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).

Registry No. $Cr(CO)_6$, 13007-92-6; $Cr(CO)_6{}^-$, 84695-79-4.

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(18) George, P. M.; Beauchamp, J. L. *J. Chem. Phys.* **1982**, *76*, 2959.

(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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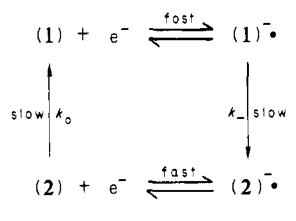
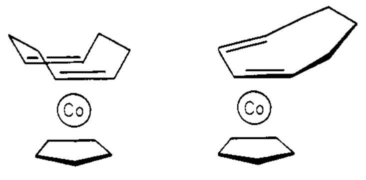
Scheme I

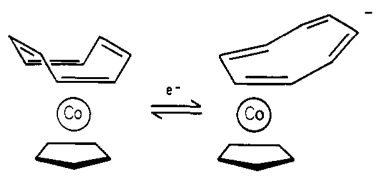


the phenomenon of fundamental interest, but structure/redox state relationships may be important in many biological and catalytic processes. One of us recently reported that C_8 polyolefins π-bonded to cobalt underwent isomerization from nonconjugated to conjugated dienes when the metal complex was reduced electrochemically to its radical anion.[3] Depending on the nature of the polyolefin, the time scale of the isomerization varied enormously. In one case involving the reduction (1,5-COD)CoCp,[3,4] (**1**), isomerization to the anion of (1,3-COD)CoCp, (**2**)$^{-}\cdot$, was slow enough to allow clear distinction between the electron-transfer step and the following isomerization step (an EC process[5]). The isomerization was reversed upon re-oxidation of (**2**)$^{-}\cdot$, so that the redox cycle could be described in terms of a sequence of EC processes using the 4-membered "square" Scheme I, in which each isomer has a defined lifetime in both redox states. The rate constant k_- was solvent dependent, but was ca. 0.1 s^{-1} in most solvents, and k_0 was 3×10^{-5} s^{-1}.



1 2

However, when the polyolefin was cyclooctatetraene (COT), the isomerization to (1,3-COT)CoCp$^{-}\cdot$, (**4**)$^{-}\cdot$, was so rapid that no existence for (1,5-COT)CoCp$^{-}\cdot$, (**3**)$^{-}\cdot$, could be obtained through cyclic voltammetry measurements at high sweep rates (100 V/s) or low temperature (230 K). Since the isomerization was so rapid, the structure change appeared to be simultaneous to the charge transfer, as in (**3**) + $e^- \rightleftharpoons$ (**4**)$^{-}\cdot$. The question of whether a structure change (whether it be a conformational change or bond cleavage) occurs concomitant with or subsequent to charge transfer is crucial to our understanding of electron-transfer mechanisms.[6] For the metal π-complex, (COT)CoCp, earlier ac polarographic measurements[3] failed to address this important mechanistic question because the frequency range of the measurements was insufficient to distinguish between the two possibilities. For example, the earlier reported polarographic peak cot ϕ plots (cot ϕ vs. $\omega^{1/2}$) for the reduction of the 1,5 isomer were linear with a rather large slope, which is consistent with a slow electrode reaction *or* with the low-frequency limit for a mechanism with a fast follow-up chemical reaction.[7] Thus, reexamination of this process was undertaken using the SYDAGES-based computerized Fast Fourier Transform Faradaic Admittance Measurement (FFT-FAM) device.[8] Cot ϕ bandwidths in dipolar organic solvents can be as high as 20–25 kHz under favorable conditions. This measurement bandwidth enhancement dramatically improved the ability to make the required mechanistic judgment concerning the (1,5)$^{-}\cdot$ → (1,3)$^{-}\cdot$ isomerization, and the results provide the first available estimates for the lifetime of the un-isomerized anion, (1,5-COT)CoCp$^{-}\cdot$.



3 4⁻

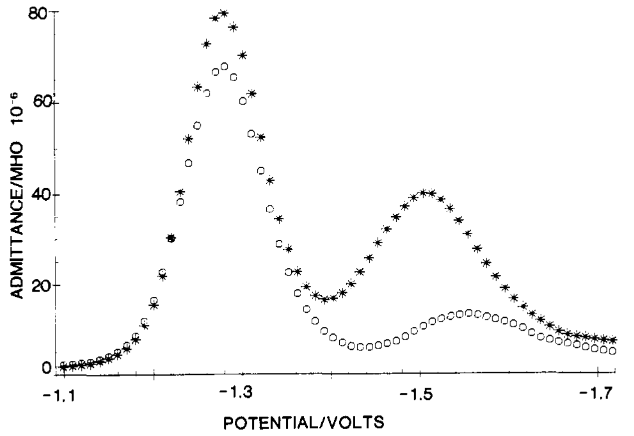
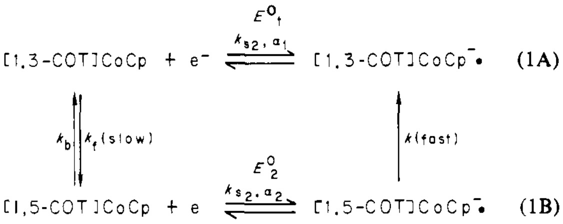


Figure 1. Faradaic admittance polarogram for reduction of 1.9 mM (COT)CoCp in 0.1 M TBATFB–DMF solution at 25 °C; $t = 2$ s, $\omega = 136.7$ Hz; * in-phase and (○) quadrature components of Faradaic admittance, respectively. Potentials vs. Ag, AgI/0.1 TEAI–DMF reference electrode.

Scheme II



Experimental Section

Reagents. Dimethylformamide (DMF) (Burdick and Jackson Laboratories, Inc.), after 1-day treatment with molecular sieves (4A, 8–12-mesh, Aldrich), was used as solvent in this study. Tetrabutylammonium tetrafluoroborate (TBATFB) (electrometric grade, Southwestern Analytical Chemicals, Inc.) was used as supporting electrolyte without further purification. (Cyclooctatetraene)cyclopentadienylcobalt (COT)CoCp was synthesized as noted earlier.[3] No noticeable decomposition was indicated during two months, according to analytical results of dc and ac polarography. Argon (Matheson Gas Products) was used to degas the solution in the cell. It was passed through two columns, one filled with molecular sieves and the second with an oxygen scavenger (Ridox), and then saturated with solvent vapor using a gas bubbler. All measurements were performed under a blanket of argon with a temperature of 25.0 ± 0.5 °C.

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(2) See, for example: (a) Huebert, B. J.; Smith, D. E. *J. Electroanal. Chem.* **1971**, *31*, 333. (b) Kojima, H.; Bard, A. J.; Wong, H. N. C.; Sondheimer, F. *J. Am. Chem. Soc.* **1976**, *98*, 5560. (c) Wimmer, R. L.; Snow, M. R.; Bond, A. M. *Inorg. Chem.* **1974**, *13*, 1617. (d) Bond, A. M.; Cotton, R.; Jackowski, J. J. *Ibid.* **1975**, *14*, 274. (e) Rieke, R. D.; Kojima, H.; Ofele, K. *J. Am. Chem. Soc.* **1976**, *98*, 6735. (f) Lemmen, T. H.; Kocal, J. A.; Yip-Kwai Lo, F.; Chen, M. W.; Dahl, L. F. *Ibid.* **1981**, *103*, 1932. (g) Nelsen, S. F.; Clennan, E. L.; Evans, D. H. *Ibid.* **1978**, *100*, 4012. (h) Olsen, B. A.; Evans, D. H. *Ibid.* **1981**, *103*, 839. (i) Neta, P.; Evans, D. H. *Ibid.* **1981**, *103*, 7041. (j) Holloway, J. D. L.; Geiger, W. E. *Ibid.* **1979**, *101*, 2038. (k) Anderson, L. B.; Hansen, J. F.; Kakihana, T.; Paquette, L. A. *Ibid.* **1971**, *93*, 161. (l) Ahlberg, E.; Hammerich, O.; Parker, V. D. *Ibid.* **1981**, *103*, 844.

(3) Moraczewski, J.; Geiger, W. E., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 4779.

(4) In this paper the following symbols will be used: COD = cyclooctadiene, COT = cyclooctatetraene, Cp = η^5-C_5H_5.

(5) E stands for a heterogeneous electron-transfer reaction and C designates a homogeneous chemical reaction.

(6) For a discussion of this question applied to the reduction of aromatic halides, the reader is referred to: Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; Saveant, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 3431.

(7) Smith, D. E. In "Electroanalytical Chemistry", Vol. 1, Bard, A. J., Ed.; Marcel Dekker: New York, 1966; Chapter 1.

(8) Schwall, R. J.; Bond, A. M.; Loyd, R. J.; Larsen, J. G.; Smith, D. E. *Anal. Chem.* **1977**, *49*, 1797.

Table I. Results of the FFT–FAM Study of the Reduction Process of [COT]CoCp at DME in 0.1 M TBATFB–DMF Solution at 25 °C

process	$E^{r}_{1/2}$/V	α	k_s^{app}/cm s^{-1}	ϕ_2/V	k_s^{cor}/cm s^{-1} [c]	k/s^{-1}
$[1,3\text{-COT}]\text{CoCp} \overset{e}{\rightleftharpoons} [1,3\text{-COT}]\text{CoCp}^{-\cdot}$	−1.28	0.61 ± 0.05	0.28 ± 0.02	−0.098	2.9	-
$[1,5\text{-COT}]\text{CoCp} \overset{e}{\rightleftharpoons} [1,5\text{-COT}]\text{CoCp}^{-\cdot}$	−1.52[b] ± 0.01	0.4 ± 0.1	0.06 ± 0.02[a]	−0.104	0.3	(2 ± 1) × 10³
$\downarrow k$						
$[1,3\text{-COT}]\text{CoCp}^{-\cdot}$						

[a] The observed rate can be two times faster when potential is held close to the $E^{r}_{1/2}$ during measurement. [b] The high-frequency position of the total admittance peak. [c] Calculated for the mean values of k_s^{app} and α.

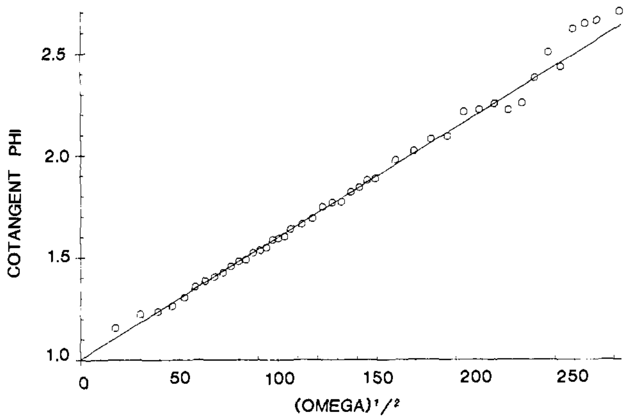

Figure 2. Cot ϕ spectrum at potential of the first admittance peak for (COT)CoCp in 0.1 M TBATFB–DMF reduction at DME.

Instrument. The computerized FFT–FAM instrument for acquisition and processing of the data previously has been described in detail.[8] Experiments encompassed frequencies between 10 Hz and 24 kHz in this work. The electrochemical cell included a dropping mercury working electrode (DME) with a 2-s drop life and mercury flow rate of 0.20 mg s^{-1}. A platinum wire was used as the auxiliary electrode and a homemade Ag,AgI/(0.1 M TEAI–DMF) was the reference electrode. All potentials are referred to this reference electrode, and are about 0.54 V positive to those previously reported for these compounds vs. the aqueous saturated calomel electrode.[3]

Correction for nonfaradaic process contributions uses the computerized extrapolation to high frequency procedure,[9,10] which allows one to determine the double-layer capacitance and electrolyte resistance values from measurements on cells with electroactive species in the solution.

Results

The reduction of (COT)CoCp reveals two ac admittance waves separated by about 0.23 V, as shown in Figure 1. The first wave (most positive) is for reduction of the (1,3-COT)CoCp isomer and the second one for reduction of the more thermodynamically stable (1,5-COT)CoCp isomer. Inspection of the broad-band "peak" cot ϕ plots, calculated from the peak admittance in-phase and quadrature response ratio for the second wave, supports the *homogeneous chemical nature* of the isomerization of (1,5-COT)-CoCp$^{-\cdot}$ anion to the (1,3-COT)CoCp$^{-\cdot}$ form. Thus, the overall mechanistic scheme for the studied reduction process is shown in Scheme II. The experimental cot ϕ plots for the first and second waves are shown in Figures 2 and 3, respectively. The quantitative analysis of the admittance data was done assuming the independence of both charge transfer processes (1A and 1B) and the literature value[3] for equilibrium constant of the neutral complex isomerization ($K = k_f/k_b = 3.26$ at 25 °C). It was assumed in calculations that diffusion coefficients for all species involved in the process are equal. Their value was calculated from the dc polarographic limiting current. It is known that even moderate deviations from this assumption will not materially alter the calculated values of k_s, α, and $E^{r}_{1/2}$. The experiments were performed for four (COT)CoCp concentration values within the range from 1.2 to 2.0 mM. The value of the diffusion coefficient was found to be 5.8×10^{-6} cm^2 s^{-1} in 0.1 M TBATFB in DMF at 25 °C.

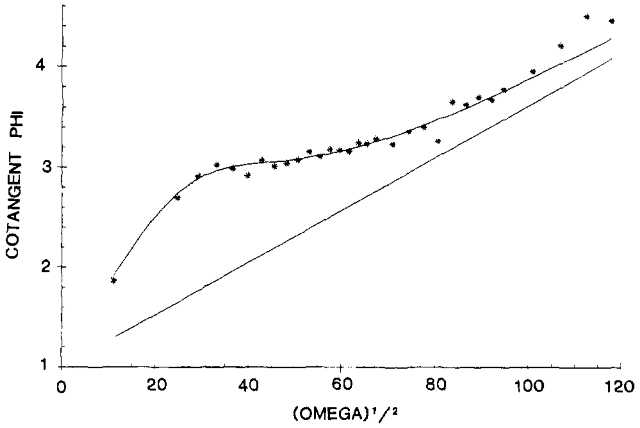

Figure 3. Cot ϕ spectrum at potential of the second admittance peak for (COT)CoCp in 0.1 M TBATFB–DMF reduction at DME: (*) experimental data for 1.9 mM solution of (COT)CoCp, at −1.52 V; (—) theoretical spectra calculated for $k = 2000$ s^{-1}, $k_s = 0.065$ cm s^{-1}, $\alpha = 0.4$, $K = 0.0$, $D = 0.58 \times 10^{-5}$ cm^2 s^{-1}, $n = 1$, $T = 298.0$ K, at $E^{r}_{1/2}$; upper, according to eq 5; lower, *pure quasi-reversibility* of the process.

Consistent with earlier conclusions,[3] the first wave is assigned to (1,3-COT)CoCp reduction to an anion radical. There is no evidence for influence of chemical reactions on kinetics of this process. The data were treated as an ac quasi-reversible electron transfer case with preceding chemical reaction at equilibrium, which is slow on the time scale of the electrochemical experiment (process 1A). The apparent standard heterogeneous rate constant, k_s^{app}, for this process was calculated from the slope of cot ϕ vs. $\omega^{1/2}$ plots at the potential of the admittance peak (Figure 2). The position of this peak does not depend on frequency, so it was assumed to equal $E^{r}_{1/2}$ for this charge transfer process. The resulting expression is[7]

$$k_s^{app} = \frac{D^{1/2}}{2^{1/2}\left(\dfrac{\partial \cot \phi}{\partial \omega^{1/2}}\right)_{E_{dc}=E^{r}_{1/2}}} \tag{2}$$

The value of the diffusion coefficient calculated from the total admittance vs. $\omega^{1/2}$ spectra using the equilibrium concentration of (1,3-COT)CoCp was in good agreement with the dc diffusion coefficient value. The transfer coefficient, α, has been determined according to the equation[7]

$$(E_{\cot\phi})_{max} = E^{r}_{1/2} + \frac{RT}{nF} \ln \frac{\alpha}{1-\alpha} \tag{3}$$

using the FFT interpolation procedure[11] for determining peak positions. The values of k_s^{app} and α obtained for experiments with

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(9) Sluyters-Rehbach, M.; Sluyters, J. H. In "Electroanalytical Chemistry"; Vol. 4, Bard, A. J., Ed.; Marcel Dekker: New York, 1970; Chapter 1.

(10) deLevie, R.; Thomas, J. W.; Abbey, K. M. *J. Electroanal. Chem.* **1975**, *62*, 111.

(11) O'Halloran, R. J.; Smith, D. E. *Anal. Chem.* **1978**, *50*, 1391.

and without scanning the potential to the range of the second wave are in very good agreement. The results are given in Table I.

The second wave is assigned to (1,5-COT)CoCp reduction to an anion radical. There is no doubt that homogeneous kinetic influence of the charge transfer by a coupled chemical reaction (EC mechanism) exists in this case (Figure 3). The admittance data for the second wave were analyzed according to the theory of the CEC mechanism with preceding chemical reaction at a very slow responding equilibrium, ac quasi-reversible charge transfer, and irreversible following chemical reaction (reaction 1B).[12] The highest frequency used in analysis of cot ϕ plots was about 2 kHz, the limit for measurement of the quite small Faradaic admittance quadrature component with proper accuracy. The kinetic parameters for the heterogeneous charge-transfer process were calculated from cot ϕ vs. $\omega^{1/2}$ plots at the "high-frequency" range, where the chemical reaction influence can be neglected (for this case it is between 800 Hz and 2 kHz) and the simple ac quasi-reversible case analysis can be used (eq 2 and 3). The $E^{\mathrm{r}}_{1/2}$ value for this process has been assumed as the "high-frequency" limit of the total admittance peak position.[12]

The possibility of the charge transfer kinetics analysis at potentials where the coupled following chemical reaction is inoperative for all frequencies was also considered. A linear cot ϕ vs. $\omega^{1/2}$ plot slope at the negative side of the ac wave occurs when the following assumption is valid

$$e^{-\alpha j} \gg e^{(1-\alpha)j} \text{ with } j = \frac{nF}{RT}\left(E_{\mathrm{dc}} - E^{\mathrm{r}}_{1/2}\right)$$

so that cot ϕ is simply related to k_s^{app} and α by the equation

$$\ln\left(\frac{\partial \cot\phi}{\partial \omega^{1/2}}\right)_{E_{\mathrm{dc}}<E^{\mathrm{r}}_{1/2}} = \ln\frac{(2D)^{1/2}}{k_s^{\mathrm{app}}} + \alpha\frac{nF}{RT}\left[E_{\mathrm{dc}} - E^{\mathrm{r}}_{1/2}\right] \quad (4)$$

The values of k_s^{app} and α obtained by this procedure (0.06 cm s^{-1} and 0.36, respectively) were in good agreement with those obtained from the "high-frequency" range at $E^{\mathrm{r}}_{1/2}$.[13] The parameters calculated from admittance data at the second wave are included in Table I.

The best fit between experimental and calculated cot ϕ plots was used as a criterion for the estimation of the chemical reaction rate constant, k (Figure 3). The theoretical curve was calculated according to the equation for ac quasi-reversible charge transfer followed by the first order *irreversible* chemical reaction[12]

$$\cot\phi = V/U \quad (5)$$

where

$$V = \frac{(2\omega)^{1/2}}{\lambda} + \frac{e^j}{1+e^j}\left[\frac{(1+g^2)^{1/2}+g}{1+g^2}\right]^{1/2} + \frac{1}{1+e^j} \quad (6)$$

$$U = \frac{e^j}{1+e^j}\left[\frac{(1+g^2)^{1/2}-g}{1+g^2}\right]^{1/2} + \frac{1}{1+e^j} \quad (7)$$

$$\lambda = \frac{k_s}{D^{1/2}}\left[e^{-\alpha j} + e^{(1-\alpha)j}\right] \quad (8)$$

$$g = k/\omega \quad (9)$$

It is seen in Figure 4 that beginning at potentials about 70 mV more negative than $E^{\mathrm{r}}_{1/2}$, the influence of the irreversible chemical reaction on cot ϕ plots for the studied process can be neglected. The prediction which was employed in the analysis of experimental data described in eq 4 is therefore correct.

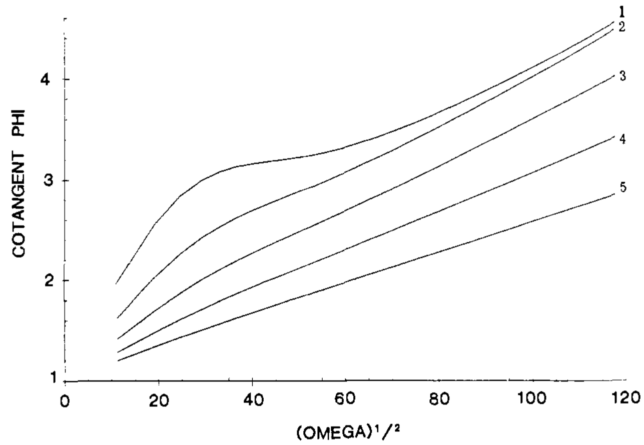

Figure 4. Calculated (eq 5) cot ϕ spectra; $n = 1$, $T = 298.0$ K, $K = 0.0$, $D = 0.58 \times 10^{-5}$ cm^2 s^{-1}, $k_s = 0.06$, $\alpha = 0.4$, $k = 2000$ s^{-1}; 1, $E_{\mathrm{dc}} = E°$; 2, $E_{\mathrm{dc}} = E° - 0.02$ V; 3, $E_{\mathrm{dc}} = E° - 0.04$ V; 4, $E_{\mathrm{dc}} = E° - 0.06$ V; 5, $E_{\mathrm{dc}} = E° - 0.08$ V.

Table I includes also the correction for the double-layer effect on values of the heterogeneous charge-transfer rate constant (Frumkin correction)[14]

$$k_s^{\mathrm{cor}} = k_s^{\mathrm{app}} \exp[-(\alpha n - z)F\phi_2/RT] \quad (10)$$

with $z = 0$ for the reduction process of the neutral molecule. The assumption which was employed was that the reaction plane potential, ϕ_2, is the Outer Helmholtz Plane potential, ϕ_{OHP}, which can be calculated according to the diffuse double-layer theory from the dependence of the double-layer capacitance on potential.[15] The double-layer capacitance vs. potential curve was determined by application of the FFT–FAM measurement to the supporting electrolyte system, followed by the extrapolation procedure.[9,10] The potential of zero charge, E_{pzc}, was determined from the position of the maximum Hg drop life in 0.1 M TBATFB–DMF solution.[16] The results are shown in Table I.

Discussion

The FFT–Faradaic admittance method is considerably advantageous relative to conventional phase-selective ac polarography. Its extended bandwidth and high accuracy allow probing of very rapid kinetics of heterogeneous and homogeneous reactions associated with electron transfer. In the present case, the combination of a very rapid following reaction and an intermediate k_s value caused the ac wave for the 1,5-isomer (**3**) to be small relative to the 1,3-isomer, especially at high frequencies, challenging the capabilities of the measurement system. However, the results allow us to separate for the first time the thermodynamic and kinetic aspects of the redox-initiated isomerization of (**3**) to $(\mathbf{4})^{-}\cdot$ as

$$(1,5\text{-COT})\mathrm{CoCp} + e^- \rightarrow (1,5\text{-COT})\mathrm{CoCp}^{-}\cdot \quad E^0,\ k_s^{\mathrm{app}}$$

$$(1,5\text{-COT})\mathrm{CoCp}^{-}\cdot \rightarrow (1,3\text{-COT})\mathrm{CoCp}^{-}\cdot \quad k$$

The measured rate constant for the isomerization reaction, $k = (2 \pm 1) \times 10^3$ s^{-1}, means that the lifetime of the anion of the nonconjugated isomer is *less than a millisecond* under these conditions. There is, therefore, a remarkable difference between the isomerization rates of the diene and tetraene complexes $(\mathbf{1})^{-}\cdot$ and $(\mathbf{3})^{-}\cdot$, respectively. In the particular solvent used in this study, DMF, $(\mathbf{1})^{-}\cdot$ is very stable and does not isomerize to $(\mathbf{2})^{-}\cdot$ over the time scale of a bulk electrolysis (ca. 20 min).[3] Thus the process $(\mathbf{3})^{-}\cdot \rightarrow (\mathbf{4})^{-}\cdot$ is at least 5–6 orders of magnitude faster than the corresponding $(\mathbf{1})^{-}\cdot \rightarrow (\mathbf{2})^{-}\cdot$ in DMF. This rate difference is

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[12] McCord, T. G.; Hung, H. L.; Smith, D. E. *J. Electroanal. Chem.* **1969**, *21*, 5.

[13] The total admittance vs. $\omega^{1/2}$ spectra are influenced by chemical reaction kinetics throughout the experimental frequency range so the admittance magnitude cannot be used as a simple method for determining the diffusion coefficient of [1,5-COT]CoCp.

[14] Frumkin, A. N. *Z. Phys. Chem.* **1933**, *164A*, 121.

[15] Delahay, P. "Double Layer and Electrode Kinetics"; Wiley: New York, 1965.

[16] Begemann, J. H., private communication.

consistent with the supposition that the isomerization mechanisms of the two radical anions are different, the process $(\mathbf{1})^{-}\cdot \rightarrow (\mathbf{2})^{-}\cdot$ probably involving a metal-hydride intermediate,[3] and $(\mathbf{3})^{-}\cdot \rightarrow (\mathbf{4})^{-}\cdot$ proceeding through a "simple" structural deformation.[17]

The heterogeneous charge-transfer rate of the 1,5-isomer, $k_s^{app} = 0.06$ cm s^{-1}, is somewhat lower than that of the 1,3-isomer, 0.28 cm s^{-1}, and that reported for the 1,3-isomer of (COT)Fe(CO)$_3$, 0.24 cm s^{-1}. It is expected that stereochemical changes during reduction will lower the electron-transfer rate,[2a,19] as predicted by the Marcus theory of electron transfer.[20] The lower electron-transfer rate for the tub-shaped 1,5-isomer may be viewed in this context as arising from structural deformations occurring during the reduction of (**3**) to its anion radical. Since the isomerization of $(\mathbf{3})^-$ to the 1,3-isomer is so facile, it may be that in the initial reduction step, (**3**) deforms part way to the chair conformation of $(\mathbf{4})^-$. Whatever the transition-state structure involved in the heterogeneous reduction of (**3**), the activation barrier to its formation is not large, since the k_s^{app} value of 0.06 cm s^{-1} is still fairly high, falling in the upper end of values associated with quasi-reversible processes.

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Registry No. 3, 84623-08-5; 4^-, 70810-91-2; (1,3-COT)CoCp, 70810-90-1.

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Solar Energy Conversion through Ligand Photodissociation

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Abstract: We examine a new technique for photochemical conversion of solar energy based on ligand photodissociation from metal complexes. We illustrate the concept with a photogalvanic cell in which voltages are generated by photodissociation of CO from carbonylferroheme and with a cell in which the illuminated electrode is coated with an iron tetraphenylporphyrin.

Research on the conversion of sunlight into heat, electricity, and burnable fuels has accelerated in recent years.[1] We here discuss the possibility of a new technique for photochemical conversion of solar energy, one based on ligand photodissociation from metal complexes.[2] The concept is illustrated with a photogalvanic cell[1a,e] in which voltages are generated by the photodissociation of CO from carbonyl ferroporphyrins.[3] We also report a cell in which the carbonyl ferroporphyrin is coated on an optically transparent electrode.

Ligand photodissociation can form the basis of a solar cell if light can appreciably perturb the ligation equilibrium in the vicinity of an illuminated electrode. For example, a cell with one illuminated and one dark electrode and containing a dissolved photodissociable complex will behave as a photogalvanic cell. Bonaventura et al.[4] have shown that the CO binding by illuminated myoglobin can be described by a light-dependent equilibrium constant. Similarly, CO binding to an iron porphyrin such as $\mathrm{Fe^{II}P}$[5] near an electrode in the presence of excess imidazole and CO can be represented by Scheme I, where the bracket indicates that the concentration of the five-coordinate $\mathrm{Fe^{II}P(Im)}$ is very low if [Im] > 0.25 M. Under illumination, l, the dark rate constant for release of CO by the six-coordinate $\mathrm{Fe^{II}P(Im)(CO)}$, is augmented by the CO photodissociation rate, κ, which is proportional to the intensity of the actinic light: $\kappa \propto I$. The ratio of concentrations between the bis(imidazole) and CO-bound species is then light dependent:

Scheme I

$$\mathrm{Fe^{II}P(Im)_2} \underset{k_2}{\overset{k_2'[\mathrm{Im}]}{\rightleftharpoons}} [\mathrm{Fe^{II}P(Im)}] \underset{l+\kappa}{\overset{l'[\mathrm{CO}]}{\rightleftharpoons}} \mathrm{Fe^{II}P(Im)(CO)}$$

$$\frac{[\mathrm{Fe^{II}P(Im)_2}]}{[\mathrm{Fe^{II}P(Im)(CO)}]}\ \frac{(l+\kappa)k_2'}{l'k_2}\ \frac{[\mathrm{Im}]}{[\mathrm{CO}]} \equiv \frac{K_2[\mathrm{Im}]}{L(I)[\mathrm{CO}]} \qquad (1)$$

where $K_2 = k_2'/k_2$ is the equilibrium constant for binding the second imidazole and $L(I) = l'/(l+\kappa)$ is the apparent equilibrium constant for CO binding under illumination; $L_0 = l'/l$ is the dark value. The potential of the illuminated electrode will vary with I insofar as this ratio (eq 1) deviates from its dark value. Metal complexes such as the ferroporphyrins are particularly intriguing for light-harvesting applications because of their broad and intense absorption envelope[6] and because the quantum yield for CO dissociation is essentially unity over the entire envelope.[3] Moreover, CO dissociations occur within 1 ps after excitation, and thus the dissociation process is not susceptible to quenching.[7]

Experimental Methods

The electrochemical cell for measurement of photovoltages (ΔV_P) typically employed an illuminated working electrode of optically trans-

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[5] Abbreviations: FeP, iron protoporphyrin IX; Im, imidazole; I_0, maximum light intensity; I, incident light intensity; TPP, tetraphenylporphinato.

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