metal carbonyl, intersect a molecular beam of the neutral, prepared by supersonic expansion of a 10% acetaldehyde/90% hydrogen mixture through a 100-μm nozzle. We detect reactively scattered products with an energy analyzer/quadrupole mass filter which rotates about the collision center.

Our initial experiments were performed at collision energies of 12.0 kcal mol^{-1} and 20.8 kcal mol^{-1} for Fe$^+$ and Cr$^+$, respectively. The measured fluxes are transformed to the center of mass collision system to yield product angular and kinetic distributions.[13,14] Figure 1 shows these distributions; the barycentric angular distribution for FeCO$^+$ formation shows clear symmetry about $\theta = 90°$, providing evidence that one or more intermediates in Scheme I live at least several rotational periods.[15] In contrast, CrCO$^+$ formation proceeds with an angular distribution that is quite broad but shows a significant peak at $\theta = 180°$. Although the collision energy for CrCO$^+$ formation is only 8.8 kcal mol^{-1} higher than for FeCO$^+$ formation, the reactive intermediate lives only a fraction of a rotational period,[16,17] or $\sim 10^{-13}$ s in the Cr$^+$ case.

The top panel of Figure 2 shows the reaction coordinate for Scheme I decarbonylation by Fe$^+$, indicating approximate energetics for the reaction of the ground-state cation. Although the energies of the various intermediates and the barriers separating them are unknown, the Fe$^+$–H and Fe$^+$–CH$_3$ bond strengths of 71 and 59 kcal mol^{-1}, respectively[18] allow us to make some estimates of the energies of intermediates I–III relative to the reaction products, as shown in Figure 2. The expected nonreactivity of the 3d^5 Cr$^+$ ground-state configuration and the clear evidence for excited states in Cr$^+$ produced by electron impact[12] suggest strongly that excited states of this ion participate in the decarbonylation reaction. The larger available energy for the excited-state reaction, coupled with smaller Cr$^+$–H and Cr$^+$–CH$_3$ bond strengths[19] relative to the Fe$^+$ system, yields a potential energy profile shown in the bottom panel of Figure 2, where several low-lying quartet states of Cr$^+$ are included. Simple thermochemical arguments[20] suggest that intermediate III in the Cr$^+$ system may lie above the products, leading to an exit barrier to product formation. The additional electrons in Fe$^+$ lead to stabilization of the Fe$^+$ intermediates relative to their Cr$^+$ analogues, resulting in deeper potential energy wells. Coupled with a higher total energy in the Cr$^+$ system arising from excited electronic states in the metal ions, the reaction intermediates exhibit substantially shorter lifetimes.

The kinetic energy distributions shown in the lower panel of Figure 1 also illustrate the differences between these two systems: the narrow distribution for FeCO$^+$ production peaks near 2 kcal mol^{-1}, with the significantly broader CrCO$^+$ distribution peaking near 5 kcal mol^{-1}. These results are consistent with the larger total energy accessible to this product, the shorter lifetimes of the transient intermediates, and the possibility of an exit channel barrier[21] in the formation of CrCO$^+$. These and related questions of excited-state reactivity suggest that additional experiments over a range of collision energies and with ground-state ions, in conjunction with theoretical calculations of the requisite surfaces, will lead to an enhanced understanding of organometallic reaction dynamics in the gas phase.

Acknowledgment. This research was supported by the U. S. Department of Energy. D.M.S. thanks the University of Rochester for support through Sherman Clarke and Hooker Foundation fellowships. We thank Prof. W. D. Jones for his comments on this manuscript.

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(12) Electron impact on metal carbonyls may generate significant excited-state populations. Reents et al. (Reents, W. D.; Strobel, F.; Freas, R. B.; Wronka, J.; Ridge, D. P. *J. Phys. Chem.* **1985**, *89*, 5666) have shown that Cr$^+$ produced by electron impact on Cr(CO)$_6$ is $\sim$70% in excited states. Recent work by Halle et al. (Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 962) provides kinetic evidence that some of these states are quartet states. There was no *kinetic* evidence for more than one Fe$^+$ electronic state produced by electron impact on Fe(CO)$_5$ in the work of Reents et al. Recent work by Elkind and Armentrout (Elkind, J. L.; Armentrout, P. B., unpublished results) suggests enhanced reactivity with D$_2$ for Fe$^+$(^{4}F) relative to ground-state Fe$^+$(^{6}D). This study also indicates that Fe$^+$ reactivity with larger molecules is relatively insensitive to the electronic state of Fe$^+$. Extant data thus suggest that excited electronic state reactivity may be greater for Cr$^+$ than for Fe$^+$.

(13) References for kinematic transformations include: Warnock, T. T.; Bernstein, R. B. *J. Chem. Phys.* **1968**, *49*, 1878. Catchen, G. L.; Husain, J.; Zare, R. N. *J. Chem. Phys.* **1978**, *69*, 1737.

(14) Our method of extracting barycentric polar fluxes from laboratory data is direct iterative deconvolution; see: Siska, P. E. *J. Chem. Phys.* **1973**, *59*, 6052.

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(20) A very crude estimate of the stability of intermediate III relative to the products can be computed from the C–H bond srength in CH$_4$, 103 kcal mol^{-1}, and the appropriate M$^+$–H and M$^+$–CH$_3$ bond energies. Thus FeCO(CH$_3$)H$^+$ lies $\sim$27 kcal below the products, while CrCO(CH$_3$)H$^+$ lies $\sim$31 kcal *above* the products. Comparable calculations for intermediate II using the C–C bond strength in acetone (80 kcal mol^{-1}) give stabilities shown in Figure 2. These calculations ignore the increase in the M$^+$–CO bond strength in the transformation from II and III to products and must be viewed as qualitative only.

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pH Dependence of the Electrochemical Behavior of Surfaces Modified with a Polymer Derived from a Monomer Consisting of Two Viologen Subunits Linked by a Quinone: Evidence for "Rectification" by Synthetic Molecular Materials

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We report results concerning use of the surface-derivatizing reagent I that demonstrates a kind of rectification that is important in systems such as the photosynthetic apparatus. The important finding is that an electrode-bound redox polymer formed via hydrolysis of the Si–OMe bonds of I, (BV–Q–BV^{6+})$_n$, undergoes a 4e$^-$/2H$^+$ reduction, but below pH 5 only 2e$^-$ can be electrochemically withdrawn from the reduced material. Reduction of quinone centers, Q, in the (BV–Q–BV^{6+})$_n$ polymer to their dihydroxy form, QH$_2$, is mediated by the viologen, BV$^{2+/+}$, redox system, but the process cannot be reversed at low pH because the QH$_2$ is thermodynamically incapable of delivering charge back to the BV^{2+} centers. Direct equilibration of the electrode with the Q/QH$_2$ centers in the (BV–Q–BV^{6+})$_n$ polymer does not occur.

Relevance of our new finding to systems like the photosynthetic apparatus rests in the fact that charge separation in the photosynthetic system is achieved by a kind of rectification: the charge transport process involves a series of effectively unidirectional e$^-$ transfer events.[1] Such rectification in immobilized (BV-Q-BV^{6+})$_n$ occurs for a range of coverages: approximately a monolayer (1.8 × 10^{-10} mol/cm^2) to thick polymers (>10^{-8} mol/cm^2). Recent demonstrations[2,3] of rectification using electrode-bound redox polymer bilayer assemblies provide evidence that an effectively unidirectional e$^-$ transfer event can be observed between molecular materials having sufficiently different redox potentials. New

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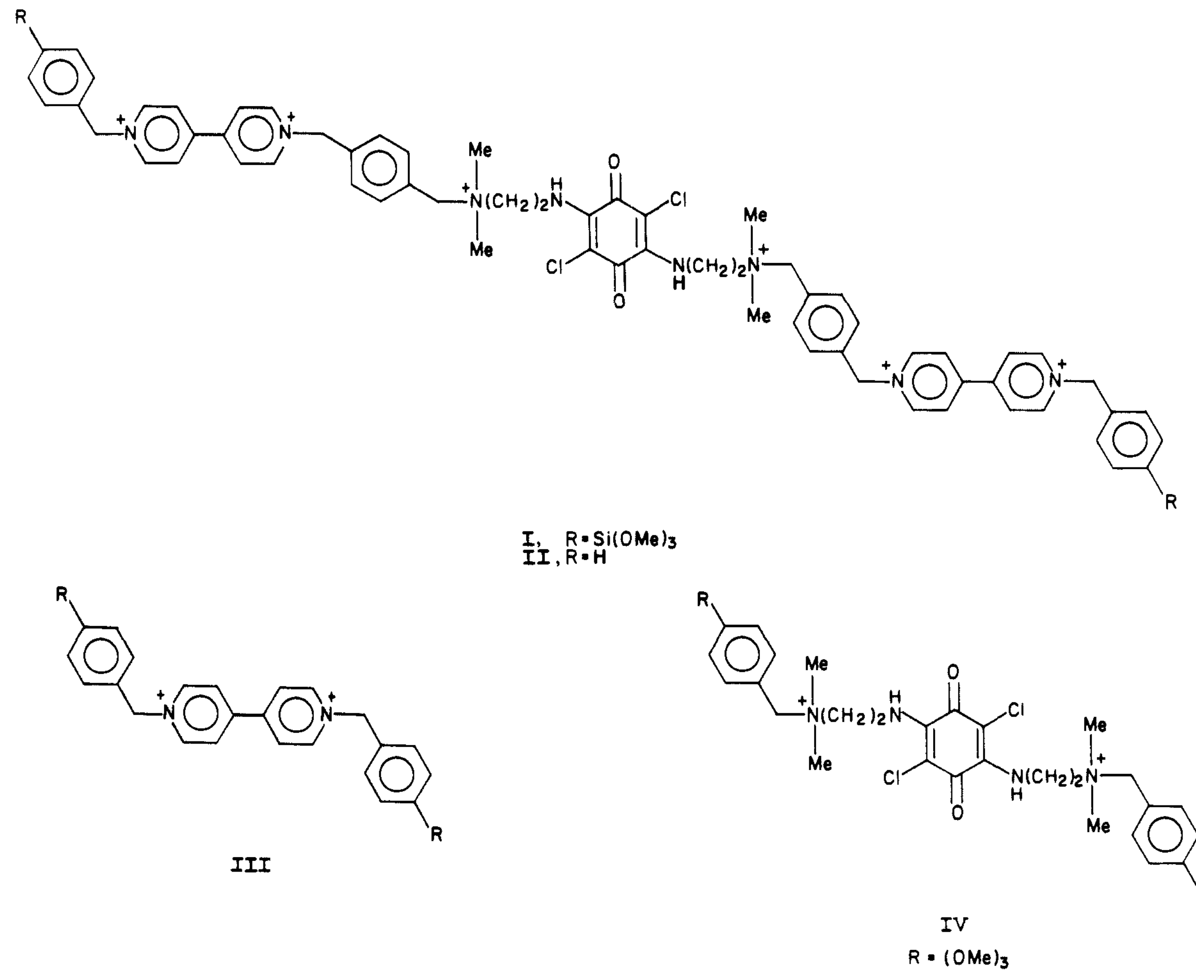
Chart I



I, R = $Si(OMe)_3$
II, R = H

III

IV
R = $(OMe)_3$

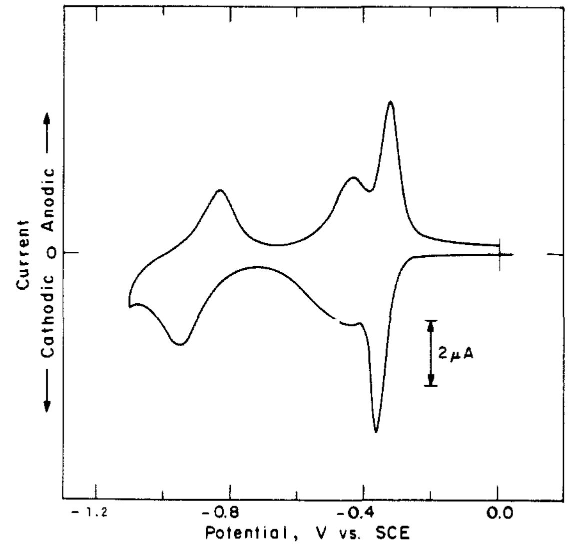


Figure 1. Cyclic voltammogram (5 mV/s) at 298 K in aqueous 1 M LiCl, pH 7.2 (tris buffer), of SnO_2 derivatized with I. The coverage of $(BV\text{–}Q\text{–}BV^{6+})_n$ is approximately 7 × 10^{-10} mol/cm^2 of monomer units.

results reported here suggest that charge can be trapped on an electrode-bound molecular subunit when there is no more than one molecular spacer between a conductor and the molecular subunit holding the charge.

Electrochemistry[4] of I or its analogue having no $Si(OMe)_3$ groups, II,[5] in aqueous electrolyte solution is difficult to study, owing to the precipitation of the reduction product onto the electrode. However, results obtained are consistent with the nature of the molecule in that a response due to BV^{2+} and Q components is observed, consistent with behavior of solutions of models of BV^{2+}, III, or Q, IV.[6,7] UV-vis spectral changes[8] accompanying chemical reduction of II with $S_2O_4^{2-}$ in aqueous solution, compared with the spectral changes accompanying reduction of model subunits III and IV, support the conclusion that the molecule behaves as a system consisting of 2 BV^{2+} centers reducible by 1e$^-$ each to BV^+ and a Q center reducible by 2e$^-$/2H$^+$ to QH_2.

Electrodes (Pt or SnO_2) can be derivatized with reagent I as has been done for other viologen-based reagents having terminal $Si(OMe)_3$ groups.[6] Electrodes to be derivatized with I are potentiostated at −0.7 V vs. SCE in a deoxygenated aqueous solution of 0.2 M KCl/0.1 M KH_2PO_4 and about 5 mM I. Under these conditions I is reduced and precipitates onto the electrode, thereby accelerating the rate of formation of polymer.[6] Coverage of $(BV\text{–}Q\text{–}BV^{6+})$ can be assessed from the integral of a current-voltage scan from 0.0 to −0.7 V vs. SCE like that shown in Figure 1. Coverages of the order of 10^{-10} mol/cm^2 can be obtained in

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(4) Electrochemical measurements were carried out in buffered, aqueous electrolyte under Ar or N_2 at 298 K using single-compartment electrochemical cells with a saturated calomel reference electrode (SCE), a Pt counter electrode, and a working electrode of Pt or SnO_2 on glass either nonderivatized (for study of II) or derivatized with I. A PARC 173/175 potentiostat/programmer was used to obtain the data recorded on a Houston 2000 X-Y recorder.

(5) The syntheses of I, II, and IV are given in the supplementary material.

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(8) Reduction of 1 × 10^{-5} M II was carried out at pH 7.2 (tris buffer) in 1 M LiCl by adding $Na_2S_2O_4$ to the deoxygenated solution. The oxidized form of II shows absorptions at 260 nm (ϵ 51 000) and 348 nm (ϵ 23 800) and reduction gives a visible absorption at 556 nm (ϵ 21 000) consistent with two BV^+ centers per unit of II.

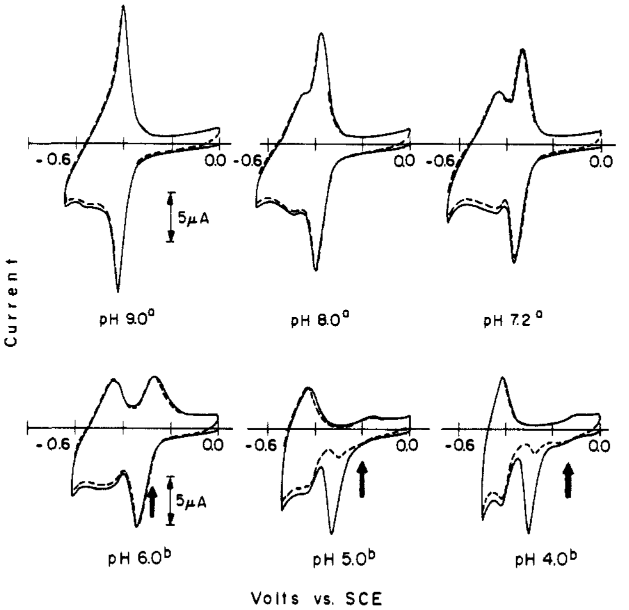


Figure 2. Cyclic voltammograms (10 mV/s) as a function of pH for a Pt electrode derivatized with I (about 5 × 10^{-10} mol/cm^2 of monomers). The electrolyte solution contains 1 M LiCl and either tris (pH 7.2–9) (a) or acetate (pH 4–6) (b) buffer. The first scan (starting from 0.0 V vs. SCE) with the fully oxidized (BV–Q–BV^{6+}) is the smooth curve and the second scan is the dashed curve. Essentially the same results illustrated for pH 4 are also found at pH 1 (aqueous 0.5 M $NaHSO_4$) where the positive limit in the scan was increased to +0.2 V vs. SCE. The arrows in the figure for the low pH's indicate the position of $E^{0\prime}(Q/QH_2)$ determined from the position of the wave for electrodes modified with IV.

a few minutes and about 10^{-8} mol/cm^2 can be obtained in 0.5 h. The electrochemical response of electrode-bound $(BV\text{–}Q\text{–}BV^{6+})_n$ is persistent in deoxygenated aqueous media from pH 1 to 9. At higher pH's the polymer is degraded, and at low pH evolution of H_2 becomes significant at the potentials needed to reduce BV^{2+} units.

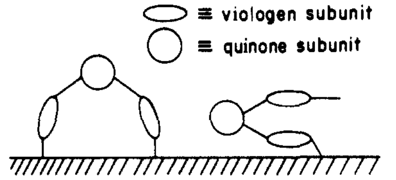
Cyclic voltammograms at pH 7.2 of SnO_2 derivatized with I, Figure 1, show waves expected for the $Q \rightleftarrows QH_2$, $BV^{2+} \rightleftarrows BV^+$, and $BV^+ \rightleftarrows BV^0$ interconversions at about −0.35, −0.45, and −0.9 V vs. SCE, respectively. The integral of the waves is consistent with the 2:1 ratio of BV^{2+} to Q. For pH >5 the electrochemical response is consistent with the reversible $4e^-/2H^+$ reduction of $(BV\text{–}Q\text{–}BV^{6+})_n$. The surprising pH-dependent results are illustrated in Figure 2. For pH <5 the first scan (starting at 0.0 V vs. SCE with the fully oxidized $(BV\text{–}Q\text{–}BV^{6+})_n$) shows a mediated $2e^-/2H^+$ reduction of Q to QH_2 followed by a reversible $BV^{2+/+}$ wave, but the return portion of the scan does not show a significant wave attributed to the oxidation of QH_2. We conclude that the Q to QH_2 reduction is mediated by the $BV^{2+/+}$ system because the reduction of Q occurs at the foot of the BV^{2+} reduction wave, substantially more negative than the reversible Q/QH_2 redox potential indicated in Figure 2. [Arrows in Figure 2 show the position of $E^{\circ\prime}(Q/QH_2)$ determined from study of electrodes modified with IV.] On the second scan there is only a very small wave attributable to the reduction of Q to QH_2, but the reversible wave for the $BV^{2+/+}$ system is the same as in the first scan. The result from the second scan is consistent with the conclusion that the first scan reduces essentially all Q centers to QH_2, and QH_2 is not electrochemically oxidized back to Q even at electrode potentials substantially positive of $E^{\circ\prime}(Q/QH_2)$. Thus, eq 1 and 2 summarize the electrochemistry of $(BV\text{–}Q\text{–}BV^{6+})_n$ above and below pH 5, respectively. Ultimately, trapped QH_2 can be oxidized by oxidants present in the solution; deliberate introduction of O_2 into solution regenerates reducible Q. QH_2 is expected to react rapidly with O_2 to generate H_2O_2 and Q.[7]

$$(BV^{2+}\overset{+}{-}Q\overset{+}{-}BV^{2+})_n + 4ne^- + 2nH^+ \overset{>pH\ 5}{\rightleftarrows} (BV^{+}\overset{+}{-}QH_2\overset{+}{-}BV^{+})_n \quad (1)$$

$$(BV^{2+}\overset{+}{-}Q\overset{+}{-}BV^{2+})_n + 4ne^- + 2nH^+ \xrightarrow{<pH\ 5} (BV^{+}\overset{+}{-}QH_2\overset{+}{-}BV^{+})_n \underset{+2ne^-}{\overset{-2ne^-}{\rightleftarrows}} (BV^{2+}\overset{+}{-}QH_2\overset{+}{-}BV^{2+})_n \quad (2)$$

Essentially the same results illustrated in Figure 2 for approximate monolayer coverage of $(BV\text{–}Q\text{–}BV^{6+})_n$ are also found for large coverages, greater than 10^{-8} mol/cm^2 of monomer units and corresponding to a thickness of several thousand angstroms. The charge trapping in the form of QH_2 is a kind of rectification like that found previously with bilayers of redox polymers.[2,3] At pH 4 the QH_2 can be trapped for at least 10 min when the electrode is held at 0.0 V vs. SCE; preservation of QH_2 appears to be limited by the O_2 impurity level. The surprising fact is that both monolayer coverage and thick polymers show the charge trapping phenomenon. Trapping depends on the ability to change the Q/QH_2 potential to a value such that the QH_2 is incapable of reducing BV^{2+} and on the ability to keep the Q/QH_2 system from directly equilibrating with the electrode surface. Disparate redox potentials of the Q/QH_2 and $BV^{2+/+}$ systems can be achieved by changing pH to low values, because the Q/QH_2 potential moves more positive while the $BV^{2+/+}$ potential remains fixed at about −0.45 V vs. SCE. The ability to prevent the Q/QH_2 system from directly transporting charge to and from the electrode is likely a consequence of the structure of the polymer; functional groups leading to polymer are on the ends of the BV^{2+} centers, and there is only one Q center for every three redox subunits. These features lead to a path for transporting charge between $BV^{2+/+}$ centers but not between Q/QH_2 centers. Additionally, study of electrodes modified with IV show that the Q/QH_2 system has relatively poor charge transport compared to the $BV^{2+/+}$ system as judged from the behavior of electrodes modified with III.[6] In any event, the point is that the only way to access the Q/QH_2 systems in the $(BV\text{–}Q\text{–}BV^{6+})_n$ polymer is via the $BV^{2+/+}$ system; at low pH the reduction of Q by BV^+ is so far downhill that the reverse reaction has negligible rate. In many respects, the results found here for the immobilized $(BV\text{–}Q\text{–}BV^{6+})_n$ system are similar to those reported[9,10] for mobile "mediators" in equilibrating redox polymers with an electrode; in the $(BV\text{–}Q\text{–}BV^{6+})_n$ case the $BV^{2+/+}$ system serves as the mediator.

It is especially significant that rectification can still be observed for very low coverage (1.8 × 10^{-10} mol/cm^2) of $(BV\text{–}Q\text{–}BV^{6+})_n$. Such a low coverage is about half the coverage found for a ferrocene reagent (smaller than I) that can only form a monolayer on electrode surfaces.[11] The fact that rectification still occurs at near monolayer coverage suggests that only a single molecular spacer is required to trap charge in the form of the QH_2. However, for the case at hand both of the BV^{2+} centers are accessible suggesting two structural possibilities:



Cyclic voltammograms, Figure 2, pH <6, show small waves for the reversible reduction of Q to QH_2 showing substantially less than 10% of Q in the polymer to be directly electrochemically accessible; presumably some of the units attached to the electrode are oriented such that this can occur.[12] Studies of charge transport properties and structure of $(BV\text{–}Q\text{–}BV^{6+})_n$ will be reported sub-

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(12) For a range of converages of $(BV\text{–}Q\text{–}BV^{6+})_n$ of 1.8 × 10^{-10} to 1.2 × 10^{-10} mol/cm^2 we observe a reversible wave at pH 1 for the Q/QH_2 centers corresponding to 4 × 10^{-11} mol/cm^2, substantially less than the total Q present in all cases. Since I is a relatively large molecule the 4 × 10^{-11} mol/cm^2 may, in fact, reflect the amount of material in the first monolayer.

sequently, but results so far establish that rectification can be achieved with a relatively small assembly of molecular materials.

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Supplementary Material Available: A scheme and experimental details for the synthesis of I, II, and IV and ^1H NMR data (4 pages). Ordering information is given on any current masthead page.

C-H vs. O-H Reductive Elimination of Methanol from a Metal Complex. Which Is a More Likely Process?

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Elimination of methanol from a metal complex, which constitutes the product-forming step in CO hydrogenation to this product, may, in principle, involve C–H reductive elimination of a hydroxymethyl hydride complex or O–H reductive elimination of a methoxy hydride intermediate[1] (eq 1). Although intramo-

$$\text{H–M–CH}_2\text{OH} \xrightarrow{1} \text{CH}_3\text{OH} \xleftarrow{11} \text{H–M–OCH}_3 \qquad (1)$$

lecular C–H reductive elimination is now well documented,[2] examples for processes of the type I or II are exceedingly scarce. *cis*-$[HIr(PMe_3)_4CH_2OH]^+$ does not eliminate methanol[3] whereas methanol is formed on reaction of $Rh(OEP)(CH_2OH)$ with $Rh(OEP)H$[4] and hydrogenation of $(CO)_4MnCH_2OR$ (R = Et, $COCMe_3$) yields CH_3OR.[5] Protonation of $(\eta^5\text{-}C_5Me_5)_2Zr(OCH_3)H$ yields methanol[6] and $\eta^5\text{-}C_5Me_5Ir(OEt)(PPh_3)H$ photochemically eliminates ethanol.[7] Hydroxyplatinum hydride complexes undergo reductive elmination of water[8] and decomposition of methoxyplatinum complexes leads to methanol via postulated intermediacy of a methoxy hydride complex.[9]

Ideally, for the best possible comparison of processes I and II, complexes containing the same metal, ligands, and stereochemical arrangement have to be employed. Here we describe such a study, leading to the conclusion that under identical conditions, methanol production via process II is preferred.

We have previously described[10] the preparation and preliminary decomposition data of the hydroxyacetyl complex **1**. The structural isomer of **1**, the carbomethoxy complex **2**, is obtained in 79% yield by addition of excess methyl formate to a toluene solution of $Rh(PMe_3)_3Cl$ at 25 °C followed by removal of the solvent in vacuo and crystallization of the resulting solid from toluene/pentane. **2**, obtained as yellow crystals, is unambiguously characterized by ^1H NMR, ^{31}P NMR, IR, and elemental analysis.[11]

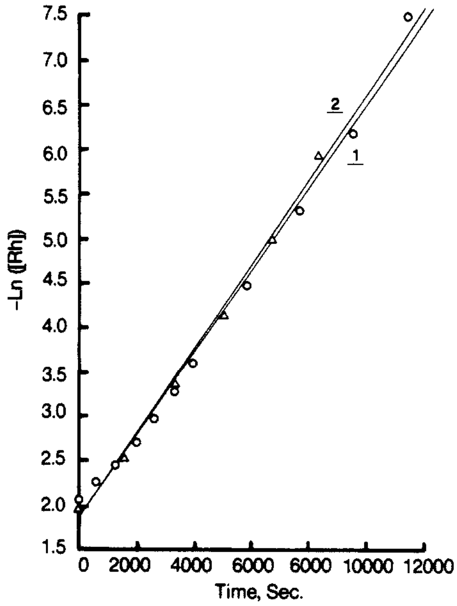
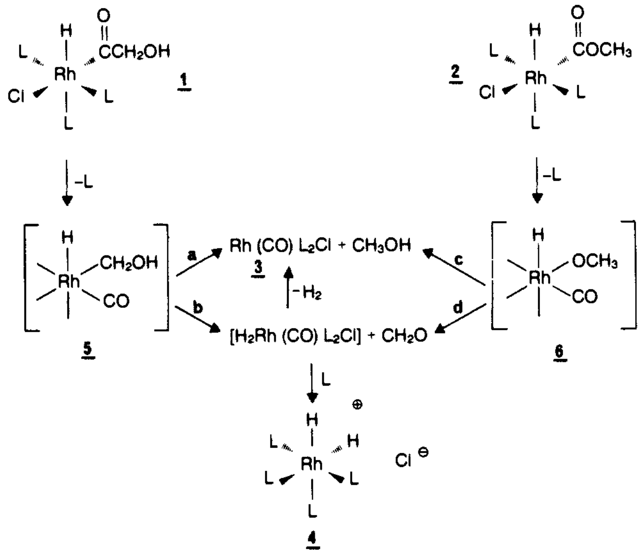


Figure 1. First-order plot for the decomposition of **1** and **2** in dioxane at 70 °C.

Scheme I



L = PMe_3

Isomers **1** and **2** are stable at 25 °C in the solid state but slowly decompose in solution. Upon heating 0.1 M solutions of the complexes in acetone or dioxane at 70 °C in sealed tubes for 12 h under identical conditions, **1** and **2** undergo complete decomposition, leading to formation of the same products but in very different amounts. **1** yields formaldehyde as the major organic product[10] (87% yield based on **1**) in addition to methanol (13%), $Rh(CO)(PMe_3)_2Cl$ (**3**) (61%), and $H_2Rh(PMe_3)_4{}^+Cl^-$[12] (39%),

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[10] Milstein, D.; Fultz, W. C.; Calabrese, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1336.

[11] IR (film) 1960 cm^{-1} (m, ν_{Rh-H}), 1630 (s, $\nu_{C=O}$), 1035 (s, ν_{C-O}); ^1H NMR (C_6D_6) δ 1.24 (d, J = 7.3 Hz, 9 H, PMe_3), 1.39 (t, J = 3.3 Hz, 18H, $2PMe_3$), 3.41 (s, 3H, OCH_3), −8.93 (d of q, J_{H-P}(trans) = 200.5, J_{H-P}(cis) = 15.7, J_{H-Rh} = 15.8 Hz); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −5.21 (d of d, J_{Rh-P} = 105.2, J_{P-P} = 27.6 Hz, 2 P), −24.16 (d of t, J_{Rh-P} = 86.2, J_{P-P} = 27.6 Hz, 1 P).

[12] This complex is reported in: Jones, R. A.; Mayor, Real, F.; Wilkinson, G.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans* **1980**, 511.

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