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Thermodynamic Measurements on Unsubstituted Cyclopropenyl Radical and Anion, and Derivatives, by Second Harmonic Alternating Current Voltammetry of Cyclopropenyl Cations

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Abstract: Cyclopropenyl cation has been reversibly reduced electrochemically to the unsubstituted 3-cyclopropenyl radical, and with two electrons to the unsubstituted 3-cyclopropenyl anion. Reversible thermodynamic reduction potentials for both processes have been determined using second harmonic ac voltammetry. The same technique has been used to determine thermodynamic potentials for the one- and two-electron reduction of triphenylmethyl, cycloheptatrienyl, triphenylcyclopropenyl, trimethylcyclopropenyl, tri-*tert*-butylcyclopropenyl, and dipropylphenylcyclopropenyl cations. Adsorption effects were detected for two of these cations at a Pt, but not at an Au, electrode. The data were used in thermodynamic sequences to evaluate the basicity of various cyclopropenyl anions; a set of pK_a 's ranges from +50 to +74. Another thermodynamic sequence was used to evaluate the C–O bond dissociation energy of various cyclopropenols. Two unusual effects emerge: cyclopropenyl radicals are destabilized by alkyl groups, and they also appear to be destabilized relative to unconjugated radicals.

Introduction

We have reported a number of studies in which stable carbonium ions, such as tropylium cation and various derivatives of cyclopropenyl cation, have been converted electrochemically by one-electron reduction to the corresponding radical and by two-electron reduction to the corresponding anion.¹ For these systems the radicals are unstable and undergo irreversible dimerization. The carbanions generated electrochemically are also highly reactive and are irreversibly quenched either by the cation in solution or by suitable proton donors. In spite of this problem close approximations to reversible thermodynamic potentials have been obtained^{1d} for a variety of these systems. Good thermodynamic information is available for stable cations, i.e., the free-energy change on quenching of the cation to the corresponding alcohol.² Thus, the reversible potentials for reducing the cations to the corresponding radicals or anions furnishes essential information about the energy content of these latter species.

We have described elsewhere how these potentials can be incorporated in a thermodynamic cycle from which it is possible to deduce the pK_a of a hydrocarbon, such as a cyclopropene.^{1c} Conversely, the same cycle can be used in the cyclopentadienyl series by combining the oxidation potentials for converting a cyclopentadienyl anion to the radical and then to the cation with the known pK_a of the cyclopentadiene. With such a cycle the thermodynamic stability of the cyclopentadienyl cation and various of its derivatives can be estimated.³ As will be shown below, it is also possible to use such data to derive thermodynamic information on radicals.

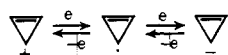
Two kinds of errors may enter into such measurements. The thermodynamic cycles combine measured ionization constants in one medium with electrochemical oxidation or reduction potentials in a different medium; the solvation changes might not be adequately compensated by running a known system through the entire cycle. The other problem is that the electrochemical data might not be reversible and thus truly thermodynamic. Most of our data in the earlier studies have been obtained by the use of cyclic voltammetry. For the most interesting systems, such as the cyclopropenyl cations, reduction by either one or two electrons to produce, respectively, the cyclopropenyl radical or anion led to very rapid subsequent radical dimerization or capture of the anion by another molecule of cation. We have discussed the magnitude of the errors which this irreversible capture can introduce.^{1c,d} The consistency of the data for a variety of related systems, together with theoretical considerations, all suggest that the errors are small. However, it clearly would be preferable to achieve true electrochemical reversibility.

It might seem a simple matter to run the cyclic voltammetric sweep at a faster rate, so as to oxidize the reduction products before they have a chance to undergo further chemical reaction. Unfortunately, with sweep rates fast enough to outrun the following chemical reaction, the use of cyclic voltammetry presents other problems.⁴ A rapid change of electrode potential induces a large double-layer charging current, i.e., the electrode-solution interface behaves like a condenser undergoing rapid charging.⁵ If this current becomes very large it is impossible to discern the small current due to a faradaic process (reduction or oxidation of the substrate) superimposed on it.

For example, we find that a two-electron reduction wave for the parent cyclopropenyl cation cannot be observed by rapid-scan cyclic voltammetry, apparently due to the magnitude of the double-layer charging current. It became clear that a fast electrochemical technique, but one in which the double-layer charging current is either absent or greatly reduced, was needed for these studies. Both of these requirements are met by second harmonic ac voltammetry,⁶ a technique that has not found wide application in organic electrochemical studies.

The method is particularly useful in the study of electrochemical processes with fast following chemical steps. McCord and Smith have demonstrated that it is capable of yielding reliable thermodynamic half-wave potentials even when the half-life of the electrode reaction product is on the order of 10^{-4} s.^{6a} Although second harmonic ac voltammetry has been discussed elsewhere,⁶ a brief description is in order. A small amplitude (e.g., 10 mV) ac signal is superimposed on the usual slow dc sweep applied to the working electrode. The double layer behaves like a capacitive linear ac circuit element and thus does not produce an ac current at harmonics of the applied frequency. On the other hand, the faradaic process results in partial rectification of the ac signal producing a nonlinear impedance. For this reason, the faradaic process generates an ac current at harmonics of the applied frequency. The selective detection of the ac current at the second harmonic using a lock-in amplifier yields information about the faradaic process and largely eliminates the double-layer charging current contribution to the measured ac current. The most important time scale of the ac polarographic experiment is the period of the ac signal employed. Additionally, the linear sweep rate (which we held constant) has a second-order effect.^{6a}

Using this technique we have found that we can determine reversible electrochemical potentials for all the processes of concern to us, including in particular the reversible reduction of unsubstituted cyclopropenyl cation to the cyclopropenyl radical and also to the cyclopropenyl anion. These highly accurate electrochemical data have been incorporated into appropriate thermodynamic cycles from which we are able to deduce the basicity of cyclopropenyl anion and various of its derivatives and in addition the stability of cyclopropenyl radicals.



Results

Triphenylmethyl and Tropylium Cations. The second harmonic ac voltammogram for the reduction of the triphenylmethyl cation at a gold disk electrode is illustrated in Figure 1. The wave shape is formally related to the second derivative of dc polarographic curves and exhibits both positive and negative lobes due to phase-sensitive detection of the ac signal. The sharpness and symmetry of the first reduction wave indicates that the process being observed is reversible under the conditions of the experiment. When charge transfer is rapid and the rate of the following chemical step is small compared with the time scale of the ac experiment, the current magnitudes of each lobe of the second harmonic response are equal and the peak-to-peak separation is $68 \text{ mV}/n$, where n is the number of electrons transferred.^{6d} Moreover, under these conditions the potential at which the second harmonic current is nulled is the thermodynamic half-wave potential. When the following chemical reaction is fast relative to the linear sweep, but slow compared with the ac modulation, the second harmonic peak can lose intensity and symmetry, but the peak-to-peak separation is still approximately $68 \text{ mV}/n$. Most important, the null potential is still the thermodynamic half-wave potential.⁶

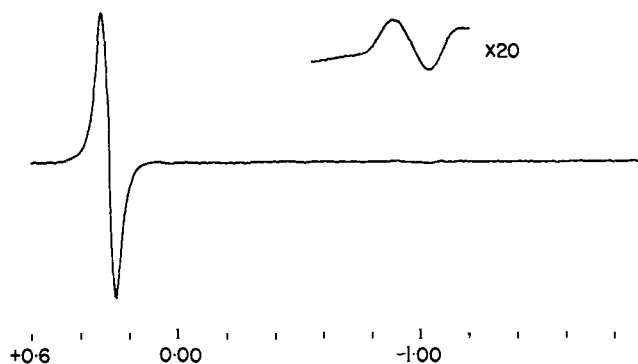


Figure 1. Second harmonic ac voltammogram of triphenylmethyl fluoroborate in CH_3CN at gold, $\omega = 45 \text{ Hz}$.

Using these criteria, the first reduction wave of triphenylmethyl cation indicates that the process is a rapid one-electron reduction (peak-to-peak separation, 65 mV) in which the following chemistry is slow relative to the 45-Hz applied frequency. The wave retained its shape and exhibited a linear relationship between the second harmonic current and $\omega^{1/2}$ over a range of frequencies from 20 to 250 Hz. Thus charge transfer is rapid under these conditions.^{6c}

An additional criterion of reversibility invokes the phase angle between the applied ac potential and the second harmonic ac current at a given dc potential. The phase angle at any dc potential may be obtained as the arc-cotangent of the ratio of the second harmonic current for the in-phase and quadrature response. Phase angles of 45 and 225° at the dc potentials of the respective lobes of the second harmonic signal indicate complete electrochemical reversibility under these conditions.⁶

These results may be compared with those we have obtained previously using cyclic voltammetry. With this technique the dc current due to reoxidation of the triphenylmethyl radical became significant only at scan rates greater than 1 V s^{-1} .^{1c} Perfect reversibility is, in fact, never obtained with cyclic voltammetry of the triphenylmethyl cation. With second harmonic ac voltammetry a fully reversible potential is obtained. Furthermore, careful examination of the base line of the second harmonic voltammogram reveals no trace of the double-layer charging current.

The second reduction potential for triphenylmethyl cation occurs at -0.97 V at the gold electrode and appears readily reversible at 45 Hz. Thus in this case the same frequency can be used for both the first and the second wave; as we will see, this situation changes with other species. The second wave for triphenylmethyl is broader than the first, but the symmetry of the wave permits ready determination of $E_{1/2}$.

Increasing the frequency of the ac signal leads to greater broadening and distortion of the second wave. In general, such broadening occurs when charge transfer from the electrode to the substrate is not rapid compared with the ac frequency.^{6a} There exists for each reduction process we have studied a kinetic window in which good reversible electrochemical behavior is observed. The ac frequency must be rapid compared with the rate of the following chemistry, but it must be kept small enough to prevent distortion of the wave due to competition with the rate of the charge-transfer process. Fortunately, with all of our compounds a sufficiently broad window exists for each process to permit determination of the thermodynamic half-wave potentials.

As Table I indicates, only a small difference was found for the potentials of triphenylmethyl cation at platinum rather than gold. Strong interaction of one of the species with the electrode, to form what might be described as an alkyl-metal bond, would of course perturb the potentials; such interaction

Table I. One- and Two-Electron Reduction Potentials of Carbonium Ions

Compd	$E_{1/2}$ vs. SCE ^a				pK _{R+}
	Second harmonic ac voltammetry ^b		Cyclic voltammetry ^c		
	Au electrode	Pt electrode	Pt electrode		
Triphenylmethyl fluoroborate	0.28 ± 0.01 -0.97 ± 0.01	0.21 ± 0.01 -0.98 ± 0.01	0.19 ± 0.05 -1.05 ± 0.05		-6.6
Cycloheptatrienyl fluoroborate	-0.16 ± 0.01 -1.63 ± 0.01	-0.18 ± 0.01 -1.55 ± 0.01	-0.23 ± 0.07 -1.51 ± 0.12		4.7
Cyclopropenyl fluoroborate	-0.62 ± 0.01 ^d -1.78 ± 0.02 ^d	-0.23 ± 0.01 ^d -1.95 ± 0.02 ^d			-7.4
Trimethylcyclopropenyl fluoroborate	-1.74 ± 0.01 -2.28 ± 0.02	-1.16 ± 0.01 -2.20 ± 0.02	-1.32 ± 0.15 -2.22 ± 0.15		7.4
Tri- <i>tert</i> -butylcyclopropenyl fluoroborate	-1.65 ± 0.01 -2.25 ± 0.02	-1.69 ± 0.01 -2.25 ± 0.02	-1.53 ± 0.15 -2.12 ± 0.15		6.5
Dipropylphenylcyclopropenyl fluoroborate	-1.16 ± 0.01 -1.90 ± 0.01	-1.17 ± 0.01 -1.91 ± 0.01			6.4
Triphenylcyclopropenyl perchlorate	-0.72 ± 0.01 -1.66 ± 0.01	-0.72 ± 0.01 -1.60 ± 0.01	-0.85 ± 0.10 -1.73 ± 0.15		3.1

^a At 25 °C. ^b In CH₃CN containing 0.10 M tetra-*n*-butylammonium perchlorate. ^c Reference 1c. In Me₂SO containing 0.10 M tetra-*n*-butylammonium perchlorate. ^d Corrected to 25 °C. At -10 °C $E_{1/2}$: -0.73 ± 0.01; -1.76 ± 0.02 at Au; -0.34 ± 0.01, -1.93 ± 0.02 at Pt. The corrections were obtained from measurements of $E_{1/2}$ for trimethylcyclopropenyl fluoroborate at -10 and 25 °C. The potential shifts observed for this model system were added directly to the cyclopropenyl fluoroborate results.

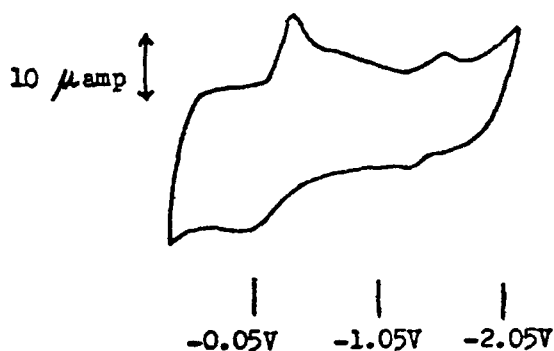


Figure 2. Cyclic voltammogram of tropylium fluoroborate in Me₂SO at platinum, scan rate 22.2 V/s, from ref 1c.

is apparently slight with triphenylmethyl. As a general proposition, interactions would be much stronger with platinum than with gold and would thus cause a change in potentials on changing the electrode metal.

The power of the second harmonic ac technique is evident in the determination of the reduction potentials of the tropylium cation. Figure 2 is the cyclic voltammogram for tropylium cation reduction at a rapid sweep rate. Both reduction waves are poorly defined, with the second wave virtually hidden by the relatively large double-layer charging current. Nevertheless, from such curves we have in the past estimated reduction potentials to be utilized in our thermodynamic pK_a cycle.^{1c} By contrast, the second harmonic ac voltammogram of the reduction is shown in Figure 3. At 45 Hz the first reduction wave exhibits the shape and symmetry indicating good reversibility on this time scale. The $E_{1/2}$ is listed in Table I; it agrees with our previous estimate, but is more precise. The process remains reversible over the frequency range 20 to 250 Hz and satisfies the same phase angle tests as those described above for triphenylmethyl. It is particularly significant in this work that the null crossing point in these voltammograms does not shift potential as the frequency is changed in this reversible region. This demonstrates clearly that these potentials are not in any way being displaced by chemical processes with a time scale competitive with the ac frequency.

An important feature of Figure 3 is the absence of a wave due to the second reduction process for the tropylium cation

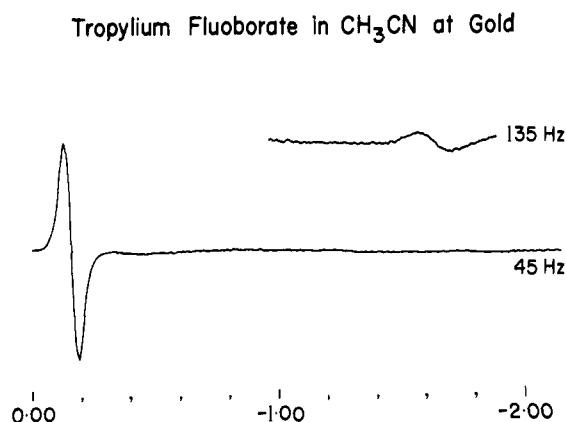


Figure 3. Second harmonic ac voltammograms of tropylium fluoroborate in CH₃CN at gold.

at 45 Hz. This second wave appears only when the frequency of the applied ac signal is increased and the magnitude of the current for the two lobes of the second harmonic response becomes equal at 135 Hz. As the frequency is increased further, significant distortion of the wave can be detected above 200 Hz. These observations indicate that good reversibility is obtained at 135 Hz, when the time scale is now much faster than the following chemical reactions, but at higher frequencies charge transfer is not fast enough and distortion results. The potential for this second reduction wave of tropylium to the cycloheptatrienyl anion agrees with that which we have estimated previously from cyclic voltammetry and simple ac methods.^{1c,7} This has been clearly identified as the potential corresponding to the reduction of tropylium cation to the cycloheptatrienyl anion, by chemical trapping of the anion at potentials more negative but not more positive than $E_{1/2}$, and from special electrochemical effects which are seen when guanidinium perchlorate is used as the supporting electrolyte.⁷ Again, very similar potentials were obtained for tropylium ion at both platinum and gold, suggesting no serious interaction of any of these species with the electrode.

Substituted Cyclopropenyl Cations. In the past we have examined several substituted cyclopropenyl cations by cyclic voltammetry and by simple ac polarography.^{1c,7} The reduction

Table II. Frequencies for Reversible Electrochemistry (Hz)

Cation	1st reduction wave	2nd reduction wave
Triphenylmethyl	20–250	20–250
Cycloheptatrienyl	20–250	75–225
Cyclopropenyl	65–85	165–185
Trimethylcyclopropenyl	20–45	95–155
Tri- <i>tert</i> -butylcyclopropenyl	65–85	105–155
Dipropylphenylcyclopropenyl	35–55	175–205
Triphenylcyclopropenyl	20–65	200–235

waves obtained were poorly behaved and rather wide error limits had to be assigned to the thermodynamic potentials for these reductions (Table I). Thus, it was of interest to obtain good reversible potentials for these processes using second harmonic ac methods.

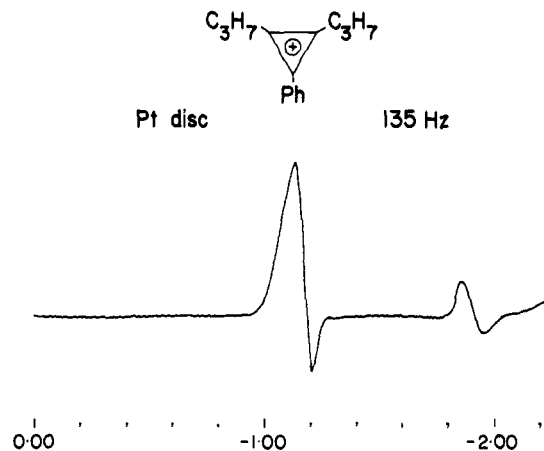
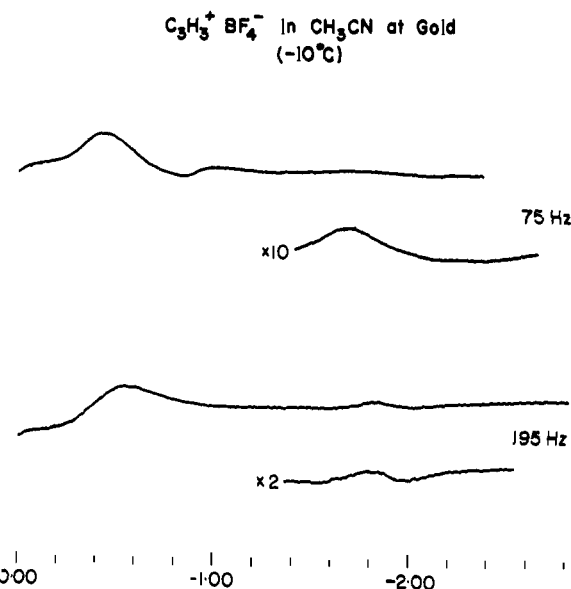
Four substituted cyclopropenyl cations were examined: triphenylcyclopropenyl perchlorate,⁸ trimethylcyclopropenyl fluoroborate,⁹ tri-*tert*-butylcyclopropenyl fluoroborate,¹⁰ and dipropylphenylcyclopropenyl fluoroborate salts.^{2b} Their behavior at the first wave, corresponding to one-electron reduction, was similar to that for the triphenylmethyl and tropylium cations. The first wave could be observed for all these species at similar frequencies; the frequencies required for reversible behavior are listed in Table II. Although the kinetic window is narrower for these species than for those previously described, good thermodynamic half-wave potentials could be obtained in each case.

A second wave could be seen for each of these cations, corresponding to reduction to their respective cyclopropenyl anions. However, as Table II indicates, the frequencies required for this second wave to be fully reversible were rather high, indicating that the chemical step following anion production is fast. The kinetic window for reversibility is narrow for these compounds, and frequently the shape of the first wave was significantly distorted at the frequencies required for reversible behavior of the second wave. An example of this is shown in Figure 4, the reduction of dipropylphenylcyclopropenyl cation at the platinum electrode. At the high frequency required for observation of the second wave there is significant broadening of the first reduction wave.

In this series of compounds the potentials are again essentially unaffected by the choice of platinum or gold electrodes, with one notable exception. Table I indicates that trimethylcyclopropenyl cation has its first reduction potential 0.58 V more negative at Au than at Pt. This of course raises the question of which, if either, of these is the true thermodynamic potential for conversion of the free cation to the free radical. As will be described below, a reasonable argument can be made that the potential at gold is indeed the correct one, unperturbed by adsorption.

Cyclopropenyl Cation. The most interesting and at the same time the most difficult case was the unsubstituted cyclopropenyl system. The cation could be prepared, as a solution of its fluoroborate salt in acetonitrile, by treatment of 3-chlorocyclopropene with silver fluoroborate at -40°C .^{2c} These solutions deteriorate (half-life 5–10 min) at 25°C , so the electrochemistry was performed at -10°C . Under these conditions a millimolar concentration of cation could be maintained for as long as 3 h.

Figure 5 illustrates the reduction of the cyclopropenyl cation. The first reduction wave exhibits severe broadening due to slow charge transfer, but at 75 Hz the effect of the chemical step following charge transfer has been minimized, and a symmetrical wave is obtained. At this same frequency a very dis-

**Figure 4.** Second harmonic ac voltammogram of dipropylphenylcyclopropenyl fluoroborate in CH_3CN at platinum.**Figure 5.** Second harmonic ac voltammograms of cyclopropenyl fluoroborate at -10°C .

torted second wave is visible. Increasing the ac frequency to 195 Hz symmetrizes the second wave, permitting the determination of a reversible potential.

The unsubstituted cyclopropenyl cation apparently undergoes very fast subsequent reaction after one- or two-electron reduction. Thus, the frequencies needed to bring about reversibility for this reduction are somewhat higher than those required for the substituted cases, and at these high frequencies some broadening is apparent as the time scale begins to approach the rate of electron transfer. However, both the first and second potentials could be measured from the symmetric second harmonic waves, and there is every reason to believe that these potentials are good thermodynamic values.

The necessity to work with this cation at -10°C introduces the need for a temperature correction to the observed potentials. The reduction potentials for the parent cation were corrected to 25°C by adding the observed difference in the reduction potentials for the trimethylcyclopropenyl cation at -10 and 25°C . The correction turns out to be relatively small for both the first and second waves (Table I).

The unsubstituted cyclopropenyl cation shows significant differences between the potentials measured at Pt and at Au electrodes. This effect is thus observed for the two smallest unhindered species listed in Table I and undoubtedly reflects

Table III. Hydrocarbon Acidities

Compd	pK_a		
	Employing second harmonic ac voltammetric data		Employing cyclic voltammetric data ^c
	Au electrode ^a	Pt electrode ^b	Pt electrode
Cycloheptatriene	38.8 ± 0.4	36.5 ± 0.4	36 ± 3 ^d
Cyclopropene (H-3)	61.3 ± 0.5	56.2 ± 0.5	
Trimethylcyclopropene	73.9 ± 0.5	61.4 ± 0.5	62 ± 5
Tri- <i>tert</i> -butylcyclopropene	72.8 ± 0.5	72.1 ± 0.5	65 ± 5
Dipropylphenylcyclopropene	58.7 ± 0.4	57.7 ± 0.4	
Triphenylcyclopropene	50.4 ± 0.4	48.1 ± 0.4	50 ± 4

^a The reliable values, free of adsorption effects. ^b Perturbed by some adsorption effects, but to be compared with the previous data. ^c From ref 1c. ^d In agreement^{1c} with equilibration data.

specific chemical adsorption effects.¹¹ As will be discussed below, we believe that these specific effects are significant only with the platinum electrode. The data at the gold electrode are thermodynamic potentials for the reduction of the *free* cyclopropenyl cation to the *free* cyclopropenyl radical and the *free* cyclopropenyl anion, respectively.

pK_a Determinations. The reduction potentials of these cations comprise a fundamental chemical characterization of the radicals and anions, but it is desirable to convert the data to more familiar quantities. As we have described elsewhere, the two potentials for sequential conversion of a cation to its radical and then to its anion can be combined with the pK_{R^+} of the cation to derive the basicity of the resulting anion.^{1c} This basicity is ordinarily expressed at the pK_a of the corresponding hydrocarbon. The values of pK_{R^+} given in Table I have been measured previously,² with the exception of that for dipropylphenylcyclopropenyl cation. This was determined by potentiometric titration of the cation in 50% aqueous acetonitrile.

The pK_a values were calculated with reference to the pK_a of triphenylmethane, which is known accurately by equilibration.¹² The data for the cyclopropenyl cation will be used in an example of such a calculation. The pK_{R^+} of the cyclopropenyl cation is -7.4, indicating that this cation is less stable (relative to the alcohol) than is the triphenylmethyl cation by 0.8 pK_{R^+} units. However, using the data obtained at the Au electrode, the cyclopropenyl cation is 1.71 V more difficult to reduce to its anion than is the triphenylmethyl cation (0.28-0.97) - (-0.62-1.78). Since at 25 °C 59.0 mV corresponds to 1 log unit in equilibrium constant, 1.71 V is equivalent to 29.0 log units. The pK_a of cyclopropene is thus 29.8 (29.0 + 0.8) units higher than that of triphenylmethane. Taking the pK_a of triphenylmethane as 31.5,¹² the pK_a of cyclopropene is 61.3. The pK_a 's derived by this technique are listed in Table III, along with the pK_a 's we have reported earlier for some of these cations using less precise electrochemical data.

Implicit in these calculations is the assumption that the free-energy change for conversion of the carbinols to their corresponding hydrocarbons is constant, or nearly so, throughout the series of compounds examined. Good data are not available which permit us to assess this energy change directly. Electropositive hydrogen might form a relatively stronger bond with the electronegative carbon orbital of cyclopropene than would electronegative oxygen; we have argued previously that this energy difference must be a few kilocalories per mol at most.^{1c} Again it should be noted^{1c} that such a correction would raise the pK_a of cyclopropene.

Discussion

Reduction Potentials. Our data indicate first of all that second harmonic ac voltammetry seems to be the method of choice for obtaining precise thermodynamic data in systems

in which the products of the electrode reaction are kinetically very unstable. Even processes as rapid as the quenching of a cyclopropenyl anion in the presence of large quantities of cyclopropenyl cation are not so fast as to prevent reversible electrochemistry using this technique.

The second point which is of interest is that the potentials we have obtained are in gratifying agreement with the less precise data derived previously from cyclic voltammetry on most of these systems. As Table I indicates, our new precise values fall within the error limits of our previous estimates, although it is of course much preferable to have these precise values. Thus, the argument we have made elsewhere^{1d} that even poorly behaved cyclic voltammetric measurements are likely to be reasonable approximations of reversible potentials seems to be confirmed.

With these precise data we were able to look carefully for effects of the nature of the electrode, and in most cases these effects were very small. However, there are two systems for which appreciable electrode adsorption effects were detected, trimethylcyclopropenyl and unsubstituted cyclopropenyl. The nature of these effects is quite interesting. The reduction of trimethylcyclopropenyl cation is 0.58 V easier at Pt than at Au; this can be most readily understood if the reduction of this cation at Pt leads to a bound radical. At Au the product cyclopropenyl radical is bound much less strongly, and we will argue below that it is probably not bound at all. However, at the second wave no significant electrode effects are seen. If the reaction occurred by reduction of the cation to a Pt bound radical, followed by reduction of this species to an unbound anion, then the second reduction at Pt should have been more difficult. The simplest picture which explains all the data is that at the second wave we are, in fact, reducing incoming cation directly to the anion without passing through strongly bound radical intermediates.

The only other system in which an appreciable electrode effect is seen is the unsubstituted cyclopropenyl cation itself. In this case reduction at the first wave is again easier at Pt, suggesting that the product is a Pt bound cyclopropenyl radical. However, in this system we do see a more negative shift of the second wave at Pt compared with Au. Thus, here the incoming cation is at least to some extent converted to bound radical at Pt before the second electron can be transferred to it, so both waves are perturbed by the binding process.

It is expected that these effects should be smaller at Au, but one must worry about whether they are, in fact, nonexistent there. We believe they are negligible at Au for the following reasons. Tri-*tert*-butylcyclopropenyl, carrying three bulky substituents, shows no electrode effects.¹³ Binding is presumably blocked by the bulky *tert*-butyl groups, and the potentials observed for this system involve unbound cation, radical, and anion. We would expect that trimethylcyclopro-

penyl would be energetically similar to the tri-*tert*-butyl case at any electrode at which binding does not occur.¹⁴ It is clear from Tables I and III that the electrochemical data at Au are similar for these two systems, as are the derived pK_a 's for the corresponding hydrocarbons. If there were residual binding in the trimethylcyclopropenyl system at Au, then the true pK_a would be even higher than the one we list; it seems unlikely that this compound could be much less acidic than is tri-*tert*-butylcyclopropene. Thus, we believe that at Au the free species are involved in the trimethylcyclopropenyl series.

The argument is related for the unsubstituted cyclopropenyl species. Thus, the interaction of this species with the electrode on reduction at Pt was not larger than was that for trimethylcyclopropenyl, so it seems likely that this interaction would also disappear at the Au electrode. Furthermore, the pK_a derived at the Au electrode seems reasonable relative to the pK_a of the substituted cyclopropenes in Table III. If the cyclopropenyl radical is strongly bound even at Au, then the pK_a listed in Table III for cyclopropene is an underestimate. We believe that it is actually the correct value.

Hydrocarbon Acidities. The pK_a 's listed in Table III are now based on sufficiently precise electrochemical data that the principal uncertainty has to do with the matter of whether the model compounds fully account for the solvation energy changes, etc., in the unknown species. No determination of pK_a 's as high as 60–70 could be performed by any direct technique, and no other method of estimating them is so nearly free of errors. When it can be applied our technique seems to be the method of choice for determining pK_a 's of very weak acids.

The chemical significance of such high pK_a 's has been discussed by us previously,^{1c,d} but there are some additional points which should be made. First of all, it is not yet possible to compare these numbers with the pK_a 's of simple saturated hydrocarbons such as methane, since no reliable pK_a for methane is yet available.¹⁵ We do not yet know whether cyclopropene is more or less acidic at the CH_2 group than is methane or cyclopropane. Several factors would in any case come into such a comparison. There is a possible angle strain effect. However, calculations¹⁶ and simple reasoning indicate that unsubstituted cyclopropenyl anion is almost certainly pyramidal, so angle strain effects may be quite unimportant here. Inductive effects of the unsaturated neighboring carbon atoms should be acidifying in cyclopropene. These considerations together suggest that cyclopropene might be considerably more acidic than is a simple saturated hydrocarbon.

The special factor in this system is of course the conjugation. As we have discussed elsewhere,¹⁷ conjugation in this case is expected to be destabilizing and thus justify the term "anti-aromatic" for the cyclopropenyl anion and various of its derivatives. If the anion remains pyramidal, such conjugative interaction is diminished but not erased. Thus, the destabilizing conjugative interaction which we have detected in various cyclopropenyl anion derivatives¹⁷ should also be operating to some extent here.

The data in Table III afford one comparison which is of interest. If three alkyl groups on cyclopropene are replaced by three phenyl groups, the pK_a changes from 73 to 50, while if only one of these three alkyl groups is replaced by a phenyl the pK_a changes from 73 to 59. Most of the anion acidification occurs with a single phenyl group, as expected in a pyramidal anion. However, the residual acidification by the other two phenyl groups suggests conjugation with the cyclopropene double bond even in a pyramidal anion structure.

It is worth noting that at the present time the pK_a 's listed in Table III are the highest for which there is good experimental support.

Cyclopropenyl Radicals. It is particularly straightforward to utilize our data to derive thermodynamic information about

Table IV. Relative Bond Dissociation Energies^a $R-OH \rightarrow R\cdot + \cdot OH$

R	$\delta\Delta G^\circ$, kcal/mol
Triphenylmethyl	0.00
7-Cycloheptatrienyl	-5.3
3-Cyclopropenyl	+21.9
1,2,3-Triphenylcyclopropenyl	+9.9
1,2,3-Trimethylcyclopropenyl	+27.6
1,2,3-Tri- <i>tert</i> -butylcyclopropenyl	+26.7
1-Phenyl-2,3-dipropylcyclopropenyl	+15.5

^a At 25 °C, relative to R = triphenylmethyl as a standard.

various radicals. Thus, the bond dissociation energy for the process $ROH \rightarrow R\cdot + OH\cdot$ can be derived from the equilibrium constant for converting the alcohol to the corresponding cation and the potential required for the addition of the one electron to that cation to produce the radical. Again, the easiest way to handle such a cycle is to use a standard compound as reference; for consistency we select the triphenylmethyl series as our standard.

As an example, conversion of cycloheptatrienol to the tropylium cation has an 11.3 pK_R unit more favorable equilibrium than does the conversion of triphenylmethanol to its cation. On the other hand, the tropylium cation is 440 mV more difficult to reduce to its radical than is triphenylmethyl cation. The combination of these two data indicates that conversion of cycloheptatrienol to the tropylium radical is 5.3 kcal/mol more favorable than is the conversion of triphenylmethanol to the triphenylmethyl radical. It should be noted that it is of no interest that the hydroxyl radical was not a product of any of these processes. Comparing one system with another in this fashion cancels all energy terms which are common to the two series. We list in Table IV the relative free-energy changes on conversion of various carbinols to carbon radicals derived by this simple procedure, taking triphenylmethanol as the standard compound.

Good data are available on the bond dissociation energies of simple saturated compounds,¹⁸ in contrast to the problems with the pK_a 's of saturated hydrocarbons. On the basis of such bond dissociation energies it has been estimated that triphenylmethane, on dissociation to the triphenylmethyl radical, undergoes an increase in resonance stabilization of 16 kcal/mol.¹⁹ From measurements on the dimer of cycloheptatriene it has been estimated²⁰ that the conversion of a covalent cycloheptatriene to the cycloheptatrienyl radical results in an increase in resonance stabilization of 21 kcal/mol. These literature data indicate that generating a cycloheptatrienyl radical from a covalent derivative is 5 kcal/mol more favorable than is generating a triphenylmethyl radical from a covalent derivative. This enthalpy difference is in precise agreement with our estimate in Table IV of a 5.3 kcal/mol free-energy advantage in the cycloheptatrienyl system. Thus, we can take the data of Table IV and translate them in Table V into "increases in resonance energies" when the radicals are produced by dissociation of the R-OH bond. Triphenylmethyl is given its literature value, and cycloheptatrienyl is also assigned its literature value which is identical with the one we have derived experimentally by our method.

The other data are striking. Thus, it is concluded from our measurements that the conversion of triphenylcyclopropenol to the triphenylcyclopropenyl radical involves only a small increase in resonance stabilization, much less than that for the triphenylmethyl system. Our measurements show that there is *no* increase in resonance stabilization in the dipropylphenylcyclopropenyl system when the radical is produced, and that there is a large "resonance destabilization" detected in the other cyclopropene systems when the radical is produced. This

Table V. Increase in "Resonance Energy"^a for the Conversion of RX → R·

R	ΔR.E. (kcal/mol)
Triphenylmethyl	-16 ^b
Cycloheptatrienyl	-21.3 ^c
Triphenylcyclopropenyl	-6.1
Dipropylphenylcyclopropenyl	-0.5
Cyclopropenyl	+5.9
Trimethylcyclopropenyl	+11.9
Tri- <i>tert</i> -butylcyclopropenyl	+10.7

^a Free energy; see the text for a discussion. ^b Reference 19. ^c Reference 20 reports -21 kcal/mol (enthalpy).

means that experimentally the dissociation of a simple alcohol to an alkyl radical, unstabilized by any kind of conjugation, is more favorable than is the dissociation of trimethylcyclopropenol to the conjugated trimethylcyclopropenyl radical.

Two sources can be considered for such relative destabilization on bond dissociation in cyclopropenes. One of them, conjugative destabilization, is the sort of thing we have invoked for the cyclopropenyl anion.¹⁷ If it is also invoked here then we would have to classify cyclopropenyl radicals as antiaromatic as well.²¹ The cyclopropenyl radical is pyramidal, not planar, from both theory^{16b} and experiment.²² However, some conjugative interaction would be present even in a pyramidal radical, and it might indeed be destabilizing. The other possibility is that we are dealing here not so much with destabilization of the radical as with stabilization of the starting alcohol. We expect the covalent bond to be stronger in a cyclopropenol because of the altered hybridization in the three-membered ring. Such an effect is presumably responsible for the observation that the bond dissociation energy of the C-H bond in cyclopropane is 5-6 kcal/mol higher than is that for simple open-chain analogues.²³ It may be that in compounds such as trimethylcyclopropenol the carbon-oxygen bond is a full 10 kcal/mol stronger than is the bond in cycloheptatrienol or triphenylcarbinol for simple hybridization reasons, but this seems like a rather large effect to be ascribed to such a cause. The other possibility is that some of the apparent resonance destabilization in this series results from stronger C-O bonds, but that some of it is also a real reflection of a conjugative destabilization in the product radical. In any case, no large amount of stabilization is detectable in the cyclopropenyl radical from these data.

A final point which is interesting about the data in Tables IV and V is the fact that alkyl groups apparently *destabilize* cyclopropenyl radicals, as judged by the bond dissociation energies. Of course alkyl groups stabilize normal radicals, but such stabilization probably involves a form of hyperconjugative electron donation from the alkyl groups. The cyclopropenyl radical system might well be destabilized, not stabilized, by hyperconjugative electron donation into the ring.

Experimental Section

Materials. Acetonitrile (Fisher reagent grade) was distilled from KMnO₄-Na₂CO₃ and again from P₂O₅ under nitrogen. The acetonitrile was distilled a final time from P₂O₅ under nitrogen before use. Tetra-*n*-butylammonium perchlorate was prepared from the corresponding bromide by treatment of an aqueous solution of the bromide with excess 70% HClO₄. The precipitate was dissolved in ethyl acetate and washed to neutrality with Na₂CO₃ solution. Evaporation of the solvent followed by two recrystallizations from distilled ethyl acetate-hexane and drying for 2 days at 50 °C in vacuo yielded electrolyte with a background current less than 5 μA out to -2.9 V vs. SCE. Triphenylmethyl fluoroborate,²⁴ tropylium fluoroborate,²⁴ triphenylcyclopropenyl perchlorate,⁸ dipropylphenylcyclopropenyl^{12b} fluoroborate, trimethylcyclopropenyl fluoroborate,⁹ and tri-*tert*-butylcyclopropenyl fluoroborate¹⁰ were prepared by literature procedures.

The salts were recrystallized once from ethyl acetate-hexane and dried in vacuo for 24 h prior to use.

Cyclopropenyl Fluoroborate. All operations were performed in a glovebox purged with dry nitrogen. Silver fluoroborate (0.016 g, 0.08 mol) was dissolved in dry acetonitrile (2 ml). The resulting solution was cooled to -40 °C in a dry ice-acetone bath. Cold (-78 °C) 3-chlorocyclopropene²⁵ was added dropwise with a micropipet to the cold silver solution until no more white precipitate formed. The cold mixture was stoppered and centrifuged. An additional drop of 3-chlorocyclopropene was added to the light yellow centrifugate. No further precipitation occurred. The ¹H NMR spectrum of the yellow solution exhibited only one strong singlet at 11.1 in addition to the solvent peak. The concentration of cyclopropenyl fluoroborate was about 0.04 M. The solution was stored at -78 °C until use. The solution was always used on the day of its preparation.

Electrochemical Cell. A three-electrode electrochemical cell was constructed from a 50-ml, three-neck, round-bottom flask modified by the addition of gas bubbler and gas outlet ports. The platinum working electrode was a 0.25-cm² disk (Beckmann No. 39273) sealed in glass. The gold working electrode was prepared by plating gold onto a 0.20-cm² platinum disk sealed in glass. The saturated calomel reference electrode was isolated from the bulk solution by a double-fritted compartment joined to a Luggin probe. The platinum wire auxiliary electrode was isolated by a single-fritted compartment. All electrochemical reductions were performed in 0.10 M solutions of tetra-*n*-butylammonium perchlorate in acetonitrile. The solutions were deoxygenated by bubbling argon through the solution until the reduction wave of oxygen was absent from a background scan of the electrolyte solution. The solutions were blanketed with argon throughout the electrochemical experiments. Typical concentrations of the cations were 2 mM.

A special jacketed version of the above cell was employed for the reduction of cyclopropenyl fluoroborate. The temperature of the cell was regulated at -10 °C by pumping cold methanol through the jacket. The cold cyclopropenyl fluoroborate solution under nitrogen was quickly introduced into the cell with a syringe. The concentration of the cation was about 2 mM. The resulting solution was stable for several hours.

Instrumentation. An ac signal with frequency ω from a Hewlett-Packard HP-3300A function generator operating in the sine wave mode was superimposed on the dc ramp of a PAR 174A polarographic analyzer via a PAR 174/50 ac polarographic interface. The amplitude of the ac signal input to the cell was 10 mV. The second harmonic of the ac current passed by the cell was detected by the phase-sensitive detector of a PAR 122 lock-in amplifier. The amplified signal drove the Y axis of a Houston Instruments Model 2000 X-Y recorder. The resistive or capacitive component of the second harmonic response could be obtained by adjustment of the phase shifter built into the Model 122. The dc scan rate v was 50 mV/s, so that $v \ll \omega \Delta E$, where ΔE is the amplitude of the ac input potential. Full ir compensation was employed.

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Flowing Afterglow Studies of the Reactions of Hydroxide, Amide, and Methoxide Ions with Ethylene Oxide and Propylene Oxide

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Abstract: Rates and mechanisms of the gas-phase reactions of OH^- , NH_2^- , and CH_3O^- with ethylene oxide and propylene oxide were studied at 300 K using the flowing afterglow technique. Helium buffer gas pressures of 0.2–1.0 Torr were employed. The reactions of OH^- and NH_2^- with ethylene oxide may be characterized as addition followed by elimination of molecular hydrogen across the newly formed carbon–oxygen or carbon–nitrogen bond. Methoxide ion adds to ethylene oxide followed by third body stabilization without hydrogen loss. All three anions react with propylene oxide exclusively by proton abstraction presumably with simultaneous opening of the three-membered ring. Rate constants for these reactions were measured and compared with the prediction of the average dipole orientation theory. For either neutral reactant, reaction probabilities decreased in the order $\text{OH}^- > \text{NH}_2^- > \text{CH}_3\text{O}^-$.

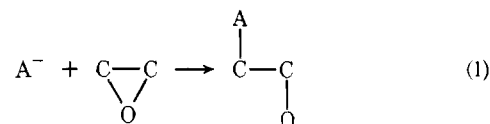
The study of organic ion–molecule reactions in the gas phase has been stimulated by a desire to discover more detail about the intrinsic properties of reactions uncomplicated by the very significant effects of solvation.¹ Unsolvated ions generated in the gas phase at low pressures often react differently from the same ions in solution, where coordinating solvent molecules cause extensive charge delocalization. These effects are most evident in the different ordering of acidities and basicities between solution and gas phase chemistry. Less is known about the effect of solvation on reaction mechanisms.

In studying differences between gas-phase and condensed-phase ion–molecule reactions, chemists have, in recent times, relied heavily on the powerful techniques of ion cyclotron resonance spectrometry,² high-pressure mass spectrometry,³ and the flowing afterglow.⁴ These techniques have added a new dimension to the understanding of the kinetics and energetics of chemical reactions. Although each technique offers its own unique advantages, several valuable assets of the flowing afterglow method can be enumerated: both the ionic and the neutral species involved in the reaction process possess thermal, i.e., Maxwell–Boltzmann, energy distributions; an unparalleled variety of ionic and neutral reactants may be prepared; the necessity of accurate time resolution for these gas phase reactions is eliminated by the equivalence of time and distance; the technique is rather easily extended to include energy variability; and finally, in a flowing gas, vapor–surface interactions can be allowed to reach a steady state so that adsorption–desorption problems do not exist.

Nucleophilic substitution reactions have been studied extensively in solution and therefore represent a fertile area for comparison with gas-phase chemistry. In 1970, Bohme and Young⁵ published the first flowing afterglow study of nucleophilic substitution reactions; they reported rates and

mechanisms for the reactions of oxide anion radical, hydroxide anion, and various alkoxide ions with methyl chloride. Recently, Brauman⁶ has shown that such nucleophilic substitution reactions occur extensively with Walden inversion much like $\text{S}_{\text{N}}2$ processes in solution chemistry. However, a rather serious constraint in the study of nucleophilic substitution and other gas-phase ion–molecule reactions is that only the ionic reactants and products are usually detected. Since much of the mechanistic and stereochemical information resides in the organic product of the reaction, it is desirable to have the organic fragment retain the charge. However, with the exception of simple proton abstraction reactions to form carbanions, this is often not the situation. For example, in the aforementioned nucleophilic substitution reactions of several anions with methyl chloride, the only ionic product is chloride ion.^{5,7}

If an analogy can be drawn with solution chemistry, the epoxides appear to be a promising class of organic substrates for gas-phase ion–molecule reaction studies. In solution, epoxides react with nucleophiles by substitution to form organic ions, the alkoxide ions, as products. In this reaction (eq 1), the



displaced moiety remains attached to the organic substrate. Two elimination processes are also observed in solution (eq 2 and 3). The opening of the three-membered epoxide ring relieves strain and contributes to the exothermicity of these reactions.

This paper reports the first gas-phase study of the reactions of two epoxides, ethylene oxide and propylene oxide, with a series of anionic nucleophiles, OH^- , NH_2^- , and CH_3O^- . The