aclacinomycin A via a 17-step sequence that proceeds regioselectively and stereospecifically.

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# A Study of the Rate of Intervalence Electron Transfer Using Time Domain Reflectometry

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It is difficult to determine the rate of intervalence electron transfer for most mixed-valence compounds by using conventional spectroscopic techniques such as EPR, NMR, Mössbauer, and ESCA.[1] We report here the first successful use of the technique of time-domain reflectometry[2] (TDR) to obtain these kinetic data. This technique has two potential advantages over the techniques mentioned above. (1) It can obtain kinetic information over the frequency range $10^6$–$10^{10}$ Hz. Calculations based on the Hush theory[3] using the energy of the intervalence transfer band indicate that for most mixed-valence systems electron-transfer rates should fall within this frequency range at reasonable temperatures. This same range is often inaccessible with commonly used techniques. (2) The measurement involves a direct observation of the electron-transfer process. It is not subject to nuclear relaxation effects and other problems which inhibit the use of magnetic resonance techniques for many nuclei and/or electronic configurations. Thus, TDR should serve to complement existing techniques for studying electron-transfer phenomena.

Time-domain reflectometry measures the dielectric relaxation properties of a sample. TDR monitors the change in the dielectric constant, $\epsilon$, as a function of time after the application of an electric field pulse as shown in Figure 1. For a typical Debye dielectric, this change can be described by

$$\epsilon(t) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)(1 - e^{-t/\tau}) \qquad (1)$$

When the electric field is applied, the sample is immediately polarized to give a dielectric constant corresponding to $\epsilon_\infty$. From this initial value, the dielectric constant continues to increase, exponentially approaching a value of $\epsilon_0$ as the dipoles which exist in the sample have a chance to orient themselves with the applied field. The dielectric relaxation time, $\tau$, is a measure of the rate at which the dipoles in the system can move to achieve this preferred orientation.

For solid mixed-valence compounds the "dipole motion" corresponds to an intervalence electron transfer between a pair of metal sites:

$$\mathrm{M_1}^{Z+}\text{—}\mathrm{M_2}^{(Z+1)+} \rightarrow \mathrm{M_1}^{(Z+1)+}\text{—}\mathrm{M_2}^{Z+} \qquad (2)$$

Here, one electron transfer changes the population difference of the two states by two electrons. Thus, the actual rate of electron transfer is

$$K = 1/2\tau \qquad (3)$$

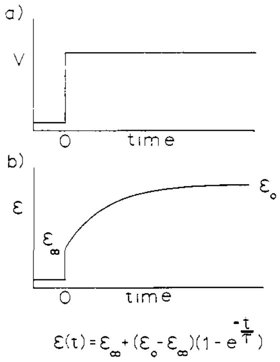

**Figure 1.** Dielectric relaxation in the time domain. (a) A representation of the external step voltage (or electric field) applied to a dielectric sample as a function of time. (b) A representation of the behavior of the dielectric constant as a function of time for the voltage pulse in (a).

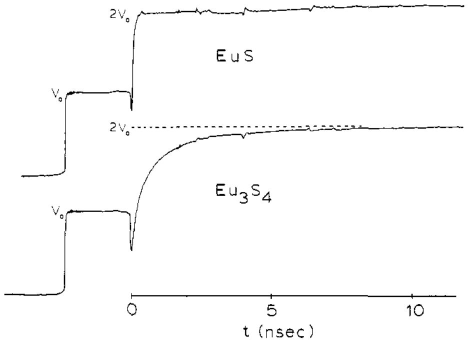

**Figure 2.** TDR spectra for europium sulfides. The top spectrum is the multiple-reflectance TDR spectrum obtained for EuS. The bottom TDR spectrum is that obtained for the mixed-valence $\mathrm{Eu_3S_4}$.

We have monitored the dielectric relaxation behavior of a sample of europium sulfide powder, $\mathrm{Eu_3S_4}$, by using a Hewlett-Packard time domain reflectometer.[4] In this device, a square wave voltage pulse, $V_0$, is propagated down a section of coaxial cable containing the sample. When this pulse encounters the surface of the sample, part of it is transmitted through the sample and part is reflected. Many such reflections eventually occur at both the front and back surfaces of the sample which represent impedence mismatches in the coaxial line. All reflected components of the pulse are eventually propogated back to the detector, and the total reflected signal, $R(t)$, is displayed on an oscilloscope. If the multiple-reflection sample-termination method developed by Cole[5] is used, the TDR data can be analyzed by the equation

$$\epsilon_\infty + (\epsilon_0 - \epsilon_\infty)(1 - e^{-[t-(1/2)T_\mathrm{r}]/\tau}) + C_\mathrm{s}/dC_\mathrm{c} = \frac{c}{d}\int_0^t \frac{P(t')}{2V_0}\,\mathrm{d}t' + \frac{c}{d}\int_0^t \frac{P(t')P(t-t')}{4{V_0}^2}\,\mathrm{d}t' + \left(\frac{c}{d}\right)\left(\frac{T_\mathrm{r}P(T_\mathrm{r})P(t)}{8{V_0}^2}\right) \qquad t > T_\mathrm{r} \quad (4)$$

where $T_\mathrm{r}$ is the rise time of the voltage pulse, $C_\mathrm{s}$ is stray end capacitance, $C_\mathrm{c}$ is coaxial line capacitance per unit length, $d$ is the length of the sample-filled section of the line, $c$ is the speed of light, and $P(t)$ is $V_0 - R(t)$.

Figure 2 shows TDR traces for $\mathrm{Eu_3S_4}$ and EuS at room temperature. The initial voltage pulse, $V_0$, encounters the sample at $t = 0$. For EuS, no dielectric relaxation is observed. However, for the mixed-valence $\mathrm{Eu_3S_4}$ sample, the reflected voltage is clearly indicative of dielectric relaxation on the TDR time scale. We attribute this dielectric relaxation to intervalence electron transfer between Eu(II) and Eu(III) sites in the sample. Analysis of the data indicates that this process has a dielectric relaxation time

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of 460 ps. Sample lengths ranging from $d = 0.3$ to 0.7 cm yielded the same relaxation time which indicates that the thin sample approximation is valid. The relaxation time corresponds to an intervalence electron-transfer rate of $10.9 \times 10^8$ Hz. Values of 22 and 3 were obtained for $\epsilon_0$ and $\epsilon_\infty$, respectively.

Berkooz has determined[6] the rate of intervalence electron transfer for $Eu_3S_4$ as a function of temperature by using Mössbauer spectroscopy. A room temperature Mössbauer spectrum of our sample has been computer simulated by using the methods outlined by Berkooz. The Mössbauer data indicate that the rate of intervalence electron transfer is $9.9 \times 10^8$ Hz, which is in good agreement with the TDR results.

The agreement between our Mössbauer and TDR results indicates that the TDR technique is a viable method for determining electron-transfer rates in mixed-valence compounds. Work is now under way to conduct variable temperature TDR and Mössbauer experiments on $Eu_3S_4$ and to compare these results with Berkooz's. The TDR technique should be able to provide important information concerning activation energies as well as intervalence-transfer rates for mixed-valence compounds.

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# Synthesis, Structural Characterization, and Molecular Orbital Calculations for a Titanium Lewis Acid Carbonyl Adduct

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The coordination of Lewis acids to the oxygen atom of a metal-bound carbonyl ligand is well-known.[2] The importance of this coordination in activating carbon monoxide for reduction has been suggested,[3,4] and the homogeneous reductions of CO to alkanes[4–6] and linear alcohols[7] in the presence of Lewis acids have been observed. We have been interested in the activation of CO in bimetallic systems[8] and report here the recent preparation of a Lewis acid carbonyl adduct by the in situ generation of a titanium(IV) Lewis acid.

The addition of $CpMo(CO)_3H$[9] to a toluene solution of $Cp'[C_5(CH_3)_4{=}CH_2]Ti(CH_3)$[10] [$Cp' = \eta^5\text{-}C_5(CH_3)_5$] resulted in an immediate color change from turquoise to dark red brown. Filtration and removal of solvent in vacuo gave an 80% yield of a dark red-brown powder characterized as $Cp'_2Ti(CH_3)(OC)_3MoCp$.[11] The IR spectrum of the compound taken in Nujol showed bands of medium intensity at 1927, 1918, 1849, 1830, and 1623 cm$^{-1}$. The absorption at 1623 cm$^{-1}$ was indicative of a bridging carbonyl ligand, and a crystallographic determination[12] was undertaken to determine its mode of coordination.

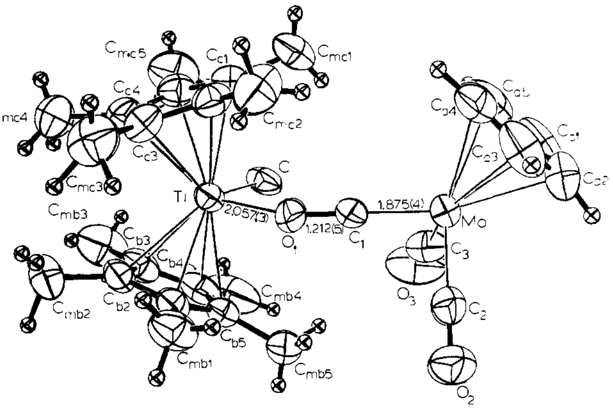

**Figure 1.** ORTEP drawing for $Cp'_2Ti(CH_3)(OC)_3MoCp$ (solvent molecule not shown). Bond lengths: $C_1–O_1 = 1.212$ (5), $C_2–O_2 = 1.154$ (6), $C_3–O_3 = 1.150$ (7), $Mo–C_1 = 1.875$ (4), $Mo–C_2 = 1.948$ (5), $Mo–C_3 = 1.940$ (5), $Ti–O_1 = 2.057$ (3), $Ti–C = 1.969$ (4) Å. Bond angles: $Ti–O_1–C_1 = 144.3$ (3), $O_1–C_1–Mo = 178.8$ (4)°. All hydrogen atoms, except those located on the methyl group attached to the Ti atom, were found.

Table I. Mulliken Gross Atomic Charges

| | C | O | total |
|---|---|---|---|
| terminal | 0.04 | −0.09 | −0.05 |
| bridging | −0.07 | −0.11 | −0.18 |

Table II. Mulliken Populations of CO Ligand Orbitals

| | $3\sigma$[15] | $4\sigma$ | $5\sigma$ | $1\pi_{\parallel}$[16] | $1\pi_{\perp}$ | $2\pi_{\parallel}$ | $2\pi_{\perp}$ |
|---|---|---|---|---|---|---|---|
| terminal | 2.00 | 2.00 | 1.13 | 2.05 | 2.05 | 0.16 | 0.25 |
| bridging | 2.00 | 1.59 | 1.06 | 1.92 | 2.04 | 0.41 | 0.45 |

The structural results are shown in Figure 1 The most interesting aspect of the structure is the coordination of the bridging carbonyl through both the carbon and the oxygen atoms. This is the first example, of a $d^0$ transition metal coordinating to a terminal carbonyl ligand.[13] The bonding of the bridging carbonyl ligand is explained as a Lewis acid interaction of the Ti(IV), $Cp'_2Ti(CH_3)$ moiety with the carbonyl oxygen atom. The observed lengthening of the $C_1–O_1$ bond and the shortening of the $Mo–C_1$ bond are expected upon Lewis acid coordination.[2a,b,e]

Fenske–Hall molecular orbital calculations[14] support this view. Table I shows the Mulliken gross atomic charges for the carbon and oxygen atoms of the terminal and bridging carbonyl ligands and the total charge on these ligands. The increase in negative charge in going from the terminal CO ligand (−0.05) to the bridging CO ligand (−0.18) indicates an increase in the $\pi^*$ orbital

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[11] Anal. Calcd for $C_{29}H_{38}O_3MoTi$: C, 60.22; H, 6.58. Found: C, 60.77; H, 6.37. Field desorption mass spectrum molecular ion at *m/e* 572-582. NMR studies in progress.

[12] Single crystals were obtained from a saturated benzene solution. The compound crystallized as $Cp'_2Ti(CH_3)(OC)_3MoCp{\cdot}0.5C_6H_6$. Space group $P2_1/n$ with $a = 10.109$ (3), $b = 18.106$ (5), $c = 16.648$ (4) Å; $\beta = 104.21$ (2)°; $Z = 4$; $R = 0.043$. The structural determination was carried out at Crystalytics Co., Lincoln, NE.

[13] (a) A similar structure has been observed for a triply bridging CO in the compound $Cp_2TiCl(OC)Co_3(CO)_9$. Schmid, G; Bätzel, V.; Stutte, B. *J. Organomet. Chem.* **1976**, *113*, 67. (b) A $V^{2+}{\cdots}OC$ bond has been observed. Schneider, M.; Weiss, E. *Ibid.* **1976**, *121*, 365.

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