Short Communications

Reactions of Aromatic Anion Radicals and Dianions. Part III.[1] Electrolyte and Solvent Effects on the Kinetics of Electron Transfers to Cyclooctatetraenes

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The first electron transfer to cyclooctatetraene (COT) to generate the anion radical has been reported to be unusually slow while reduction of the anion radical proceeds at a rate comparable to that observed for benzenoid hydrocarbons.[2] This effect was attributed to the large activation energy associated with distortion of COT to a transition state resembling planar COT.[2] Electron transfer kinetics to COT were investigated more thoroughly using A. C. polarography by Huebert and Smith[3] and a semiquantitative study by Anderson et al. indicated that the first charge transfer to a related system, 2-methoxyazocines, is even slower than

that to COT.[4] More recent studies have led to the curious conclusions that COT anion radical is electrochemically irreducible[5] in acetonitrile and THF and that benzocyclooctatetraene (BCOT) and sym-dibenzocyclooctatetraene (DBCOT) undergo reversible one electron transfers in THF to the anion radicals which are not further reducible.[6] By using "super dry" solvents[7] and taking advantage of the effect of small supporting electrolyte cations[1] on the electrochemical reversibility of cathode processes we have been able to conclusively demonstrate that the conclusions of the latter studies[5,6] are not valid. Furthermore, the kinetics of the COT reductions were found to be markedly dependent upon the nature and concentration of the supporting electrolyte cation. Under the most favorable conditions the first electron transfer to COT approaches reversibility which suggests that the flattening energy does not contribute as much to the electron transfer kinetics as previously reported.[2,3]

The cyclic voltammogram of BCOT in carefully purified THF[8] passed over neutral alumina immediately before use is illustrated in Fig. 1a (supporting electrolyte; 0.2 M Bu₄NBF₄). The shape of the voltammogram is indicative of two closely spaced one electron transfers.* When

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* The same conclusion can be arrived at by examing the voltammogram of BCOT shown in Fig. 2 of Ref. 6.
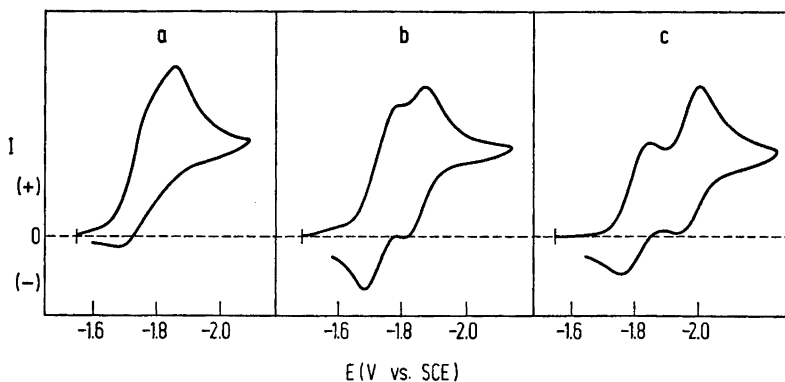

Fig. 1. Cyclic voltammograms of BCOT on mercury at 65 mV/s. (a) In THF containing Bu₄NBF₄ (0.2 M). (b) As in (a) with neutral alumina added. (c) In DMF containing Bu₄NBF₄ (0.2 M) saturated with Me₄NI.
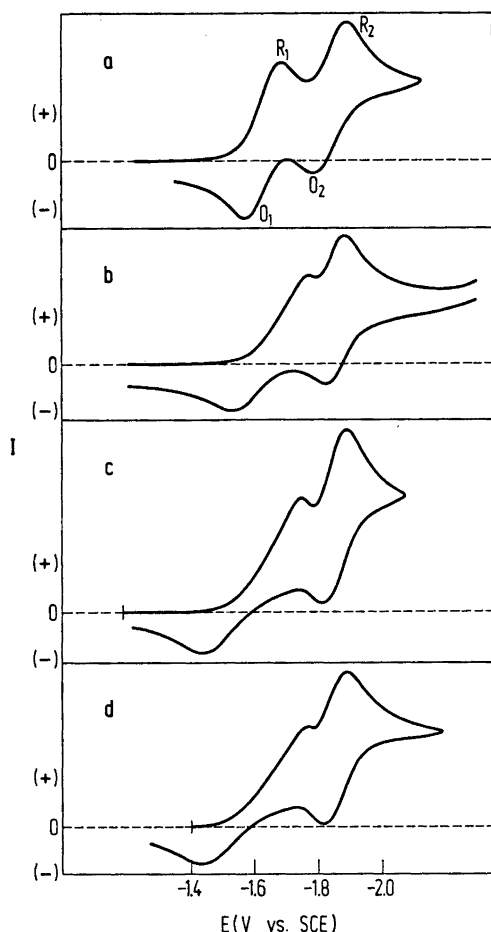
Fig. 2. Cyclic voltammograms of COT on platinum in DMF at 131 mV/s. supporting eleetrolyte (a) Me₄NI (13.5 °C), (b) Et₄NClO₄ (27.5 °C), (c) Pr₄NI (47 °C), and (d) Bu₄NBF₄ (45 °C).

an equimolar amount of azobenzene, which is reduced by two consecutive, well spaced one electron transfers, was added to the solution. The height of the first peak for azobenzene was nearly identical to the for BCOT while the peaks for the second charge transfers from both compounds overlapped and appeared as a single peak. Thus, it is apparent that BCOT is reduced by two consecutive one electron transfers to first the anion radical and then the dianion, the difference in potentials for the two processes being dependent upon the voltammetric conditions.

The latter results suggested that the reduction of COT should be re-examined. Fig. 2a – d show the cyclic voltammograms of COT in DMF at a platinum electrode containing Bu_4N^+ (d), Pr_4N^+ (c), Et_4N^+ (b), and Me_4N^+ (a) ions.* The effect is dramatic, k_s (heterogeneous rate constant for electron transfer) as judged by the separation of oxidation and reduction peaks for the first electron transfer,[9] increased uniformly as the size of the cation decreased. In fact, the rate of charge transfer in the presence of Me_4N^+ was calculated to be of the order of 10^3 times greater than when Bu_4N^+ was the supporting electrolyte cation. Electron transfer is also fast when the supporting electrolyte cation was Bu_4N^+ in the presence of low concentrations of Me_4N^+.

Apparent heterogeneous rate constants (k_{app}) for the first electron transfer to COT in DMF on platinum were determined by cyclic voltammetry[9] and data at various concentrations of Bu_4NBF_4 are summarized in Table 1. According to diffuse double layer theory[10] k_{app} is related to the electrolyte concentration (C) by eqn. (1). Using the value determined ($\alpha = 0.4$) for the transfer coefficient,[3] relative k_{app} values were

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* Electron transfer to COT is faster on mercury than on platinum and on either electrode the rate increases with increasing temperature.

Table 1. Supporting electrolyte concentration effect of COT electron transfer rate in DMF.

[Bu₄NBF₄]	k_{app}^{rel}(Exp) [a]	k_{app}^{rel}(Calc) [b]
0.01	0.4	0.5
0.05	1.0	1.0
0.10	1.4	1.3
0.15	1.6	1.6
0.30	2.2	2.0
0.75	3.1	3.0

[a] Calculated from cyclic voltammograms according to Ref. 9. Voltage sweep rate=131 mV/s
[b] Calculated according to eqn. (1), α=0.4.

all residual water is removed by adding neutral alumina to the cell and stirring immediately before recording the voltammogram, the two electron transfers are distinctly separated (Fig. 1b). The latter effect is readily understood by considering the effect of a follow up chemical reaction of the BCOT dianion. Thus the protonation of $BCOT^{2-}$ by residual water shifts the peak for the second electron transfer so that it merges with the first peak. The two peaks are completely resolved during voltammetry in DMF when the small cation, Me_4N^+, is present in the voltammetric solution (Fig. 1c). To further substantiate that the two consecutive reversible charge transfers involve one electron,

$$k_{app} = k_s(e^{\alpha n F/RT})\ C^\alpha = k_s(\text{constant})C^\alpha \qquad (1)$$

calculated and found to agree remarkably well with the observed values. These data show that when Bu_4NBF_4 is the supporting electrolyte, a significant portion of the apparent activation energy for the first electron transfer is due to the double layer effect and not to a conformational change.

It is evident that studies which involved the use of large tetraalkylammonium ions, Pr_4N^+ [2] and Bu_4N^+ [3] as supporting electrolyte cations during kinetic studies on the electron transfer to COT, were not under optimum conditions and the conformational effect may not be as important as previously [2,3] reported. Our results do show that the electrolyte and double layer effects are greater than any conformational effects but more detailed kinetic studies under optimum conditions are necessary in order to completely clarify the role of the conformational barrier to electron transfer to COT. Further studies on these and related systems are under way.

In conclusion we draw attention to the cyclic voltammogram of COT in acetonitrile containing Me_4N^+ (Fig. 3). The height of the initial reduction peak (R) was nearly identical to that of an equimolar solution of azobenzene in acetonitrile. The reduction obviously involves two consecutive one electron transfers as it does in DMF. It is not clear what the previous report, indicating that the anion radical is "irreducible" in acetonitrile, was founded on.
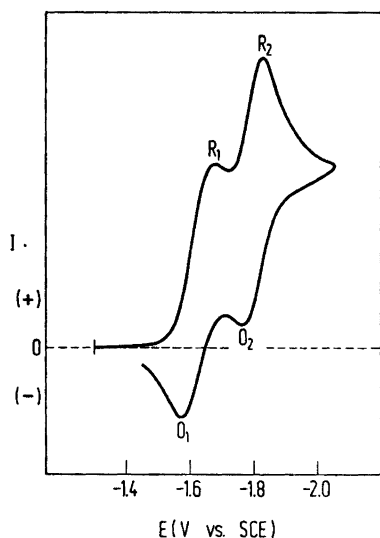
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Fig. 3. Cyclic voltammogram of COT on mercury in acetonitrile (13 °C) containing Bu_4NBF_4 (0.2 M) saturated with Me_4NI. Voltage sweep rate 131 mV/s.