occurs at an energy approximately 3.0 kcal above the reactant energies. Since other processes have been shown to proceed with no activation, it is unlikely that this process will be very important. It does, however, offer another possible explanation for the experimentally observed decrease in both total O_2 production and $O_2(^1\Delta)$ percentage as the solution pH decreases.

Conclusions

Calculations have shown that several possible processes produce $O_2(^1\Delta)$ with little or no activation. Most of these involve a two-step mechanism in which Cl_2 first reacts with basic species present in solution to form intermediates. These intermediates can then be attacked by basic species to yield $O_2(^1\Delta)$.

On the basis of our calculations, we believe that a plausible picture of what happens in the reaction zone as Cl_2 is bubbled through concentrated basic hydrogen peroxide is as follows:

(1) Cl_2 rapidly reacts ($E_a \simeq 0$) with HO_2^- (the most concentrated reactive species present) to form either (a) $HO_2Cl_2^-$ if the Cl_2 attacks the terminal O atom or (b) $HCl + Cl^- + O_2(^1\Delta)$, if the Cl_2 attacks the H atom. This supports the mechanism proposed by Hurst (reactions 4 and 5).

(2) Any $HO_2Cl_2^-$ formed will react with base, either OH^- or HO_2^-, to form $O_2(^1\Delta)$, two Cl^-, and either H_2O or H_2O_2. This is consistent with Goldberg's proposed mechanism (reactions 6–8), in that reaction of a base with the H on the intermediate (either as HOOCl alone or with the Cl^- loosely bound) is a key step in subsequent O_2 formation. MNDO calculations indicate that $OOCl^-$ is not stable in the gas phase but spontaneously decomposes to O_2 and Cl^-, so that steps 7 and 8 may be more properly combined into a single elementary step. However, in solution, $OOCl^-$ may be slightly stabilized by polar solvents, so that it may exist briefly as an intermediate.

(3) The $O_2(^1\Delta)$ diffuses into the gas phase, being deactivated to $O_2(^3\Sigma)$ to some unknown extent (but probably less than 20% deactivated based on extrapolated data) in the process.

(4) As base is consumed, as in a batch reactor, the Cl_2 must diffuse deeper into the solution to encounter reactive basic species. Thus $O_2(^1\Delta)$ undergoes more deactivation as it diffuses the longer distance into the gas phase. Furthermore, reactions involving acidic species, e.g., H_2O, H_2O_2, and HOCl, occur to a greater extent. Then reactions for which the triplet and singlet surfaces cross (see Figure 8) may cause the observed lowering of $O_2(^1\Delta)$ output at lower pH.

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Registry No. Chlorine, 7782-50-5; hydrogen peroxide, 7722-84-1; oxygen, 7782-44-7.

Hartree–Fock Calculations on Negative Ion States of Chromium Hexacarbonyl

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Abstract: Restricted Hartree–Fock calculations (RHF) have been carried out on the ground state of neutral chromium hexacarbonyl and on a number of low-lying unstable anion states of $Cr(CO)_6^-$. The results are analyzed and compared to recent electron transmission spectral data.

If the ground-state energy of a negative ion is higher than the ground-state energy of the corresponding neutral molecule, the ion is unstable with respect to spontaneous electron loss and the molecule is characterized by a negative electron affinity. The existence of these unstable negative ion states is observable, albeit somewhat indirectly, by electron transmission spectroscopy (ETS). Indeed, in electron–molecule collisions, the scattering cross section changes abruptly when the impacting electron has just enough energy to be temporarily captured into an unstable ion. This phenomenon is usually referred to as a resonance.[1,2]

Although there are several types of resonances, we will only be concerned with the so-called shape resonances, where the projectile electron may be said to be briefly retained into a normally vacant orbital of the target; such a resonance can be looked upon as a state where the electron is temporarily captured into a potential well, whose attractive portion consists of Coulomb forces, while its repulsive portion is due to the centrifugal potential associated with the angular momentum of the electron. The typical lifetime of a shape resonance is of the order 10^{-12}–10^{-15} s. Shape resonances have been observed for atoms, diatomic and triatomic molecules,[3] for unsaturated hydrocarbons, and very recently[4] also for the transition-metal hexacarbonyl compounds $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$.

From a theoretical point of view, the study of resonances requires the proper description of both the target and the projectile. Different aproximate methods have been developed to calculate the wave functions, energies, and lifetimes of the resonances.[5]

Instead, it is the purpose of the present work to discuss the results of a Hartree–Fock calculation of certain stationary negative ion states of $Cr(CO)_6^-$. Since resonances are not true bound states, such a calculation cannot be quantitative nor complete. Yet, wave functions of bound-state form that closely resemble the temporary ion states should yield a reasonable first estimate of the resonance energies. Preliminary calculations of this same type, using the $X\alpha$ formalism, have been presented by Giordan et al.[4]

Neutral $Cr(CO)_6$ Molecule

SCF calculations have been carried out within the framework of Roothaan's RHF open-shell formalism,[6] using the SYMOL program.[7,8] The $Cr(CO)_6$ molecule was taken to be perfectly

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Table I. Virtual Orbitals of Different Symmetry Types[a]

m	orbital character	$\eta_m{}^v$ (virtual) orbital	$E(^2M) - E(^1A_{1g}) = \Delta E_m$	η_m (open shell)
$9a_{1g}$	4s (Cr)	1.94	1.90	1.87
$9t_{1u}$	σ (CO); 4p (Cr)	1.96	1.54	1.07
$2t_{2u}$	π^* (CO)	3.05	2.66	2.23
$3t_{2g}$	π^* (CO); $3d\pi$ (Cr)	3.41	1.89	−0.57
$2t_{1g}$	π^* (CO)	5.30	4.84	4.36
$6e_g$	$3d\sigma$ (Cr); σ (CO)	6.67	2.16	−4.70

[a] The first column shows the $Cr(CO)_6$ virtual orbitals m under consideration; the second column gives indications on the dominant character of these MO's (atomic orbital components); the third column displays the energy $\eta_m{}^v$ of the virtual orbitals (in eV). The last two columns refer to calculations on the $Cr(CO)_6{}^-$ anions: the fourth column gives the relative energy, with respect to the $^1A_{1g}$ ground state of the neutral molecule, of the anion where the relevant orbital is occupied by one electron (^2M stands for $^2A_{1g}$, $^2T_{1u}$, etc.); the fifth column shows the open-shell orbital energies η_m. $E(^1A_{1g}) = -1719.4277$ hartree; all other energies are in eV.

Table II. Mulliken Population Analysis of the Open-Shell Orbitals in the Different $Cr(CO)_6{}^-$ Anion States ($9a_{1g}$ for $^2A_{1g}$, $9t_{1u}$ for $^2T_{1u}$, etc.)[a]

	Cr				C			O		
	4s	4p	$d\sigma$	$d\pi$	s	$p\sigma$	$p\pi$	s	$p\sigma$	$p\pi$
$9a_{1g}$	1.15				0.18	−0.35		0.02		
$9t_{1u}$		0.31			0.03	0.55			0.18	
$2t_{2u}$							0.80			0.20
$3t_{2g}$				0.48			0.43			0.09
$2t_{1g}$							0.81			0.19
$6e_g$			0.87		0.12	0.01				

[a] The populations listed under C or O are the sum populations referring to the six ligands.

octahedral, with internuclear distances of 1.140 Å for C–O and 1.914 Å for Cr–C; these bond lengths are the average values determined by means of the *X–N* method.[9]

For the chromium atom we used a (15s 11p 6d/12s 8p 4d)-GTO basis. For the metal s and p orbitals, the exponents and the contraction coefficients were those proposed by Wachters,[10] except for the following modifications: Wachters' two most diffuse s orbitals were replaced by three s orbitals with exponents 0.236, 0.086, and 0.031. These values were obtained from a linear extrapolation procedure.[11] With the use of the same procedure, the exponents of the two most diffuse p-GTO's were determined at 0.206 and 0.084. The exponents of the d orbitals were taken from Rappe et al.[12] The contraction scheme for the metal atom is identical with the one used by Nieuwpoort et al.[13] For the ligand atoms, we used the (9s 5p/5s 3p) bases proposed by Dunning.[14]

This set of orbitals should constitute a well-balanced basis, leading to results of nearly optimal quality. A full discussion of the ground and excited states of the neutral $Cr(CO)_6$ molecule will be published separately. In the present paper, we confine our attention to those aspects that are immediately relevant to the comparison between the $Cr(CO)_6$ ground state and the different anion states. The total energy of the $Cr(CO)_6$ $^1A_{1g}$ ground state is calculated at −1719.4277 hartree, as compared to the value of −1702.6129 hartree obtained by Hillier and Saunders;[15] the significant improvement of about 17 hartree is obviously connected to the size and the flexibility of the basis set.

The highest occupied orbital, $2t_{2g}$, is of predominant $d\pi$ character. At the Koopmans' level of approximation, this orbital energy should be a measure for the first ionization potential. The lowest band in the photoelectron spectrum is found at 8.4 eV, while the absolute value of the orbital energy is calculated at 9.8 eV by us, vs. 10.7 eV by Hillier and Saunders.[15]

The lowest virtual orbitals of a number of different symmetry types are listed in Table I. Only two of these six orbitals are mainly metal centered: $9a_{1g}$ is essentially the chromium 4s orbital while $6e_g$ represents predominantly the two chromium $d\sigma$ orbitals (in an antibonding combination with the carbonyl σ orbitals). The other four orbitals are either completely or predominantly ligand centered: $2t_{2u}$ and $2t_{1g}$ are pure π^* (CO) combinations; $9t_{1u}$ and $3t_{2g}$ are antibonding combinations of large ligand components (σ and π, respectively) and small metal components (4p and 3d, respectively).

$Cr(CO)_6{}^-$ Anion

To date, no Hartree–Fock calculations on metal hexacarbonyl anions have been published. Table I shows the total energies and the open-shell energies of the $Cr(CO)_6{}^-$ states, obtained by occupying the different orbitals m by one electron. The order of the doublet energies $E(^2M)$ is completely different from the order of the virtual energies $\eta_m{}^v$ or of the open-shell energies η_m. In fact, one obtains for all m

$$\eta_m < E(^2M) - E(^1A_{1g}) < \eta_m{}^v \qquad (1)$$

an inequality that is to be expected on general grounds. Indeed, if neutral molecule and anion were described by the same set of orbitals (Koopmans' approximation), one would obtain for a neutral closed-shell system

$$E^- = E + \eta \qquad (2)$$

where E and E^- are the total energy of the neutral molecule and the anion, respectively; η is the orbital energy of the singly occupied open shell. Therefore,

$$E_K(^2M) = E(^1A_{1g}) + \eta_m{}^v > E(^2M) \qquad (3a)$$

$$E_K(^1A_{1g}) = E(^2M) - \eta_m > E(^1A_{1g}) \qquad (3b)$$

where the subscript K refers to the Koopmans' approximation; in eq 3a, $E_K(^2M)$ is the anion energy, calculated from the orbitals of the neutral molecule; in eq 3b, $E_K(^1A_{1g})$ is the energy of the neutral molecule, calculated from the anion orbitals. Both inequalities of eq 3 result from the fact that the relaxation of the orbitals to their optimal shape necessarily stabilizes the system. Combination of eq 3a and 3b yields eq 1.

The most striking feature of the η_m column of Table I is the negative value for the $3t_{2g}$ and $6e_g$ orbitals. From Koopmans' point of view, a negative orbital energy would correspond to a positive electron affinity. The positive value of the corresponding ΔE_m obviously demonstrates the complete breakdown of Koopmans' theorem for the anions under consideration. This conclusion is to be contrasted to the discussion of the previous section, where a rather satisfactory treatment of cation energies was possible on a Koopmans' basis.

The relaxation phenomenon is most pronounced for the ^2E_g state. Occupation of the e_g orbitals leads to a significant contraction with respect to the virtual orbitals, resulting in a $d\sigma$ (Cr) population of 0.87 electron (Table II). However, this metal population increase is nearly completely offset by a $d\pi$ (Cr) population decrease of 0.60 electron. The $d\pi$-electron shift takes place almost exclusively within the occupied t_{2g} orbitals (Table III). As a net consequence, the added charge is essentially concentrated on the carbonyl ligands.

The open shell in $^2T_{1u}$, $^2T_{2u}$, $^2T_{1g}$, and $^2T_{2g}$ is predominantly centered on the ligands, and the relaxation of the other (closed-shell) orbitals is more limited. Yet, it remains significant, especially in the $^2T_{2g}$ state, where the $3t_{2g}$ open shell contains $d\pi$ (Cr) components. In the four cases, the occupied orbitals of the

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Table III. Total Gross Population (Mulliken Population Analysis) of the Relevant Atomic Orbitals[a]

		$Cr(CO)_6^-$					
	$Cr(CO)_6$	$^2A_{1g}$	$^2T_{1u}$	$^2T_{2u}$	$^2T_{2g}$	$^2T_{1g}$	^2E_g
Cr (4s)	−0.20	+1.15	+0.01	+0.00	+0.00	+0.00	+0.01
Cr (4p)	0.01	+0.01	+0.35	+0.03	+0.06	+0.03	+0.07
Cr (dσ)	1.00	+0.00	+0.01	+0.08	+0.06	+0.03	+0.89
Cr (3dπ)	4.86	+0.00	−0.09	−0.10	+0.02	−0.07	−0.60
C (s)	21.02	+0.16	−0.08	−0.08	−0.11	−0.03	+0.09
C (pσ)	5.38	−0.38	+0.43	−0.11	−0.09	−0.11	−0.13
C (pπ)	8.28	−0.09	−0.21	+0.63	+0.51	+0.58	+0.10
O (s)	23.34	−0.03	−0.11	−0.11	−0.10	−0.11	−0.12
O (pσ)	8.40	+0.07	+0.34	+0.14	+0.15	+0.16	+0.17
O (pπ)	17.93	+0.13	+0.34	+0.51	+0.51	+0.53	+0.52

[a] For the neutral $Cr(CO)_6$ molecules, the total populations are listed; for the different anion states, the table shows the population differences with respect to $Cr(CO)_6$. The population listed for C or O are the sum populations, referring to the six ligands.

neutral molecule have a tendency to expand upon anion formation. For instance, the total population increase of the oxygen atoms amounts to more than 0.5 electrons, although the population increase on the same atoms does not exceed 0.2 electron within the open shells—in any one of the ^2T states.

The $^2A_{1g}$ state is exceptional in that the relaxation of the closed-shell orbitals of the neutral molecule is very limited upon $9a_{1g}$ occupation: the 4s (Cr) orbital is quite diffuse and the resulting interactions are definitely smaller than for any of the other orbitals.

The relative energies of the different anion states cannot be simply rationalized in terms of qualitative arguments: the singly occupied orbital of the ground-state $^2T_{1u}$ and of the first excited anion state $^2T_{2g}$ are of predominant ligand π^* character. Contrary to naive extrapolations from optical absorption spectra, the ^2E_g state (dσ (Cr) occupation) is higher in energy, while the $^2A_{1g}$ state (4s (Cr) occupation) is nearly degenerate with $^2T_{2g}$. It is true though that the relative energy of $^2T_{2u}$ and $^2T_{1g}$ can be connected to the bonding properties of the corresponding open-shell orbitals: the interligand interactions are π^* antibonding in $2t_{2u}$, whereas they are 50% σ^* and 50% π^* antibonding in $2t_{1g}$.

Electron Transmission Spectrum

The experimental $Cr(CO)_6$ spectrum of Giordan et al.[4] exhibits three major resonances at 1.23, 1.64, and 2.42 eV, together with two small signals below 1 eV. The major resonances were assigned by the same authors[4] as the electron attachment energies to the $2t_{2u}$, $7e_g$, and $4t_{2g}$ orbitals, whereas the low-energy signals were suggested to correspond to attachment into the $10t_{1u}$, $6e_g$, and $3t_{2g}$ orbitals. According to Giordan et al., the population of $9t_{1u}$ and certain other low-lying orbitals would give rise to stable negative ions. These assignments and conclusions were based on Xα calculations of the muffin-tin variety; in order to avoid positive orbital energies, the authors had to introduce a Watson sphere of uniform charge density surrounding the molecule. Also, certain orbital and state energies were estimated rather than calculated.

We believe that most of the discrepancies with the results presented here are due to some of the severe approximations introduced by Giordan et al. At the Hartree–Fock level, *all* the anion states, including $^2T_{1u}$, are calculated with a negative electron affinity; no levels are predicted below 1 eV.

From Table I and Figure 1, a set of alternative assignments might be suggested. The resonances at 1.23, 1.64, and 2.42 eV would correspond to electron capture into the $9t_{1u}$, $3t_{2g}$, and $2t_{2u}$ orbitals.

The totally symmetric $^2A_{1g}$ state cannot be expected to be observable in electron transmission spectroscopy: the potential barrier vanishes due to the absence of a centrifugal force. Moreover, for totally symmetric states, the energy minimum is properly described by the $^1A_{1g}$ state of the neutral molecule plus one free electron.[16] Therefore the Hartree–Fock results for $^2A_{1g}$ is meaningless: the value of 1.90 eV in Table I is an artifact due to the limited size of the basis set. Table II shows that the electron density accumulates as far as possible from the center of the molecule (occupation of the very diffuse Cr 4s orbital). If the calculation were repeated with a still more diffuse basis, the unpaired electron would keep moving away to infinity. The only reason to include the $^2A_{1g}$ result in the tables is to contrast its behavior to that of the other states, where a centrifugal barrier does exist. In all those cases, the variational-Hartree–Fock calculation leads to a meaningful result if the basis is chosen in such a way that the wave function cannot attain significant density beyond the barrier.[17] In the case of N_2 (internuclear distance 2.07 au), the top of the barrier is at about 4 au from the center of the molecule.[17] If a similar situation applies in the present case, the potential barrier will have its maximum at 8 or 9 au from chromium nucleus. It is readily verified that even that the most diffuse GTF's used in this work decay sufficiently rapidly so as to satisfy the required condition. As a matter of fact, in all cases—except for $9a_{1g}$—the singly occupied orbitals have no tendency whatsoever to accumulate charge density toward the outskirts of the molecule: as shown in Table II, the population

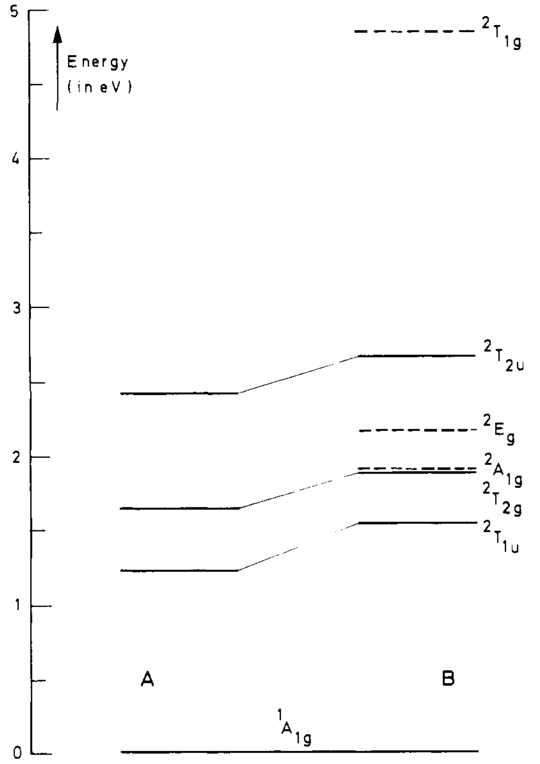

Figure 1. (A) Energy level diagram of the experimental $Cr(CO)_6$ resonances in the ETS spectrum. (B) Calculated energies of the $Cr(CO)_6^-$ states. Dotted line correspond to unobserved levels. The proposed assignments are indicated by interconnected levels.

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of the carbon atoms is always considerably larger than the population of the oxygen atoms.

An alternative way to verify whether the anion states under consideration are of pseudo-bound type is to compare the singly occupied orbitals of the anions to the corresponding orbitals of excited $Cr(CO)_6$ states. For instance, the $6e_g$ orbital of ^2E_g is barely distinguishable from the $6e_g$ orbital of the (bound) excited $^1T_{2g}$ ($2t_{2g}{}^5$ $6e_g{}^1$) state. The same conclusion holds true for $9t_{1u}$, $2t_{2u}$, $3t_{2g}$, and $2t_{1g}$, but *not* for $9a_{1g}$: comparison of the $9a_{1g}$ orbital contours of the $^3A_{1g}$ ($8a_{1g}{}^1$ $9a_{1g}{}^1$) excited state and the $^2A_{1g}$ anion shows a distinct orbital expansion in the latter case.

Beside $^2A_{1g}$, also the $^2T_{1g}$ state may be expected to be absent from the experimental spectrum: it is calculated at 4.84 eV, where the resonances are known to be broadened to the extent of being unobservable. The four remaining states between 1.54 and 2.66 eV are to be matched to the three observed resonances at 1.23, 1.64, and 2.42 eV. In a recent study on negative ion formation via dissociative electron attachment, George and Beauchamp[18] suggested that the expulsion of a CO ligand from a $Cr(CO)_6$ molecule should be facilitated by electron capture into an antibonding e_g orbital. Although this suggestion is obviously in line with classical ligand field theory, the present study does not offer conclusive evidence as to the nature of the dissociation-inducing orbital. Indeed, both the $9t_{1u}$ and the $3t_{2g}$ orbitals are equally—if not more—antibonding between the metal and the ligands; they are as likely candidates as $6e_g$ to serve as a precursor to the dissociative reaction.

In fact, we are inclined to believe that the ^2E_g state is *not* observed in the experimental ETS spectrum. Indeed, as discussed in the previous section, the formation of the ^2E_g state is accompanied by a very pronounced electronic rearrangement within the closed shells. As a consequence, the overlap between decaying and decayed state is smaller for ^2E_g than for any of the other resonances. Although the autodetachment width, and hence the cross section, is determined by matrix elements of the repulsion operator, a decrease of the overlap integral may be taken as a qualitative indication of a decrease in scattering cross section. If so, it is likely that the ^2E_g state will not be detected in the transmission spectrum. Therefore, the assignment of Figure 1 appears to be the only reasonable alternative.

If this assignment is correct, the calculated levels are somewhat too high (0.20–0.30 eV). A similar phenomenon is observed for the individual CO ligand, where the experimentally observed resonance is situated at 1.75 eV; it can be assigned to electron attachment into the 2π orbital. With the Dunning basis set, used in this work, the CO^- $^2\Pi$ state is calculated at 2.52 eV. However, the Dunning basis set has been constructed to reproduce the wave function of neutral molecules; it is less well suited to describe the more expanded anions. Indeed, adding diffuse basis functions to the Dunning set lowers the anion energy[19] with respect to the ground state of neutral CO. Similarly, the basis set used in this work was set up for neutral molecules and positive ions; there can be little doubt that part of the discrepancies should be traced back to a basis set effect.

In addition, the correlation error is certainly expected to be larger in the anion than in the neutral molecule. Both effects—basis set and correlation error—suggest that the present method places the anion levels at too high an energy with respect to the ground state. This observation further substantiates the assignment of the 2.42-eV resonance to $^2T_{2u}$ rather than to ^2E_g.

Acknowledgment. We are indebted to Professor W. C. Nieuwpoort and his group (Groningen, The Netherlands) for help with the SYMOL program. We also gratefully acknowledge financial support from the Belgium Government (Programmatie van het Wetenschapsbeleid).

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(19) If the Dunning basis set is augmented with one p-GTO of exponent 0.0365 for C, 0.0637 for O, and two d-GTO's of exponent 0.7 and 0.1 for both C and O, the energy difference between anion and neutral molecule drops to 1.84 eV.

Structural Consequences of Electron-Transfer Reactions. 8. Elucidation of Isomerization Mechanism of the Radical Anion of (η^4-Cyclooctatetraene)cyclopentadienylcobalt with FFT Faradaic Admittance Measurements

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Abstract: The reduction of (η^4-1,5-cyclooctatetraene)cyclopentadienylcobalt, (1,5-COT)CoCp, proceeds in an apparently irreversible one-electron step to an isomerized anion, $(1,3\text{-COT})CoCp^-$. The present study addressed the mechanistic question of whether the isomerization occurs concomitant with or subsequent to the electron-transfer step. Since the isomerization step was too fast to be studied by normal cyclic voltammetric or moderate frequency ac polarographic techniques, studies using Fast Fourier Transform Faradaic Admittance measurements were undertaken. Using ac frequencies up to 24 kHZ, the reduction was characterized as an EC process (isomerization reaction following the electron-transfer step) with a rate constant for the isomerization step (at 298 K) of $(2 \pm 1) \times 10^3$ s^{-1} in dimethylformamide containing 0.1 M Bu_4NBF_4 as supporting electrolyte. The heterogeneous electron-transfer rates of the reductions of both isomers were evaluated as $k_s^{app} = 0.28$ cm/s for the 1,3-isomer and 0.06 cm/s for the 1,5-isomer.

The relationship between the redox state[1] of a molecule and its structure is perhaps the most important aspect of an electron-transfer process. There has been increasing interest in redox processes which alter the molecular structure of a compound, especially its conformation, in a definable way.[2,3] Not only is

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(1) The term "redox state" of a molecule refers to the overall number of electrons it possesses (i.e., an electron count).

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