

Oxidatively Promoted Alkyl to Acyl Migratory Insertion Reactions: A Thermodynamic Assessment for Iron Methyl Complexes

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We report evidence for a trillionfold increase in the equilibrium constant for the alkyl to acyl migratory insertion reaction¹⁻⁴ with acetonitrile (AN) incorporation occurring on one-electron oxidation of complexes of the type Cp(L)(CO)Fe(CH₃),⁵ the first direct demonstration of a facile equilibrium between methyl carbonyl and acetyl forms in the formally Fe(III) oxidation state, and an evaluation of the thermodynamic parameters for one of these equilibria. In addition evidence is presented that shows the oxidative enhancement to be associated primarily with large changes in the forward rates (rather than a decrease in the reverse rate).

Spectroscopic evidence (IR and PMR) shows that the equilibrium positions in the formally Fe(II) oxidation state lies well in favor of the alkyl form, **1a-c** (Scheme I), over the solvent incorporated acyl form, Cp(L)(Sol)Fe(COCH₃), in acetone or acetonitrile solution. In weakly coordinating solvents such as acetone or methylene chloride, the predominance of the alkyl form in the formally Fe(III) oxidation state is maintained for **1a,b**. Thus, the cyclic voltammograms (CV) in acetone at 0 °C exhibit an anodic wave, I,⁶ and a coupled cathodic wave, II, representing the quasi-reversible oxidation of **1** to **3** (*i_a/i_c* = 0.95-1.04; *E_a* - *E_c* = 107-120 mV; Table I). For these derivatives the addition of aliquots of the more strongly coordinating AN in greater than stoichiometric amounts progressively suppressed the alkyl cathodic wave, II, and caused the appearance and growth of a new cathodic wave, III, attributed to the reduction of a solvated acetyl cation radical, **4a** or **4b**.⁷ Neither the cathodic wave, III, nor its anodic partner, IV, was present unless the alkyl oxidation wave, I, had been scanned initially. In neat AN the equilibrium is shifted far in favor of the acyl cation radicals and must be established rapidly since only waves I, III, and IV are observed in cycles with scan rates as high as 20 V s⁻¹.

The kinetic stability of the neutral acyl complexes, **2**, is apparently diminished by increasing the electron donicity of the ancillary ligand L. Thus, the reduction of **4c** is quasi-reversible

Scheme I

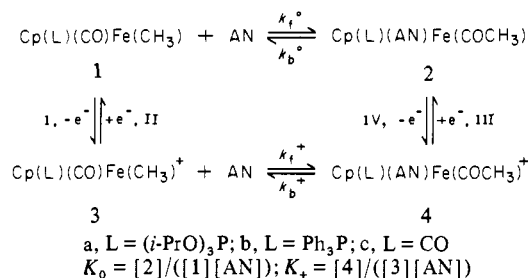


Table I. Electrochemical Potentials

couple	solvent	(<i>E_a</i> + <i>E_c</i>)/2 ^a
3a + e ⁻ ⇌ 1a	acetone	0.41
	AN	0.38 ^b
3b + e ⁻ ⇌ 1b	acetone	0.37
	AN	0.29 ^b
3c + e ⁻ ⇌ 1c	acetone	1.3 ^b
	AN	0.92 ^b
4a + e ⁻ ⇌ 2a	AN	-0.36 ^c
	AN	-0.35 ^d
4b + e ⁻ ⇌ 2b	AN	-0.32 ^c
	AN	-0.33 ^e
4c + e ⁻ ⇌ 2c	AN	0.18
Fc ⁺ + e ⁻ ⇌ Fc	acetone	0.47
	AN	0.39

^a Reduction Potentials (V) from CV measurements at 0 vs. SCE (at 20 °C, contact via Luggin capillary), 0.10 M TBAP, 100 mV s⁻¹.
^b No cathodic wave observed in this medium, *E_a* given. ^c 500 mV s⁻¹. ^d 4.0 V s⁻¹. ^e 10.0 V s⁻¹.

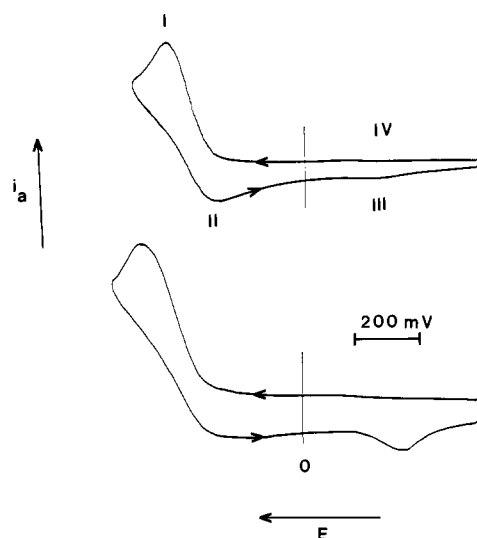


Figure 1. Cyclic voltammograms of **1a** (3 mM) in 50 mM AN in acetone, 0.10 M TBAP, 25 °C, SCE reference: (top) 50 mV s⁻¹; (bottom) 400 mV s⁻¹.

at 0.10 V s⁻¹, whereas the anodic waves, IV, for the reoxidation of **2a** and **2b** become distinct at 0.20 and 0.5 V s⁻¹ and quasi-reversible at 4 and 10 V s⁻¹, respectively. Both **2a** and **2b** rapidly generate **1a** and **1b**, as evidenced by the following CV observations made at slower scan rates. Repeated cycles (AN) over a range including the alkyl anodic wave I but not waves III and IV resulted in a diminution of current. In contrast, when the cathodic acyl wave, III, was included in the scan range anodic wave, IV was not observed (indicating the chemical decomposition of **2**), and no loss in current of I was observed over repeated cycles. This behavior is consistent with the closed electrochemical/chemical system presented in Scheme I.

The CV's of acetone solutions of acetonitrile and **1a** or **1b** showed scan-rate and temperature dependencies that are rather unusual but are diagnostic of an *E_rC_r* mechanism⁸ in which the

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(5) Abbreviations used: Cp = η⁵-cyclopentadienyl, i-Pr = 2-propyl, AN = acetonitrile, TBAP = tetrabutylammonium perchlorate, Fc = ferrocene.

(6) Roman numerals designate CV waves, which are assigned in Scheme I.

(7) Oxidation of **1a** with 1 equiv of AgBF₄ at 0 °C in AN afforded Ag⁰ and a green solution, which exhibited only a single carbonyl absorption at 1645 cm⁻¹, attributed to the acetyl ligand of **4a**. (Comparable results were reported for the oxidation of **1c**.)³ Species **4a** was moderately stable and disproportionated slowly (τ_{1/2} = 43 min, 0.02 M, 24 °C, AN) to give **1a** as one of the products. CV's of chemically oxidized solutions in AN show waves III and IV without scanning over wave I.

Table II. Equilibrium Data for Migratory Insertion Processes

L	T, °C	K_+/K_0	$10^2 K_+$, M ⁻¹	K_0 , M ⁻¹
(<i>i</i> -PrO) ₃ P	0 ^a	4×10^{12}	5.2 ± 0.6	1.3×10^{-10}
Ph ₃ P	0 ^b	2×10^{11}	0.23 ± 0.02	1×10^{-10}
	-12 ^b		0.78 ± 0.22	
	-22.5 ^a		2.4 ± 0.3	

^a [AN] = 3=30 mM in acetone/0.10 M TBAP, [Fe] = 1.0 mM.

^b [AN] = 10-100 mM, [Fe] = 3.0 mM.

scan rate is competitive with the alkyl-acyl (**3** → **4**) equilibration rate. For example, a decrease in the scan rate for **1a** or **1b** increased the relative cathodic peak current for wave II and decreased the peak current of the acyl cathodic wave III (Figure 1). Increasing the temperature had the same effect. It must be noted that the shape of the cathodic wave II does not conform to Cottrell behavior. Rather the current decay between waves II and III is substantially slower and depends on the concentration of AN, implying coupled homogeneous kinetics.

The utilization of the recently developed technique of reverse pulse voltammetry⁹ has permitted the direct determination of K_+ for the phosphite, **1a**, and phosphine, **1b**, derivatives. In this method, the potential at a planar Pt electrode, dipped into an acetone solution of AN and **1a** or **1b**, was stepped for 8 s to 150 mV above $(E_a + E_c)/2$ for the alkyl couple. This was sufficient time to oxidize the complex near the electrode surface and for the alkyl-acyl equilibrium to be established.¹⁰ A pulsed scan toward negative potentials gave two clearly defined waves at potentials corresponding to the reduction of the alkyl and acyl cation radicals. On the basis of the assumption that the diffusion coefficients of the alkyl and acyl cation radicals are the same, the plateau currents were used to determine the concentration ratios and thus the equilibrium constants, K_+ , for a range of AN concentrations. The data in Table II show that the K_+ values at 0 °C parallel the electron-withdrawing power and a decrease in steric requirements of the ancillary ligands.

From the temperature dependence of K_+ for the equilibrium between **3b** and **4b**, ΔH° and ΔS° were computed to be -15 ± 2 kcal/mol and -50 ± 10 eu, respectively. A large negative entropy change seems to be characteristic of the carbon monoxide insertion reaction, although thermodynamic information is limited.¹¹

The thermodynamic enhancements (K_+/K_0 in Table II) of the migratory insertion that occur on oxidation were readily computed for the alkyl and acyl redox processes via the expression

$$\ln(K_+/K_0) = (nF/2RT)[(E_a + E_c)_{\text{alkyl}} - (E_a + E_c)_{\text{acyl}}]$$

Data were obtained in acetone for the alkyl complexes and in AN for the acyl complexes. Medium corrections were made by comparison to the ferrocene couple. The ratios of 10^{11} - 10^{12} correspond to a free energy promotion of 14-15 kcal/mol (0 °C) for the Fe(III) state over the Fe(II) state for the migratory insertion. While K_0 cannot be determined directly because of its intrinsically low value, the thermodynamic cycle of Scheme I permits its calculation whenever K_+ and electrochemical information are available (Table II).

The changes in the equilibrium positions on oxidation appear to be associated with changes principally in the forward dynamics

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(10) A PAR Model 174A polarograph, with an intrinsic pulse width of 57 ms and current sampling during the last 17 ms, was used at a scan rate of 20 mV s⁻¹ with 1 s between pulses. The moderately rapid scan rate was necessary to minimize decomposition of the radical species. The success of this method depends on the rapid restoration of the equilibrium between pulses (supported by CV data) and the relatively small current attributable to back reaction and reduction during the pulse (supported by chronoamperometry). A small correction for the latter was made, as well as for complexation of AN.

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rather than in the reverse dynamics. Predicated on the scan rates necessary to detect the anodic waves IV for phosphite and phosphine complexes in neat AN (vide supra), we estimate half-lives for the conversion of the neutral acyl to alkyl complexes to be on the order of 10^{-1} s at 0 °C. Hence the forward pseudo-first-order rate constant k_f° under these conditions is estimated to be about 10^{-11} s⁻¹.¹² For the oxidation step no cathodic wave II was observed for either of the phosphorous derivatives at scan rates up to 20 V s⁻¹, thereby placing lower bounds on the observed k_f° of 10^2 s⁻¹.

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Registry No. **1a**, 83006-06-8; **1b**, 12100-51-5; **1c**, 12080-06-7; **2a**, 83006-07-9; **2b**, 83006-08-0; **2c**, 83006-09-1; **3a**, 83006-10-4; **3b**, 83006-11-5; **3c**, 83006-12-6; **4a**, 83006-13-7; **4b**, 83006-14-8; **4c**, 75778-51-7; Fc, 102-54-5; acetonitrile, 75-05-8.

(12) This assumes pseudo-first-order behavior for solvent incorporation, and K_0 has been adjusted for [AN].

¹³C{²H} Insensitive Nuclei Enhanced by Polarization Transfer (INEPT): A New NMR Strategy for Isotopic Labeling Studies

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Isotopic labeling studies are commonly used to elucidate mechanistic and structural features in chemistry and biochemistry, either as a tracer or as a structural probe for a selected environment in a large molecule. One method by which this has been accomplished is by selectively labeling sites of interest with enriched NMR-active nuclei such as ¹³C¹ or ²H.² In many instances, ¹³C labeling of selective sites is expensive and difficult to accomplish synthetically. ²H is generally easier to incorporate in organic molecules, and ²H-labeled reagents are much less expensive. However, ²H NMR in isotropic systems has the disadvantage of much smaller chemical shift dispersion.

A new strategy has been developed for studying selected ¹³C sites in low concentrations that takes advantage of both the ¹³C chemical shift dispersion and the expediency of ²H incorporation. In those cases where ²H labeling of a site is easier, polarization transfer from ²H to ¹³C via an INEPT (insensitive nuclei enhanced by polarization transfer) pulse sequence provides the needed selectivity.

The INEPT pulse sequence was designed to tap the reservoir of the larger spin population difference of high γ nuclei (especially of protons) coupled to spins of low γ nuclei.^{3,4} The enhancement results from polarization transfer by way of the internuclear scalar coupling (J) between the observed (I) and coupled (S) spins. The sequence for accomplishing this is

$90^\circ_x(S) - \tau - (180^\circ_x(S), 180^\circ(I)) - \tau - (90^\circ_y(S), 90(I))$ - acquisition
if coupled spectra are obtained or
 $90^\circ_x(S) - \tau - (180^\circ_x(S), 180^\circ(I)) - \tau - (90^\circ_y(S), 90(I)) - \Delta - 180(I) - \Delta$ - (decouple(S), acquisition)

if decoupling is desired, where $\tau = 1/4J$, and $\Delta = 3/8J$ for triplets.

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