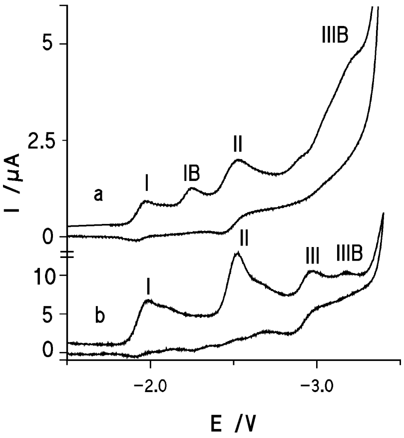


Figure 2. Cyclic voltammograms of: (a) 0.1 and (b) 1 mM solutions of 9,10,11-triptindanetrione (**3**) in DMF, 0.1 M TBAP; scan rate 1 V s^{-1}.

The above results can be explained taking into account the chemical reaction of the triketone **3** with some contamination in a solution, most probably the residual water. Indeed, the addition of water influences peak IB. In the solution containing 0.028 M of added water, i_{pc} of peak IB increased without a change in the E_{pc} value and in the solution containing 1.14 M of water the height of peak IB increased 1.7 times in respect to the peak in the solution without added water and its E_{pc} was shifted to more positive potentials. On the other hand, peak I remained practically unchanged and the height of peak II also increased (finally by a factor of two) but without changing the E_{pc} value. It should be added here that the hydration/dehydration processes play an important role in the electrochemistry of 1,2,3-indanetrione [1,2] and that the oxidation peak for a dehydrated form was observed at the potential being 960 mV more positive than the original peak of ninhydrin hydrate. A similar behavior was found for triketone **3**: when the potential scanning is reversed just after the reduction peak IB, the new oxidation peak was found at the potential approximately –0.95 V and this peak increases markedly in solutions with added water. Thus, for the reactants under investigation the reduction of hydrated or protonated ketone may be suggested for the process IB but as yet it is impossible to distinguish between these reaction pathways. For diketone **2** a small anodic peak corresponding to the reduction process IB is observed if the potential scan is reversed early enough (Fig. 1) and then the sum of the anodic peak currents I and IB is equal to the cathodic peak current for the process I.

For triketone **3,** on the other hand, it was found that the product of the reduction at the potential of peak IB is unstable and gives no oxidation peak; only a bow can be observed in the course of the oxidation current. However, if the potential scan is terminated for 60 s at the potential –2.28 V, *i.e.*, just after the E_{pc} of peak IB and then reversed, the new anodic peak at –2.05 V is observed. This indicates a slow chemical step consuming the product of the reduction IB. The last conclusion was also confirmed by the shift of E_{pc} (recorded in the low triketone concentration equal to 0.1 mM) with the scan rate giving $\partial E_{pc}/\partial \log v = -29.4$ mV as for the EC mechanism, *i.e.*, with the first order reaction following the electron transfer. At higher scan rates starting from 0.9 $V s^{-1}$ the reduction process is reversible and E_{pc} does not change. Thus, it was possible to determine the rate constant for the decay of the product of the step IB: $k = 18 \pm 4\ s^{-1}$. It should be added that peak currents for peaks IB as well as I and II depend linearly on $v^{1/2}$ giving null intercepts and thus they have a diffusional character.

The reduction process III is not fully reversible giving $E_{pc} - E_{pc/2} = 58$ mV, but $i_{pa}/i_{pc} = 0.8$, $\Delta E_p = E_{pc} - E_{pa} = 134$ mV (for $v = 1\ V s^{-1}$) and E_{pc} is shifted to more negative potentials with an increase in v, giving $\partial E_{pc}/\partial \log v = -32$ mV, but also E_{pc} is shifted to more negative potentials with an increase in the reactant concentration. Moreover, it was found that processes III and IIIB are mutually related. An increase in the reactant concentration results in an increase of peak III at the cost of peak IIIB as is evident from Fig. 2. On the other hand, a reverse behavior was observed with an increase in the scan rate: the peak IIIB increases at the cost of peak III as illustrated in Fig. 3.

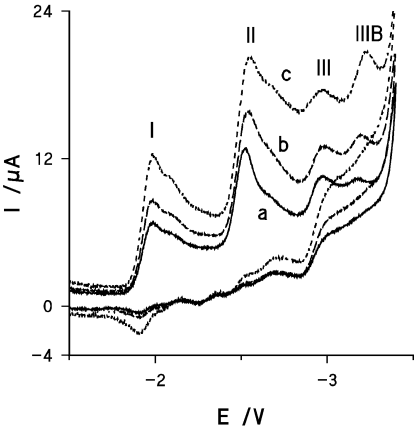


Figure 3. Cyclic voltammetric curves of the solution of 1 mM 9,10,11-triptindanetrione (**3**) in DMF at scan rates: (a) 1 $V s^{-1}$, (b) 2 $V s^{-1}$, (c) 5 $V s^{-1}$.

This latter effect is also caused by adding water. For the reactant concentration 0.5 mM peak III disappeared completely in the solution containing 1.14 mM of added water, and E_{pc} for peak IIIB was shifted then to more positive potentials indicating an interaction of the product with water. Moreover, increasing the supporting electrolyte concentration from 0.1 to 0.2 mM results in a significant decrease of the IIIB peak current (1.6 times) whereas the height of other peaks remains practically unchanged. It is evident from the obtained results that the primary product of the process II, *i.e.*, the biradical dianion is reduced at the potential around –3.2 V giving the completely irreversible peak IIIB, without any oxidation response, which looks reasonable taking into account a high electron density at the dianion. On the other hand, the dianion undergoes a slow chemical reaction with the participation of TBA^+ cations and the residual or added water yielding a more easily reducible product which is responsible for the reversible peak III. The association with cations as well as protonation or hydration of the dianion should be rather fast processes. Therefore, a slow conformational change involving the bulky TBA^+ cations and/or the electrostatic repulsion between oxygen atoms of three carbonyl groups can be suggested instead. Certainly, these assumptions require further experimental support.

The change of the TBAP concentration from 0.1 to 0.2 M for diketone **2** results in a 22 mV shift of the peak potential for process II to a more positive direction but practically does not influence E_{pc} for process I. On the other hand, the E_{pc} values for triketone **3** for all cathodic processes are shifted by increasing the TBAP concentration and the shift increases for each successive process giving $\partial E_{pc}/\partial \log [TBAP] = 52$ mV and 175 mV for processes I and IIIB, respectively (for the concentration of **3** equal to 0.5 mM, the concentration range of TBAP from 0.1 to 0.3 M and $v = 1\ V\ s^{-1}$). This means that the formation of ion pairs with TBA^+ cations by radical anions of **1** and **2** can be neglected, but that radical anions of **3** and products of further reduction (also for diketone **2**) have an increasing tendency to form associates even with big TBA^+ cations. Thus, the Lewis basicity found for radical anions of spatial triketone **3** is much higher than that of radical anions of planar 1,2,3-indanetrione, which do not formed associates in DMF even with Na^+ and K^+ ions [2].

Finally, from a comparison of the first reduction step yielding the radical anion for reactants **1**, **2**, and **3** it is evident that peak potentials and heights are changing with the reactant nature (Fig. 4). The ratio of peak currents 1.3:1.2:1.0 was found for **1, 2** and **3**, respectively, most probably reflecting the slight decrease of the reactant diffusion coefficient with the increase in the number of carbonyl groups. The values of E_{pc} shift in a positive direction in the same order, indicating that the electron transfer becomes easier then. The observed shifts of E_{pc} are equal to 300 mV and 119 mV for the reactant with two and three carbonyl groups, respectively. This means that the energy of LUMO is decreased in the same order and that the solvation of radical anions increases with the increasing number of carbonyl groups. This behavior could be expected from the literature data for other ketones, *e.g.*, in aqueous 48% ethanol solutions at pH 12 the difference in polarographic half-wave potentials for 1,3-indanedione and 1,2,3-indanetrione is 440 mV [1]. However, a straightforward comparison of the behavior of different ketones is not possible yet because of combined effects of the LUMO energy and the solvation of the reactants.

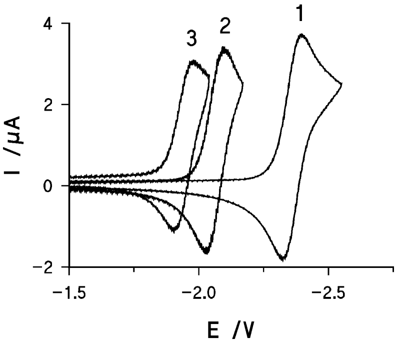


Figure 4. Cyclic voltammograms of 0.5 mM solutions of: 9-triptindanone (**1**), 9,10-triptindanedione (**2**), and 9,10,11-triptindanetrione (**3**) in DMF, 0.1 M TBAP showing only the first electron-transfer steps; scan rate 1 V s^{-1}.

In conclusion, the electroreduction of triptindanones is rather complicated due to adsorption phenomena and to chemical reactions involving supporting electrolyte cations and residual water, but it is evident that every carbonyl group can be reduced and that the radical anions formed in the first electron transfer step are relatively stable.

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