THE ELECTROCHEMICAL REDUCTION OF TRANS-15,16-DIMETHYL-
DIHYDROPYRENE IN DIMETHYLSULFOXIDE

Albert J. Fry* and Ling Ling Chung[1]
Hall-Atwater Laboratories of Chemistry
Wesleyan University, Middletown, Conn. 06457

Virgil Boekelheide*
Department of Chemistry, University of Oregon
Eugene, Oregon 97403

A number of studies of the chemical and physical properties of trans-15,16-dimethyldihy-
dropyrene (1) and its derivatives have been reported.[2] Interest in 1 derives from the fact that
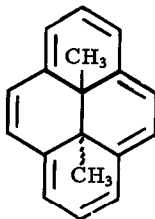
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it possesses a cyclic 14 π-electron system and consequently exhibits the chemical and physical
properties expected for an aromatic system. Some years ago Gerson, Heilbronner, and
Boekelheide reported a study of the E. S. R. spectrum of the radical cation and radical anion
of 1.[3] As part of their study, they examined the polarographic behavior of 1 in 75% aqueous
dioxane, and found a wave at -1. 83V (vs. s. c. e.) whose height corresponded to an overall two-
electron reduction. Unfortunately however, fundamental aspects of the electrochemistry of
aromatic hydrocarbons are frequently obscured in protic media such as 75% dioxane.[4] Fur-
thermore, the interesting behavior of the dianion of 1, which exhibits a strong paramagnetic
effect, in contrast with the induced diamagnetic ring current exhibited by 1 itself,[5] suggested
the desirability of examining the electrochemistry of 1 under aprotic conditions, where it ought
to be possible to study the generation of the dianion of 1. Inter alia, it was of interest to deter-
mine whether electron-transfer to 1 or its radical anion might be slow, since reduction of 1
results in conversion of a Huckel 4n+ 2 system successively to 4n+ 3 (radical anion) and 4n
(dianion) systems.

Two well-defined diffusion-controlled polarographic waves of approximately equal height
were exhibited by 1 in dimethyl-sulfoxide (DMSO) containing tetraalkylammonium salts as
supporting electrolytes; when lithium bromide was used as the supporting electrolye, reduction
of lithium ion precluded observation of the second wave (Table I). The potential of the first
wave was independent of the nature of the supporting electrolyte; the second wave however was

Table I. Polarographic Behavior of Aromatic Hydrocarbons in Dimethylsulfoxide[a]

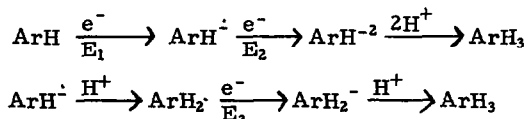| Hydrocarbon	Electrolyte	$-E_{1/2}, 1$(V)	$-E_{1/2}, 2$(V)	$\Delta E_{1/2}$(V)[d]	$\Delta G°$(kcal/mole)
1	Me_4NPF_6	1.59[c]	2.15	0.56	+12.9
1	Bu_4NClO_4	1.59[c]	2.27	0.68	+15.7
1	LiBr	1.59[c]	--[b]	---	---
Pyrene(2)	Me_4NPF_6	1.89	2.37	0.48	+11.1
Pyrene(2)	Bu_4NClO_4	1.88	2.43	0.55	+12.7
9,10-Diphenyl-anthracene(3)	Me_4NPF_6	1.83	2.29	0.46	+10.6
9,10-Diphenyl-anthracene(3)	Bu_4NClO_4	1.82	2.35	0.53	+12.2

[a]Solutions were 1mM in hydrocarbon and 0.1M in supporting electrolyte. Potentials are rela tive to s. c. e. [b]Reduction of lithium ion obscures the second wave. [c]Tomes' criterion, $E_{1/4}-E_{3/4}$,[9] was equal to 57, 54, and 55mV for the first wave of 1 in the presence of Me_4NPF_6, Bu_4NClO_4, and LiBr, respectively. [d]$\Delta E_{1/2}=E_{1/2, 2}-E_{1/2, 1}$

observed at distinctly more negative potential when the cation of the electrolyte was tetrabutyl-ammonium than when it was tetramethylammonium.[6] This appears to be a general phenomenon; representative data for two polycyclic aromatic hydrocarbons, pyrene (2) and 9,10-diphenyl-anthracene (3) are also included in Table I. Discussion of this point appears later in this paper. The number of electrons involved in the first polarographic wave of 1 (and therefore also in the second wave) was evaluated by two methods: (a) Polarographic currents for equal concentrations of 1 and pyrene, a molecule of similar size and shape, are identical within experimental error. Since the first wave for pyrene involves a one-electron transfer,[7] that for 1 must also involve one electron. (b) Malachesky's method for determination of n,[8] in which one measures the ratio of $iv^{-1/2}/it^{1/2}$ [where $it^{1/2}$ is the constant obtained from a chronoamperometric (potential-step) experiment and $iv^{-1/2}$ is the corresponding constant obtained by linear-sweep voltammetry] afforded a value for this ratio of 4.3; values between 4 and 5 correspond to a one-electron reduction process.[8] The polarographic diffusion current constant, $I_d^9(=708nD^{1/2})$, was found to be 1.63. Since n=1, this corresponds to a diffusion coefficient of 1 of 5.3×10^{-6} cm^2 sec^{-1}, a reasonable value.[9] The two polarographic waves of 1 correspond to stepwise succes-sive formation of the corresponding radical anion (1$^-$) and dianion (1^{-2}).

The initial electron-transfer to 1 is rapid and reversible. Thus, by Tomes' criterion,[10] the value of $E_{1/4}-E_{3/4}$ varies from 54 to 57mV, depending upon electrolyte, but always within ex-perimental error of the value of 56mV predicted for a reversible process.[10] The Nicholson-Shain cyclic voltammetric criteria for a rapid reversible process[11] were also satisfied for the first electron-transfer. When the direction of potential scan was reversed after the second re-duction peak, no corresponding anodic peak was observed even at scan rates as high as 100V/sec;

a small anodic peak was however observed at a potential corresponding to the first cathodic peak. Similar cyclic voltammetric behavior is exhibited by aromatic hydrocarbons such as $\underset{\sim}{2}$ or $\underset{\sim}{3}$ in DMSO.

Addition of either 2, 4, 5-trimethyl-phenol or benzoic acid resulted in an increase in the height of the first polarographic wave of $\underset{\sim}{1}$ at the expense of the second wave. When a large amount of benzoic acid (ten-fold excess) was added, the first wave doubled in height and the second wave was no longer evident. This behavior is characteristic of the following reduction scheme common to many polycyclic aromatic hydrocarbons:[4]

$$ArH \xrightarrow[E_1]{e^-} ArH^{\cdot} \xrightarrow[E_2]{e^-} ArH^{-2} \xrightarrow{2H^+} ArH_3$$

$$ArH^{\cdot} \xrightarrow{H^+} ArH_2 \cdot \xrightarrow[E_3]{e^-} ArH_2^- \xrightarrow{H^+} ArH_3$$

where E_2 is negative of E_1 but E_3 is positive of E_1. Protonation of the initially-formed radical anion affords a neutral radical (ArH$_2$·) which is reduced rapidly to afford, after protonation, a dihydro derivative of the original aromatic compound. No new polarographic wave appeared for $\underset{\sim}{1}$ in the presence of proton donors, hence either the dihydroderivative of $\underset{\sim}{1}$ is not reducible at accessible potentials, or else its reduction wave is obscured by the polarographic wave associated with hydrogen discharge from the proton donor.[12] Simple M. O. theory predicts $\underset{\sim}{4}$ to be the major product of this reduction, and 4 is undoubtedly harder to reduce than any other dihy-

$$\underset{\sim}{4}$$
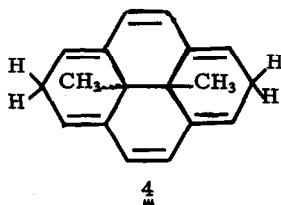
dro derivative of $\underset{\sim}{1}$ (since all others would contain more extended conjugation) but a mixture of dihydro compounds is very likely formed. The limited quantities of $\underset{\sim}{1}$ available to us did not permit examination of this reduction on a preparative scale.

All of the data demonstrate that the electrochemical behavior of 1 very closely parallels that exhibited by typical polycyclic aromatic hydrocarbons. There is however one respect in which $\underset{\sim}{1}$ does differ from such compounds. The difference $\Delta E_{1/2}$ between the first and second polarographic half-wave potentials of $\underset{\sim}{1}$ is substantially larger than for aromatics such as $\underset{\sim}{2}$ or $\underset{\sim}{3}$ (Table I). Making the not unreasonable approximation that both electron transfers are reversible,[13] one may show that $\Delta G°$ for disproportionation of an aromatic radical anion, i. e. ,

$$2 \, ArH^{\cdot -} \rightleftharpoons ArH + ArH^{-2}$$

is given by $\Delta G° = n \mathcal{F} \Delta E_{1/2}$. From the data of Table I, two effects may be noted: $\Delta G°$ is always larger when the cation of the electrolyte is tetrabutylammonium than when it is tetramethyl-

ammonium, and $\Delta G°$ is distinctly larger for 1 than for 2 or 3. We believe that the first of these two phenomena is associated with a greater degree of ion pairing when R in R_4N^+ is methyl than when it is butyl. Ion pairing ought to be more important with the dianion ArH^{-2} than for the radical anion, hence increased ion pairing should favor disproportionation. We believe that the differences in $\Delta G°$ between 1 and the other aromatic hydrocarbons is associated with steric hindrance to ion-pairing caused by the methyl groups in 1, which should restrict close approach of the cation of the electrolyte toward either face of the π-system. This should be particularly true for large cations, and indeed $\Delta G°$ is strikingly large for reduction of 1 in the presence of tetrabutylammonium ion.[14] Cox, et al., have observed steric hindrance to ion-pairing of lithium ion to the radical anion of 1.[15]

References

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6) The second wave for 1 in the presence of lithium ion is obscured by the reduction of lithium to its amalgam at mercury, but presumably this wave would be observable at platinum or other inert electrode material. See J. Perichon and R. Buvet, Bull. Soc. Chim. Fr., 1279, 1282 (1968).
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12) A third possibility, that protonation of the monoanion (ArH_2^-) of 1 is slow on the polarographic time scale, and that this species is not reducible, is considered unlikely, since protonation of the monoanion should be rapid in the presence of an excess of benzoic acid.
13) The cyclic voltammetry data clearly justify this assumption for the first wave of all compounds studied. The data indicate further that the second wave is not reversible due to follow-up chemical reactions. The $E_{1/2}$'s of the second waves will be in error for this reason, but we assume that the error is minimized when comparing a set of similar compounds because all $E_{1/2}$'s should be shifted in the same direction. The $\Delta G°$'s then calculated will also be in error, however, trends will still be meaningful. We believe that this factor results in a fairly small deviation of the measured values of $\Delta G°$ from the true ones.
14) For a further discussion of the role of ion-pairing in electrochemical reduction of aromatic hydrocarbons, see L. A. Avala and A. Bewick, J. Electroanal. Chem., 41, 405 (1973).
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