THE APPLICATION OF ELECTROCHEMISTRY TO SOME PHYSICAL ORGANIC PROBLEMS

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ABSTRACT

Carbonium ions, radicals and carbanions are simply different oxidation states of trivalent carbon, which can be electrochemically interrelated. By use of electrochemical techniques, along with thermodynamic information, the pK_as of various cyclopropenes can be calculated. Furthermore, cyclopentadienyl cations can be produced by electrochemical oxidation and their pK_{R+}s determined in an indirect way. Cyclobutadiene derivatives can also be electrochemically generated and the cyclobutadiene resonance energy thereby deduced.

The electrochemistry of some of these very unstable species is non-ideal, but theoretical and experimental evidence shows that the resulting errors are small. Thus, electrochemical methods are probably the best technique by which to obtain thermodynamic information on unstable species.

Trapping experiments have led to the development of a novel electrolyte. This work confirms the assignment of potentials and indicates a striking effect of charge on trapping effectiveness.

For a number of years we have been interested in conjugated systems with $4n\pi$ electrons; on the basis of a variety of physical studies, we have concluded that some of these species are anti-aromatic, i.e. destabilized by conjugation[1]. Recent work has utilized electrochemistry to study such unstable species. With electrochemical techniques, when they are applicable, one can generate extremely unstable and otherwise inaccessible species and also, from the potentials required, get information about the energies of the reaction products.

Under ideal conditions electrochemical information is thermodynamic, but under less than ideal conditions it begins to approach information which is kinetic in character. Really interesting chemical cases hardly ever turn out to be ideal, so our studies have perforce involved some non-ideal electrochemistry. We are thus concerned with the question of how much error is thereby introduced.

The species of interest to us are the cyclopropenyl anion, the cyclobutadiene system, the cyclopentadienyl cation and the cycloheptatrienyl anion. In some of the cyclobutadiene work we have also examined the electrochemistry of benzenoid systems. Since our work covers the range of three- to seven-membered rings, I should like to thank the organizers of this symposium for kindly adopting as its symbol a superimposed set of polygons ranging over the same ring sizes. This was doubtless in anticipation of my lecture! The first system we will consider is the cyclopropenyl anion. Although we

had observed[2] base-catalysed deuterium exchange in cyclopropene derivatives carrying strong activating groups, such as cyano or benzoyl substituents, we had found[3] that all attempts to remove the ring hydrogen from triphenylcyclopropene were unsuccessful. This includes both attempts to equilibrate this compound with its anion and also even attempts to detect deuterium or tritium exchange under vigorous basic conditions. Thus, there was available no thermodynamic information on the 1,2,3-triphenylcyclopropenyl anion.
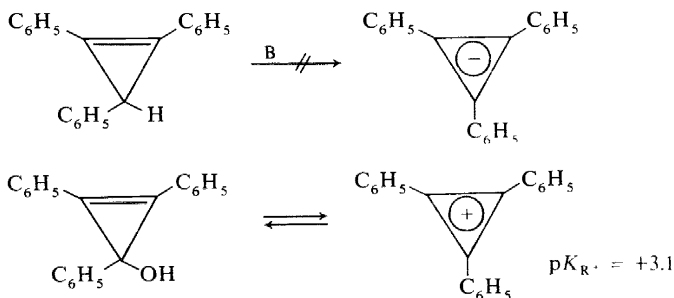
We had excellent thermodynamic information on the corresponding cation[4], which can be reversibly equilibrated with the corresponding covalent alcohol. Our work involved the realization that carbonium ions and carbanions are simply different oxidation states of carbon, and that any information on carbonium ions in a given series could be utilized along with reduction potentials to obtain thermodynamic information about the corresponding anion. Carbon radicals are of course an intermediate oxidation state between cation and anion; the three different classes of reactive trivalent carbon intermediates can thus be directly linked with one another if the electrochemical connections can be made. I might add that in inorganic chemistry the electrochemical interrelation of different oxidation states of the central atom is a common activity.

The thermodynamic cycle used for pK_a determination[5] is as shown. By this cycle a hydrocarbon can be converted to its corresponding anion even if this

$$RH \rightarrow ROH \rightarrow R^+ \rightarrow R^{\cdot} \rightarrow R^-(\rightarrow RH)$$
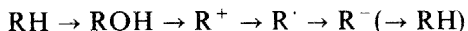
process cannot be directly achieved.

The first step, conversion of a hydrocarbon to the corresponding alcohol, is the kind of process in which thermodynamics specializes. That is, we do not directly carry out such a conversion, but rather we consult tables of heats of formation. They indicate that the energy involved in conversion of a hydrocarbon to the corresponding alcohol is relatively constant for various R groups and can be empirically corrected to a minor extent for the known differences in these heats of formation among different classes of compounds. For instance, the energy difference between a tertiary alcohol and the corresponding hydrocarbon is not quite the same as that between a secondary alcohol and its related hydrocarbons. In practice, we make such corrections by using a reference compound for which all the steps in the thermodynamic cycle are known.

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The conversion of an alcohol to a carbonium ion is, for cyclopropenyl cations, an observable reversible equilibrium which can be characterized by the pK_{R+} determinable[4] by use of acidity function techniques. Reversible conversion of a carbonium ion such as triphenylcyclopropenyl cation to the corresponding radical is an electrochemical process[6]. The second step, reduction of the radical to the corresponding anion, is also an electrochemical process. Our studies of the cyclopropenyl cation reductions were done simultaneously with work on tropylium ion and on substituted triphenylmethyl cations, which systems helped us to calibrate the method and establish its reliability.

We have examined various electrochemical techniques to determine reversible thermodynamic potentials for the interconversions between ion and radicals. The simplest and best-known electrochemical method, polarography at a dropping-mercury electrode, involves a slow continuous sweep in the potential applied at the electrode as the current is monitored. Slightly more sophisticated versions involve applying pulses of increased amplitude as a function of time and also sampling the resulting current at a particular time with relation to the pulse. These techniques produce somewhat cleaner versions of a classical polarogram.

A.C. polarography, by contrast, involves superimposing a high-frequency a.c. modulating signal on the polarographic sweep; the detector is set to monitor the resulting current, which fluctuates at the same a.c. frequency. By adjusting the phase relationship between the applied signal and the detected current it is possible to obtain important extra information about the process. In general, when a potential sweep is applied to an electrode system, two processes can occur which involve passage of current. One is electron transfer to electroactive species, such as the substrate. The resulting faradaic current is what is of interest. In addition, current passes as a result of restructuring of the double layer of electrolyte near the electrode surface. This process, analogous to charging a capacitor, involves the capacitative current; it is not related to electron transfer to or from the substrate of interest. The capacitative and faradaic a.c. signals occur with a different phase relationship relative to the applied signal, so a.c. polarography makes it possible to tune out the capacitative component and detect only the charge transfer process, which is of chemical interest. An incidental advantage of a.c. polarography is that the polarogram is presented as a derivative curve, and thus inflection points in a normal polarogram are instead peak maxima in the a.c. polarogram. As we will describe, we have utilized this technique for some of our studies.

In general, electrochemical processes which produce very unstable species, such as anti-aromatic ions, present an additional difficulty. The products are kinetically unstable and rapidly disappear through chemical processes such as dimerizations. The result of this is to perturb the apparent potential required to produce such a species, since the subsequent chemical reaction removing products of the electrochemical step makes it easier to carry out that step. Thus, it is necessary to have a technique which minimizes the effect of such subsequent chemical reaction, and for this we use cyclic voltammetry. The measurement is performed with a stationary electrode, commonly platinum, and it utilizes a triangular potential sweep. Potential is rapidly changed

to pass through the potential required for an electrochemical process, and it is then rapidly reversed to reverse that process. If a carbonium ion is reduced to a radical by such a rapid sweep and the sweep is reversed sufficiently quickly for the radical (or at least some of it) to be oxidized again, then signals will be obtained for both the reduction and the oxidation processes. Under these circumstances it is easy to correct for the effect of the subsequent reaction and to obtain a good thermodynamic potential. Our best data are obtained with this technique, but in some cases we have been able to confirm them by other methods.

To illustrate the problems, *Figure 1* shows the ordinary d.c. polarogram[7]
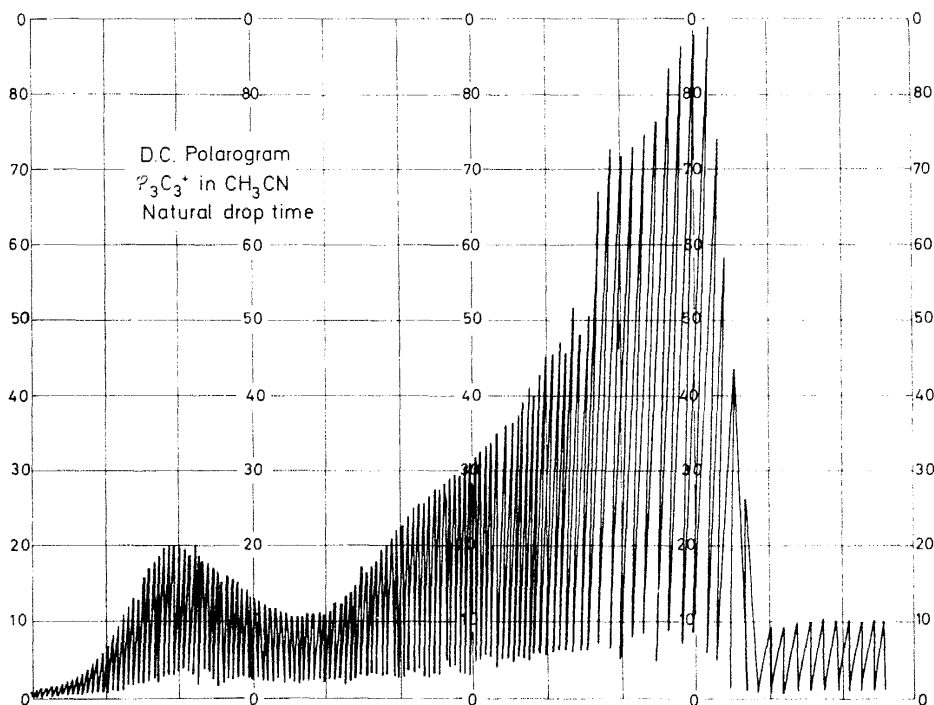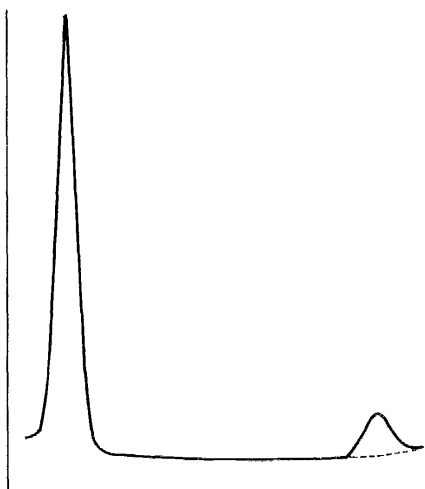

Figure 1. DC polarogram of triphenylcyclopropenyl cation in acetonitrile

of triphenylcyclopropenyl cation in acetonitrile solvent with tetrabutyl-ammonium perchlorate as supporting electrolyte. The potential sweep covers the entire region in which first one and then the second electron is being added to the cation. From such a curve no useful electrochemical information can be extracted. Applications of pulsed or current sampled techniques to this system do not significantly improve the polarogram. In fact, only with cyclic voltammetry could potentials for the first and second reduction process be obtained, and these were then confirmed by controlled potential electrolyses, as discussed below.

Studies[7] on the reduction of tropylium ion revealed an interesting new phenomenon. This system gives somewhat cleaner polarographic waves, and

in particular (under special conditions described below) the a.c. polarogram of tropylium cation (*Figure 2*) shows nice maxima for the first and second waves at the same potentials derived from cyclic voltammetry studies. However, with cyclic voltammetry the first and second waves are both observable with tetrabutylammonium perchlorate as a supporting electrolyte. With polarography, including a.c. polarography, only the first wave can be discerned with this electrolyte and the second wave is invisible.

Figure 2. AC polarogram of tropylium cation in acetonitrile, with guanidinium perchlorate as supporting electrolyte. The dashed line is with tetrabutylammonium perchlorate electrolyte instead; the curves are otherwise identical

The distinction has to do with a fundamental difference in the processes involved in these techniques. Cyclic voltammetry involves a time scale so short that material does not diffuse to the electrode, and instead one observes electrochemical processes involving the substrate in a layer close to the electrode to start with. At the first reduction potential tropylium cation can be reduced to the radical; if we then get rapidly to the second potential, some of this radical can be reduced again to the anion in competition with its dimerization. This anion then diffuses into solution to undergo further chemical changes. Thus, at the second potential there is an increase in current when some radical is converted to anion and this results in an observable second wave.

By contrast, polarographic methods are controlled by diffusion processes, and the faradaic current reflects the chemistry which occurs at the electrode as substrate diffuses to it. At the first potential tropylium cation diffuses to the electrode and is reduced to the radical, which then undergoes dimerization. This leads to a certain level of current. At the second potential tropylium cation will diffuse to the electrode and pick up two electrons to be converted to the anion. However, this anion then reacts with a second tropylium cation which has diffused to the electrode. The result is that again the dimer, bis-

cycloheptatrienyl, is formed. Furthermore, by the process just described there has been no increase in current. Again the current is limited by the rate of diffusion of tropylium cation to the electrode, and again the process has involved the addition of two electrons to two tropylium cations to afford the dimer. Since there is thus no increase in current at the second potential, the second wave cannot be detected.

The only solution to this problem is to divert the chemistry of cycloheptatrienyl anion so that it does not quench an incoming tropylium cation. Interestingly, it is not possible to do this by incorporating even 50 mol per cent of acetic acid into the solvent. Although tropylium anion should be rapidly trapped by acetic acid, this does not occur in the electrochemical system as described. Instead, even at the second potential only the dimer is formed and no second wave can be detected in polarography.

We reasoned that the chemistry involved in trapping must be occurring within the layer of electrolyte itself which surrounds the electrode, and that acetic acid may be excluded from this layer while tropylium cation is incorporated in it. Accordingly, we examined the possibility of using an electrolyte which could serve as a proton donor to trap the electrolyte product and found that this is very readily achieved with the novel electrolyte guanidinium perchlorate. As *Figure 2* shows, using this electrolyte we can indeed see a second wave for tropylium which turns out to be at the same potential as that revealed by cyclic voltammetry.

The products of controlled potential electrolyses at the two reduction potentials under various conditions are listed in *Table 1*. It is apparent that acetic acid is completely ineffective in trapping the cycloheptatrienyl anion or the triphenylcyclopropenyl anion. However, guanidinium ion is able to trap these anions, and thus lets us confirm the assignment of the chemistry which occurs at the first and second potentials. An additional point of interest is that guanidinium ion is still less effective than tropylium cation or triphenylcyclopropenyl cation in trapping the corresponding anions, remarkable since the supporting electrolyte guanidinium cation is present in one-hundred-fold excess over the substrate cations themselves. Proton transfer from guanidinium cation to these anions should be extremely fast, so the coupling process must proceed by a mechanism which is even faster. Since ordinarily carbon–carbon bond formation would seem to be subject to much more steric hindrance than is a proton transfer, we conclude that the

Table 1. Products of controlled potential electrolysis

	Electrolyte	First wave	Second wave
Tropylium	0.4 M TBAP	Dimer (99 %)	Dimer (99 %)
	with HOAc (50 %)	Dimer (99 %)	Dimer (99 %)
	0.4 M C(NH$_2$)$_3$$^+$	Dimer (99 %)	Dimer (65 %), cycloheptatriene (29 %)
Triphenylcyclopropenyl	0.4 M TBAP	Dimer	Dimer
	with HOAc (50 %)	Dimer	Dimer
	0.4 M C(NH$_2$)$_3$$^+$	Dimer	Dimer plus triphenylcyclopropene (12 %)

reaction of carbanion with carbonium ion probably involves prior electron transfer, followed by coupling of the resulting radicals.

The effectiveness of 0.4 M guanidinium perchlorate at trapping these anions, compared with 50 mol per cent of the more acidic proton donor acetic acid, indicates that the electrochemical process is indeed occurring within essentially a fused salt medium, from which neutral solvent is excluded. However, this is not necessarily a special problem in the interpretation of the reduction potentials. In all of our studies a related compound is submitted to the same reaction conditions to calibrate any changes in solvation effects.

The pK_a method was first calibrated with a series of substituted triphenyl-methyl cations. These are moderately well-behaved electrochemically, but even they show some kinetic complications associated with subsequent chemical reactions. Thus, as *Figure 3* shows, we cannot detect the reoxidation
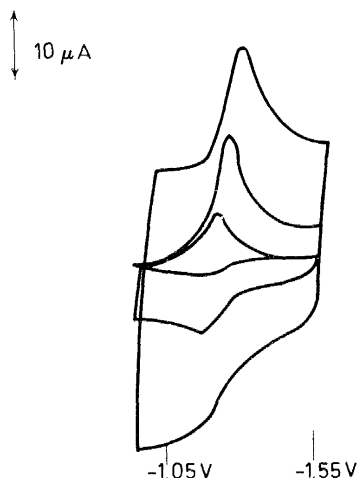
Figure 3. Cyclic voltammetry of p-dimethylaminophenyldiphenylmethyl perchlorate in dimethyl sulphoxide at platinum disc electrode. Triarylmethyl perchlorate concentration 3 mM; 0.1 M tetrabutylammonium perchlorate supporting electrolyte; cyclic voltammetry sweep rates of 0.12, 1.2 and 6.2 V/s

in the second wave for p-dimethylaminotriphenylmethyl cation. *Figures 4* and *5* show that this is also a problem with tropylium and trimethylcyclo-propenyl cation reductions. Thus, we must consider what the likely errors are in the reduction potentials for such systems.

Certain errors can be introduced into such potentials because of uncom-pensated resistance in the electrochemical cell, but this can be avoided with careful experimental control. In addition, the electrochemical processes themselves can be 'irreversible'. This essentially involves the possibility that there is some kind of activation energy associated with electron transfer. In general, it would have to reflect bond breaking, which is not involved in our processes, or strong solvation changes, or large conformation changes. In our systems no such difficulties are likely. The ions are large and well-
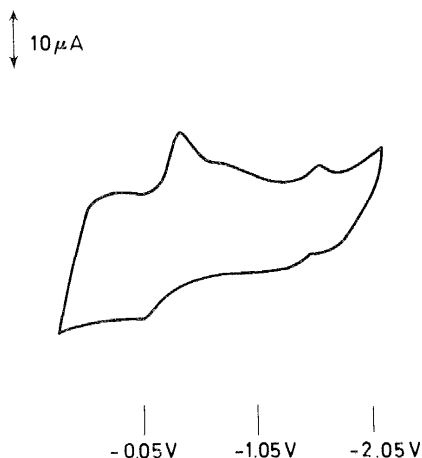
Figure 4. Cyclic voltammetry of tropylium fluoroborate in dimethyl sulphoxide at platinum disc electrode. Tropylium fluoroborate concentration 2 mM; 0.1 M tetrabutylammonium perchlorate supporting electrolyte; cyclic voltammetry sweep rate of 22.2 V/s
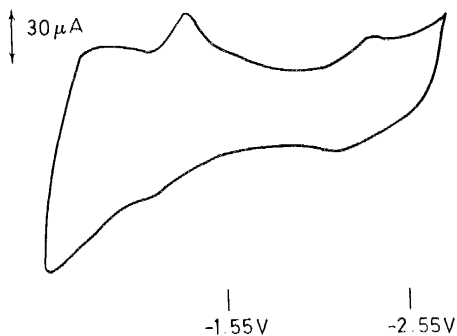

Figure 5. Cyclic voltammetry of trimethylcyclopropenium perchlorate in dimethyl sulphoxide at platinum disc electrode. Trimethylcyclopropenium perchlorate concentration 3 mM; 0.1 M tetrabutylammonium perchlorate supporting electrolyte; cyclic voltammetry sweep rate of 22.2 V/s

delocalized, so that specific local solvation effects will be minimal and corrected for by the model compounds in any case. Furthermore, geometric changes accompanying the changes in oxidation state should be very small. Accordingly, the major problem in all the electrochemistry we are considering is the chemical reaction of the unstable products resulting from the electrochemical step. We must consider what effect this could have on the observed potentials.

Saveant and his colleagues[8] have formulated the relationship between the observed peak potential in a cyclic voltammogram and the true thermodynamic potential as influenced by the dimerization of the electrochemical product. For a reduction process which generates, e.g. a radical, which then dimerizes (at a rapid rate):

$$E_{\text{peak}} = E^\circ - 0.058 + 0.0197 \log (kC_0/V)$$

Even if we assume a second-order dimerization of the product with a diffusion-controlled rate constant k of 10^{10} M^{-1} s^{-1}, with a concentration of 10^{-4} M for the substrate and at a scan rate of 10 V s^{-1}, the second term in the equation corresponds to 100 mV, or 2.3 kcal/mol for a one-electron process. In general, the dimerization will have *some* activation energy, while it is possible to scan at even faster rates than this, so the error should be smaller. Furthermore, for processes in which we see no sign of reversibility we can take the peak potential as a better approximation to the true potential, and the error in this is then even smaller than our estimate above. Thus, kinetic complications introduce a problem, but this problem is of limited magnitude. It is less serious than the difficulty we commonly accept when we hope that rate constants in solvolytic studies, for instance, have some relationship to the stabilities of the intermediates in the reactions. It should also be noted that the kinetic complications introduce errors in the direction in which we underestimate the instability of the unstable species we are producing. In this sense estimates of anti-aromaticity based on such studies are in fact lower limits, although, as described above, the errors must be small.

	$\phi_3 C$	$\phi_3 C_3$	Δ
$R - OH \rightleftarrows R^+$	$pK_{R^+} = -6.6$	$+3.1$	$9.7\,pKs$
$R^+ \overset{e}{\rightleftarrows} R\cdot$	$E_{\frac{1}{2}} = -0.08$ V	-1.11 V	-1.0 V
$R\cdot \overset{e}{\rightleftarrows} R^-$	$E_{\frac{1}{2}} = -0.83$ V	-1.56 V	-0.7 V
$R - H \rightleftarrows R^-$	$pK_a = +33$	X	Y
$R - H \rightleftarrows R - OH$	assumed the same		~ 0

1.7 eV = 39 kcal/mol = 28 pK units

$\therefore X = 33 + 28 - 9.7 = 51$

Figure 6. A typical pK_a calculation

The data are treated as illustrated in *Figure 6*. From this calculation we estimate that triphenylcyclopropene has a pK_a 20 units higher than that of triphenylmethane. Thus, the hydrogen on the cyclopropene ring is probably less acidic than is a proton on one of the phenyl rings. Our technique not only permits us to determine a pK_a which is otherwise inaccessible but even permits us to determine the pK_a of a hydrogen which is not the most acidic in the molecule.

A collection of all the data derived from the same kind of treatment is given in *Table 2*. It is particularly gratifying that the data on triphenylmethane acidities correlate with direct equilibration results. Of course the uncertainties in these data are significant, as the table indicates, but no gross errors in the method are suggested by these comparisons. More significantly, the pK_a of cycloheptatriene is also correctly predicted by this technique. All of this makes it likely that the pK_as of the cyclopropene derivatives are also of the correct general magnitude.

We have also applied electrochemical techniques in determining the stability of cyclopentadienyl cations[9]. In this case the thermodynamic properties of the corresponding anions are known, in the sense that they are

Table 2. pK_a Determinations

R	Anion (salt)	$E_{1/2}$ in V versus source		pK_{R^+}	pK_a(calcd)	pK_a (by equilibration)
		first wave	second wave			
Triphenylmethyl	ClO_4^-	0.19 ± 0.05	-1.05 ± 0.07	-6.6	31.5	31.5
Tris(p-chlorophenyl)methyl	ClO_4^-	0.23 ± 0.05	-0.87 ± 0.07	-7.7	28.9 ± 2.0	30.1 ± 0.5
Dimethylaminophenyldiphenylmethyl	ClO_4^-	-0.35 ± 0.05	-1.22 ± 0.07	3.6	33.1 ± 2.0	34.8 ± 0.5
Tris(p-dimethylaminophenyl)methyl	Cl^-	-0.74 ± 0.05	-1.61 ± 0.07	9.4	40.3 ± 2.0	High
p-Methoxyphenyldiphenylmethyl	ClO_4^-	0.09 ± 0.05	-1.22 ± 0.07	-3.4	32.8 ± 2.0	32.5 ± 0.5
Tris(p-methoxyphenyl)methyl	ClO_4^-	-0.07 ± 0.05	-1.42 ± 0.07	0.8	34.6 ± 2.0	33.3 ± 0.05
7-Cycloheptatrienyl	BF_4^-	-0.23 ± 0.07	-1.51 ± 0.12	4.7	36 ± 3	36
Triphenylcyclopropenyl	ClO_4^-	-0.85 ± 0.10	-1.73 ± 0.15	3.1	50 ± 4	
Trimethylcyclopropenyl	ClO_4^-	-1.32 ± 0.15	-2.22 ± 0.15	7.4	62 ± 5	
Tripropylcyclopropenyl	BF_4^-	-1.36 ± 0.15	-2.30 ± 0.15	7.0	64 ± 5	
Tri-tert-butylcyclopropenyl	ClO_4^-	-1.53 ± 0.15	-2.12 ± 0.15	6.5	65 ± 5	

related to hydrocarbons by known pK_as. Since the carbonium ion is formally derived by a two-electron oxidation, the thermodynamic cycle in this case is

$$\text{ROH} \rightarrow \text{RH} \rightarrow \text{R}^- \rightarrow \text{R}^\cdot \rightarrow \text{R}^+ (\rightarrow \text{ROH})$$
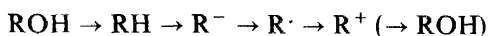
For a few cyclopentadienyl cation derivatives the value of pK_{R+} was already known. These data, included in *Table 3*, were derived by acidity-function measurements.

Table 3. pK_{R+} Determinations for cyclopentadienyl cations[a]

System	pK_a	E_1	E_2	pK_{R+} (derived)	pK_{R+} (known)
Triphenylmethyl	31.5	-1.335^c	$+0.312^d$ $+0.36^{b,d}$	—	-6.63
9-Phenylfluorenyl	18.5	-0.77^d	$+0.76^d$	-10.8	-10.5
1,2,3-Triphenylindenyl	17.8	-0.567^c	$+0.76^d$	-12.6	-12.6
Pentaphenylcyclopentadienyl	16.9	-0.354^c	$+0.94^d$	-18.9	< -16
Cyclopentadienyl	18.5	-0.03^d	$+1.77^d$	-40	—

[a] In 0.2 M LiClO$_4$/DME at a platinum electrode measured versus Ag/AgCl(s).
[b] From reduction of triphenylmethyl perchlorate.
[c] Near-reversible behaviour.
[d] Irreversible behaviour.

Pentaphenylcyclopentadienyl cation had been prepared at low temperature, but it was not possible to determine the pK_{R+} by equilibration, since the cation rearranges at room temperature to a phenanthrene derivative. Furthermore, there is no chance at all of applying acidity-function measurements to determine the stability of unsubstituted cyclopentadienyl cations. Thus, our solvolytic studies[10] on 5-iodocyclopentadiene indicate that it is kinetically inert with Ag$^+$ under conditions in which even saturated cyclopentyl iodide undergoes solvolysis. Unsubstituted cyclopentadienyl cation can be made[11] by using very strong Lewis acids at very low temperatures (and it proves to be a ground state triplet), but it is much too unstable for direct physical equilibration studies.

Thus, we applied our electrochemical thermodynamic method. Again we have chosen triphenylmethyl as the model compound for various bond energy and solvation changes. As *Table 3* shows, we are able to make estimates of the first and second oxidation potentials, again using cyclic voltammetry as the electrochemical method. The electrochemistry is again non-ideal, in the sense that subsequent kinetic processes are rapid. However, our above discussion of errors is also relevant here, suggesting that they are small in magnitude. The results confirm this.

Combining these potentials with those for the triphenylmethyl series in the standard way yields the set of pK_{R+}s indicated in *Table 3*. It is gratifying to note that for the two cyclopentadienyl cation derivatives for which we had independent pK_{R+} data the agreement between the two methods is excellent. For pentaphenylcyclopentadienyl cation the pK_{R+} by the electrochemical technique is consistent with that which we had estimated previously, based on the rate of conversion of the corresponding carbinol to the (unstable) cation. For unsubstituted cyclopentadienyl cation itself there is of course no independent determination of its pK_{R+}, but the very low value derived from

these electrochemical thermodynamic studies is certainly consistent with our observations that only an extremely strong Lewis acid can remove halogen from a 5-halocyclopentadiene.

In all of these treatments we have been concerned only with the two-electron processes and have ignored the thermodynamic information available on the intermediate radicals. Of course, thermodynamic cycles can be constructed by which bond-dissociation energies of the hydrocarbons (or alcohols) to the corresponding radicals can be derived. We expect that this also may prove to be a useful application of electrochemical methods.

Electrochemical studies on cyclobutadiene[12, 13] have had to involve a different approach. We have used naphthoquinone as a probe to be fused to the cyclobutadiene ring and have determined the perturbation of the naphthoquinone reduction potentials which accompanies such fusion. Reduction of naphthoquinone to the corresponding hydroquinone dianion is accompanied by a decrease in the 2–3 bond order, from a full double bond to one with less than 50 per cent π bonding. Only very slight geometric changes accompany this bond-order change. Thus, the effect of fusion of a ring at the 2–3 position on the reduction potential of naphthoquinone can be used to assess the energy consequences of changing the bond order in that fused ring.
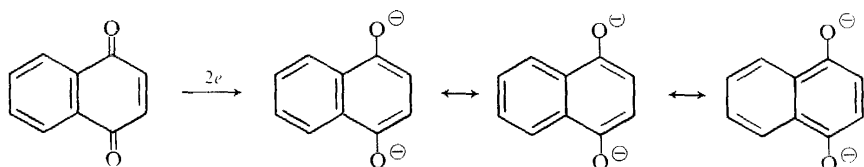

To illustrate, reduction of naphthoquinones is easier than reduction of anthraquinone. The 2–3 bond is part of another benzene ring in anthraquinone. A decrease in bond order will thus raise the energy of the system, and the difference in reduction potential between the two systems contains information related to the aromatic stabilization of a benzene ring. We have examined similar comparisons[14] in probing the aromaticity of some large ring annulene diones as well.

For cyclobutadiene, the prediction is the contrary. If a cyclobutadiene ring is fused to naphthoquinone, as in compound 1, this should be more easily reduced than is unsubstituted naphthoquinone. Now a decrease in the 2–3 bond order on reduction will lead to a desirable decrease in the cyclobutadiene character of the right-hand ring, since cyclobutadiene interaction proves to be an anti-aromatic destabilizing one. A variety of naphthoquinone derivatives were synthesized involving not only the potential cyclobutadiene ring but also various model systems designed to correct for steric and inductive effects. Since it is the naphthoquinone system itself which contains the very unstable cyclobutadiene system more or less unperturbed, we actually synthesized the corresponding naphthohydroquinone dianions and determined their oxidation potentials.

The treatment of these data is of course different from that for the ions we

have been discussing, and it is described in detail in our recent publication[13]. However, there is one respect in which the two lines turn out to be closely related: the electrochemistry is sometimes non-ideal, becoming more poorly behaved as the compounds involved are more closely related to anti-aromatic cyclobutadiene itself. Thus, the cyclic voltammogram (*Figure 7*) of
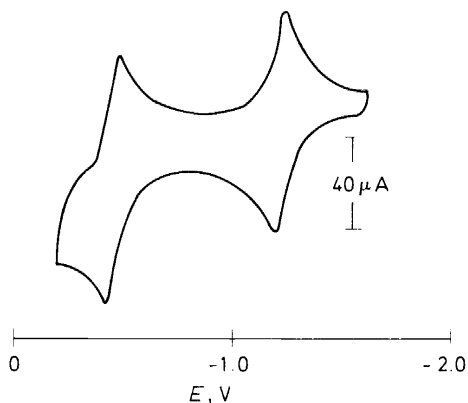
Figure 7. Steady-state stationary electrode polarogram of dibenzylidenecyclobutenonaphtho-hydroquinone dianion (2)(⩽ 0.5 mM) in DMF, 0.5 M TBAP, at a platinum disc electrode at 20°C for a sweep rate of 0.54 V/s

compound **2** is almost classical. Two oxidation waves are seen and both are reversible, accompanied by corresponding reduction waves when the cyclic voltammogram sweep is reversed. In this case the corresponding quinone is not a cyclobutadiene derivative but instead a dimethylenecyclobutene, a stable molecule on the electrochemical time scale.
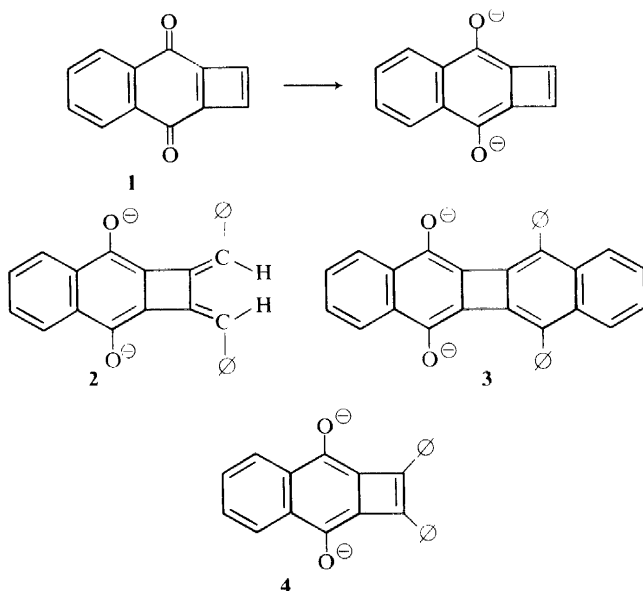
By contrast, when we oxidize compound **3**, the product of oxidation is a naphthoquinone fused to a 2,3-cyclobutadienonaphthalene. The first oxidation wave (*Figure 8*) is still nicely reversible but the second wave is
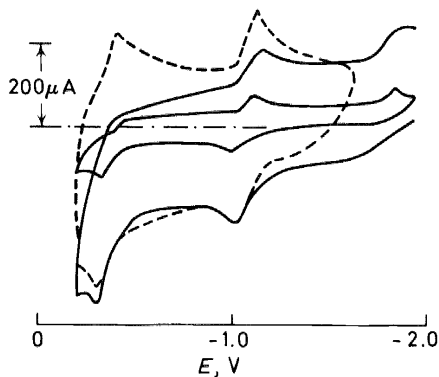

Figure 8. Stationary electrode polarogram of diphenyldibenzobiphenylenehydroquinone dianion (3) in DMF at a platinum disc electrode at 20°C. Full lines are for a concentration of > 1 mM, with 0.2 M TBAP at sweep rates of 0.108 and 1.08 V/s. The dashed lines correspond to a concentration of ≤ 0.5 mM, with 0.5 MTBAP, for a sweep rate of 11.2 V/s. The current scale is shown for the latter experiment
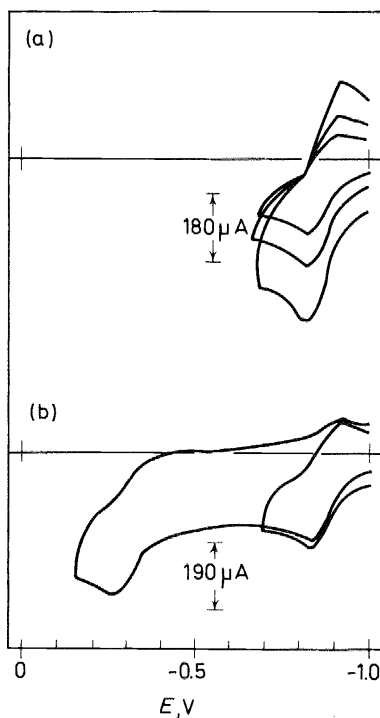
Figure 9. Cyclic voltammetry of diphenylcyclobutadienonaphthohydroquinone dianion (**4**) (~0.8 mM) in DMF, 1.0 M TBAP, at a platinum disc electrode at 20°C. (a) First wave isolated for sweep rates of 1, 4 and 9 V/s. (b) Extension of the potential sweep to include the second anodic process at 4 V/s

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irreversible at slow sweeps and only shows a re-reduction wave, at the second potential, when low concentrations and fast sweep rates are used in order to suppress dimerization processes. When compound **4** is oxidized, its product would be a naphthoquinone with a diphenylcyclobutadiene ring fused in position 2–3. This is of course most closely related to cyclobutadiene itself and it also is the least stable compound in the series. The cyclic voltammo-gram (*Figure 9*) shows an irreversible second wave. Again, various tech-niques involving variation of sweep rate and concentration can be used to try to permit the electrochemistry to 'catch up' with the disappearance of the product by chemical reaction. Again, the theoretical treatment indicates the magnitude of the residual error, and it must be small. Furthermore, it is experimentally clear that the second wave is quite close to the true potential. This is shown in a plot (*Figure 10*) which suggests that an asymptote is being
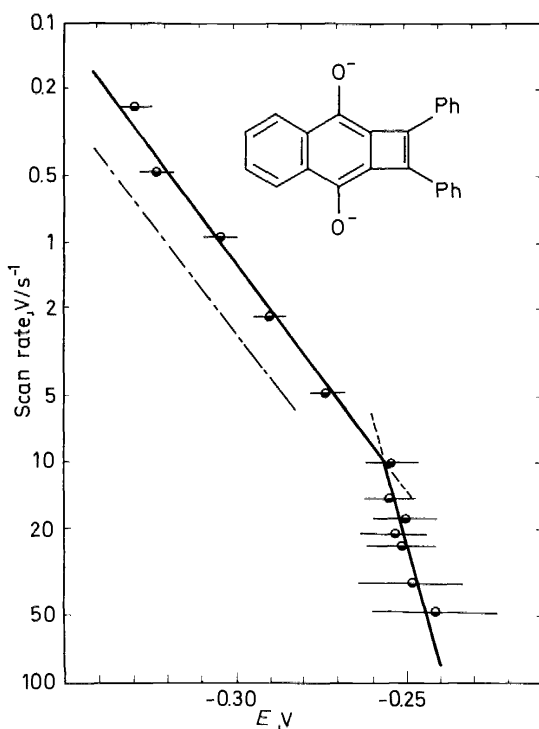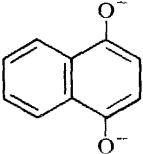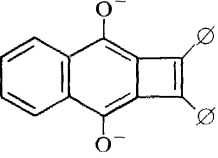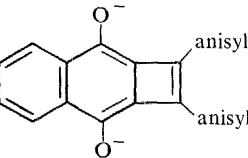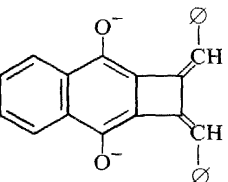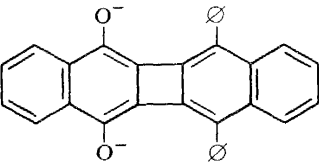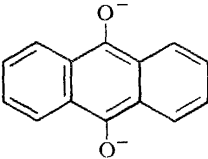

Figure 10. The behaviour of the second anodic peak potential of dianion 4 with increasing scan rate

approached with increasing sweep rate, as expected if the rate is becoming competitive with the chemical dimerization. It is also suggested by the column $E_1 - E_2$ in *Table 4*, which should be relatively constant through the series. The 'irreversible' cases, such as **4**, are not out of line with the well-behaved cases.

On the basis of the numbers in *Table 4*, we have estimated that cyclobuta-diene is destabilized through conjugation by at least 15 kcal/mol. Further-

Table 4. Oxidation potentials[13]

	E_1	E_2	$E_2 - E_1$	$E_1 + E_2$	$\Delta(E_1 + E_2)$
	-1.50	-0.68	0.82	-2.18	—
	-0.90	-0.25	0.65	-1.15	1.03
	-1.00	-0.38	0.62	-1.38	0.80
	-1.22	-0.45	0.77	-1.67	0.51
	-1.17	-0.36	0.81	-1.53	0.65
	-1.67	-0.96	0.71	-2.63	-0.45

more, we have evidence for a special push–pull effect in this system. The arguments have been detailed elsewhere[13].

The conclusion of all these studies is that non-ideal behaviour is the rule rather than the exception when electrochemical methods are used to generate

and study very unstable compounds, such as the four-π-electron anti-aromatic rings. However, the errors involved in such non-ideal behaviour are reasonably well understood, and their magnitudes are small and can be estimated. Thus, these electrochemical thermodynamic techniques must take their place alongside more familiar methods for the estimation of energies of very unstable species.

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