Electrochemical Reduction of Substituted 15,16-Dihydropyrenes in Dimethylformamide

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The electrochemical reduction of a series of 15,16-disubstituted 15,16-dihydropyrenes and some benzannelated derivatives was studied by differential pulse polarography in dimethylformamide. The large spacing between the first and second reduction waves, compared to polycyclic benzenoid hydrocarbons, is probably due to (a) steric inhibition of ion-pairing to the electrolyte cation by the 15,16-substituents and (b) the conversion of the Huckel 14-electron ($4n+2$) starting material to a 16-electron dianion. The first reduction potentials of the compounds correlate fairly well with the Huckel LUMO energy, and with an equation previously derived by Streitwieser for benzenoid hydrocarbons.

Some of the most significant insights which organic electrochemists have attained into the principles underlying the cathodic behavior of organic compounds have come from studies of the electrochemical behavior of aromatic hydrocarbons in aprotic media.¹ Such studies provide information concerning the thermodynamics and kinetics of the injection of electrons into unfilled orbitals of the hydrocarbon to form successively the corresponding radical anion at potential E_1 , (eqn. 1), and dianion at potential E_2 , (eqn. 2), without complications introduced by either coupled chemical reactions or the presence of electro-active substituents. Almost all of the

hydrocarbons which have been investigated in this manner have been polycyclic benzenoid substances, since they are available in diversity. For this reason, however, one may reasonably inquire whether in fact any of the electrochemical behavior exhibited by such substances derives specifically from their benzenoid nature. Are there any aspects of such behavior which are not shared by nonbenzenoid hydrocarbons? A brief study of the electrochemical behavior of *trans*-15,16-dimethyl-15,16-dihydropyrene (*1a*) which we carried out several years ago² first forced us to address this question. As will be elaborated in the Discussion section, we observed that ΔE , the spacing between the first and second reduction potentials in aprotic media, is significantly larger for *1a* than for a variety of polycyclic benzenoid hydrocarbons. We interpreted the difference as due to steric hindrance to ion-pairing between the dianion of *1a* and the cation of the supporting electrolyte, caused by the methyl groups at the 15,16-positions. However, our subsequent observation³ that ΔE is actually *smaller* for cyclooctatetraene (COT) than for benzenoid hydrocarbons suggested that something more might be involved.

As a consequence of considerable recent synthetic activity in this area, a number of substi-

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tuted 15,16-dihydropyrenes are now available.⁴⁻⁶ We wish to report a study of the electrochemical behavior of 1-8, which has permitted us to derive further insights into this ring system and into the question posed above. The electrochemical technique employed was differential pulse polarography (DPP)⁷ at a dropping mercury electrode, because (a) the high signal-to-background ratio characteristic of this technique enabled us to make measurements upon the limited amounts of samples available, and (b) the sharply peaked signals permitted accurate measurements of reduction potential.

RESULTS

Precision of DPP measurements. It was necessary to establish at the outset that data of sufficiently high precision could be obtained by the DPP technique, which is widely used in analytical work but only infrequently in mechanistic studies. A series of 4-8 polarograms were recorded on an expanded voltage scale (1 volt=30 cm) and at low potential scan rate (2 mV/s) and short polarographic drop time (1 s) to minimize instrumental artifacts;⁸ the DPP peak potentials could be corrected where desired to normal DC polarographic half-wave potentials

- 2a, R₁=R₂=Me
2b, R₁=Me; R₂=Et
2c, R₁=Me; R₂=n-Pr
2d, R₁=R₂=Et
2e, R₁=Et; R₂=n-Pr
2f, R₁=R₂=n-Pr
2g, R₁=R₂=n-Bu

($E_{1/2}$) by the method described in the Experimental section. The standard deviation of a set of DPP peak-to-peak measurements was typically 0.8 to 2 mV; for example, for 2d, ΔE was measured as 762, 764, 763, 763, 764 and 764 mV, corresponding to a mean value of 763 mV and standard deviation of 1 mV. The ΔE values are therefore considered to be reliable to $\pm 1-2$ mV.

Series 1 and 2. Compounds 1a-b and 2a-g all exhibit the same electrochemical behavior: two DPP polarographic peaks are observed in dimethylformamide (DMF) containing tetrabutylammonium perchlorate. The values of E_1 , E_2 and ΔE measured for these substances are presented in Table 1, together with data for pyrene (3a) and 2,7-di-*t*-butylpyrene (3b). A representative voltammogram is shown in Fig. 1.

Fig. 1. Derivative pulse polarogram of 2,7-di-*t*-butyl-15,16-dibutyl-15,16-dihydropyrene (2g) in dimethylformamide containing 0.1 M Bu₄NClO₄; 2 mV/s, 1 s drop time.

Table 1. Reduction potentials of substituted 15,16-dihydropyrenes and pyrenes.^a

Compound	$-E_1/V$	$-E_2/V$	$\Delta E/V$
1a	2.22	3.01	0.69
1b	2.150	2.893	0.743
2a	2.344	3.080	0.736
2b	2.357	3.104	0.747
2c	2.348	3.100	0.752
2d	2.331	3.094	0.763
2e	2.333	3.098	0.765
2f	2.332	3.103	0.771
2g	2.334	3.108	0.774
3a	2.521	3.104	0.583
3b	2.580	3.173	0.593

^a Potentials are differential pulse polarographic peak potentials in dimethylformamide/0.1 M Bu₄NClO₄, relative to Ag/0.1 M AgNO₃.

Benzo series. The benzodihydropyrenes 4–8 were found to exhibit diverse cathodic behavior, characterized in general by more than two voltammetric waves. The first wave in each case is presumably associated with formation of the radical anion; we have not chosen to speculate upon the processes responsible for the waves at more negative potential, and the very small available amounts of sample (1–3 mg) precluded preparative experiments which might have provided information on this point. The [a]-ring benzannelated compound was examined by conventional DC polarography and exhibited three

Fig. 2. Derivative pulse polarograms of benzo-dihydropyrenes 5 and 8 in dimethylformamide containing 0.1 M Bu₄NClO₄; curve 1, compound 5; curve 2, compound 8.

Fig. 3. Derivative pulse polarograms of benzo-dihydropyrenes 6 and 7 in dimethylformamide containing 0.1 M Bu₄NClO₄; curve 1, compound 6; curve 2, compound 7.

waves at -2.08 , -2.62 and 3.1 V. The other substances were examined by differential pulse polarography. (Figs. 2 and 3). The first voltammetric wave for each substance was found to be as follows: 5, -2.04 V; 6, -1.68 V; 7, -2.220 V; 8, -1.91 V.

DISCUSSION

By subtraction of eqn. (2) from eqn. (1) (Introduction) one obtains eqn. (3), from which it may be noted that the ΔE , the spacing between E_1 and E_2 , provides a measure of the position of the disproportionation equilibrium illustrated in eqn. (3).

$$\Delta G = -F(E_1 - E_2) = -F\Delta E$$

It is important to note that theoretical calculations,³ which predict values of ΔE for eqn. (3) of upwards of 5V, are in severe disagreement with experiment. Typical values of ΔE lie in the range 0.5–0.6 V for a wide variety of hydrocarbon structures; it is generally believed that the dianion on the left side of the equilibrium of eqn. (3) is more extensively solvated and ion-paired to the supporting electrolyte cation than is the

radical anion, thus driving the equilibrium much more to the left than the calculations, which do not take this effect into account, would indicate. The fact that ΔE lies within the narrow range 0.5 to 0.6 V for a variety of aromatic structures suggests that solvation effects on eqn. (3) are roughly similar for most benzenoid aromatic structures. Though surprising, this seems to be in fact a rather good approximation. Indeed, there seem to be only minor differences between the electrochemical reduction potentials of such substances in solvents as remarkably diverse as aqueous dioxane, 2-methoxyethanol, and DMF.^{9,10}

We noted previously² that ΔE is larger for *1a* in dimethylsulfoxide (0.68 V) than for the general run of benzenoid aromatic hydrocarbons; e.g., 0.55 V for pyrene (*3a*). We argued that the methyl groups in *1a* sterically inhibit approach of a tetraalkylammonium ion to either face of the π -system. However, we subsequently observed³ that ΔE is unusually small (<0.2 V) for COT, even though the degree of ion-pairing to the planar COT dianion should be sterically similar to species such as pyrene dianion. It was clear, therefore, that the steric argument might not be sufficient to explain the data. The results obtained in the present study provide useful information on this problem. Generally speaking, the data in Table 1 confirm beyond question the existence of a steric effect upon association of 15,16-dihydropyrene dianions with tetrabutylammonium ion, inasmuch as ΔE increases in a regular way as the R_1 and R_2 groups increase in size. More specific conclusions are possible, however. Note that one face of the π -system becomes increasingly hindered as one proceeds through both the series *1a,b* and *2a-c*. Since ΔE also increases concomitantly, we can conclude, contrary to what one might have guessed, that such systems do not respond to increased hindrance on one face of the π -system simply by correspondingly greater ion-pairing and solvation on the other face, although this presumably does occur to some extent. A more significant conclusion may be reached by examining the symmetrically substituted series, *2a,d,f,g*; ΔE increases by 27 mV in going from *2a* to *2d*, but subsequent increases are small, i.e., 8 mV from *2d* to *2f*, and only 3 mV from *2f* to *2g*. Examination of space-filling models leads to the same conclusion, that the largest increase in effective group size in

this system comes in going from *2a* to *2d*. This is not what one would expect from some other measures of effective group size, e.g., conformational A-values,¹¹ Taft steric constants,¹² or effects of group size upon the rates of S_N2 displacements,¹³ but these generally describe the steric constraints upon attack on an alkyl chain from a direction *normal* to the (average) axis of the chain, whereas ion-pairing to anions derived from *2a-f* involves approach along an axis *parallel* to the axis defined by C-15 (or C-16) and the carbon directly bound to it.

What one would really like to know, however, is what ΔE would be in the absence of the two methyl groups of *2a*. Would it be 0.59 V, the value for *3b*, or would it be larger? We think the latter is more likely, because even if the methyl groups were removed the tetrabutylammonium ion could not approach much closer than with *2a* anyway because of the intrinsic bulk of the π -system itself (recall that the van der Waals' "thickness" of substances such as benzene is *ca.* 3.7 Å).¹⁴ If we accept the latter argument, we are left with the conclusion that the large values of ΔE observed for *1* and *2* are not primarily steric in origin, but that a second effect is involved. We believe that this effect is electronic. Addition of two electrons to the diatropic¹⁵ Huckel $4n+2$ dihydropyrene system converts it to a paratropic¹⁵ $4n$ system, the relative instability of which will drive eqn. (3) to the right; conversely, reduction of COT to its dianion converts a $4n$ system to a $4n+2$ species, the stability of which would drive eqn. (3) to the left. In general, ΔE should therefore be small for Huckel $4n$ systems and large for $4n+2$ systems. Data in the literature support this hypothesis. Thus, a number of nearly planar bridged [14] annulenes exhibit ΔE values in the range 0.6–0.7 V,¹⁶ while [16]annulene,¹⁷ a doubly-bridged [16]annulene,¹⁸ and two bridged [12]annulenes¹⁹ all have ΔE in the range 0.2–0.3 V, and, as already noted, COT or [8]annulene exhibits a ΔE value of less than 0.2 V.² The only apparent exception to this generalization in the literature is the ΔE of 0.65 V for an isomer of [12]annulene,¹⁹ but this substance *and* its dianion (unlike COT) are both non-planar and could be expected to behave anomalously. It may be inappropriate to include COT in this list because of the large geometrical change involved in reduction of the tub-shaped neutral molecule to the nearly-planar radical anion, but it is notable

that a small value of ΔE is observed for all of the other $[4n]$ annulenes, despite the variety of geometrical situations represented among them.

The electrochemical data on benzo derivatives 4–8 is instructive. It may initially seem surprising that while annelation of a single benzene ring onto the nucleus of *1a* lowers the reduction potential (4 and 5), a second benzannellation either lowers the reduction potential (6) or increases it (7) depending upon the position of annelation. However, the data are better understood by examining the degree of correlation between the polarographic half-wave potentials and m_{n+1} , the coefficient of the lowest unoccupied molecular orbital (LUMO) computed by the Huckel M. O. method (Table 2). The experimental half-wave potentials can be compared with values computed by the empirical correlation found by Streitwieser¹⁰ for a series of hydrocarbons in DMF containing tetrabutylammonium iodide (eqn. (4))

$$E_{1/2} = (2.407 \pm 0.182)M_{n+1} - (0.396 \pm 0.093) - 1.010 \quad (4)$$

where $E_{1/2}$ is the polarographic half-wave potential relative to Ag/0.1 M AgNO₃ and the last term is the correction factor necessary to correct potentials measured relative to this reference to the mercury pool reference used by Streitwieser. As Table 2 shows, there is rather good agreement

between the calculated and observed reduction potentials. In every case the dihydropyrene is easier to reduce than predicted by the empirical relationship, but the variations are close to or within the error limits of the Streitwieser correlation, hence the effect may not be real. It is interesting to note that there is an especially large deviation with the dibenzo compound 6, for which other evidence²⁰ indicates the possibility of a low-lying triplet state; on the other hand, the parent substance of the series, *1a*, deviates equally from the Streitwieser line. An alternate way to view the data is to construct a Streitwieser-type correlation line for the data of Table 2 (eqn. (5)).

$$E_{1/2} = (2.488 \pm 0.302)M_{n+1} - (0.208 \pm 0.0336) - 1.010 \quad (5)$$

Examination of eqn. (5), in which the intercept is written in two parts to facilitate comparison with eqn. (4), shows that the line has the same slope (within experimental error) as the Streitwieser line, but different intercept. This could perhaps be related to a somewhat different degree of solvation of the radical anions of these substances compared to polycyclic benzenoid hydrocarbons.

Finally, the similarity of the ΔE values for *1a* and *2a* and for *3a* and *3b* demonstrate the minimal effect of groups at positions 2 and 7 upon ion-pairing, in contrast with the systematic changes associated with substituents at positions 15 and 16. The space-filling models show that substituents at the latter positions should indeed play a much greater role in shielding the π -system, even when the groups at 2 and 7 are *t*-butyl.

CONCLUSIONS

The two-electron reduction of dihydropyrenes in DMF affords dianions which are destabilized relative to those from benzenoid aromatic hydrocarbons. The effect is thought to arise (a) because the 15, 16 substituents create steric hindrance to solvation and ion-pairing of the corresponding dianion, and (b) from the fact that dihydropyrene dianions, as Huckel $4n$ systems, are electronically destabilized compared to those from benzenoid aromatic species. It is concluded that ΔE will

Table 2. Correlation between first reduction potential and Huckel LUMO energy.

Compound	$-m_{n+1}^a/\beta$	$-E_{1/2}/V$	
		Experimental ^b	Calculated ^c
6	0.226	1.70	1.95 ± 0.14
8	0.285	1.93	2.09 ± 0.15
5	0.325	2.06	2.19 ± 0.15
4	0.325	2.08	2.19 ± 0.15
7	0.357	2.22	2.27 ± 0.15
1a	0.445	2.23	2.48 ± 0.16

^a Energy of Huckel LUMO. ^b Differential pulse polarographic peak potentials were corrected to DC half-wave potentials by the addition of 0.015 V (see Experimental). ^c Calculated by the equation $E_{1/2} = (2.407 \pm 0.182)m_{n+1} - (0.396 \pm 0.093) - 1.010$; note that m_{n+1} is a negative number (see Ref. 10).

generally be large (>0.6 V) for reduction of $4n+2$ annulenes, and small (<0.4 V) for $4n$ systems. It may be, therefore, that the ΔE value can be used to estimate the diatropic or paratropic nature of a new dianion.

Finally, the sensitivity of the voltammetry to small steric differences deserves comment. The total change in ΔE across the series $2a-g$ corresponds to an overall change in ΔG for eqn. (4) of less than 1 kcal, yet each steric increment, even those as minor as the change from $2d$ to $2e$, is faithfully mirrored in the DPP voltammetric data.

EXPERIMENTAL

Dimethylformamide was distilled from calcium hydride at aspirator pressure. Tetrabutylammonium perchlorate (G. Frederick Smith Chem. Co.) was dried overnight in an Abderhalden apparatus at 56°C . Differential pulse polarography (DPP) was carried out using a PAR Model 170 Electrochemistry System with Model 172 drop timer. DPP peak potentials were found to be positive of polarographic half-wave potentials. The appropriate correction factor was found to be 0.015 V by measuring the difference between the DPP peak potential of pyrene on an expanded scale and the polarographic half-wave potential, defined as the point where $\log i/(i_d - i) = 0$ and located by an appropriate computer program. $E_{p,DDP}$ and $E_{1/2}$ were found to be -2.521 and -2.536 V, respectively. Potentials were measured relative to a reference electrode consisting of a silver wire immersed in a 0.1 M solution of silver nitrate in acetonitrile, contained in a length of heavy-walled Teflon tubing closed at one end by a short length of porous Vycor rod.

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