Table II. Preparation of 1-Arylcyclohexyl and 1-Arylcyclohex-2-enyl p-Nitrobenzoates

System	Substituent in aryl	% yield	Mp, °C	Analyses
Cyclohexyl	p-CH_3O[a]	87	104–105	C, H
	p-CF_3	70	135	C, H, N, F
	3,5-$(CF_3)_2$	78	124.5–125	C, H, N, F
Cyclohex-2-en-1-yl	p-H[a]	26	101–101.5	C, H
	p-CF_3	31	98–99	C, H, N, F
	3,5-$(CF_3)_2$	39	122–122.5	C, H, N, F

[a] Benzoate.

or **14**, not involving π bridging. In the solvolysis of 1-arylcyclopent-3-enyl p-nitrobenzoates (**5**), no π participation is observed, and hence there would appear to be no reason in this case to postulate π bridging either in the transition state or in the intermediate.

π conjugation should be clearly distinguished from π participation. The introduction of an allylic double bond into the cyclohexane ring causes ρ^+ to change from -4.60 to -2.52. This major change is clearly the result of π conjugation.

Consequently, it appears that the tool of increasing electron demand can detect unambiguously either π participation, when it occurs in homoallylic systems, or π conjugation when it occurs in allylic systems.

It is of major interest to establish unambiguously in various systems the presence and magnitude of σ bridging and σ conjugation (hyperconjugation). Consequently, we are continuing our exploration in appropriate systems with this tool to test its ability to detect σ participation and σ conjugation in such systems.

Experimental Section

Preparation of 1-Arylcylcohexyl (8) and 1-Arylcyclohex-2-enyl p-Nitrobenzoates (9). 1-Arylcyclohexanols and 1-arylcyclohex-2-enols were obtained by the addition of the appropriate Grignard reagents to cyclohexanone or cyclohex-2-en-1-one. The alcohols were purified by distillation or crystallization. The p-nitrobenzoates were prepared by treating the lithium salt of the alcohols with p-nitrobenzoyl chloride. The physical and analytical data are listed in Table II.

Kinetic Procedure. The procedure employed in determining the rate constants of p-nitrobenzoates followed that described earlier.[14]

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Low-Energy Singlet–Triplet and Singlet–Singlet Transitions in Cycloalkenes

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Abstract: The lowest energy singlet–triplet and singlet–singlet transitions of cis cycloalkenes, ranging from cyclopropene to cyclooctene, as well as *trans*-cyclooctene, have been investigated using the technique of ion-impact energy-loss spectrometry. In the cis cycloalkenes the maximum of the T ← N transition occurs at 4.2 eV regardless of ring size. The V← N transition energy decreases from 7.2 to 6.5 eV with increasing ring size. The T ← N maximum for *trans*-cyclooctene decreases to 3.85 eV in agreement with predictions of the Franck–Condon principle.

The electronic spectra of ethylene and its alkyl derivatives have the potential of providing much valuable information about the structural and chemical nature of the carbon–carbon double bond. The spectra associated with the electrons in the double bond are often diffuse and of anomalous intensity and the interpretation of these spectra is currently a problem of considerable interest.

The lowest energy olefinic transition is a $\pi \rightarrow \pi^*$ transition from the ground state (the N state) to the lowest triplet state (T) which lies about 4.2 eV above the ground state. Ground-state ethylene is planar, whereas the molecule in the triplet state is relatively free to twist about the double bond and is most stable in the 90° twisted conformation. For this reason the T ← N transition is of importance in photochemical isomerization processes requiring rotation about the C=C bond. The corresponding singlet–singlet $\pi \rightarrow \pi^*$ transition in ethylene is identified as the V ← N transition and lies about 3.5 eV above the T ← N transition. However, the V ← N transition in many substituted ethylenes is only 3.0 eV or less above the T ← N.[1] Much of the intensity in the V ← N absorption spectrum of ethylene has been ascribed[2-5] to transitions to excited states in which the molecules are significantly twisted from the planar conformation (so-called nonvertical transitions). It has also been

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suggested[6-8] that underlying valence state transitions or transitions to Rydberg states (R ← N) account for much of the apparent V ← N intensity. The general nature of the uv spectra of ethylene and its derivatives has been reviewed by Merer and Mulliken.[9]

In the present research, the nature of the interaction between molecular structure and electronic structure in the double bond has been investigated by examining electronic spectra of the series of cis cycloalkenes extending from cyclopropene through cyclooctene. In this series of molecules the rotational freedom about the σ component of the double bond varies from a weak constraint in the larger rings which is similar to that in ethylene to the extreme case of cyclopropene which is forced to remain planar in all electronic states. In addition, spectra of *trans*-cyclooctene have been studied in order to investigate the effects in a double bond which is torsionally distorted in the ground state. It is expected that the σ states and Rydberg states will be a strong function of ring size, while the more localized π and π^* levels will be less sensitive to this parameter. The T ← N transition has been of special interest in this work because, in contrast to optical spectroscopy, singlet–triplet transitions are readily observable by the ion-impact technique employed here. In addition, the T ← N transition is isolated and positively identifiable as a $\pi \rightarrow \pi^*$ transition.

Previous experimental work on this class of molecules is sparse and consists primarily of uv absorption spectra in the 6–9-eV range.[10-16] There have been no previous observations of the T ← N transition in cycloalkenes. The bulk of the theoretical work on cycloalkenes is concerned with cyclopropene,[6,8,13,17] although Watson et al.[6] have dealt with cyclobutene, cyclopentene, and cyclohexene and Yaris et al.[16] have made calculations on *trans*-cyclooctene.

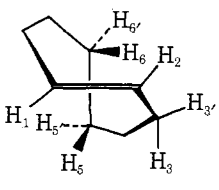
Experimental Method

The apparatus has been described elsewhere[18] and only a brief outline of the ion-impact energy-loss method will be given here. A monoenergetic beam of ions with several keV of energy is passed through the sample gas at a sufficiently low pressure to assure that only single collisions occur. Under these conditions the kinetic energy lost through inelastic collisions corresponds to the excitation energy of the target molecules. A plot of the intensity of scattered ions as a function of energy loss constitutes a spectrum of the sample which is analogous in many ways to an optical absorption spectrum. The choice of projectile ion is important. Proton impact spectra correspond only to singlet–singlet transitions. This is because the total electron spin of the collision system must be conserved and, since a proton has no electron spin, the spin of the target is conserved. However, singlet–triplet transitions occur with high probability[1,19] upon He^+ impact as a result of electron exchange.

The energy resolution in these experiments is about 0.25 eV, and the energy-loss scale is believed to be accurate to better than 0.05 eV. Target gas pressures are in the 10–20 mTorr range with a collision length of 2.5 cm.

Cyclopentene, cyclohexene, cycloheptene, and *cis*-cyclooctene were obtained commercially. Cyclopropene was prepared under a positive pressure of helium by the procedure of Closs and Krantz[20] and was purified by several trap-to-trap distillations,[21] also under a positive pressure of helium. An NMR spectrum indicated the presence of only cyclopropene in the sample.

Cyclobutene was prepared by the method of Cope et al.[22] The cyclobutene contained a small butadiene impurity which was deemed acceptable for the present work. *trans*-Cyclooctene was prepared by the irradiation of the cuprous chloride complex of *cis*-cyclooctene.[23] The 220-MHz NMR spectrum[24] of *trans*-cyclooctene (in CCl_4) displays multiplets at δ 5.39 (H_1 and H_2), 2.35 ($H_{3'}$ and $H_{8'}$), 2.02–1.75 (6 H), 1.41 ($H_{5'}$ and $H_{6'}$), and 0.82 (H_5 and H_6). These data complement the data obtained at lower field strengths by other workers[25] and support the twist conformation (**1**) for *trans*-cyclooctene. In particular, note the newly discovered shielding of $H_{5'}$ and $H_{6'}$ as well as the previously recognized shielding of H_5 and H_6 relative to H_4 and H_7.



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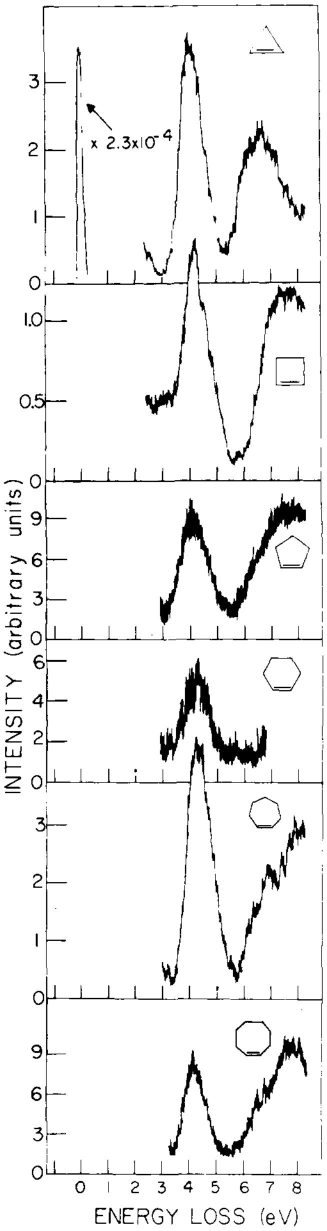

Figure 1. Energy-loss spectra of 3.5 keV He^+ scattered from cis cycloalkenes. The sample gas pressure was about 20 mTorr.

Results and Discussion

A composite of the energy-loss spectra of 3.5 keV He^+ scattered from the cis cycloalkenes is given in Figure 1. The peak at about 4.2 eV in each spectrum is the result of the T ← N transition. The remarkable feature of these spectra is the invariance of the shape and position of the T ← N peak with respect to the ring size. The butadiene impurity gives rise to a shoulder at 3.2 eV in the cyclobutene spectrum. A similar composite of the energy-loss spectra of 3.5 keV H^+ scattered from the cis cycloalkenes is given in Figure 2. The

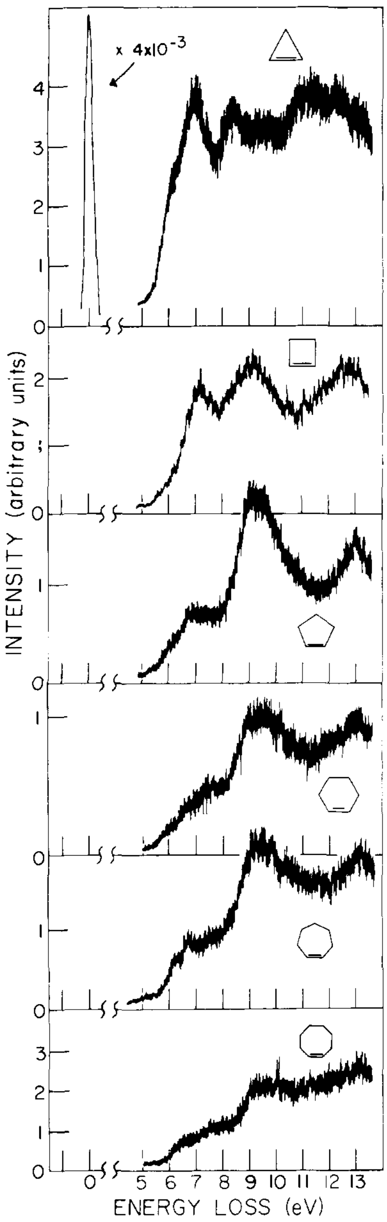

Figure 2. Energy-loss spectra of 3.5 keV H^+ scattered from cis cycloalkenes. The sample gas pressure was about 20 mTorr.

proton impact spectra are distinctly more complicated, exhibiting three broad peaks at roughly 7, 9, and 13 eV; no intensity is seen in the 3-5-eV range. The 7-eV peak is well defined in cyclopropene and cyclobutene but becomes broad and irregular in the larger ring compounds. These peaks are believed to be a composite of the V ← N and R ← N transitions.[9] The 9-eV peaks are transitions to a higher Rydberg state or states,[9] and the 13-eV peaks are well above the ionization potential and are presumed to correspond to transitions to states of the ion. The insensitivity of the singlet-triplet $\pi \rightarrow \pi^*$ transition to ring size suggests that the π and π^* orbitals are located mostly in the region between the double bonded carbon atoms. It follows that the splitting energy between the ${}^3(\pi,\pi^*)$ and ${}^1(\pi,\pi^*)$ states—the T and V states—is also relatively insensitive to ring size. This assumption is borne out by previous observations by Moore[1] on the singlet-triplet splitting of the π^* state in various substituted ethylenes. The apparent broadening and decrease in energy of the 7-eV peak with increasing ring size is at least in part a result of a stabilization of the R state with increasing ring size. That is, it is the underlying R ← N transition which broadens and decreases in energy as the ring size increases. Thus, as indicated in Figure 2 and Table I, the location of the V ← N peak is uncertain in the cycloalkenes larger than cyclopentene.

Table I. Assignment of Prominent Peaks in the Ion-Impact Energy-Loss Spectra of Cycloalkenes

Cycloalkene[a]	T ← N, eV	V ← N, eV	V ← N, eV, other work
Cyclopropene	4.16	7.0	7.2 (ref 13)
Cyclobutene	4.23	7.2	6.2-8.1 (ref 12)
Cyclopentene	4.15	6.9	7.0 (ref 11)
Cyclohexene	4.24	7.0-7.7	
Cycloheptene	4.30	~6.7	
cis-Cyclooctene	4.16	~6.5	
trans-Cyclooctene	3.85	~6.3	6.33 (ref 14-16)

[a] Cis isomer unless designated otherwise.

Comparison of the present spectra with previous theoretical work can only be made in the case of cyclopropene and *trans*-cyclooctene. The first singlet-triplet transition for cyclopropene has been calculated by Peyerimhoff and Buenker[17] and by Robin et al.[13] to be a $\pi \rightarrow \pi^*$ transition. Their values, 4.57 and 4.38 eV, respectively, compare well with the experimental value of 4.16 eV. An assignment of the higher transitions is not so clear-cut since there are numerous singlet transitions which may occur, including $\pi \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$, and $\sigma \rightarrow \pi^*$, as well as Rydberg $\pi \rightarrow$ nl transitions. Peyerimhoff and Buenker[17] predict the first singlet-singlet $\pi \rightarrow \pi^*$ transition to be at 8.24 eV which is more than an electron volt higher than the transition observed here. Basch's[8] calculated $\pi \rightarrow \pi^*$ transition at 7.24 eV, is much closer. He predicts two additional transitions in this region, one to a Rydberg state at 6.14 eV and another to a (σ,π^*) state at 6.5 eV. The shoulder at ~6.1 eV on the 7-eV peak for cyclopropene (Figure 2) possibly indicates the Rydberg transition, while transitions to both the (π,π^*) and (σ,π^*) states may lie within the envelope centered at ~7 eV. Although Robin's[13] calculated value for the singlet-triplet $\pi \rightarrow \pi^*$ transition agrees well with the present work, the corresponding singlet-singlet energy of 8.51 eV does not. For *trans*-cyclooctene, the calculation of Yaris et al.[16] places the V ← N transition at 5.84 eV, whereas this peak appears at 6.3 eV in the proton-impact spectrum.

It is interesting to note in the present work, as well as in previous work on ethylene and substituted ethylenes,[1] that the splitting between the V and T states of substituted ethylenes is at least 0.5 eV less than in the parent molecule. Peyerimhoff and Buenker[5] have recently suggested that the V state of the ethylene is split into two components—V_u and V_g—corresponding to the symmetry species of the planar and 90° twisted conformations, respectively. They calculate that the bulk of the intensity in the V ← N absorption is due to transitions to the V_u state, which is uppermost in energy. Due to the lower symmetry of the substituted ethylenes, there will be mixing between the V_u and V_g states in the substituted molecules and a corresponding decrease in the V_u potential energy for at least some twist angles. This may explain in part the decrease in the splitting between the V and T states in the ethylene derivatives. Note that other effects, such as hyperconjugation, may also affect the T-V splitting.

The nature of the $\pi \rightarrow \pi^*$ transition with regard to twisting about the double bond before or during excitation may be considered in terms of the well-defined T ← N peak in the He^+ spectra. The *cis*-cyclooctene molecule is sufficiently large and flexible to accommodate considerable twisting about the σ component of the double bond, and in this re-

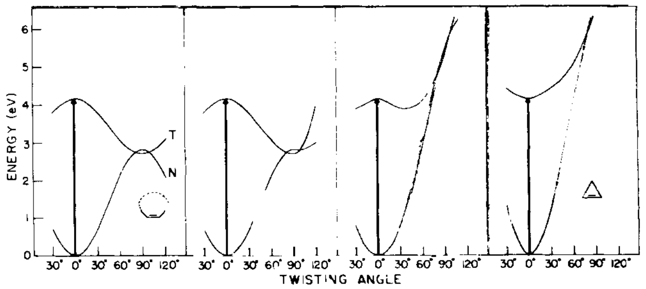

Figure 3. Schematic representation of the N- and T-state potential energy curves of the cis cycloalkenes as a function of the double bond dihedral angle. From left to right the curves refer to decreasing ring size. The curves in the left panel correspond to those expected for ethylene (see text).

spect possible nonvertical transitions to a twisted excited state in cyclooctene are expected to be similar to ethylene transitions. The potential energy curves as a function of dihedral angle for the N and T states of *cis*-cyclooctene are shown schematically in the first panel of Figure 3. For this pair of curves the vertical transition energy for the T ← N transition from the minimum of N-state curve is taken to be 4.16 eV as observed here. The maximum of the N-state curve, 2.82 eV, is the experimentally established barrier[27] to internal rotation of this state. The T-state minimum at 90° is assumed to be slightly lower (0.10 eV) than the N-state maximum in accordance with Hund's rules.[9] The constraining effect of decreasing ring size is illustrated by the remaining three panels in Figure 3. The constraint is manifested by a progressive increase in the energy of both the T and the N states as the dihedral angle increases from 0 to 180°. Clearly the lowest energy transition in cyclopropene must be a vertical transition as indicated in Figure 3. A nonvertical transition would be expected to result in a significant decrease in the observed T ← N transition energy in the larger-membered rings. In fact, the T ← N transition occurs at about 4.2 eV in all of the cis cycloalkenes and at 4.3 eV in ethylene.

A critical test of the hypothesis that the T ← N transition is a vertical transition can be made by measuring the transition energy in a molecule which does not have a planar conformation about the double bond in the ground state. In such a case an upward transition can be expected to be initiated from a nonzero dihedral angle and the apparent T ← N energy gap should decrease.

A recent electron diffraction study[28] indicates that *trans*-cyclooctene has a C—C=C—C dihedral angle of 136°. It can reasonably be assumed that the strain energy,[29] which thus creates a double minimum in the N-state potential curve of *trans*-cyclooctene,[30] will have a similar effect on the T-state curve and can be ignored when considering energy differences between these two states. Thus, the energy of a vertical T ← N transition in the trans isomer is expected to be below that of the cis isomer since the T and N curves converge as the dihedral angle increases from 0 to 90°.

The He^+ impact spectra of *cis*- and *trans*-cyclooctene are given in Figure 4. The peak of the T ← N transition is located at 4.16 eV in *cis*-cyclooctene, whereas this peak occurs at 3.85 eV in *trans*-cyclooctene. This transition energy corresponds to an angle of 17° in the first panel of Figure 3. This angle can be taken as the *interorbital* angle for the p orbitals of the double bond of *trans*-cyclooctene. This is in reasonable agreement with the conclusions of other workers (20° by electron diffraction,[28] and 20°,[31] and 23°[32] by photoelectron spectroscopy) and supports the aforementioned assumption that the strain energy in *trans*-cyclooctene and other strained ethylenes will have a similar effect on both the N-and T-state potential surfaces.

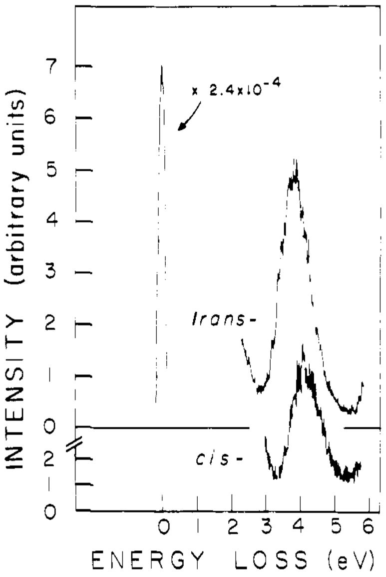

Figure 4. Energy-loss spectra of 3.5 keV He^+ scattered from *cis*-cyclooctene and *trans*-cyclooctene.

Conclusions

The invariance of the T ← N transition energy and the weak dependence of the V ← N energy on ring size in the cis cycloalkenes illustrates the highly localized nature of the π and π^* orbitals associated with the olefinic double bond. Furthermore, the observation that the T ← N transition energy depends only upon the π orbital dihedral angle of the equilibrium conformation strongly supports the hypothesis that the T ← N transition is a Franck–Condon transition originating from the equilibrium conformation of the ground state.

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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.