

which proceed by way of free-radical intermediates are also subject to polar influences.³² Without further data, such as reaction kinetics and salt and solvent effects on the rate of reaction, a radical pathway involving transfer of a hydrogen atom cannot be eliminated at this time. Regardless of the details of mechanism, the model system has apparently led to satisfactory reaction by substituting an electrostatic acceleration by a trifluoromethyl group or a carboxyl group for the catalysis by the enzyme.

Unfortunately, the available examples of the model system are few. Several attempts to extend the generality of the reaction failed. A number of other dihydropyridines were tried without success; the list includes N-benzyl-dihydronicotinamide, 3,5-dicarboethoxy-1,4-dihydropyridine, 3-cyano-N-methyl-1,4-dihydropyridine, 3-cyano-N-phenyl-1,4-dihydropyridine, N-phenyldihydronicotinamide, N-benzyl-3,5-dicarboxamyl-1,4-dihydropyridine. The sharp requirements with respect to the structure of those ketones which can be reduced has already been mentioned. These restrictions probably arise because of the limitations in experimental conditions which are imposed upon the reduction. The reaction cannot

(32) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 384.

be conducted except in slightly acid or neutral solution, since the trifluoromethyl olefin is extraordinarily sensitive to Michael addition. In the presence of an acetic acid-sodium acetate buffer, or even of a methoxyacetate-methoxyacetic acid buffer, the Michael addition of methanol to the double bond takes precedence over reduction; the successful experiments were carried out in the presence of added methoxyacetic acid or pyridinium perchlorate. (In mildly alkaline solution, N-alkyl pyridinium salts are also unstable.) On the other hand, strongly acid conditions (or in some cases even mildly acid conditions) are not tolerated by the notoriously acid-sensitive dihydropyridines. Presumably in enzyme systems, the protein can catalyze the reaction sufficiently to allow reduction even under very mild conditions, where the dihydropyridines are stable.

Acknowledgments.—The authors take pleasure in acknowledging a grant (N.I.H. 8486) from the National Institutes of Health which enabled us to carry out this investigation. P.E.K. wishes further to acknowledge his support from a Postdoctoral Fellowship awarded to him by the National Science Foundation. The authors also wish to express their indebtedness to Dr. John L. Graves, who carried out some of the preliminary experiments on the reduction of benzoylacrylic acid.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

Electrolytic Reduction of Cyclooctatetraene

BY THOMAS J. KATZ, WILLIAM H. REINMUTH AND DONALD E. SMITH

RECEIVED JULY 6, 1961

The electrolytic reduction of cyclooctatetraene in 96% dioxane-water is shown by oscillogpolarography to proceed by reversible addition of two electrons to the hydrocarbon followed by an irreversible pseudo-first-order reaction of the resulting dianion with the solvent. The kinetics of the latter reaction are determined. The observed behavior supports the conclusions based on e.s.r. and n.m.r. studies that the geometries of the cyclooctatetraenyl anions are similar and unlike that of the hydrocarbon. The significance of the observed half-wave potential is discussed in terms of the compressional energy required to aromatize the cyclooctatetraene molecule and the energy level of the hydrocarbon m.o. being filled. It is concluded that this m.o. is non-bonding, consistent with a regular octagonal geometry for the cyclooctatetraenyl dianion.

Introduction

The high degree of stabilization due to π -electron delocalization which is characteristic of carbocyclic aromatic systems and which had been sought but found absent in the hydrocarbon cyclooctatetraene is to be found in the cyclooctatetraenyl anions.¹ Since the available observations² concerning the electrolytic reduction of cyclooctatetraene had suggested this hypothesis to us before our own experiments were begun, we submitted the polarographic behavior of cyclooctatetraene to further scrutiny. The results of this study, which are elaborated below, bear out the hypothesis and further confirm the conclusions derived by means of proton nuclear magnetic and electron spin resonance techniques.

(1) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960); **82**, 3785 (1960); T. J. Katz and H. L. Strauss, *J. Chem. Phys.*, **32**, 1973 (1960).

(2) (a) R. M. Eloffson, *Anal. Chem.*, **21**, 917 (1949); (b) J. H. Glover and H. W. Hodgson, *Analyst*, **77**, 473 (1952); (c) L. E. Craig, R. M. Eloffson and I. J. Ressa, *J. Am. Chem. Soc.*, **75**, 480 (1953).

Mechanism of Aromatic Hydrocarbon Reductions

As a result of extensive investigation,³⁻⁵ the mechanisms of the electrode reactions of a number of unsaturated hydrocarbons have come to be recognized, and some of their essential features are briefly stated. (1) Electron transfer occurs between the electrode and the first unfilled molecular orbital of the unsaturated hydrocarbon molecule.⁶⁻⁸ (2) Electronic repulsion results in a decrease in the facility with which a second electron transfer occurs.^{8,9} (3) Solvation and ion pairing

(3) G. J. Hoijtink, J. Van Schooten, E. de Boer and W. I. Aalbersberg, *Rec. trav. chim.*, **73**, 355 (1954).

(4) (a) H. A. Laitinen and S. Wawzonek, *J. Am. Chem. Soc.*, **64**, 1765 (1942); (b) S. Wawzonek and H. A. Laitinen, *ibid.*, **64**, 2365 (1942); (c) S. Wawzonek and J. W. Fan, *ibid.*, **68**, 2541 (1946).

(5) I. Bergman, *Trans. Faraday Soc.*, **50**, 829 (1954).

(6) A. Maccoll, *Nature*, **163**, 178 (1949).

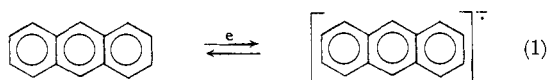
(7) A. Pullman, B. Pullman and G. Berthier, *Bull. soc. chim. France*, 591 (1950).

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

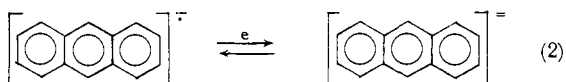
(9) N. S. Hush and J. Blackledge, *J. Chem. Phys.*, **23**, 514 (1955).

diminish this effect of electron repulsion. The effects 2 and 3 have been more closely defined by theoretical calculations,⁹⁻¹¹ although quantitative agreement with experiment has not yet been achieved. Empirical data, however, clearly bear out these suggestions, for it is generally observed that the addition of two electrons to a hydrocarbon occurs in two one-electron steps.^{3,10-14}

Manifestation of these effects was first discerned by Hoiijtink in d.c. polarographic experiments conducted in aprotic solvents.^{3,11,12,15} The polarographic behavior typical of an aromatic hydrocarbon, such as anthracene, is that as the variation of current with electrode potential is observed, two separate waves are seen, the limiting diffusion current for each wave corresponding to the transfer of one electron. These waves represent, respectively, the reversible one-electron reduction of the hydrocarbon to its anion-radical



and the more difficult reduction of the anion-radical to the dianion



The operation of this mechanism is rendered most clearly apparent by an oscillopolarographic study. Figure 1A shows a large amplitude triangular wave potential oscillopolarogram for the reduction of anthracene. On the cathodic scan two peaks are observed, each of height and shape essentially that to be expected for a reversible one-electron reduction. The anodic half cycle, however, produces no observable reoxidation of the product of the second reduction. This is in accord with Hoiijtink's evidence and conclusion^{3,15} that the dianion produced in the second reduction undergoes a rapid irreversible chemical reaction with the solvent. A reoxidation which corresponds to the first reduction peak is readily apparent. The reoxidation peak is smaller than the corresponding reduction peak because part of the first reduction product is removed irreversibly in the second reduction step. It is, thus, unavailable for reoxidation. As the amplitude of the scan is decreased so that the irreversible second step is prevented, the cathodic and anodic peak heights of the first step become more nearly equal (Fig. 1B).

In solvents in which rapid protonation of the monoanion occurs, perception of the fundamental reduction mechanism is obscured in the conventional polarographic experiment. The protona-

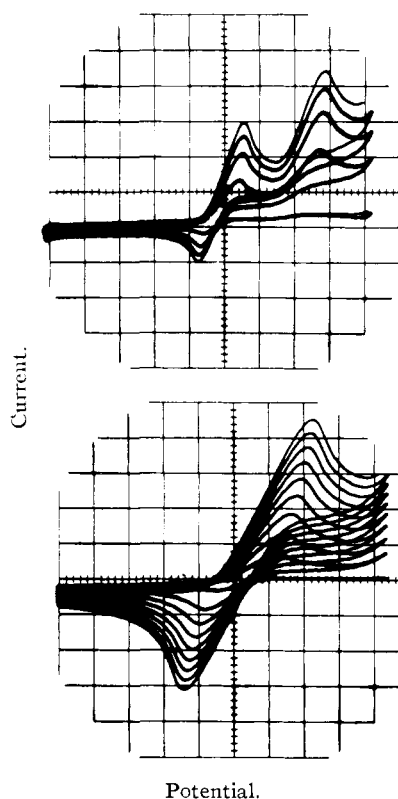
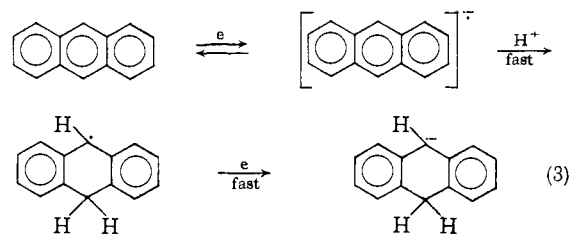


Fig. 1A (above) and 1B (below).—Large amplitude triangular wave oscillopolarograms of anthracene in 95% dioxane-water. The triangular frequency is 1 c.p.s.

tion reaction results in the formation of an uncharged free radical the reduction potential of which is lower than that of the hydrocarbon, anthracene. This species, therefore, abstracts another electron from the electrode



This chemically diverted reduction manifests itself in the polarographic experiment as a single reduction wave corresponding in limiting diffusion current to the uptake of two electrons. This is, of course, the same result as would obtain were the electrode process a two-electron transfer, and thus, the observation that the limiting diffusion current implies the involvement of two electrons in the reduction cannot be considered prognostic of a simple two-electron electrode reaction. The distinction between a fundamentally one-electron reduction diverted by a succeeding rapid chemical reaction and a simple two-electron reduction is, therefore, not easily made. When these mechanisms have been distinguished, it has usually been found that the initial reaction in the reduction of hydrocarbons entails but one electron.^{2,11-13,15}

(10) G. J. Hoiijtink, E. de Boer, P. H. van der Meij and W. P. Weijland, *Rec. trav. chim.*, **75**, 487 (1956).

(11) S. Wawzonek, E. W. Blaha and M. E. Runner, *J. Electrochem. Soc.*, **102**, 235 (1955).

(12) P. H. Given, *ibid.*, **105**, 2684 (1958); P. H. Given and M. E. Peover, *Collection Czechoslov. Chem. Commun.*, **25**, 3195 (1960).

(13) D. E. Paul, D. Lipkin and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).

(14) T. L. Chu and S. C. Yu, *ibid.*, **76**, 3367 (1954).

(15) A. C. Aten, C. Buthker and G. J. Hoiijtink, *Trans. Faraday Soc.*, **55**, 324 (1959).

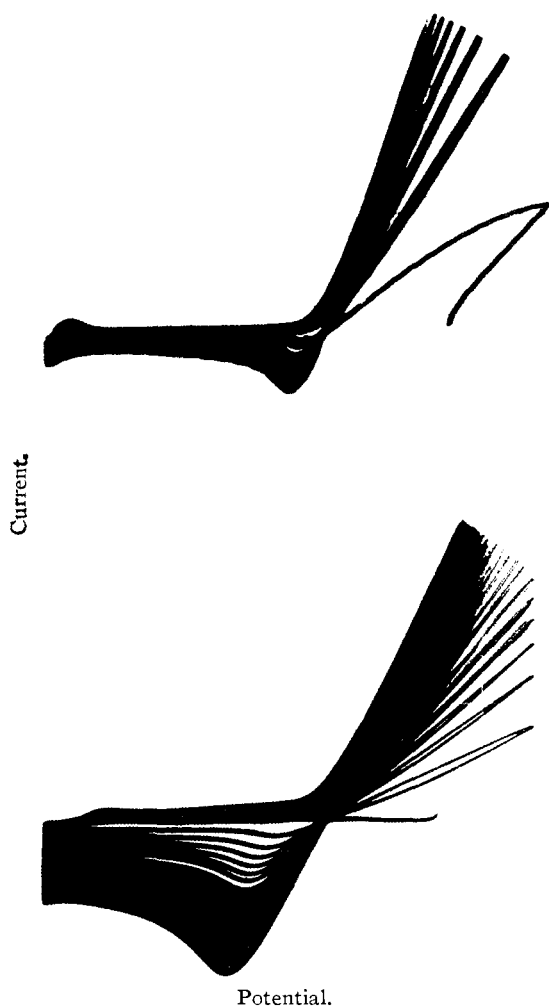


Fig. 2.—Large amplitude triangular wave oscillograms (foot-of-wave) of cyclooctatetraene in 96% dioxane-water. A (above): triangular wave frequency is 1 c.p.s. B (below): triangular wave frequency is 10 c.p.s.

Polarographic Behavior of Cyclooctatetraene

Experimental Results.—The reported² behavior of cyclooctatetraene on polarographic reduction in 50% ethanol-water is striking in that the shape of the line formed on plotting $\ln(i_a - i)/i$ as a function of the electrode potential is $RT/2F$, implying that the initial electrode reaction involves the transfer of two electrons. Other characteristics of the reaction appear unexceptional: in aqueous ethanol containing tetramethylammonium hydroxide the reduction of cyclooctatetraene produces a single well-defined polarographic wave, the limiting diffusion current corresponds to the uptake of two electrons, and the products of this reduction have been identified as 1,3,6- and 1,3,5-cyclooctatriene.¹⁶ The formal similarity between the behavior of cyclooctatetraene and that of benzenoid aromatic hydrocarbons extends also to their reactions with alkali metals in ethereal solution and with alkali metals and mild acids in

(16) The latter might be a spurious reaction product formed subsequent to the reduction step, since it is known that the unconjugated triene undergoes a ready alkali-catalyzed isomerization to the fully conjugated isomer.¹⁰

liquid ammonia. The cyclooctatrienes obtained as products of the Birch reduction of cyclooctatetraene¹⁷ are analogous to the dihydro products formed from benzenoid aromatics.^{18,19} The behavior of cyclooctatetraene on electrolytic reduction is, however, in direct contrast to that of benzenoid aromatic hydrocarbons in that the initial electrode reaction appears to involve two—not one—electrons.

Our own polarographic studies conducted in 96% dioxane with tetra-*n*-butylammonium iodide as supporting electrolyte yielded results similar to those in 50% ethanol: a single well-formed wave, a linear $\log(i_a - i)/i$ vs. E plot of slope 0.03 volt, and a half-wave potential of -1.12 volts vs. mercury pool. The diffusion current constants and the slopes of the log plots suggested that the reduction in both media involves the reversible addition of two electrons. Since the cyclooctatrienes are formed on macro controlled potential reduction, the insensitivity of the half-wave potential to change in the hydroxyl ion concentration^{2a,b} in the range from neutral to strongly basic can be interpreted in one of two ways: either the lifetime of the initially formed dianion with respect to protonation is long compared with the drop time in the polarographic experiment but short compared with the much longer (ten hours) time of the macroelectrolysis, or the lifetime of the dianion is short, it undergoing a rapid (compared with diffusion) and irreversible pseudo-first-order chemical decomposition in which a water molecule (or molecules) rather than a proton (or protons) participates.

These alternatives can be distinguished by examination of the triangular wave potential oscillographic behavior of the system. In the oscillogram of cyclooctatetraene in 96% dioxane at 1 c.p.s., the current peak on the cathodically scanned half-cycle is well formed. The half-peak potential is approximately the same as the polarographic half-wave potential. However, on the anodically scanned half-cycle there is no hint of a peak due to reoxidation of the reduction product. Shifting the d.c. bias so as to confine the cathodic portion of the scan to the foot of the wave makes visible a small anodic peak (Fig. 2A). Increasing the frequency to 10 c.p.s. makes the areas under the cathodic and anodic portions of the current potential curve more closely comparable (Fig. 2B). The oxidation peak immediately follows the decay of the cathodic current, indicating that the charge transfer proceeds without appreciable activation overpotential.

These observations strongly suggest a mechanism in which reversible charge transfer is rapidly followed by an irreversible chemical decomposition. The Nernstian slope of the d.c. polarographic $\log(i_a - i)/i$ vs. E plot indicates that the irreversible step occurs subsequent to the addition of both electrons. The linearity of the plot suggests that this reaction is first order in the primary reaction

(17) A. C. Cope and F. A. Hochstein, *J. Am. Chem. Soc.*, **72**, 2515 (1950).

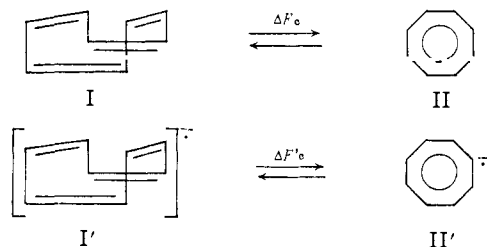
(18) A. J. Birch and H. Smith, *Quart. Revs. (London)*, **12**, 17 (1958).

(19) A. P. Krapcho and A. A. Bothner-By, *J. Am. Chem. Soc.*, **81**, 3658 (1959).

product. If an irreversible chemical step had occurred after addition of a single electron, the slope would have been 0.06 or larger, rather than 0.03. If the second charge transfer had been irreversible, the slope would have been approximately 0.04, the apparent number of electrons corresponding to one (for the reversible first step) plus the charge-transfer coefficient for the second step. If reversible two electron addition had been followed by a chemical reaction second order in the initial charge-transfer product, the slope of a plot of $\log(i_d - i)/i^2$ vs. E would have been 0.03, and a plot of $\log(i_d - i)/i$ vs. E would have been 0.045.³

While these considerations do not preclude a four-step mechanism consisting successively of reversible electron addition, reversible chemical reaction, reversible electron addition and irreversible chemical reaction, the independence of the half-wave potential and the pH of the solution eliminates hydrogen and hydroxyl ions as participants in the chemical steps. Moreover, reversible chemical reactions of the cyclooctatetraene mono-anion with species other than protons—at least reactions more substantial than ion pairing with the cation of the supporting electrolyte—seem unlikely. The only conclusion which appears tenable is that reduction of cyclooctatetraene proceeds through simple reversible addition of two electrons followed by rapid irreversible decomposition of the dianion.

The Significance of Reversible Multielectron Reduction.—The addition of one electron to cyclooctatetraene in its stable conformation (I) would result in an anion radical with the odd electron in a high energy anti-bonding orbital. If the hydrocarbon were compressed to a planar regular octagonal conformation (II), however, its lowest unfilled molecular orbital would be non-bonding. If the assumptions of Hückel theory be made, the energy change on aromatization of the anion radical



differs from that for aromatization of the parent hydrocarbon just by the energy of this orbital. Since the energy of skeletal compression is the same in both cases, while the delocalization energy gained in the former is considerably greater than in the latter, it is possible that the radical anion in contrast to the hydrocarbon²⁰ possesses a stable

(20) It is known that the cyclooctatetraene molecule exists in the puckered, so-called "tub" conformation, that the carbon-carbon bond distances alternate between long and short around the ring, and that little conjugation occurs among the four isolated π -electron systems.²¹ Since the structural basis of an aromatic system—a regular polygonal conformation—is lacking in cyclooctatetraene, the extensive π -electron delocalization energy (1.6β , as compared with 2β for benzene by the Hückel theory) expected of the regular octagonal molecule must fail to compensate for the exceptionally large compressional strain associated with the angular distortion of the framework.

aromatic conformation, *i.e.*, $\Delta F'_c$ can be negative although ΔF_c is positive.²² The requirement for this is that ΔF_c not be greater than $|\beta|$, the absolute value of the carbon-carbon exchange integral. Since $|\beta|$ is very large, an estimated 2.2 e.v.,²⁴ this expectation seems warranted. Conformations other than the two extremes considered above are possible. Since the discussion does not explicitly depend on the conformation of the delocalized species, we will simply refer to it as the aromatic one, although, as will be seen, we favor the regular octagonal structure.

If the three oxidation states of cyclooctatetraene possessed the same skeletal geometry, addition of the second electron would necessarily be much less facile than the first because of the coulombic barrier to further reduction of the mono-anion. If, however, as in reality, the first step is encumbered by an energy of compression to the aromatic conformation, this need not be so. Indeed, if the compressional barrier to the initial reduction is sufficiently great, the second reduction step could be less difficult than the first. Because of these considerations the observed reversible two electron reduction of cyclooctatetraene seems explicable only if the anion radical and the dianion are similar in geometry and unlike the parent hydrocarbon.

The general conclusion which cyclooctatetraene thus exemplifies is this: despite the coulombic barrier to multielectron addition, reversible reduction of a hydrocarbon can, if it is accompanied by a geometrical change, involve the addition of more than a single electron.

The Reduction Potential of Cyclooctatetraene

Experimental Results.—The reduction potential of the hydrocarbon can readily be estimated by observation of the half-wave potential in the polarographic experiment. The half-wave potential and the standard reduction potential are essentially interchangeable if the Nernst equation is obeyed and no chemical reactions precede or follow the charge transfer process, for the two potentials differ only by $(RT/2nF) \ln(D_o/D_R)$ where D_o and D_R are the diffusion coefficients for the oxidized and reduced forms. The magnitude of this quantity is seldom more than a few millivolts.

When, however, the rate of the charge-transfer process is slow compared to the rate of diffusion or when chemical kinetic complications are present, the standard and half-wave potentials differ by quantities logarithmically related to the rate or equilibrium constants of the complicating reactions. Insofar as the complications are responsive to the same factors which determine the free energy of the primary charge-transfer and the compounds compared are all subject to the same complications, empirical correlation of half-wave potentials with

(21) R. A. Raphael, "Non-Benzenoid Aromatic Compounds," D. Ginsburg, editor, Interscience Publishers, Inc., New York, N. Y., 1959.

(22) ΔF_c and $\Delta F'_c$, the compression energies of the hydrocarbon and of the anion radical, respectively, are here defined to include the delocalization energy gained on compression (*cf.* ref. 23).

(23) C. A. Coulson and S. L. Altman, *Trans. Faraday Soc.*, **48**, 293 (1952).

(24) A. Streitwieser, Jr., and P. M. Nair, *Tetrahedron*, **5**, 149 (1959).

other parameters still yields useful results. Extraneous factors are of more importance in such situations and, in extreme cases, their influence may obscure that of the factor of interest. In cases of slow charge transfer, for example, salt effects similar in principle to Debye-Hückel interactions cause the effective electrode potential to differ from the applied potential. Cases of this type are easily distinguished experimentally because the change of current with potential, as measured by the slope of a plot of $\ln(i_a - i)/i$ (where i_a is the diffusion plateau current and i the current at potential E) vs. E , usually differs significantly from the Nernstian value of $RT/n\mathcal{F}$. Cases in which the charge transfer obeys the Nernst equation but is followed by rapid irreversible first-order chemical decomposition cannot be distinguished by this criterion from cases uncomplicated by chemical reactions. Provided the chemical reaction is sufficiently rapid, Koutecky's²⁵ theoretical treatment, given originally for cases of slow charge transfer, can be applied. Kern's²⁶ calculations based on Koutecky's theory indicate that in these cases for currents averaged over drop life, plots of $\ln(i_a - i)/i$ should be linear and of slope $RT/n\mathcal{F}$. Our own calculations, again based on Koutecky's theory, indicate that if instead instantaneous currents measured at time of drop fall are used, the slope should be $RT/1.095n\mathcal{F}$. Unfortunately, the difference between this value and that for cases uncomplicated by chemical reaction, $RT/n\mathcal{F}$, normally lies within the range of experimental error. Thus, although the wave slope criterion of polarographic reversibility is a necessary condition, it is not sufficient to ensure the absence of kinetic complications.

When such complications occur, for $kt \gg 1$, the polarographic half-wave potential is related to the standard potential by the eq. 4 where k is the (pseudo) first-order rate constant for the

$$E_{1/2} = E^{0'} + \frac{RT}{n\mathcal{F}} \ln \frac{12k t^{1/2}}{7D} \quad (4)$$

following chemical reaction, D the diffusion coefficient of the initial reactant, t the drop time of the dropping electrode, and the other symbols have their usual thermodynamic significance. In order to obtain the standard potential polarographically it is necessary to correct the observed $E_{1/2}$ for the effect of the kinetic complication.

For hydrocarbon reductions conducted in aqueous media this means that it is necessary to consider the extent to which the protonation of the anionic species formed displaces the half-wave potentials observed. That hydrocarbon anion-radicals protonate slowly in 96% dioxane, while dianions protonate much more rapidly, was pointed out by Hoijsink,³ and is observable in the anthracene oscillogram (Fig. 1A). The protonation of the hydrocarbon anion radicals is, in fact, sufficiently slow as not to influence detectably the half-wave potentials observed, while the more rapid protonation of the dianion produces small, but observable, shifts. The pseudo-first-order rate constant for the protonation of the

cyclooctatetraenyl dianion in 96% dioxane and, hence, the magnitude by which this reaction displaces the half-wave potential for the reduction of cyclooctatetraene in this medium, was directly determined by use of an oscillographic method based on comparison of the areas under the anodic and cathodic peaks as a function of frequency. A detailed discussion of this method—the theory, experimental conditions and verification on a system of known kinetics—will be presented elsewhere.²⁷ The rate constant as determined from measurements conducted at 1 and 10 c.p.s. is $32 \pm 4 \text{ sec.}^{-1}$. With the aid of Koutecky's theoretical treatment of the proposed reaction mechanism, the extent by which the kinetic complications displaces $E_{1/2}$ from its value in the absence of such influences can be calculated to be only 0.04 v. This difference is sufficiently small to be insignificant in this case, and any corrections for this effect will, therefore, similarly be neglected in the consideration of the other hydrocarbon reductions discussed below.

The half-wave potential observed in the polarographic reduction of cyclooctatetraene in 96% dioxane containing 0.175 *M* tetra-*n*-butylammonium iodide is -1.12 v. with reference to the mercury pool.

Experimental Reduction Potential of the Anion-Radical.—In the present section the polarographic data will be used to derive the reduction potential of the cyclooctatetraenyl anion radical. This will then be compared to a theoretical estimate based on the assumption that the cyclooctatetraenyl anions both possess the planar regular octagonal geometry.

The free energy of reduction of cyclooctatetraene can be divided hypothetically into four component parts: ΔF_{c1} , the compression energy required to distort the parent to the conformation of the monoanion; $-\mathcal{F}E_1$, the energy of electron addition to this species; ΔF_{c2} , the compression energy required to distort the monoanion to the structure of the dianion; $-\mathcal{F}E_2$, the energy of electron addition to this species.

The observed half-wave potential, E_{obs} , for cyclooctatetraene is related to these components by the equation

$$-2 \mathcal{F}E_{\text{obs}} = (\Delta F_{c1} - \mathcal{F}E_1) + (\Delta F_{c2} - \mathcal{F}E_2) \quad (5)$$

The individual bracketed terms in this equation could be determined if the free energy of disproportionation of the cyclooctatetraenyl radical anion into the hydrocarbon and the dianion, ΔF_d , were evaluated, for

$$\Delta F_d = -(\Delta F_{c1} - \mathcal{F}E_1) + (\Delta F_{c2} - \mathcal{F}E_2) \quad (6)$$

The concentrations of the anion radical present in solutions of cyclooctatetraene and potassium or lithium in tetrahydrofuran have been determined by electron spin resonance.^{1,28} If these concentrations are defined by the disproportionation equilibrium, and if the equilibrium constant is insensitive both to the nature of the medium (tetrahydrofuran or 96% dioxane-water) and to the nature of the cation—as is suggested by the

(27) D. E. Smith and W. H. Reinmuth, *Anal. Chem.*, submitted for publication.

(28) H. L. Strauss, Dissertation, Columbia University, 1960.

(25) J. Koutecky, *Coll. Czechoslov. Chem. Commun.*, **18**, 597 (1953).

(26) D. M. H. Kern, *J. Am. Chem. Soc.*, **76**, 4234 (1954).

similarity of the constants at 25° for the potassium (2.7×10^8) and lithium (1.1×10^8) salts and the similarity of the differences between the first and second half-wave potentials of a number of benzenoid aromatics measured in 96% dioxane containing tetra-*n*-butylammonium iodide⁸ and the reduction potential difference measured in tetrahydrofuran with sodium cations¹⁰—then ΔF_d is approximately -11.2 kcal./mole or -0.49 ev.

Thus

$$\Delta F_{c1} - \bar{\mathfrak{F}}E_1 = 1.4 \text{ e.v.} \quad (7)$$

and

$$\Delta F_{c2} - \bar{\mathfrak{F}}E_2 = 0.9 \text{ e.v.} \quad (8)$$

ΔF_{c2} is probably very small. This is suggested by the finding that $(\Delta F_{c1} - \bar{\mathfrak{F}}E_1) > (\Delta F_2 - \bar{\mathfrak{F}}E_{c2})$, which is implied both by the observations in magnetic resonance experiments that ΔF_d is negative and in the polarographic experiments that cyclooctatetraene undergoes a one-step two-electron reversible reduction. Moreover, the rapid electron exchange which has been observed to occur between the dianion and the anion radical contrasts sharply with the immeasurably slow exchange which occurs between the dianion and the hydrocarbon, and can be accounted for readily if the dianion and the anion radical are similar in geometry and unlike the hydrocarbon¹—that is, if ΔF_{c2} is small. If $\Delta F_{c2} = 0$, then the reduction potential of the anion radical is about -0.9 v.

For an aromatic hydrocarbon, the reduction potential is, theoretically, linearly related to the energy level of the molecular orbital filled in the reduction process.⁶ Experimentally for a large number of benzenoid aromatic hydrocarbons a good correlation is found between the polarographic half-wave potentials for both the first and second electron additions and a , the calculated coefficient of β for the first unfilled molecular orbital. The success of this test lends added credence to the Hückel treatment and suggests the general feasibility of inferring reduction potentials from structural concepts. Hoiijtink⁸ gives the following equation for $E_{1/2}$ versus mercury pool²⁹ in 96% dioxane-water with 0.175 *M* tetra-*n*-butylammonium iodide as supporting electrolyte

$$E_{1/2} = -2.54a - 0.29 \quad (9)$$

The mean square regression line of a on $E_{1/2}$ for the twelve alternant hydrocarbons³⁰ which Hoiijtink examined is slightly different

$$E_{1/2} = -2.82a - 0.17 \quad (10)$$

The correlation as measured by the correlation coefficient (0.95) and the standard error of estimate in a (0.036)³¹ is very good.

(29) The equation given by Hoiijtink⁸ is $E_{1/2} = -2.54a - 0.85$ with potentials measured with reference to the saturated calomel electrode (SCE). Since the actual experimental measurements were made with reference to the mercury pool and then adjusted by the measured anode potential (-0.56 v.) with respect to SCE, and since the mercury pool anode has itself proved to be very stable in numerous related experiments,¹² we have simply readjusted the measurements to the mercury pool reference.

(30) Naphthalene, phenanthrene, anthracene, pyrene, tetracene, triphenylene, coronene, 1,2-benzopyrene, 1,2,5,6-dibenzanthracene, 1,2-benzanthracene and perylene.

(31) R. S. Burlington and D. C. May, Jr., "Handbook of Probability and Statistics," Handbook Publishers, Inc., Sandusky, Ohio, 1953, pp. 116 ff.

The half-wave potentials for the second reduction steps are, surprisingly enough, similarly related to the energies of the hydrocarbon m.o.'s being filled³²

$$E_{1/2} = -2.71a - 0.57 \quad (11)$$

For all sixteen hydrocarbons which Hoiijtink studied in 96% dioxane the second polarographic wave follows the first by 0.34 ± 0.10 v., while for the eight alternant hydrocarbons this difference is 0.37 ± 0.05 v. The difference in standard potentials is expected to exceed this slightly because the greater rate of protonation of the dianions in the solvent tends to shift the second polarographic wave anodically but, as was discussed above, this effect is probably small. The actual reduction potentials for a few hydrocarbons in related solvent media have been measured directly by potentiometric titration with sodium biphenylide,¹⁰ and the first and second reduction potentials for two hydrocarbons in tetrahydrofuran are found to differ by only 0.40 ± 0.06 v., and for eight hydrocarbons in dimethoxyethane by 0.58 ± 0.04 v. The significant observation is that for all the hydrocarbons examined this difference, which is a measure of the effect of electronic repulsion attenuated by solvation and ion-pairing, is found to be small and quite constant at 0.40 v.

The first and second reduction potentials of the hypothetical aromatic regular octagonal cyclooctatetraene molecule might, since the first unfilled molecular orbital is non-bonding, be expected in 96% dioxane 0.175 *M* in tetra-*n*-butylammonium iodide to be -0.17 (by eq. 10) and -0.57 v. (by eq. 11), respectively. Considering the similarity in the size of cyclooctatetraene and the benzenoid hydrocarbons which define the experimentally observed curves, the use of these curves in this special case seems, at least as a first approximation, not unwarranted. What are expected to be more reliable estimates of these reduction potentials can, however, be made as follows.

The effects which the specific consideration of electronic repulsion terms neglected in the Hückel theory have on the calculated polarographic half-wave potentials might be considered in the manner employed by Streitwieser^{24,33} in his elegant treatment of gas phase ionization potentials. Streitwieser demonstrated that a general correlation relates the theoretical and the observed ionization potentials of a variety of organic compounds if, by a simple device, account is taken of the varying effects of electronic repulsion. For benzenoid aromatic hydrocarbons the vertical ionization potentials calculated by use of the simple Hückel theory and by use of the ω treatment do not differ appreciably, but the difference between the computed ionization potentials of aromatic cyclooctatetraene derived by the two methods (7.07 ev. by the Hückel method; 7.29 ev. by the ω technique) suggests that the reduction potentials given above are somewhat (*ca.* 0.2 v.) cathodic. It is

(32) This is the mean square regression line of $E_{1/2}$ on a for eight of the above alternant hydrocarbons. The correlation coefficient is 0.97 and the standard error of estimate in a is only 0.019. Hoiijtink gives the equation $E_{1/2} = -2.82a - 0.49$ as best fitting all the hydrocarbons he examined.

(33) A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **82**, 4123 (1960).

interesting to observe that the half-wave potentials for hydrocarbon reductions appear to be linearly related to Streitwieser's χ 's (the changes in the coefficients of β on ionization), and for five alternating hydrocarbons (naphthalene, phenanthrene, anthracene, pyrene and tetracene) the mean square regression line of χ on $E_{1/2}$ (96% dioxane; 0.175 *M* tetra-*n*-butylammonium iodide; *vs.* mercury pool) is

$$E_{1/2} = 2.48\chi - 3.49 \quad (12)$$

with correlation coefficient 0.99 and standard error of estimate in χ of 0.024. Extrapolating to $\chi = 1.225$ for aromatic cyclooctatetraene yields

$$E_1 = -0.46 \text{ v.} \quad (13)$$

for the expected first half-wave potential.³⁴ If the first reduction potential of aromatic cyclooctatetraene is -0.46 v. (eq. 12), then the second reduction potential would be expected to be

$$E_2 = -0.86 \text{ v.} \quad (14)$$

Yet a third consideration can be brought to bear on the estimation of the reduction potentials of aromatic cyclooctatetraene. The χ -value for the hydrocarbon (1.225) is almost identical with that of the triphenylmethyl radical (1.239), for which polarographic data in the desired solvent system are available. The half-wave potential of the single wave observed on reduction of hexaphenylethane is -0.49 v. *vs.* mercury pool.⁸ From the known dissociation constant of hexaphenylethane,³⁵ its percentage dissociation in solutions of 1 to 5×10^{-3} formality can be calculated as 10–25%. Since the observed wave undoubtedly represents the reduction of triphenylmethyl radicals which diffuse to the electrode as such or as the dimer (which undergoes dissociation more rapidly than reduction), the actual reduction potential of triphenylmethyl radical is probably about 30 millivolts more anodic than the observed half-wave potential. That is, $E^\circ = -0.46$ v. The expected potential by eq. 12 is -0.42 v., in excellent agreement with the observed potential. The first two reduction potentials expected of aromatic cyclooctatetraene are, therefore, most probably those given by eq. 13 and 14: -0.46 v. and -0.86 v.

The latter is exactly the potential which was experimentally found for the anion radical by assuming only that it had the same geometry as the dianion; that is, that $\Delta F_{c2} = 0$. This in turn strongly suggests that the geometry of the anion radical and of the dianion is in fact the planar

(34) By contrast, the half-wave potentials of the same five hydrocarbons are linearly related to the coefficient, a , of β of the m.o. being filled by the regression line

$$E_{1/2} = -3.05a - 0.17$$

with correlation coefficient $r = 0.995$, and standard error of estimate in a of 0.012, suggesting again (probably incorrectly) that $E_{1/2}$ for aromatic cyclooctatetraene be only -0.17 v.

(35) K. Ziegler and L. Ewald, *Ann.*, **478**, 163 (1929).

aromatic structure. The great sensitivity of the reduction potential to the coefficient of β associated with the hydrocarbon m.o. being filled (eq. 11) indicates that any errors made in this analysis would not significantly alter the conclusion that the coefficient is in this case zero, or much closer to zero than to one.

Moreover, if $\Delta F_{c2} = 0$ and E_2 is known, the compression energy of cyclooctatetraene, ΔF_{c1} , can be derived, since E_1 is also known. E_1 is expected (eq. 13) to be -0.46 v., and, thus, by eq. 7, the energy required to compress cyclooctatetraene to the "aromatic" conformer is about 0.94 ev. = 22 kcal./mole.

The assumption that ΔF_{c2} is zero or very small requires further comment since the symmetrical anion radical would be expected theoretically to undergo Jahn-Teller distortions^{36,37} to which the symmetrical closed shell dianion would not be subject. Snyder^{37,38} has calculated that a planar anion radical with alternating long and short bonds should be more stable than a symmetrical species by as much as 2.4 kcal. Strictly, account of this correction should be made, but although the effect is remarkably large, it is not large enough that its neglect radically alters the conclusions drawn.

Experimental Methods

Conventional polarograms were recorded automatically with an all electronic instrument identical in principle with ones described in the literature,^{39,40} with scan rate of 0.1 volt/minute. Readout was to a Sargent model SR recorder. Oscillograms were obtained with apparatus which will be described elsewhere.²⁷ The electrolysis cell was a Sargent model s-29390. Solutions 0.001 *M* in cyclooctatetraene or anthracene and 0.175 *M* in tetra-*n*-butylammonium iodide were prepared in 96% dioxane and thermostated at 30°.

While the use of 96% dioxane in the major portion of our experiments was dictated by the availability of data on other electrode reactions in this medium, some experiments were performed in dimethylformamide. Unfortunately the conventional polarographic results were complicated here by the appearance of extra waves at -2.4 and -2.9 v. *vs.* Ag/AgClO₄ (satd.), which we recognized as arising from the elimination of carbon monoxide from the solvent. The solution becomes yellow on saturation with carbon monoxide, and the intensities of the extraneous waves are concomitantly enhanced.

Acknowledgments.—We wish to acknowledge the assistance of Mr. William Bahary, who performed preliminary experiments on the cyclooctatetraene system. We are grateful to the Badische Anilin and Sodafabrik for a gift of cyclooctatetraene, to L. C. Snyder and A. D. McLachlan for prepublication manuscripts, and to the National Science Foundation for a grant (NSFG-15561) in support of this research.

(36) H. M. McConnell and A. D. McLachlan, *J. Chem. Phys.*, **34**, 1 (1961).

(37) A. D. McLachlan and L. C. Snyder, *ibid.*, Feb. (1962).

(38) L. C. Snyder, private communication.

(39) D. D. Deford, Division of Analytical Chemistry, 133rd Meeting, A.C.S., San Francisco, Calif., April, 1958.

(40) M. T. Kelley, D. J. Fisher and H. C. Jones, *Anal. Chem.*, **31**, 1475 (1959); **32**, 1262 (1960).