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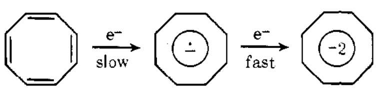
Electrolyte Effects upon the Electrochemical Reduction of Cyclooctatetraene in Dimethyl Sulfoxide

Albert J. Fry,* Clyde S. Hutchins, and (in part) Ling Ling Chung

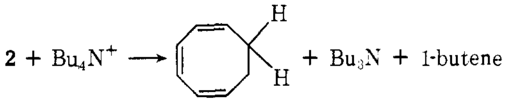
Contribution from the Department of Chemistry, Wesleyan University, Middletown, Connecticut 06457. *Received February 14, 1974*

Abstract: The electrochemical reduction of cyclooctatetraene in dimethyl sulfoxide was studied by a variety of techniques, principally dc and phase-sensitive ac polarography, using tetra-*n*-alkylammonium salts as supporting electrolytes, with the alkyl group ranging in size from methyl to heptyl. Cyclooctatetraene (COT) shows two polarographic waves, associated with its stepwise reduction to the corresponding radical anion and dianion, respectively, in the presence of all electrolytes studied. The rate of heterogeneous electron-transfer to COT decreases markedly as the size of the tetraalkylammonium ion increases. The results are discussed, with emphasis upon the role of electrolytes.

A number of studies of the electrochemical reduction of cyclooctatetraene (COT) (**1**) in aprotic solvents have been reported.[1] Two polarographic waves have generally been observed, with the first wave somewhat drawn out (log-plot slope[2] > 59 mV), suggesting an element of irreversibility to be associated with this reduction step. This behavior contrasts with that exhibited by aromatic hydrocarbons; the first reduction step of such compounds under aprotic conditions is rapid and reversible using a variety of electrochemical criteria and techniques.[3] The generally accepted interpretation of the electrochemical reversibility of the first reduction step of aromatic hydrocarbons is that the electron-transfer step simply involves injection of an electron into the lowest unoccupied molecular orbital of the hydrocarbon, a process involving no bond breaking and little change in molecular geometry and hence has a very low activation energy.[3] The conventional explanation of the polarographic behavior of COT has on the other hand been that the first electron transfer involves a change in molecular geometry, from the initially tub-shaped COT neutral molecule to a planar or nearly planar radical anion, COT$^{\cdot -}$ (**2**), this geometrical change being associated with an increase in the activation energy for electron transfer and hence the observed irreversibility of the first reduction step.[1] This interpretation also implies that the second reduction step of COT should be reversible or nearly so since a minimum of geometrical change would be involved in converting **2** to the planar dianion **3**, and the data apparently support this corollary.[1a,c] The conventional interpretation of the electrochemical behavior of COT has, however, recently been challenged by Thielen and Anderson.[4] They reported the usual two-wave polarogram for **1** in anhydrous acetonitrile containing tetrabutylammonium hexafluorophosphate (TBAHFP) but claimed that the second wave is not observed when tetramethylammonium hexafluorophosphate (TMAHFP) is employed as the supporting electrolyte. They suggested that the second reduction step previously observed for COT and thought to correspond to the reduction of **2** to **3** was actually associated with the reduction of the radical HCOT· (**4**) generated by a Hofmann elimination by **2** upon the tetrapropyl- (TPA) or tetrabutylammonium (TBA) salts previously employed as supporting electrolytes in the reduction of **1**, *e.g.*



1 2 3



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They argued further that when this elimination is prevented through use of tetra*methyl*ammonium (TMA) ion, no second wave for reduction of **2** to **3** could be observed, supported their argument by reference to the calculations of Dewar and coworkers[5] on the relative energies of **1**, **2**, and **3**, and expressed doubts concerning the possibility of reduction of **2** to **3** by alkali metals. We were led to question the conclusions of Thielen and Anderson for a number of reasons, however. First, the evidence from nmr, uv, and ir spectroscopy[6,7] that the product of reaction between 1 mol of **1** and 2 gram-atoms of potassium is indeed the dipotassium salt of **3** seems very strong. Second, an apparent internal inconsistency appeared in the paper; it was claimed that **4** is *easier* to reduce than **1** when formed *via* protonation of **2** by added water but *harder* to reduce than **1** when formed *via* protonation of by tetrabutylammonium ion. Third, it had been reported previously that COT does in fact exhibit two polarographic waves in the presence of tetramethylammonium ion.[8] Finally, it was clear, and in fact has previously been pointed out,[9] that MO calculations, such as those of Dewar,[5] may not be applied to electrochemical measurements in solution, because ion pairing and solvation both act to decrease the energy necessary to add a second electron to hydrocarbon radical anions. Even in a solvent as polar as dimethyl sulfoxide (DMSO), ion pairing of aromatic radical anions and dianions with tetraalkylammonium ions is significant,[10] and indeed it is generally recognized that ion pairing must be considered examining the electrochemical behavior of aromatic and other species in aprotic organic solvents.[11] Because of the considerable im-

Table I. Polarographic Behavior of Some Hydrocarbons in Dimethyl Sulfoxide

Hydrocarbon[a]	Supporting electrolyte[b,c]	First wave $-E_{1/2}$, V[d]	First wave i_d, μA	First wave Slope, mV[e]	Second wave $-E_{1/2}$, V[d]	Second wave i_d, μA	Second wave Slope, mV[e]
COT	$(CH_3)_4NPF_6$	1.87	2.92	68	2.03	1.52	44
COT	$(C_2H_5)_4NBr$	1.87	3.17	88	2.11	1.58	43
COT	$(C_3H_7)_4NBF_4$	1.87	2.44	92	2.10	1.47	54
COT	$(C_4H_9)_4ClO_4$	1.92	2.48	123	2.11	1.44	51
COT	$(C_5H_{11})_4NI$	2.04	2.58	122	2.11	1.39	53
COT	$(C_6H_{13})_4NClO_4$[j]	2.03	1.6	100	2.16	1.9	~80
COT	$(C_7H_{15})_4NI$[j]	2.02	~1.3	~130	2.14	1.1	~80
Anthracene[f]	$(CH_3)_4CPF_6$[h]	2.21	2.30	60	2.68	1.55	48
Anthracene[f,g]	$(CH_3)_4NPF_6$[h]	2.19	1.80	56	2.60	1.25	46
Anthracene[f]	$(C_4H_9)_4NClO_4$	2.14	3.85	62	2.75	2.25	52
9,10-Diphenylanthracene[i]	$(CH_3)_4NPF_6$	2.26	1.5	55	2.72	0.78	50
9,10-Diphenylanthracene[i]	$(C_4H_9)_4NClO_4$	2.25	0.85	60	2.78	0.86	53
Pyrene[f]	$(CH_3)_4NPF_6$[h]	2.32	2.20	58	2.80	1.70	70
Pyrene[f,g]	$(CH_3)_4NPF_6$[h]	2.31	1.70	60	2.70	1.39	40
Pyrene[f]	$(C_4H_9)_4NClO_4$	2.31	2.10	60	2.86	1.30	75

[a] Concentration of electroactive substance is 1 m*M*, except where noted. [b] Electrolyte concentration is 0.1 *M*. [c] Groups larger than ethyl are all *n*-alkyl. [d] Potentials measured relative to Ag|0.1 *M* $AgNO_3$–0.1 *M* Bu_4NClO_4. [e] Slope of a plot of log $i/(i_d - i)$ *vs.* *E*. [f] 0.74 m*M*. [g] Added water (2.8 *M*). [h] 0.15 *M*. [i] 0.5 m*M*. [j] Polarographic diffusion currents and slopes are considered unreliable for these two electrolytes because of the poorly defined nature of the waves.

portance of the conclusions of Thielen and Anderson, should they prove correct, and in connection with concurrent experiments involving electrolyte effects upon the polarographic reduction of alkyl halides[12] and aromatic hydrocarbons,[10] it was decided to investigate electrolyte effects upon the electrochemical reduction of COT.[13] The solvent was DMSO; supporting electrolytes were a series of tetraalkylammonium (R_4N^+) salts, in which R ranged in size from methyl through *n*-heptyl. The electrochemical techniques employed consisted of dc and phase-sensitive ac polarography.[13,14] The results are relevant not only to the question of the electrochemical reducibility of **2** to **3** but also demonstrate a substantial and unexpected correlation between the size of the tetraalkylammonium ion and the rate of heterogeneous electron transfer to **1**. We also offer some comments upon ion pairing and the use of data such as Dewar's[5] to estimate reduction potentials of intermediates.[15]

Experimental Section

General. Electrochemical measurements were carried out using a Princeton Applied Research (PAR) Model 170 electrochemical instrument. Electrolytes were recrystallized from water whenever necessary to remove traces of electroactive materials and dried overnight in an Abderhalden drying pistol. Cyclooctatetraene was distilled *in vacuo* at roughly 2-month intervals, then stored under nitrogen at −78° to inhibit autoxidation and thermal dimerization.[16] Dimethyl sulfoxide (Matheson Colemen and Bell reagent grade) was used as received. The polarographic behavior of cyclooctatetraene was found to be unchanged in a sample of this solvent dried over molecular sieve. The reference electrode consisted of a silver wire immersed in a solution of 0.1 *M* silver nitrate and 0.1 *M* tetrabutylammonium perchlorate in dimethyl sulfoxide and was separated from the polarographic solution by a fine porosity ceramic plug. A fresh reference electrode was prepared each day.

Computations. The closely-spaced dc polarographic waves for COT were resolved in all cases using the multiparameter least-square curve-fitting computer program CFT3 developed by Meites;[17a] the two-wave polarograms were fitted to the five-parameter equation[17b]

$$i = \frac{i_{d_1}}{1 + \exp[(E - E_{1/2,1})/S_1]} + \frac{i_d - i_{d_1}}{1 + \exp[(E - E_{1/2,2})/S_2]}$$

where i_{d_1} and $i_d - i_{d_1}$ ($\equiv i_{d_2}$), $E_{1/2,1}$ and $E_{1/2,2}$, and S_1 and S_2 are the heights, half-wave potentials, and log-plot slopes (to the base *e*) of the first and second waves, respectively, and i_d is the combined height of the two polarographic waves, using the measured value of i_d and values of *E* and *i* measured at a large number (17–45, depending upon the run) of points along the rising portion of the polarograms. A number of computations were carried out for each electrolyte, some on the same polarogram, some on replicate polarograms. The data in Table I represent an average of four computations per electrolyte.

Results

Dc Polarography. Dc polarograms for COT (10^{-3} *M*) in DMSO containing a variety of supporting electrolytes (0.1 *M*) are illustrated in Figure 1. Several characteristic quantities measured from these polarograms using the computer technique described in the Experimental Section are tabulated in Table I, along with data measured from the polarograms of the polycyclic aromatic hydrocarbons anthracene (**5**), 9,10-diphenylanthracene (**6**), and pyrene (**7**) which are presented for comparison purposes.

The dc polarographic behavior of COT in the presence of tetrabutylammonium ion closely resembles that reported by others.[1,4,18] Noteworthy features of the series of polarograms shown in Figure 1 include the following: (a) COT exhibits two polarographic waves in the presence of all electrolytes studied; (b) the polarograms exhibit a continuous change in appearance with increasing size of the cation of the supporting electrolyte; (c) this change is in the direction of increasingly irreversible behavior as judged by the increasingly drawn-out appearance and loss of definition as the cation size increases;[19] (d) spacing between the two polarographic waves, $\Delta E_{1/2}$, defined as the difference (in volts) between the half-wave potentials of the two waves, is less with tetramethylammonium ion that with tetrabutylammonium (*cf.* Table I); (e) except for the polarograms with the two largest electrolytes, the ratio of the height of the first wave to that of the second remains essentially constant (1.9 ± 0.2) with changes in the supporting electrolyte. Because of the loss of definition in the polarograms with the two largest electrolytes, computed values of the various parameters are very sensitive to the number of points chosen for analysis and are regarded as less reliable than the others. It may also be that $k_{s,h}$ has become so small with these electrolytes (*vide infra*) that the polarogram is not described by the five-parameter equation given in the Experimental Section.

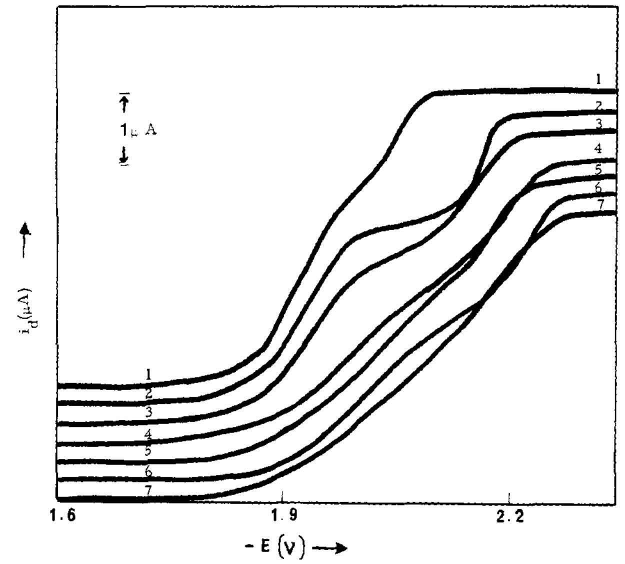

Figure 1. Dc polarograms of cyclooctatetraene in dimethyl sulfoxide. Electrolytes: **1**, $(CH_3)_4NPF_6$; **2**, $(C_2H_5)_4NBr$; **3**, $(n\text{-}C_3H_7)_4NBF_4$; **4**, $(n\text{-}C_4H_9)_4NClO_4$; **5**, $(n\text{-}C_5H_{11})_4NI$; **6**, $(n\text{-}C_6H_{13})_4NClO_4$; **7**, $(n\text{-}C_7H_{15})_4NI$. [Electrolyte]: 0.1 *M;* [cyclooctatetraene]: 1 m*M*. Reference: Ag|0.1 *M* $AgNO_3$–0.1 *M* $(C_4H_9)_4NClO_4$. Polarograms are displaced vertically and scaled to uniform wave height for ease of comparison.

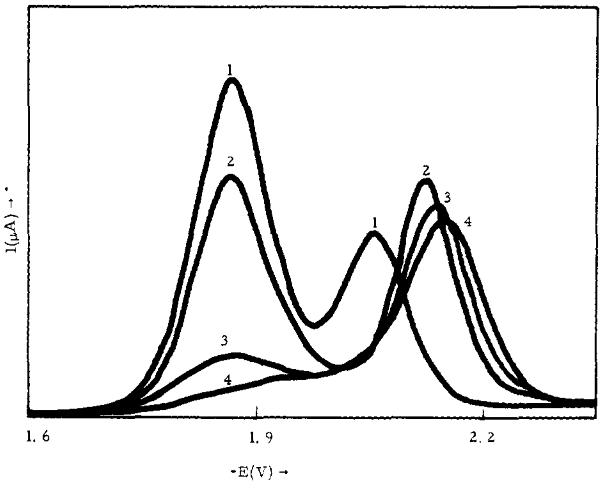

Figure 2. Ac polarograms of cyclooctatetraene in dimethyl sulfoxide. Electrolytes: **1**, $(CH_3)_4NPF_6$; **2**, $(C_2H_5)_4NBr$; **3**, $(n\text{-}C_3H_7)_4NBF_4$; **4**, $(n\text{-}C_4H_9)_4NClO_4$. Superimposed ac signal: 10 m*V* peak-to-peak, 85 Hz. Other conditions as in Figure 1.

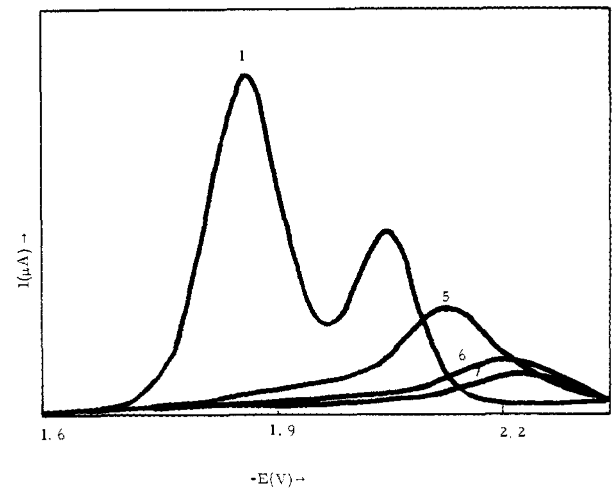

Figure 3. Ac polarograms of cyclooctatetraene in dimethyl sulfoxide. Electrolytes: **1**, $(CH_3)_4NPF_6$; **5**, $(n\text{-}C_5H_{11})_4NI$; **6**, $(n\text{-}C_6H_{13})_4NClO_4$; **7**, $(n\text{-}C_7H_{15})_4NI$. Other conditions as in Figure 2.

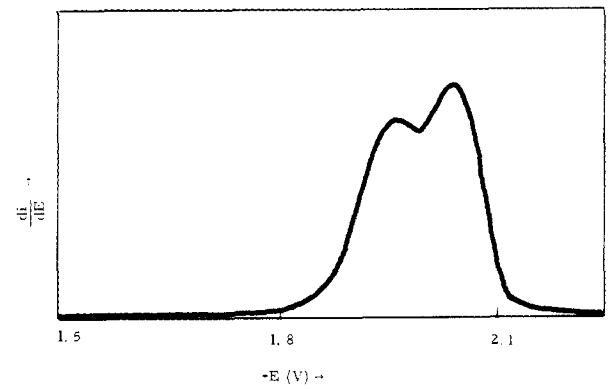

Figure 4. Derivative pulse polarogram of cyclooctatetraene in dimethyl sulfoxide containing 0.1 *M* $(CH_3)_4NPF_6$ and 5 *M* water.

Because the appearance of the dc polarograms suggested that the nature of the heterogeneous electron-transfer process is affected by the supporting electrolyte, COT was examined by phase-sensitive ac polarography, using the same electrolytes as in the dc experiments. It is recognized that ac polarography is an excellent technique for studying heterogeneous electron-transfer, and it has in fact previously been applied to the electroreduction of COT in dimethylformamide containing tetrabutylammonium ion.[1c] The faradaic component of the total ac current resulting from application of a 10 mV (peak-to-peak) signal to the dc ramp was phase selected and recorded. The ac polarographic dependence upon the nature of the supporting electrolyte is illustrated by the set of polarograms shown in Figures 2 and 3. (The data are presented in two sets for improved ease of examination.) These polarograms were all recorded at 85 Hz. As the frequency of the applied ac signal was increased, the first peak generally became smaller. The first peak in the presence of tetramethylammonium ion was of substantial magnitude at all frequencies examined; at the highest frequency, 800 Hz, the first peak had diminished to the point that the two peaks were of equal height. Conversely, the first ac peak in the presence of large ions, *e.g.*, tetrabutylammonium, was only slightly enhanced at the lowest frequency examined (10 Hz). As with the dc polarograms, a continuous progression in the ac polarographic behavior of COT is observed as the size of the supporting electrolyte is increased. The fact that the ac polarogram in the presence of tetrabutylammonium ion closely resembles that observed by Huebert and Smith under similar conditions in DMF[1c] again indicates that the electrochemical behavior of COT is not anomalous in DMSO.

Addition of 2,4,5-trimethylphenol (TMP) (8 m*M*) to a 0.7 m*M* solution of COT in DMSO containing TMAHFP caused an increase in height of the first wave by a factor of 2 and the disappearance of the second wave. This is consistent with behavior previously reported for COT[4] and indicates that radical **4** must be more easily reduced than **1**.[3] Addition of small amounts of water (<50 mmol) had no effect upon the polarographic behavior of COT; this is as expected, in view of the fact that water is a very poor proton donor in DMSO because of strong association between water and DMSO.[20,21] Addition of large amounts of water (0.5–5.0 mol) caused the two polarographic waves to coalesce into a single two-electron wave. Unlike the TMP result, however, this wave is *not* simply due to an ECE process[3] involving protonation of **2** to form **4** and reduction of the latter. This was demonstrated by measuring a derivative dc pulse polarogram of COT in the presence of 5 mol of water (Figure 4). Two reduction steps are clearly visible, indicating that this apparent two-electron wave actually corresponds to two very closely spaced one-electron waves, *i.e.*, that the two waves observed in the absence of added water have merely shifted closer together in the presence of water. This type of behavior is general and has been observed before with aromatic hydrocarbons.[3] It is associated with a shift of the second wave to more positive potentials as a consequence of protonation of the corresponding dianion; other examples are shown in Table I, where it may be seen that addition of water to the medium decreases the spacing ΔE between the two polarographic waves of anthracene and pyrene.

The fact that even 5 mol of water does not protonate **2** is a vivid demonstration of the fact noted above, that water is a very poor proton donor in DMSO. This can be observed in an equally striking manner by observing the effect of added water upon the polarographic wave heights of **5** and **7** in DMSO (Table I). Addition of a large amount (2.8 mol) of water to the polarographic medium, far from causing an increase in the height of the first wave due to incursion of the ECE process, actually causes a *decrease* in the height of the two polarographic waves. This behavior is undoubtedly a consequence of the increased viscosity of DMSO–water solutions over DMSO itself.[20] Even if water did not associate with DMSO, one would expect the effects of added water to be less significant than in low-viscosity solvents such as acetonitrile or tetrahydrofuran, although not to the extent noted here.

Discussion

The results of dc and ac polarographic experiments upon COT in the presence of a wide variety of supporting electrolytes conclusively demonstrate that reduction of the COT radical anion to the corresponding dianion is feasible at potentials accessible in organic solvents, in agreement with the conclusion of a number of other investigators[1,8] and in contrast to the interpretation of Thielen and Anderson.[4] More important, however, there is a striking electrolyte effect upon the polarographic reduction of COT. The dc and ac polarographic experiments, particularly the latter, demonstrate clearly that the rate constant for the first heterogeneous electron transfer to COT, $k_{s,h}$, increases as the size of the supporting electrolyte decreases, such that reduction in the presence of the TMA ion is almost reversible by the criterion of polarographic log-plot slope.[2] At the same time, the log-plot slope is independent of the nature of the supporting electrolyte for the aromatic hydrocarbons **5–7**. It is possible that an electrolyte effect may even be operating upon electron-transfer rates to the latter compounds, but that the inherently high values of $k_{s,h}$ exhibited by such compounds[3] are such that even with large electrolytes the rates are too high for electrolyte-induced changes to be detected by ac or dc polarography. Electron transfer to COT is rather slow, however ($k_{s,h} = 2.0 \times 10^{-3}$ cm sec^{-1} at 25° in DMF containing TBAP),[1c] and hence is in the range in which electrolyte effects upon $k_{s,h}$ can be detected. If this interpretation is correct, one would expect behavior similar to that of COT to be exhibited by other quasi-reversible systems, and that in fact the electrolyte effects upon $k_{s,h}$ which we observe may be very general. Evidence is accumulating that this is very likely the case. While our experiments were in progress, a paper appeared describing similar behavior for some rate earth ions in the presence of tetraalkylammonium salts,[22] and there is some evidence that long chain tetraalkylammonium ions can on occasion partially or totally inhibit electron transfer to a substrate because of their strong absorption at the mercury–solution interface.[23] However, all examples of such behavior previously discovered have been observed in aqueous media. It is generally believed that the decreasing aqueous solubility of tetraalkylammonium salts with increasing cation size results in an increasing tendency of the cation to accumulate at the solution–electrode interface, *i.e.*, to be adsorbed on the electrode and thus inhibit electron transfer. To our knowledge, our observations represent the first case of such behavior in an aprotic organic solvent, in which the solubility of the tetraalkylammonium salts *increases* with increasing cation size. We expect that totally irreversible systems ought to exhibit such effects to a very marked degree, and this appears to be true from studies of the dependence of the electrolyte dependence of the polarographic behavior of alkyl halides.[10,24] The origin of this electrolyte effect remains to be elucidated.

It will be noted that $\Delta E_{1/2}$ for all substrates in Table I is smaller for TMA as counterion that for TBA. This is undoubtedly a consequence of the facts that[9,10,25] (a) for steric reasons, ion pairing will be less important as cation size increases; (b) dianions will ion-pair much more effectively than monoanion radicals;[25] and (c) $\Delta G°$ for the disproportionation reaction

$$2R\cdot^{-} \rightleftharpoons R + R^{2-}$$

will be approximated by $-n\mathcal{F}\Delta E_{1/2}$. Ion pairing should become more important, and hence $\Delta E_{1/2}$ should decrease, as one proceeds through this series: (1) TBA counterion, polar solvent; (2) TMA counterion, polar solvent; (3) alkali metal counterion, nonpolar solvent. Our observations satisfy this prediction for the first two, and the nmr experiments of Katz complete the series by demonstrating that under the last-named set of conditions, disproportionation of the radical anion is actually exothermic.[6] Under the latter conditions, one would then expect a single two-electron polarographic wave for COT, and indeed this has now been observed by Lehmkuhl.[15b] Such behavior has been observed with several other substrates. Azobenzene, for example, exhibits two one-electron waves in DMF in the presence of tetraalkylammonium ions[26,27] but a single two-electron wave in the presence of lithium ion,[27] and chemical experiments show that disproportionation is exothermic only in the presence of lithium ion.[27] Completely analogous behavior has been observed with benzil.[28,29] Extension of this reasoning suggests that the polarogram observed by Anderson and Thielen may represent two coalesced one-electron waves, which would also be consistent with the report that the one wave in the presence of TMAHF (a) has $E_{1/2}$ *negative* of the first wave in the presence of TBAHFP, and (b) encompasses a total potential span as wide as both waves in the presence of TBAHFP.[4] The height of this wave was reported, however, to correspond only to a one-electron reduction.[4] We are unable to resolve this apparent discrepancy.

Thielen and Anderson[4] referred to MO computations by Dewar, *et al.*,[5] to support the contention that reduction of **2** to **3** is not feasible at potentials accessible in organic solvents. As mentioned in the introductory section it is known that such calculations are not transferable to electrochemical measurements in solution since the calculations (essentially gas-phase data) do not include effects of ion pairing and solvation.[9] These effects are very sizable; the computed heats of atomization, for example, of the anthracene molecule, radical anion, and dianion by the π-MO method[30] are 2856.6, 2651.0, and 2342.4 kcal/mol,[31] respectively, from which one may calculate that disproportionation of the anthracene radical anion should be endothermic by 103.1 kcal/mol, *i.e.*, that the two polarographic waves for anthracene should be separated by *ca.* 4.47 V; the experimental values (Table I) are far smaller (0.4–0.5 V).

The second wave for COT in the presence of TBA ion cannot be due to the reduction of **4** generated by a Hofmann elimination by **2** upon the supporting electrolyte. Two arguments may be adduced in support of this conclusion. (a) The relative heights of the first and second waves remain remarkably constant (*cf.* Table I) as the size of the electrolyte is changed, even with tetramethylammonium ion, which cannot undergo a Hofmann elimination. (b) Using this ratio measured for COT in the presence of tetrabutylammonium ion, in conjunction with polarographic theory for the ECE process as developed by Nicholson,[32] and using the postulate that the second wave is indeed due to the reduction of **4,** we calculate that the half-life of **2** in the presence of an electrolyte undergoing the Hofmann elimination should be on the order of 0.5–1.0 sec, while Allendoerfer and Rieger have observed, using esr spectroscopy, that the half-life of **2** in dimethylformamide containing tetrapropylammonium perchlorate is 1.0 ± 0.1 hr.[33] The fact that the second polarographic wave is smaller than the first may be a consequence of decreased polarographic drop-times with increasingly negative potentials and/or repulsion of negatively charged COT species from the negative electrode surface. The second wave for anthracene, whose electrochemistry proceeds in straightforward fashion through the radical anion and dianion,[3] is also smaller than the first (Table I).

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(13) Derivative dc, pulse, and derivative pulse polarograms were also measured for COT in the presence of each electrolyte, but these techniques provided little information not also contained in the dc and ac polarograms; hence they are not reported herein, although the data are available from the senior author.

(14) Petrovich carried out a dc polarographic study of COT in dimethylformamide, also using electrolytes of varying size.[8] The polarograms were not shown; rather, half-wave potentials (presumably visually estimated) for each wave were presented in tabular form. Because of the closeness of the two waves, we believe that they are best resolved by computational techniques, hence we believe our data to be more reliable, as well as more extensive.

(15) (a) After our experiments were completed, there appeared a paper by Lehmkuhl, *et al.*,[15b] presenting conclusions similar to ours with respect to the role of ion pairing in COT electrochemistry and to the validity of the Anderson–Thielen mechanism. This paper, however, related data taken in tetrahydrofuran, in which ion pairing is more important than in DMSO. These authors did not use ac polarography; hence the effect of electrolytes upon electron-transfer rates to COT was not discovered by them. (b) H. Lehmkuhl, S. Kintopf, and E. Janssen, *J. Organometal. Chem.*, **56**, 41 (1973).

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