ELECTROCHEMICAL REACTIONS OF ORGANIC COMPOUNDS IN LIQUID AMMONIA

PART IV. REDUCTION OF CYCLOOCTATETRAENE

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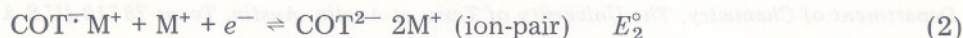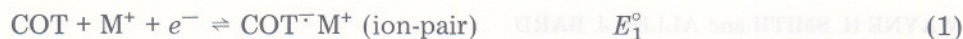(Received 3rd November 1975; in revised form 11th March 1976)

ABSTRACT

The electroreduction of COT in liquid ammonia at —38° and —65°C was investigated by cyclic voltammetric and controlled potential coulometric techniques. The results are interpreted by a two-step two-electron transfer reaction with strong ion-pairing of the COT dianion. Values for the heterogeneous electron transfer rate constants and the equilibrium constant of the disproportionation of the radical anion are estimated, based on a digital simulation of the cyclic voltammogram.

INTRODUCTION

In recent years there have appeared in the literature several reports on the electrochemical behavior of cyclooctatetraene (COT) and its derivatives in aprotic solvent systems [1—4, 15]. From these works two different mechanisms for the reduction of COT have been proposed. Thielen and Anderson [3] observed two closely spaced reduction waves of COT in acetonitrile (ACN) when using a tetrabutylammonium salt as supporting electrolyte, but only one reduction wave when the tetramethylammonium salt was employed. These results were explained on the basis of an ECE type mechanism where the electrochemically generated COT radical anion abstracts a proton from the tetrabutylammonium salt in a Hoffman-type elimination reaction to yield a radical species. The radical species is reducible at a slightly more negative potential than the parent compound accounting for the second reduction wave. Since the tetramethylammonium salt is incapable of under going the Hoffman reaction, they claimed that when it is employed as the supporting electrolyte the intervening chemical reaction cannot occur and only a single reduction wave, corresponding to the formation of the radical anion, is observed. The anion radical was said to be reduced at a very negative potential, beyond the limit of solvent reduction, and does not appear in the polarogram.

An alternate explanation advanced by several researchers takes into account the effect of ion-pairing phenomena on the electrochemical reduction

waves. According to this scheme COT is reduced in two closely-spaced one-electron reduction waves to yield the radical anion and dianion respectively. However, in solvents of low dielectric constant these anionic species can interact with the supporting electrolyte cation to form tight ion pairs. The strength of the ion-pair formation can sometimes be determined from the differences between the observed peak potentials and the standard potentials of the electron transfer reactions. Expressed in standard notation these reactions are:

$$COT + M^+ + e^- \rightleftharpoons COT^- M^+ \text{ (ion-pair)} \qquad E_1^\circ \qquad (1)$$

$$COT^- M^+ + M^+ + e^- \rightleftharpoons COT^{2-} 2M^+ \text{ (ion-pair)} \qquad E_2^\circ \qquad (2)$$

where E_1° and E_2° are the reduction potentials and M^+ represents the supporting electrolyte cation. In the presence of ion pairing both reduction waves shift to more positive potentials as was clearly demonstrated by Fry et al. in their study of the reduction in dimethyl sulfoxide. They found that a decrease in the size of the supporting electrolyte cation from R = n-heptyl to R = methyl in the tetraalkylammonium salt (R_4N^+) resulted in an increase in the ease of reduction with a potential shift greater than 0.1 V for each electron transfer, presumably due to a greater tendency of the smaller cation to ion pair. Also significant in their work was the observed decrease in potential between successive reduction waves in changing the supporting electrolyte from the tetrabutyl to the tetramethylammonium salt, showing that the strength of ion-pairing is greater for the dianion than for the anion radical so that the second electron transfer wave is shifted to a greater extent than the first.

We report here the electrochemical behavior of COT in liquid ammonia using potassium iodide as a supporting electrolyte. In this solvent system reduced species, even dianions, are very stable, especially with regard to protonation [5—7], and ion-pairing effects are marked. We will show that the reduction of COT under these conditions follows the two-step reduction mechanism and estimate kinetic parameters for the electrode reactions.

EXPERIMENTAL

COT (Columbia Organic Chemicals) was vacuum distilled at approximately 40°C and stored frozen under nitrogen in a septum sealed flask. Infrared analysis of the final product failed to detect the presence of styrene, a common impurity, and no extraneous waves were detected during electrochemical analysis. Potassium iodide (Baker and Adamson) was crushed into a fine powder and dried in air at 120°C.

A description of the cell apparatus and techniques used in the electrochemical measurements has been given previously [6]. The general procedure was to fill the cell with supporting electrolyte, attach it to a vacuum line and evacuate it for 24 h. During the same time period the liquid ammonia (Matheson 99.9%) was allowed to remain in contact with sodium metal at ap-

proximately —50°C. The ammonia was then vacuum distilled into the reaction cell and the temperature was maintained at ±1°C between —35°C and —70°C with a dry ice-isopropanol bath. Aliquots of COT were injected into the cell through a silicone gum rubber septum by means of an air-tight microliter syringe. All experimental measurements were made with a Princeton Applied Research Model 170 electrochemical system.

RESULTS AND DISCUSSION

In liquid ammonia containing 0.1 M KI as supporting electrolyte COT is reduced in a single two-electron reduction process characterized by a large separation between anodic and cathodic peak potentials (Fig. 1). At a scan of 200 mV s^{-1} the peak potential separation is approximately 440 mV at —38°C; this increases to greater than 600 mV at —65°C. Noticeably absent in the cyclic voltammogram is the wave usually observed in other aprotic solvents approximately 800 mV negative of the COT wave which corresponds to the reduction of 1,3,5-cyclooctatriene, a product obtained as a result of protonation of the COT dianion. This wave can be made to appear in liquid ammonia by the addition of a proton donor such as water or an alcohol. The use of the ammonia-soluble quaternary ammonium salt, methyl-tri-butyl ammonium iodide, as a supporting electrolyte resulted in a large adsorption wave on the anodic portion of the scan which masked the wave corresponding to the reoxidation of the COT dianion, thus eliminating the possibility for quantitative
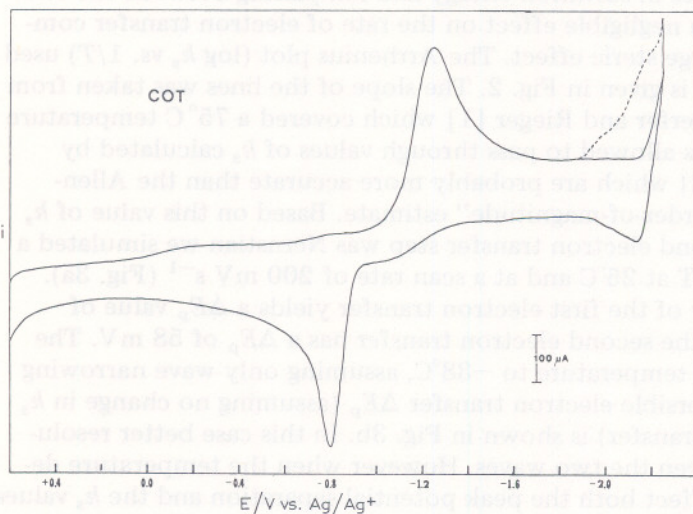

Fig. 1. Cyclic voltammogram of cyclooctatetraene in liquid ammonia containing 0.1 M KI at a gold disk electrode, Scan rate 500 mV s^{-1}; temperature —38°C; concentration 6.3 mM. (— — —) Addition of isopropyl alcohol.

measurements. However, the cathodic portion of the scan still exhibited only a single reduction wave. Controlled potential coulometric reduction resulted in a pale yellow solution and an n_{app} value of 2.01 electrons/COT molecule, demonstrating production of the COT dianion. Reoxidation of the dianion back to parent compound occurred with an n_{app} value of 1.93. Cyclic voltammograms of the solution following coulometric reduction and reoxidation were identical to voltammograms of starting material with no new waves apparent.

The large peak potential separation (ΔE_p) in the cyclic voltammogram of COT is consistent with a quasi-reversible electron transfer process. Similarly the increase in ΔE_p with decreasing temperature is opposite to the effect expected for a Nernstian reaction (where peaks narrow and ΔE_p decreases with decreasing temperature) and suggests rather a decrease in the heterogeneous rate constant with decreasing temperature. This temperature effect on the of electron transfer has also been observed in dimethylformamide (DMF) [1], and has been attributed to the fact that at lower temperatures there is less thermal motion in the COT ring, and therefore more energy, in the form of higher overpotential, must be applied to flatten the ring from a tub conformation as it exists in the parent to the planar conformation it exhibits in the reduced state. To simulate the cyclic voltammetric behavior of COT in liquid ammonia and to illustrate the effect of different factors (e.g., temperature, ion pairing) on the voltammograms, a series of digital simulations were undertaken. An initial estimate for the heterogeneous rate constant for the first electron transfer at the temperatures used in this study was made from the previously calculated value obtained in DMF. The major assumption in this procedure is differences in solvation energy and ion-pairing between the two solvent systems have a negligible effect on the rate of electron transfer compared to the rather large steric effect. The Arrhenius plot ($\log k_s$ vs. $1/T$) used to obtain these values is given in Fig. 2. The slope of the lines was taken from data given by Allendoerfer and Rieger [1] which covered a $75°C$ temperature range, and the line was allowed to pass through values of k_s calculated by Huebert and Smith [2] which are probably more accurate than the Allendoerfer and Rieger "order-of-magnitude" estimate. Based on this value of k_s and assuming the second electron transfer step was Nernstian we simulated a voltammogram of COT at 25°C and at a scan rate of 200 mV s^{-1} (Fig. 3a). The quasi-reversibility of the first electron transfer yields a ΔE_p value of about 200 mV while the second electron transfer has a ΔE_p of 58 mV. The effect of lowering the temperature to $-38°C$, assuming only wave narrowing and change in the reversible electron transfer ΔE_p (assuming no change in k_s for the first electron transfer) is shown in Fig. 3b. In this case better resolution is obtained between the two waves. However when the temperature decrease is allowed to affect both the peak potential separation and the k_s values of both electron transfers, with values of k_{s_1} and k_{s_2} extracted from the Arrhenius plot of Fig. 2, Fig. 3c results. Here, the much lower value of k_s for the first electron transfer causes the reduction wave to shift in the negative
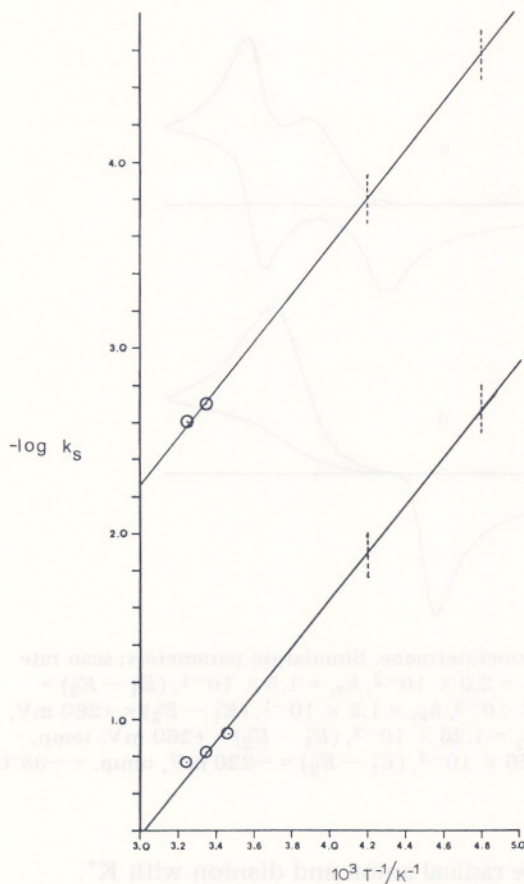
Fig. 2. Arrhenius plot of heterogeneous rate constant versus temperature for electron transfer to cyclooctatetraene. (○) Data of ref. 3, slope taken from ref. 2.

direction until the two reduction waves over lap, approximating the behavior observed in liquid ammonia. However, the anodic portion of this simulated voltammogram shows two one-electron oxidation waves whereas the experimental voltammogram shows only a single two-electron oxidation wave. Further refinement in the simulated voltammogram was then made by allowing the standard reduction potential of the second electron transfer (E_2^o) to shift in a positive direction until the two anodic waves overlapped producing a single two-electron oxidation wave (Fig. 3d). Since the controlled potential coulometry results indicate the absence of any following chemical reaction with the dianion species, the positive shift in potential of the second electron transfer cannot be explained on this basis. This behavior can be explained,
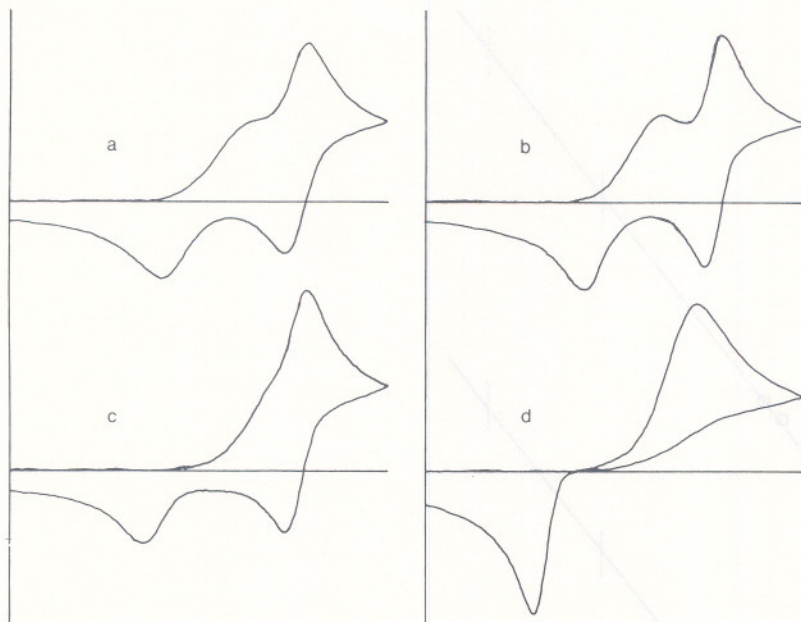
Fig. 3. Simulated voltammograms of cyclooctatetraene. Simulation parameters; scan rate 200 mV s^{-1}; α_1 = 0.40, α_2 = 0.50. (a) k_{s_1} = 2.0 × 10^{-3}, k_{s_2} = 1.5 × 10^{-1}, $(E_1^\circ - E_2^\circ)$ = = +260 mV, temp. = 25°C; (b) k_{s_1} = 2.0 × 10^{-3}, k_{s_2} = 1.5 × 10^{-1}, $(E_1^\circ - E_2^\circ)$ = +260 mV, temp. = −38°C; (c) k_{s_1} = 1.58 × 10^{-4}, k_{s_2} = 1.26 × 10^{-2}, $(E_1^\circ - E_2^\circ)$ = +260 mV, temp. = −38°C; (d) k_{s_1} = 1.58 × 10^{-4}, k_{s_2} = 1.26 × 10^{-2}, $(E_1^\circ - E_2^\circ)$ = −220 mV, temp. = −38°C.

however, based on ion-pairing of the radical anion and dianion with K$^+$.

Several electron spin resonance (E.S.R.) studies of the COT system have been carried out in hexamethylphosphotriamide [8], tetrahydrofuran [4—11], and liquid ammonia [9—11] where generation of the COT$^{\cdot-}$ was accomplished by chemical reduction with alkali metals. In all three solvents the COT$^{\cdot-}$ concentration was very low compared to the dianion and parent molecule concentrations, and the E.S.R. spectra displayed hyperfine splitting caused by tight ion-pair formation between COT$^{\cdot-}$ and the alkali metal cation (M$^+$). These findings suggested that in the presence of appreciable ion-pairing the disproportionation of COT$^{\cdot-}$, eqn. (3), is exothermic.

$$2 \; COT^{\cdot-}, M^+ \rightleftharpoons COT + COT^{2-}, 2 \; M^+ \tag{3}$$
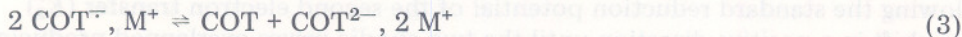
The equilibrium constant for this reaction, K_{eq}, is given by the thermodynamic relationship in eqn. (4)

$$RT \ln K_{eq} = nF(E_1^\circ - E_2^\circ) \tag{4}$$

where E_1° and E_2° are the standard potentials of reactions (1) and (2). It follows that if in the presence of ion-pairing the position of equilibrium of reac-
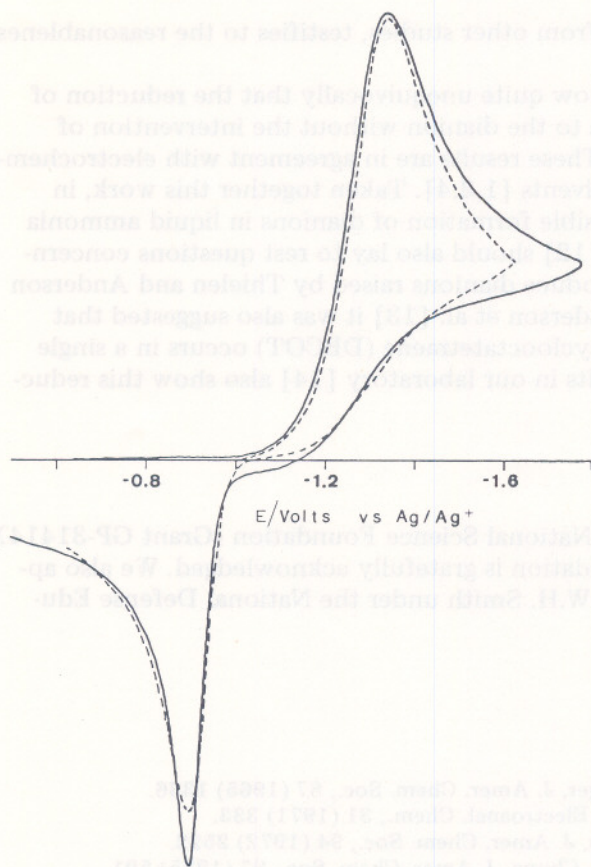
Fig. 4. Simulated voltammogram of cyclooctatetraene (— — —) versus experimental voltammogram (————). Electron transfer parameters same as Fig. 3d.

tion (3) lies to the right, then E_2° must be more positive than E_1°. We found that a value of -220 mV for $(E_1^\circ - E_2^\circ)$ along with the value of k_{s_1} and k_{s_2} obtained from the Arrhenius plot yielded a simulated voltammogram very similar to the one obtained experimentally at a temperature of $-38°C$ (Fig. 4), while at a temperature of $-65°C$, a ΔE° value of -272 mV was necessary to give the proper peak potential separation (610 mV). The K_{eq} calculated from these ΔE° values are 2.2×10^{-5} ($-38°C$), and 2.6×10^{-7} ($-65°C$), in reasonable agreement with a reported value of 1.4×10^{-6} obtained from E.S.R. measurements of the COT system in the presence of potassium ion in liquid ammonia at $+22°C$ [9]. Of course the number of adjustable parameters involved in fitting this cyclic voltammogram suggests that exact quantitative significance should not be attached to the k_{s_1}, k_{s_2} and K_{eq} values. The ability to fit the voltammogram within the framework of the two-step mechanism,

using estimates of parameters from other studies, testifies to the reasonableness of this model.

The results obtained here show quite unequivocally that the reduction of COT occurs in liquid ammonia to the dianion without the intervention of following chemical reactions. These results are in agreement with electrochemical studies of COT in other solvents [1,2,4]. Taken together this work, in addition to the clear and reversible formation of dianions in liquid ammonia [5,6] or carefully dried DMF [12] should also lay to rest questions concerning the energies required to produce dianions raised by Thielen and Anderson [3]. In a previous study by Anderson et al. [13] it was also suggested that the reduction of sym-dibenzocyclooctatetraene (DBCOT) occurs in a single one-electron step. Recent results in our laboratory [14] also show this reduction to be a two-electron one.

ACKNOWLEDGMENTS

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