

H_3O_4^+ or at least it is highly hydrated.²² In experiments related to these, ions of mass as high as H_3O_4^+ have been observed as products of ionic reactions in water at pressures up to several tenths of a torr at about 200°, but in dimethyl ether the highest protonated

(22) See the article by M. Eigen and L. DeMayer in "Structure of Electrolytic Solutions," W. J. Hamer, Ed., John Wiley and Sons, Inc., New York, N. Y., 1959.

species observed was $(\text{CH}_3\text{OCH}_3)_2\text{H}^+$. These are preliminary results which will be studied further, but they indicate the marked differences in solvation of ions by different solvents.

Acknowledgment. The author is grateful to Mr. W. C. Gieger for performing these experiments with his accustomed excellence and to Dr. F. H. Field for his helpful discussions.

Electrolytic Reduction of Cyclooctatetraene¹

Robert D. Allendoerfer² and Philip H. Rieger

Contribution from the Metcalf Chemical Laboratories, Brown University, Providence, Rhode Island 02912. Received December 28, 1964

The reduction of cyclooctatetraene has been studied in *N,N*-dimethylformamide and dimethyl sulfoxide by the techniques of d.c. polarography, triangular wave oscillopolarography, and a.c. polarography. It was found that cyclooctatetraene is reduced in two one-electron steps. Previous experiments in which the anion radical was found to disproportionate have been explained on the basis of reactions of the cyclooctatetraene dianion with alkali metal ions to form tightly bound complexes or with water to form cyclooctatrienes. The electron spin resonance spectrum of cyclooctatetraene anion radicals, produced by controlled-potential electrolysis in DMF, was virtually identical with previous results. The first electron transfer to cyclooctatetraene was found to be slow and to proceed through a transition state which resembles planar cyclooctatetraene. The cathodic transfer coefficient was found to be significantly less than 0.5, and a suggestion is made regarding its interpretation. Rapid electron transfer to the anion radical was observed, and the significance discussed. The difference between the two half-wave potentials of the hypothetical planar conformer was estimated to be about 0.80 v.

Introduction

Cyclooctatetraene, the mechanism of its reduction, and the nature of its reduction products have attracted considerable interest in recent years.³⁻¹¹ It has been shown polarographically that cyclooctatetraene in 50% aqueous ethanol^{3,5} or 96% dioxane-water⁹ undergoes a two-electron reduction. In tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) cyclooctatetraene is reduced by alkali metals primarily to the dianion.

(1) Supported in part by a grant from the National Science Foundation and by the ARPA program at Brown University.

(2) Du Pont Teaching Fellow, 1964-1965.

(3) R. M. Eloffsen, *Anal. Chem.*, **21**, 917 (1949).

(4) A. C. Cope, *J. Am. Chem. Soc.*, **72**, 2515 (1950).

(5) J. H. Glover and H. W. Hodgson, *Analyst*, **77**, 473 (1952).

(6) L. E. Craig, R. M. Eloffsen, and I. J. Ressa, *J. Am. Chem. Soc.*, **75**, 480 (1953).

(7) T. J. Katz, *ibid.*, **82**, 3784, 3785 (1960).

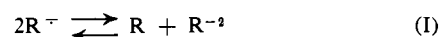
(8) T. J. Katz and H. L. Strauss, *J. Chem. Phys.*, **32**, 1873 (1960).

(9) T. J. Katz, W. H. Reinmuth, and D. E. Smith, *J. Am. Chem. Soc.*, **84**, 802 (1962).

(10) H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *ibid.*, **85**, 2360 (1963).

(11) A. Carrington and P. F. Todd, *Mol. Phys.*, **7**, 1525 (1964).

Under these conditions, the equilibrium



lies very far to the right with $\Delta F_d = -0.48$ e.v. although the anion radical of cyclooctatetraene was detected by electron spin resonance (e.s.r.) spectroscopy.^{8,10} Evidence for the planarity of both anions has been presented.^{7,8,10,11}

The position of the disproportionation equilibrium, reaction I, for aromatic hydrocarbons has been found, in general, to lie far to the left,^{12,13} primarily because of electron repulsion in the doubly filled molecular orbital of the dianion.¹⁴ Katz^{9,10} has pointed out that if the compression energy required to flatten the cyclooctatetraene ring exceeds the electron repulsion energy, attenuated by solvation, then the disproportionation equilibrium may lie to the right. For most aromatic hydrocarbons, the free energy of reaction I is on the order of $\Delta F_d = +0.4$ e.v.^{9,12,13}; thus, assuming the same value for hypothetical planar aromatic cyclooctatetraene, the compression energy must be approximately 21 kcal./mole to account for the observed results.¹⁰

In the present work, we have investigated the reduction of cyclooctatetraene by a number of polarographic techniques as well as by e.s.r. spectroscopy. The polar aprotic solvents *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were used to avoid the effects of water or alkali metal ions.

In the following, we shall show that: (1) the monoanion is stable to disproportionation in DMF or DMSO in the absence of alkali metal ions; (2) the e.s.r. spectrum of the monoanion radical in DMF is virtually identical with those obtained previously in THF or DME; (3) the electron-transfer reaction, $\text{R} + \text{e}^- \rightleftharpoons \text{R}^-$, is slow with an activation free energy comparable with the energy estimated to be required to flatten the cyclooctatetraene ring; (4) electron transfer to the monoanion to form the dianion is very rapid; (5) in the presence of water, both anions are rapidly protonated, thus coalescing the two polarographic

(12) G. J. Hoijtink, *Rec. trav. chim.*, **74**, 1525 (1955).

(13) G. J. Hoijtink, E. de Boer, P. H. van der Meij, and W. P. Weijland, *ibid.*, **75**, 487 (1956).

(14) N. S. Hush and J. Blackledge, *J. Chem. Phys.*, **23**, 514 (1955).

waves to one apparent two-electron wave; and (6) the product resulting from protonation of the anions in DMF is principally 1,3,5-cyclooctatriene rather than a mixture of the two possible isomers as had been observed in more protic solvents.

Experimental

Polarographic Measurements. An electronic polarograph similar to that described by Kelley, *et al.*,¹⁵ with modifications to permit a.c. and oscillopolarographic work,¹⁶ was used.

The a.c. polarographic experiments were performed with an applied voltage of 5.0 mv. (peak to peak). Polarograms were determined at nominal frequencies of 9, 36, 81, 144, 225, 441, and 1000 sec.⁻¹. Alternating current in the a.c. polarographic experiments was measured with an Electronics, Missiles and Communications Model RJB lock-in amplifier. The phase of the reference signal in the lock-in amplifier was adjusted so as to measure the component of the current in phase with the a.c. voltage applied to the cell. Experiments using an RC dummy cell¹⁷ indicated that negligible error resulted from this method of detection over the frequency range covered.

A thermostated cell was used for all polarographic measurements except the room temperature oscillopolarographic work. Temperature of the heat exchange liquid (heptane or ethylene glycol) was maintained constant to $\pm 0.1^\circ$ although the temperature of the polarographic solutions was as much as 0.5° higher or lower at the extreme temperatures.

All polarographic work was done in a three-electrode configuration, with a dropping mercury electrode cathode and mercury pool anode. Solution potentials in the d.c. and oscillopolarographic experiments were measured using a saturated calomel electrode (s.c.e.) with a 1.2-mil Teflon film¹⁸ as the liquid junction membrane. In order to further prevent contamination of the solutions by water or potassium ions, the reference electrode was isolated from the bulk of the solution by an ultrafine fritted glass disk. Tests of systems of known half-wave potentials and wave shapes failed to show any effects of *IR* drop in the reference circuit of the polarograph. In the a.c. polarographic measurements, a second mercury pool electrode was used as the reference.

Electron Spin Resonance Experiments. Electron spin resonance spectra were obtained with a superheterodyne spectrometer similar to that described by Hirshon and Fraenkel.¹⁹ Radicals were generated by controlled potential electrolysis in a cell external to the resonance cavity.²⁰

Purification of Chemicals. Cyclooctatetraene was obtained from Aldrich Chemical Co. and was distilled twice, b.p. 48° at 31 mm., n_D^{25} 1.5340 (literature value 1.5348).⁴ The sample was stored frozen. The purity of the sample was checked by n.m.r., gas-liquid chromatography, and infrared spectroscopy.²¹ Styrene-

free cyclooctatetraene prepared according to the method of Cope⁴ gave a polarogram identical with that of the freshly distilled sample, as did a sample purified by repeated freezing.

Dimethylformamide was refluxed with benzene and vacuum distilled twice from sodium carbonate. Dimethyl sulfoxide was refluxed with benzene and vacuum distilled. Tetra-*n*-propylammonium perchlorate was prepared from Eastman tetra-*n*-propylammonium hydroxide by neutralization with perchloric acid, recrystallization from 20% aqueous acetonitrile, and a second recrystallization from 2:1:1 ether-methanol-acetonitrile. The salt was dried over P_2O_5 *in vacuo*. Eastman tetra-*n*-butylammonium iodide was recrystallized from 20:1 ether-methanol and dried over P_2O_5 . Potassium perchlorate was dried overnight at 110° and stored over P_2O_5 .

Cyclooctatrienes. A 5-ml. sample of cyclooctatetraene was reduced by sodium in an *N*-ethylaniline-ethyl ether mixture according to the method of Craig, *et al.*⁶ The product mixture was separated by fractional distillation at reduced pressure. The 2-ml. fraction, collected at $55-56^\circ$ and 40 mm., was light yellow, probably owing to a small amount of cyclooctatetraene and showed an inflection at 265 $m\mu$ in its absorption spectrum. The 1-ml. fraction, collected at $62-64^\circ$ and 40 mm., was clear and showed a maximum of 263 $m\mu$ in its absorption spectrum. The relative boiling points and ultraviolet spectra served to identify the fractions as 1,3,6- and 1,3,5-cyclooctatriene, respectively.⁴

Results

Direct Current Polarography. Polarograms of cyclooctatetraene in DMF or DMSO, containing 0.1 *M* tetra-*n*-propylammonium perchlorate as the supporting electrolyte, showed three well-defined waves and a fourth much smaller wave. Half-wave potentials, reciprocal slopes from plots of $\log(i_d - i)/i$ vs. ϵ , and relative diffusion currents are given in Table I.²² The fourth wave was only barely detectable in the d.c. polarograms in DMF and could not be investigated in detail. The slopes for the first two waves are sufficiently close to the theoretical value of 0.059 that these waves may be considered to involve one electron each and represent reduction of cyclooctatetraene to the radical anion and dianion, respectively.

Table I. Polarographic Constants of Cyclooctatetraene at 25°

Wave	DMF			DMSO		
	$\epsilon_{1/2}^a$	Slope ^b	i_d^c	$\epsilon_{1/2}^a$	Slope ^b	i_d^c
I	-1.62	0.063	1.11	-1.56	0.065	1.03
II	-1.86	0.056	0.89	-1.79	0.057	0.97
III	-2.38	0.044	0.84	-2.32	0.045	1.18
IV	-2.55	...	0.09

^a Half-wave potentials vs. s.c.e., estimated accuracy ± 0.01 v. ^b Reciprocal slope from plot of $\log(i_d - i)/i$ vs. ϵ ; estimated accuracy ± 0.001 . ^c Diffusion current in arbitrary units; third and fourth waves corrected for drop time; estimated accuracy ± 0.05 .

Polarograms were determined for DMF solutions of

(21) E. R. Lippincott, R. C. Lord, and R. S. McDonald, *ibid.*, 73, 3370 (1951).

(22) Similar results have been obtained by A. H. Maki, private communication.

(15) M. T. Kelley, D. J. Fisher, and H. C. Jones, *Anal. Chem.*, 31, 1475 (1959).

(16) D. E. Smith, *ibid.*, 35, 1811 (1963).

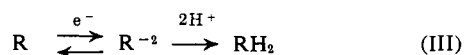
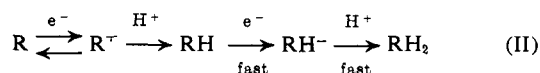
(17) M. E. Peover, *J. Chem. Soc.*, 4540 (1962).

(18) Obtained from Dilectrix, Inc., Farmingdale, L. I., N. Y.

(19) J. M. Hirshon and G. K. Fraenkel, *Rev. Sci. Instr.*, 26, 34 (1955).

(20) P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Am. Chem. Soc.*, 85, 683 (1963).

1,3,5- and 1,3,6-cyclooctatriene. The half-wave potentials were -2.38 and -2.55 v., respectively. Reduction of aromatic hydrocarbons generally has been found to lead to a two-electron reduction product, but by two different routes.^{13,23}



Protonation of a radical anion leads to a radical which is more easily reduced than the parent hydrocarbon and, so, is reduced at the same potential to the two-electron product. On the other hand, if the monoanion is stable or is only slowly protonated, the dianion formed at a more cathodic potential may be attacked by the proton donor, generally to give the same product. Hoijtink²³ showed that, in 96% dioxane-water, the polarographic diffusion current ratio of the first to second waves of anthracene increased as the pH was decreased and attributed this to the increased speed of the protonation step in reaction II. In the present experiments, the ratio of the first to second wave and, similarly, the ratio of the third to the sum of the first two waves increased with temperature and with the amount of water in the solvent. Table II summarizes the temperature effect for a DMF solution of cyclooctatetraene containing a slightly greater amount of water than the solutions from which the data of Table I was obtained. The temperature effect is readily understandable since the rate of protonation of the monoanion is expected to increase with temperature. The total height of the first two waves, however, represents the over-all addition of two electrons to cyclooctatetraene, regardless of the mechanism.

The principal temperature dependence of the polarographic diffusion current is through changes in the diffusion coefficient²⁴ which is related to the diffusion current by the Ilkovic equation.^{25,26} The approximate activation enthalpy of diffusion may be determined by an Arrhenius plot of $\log i_d$ vs. $1/T$. Thus, we find for the data of Table II, $\Delta H_D^* = 3.86 \pm 0.18$ kcal./mole for diffusion of cyclooctatetraene in DMF. The total diffusion current of the first and second waves was used in the plot to avoid complications from the protonation reactions.

The wave shapes, measured by the reciprocal slopes or by $\epsilon_{3/4} - \epsilon_{1/4}$ and given in Tables I and II, show two effects. The first wave at -25 and 0° shows $\epsilon_{3/4} - \epsilon_{1/4}$ greater than 0.047, the reversible value, while at 75° , the opposite effect is seen. This is indicative of significant irreversibility at low temperatures, and, at high temperatures, the increased rate of the following protonation reaction which leads to an increase in the number of electrons involved in the reduction. The second wave at low temperatures, shows a width close to the reversible value, and decreases, compared with theory, only slightly as the temperature is raised.

(23) G. J. Hoijtink, J. van Schooten, E. de Boer, and W. I. Aalbersberg, *Rec. trav. chim.*, **73**, 355 (1955).

(24) L. Meites, "Polarographic Techniques," Interscience Publishers, Inc., New York, N. Y., 1955, pp. 55, 56.

(25) J. Heyrovsky and D. Ilkovic, *Collection Czech. Chem. Commun.*, **7**, 198 (1935).

(26) H. Matsuda and Y. Ayabe, *Bull. Chem. Soc. Japan*, **28**, 422 (1955).

Since one electron is added per monoanion reduced, regardless of the rate of succeeding protonation reactions, this effect is expected. The width of the third wave is much more difficult to interpret since it depends upon the speed of the protonation reaction following the second wave and is also affected by protonation of the product.

Triangular Wave Oscillopolarography. Room temperature oscillopolarograms of cyclooctatetraene in DMF at 1.0 and 20 v./sec. are shown in Figure 1. At the lower scan rate, a reduction trace similar to the d.c. polarogram is seen; reoxidation of both reduction products takes place, indicating their short-term stability. As the frequency is increased, the first reduction peak broadens, shifts cathodically, and, at 20 v./sec., is masked by the second peak. This behavior is characteristic of a moderately slow or "quasi-reversible" electron-transfer step with a cathodic transfer coefficient of less than 0.5.²⁷ An alternative explanation, discussed below, would involve a prior equilibrium which limits the rate at sufficiently high voltage scan rates.

With the d.c. bias adjusted so that the scan included the third and fourth waves, the reoxidation peak current corresponding to the second wave increased with increasing frequency as the reduction peak corresponding to the third wave decreased, and, at high scan rates, the third reduction peak was virtually unobservable. The reoxidation peak corresponding to the first wave was relatively insensitive to changes in the scan rate. The pseudo-first-order rate constant for the protonation of the cyclooctatetraene dianion, formed at the second peak, may be estimated by comparison of the second and third oscillopolarographic peak heights, assuming that the third wave represents reduction of the protonated product. The measured rate constant varied from less than 10 sec.^{-1} to more than 1000 sec.^{-1} depending upon the water content of the solvent.

A reoxidation peak corresponding to the third wave was usually visible in the oscillopolarogram although the reduction product was apparently somewhat less stable than the cyclooctatetraene dianion. The fourth oscillopolarographic peak appeared to arise from a slower process than the third peak and disappeared at high scan rates. No reoxidation peak attributable to this product was ever observed. A small oxidation peak at -1.1 v. was observed whenever the oscillopolarographic scan included the third and fourth waves. The identity of the species involved was not established although it apparently was some protonation product since the peak is frequency and temperature dependent and water sensitive in the same way as were the third and fourth peaks.

Effect of Water on Polarograms. Addition of small amounts of water to DMF solutions of cyclooctatetraene had two effects on the polarogram: (1) the diffusion current of the first wave increased at the expense of the second wave and (2) the second wave shifted anodically, until, in approximately 80% DMF-water, the two waves were coalesced to an apparent two-electron wave, distorted by a small maximum at -1.60 v. The apparent half-wave potential was -1.58 v., and the reciprocal slope of the plot of \log

(27) H. Matsuda and Y. Ayabe, *Z. Elektrochem.*, **59**, 494 (1955).

Table II. Temperature Effect on Polarogram in DMF

T, °C.	Wave I		Wave II		Wave III		Rev. width ^{a,c}
	Width ^a	i_d^b	Width ^a	i_d^b	Width ^a	i_d^b	
-25	-0.084 ^d	0.55	-0.045 ^d	0.55	-0.035	0.26	-0.047
0	-0.076 ^d	0.86	-0.045 ^d	0.65	-0.038	0.62	-0.052
25	-0.060	1.28	-0.053	0.72	-0.042	1.22	-0.056
50	-0.060	1.94	-0.056	0.88	-0.050	1.89	-0.061
75	-0.060	2.38	-0.060	0.73	-0.050	2.24	-0.066

^a Width = $\epsilon_{3/4} - \epsilon_{1/4}$; estimated accuracy ± 0.003 except where noted. ^b Diffusion current in arbitrary units; third wave corrected for drop time; estimated accuracy ± 0.05 . ^c Reversible width = $RT/n\bar{\nu} \ln 9$. ^d Estimated accuracy ± 0.005 .

$(i_d - i)/i$ was 0.038. The fourth wave, which was ordinarily very small, was increased markedly by the addition of water.

The oscillographic oxidation peak, corresponding to reoxidation of the dianion, vanished on the addition of only small amounts of water. The reoxidation peak owing to the monoanion was affected by water but decreased only slowly with the addition of water, and some reoxidation was observed even in 80% DMF-water.

The observation of a two-electron polarographic wave in 96% dioxane-water⁹ and 50% ethanol-water^{3,5} thus seems explicable. It is not unreasonable to suppose that the effective activity of water in the ion solvation spheres is higher in dioxane-water than in DMF-water mixtures so that the anodic shift of the second reduction wave might occur at lower concentrations in the former solvent. The small reoxidation peak observed oscillographically in dioxane-water⁹ was undoubtedly due to the small amount of unreduced monoanion still present in the vicinity of the electrode. The two-electron wave in aqueous dioxane or ethanol is thus actually two one-electron waves coalesced by kinetic complications. An explanation can also be offered for the pH independence of the half-wave potential in 50% ethanol-water.^{3,5} If the monoanion reacts only slowly with water and the electron transfer takes place in discrete steps, the over-all reduction potential is determined by the first electron transfer, the potential of which is unaffected by changes in the proton activity.

Effect of Tetra-n-butylammonium Iodide and Carbon Monoxide. Katz, Reinmuth, and Smith⁹ reported a brief polarographic study of cyclooctatetraene in DMF using tetra-n-butylammonium iodide as the supporting electrolyte. They observed extra waves at -2.4 and -2.9 v. (vs. a saturated Ag-AgClO₄ electrode)²⁸ which were enhanced by the addition of carbon monoxide. In our work, polarograms, either containing cyclooctatetraene or blank, with unpurified tetra-n-butylammonium iodide showed a wave at -1.9 v. (vs. s.c.e.) which was indeed enhanced by the addition of CO.²⁹ When the supporting electrolyte was recrystallized, this spurious wave was not observed. The normal third wave at -2.38 v. was slightly enhanced by the addition of CO in the presence of impure supporting electrolyte. Using recrystallized supporting electrolyte, either tetra-n-butylammonium iodide or tetra-n-

propylammonium perchlorate, CO had no effect whatever on the polarogram of cyclooctatetraene.

Macroelectrolyses of Cyclooctatetraene. A 0.002 M solution of cyclooctatetraene was electrolyzed at -1.8

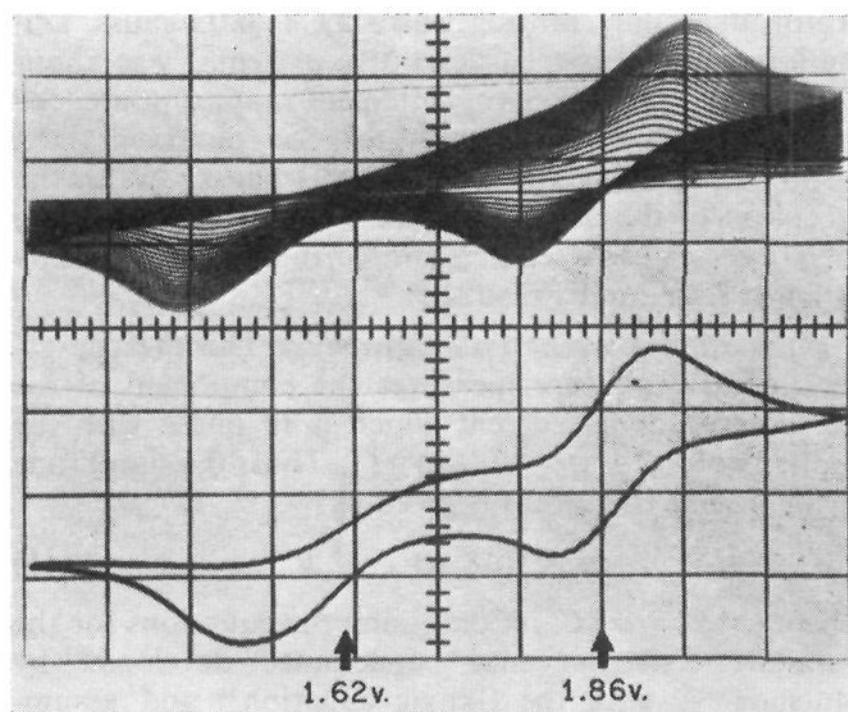


Figure 1. Oscillograms of cyclooctatetraene in DMF. Scan rates are 1.0 v./sec. (lower curve) and 20 v./sec. (upper curve).

v. vs. s.c.e. in 50% aqueous ethanol, and the concentration of cyclooctatetraene was followed polarographically during the electrolysis. Reduction was stopped at 80% completion, and the solution was extracted with isooctane, which in turn was extracted with DMF; supporting electrolyte was added, and the polarogram determined. Waves were observed as expected for cyclooctatetraene, except that the ratio of the diffusion currents was approximately (I + II):III:IV = 3:3:2. Since pure cyclooctatetraene in the same batch of solvent gave a diffusion current ratio of approximately 3:2:0.2, we conclude that an approximate 1:2 ratio of the 1,3,5- to 1,3,6-cyclooctatriene was formed on electrolysis in aqueous ethanol, in agreement with previous work by Elofson, who obtained a 1:3 ratio.⁶ We have assumed that the distribution coefficients of the two trienes are identical in the extractions.

A 0.01 M solution of cyclooctatetraene in DMF was electrolyzed to 92% completion (determined polarographically) at -2.1 v. vs. s.c.e. The final polarogram showed the ratio of the waves (I + II):III:IV = 1:4:0.3, that is, with the ratio of the third to fourth waves approximately unchanged from that given by unelectrolyzed cyclooctatetraene. This solution was

(28) The potential of the Ag-AgClO₄ electrode in DMF is approximately -0.5 v. vs. s.c.e.

(29) An approximate fivefold increase in DMSO, but only 20% in DMF.

extracted with isoctane, and the principal product identified as 1,3,5-cyclooctatriene by its ultraviolet spectrum.

Electrolysis in DMF at -1.8 v. vs. s.c.e., under conditions which had been shown by electron spin resonance to lead to the anion radical, followed by addition of an excess of water, extraction with isoctane, and resolution in DMF, showed that the principal product was 1,3,5-cyclooctatriene, with only a small amount of the other isomer. Thus, electrolysis in proton-active solvents—ethanol–water or DMF–water—produces a mixture of the two cyclooctatrienes, whereas in DMF, the product is the 1,3,5-isomer almost exclusively.

Electron Spin Resonance of Cyclooctatetraene Anion Radicals. Electrolysis of a 0.001 M solution of cyclooctatetraene in DMF at -1.8 v. vs. s.c.e. gave a pale yellow solution which showed a strong e.s.r. spectrum consisting of nine lines having the appropriate intensity ratios for eight equivalent protons.²² The proton hyperfine splitting was 3.23 ± 0.03 gauss, and the line width (between derivative extrema) was about 0.18 gauss. Satellites of intensities appropriate for carbon-13 hyperfine lines were also observed; the carbon-13 splitting was 1.30 ± 0.03 gauss. With the exception of the absence of alkali metal splittings, the spectrum was in all respects similar to those reported by Strauss, Katz, and Fraenkel.^{8, 10}

Alternating Current Polarography. The present experimental procedure measures the component of the a.c. polarographic current which is in phase with the applied voltage $\mathcal{E}(t) = \Delta\mathcal{E} \sin \omega t$. Thus, the amplitude of the measured current is given by

$$i = (\Delta\mathcal{E}/R) \cos^2 \theta \quad (1)$$

where $\cot \theta = \omega RC$. Combining the equations for the Faradaic resistance and capacitance developed by Matsuda^{30, 31} with the Ilkovic equation²⁶ and assuming that $D = D_O$,³² we obtain

$$i_d/i = B\nu^{-1/2} \{1 + [1 + (4\pi\nu)^{1/2}/\lambda]^{-1}\} + B(4\pi)^{1/2}/\lambda \quad (2)$$

where

$$B = (7/12\pi^2)^{1/2} (RT/n\mathcal{F}) [\Delta\mathcal{E}t^{1/2} F(\lambda t^{1/2})]^{-1} \quad (3)$$

$$F(\lambda t^{1/2}) = 1/4 [1 + (7/3\pi)^{1/2} (\alpha e^{-j} - \beta)(1.61 + \lambda t^{1/2}) / (1.13 + \lambda t^{1/2})] \quad (4)$$

$$\lambda = k_h f D^{-1/2} (e^{-\alpha j} + e^{\beta j}) \quad (5)$$

$$D = D_O^\beta D_R^\alpha \quad (6)$$

$$f = f_O^\beta f_R^\alpha \quad (7)$$

$$k_h = k_{fh}^\beta k_{bh}^\alpha \quad (8)$$

$$j = (n\mathcal{F}/RT)(\mathcal{E}_{dc} - \mathcal{E}_{1/2}^\dagger) \quad (9)$$

Here D_O and D_R are the diffusion coefficients of the oxidized (O) and reduced (R) forms of the electroactive species, respectively; k_{fh} and k_{bh} are the forward and

backward heterogeneous rate constants; f_O and f_R are the activity coefficients of O and R; $\alpha = 1 - \beta$ is the cathodic transfer coefficient; \mathcal{E}_{dc} is the applied d.c. potential; and $\mathcal{E}_{1/2}^\dagger$ is the reversible half-wave potential. The other symbols have their usual significance.

In the treatment of the experimental data, the a.c. polarographic peak currents, measured at drop fall, were normalized to 25° and to a drop time of 4 sec. The normalized currents were then used to form the ratio i_d/i , and the ratios plotted vs. $\nu^{-1/2}$. The d.c. diffusion current was taken as half the total diffusion current for the first two waves, measured on the same solution and under identical conditions, thus eliminating the d.c. effects of the protonation reactions. Examination of eq. 2 shows that an approximate straight line should result provided that $\nu^{1/2}$ is either much larger or much smaller than $\lambda/(4\pi)^{1/2}$.

On the first inspection, data for the first wave gave moderately good straight lines, but sizable values of $(4\pi)^{1/2}/\lambda$ on extrapolation to infinite frequency. The curves were then corrected for nonlinearity by plotting the same i_d/i vs. $\nu_c^{-1/2}$ where

$$\nu_c^{-1/2} = \nu^{-1/2} \{1 + [1 + (4\pi\nu)^{1/2}/\lambda]^{-1}\} \quad (10)$$

A new value of $(4\pi)^{1/2}/\lambda$ was obtained, and the process was repeated until the intercept was constant; usually about three iterations were necessary. The final plots for the first wave are given in Figure 2. Although a.c. polarograms were determined at -25° , virtually no current was observed at the potential of the first wave. Similarly, at the higher frequencies, the current measured at 0° was very small so that large uncertainties attach to these data points, and they were not included in the least-squares analysis. Values of B and $\lambda/(4\pi)^{1/2}$ are given in Table III.

Table III. A.c. Polarographic Parameters—First Wave

T , °C.	B , sec. ^{-1/2} , ^{a, b}	$\lambda/(4\pi)^{1/2}$, sec. ^{-1/2} , ^{b, c}
0	5.93 ± 0.26	0.42 ± 0.02
25	5.72 ± 0.20	1.49 ± 0.05
50	4.62 ± 0.11	2.64 ± 0.06
75	4.32 ± 0.03	4.79 ± 0.05

^a Slope of plot of i_d/i vs. $\nu_c^{-1/2}$. ^b Uncertainties are standard deviations of the least-squares fit. ^c Ratio of slope to intercept at $\nu_c^{-1/2} = 0$ from plot of i_d/i vs. $\nu_c^{-1/2}$.

Assuming that $F(\lambda t^{1/2}) = 0.25$ and with $\Delta\mathcal{E} = 2.5$ mv. ($\pm 10\%$), one may calculate the slope, $B = 5.0$ sec.^{-1/2}. The experimental values of B are seen to decrease slightly with increasing temperature. If k_h is small and $\alpha < \beta$, $F(\lambda t^{1/2})$ is expected to increase with temperature so that the slope should decrease. A following chemical reaction would increase B with increasing temperature (see below) so that this is apparently not the major effect. It is not possible to obtain k_h directly from these data since D , f , α , and j are all unknown. At high temperatures, it is probably safe to assume that the peak potential is sufficiently close to the reversible half-wave potential that j may be taken equal to zero and $\lambda/(4\pi)^{1/2} = k_h f / (\pi D)^{1/2}$. At low temperatures, however, the decreased rate should cause deviation of the peak potential from the reversible half-wave potential, leading to a value of $\lambda/(4\pi)^{1/2} > k_h f / (\pi D)^{1/2}$. In

(30) H. Matsuda, *Z. Elektrochem.*, **61**, 489 (1957).

(31) H. Matsuda, *ibid.*, **62**, 977 (1958).

(32) If O is cyclooctatetraene and R is the monoanion, we might expect that $D_O > D_R$ and that the activation enthalpy for diffusion of O is less than for diffusion of R since the effective anion radius is undoubtedly greater through increased solvation. See S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 516-525.

fact, however, an Arrhenius plot of $\log \lambda/(4\pi)^{1/2}$ vs. $1/T$ gives a moderately good straight line. The resulting activation enthalpy is $\Delta H^* = 5.85 \pm 0.46$ kcal./mole, where the uncertainty is the standard deviation of the least-squares fit. Assuming that the activity coefficient is constant with temperature, the enthalpy of activation for electron transfer ΔH_h^* is related to the measured quantity by

$$\Delta H_h^* = \Delta H_{\text{meas}}^* + \frac{1}{2}\Delta H_D^* \quad (11)$$

where ΔH_D^* is the average activation enthalpy of diffusion (see eq. 6). Assuming that $\Delta H_D^* = \Delta H_{D0}^*$ ³² which was estimated above, we have $\Delta H_h^* = 7.7$ kcal./mole.

An order of magnitude estimate of the rate constant may be made if we assume $f = 1$, $D = 10^{-5}$ cm.²/sec.^{33,34} At 25°, we obtain $k_h = 0.0085$ cm./sec. According to the absolute rate theory, the heterogeneous rate constant is given by³⁵

$$k_h = \rho(kT/h) \exp(-\Delta H_h^*/RT) \exp(\Delta S_h^*/R) \quad (12)$$

where ρ is a distance parameter thought to be of the order of a few Ångstrom units. Substituting the estimated values of k_h and ΔH_h^* we obtain

$$\Delta S_h^* = -(5.6 + R \ln \rho) \text{ cal./mole } ^\circ\text{K}. \quad (13)$$

where ρ is in Ångstrom units. Thus, ΔS_h^* is probably in the range -6 to -10 cal./mole $^\circ\text{K}$.

Plots of i_d/i for the a.c. polarographic peak currents of the second wave, normalized as described for the first wave, are given in Figure 3. The intercepts at infinite frequency are zero within experimental error except at -25° where the ratio of slope to intercept gives a value of $\lambda/(4\pi)^{1/2} = 33$. The corresponding value for the first wave, extrapolated from the data of Table III, is 0.17, so that, at -25° , neglecting differences in D and j , the electron-transfer rate is some 200 times faster for the second wave than for the first.

The plots shown in Figure 3 show considerable nonlinearity at low frequencies, and the limiting high-frequency slopes increase markedly with temperature. Because of the apparent large values of $\lambda(4\pi)^{1/2}$ for this electron-transfer process, however, the nonlinear term in eq. 2 would not be expected to contribute, and straight lines of slope $B = 10 \text{ sec.}^{-1/2}$ are expected. It is seen that, as the temperature is decreased, the lines become less nonlinear and that the slope approaches the theoretical value. Apparently, deviations are caused by the effects of the following protonation reaction. The DMF solvent used in the a.c. polarographic experiments, although relatively dry, had a greater water content than, for example, the solutions from which the data of Table I were obtained. The room temperature rate of protonation of the dianions, estimated oscillographically, was probably on the order of $100\text{--}500 \text{ sec.}^{-1}$.

The change in high-frequency slope with temperature may be qualitatively explained by noting that if, on

(33) The corresponding average diffusion coefficient has been estimated by Aten and Hoijtink³⁴ for several aromatic hydrocarbons; the values obtained ranged from 0.5 to 1.3×10^{-5} cm.²/sec.

(34) A. C. Aten and G. J. Hoijtink, "Advances in Polarography," I. S. Longmuir, Ed., Pergamon Press Inc., New York, N. Y., 1960, p. 777.

(35) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, p. 42.

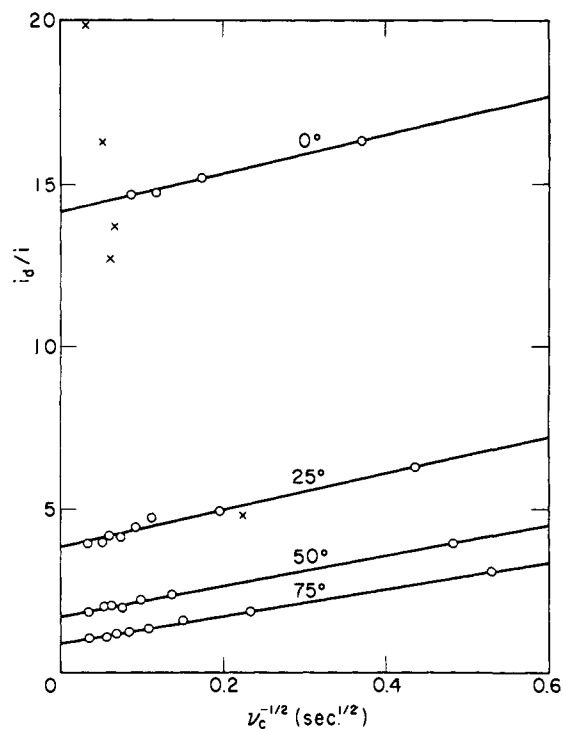


Figure 2. Plots of i_d/i vs. $\nu_c^{-1/2}$ for the first a.c. polarographic wave of cyclooctatetraene in DMF. Points not included in the least-squares analysis are indicated by crosses.

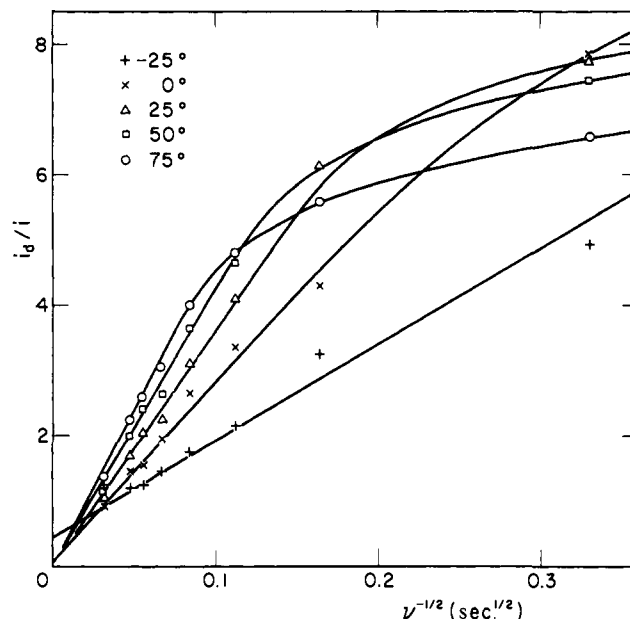


Figure 3. Plot of i_d/i vs. $\nu^{-1/2}$ for the second a.c. polarographic wave of cyclooctatetraene in DMF.

application of an a.c. voltage, R is removed irreversibly by a chemical reaction, the anodic half-cycle of the current will be smaller than the cathodic half-cycle, giving rise to rectification and higher harmonic content in the current. Thus, at the fundamental frequency, the a.c. current is expected to decrease with increasing chemical rate constant and thus with temperature.

Smith³⁶ has formulated a theory of a.c. polarographic

(36) D. E. Smith, *Anal. Chem.*, **35**, 602 (1963). See also ref. 35, pp. 159-165, and papers referred to therein.

currents with preceding and following first-order chemical reactions, using the methods of Matsuda.³¹ For a following reaction, he obtains a function $Q_1(t)$ which is proportional to the a.c. current and can easily be arranged to give the resistive component of the current, of interest in these studies.

$$Q_{IR}(t) = G_0(t)T/(T^2 + U^2) \sin \omega t \quad (14)$$

where T and U are functions defined by Smith's eq. 64 and 65, $G_0(t)$ is the solution of an unsolved integral equation and is a function of k , α , and j as well as t , where k is the pseudo-first-order rate constant for the following reaction. Since $G_0(t)$ is not a function of frequency, a plot of $(T^2 + U^2)/T$ vs. $\nu^{-1/2}$ should give curves of the correct shape for comparison with the experimental plots of current vs. frequency. Thus, for the purposes of comparison, we take $k_h \gg (2\omega)^{1/2}$, assume the chemical reaction completely irreversible, and let $\alpha = \beta = 1/2$. We then further assume that the a.c. polarographic peak potential is kinetically shifted to the same extent as the d.c. half-wave potential and that the shift is given by³⁷

$$\Delta E_{1/2} = (RT/nF) \ln 0.81(kt)^{1/2} \quad (15)$$

Figure 4 shows plots of $(T^2 + U^2)/T$ vs. $\nu^{-1/2}$ for assumed rate constants of 0, 10, 100, and 1000 sec.⁻¹. The similarity of the shapes of these curves to those of Figure 3 is striking and suggests that Smith's theory provides at least a qualitative explanation of the present results. Because of lack of knowledge of $G_0(t)$ and uncertainty regarding the validity of eq. 15 in this case, no quantitative understanding of the relative values of the slopes is possible. The range of rate constants required to give curves of the same general shape as those experimentally determined is, however, in agreement with the semiquantitative estimates made oscillographically.

The a.c. polarographic data for the third wave, plotted as in Figures 2 and 3, give curves which are qualitatively similar to those obtained from the second wave. However, in this case, there is no clear choice of d.c. diffusion current since the measured value is a function of the rates of both the preceding and the following protonation reactions, and, since the concentration of 1,3,5-cyclooctatriene in the vicinity of the electrode is not necessarily proportional to the bulk concentration of cyclooctatetraene, the d.c. diffusion current of the first and second waves cannot be justifiably used.

Discussion

Alkali Metal Complexes with Cyclooctatetraene Anions. Strauss, Katz, and Fraenkel¹⁰ found that for potassium ions in THF the disproportionation equilibrium of reaction I lies very far to the right with an equilibrium constant of about 10^8 . In the absence of alkali metal ions, this work indicates that the equilibrium lies to the left with $\Delta F_d = 0.24$ e.v. or an equilibrium constant of about 10^{-4} . These figures suggest that the shift in equilibrium may be due to the formation of a strong alkali metal-dianion complex. If K_1 is the formation constant of the monoanion-

potassium complex KR and K_2 is the formation constant of the dianion complex K_2R , we would have $K_2/K_1^2 = 10^{12}$.

Electron spin resonance spectra of cyclooctatetraene anions in the THF or DME solutions show alkali metal nuclear hyperfine splittings, and it was estimated that 60–70% of the radical was present as the alkali metal complex.¹⁰ Since the free alkali metal ion concentration was apparently very small, the formation constant K_1 must be quite significant. Hoijtink and co-workers^{13,38} have shown that, in solvents of low dielectric constant, aromatic hydrocarbon dianions are, in general, very much more associated with alkali metal ions than are the corresponding monoanions. The extremely large difference in the case of cyclooctatetraene suggests that there may be something special about the structure of the alkali metal-dianion complex.

In the present work, we observed that addition of a very small concentration of potassium ions to DMF solutions of cyclooctatetraene was sufficient to shift the second reduction wave by about 0.14 v. Considering that the potassium and cyclooctatetraene concentrations were approximately 10^{-3} M, this is a very large effect and shows that, even in a relatively strongly solvating medium, the formation constant K_2 must be very large indeed.

While providing a qualitative explanation of the position of the disproportionation equilibrium, the present work does not suggest a rationalization for the magnitude of the formation constants or for the entropy and enthalpy changes associated with reaction I.¹⁰

First Electron-Transfer Mechanism. The rate constant for bond isomerization in cyclooctatetraene has been estimated by Anet³⁹ at -10° from C¹³ n.m.r. measurements. If the transition state of this reaction is the planar conformer with equal bond lengths, the corresponding activation free energy of 13.7 kcal./mole may be taken as an estimate of the difference in free energy between the tub and symmetric planar conformations of cyclooctatetraene. Similar measurements on cyclononatetraene by Untch and Kurland⁴⁰ resulted in an almost identical value for the free energy of activation, and a complete analysis gave an entropy of activation of -16 cal./mole $^\circ\text{K}$. If we assume the same value for cyclooctatetraene, the free energy, corrected to 25° , is about 14.3 kcal./mole. Snyder's calculations for cyclooctatetraene indicate that the planar conformation with unequal bond lengths is more stable than the planar symmetric conformation by about 1.3 kcal./mole.⁴¹ Thus, the most stable planar form of cyclooctatetraene is expected to be approximately 13 kcal./mole higher in energy than the usual tub conformation.

In the present experiments, we find that the enthalpy of activation for electron transfer is 7.7 kcal./mole; the entropy term (see eq. 13) is probably about 2–3 kcal./mole at 25° , so that the free energy of activation is on the order of 10–11 kcal./mole. The similarity of this result to the estimated energy of hypothetical planar cyclooctatetraene strongly suggests that the

(38) G. J. Hoijtink and P. H. van der Meij, *Z. physik. Chem.*, **20**, 1 (1959).

(39) F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 671 (1962).

(40) K. G. Untch and R. J. Kurland, *ibid.*, **85**, 346 (1963).

(41) L. C. Snyder, *J. Phys. Chem.*, **66**, 2299 (1962).

(37) R. Brideka, V. Hanus, and J. Koutecky, "Progress in Polarography," Vol. 1, P. Zuman, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, Chapter 7.

transition state for electron transfer resembles the planar anion. The present estimate of the activation energy for charge transfer should not, however, be taken as an approximation to the free energy of planar cyclooctatetraene since it must also include a contribution from solvent reorganization, expected to amount to 2–3 kcal./mole.⁴² In addition, there is no reason for assuming that the transition state is entirely planar; electron transfer most likely occurs before the molecule is completely flattened, and the precise conformation of the transition state is probably a function of potential.

The shapes of the first d.c. polarographic wave at low temperatures and of the oscillopolarographic reduction and reoxidation peaks are indicative of a quasi-reversible electron-transfer step with the cathodic transfer coefficient significantly less than 0.5. Alternatively, these results could be explained by postulating a prior equilibrium



where Y is normal cyclooctatetraene, O might be the planar conformer, and R is the anion radical. A number of lines of evidence suggests, however, that there is no metastable intermediate along the reaction coordinate, at least not near the transition state. The height of the d.c. polarographic waves is normal, and the variation with temperature leads to an activation enthalpy of the correct order of magnitude for a diffusion-controlled process. Similarly, the slope of plots of i_d vs. $\nu^{-1/2}$ obtained from the a.c. measurements is in excellent agreement with the value predicted from Matsuda's theory³¹ which assumes straightforward electron transfer. Smith's extension of this theory³⁶ to kinetically complicated processes suggests that the slope of these plots should be a function of equilibrium constant and therefore a much stronger function of temperature than is observed. If the supposed metastable intermediate were the planar conformer, the free energy of activation would be greater than the estimated 13 kcal./mole by 2–3 kcal./mole of solvent reorganization free energy and thus significantly larger than is actually observed. Finally, if most of the observed free energy of activation were due to the free energy of a potential-independent equilibrium, then only a small increase in rate could be expected if a cathodic overvoltage were applied; thus, electron transfer to cyclooctatetraene at the potential of the second wave would be slow as well. In fact, Figure 1 shows that the integrated current passed in the second peak at 20 v./sec. is very much greater than twice that passed in the first (almost invisible) peak; this can only be explained if the charge-transfer rate increases significantly with overvoltage.

According to Marcus' theory of electron transfer,⁴² the electrochemical transfer coefficient is expected to depend primarily on the differences in the work required to bring the reactants and products to the electrode. Here the reactant, cyclooctatetraene, is uncharged so that the transfer coefficient is expected to

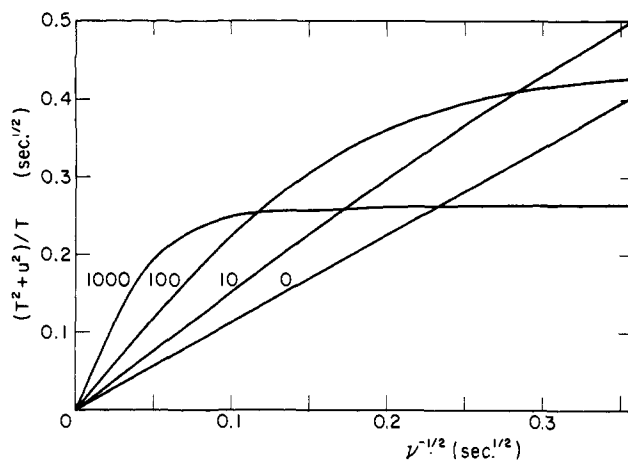


Figure 4. Plots of $(T^2 + U^2)/T$ vs. $\nu^{-1/2}$, calculated for chemical reaction rate constants of 0, 10, 100, and 1000 sec.⁻¹.

be slightly greater than 0.5. Thus, if we exclude the possibility of a prior equilibrium we see that another interpretation of the small transfer coefficient must be sought. It is not surprising that Marcus' theory fails in this case since the process involves considerably more "inner sphere" conformational change than can be dealt with by the theory.⁴²

The significance of an increase in charge-transfer rate with potential must be that, because of the increased free energy of electrons in the electrode, electron transfer can take place through a less favorable transition state than at equilibrium. If the cathodic overvoltage is made large, the charge-transfer rate becomes fast and the over-all reaction exothermic; according to the Hammond postulate,⁴³ the transition state under such conditions resembles the reactants. Conversely, for a large anodic overvoltage, the slow endothermic reaction goes through a transition state which, according to the Hammond postulate, resembles the products. In the present example, the reduction of cyclooctatetraene, an abnormally large cathodic overvoltage is required to make the reaction fast and exothermic; this is represented by the appearance of a small cathodic transfer coefficient. On this basis, since a large change in potential is required to make the transition state resemble reactants whereas only a small change is required to make it resemble products, we might expect that the equilibrium transition state is closer to the product conformation; this expectation is substantiated by the above arguments based on the measured free energy of activation for the reaction. These observations suggest that in general the transfer coefficient might profitably be interpreted in an extension of the Hammond postulate: *a small electrochemical transfer coefficient indicates that the transition state at equilibrium resembles products; conversely, a large transfer coefficient indicates that the equilibrium transition state resembles reactants.*

Anion-Dianion Electron-Transfer Rates. According to the a.c. polarographic experiments of Aten and Hoijtink,³⁴ the rate constants for electron transfer at the second reduction potential of ordinary aromatic hydrocarbons are small, of the order of 0.01 cm./sec. However, their data for the second wave are somewhat

(42) R. A. Marcus, "Transactions of the Symposium on Electrode Processes," E. A. Yeager, Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 239; H. Eyring, C. J. Christensen, and H. S. Johnston, Ed., "Annual Review of Physical Chemistry," Annual Reviews, Inc., Palo Alto, Calif., 1964, p. 155, and papers referred to therein.

(43) G. S. Hammond, *J. Am. Chem. Soc.*, 77, 334 (1955).

suspect because of the lack of agreement of the slopes of the $1/i$ vs. $\nu^{-1/2}$ plots with theoretical estimates with which agreement was obtained for the data from the first reduction waves. It is probable that a rapid protonation reaction following the addition of the second electron is responsible for this difficulty. In fact, since Aten and Hoijtink used a frequency range of about 20–60 sec.⁻¹, the extrapolation to infinite frequency is quite long, and the experimental frequency range might well be in the horizontal region of the curves of Figure 4, leading to a very low estimate of the electron-transfer rate constant.

Previous evidence⁷ does suggest that electron exchange between the cyclooctatetraene anions is considerably faster than between the naphthalene⁴⁴ anion and dianion. The rate of exchange is, however, strongly affected by the cation present and, for example, proceeds about 10⁴ times faster in the presence of potassium ion than in the presence of lithium ion.⁷ These data suggest that the exchange is really alkali metal atom transfer. Unfortunately, the dianion is unstable in DMF so that homogeneous electron-exchange rates cannot be measured. The a.c. polarographic data suggest that this rate is rapid and comparable with the rates measured by Aten and Hoijtink³⁴ at the first reduction potential of ordinary aromatic hydrocarbons.

According to the Marcus theory of electron-transfer processes,⁴² the free energy of activation for electron transfer consists of four terms: the work terms required to bring the reactants together and to remove the products; the free energy associated with reorganizing "outer sphere" solvent molecules in the transition state; the free energy associated with "inner sphere" reorganization; and the over-all free energy of the reaction which includes activation overvoltage in the electrochemical case. The work terms should be of importance in low dielectric constant solvents if the ions are free; in DMF or DMSO, in the presence of a large excess of supporting electrolyte, the work terms may conveniently be neglected. The outer-sphere

solvent reorganization term might be expected to be more important in these solvents, however, and will probably be larger for electron transfer between a neutral molecule and an anion than between the anion and the dianion. The last term involving the over-all free energy of the reaction is, of course, zero for homogeneous electron transfer between a hydrocarbon and its anion.

Providing then that inner-sphere reorganization can be neglected (which of course it cannot for the first electron transfer to cyclooctatetraene), we expect that electron-transfer rates between the anion and dianion might well be as fast as or faster than those between the neutral molecule and the monoanion when a high dielectric constant solvent and a large excess of supporting electrolyte are used. In a solvent of low dielectric constant (with no supporting electrolyte), the work terms should become of dominant importance, and the R–R⁻ electron exchange should proceed faster than the R⁻–R⁻² exchange. In cases where ion pairing occurs, of course, the process is not merely electron exchange, and these simple ideas should not hold.

Separation of the Half-Wave Potentials. The difference between the first and second half-wave potentials of cyclooctatetraene, measured in DMF or DMSO, is 0.24 v. In order to compare this value with half-wave potential differences measured for other aromatic hydrocarbons, we must first remove the effect of the conformation change. If we take 13 kcal./mole as the energy required to flatten the cyclooctatetraene ring, then the half-wave potential of the hypothetical planar cyclooctatetraene molecule should be approximately 0.56 v. more anodic than that observed for the tub conformation. The difference in half-wave potentials for the planar molecule would be of the order of 0.80 v., a considerably larger difference than has been observed for any other aromatic hydrocarbon.

Acknowledgments. We are particularly grateful to Professor A. H. Maki who communicated to us a number of preliminary results and suggested the problem to us. Discussions with Professors W. H. Reinmuth and J. O. Edwards have proven most helpful.

(44) R. L. Ward and S. I. Weissman, *J. Am. Chem. Soc.*, **76**, 3612 (1954); **79**, 2086 (1957); P. J. Zandstra and S. I. Weissman, *J. Chem. Phys.*, **35**, 757 (1961).