methods of ab initio quantum chemistry. However, it serves a purpose in warning one to be careful of situations in which correlation effects will have opposing ramifications. An obvious closely related problem would be the comparison between the C–C single bond distances of triplet methylcarbene (CH_3–CH) and ethane. Since experiments of the type reported by Engelking, Bermath, and co-workers[15,17,18] may soon be possible for triplet methylcarbene, one should make note of this problem in advance.

Acknowledgment. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Fundamental Interactions Branch, Grant DE-FG09-87ER13811.

Registry No. $CH_2{=}NH$, 27770-42-9; NCH_3, 74-89-5.

Electron-Transfer Reactions of Rhenium Carbonyl Radicals with *N*-Methylpyridinium Cations: Application of Marcus-Type Relationships

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Abstract: Rhenium carbonyl radicals, $Re(CO)_4L^\bullet$ (L = PMe_3 or $P(O\text{-}i\text{-}Pr)_3$), generated via flash photolysis at 22 °C of acetonitrile solutions of the corresponding dinuclear compounds, $Re_2(CO)_8L_2$, are observed to undergo electron transfer to substituted *N*-methylpyridinium cations. Reaction rates were measured by observing the disappearance of the transient absorption due to $Re(CO)_4L^\bullet$ or appearance of the absorption due to the product pyridinyl radical. Measured bimolecular rate constants, k_T, for electron transfer of the $Re(CO)_4PMe_3^\bullet$ radical fall in the range 2.6×10^9–4.0×10^6 M^{-1} s^{-1}. For $Re(CO)_4P(O\text{-}i\text{-}Pr)_3^\bullet$ the rate constants fall in the range 6.0×10^8–3.5×10^6 M^{-1} s^{-1}. Correlation of the relationship between log k_T and $-E_{p,c}$, the cathodic peak potential for reduction of the pyridinium cations, using both the Marcus/Agmon–Levine and Marcus quadratic equations led to values of the intrinsic barrier, $\Delta G^*(0)$, of approximately 3 kcal mol^{-1} for each rhenium radical. Application of the above-mentioned equations to extant transition-metal-mediated electron transfer returns *C* parameters (essentially the oxidation potential of the electron-donor species) in reasonable agreement with values estimated in other ways. The electron-transfer results provide insight into the differences in the electron-transfer and atom-transfer processes for the carbonyl radicals.

The chemistry of metal carbonyl radicals now encompasses a wide variety of reaction types, including disproportionation,[1] recombination,[2] ligand substitution,[3] and atom transfer.[2e,3c,4] Interestingly, and in spite of the premise that these radicals are both better oxidants and reductants than their parent molecules, the electron-transfer chemistry of metal carbonyl radicals remains largely unexplored.[4b,5] These transient organometallic species are ideal subjects for study employing flash photolysis methods; the radicals can be generated from metal–metal bonded dinuclear precursors via irradiation into the $\sigma_{M-M} \rightarrow \sigma^*_{M-M}$ manifold.[6] In this manner, the oxidation of $Mn(CO)_5^\bullet$ by several pyridinium complexes has been studied.[5b] The rate of electron transfer exhibits a monotonic dependence on the pyridinium reduction potential. An analogous trend has been observed elsewhere where pyridinium ions serve as the electron acceptor.[7] The attractiveness of pyridinium complexes as acceptors resides in their high electron affinity and, of equal importance, the potential for modifying the reduction potential while maintaining a fairly fixed structure. In addition, the product of electron transfer, the pyridinyl radical,[8] is generally a stable entity with characteristic absorptions in the UV–visible region, which in favorable cases provide a useful probe in the flash photolysis experiment.

Recent efforts from our laboratory have centered on both the atom[4d-g]- and electron[5c]-transfer reactivities of $M(CO)_4L^\bullet$ radicals (M = Mn, Re; L = CO, phosphine, phosphite, arsine). Particular attention has been paid to the applicability of Marcus theory[9] and related models[10] to the halogen atom transfer reactions of Re-

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Table I. Analytical Data for X-*N*-Methylpyridinium Tetrafluoroborates

		elemental analysis							
		calcd			found				
X	formula	C	H	N	C	H	N	mp, °C	yield, %
a. 3,4-$(CN)_2$	$C_8H_6BF_4N_2$	41.60	2.62	18.19	41.77	2.48	18.14	150–2	52
b. 2,4-$(CN)_2$	$C_8H_6BF_4N_2$	41.60	2.62	18.19	41.56	2.38	18.09	166–8	29
c. 2-Cl-3-NO_2	$C_6H_6BClF_4N_2O_2$	27.68	2.32	10.76	27.68	2.28	10.70	230 (d)	33
d. 2-CN	$C_7H_7BF_4N_2$	40.82	3.43	13.60	40.93	3.39	13.49	130–1	80
e. 2-Cl-3-CN	$C_7H_6BClF_4N_2$	34.97	2.52	11.65	34.83	2.53	12.07	139–40	31
f. 4-CN	$C_7H_7BF_4N_2$	40.82	3.43	13.60	40.73	3.39	13.62	119–21	70
g. 4-C_6H_5CO	$C_{13}H_{13}BF_4NO$	54.78	4.24	4.91	54.89	4.19	4.96	168	86
h. 2-C_6H_5CO	$C_{13}H_{13}BF_4NO$	54.78	4.24	4.91	54.62	4.20	4.87	93–4	72
i. 4-$COCH_3$	$C_8H_{10}BF_4NO$	43.09	4.51	6.28	42.74	4.58	6.22	105–7	96
j. 3,4,5-Cl_3	$C_6H_5BCl_3F_4N$	25.35	1.77	4.93	25.40	1.69	4.79	207–8	57
k. 2-(2′-*N*-Me(py)$^+$)	$C_{12}H_{14}B_2F_8N_2$	40.05	3.92	7.78	39.96	3.87	7.75	>300	51
l. 2-$COCH_3$	$C_8H_{10}BF_4NO$	43.09	4.52	6.28	43.01	4.50	6.25	88–9	84
m. 4-CO_2CH_3	$C_8H_{10}BF_4NO_2$	40.21	4.22	5.86	40.16	4.22	5.89	104–6	83
n. 3-CN	$C_7H_7BF_4N_2$	40.82	3.43	13.60	40.95	3.37	13.70	112	88
o. 3-C_6H_5CO	$C_{13}H_{13}BF_4NO$	54.78	4.24	4.91	54.68	4.11	4.84	95	89
p. 4-$CONH_2$	$C_7H_9BF_4N_2O$	37.54	4.05	12.51	37.32	3.95	12.63	175–8	90
q. 3-$COCH_3$	$C_8H_{10}BF_4NO$	43.09	4.52	6.28	43.26	4.55	6.19	109	73
r. 3-CO_2CH_3	$C_8H_{10}BF_4NO_2$	40.21	4.22	5.86	40.15	4.23	5.78	77	89

$(CO)_4L^\bullet$ (L = PMe_3, **2a**; P(O-*i*-Pr)$_3$, **2b**).[4g] Analysis of log k_T vs $-E_{1/2}$(red) data via the Marcus/Agmon–Levine equation (or the closely related Rehm–Weller equation[11]) revealed that assumptions made concerning the constancy of the intrinsic barrier, $\Delta G^*(0)$, for reaction of a series of related halogen donors with a given metal carbonyl lead to good agreement with experimental results.[4g]

To better understand the role of electron transfer in the atom-transfer process, we embarked on the first systematic study of the electron-transfer reactivity of metal carbonyl radicals. As an initial exercise to test the applicability of the Marcus/Agmon–Levine[4g] and Marcus quadratic[9a,12] equations to this type of system, we analyzed the log k_T vs $-E_{p,c}$ (or $-E_{1/2}$) data for three examples of transition-metal-mediated electron-transfer reactions.[7a,d,g,13] The reasonably close correspondence between the reported estimates of oxidation potentials for the reactive metal species and the *C* parameters derived from the analysis suggest that it should be valid to apply these equations to the analysis of data for the rhenium radical systems. The present results, together with a number of reported free energy parameters[14–16] and those from the halogen atom transfer studies,[4g] provide a basis for assessing the nature of the intrinsic barriers to electron transfer from metal carbonyl radicals and the contribution of electron transfer to the atom transfer process.

Experimental Section

Materials. Acetonitrile was dried successively over 4-Å molecular sieves (Davison) and CaH_2 (Alfa) then distilled under nitrogen from P_2O_5 (Mallinckrodt). The solvent was freed from oxygen by three freeze–pump–thaw cycles and stored in an inert atmosphere drybox. All other solvents were reagent grade and used immediately without further purification. The substituted pyridines (Aldrich and Lancaster) and $Me_3O^+BF_4^-$ (Alfa) were used as received. The dimers $Re_2(CO)_8(PMe_3)_2$ and $Re_2(CO)_8[P(O\text{-}i\text{-}Pr)_3]_2$ were prepared as previously described.[4f]

The *N*-methylpyridinium complexes were synthesized as the tetrafluoroborate salts in the following manner: a slight excess of $Me_3O^+BF_4^-$ was added slowly at room temperature under nitrogen to a stirring acetone solution of the substituted pyridine. The resulting mixture was allowed to stir overnight. Any precipitated salt was filtered off while the filtrate was treated with pentane to induce further precipitation. In the absence of solids, the reaction solution was either treated with pentane or reduced to solids, redissolved in either acetonitrile or methanol, and then treated with ether to separate the pyridinium salts. The white salts were recrystallized twice either from acetone/pentane or (acetonitrile or methanol)/ether mixtures, filtered, washed with pentane or ether, and dried in vacuo. Analytical data for the pyridinium complexes appear in Table I.

Physical Techniques. The N_2 laser flash photolysis (337 nm) and data acquisition apparatus have been described earlier.[4e] Several constraints imposed on the present reaction system are noteworthy. The range of measurable rates is bound in the fast regime by the laser pulse decay and at the slow end by recombination of the rhenium carbonyl radicals. Adjustment of the electron-acceptor concentration to cause the observed rates to fall within these boundaries is limited in these systems by the fact that electron transfer occurs predominantly to the free pyridinium cation,[5c] the concentration of which is affected by ion-pair and triple-ion formation. The concentration of free ion, α, was calculated for each concentration as described earlier.[5c] K_D and K_T, the ion-pair and triple-ion dissociation constants, respectively, were determined for three different pyridinium salts. They differed little from the original values quoted for the 4-cyano derivative;[5c] therefore, average values (K_D = 0.015 M, K_T = 0.15 M) were used for all salts. Samples were prepared ca. 0.6 mM in metal carbonyl dimer and ca. 0.02 M in pyridinium acceptor in an inert atmosphere drybox and sealed by Teflon stoppers in 25-mL round-bottom flask to which 1-cm quartz cuvettes had been attached. Following the flash, signals were detected by monitoring either at 540 ± 10 or 600 nm (Re carbonyl radicals) or at 450 ± 20 nm (pyridinyl radicals). In only one instance (Table II, entry e, L = P(O-i-Pr)$_3$ was it possible to obtain reliable data for both species. Reported rate constants are averaged from 5 single shots or from 5 traces, each of which is an average of 5–10 shots, depending on signal/noise levels in the particular system.

Conductivity measurements were performed on a Beckman RC-19 conductivity bridge with a Fischer Scientific 3403 cell. A cell constant of 1.033 cm^{-1} was determined by measuring the conductivity of a 0.1 M KCl solution. All measurements were taken at 25 °C.

Reduction potentials were obtained on a BAS-100 electrochemical analyzer operating in the cyclic voltammetry mode. Solutions were prepared 6–10 mM in pyridinium complex in acetonitrile with 0.1 M $Bu_4N^+BF_4^-$ as supporting electrolyte. A Ag/AgCl (3.0 M NaCl) reference electrode was used in conjunction with a Pt wire working electrode and a Pt disk as counter electrode. Cyclic voltammograms were obtained with a negative sweep rate of 200 mV s^{-1} and were compensated for *iR* drop. $E_{1/2}$ values are reported for those species exhibiting reversible behavior (Table II); in all other cases and for plotting purposes the $E_{p,c}$ value is quoted. The ferrocene/ferricinium couple showed a reversible wave at +477 mV vs the Ag/AgCl electrode and was used as the standard for all experiments.

Melting points (uncorrected) were determined on a Büchi melting point apparatus in glass capillaries sealed with silicone grease.

Multivariable nonlinear regression analysis was carried out using the SHAZAM program.[17] Both the Marcus/Agmon–Levine relationship, eq

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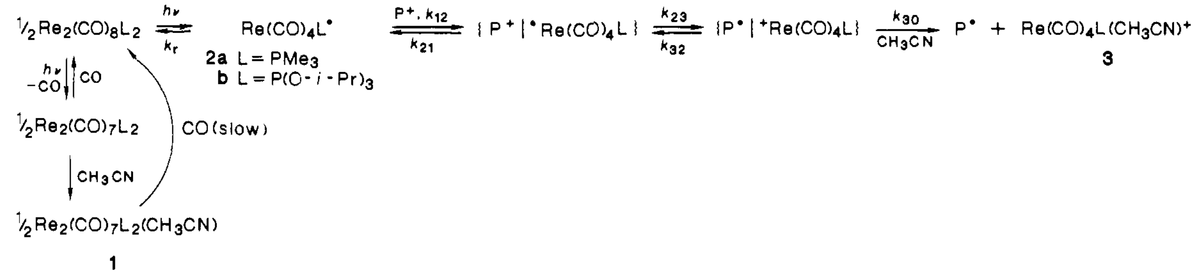
Table II. Rate Data for Reaction of Re(CO)$_4$L$^\bullet$ with X–*N*-Methylpyridinium Cations

X	$-E_{p,c}$,[a] V vs Ag/AgCl	L = PMe$_3$ (**2a**) α,[b] M	k_T[c] 10^{-7} M^{-1} s^{-1} (M)	λ,[d] nm	L = P(O-*i*-Pr)$_3$ (**2b**) α,[b] M	k_T,[c] 10^{-7} M^{-1} s^{-1} (M)	λ,[d] nm
a. 3,4-(CN)$_2$	0.06	0.00656	260 ± 8 (0.994)	470	0.00707	47.3 ± 0.1 (0.996)	450
b. 2,4-(CN)$_2$	0.09 (0.07)	0.00811	171 + 9 (0.996)	450	0.00854	35.3 ± 0.3 (0.997)	450
c. 2-Cl-3-NO$_2$	0.32	0.00685	223 ± 7 (0.999)	450	0.00712	59.5 ± 0.4 (0.995)	450
d. 2-CN	0.57	0.0171	6.4 ± 0.14 (0.999) 6.13 ± 0.05 (0.999)	540 600	0.0172	1.40 ± 0.04 (0.999)	450
e. 2-Cl-3-CN	0.59	0.0119	2.6 ± 0.2 (0.995)	600	0.0117	0.37 ± 0.03 (0.997) 0.70 ± 0.04 (0.996)	430 600
f. 4-CN	0.60 (0.57)	0.0175	18.1 ± 0.2 (0.985)	540	0.0187	3.2 ± 0.2 (0.991)	450
g. 4-C$_6$H$_5$CO	0.62 (0.59)	0.0114	26.8 ± 0.04 (0.999)	450	0.0121	4.97 ± 0.05 (0.999)	450
h. 2-C$_6$H$_5$CO	0.64 (0.61)	0.0128	11.7 ± 0.07 (0.999)	430	0.0122	1.59 ± 0.08 (0.999)	430
i. 4-COCH$_3$	0.66 (0.63)	0.0116	13.3 ± 0.01 (0.999)	450	0.0114	2.23 ± 0.07 (0.999)	450
j. 3,4,5-Cl$_3$	0.66	0.0122	4.3 ± 0.1 (0.997)	540	0.0114	0.39 ± 0.01 (0.995)	540
k. 2-(2′-*N*-Me(py)$^+$)	0.67	0.0128	1.01 ± 0.05 (0.994)	540	0.0120	0.57 ± 0.02 (0.996)	540
l. 2-COCH$_3$	0.69 (0.67)	0.0140	2.8 ± 0.1 (0.993)	450	0.0131	2.14 ± 0.05 (0.998)	540
m. 4-CO$_2$CH$_3$	0.72 (0.70)	0.0176	4.32 ± 0.07 (0.997)	540	0.0249	1.24 ± 0.05 (0.997)	600
n. 3-CN	0.76	0.0173	1.53 ± 0.06 (0.998)	450	0.0194	1.22 ± 0.04 (0.997)	540
o. 3-C$_6$H$_5$CO	0.81		*e*		0.0175	2.53 ± 0.04 (0.997)	450
p. 4-CONH$_2$	0.88 (0.85)	0.0115	3.38 ± 0.03 (0.999)	430	0.0116	0.76 ± 0.01 (0.999)	430
q. 3-COCH$_3$	0.88	0.0194	4.1 ± 0.1 (0.997)	450	0.0193	0.35 ± 0.01 (0.997)	450
r. 3-CO$_2$CH$_3$	0.91	0.0251	0.40 ± 0.02 (0.995)	540		*f*	

[a] Cathodic reduction potential, in V vs Ag/AgCl (Cp$_2$Fe/Fe$^+$ = +0.477 V); numbers in parentheses correspond to $E_{1/2} = (E_{p,c} + E_{p,a})/2$ where available. [b] Free pyridinium cation concentration. [c] $k_T = k_{obsd}/\alpha$; number in parentheses indicates correlation coefficient for linear least-squares fit. [d] Monitoring wavelength. [e] Unanalyzable traces. [f] Recombination only.

Scheme I



1, and the Marcus quadratic expression, eq 2, were used in the analyses following modification to accommodate half-wave reduction potentials.[4g]

$$\log k_T = \log k_{12} - \log\left[1 + A\exp\left(\frac{-23.06E_{1/2}}{RT} + \frac{C}{RT}\right)\exp\left\{\frac{\Delta G^*(0)}{RT\ln 2}\ln\left[1 + \exp\left(\frac{23.06(\ln 2)E_{1/2}}{\Delta G^*(0)} - \frac{C\ln 2}{\Delta G^*(0)}\right)\right]\right\} + B\exp\left(\frac{-23.06E_{1/2}}{RT} + \frac{C}{RT}\right)\right] \quad (1)$$

$$\log k_T = \log k_{12} - \log\left[1 + A\exp\left\{\frac{1}{RT}\left(\Delta G^*(0) - 11.53E_{1/2} + 0.5C + \frac{(-23.06E_{1/2} + C)^2}{16\Delta G^*(0)}\right)\right\} + B\exp\left(\frac{-23.06E_{1/2} + C}{RT}\right)\right] \quad (2)$$

The employment of both equations was carried out in a similar fashion. The diffusion rate constant, k_{12}, was calculated as 1.9 × 10^{10} M^{-1} s^{-1} for acetonitrile solvent.[18] The program containing the appropriate equation was allowed to iterate with varying fixed values for A-$(=k_{21})/k^\circ_{23}$, where k°_{23} is the frequency factor for the electron-transfer step; see Scheme I) and B $(=k_{21}/k_{30}$; see Scheme I) to generate the parameters C (approximately the oxidation potential for the reducing species) and $\Delta G^*(0)$, the intrinsic barrier to electron transfer. In general, the nonlinear fitting for all data sets showed little sensitivity to a wide range of B values,[19] and subsequently a value of 2 was set for this parameter in most cases. The final values for C and $\Delta G^*(0)$ thus were ascertained via error analysis features (maximum likelihood of variance and coefficient of determination) of the SHAZAM program package.

Results

Reaction of Re(CO)$_4$L$^\bullet$ with Substituted Pyridinium Ions. N$_2$ laser flash photolysis (337 nm) of acetonitrile solutions containing Re$_2$(CO)$_8$L$_2$ (L = PMe$_3$, P(O-*i*-Pr)$_3$) and a sufficient concentration of substituted pyridinium ion, P$^+$, to provide pseudo-first-order reaction conditions, gives rise to transient absorptions across a broad range of wavelengths (400–600 nm). The overall reaction can be described best by Scheme I.[4g,5c]

The multiple absorptions can be assigned readily to the appearance or disappearance of three distinct species following the flash. Within the lifetime of the flash (ca. 20 ns), the solvated dinuclear CO-loss product **1** (λ_{max} 390 ± 10 nm) forms and then decays away over a much longer period of time (>10 ms). Absorption arising from the organometallic radicals **2** (λ_{max}, 550 ± 20 nm) also is prevalent (see Figure 1) and in many cases provides analyzable data for rate constant determination. However, the rich absorption spectra of the pyridinyl radicals (λ_{max} (ε, M^{-1} cm^{-1}), ca. 300 (10^4), 400 (10^3), 630 (10^2) nm)[8] complicates detection of the rhenium radicals. The broad band at ca. 400 nm for the organic radical overlaps the metal carbonyl absorption, and a nonzero base line obtains following the decay. In those cases where the base-line absorptivity is less than approximately 50% of the maximum absorptivity observable for the radical, the transient decay proved analyzable. Inasmuch as the rhenium radical disappearance is concurrent with appearance of the pyridinyl radical when electron transfer is substantially faster than recombination (in most cases, vide infra), the electron-transfer reaction

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(19) For two series,[7a,g] varying B over several orders of magnitude resulted in a less than 10% change in both $\Delta G^*(0)$ and C.

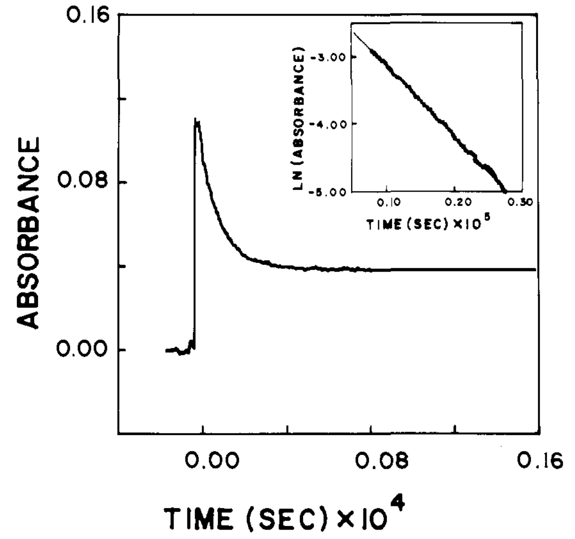

Figure 1. Transient decay of $Re(CO)_4(PMe_3)^\bullet$ (**2a**) observed at 600 nm upon photolysis of $Re_2(CO)_8(PMe_3)_2$ (ca. 0.6 mM) and 2-cyano-*N*-methylpyridinium tetrafluoroborate (0.04 M) in CH_3CN solution. The solid line through the trace is the first-order least-squares fit of the data. The insert shows the linear least-squares fit of the data to a first-order rate expression over ca. 3.0 half-lives.

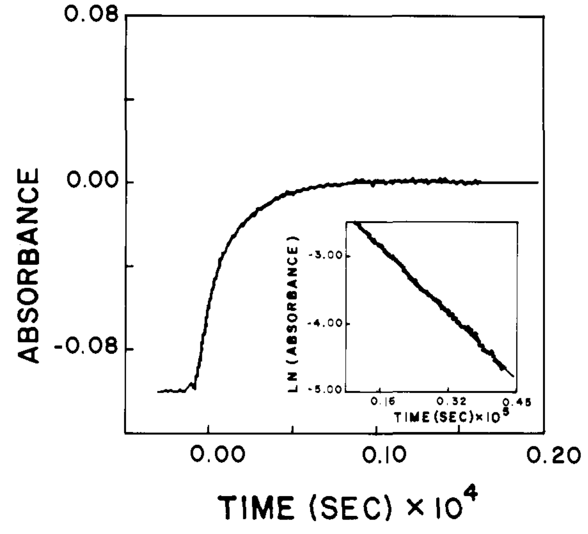

Figure 2. Appearance trace of the 4-benzoyl-*N*-methylpyridinyl radical (**3g**) observed at 450 nm upon photolysis of $Re_2(CO)_8[P(O\text{-}i\text{-}Pr)_3]_2$ (ca. 0.6 mM) and 4-benzoyl-*N*-methylpyridinium tetrafluoroborate (0.02 M) in CH_3CN solution. The solid line through the trace is the first-order least-squares fit of the data. The insert shows the linear least-squares fit of the data to a first-order rate expression over ca. 3.1 half-lives.

also can be monitored by observing the appearance with time of the organic radical in the wavelength range 450 ± 20 nm. Figure 2 shows a typical trace for the appearance of the pyridinyl radical following the laser flash. The initial abrupt increase in absorption is attributable to the aforementioned CO-loss product, **1**. Because **1** disappears orders of magnitude more slowly than the rate at which electron transfer occurs, **1** simply provides a constant added absorption that does not affect the kinetics analysis. This is borne out in the high correlation coefficients for the linear least-squares fit of the appearance trace (Figure 2, inset). It should be noted that, with two exceptions mentioned below, the rates of disappearance of the transients are much greater than the rate characteristic of the recombination process.

To correlate the electron-transfer rate constants with overall driving force of the reactions, we chose pyridinium complexes whose reduction potentials[20] spanned as large a voltage range as could be accommodated under the experimental conditions (see Experimental Section). In Table II are listed cathodic reduction potentials, $E_{p,c}$, as determined by cyclic voltammetry. Although several ions in the series exhibit reversible behavior, the peak cathodic potentials were used to ensure consistency within the data set. It has been established that reduction of the cation is a one-electron process.[21] A second reduction is observable in those cases where the first reduction is reversible. However, the potential (<-1.1 V vs Ag/AgCl) is far too negative to affect the flash experiments.[22] The irreversible behavior observed for many of the compounds, to sweep rates of 1.6 V s^{-1}, can be attributed to dimerization or a more complex reaction.[8] We were not concerned with secondary reaction of the radicals since they do not affect the primary electron transfer or detection of signals.

Rate constants thus collected for the 18 different pyridinium ions with the laser-light-generated radicals **2a** and **2b** appear in Table II. The values k_T are taken as k_{obsd}/α for measurements at single concentrations, where α is the effective concentration of free pyridinium cation. Inspection of the data reveals that electron transfer is a generally fast process, as noted in earlier work.[5c] The radical **2a** yielded rate constants in the range 2.6×10^9–4.0×10^6 M^{-1} s^{-1}. When L = $P(O\text{-}i\text{-}Pr)_3$, a bulkier and weaker donor ligand than PMe_3,[23,24] the rate constants are lower, in the range 6.0×10^8–3.5×10^6 M^{-1} s^{-1}. Even the fastest rates observed are significantly lower than the estimated diffusion-limited rate constant value of 1.9×10^{10} M^{-1} s^{-1}. They are in the range of values estimated by Hepp and Wrighton for reaction of the radicals $CpW(CO)_3^\bullet$, $Mn(CO)_5^\bullet$, and $Re(CO)_5^\bullet$ with ferricinium ion, a powerful oxidant.[4b]

A number of data points in Table II deserve special attention. In one instance (entry e, L = $P(O\text{-}i\text{-}Pr)_3$), traces for both the rhenium radical **2b** and product pyridinyl radical **3e** could be analyzed: the difference in derived rate constants is about 2-fold (3.7 vs 7.0×10^6 M^{-1} s^{-1} for 430- and 600-nm monitoring, respectively). The value obtained at 600 nm we believe to be the more reliable for this reaction, since at the longer wavelength we observe little interference of the CO-loss product and pyridinyl absorptions (the base line returns close to the preflash value). Of equal significance is the small wavelength dependence of the measured electron-transfer rate constant in the range 540–600 nm (see entry d, L = PMe_3, Table II), allowing for data acquisition at longer wavelengths than potentially interfering absorptions due to the pyridinyl radicals. In most cases, however, transient decays when available at 540 nm were adequate to provide reliable rate data.

The measured rate constants for 2-chloro-3-cyanopyridinium tetrafluoroborate (entry e) and *N*,*N'*-dimethyl-2,2'-bipyridinium tetrafluoroborate (entry k) may represent the *upper* limit for electron transfer. Due to restrictions imposed by ion pair and triple ion formation (see Experimental Section), the concentration of free pyridinium cation could not be made high enough to render the electron-transfer process several times faster than the rhenium radical recombination. Linear least-squares analysis, although not affording strictly linear fits, gave reasonable correlations, leading to rate parameters consistent with the expected pseudo-first-order behavior.[25] However, there might be some contribution to the calculated k_T in these two systems due to recombination.

Marcus-Type Relationships. With a large body of electron-transfer rate constants at hand, covering a moderate range of reduction potentials (or equivalently, ΔG_{23} values), we were interested in determining whether there exists a reliable correlation between log k_T and the overall driving force for the rhenium radical

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[20] The reduction potential is converted to free energy terms by the expression[4g] $\Delta G_{23} = -23.06E_{1/2} + C$ (kcal mol^{-1}).

[21] Mackay, R. A.; Landolph, J. R.; Poziomek, E. J. *J. Am. Chem. Soc.* **1971**, *93*, 5026.

[22] The free pyridinium cation concentration cannot be increased sufficiently to make electron transfer competitive with radical recombination for these potentials.

[23] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

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[25] In comparison, analysis of transient decays of $Re(CO)_4L^\bullet$ when only recombination operates gives distinct deviation from linear least-squares fittings.

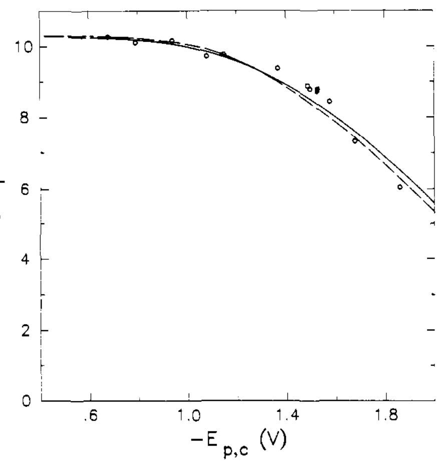

Figure 3. Plot of the log k_T for the reactions of excited state $Ir_2(COD)_2(\mu\text{-}pz)_2$[7d,g] with N-alkylpyridinium complexes vs $-E_{p,c}$ values for the acceptors (CH_3CN, 0.1 M Bu_4NPF_6, vs SCCE). The solid line represents the fit using eq 1; the broken line, using eq 2 (Table III for parameters).

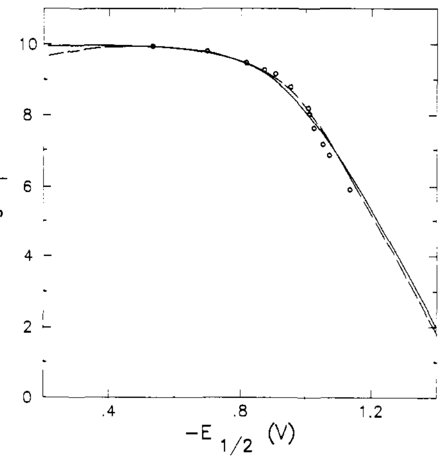

Figure 4. Plot of the log k_T for the reactions of excited state $Ru(bpy)_3^{2+}$[13] with nitroaromatics vs $-E_{1/2}$ values for the acceptors (CH_3CN, 0.1 M $(n\text{-}Pr)_4NClO_4$, vs SCE). The solid line represents the fit using eq 1; the broken line, using eq 2 (Table III for parameters).

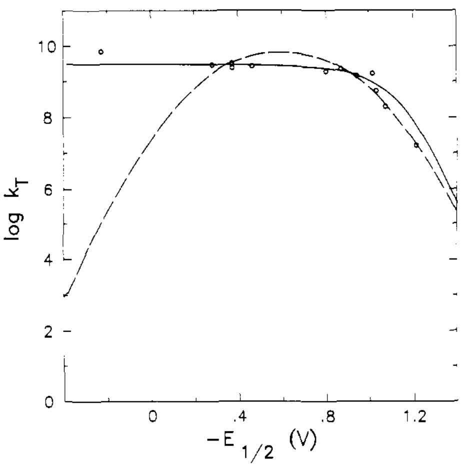

Figure 5. Plot of log k_T for reactions of excited-state $Re(CO)_3Cl(phen)$[7a] with N-alkylpyridinium complexes and nitrobenzenes vs $-E_{1/2}$ values for the acceptors (see reference for details). The solid line represents the fit using eq 1; the broken line, using eq 2 (Table III for parameters).

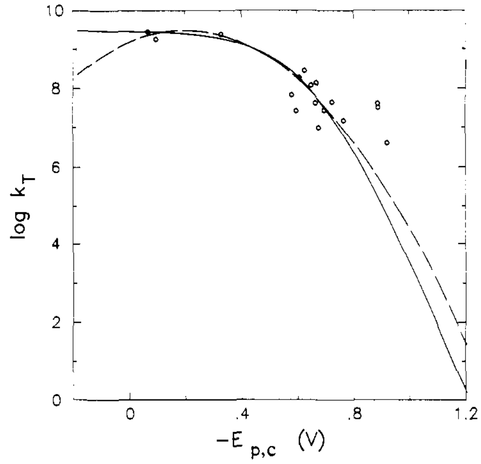

Figure 6. Plot of the log k_T for reactions of $Re(CO)_4(PMe_3)^•$ (**2a**) with N-methylpyridinium cations vs $-E_{p,c}$ values for the acceptors (CH_3CN, 0.1 M Bu_4NBF_4, vs Ag/AgCl). The solid line represents the fit using eq 1; the broken line, using eq 2 (Table III for parameters).

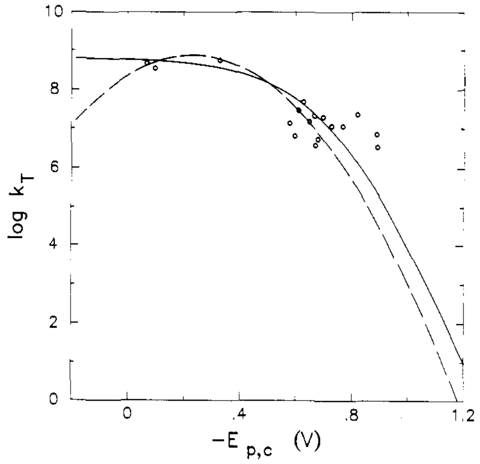

Figure 7. Plot of log k_T for reactions of $Re(CO)_4(P(O\text{-}i\text{-}Pr)_3)^•$ (**2b**) with N-methylpyridinium cations vs $-E_{p,c}$ values for the acceptors (CH_3CN, 0.1 M Bu_4NBF_4, vs Ag/AgCl). The solid line represents the fit using eq 1; the broken line, using eq 2 (Table III for parameters).

systems. The data for both rhenium radical series unfortunately exhibit considerable scatter and do not extend as far in the direction of more negative potentials as desirable. Thus, before attempting to analyze these data, we tested the application of the Marcus/Agmon–Levine (MAL) equation (eq 1), employed earlier in the analysis of the halogen atom abstraction reactions,[4g] and the Marcus quadratic equation (eq 2),[9a] by applying them to well-behaved electron-transfer rate data. We chose three transition-metal systems,[7a,g,13] the data for which were fit via a nonlinear regression analysis.[17]

The resulting fits from both equations for the literature data are depicted in Figures 3–5. Two main features of the analyses were clearly evident: (1) over the potential ranges considered (i.e., not strongly exergonic in overall driving force), the two theoretical models returned comparable C and $\Delta G^‡(0)$ parameters (see Table III); (2) the derived C parameters reasonably approximate the reported estimates of oxidation potentials for the reacting transition-metal reductants. From this we conclude that if acceptable minima in the error function analyses could be obtained in fitting eq 1 and 2 to the rhenium radical data, the generated parameters should represent the free-energy characteristics for the reacting systems.

Analysis of the data for **2a** and **2b** did yield distinct error minima for particular values of $\Delta G^‡(0)$ and C over a wide range of A values. The line fits from both the MAL and quadratic equations for **2a** and **2b** are shown in Figures 6 and 7, respectively. A value of approximately 3 kcal mol^{-1} for the intrinsic barrier in each case is similar to the values reported for the atom transfer reactions (3–5 kcal mol^{-1} [4g]), while the C parameter, on average −16 kcal mol^{-1}, is far below the values earlier obtained for the same radicals (−40.5 and −38.5 kcal mol^{-1} for **2a** and **2b**, respectively).

Table III. Marcus-Type Parameters for Various Electron-Transfer Reaction Systems

electron donor	electron acceptor[a]	A	B	$\Delta G^{\ddagger}(0)$[b]	C[b]	ext donor oxid potential[b]	ref
$Ir_2(COD)_2(\mu\text{-pz})_2$[c]	P^+					−41	7d,g
MAL		0.01	2	11	−51		
quadratic		0.05	2	11	−53		
$Ru(bpy)_3^{2+}$[d]	N					−18	13
MAL		1	2	2.1	−22		
quadratic[e]		0.5	10^5	4.1	−27		
$Re(CO)_3Cl(phen)$[d]	P^+, N					−30	7a
MAL		5	2	2.1	−27		
quadratic		0.8	2	3.4	−27		
$Re(CO)_4(PMe_3)^{\bullet}$ (**2a**)	P^+					−14	*f*
MAL		6	2	2.3	−15		
quadratic		4	2	3.1	−17		
$Re(CO)_4(P(O\text{-}i\text{-}Pr)_3)^{\bullet}$ (**2b**)	P^+					−14	*f*
MAL		29	2	2.8	−17		
quadratic		18	2	2.5	−15		

[a] P^+, pyridinium cations; N, nitroaromatics. [b] In kcal mol^{-1}; C values referenced to SCE. [c] Metal-centered excited state. [d] $d\pi \rightarrow \pi^*$ excited state. [e] In this reaction series, when B is constrained to a value of 2, the fitting procedure returns values for $\Delta G^{\ddagger}(0)$ and C of 3.5 and −25 kcal mol^{-1}, respectively.[19] The value of 10^5 provides a marginally better fit to the data in the most endergonic region. [f] See text for estimation of oxidation potential.

A test of the reliability of the fit in each case could be accomplished by varying A while holding B constant and examining the sharpness of the error minimum at the derived values for $\Delta G^{\ddagger}(0)$ and C. In general, it was found that for changes in A no greater than 2-fold, $\Delta G^{\ddagger}(0)$ and C varied by not more than 10%. Larger changes in A produced unreasonably large changes in $\Delta G^{\ddagger}(0)$ and C and returned much larger error values. There is some basis, therefore, to believe that the values listed in Table III for the application of eq 1 and 2 to the $Re(CO)_4L^{\bullet}$ electron-transfer data represent real minima in the fitting procedure and reflect intrinsic properties of these systems.

Discussion

The choice of solvent and counterion were crucial to this study. Acetonitrile is a moderately polar solvent and is thought to stabilize the product pyridinyl radical.[21] Electron transfer occurs to the free pyridinium ion, the concentration of which is exceedingly limited in less polar solvents, such as CH_2Cl_2.[21] In addition, halogen atom transfer from halogen-containing solvents could interfere with the determination of electron-transfer rate constants.

The tetrafluoroborate ion was chosen as counterion because the pyridinium salts are generally soluble in acetonitrile. The more familiar iodide salts are rather insoluble in many solvents and display their own charge-transfer photochemistry.[21,26]

Because acetonitrile is nucleophilic in character, the question arises as to whether the electron transfer occurs from a 19-electron metal carbonyl radical, formed via interaction of solvent with the 17-electron $Re(CO)_4L^{\bullet}$ radical. This question has already been addressed;[5c] it is our view that the evidence argues against a significant role for the solvent in this sense. The present results do not add anything new to what has already been said on this point.

Although there is scatter in the data, the rate constants in each of the radical reaction series are seen to decrease with increasingly negative reduction potential of the pyridinium ion electron acceptor (Figures 6 and 7). Much of the scatter can be ascribed to variations in steric requirements of the various cations. In this connection, it is noteworthy that the rate constants for the 2-substituted cations are generally lower than for the 3- and 4-substituted species. The problems associated with linear free energy correlations involving 2-substituted aromatic systems are well-documented.[27] In the present context the fact that there is apparently a greater steric impediment to reaction of the 2-substituted derivatives suggests that the nitrogen atom may be the locus of the interaction that leads to electron transfer. Our knowledge of the geometries of the precusor complexes is too limited to draw further conclusions.

Application of Marcus-Type Relationships. The relationship between log k_T and $-E_{p,c}$ for the electron-acceptor cation has been analyzed in terms of both the MAL equation, eq 1, and the Marcus quadratic equation, eq 2. For systems in which the overall driving force does not extend to the strongly exergonic region, these two expressions predict rather similar behavior.[12] Much has been written of late regarding the behavior of electron-transfer systems in the strongly exergonic region, in which eq 2 predicts an inversion to lower rate constants.[9a] In general, inverted behavior is not observed in systems in which the rate of electron transfer is determined in the limit by diffusion. We have employed both forms in the analysis of our data in the hope that it would assist in selecting appropriate sets of $\Delta G^{\ddagger}(0)$ and C values.

The value chosen for B is not critical for fitting data that lie mainly in the exergonic ΔG_{23} region of the relationship between activation free energy and overall free energy change. The fit is more sensitive to the value chosen for A. However, we have found that, having chosen an appropriate value for the diffusion-limited rate constant, k_{12}, the values for A that lead to best fits in terms of regression coefficients and acceptable C and $\Delta G^{\ddagger}(0)$ are limited.

Application of eq 1 and 2 to extant data for the electron-transfer reactions of other transition-element compounds provides a basis for comparisons regarding the quality of fits with the present data, and comparative interpretations of the important C and $\Delta G^{\ddagger}(0)$ parameters. The parameters obtained via nonlinear regression analysis for three such systems are listed in Table III along with the results for the rhenium carbonyl systems.

In general, there is considerably less scatter for the literature data than for ours. As a result the analyses yield well-conditioned best fits. Thus, under the assumption that the systems are behaving in general accord with the predictions of eq 1 or 2, it is possible to achieve reasonable fits of the data to the theoretical model for the literature electron-transfer data. It is noteworthy that the derived parameters obtained from use of eq 1 and 2 are closely comparable for each of these three systems (Table III), particularly with respect to values for C and $\Delta G^{\ddagger}(0)$.

The $Ir_2(COD)_2(\mu\text{-Pz})_2$ system reported by Gray and coworkers[7d,g] most closely resembles the rhenium radical systems in the sense that the orbital from which the transferred electron emanates is largely metal-centered and in the use of the same series of acceptors (although not with the same substituents). The obtained line fits (Figure 3, Table III) yield an average value for C of −52 kcal mol^{-1}, 11 kcal mol^{-1} more negative than the estimated oxidation potential of −1.8 V (−41 kcal mol^{-1}) for the excited state from which electron transfer occurs.[7d] The value of the intrinsic barrier (11 kcal mol^{-1}) presumably reflects the Ir–Ir bond distance change occasioned by oxidation of the dinuclear metal center in its excited state. The electron-transfer reactions of

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Table IV. Kinetic and Thermodynamic Free Energy Parameters for Some Transition-Metal Electron-Transfer Reactions

metal complex	redox partner[a]	$\Delta G^\ddagger(0)$[b]	C[b]	ref
$Re(CO)_3Cl(phen)$[c,d]	P^+	2.0	−27	7a
$Ru(bpy)_3^{2+}$[c,d]	N	2.3	−22	13
$Ru(bpy)_3^{2+}$[d,e]	A	4	−16	14
$Cr(bpy)_3^{3+}$[e,f]	A, MB	3	−30	14
$Ir(Me_2phen)_2Cl_2^+$[d,e]	A, MB	2	−30	14
$Ru(NH_3)_6^{3+}$[e]	MP	8		15
$Fe(aq)^{3+}$[e]	MP	12		15
$Co(bpy)_3^{3+}$[e]	MP	10		16
$Co(en)_3^{3+}$[e]	MP	11		16
$Co(NH_3)_6^{3+}$[e]	MP	15		16
$Ir_2(COD)_2(\mu\text{-}Pz)_2$[c,f]	P^+	11	−51	7d,g

[a] P^+, pyridinium cations; N, nitroaromatics; A, amines; MB, methoxybenzenes; MP, metal polypyridine complexes. [b] In kcal mol^{-1}. [c] Based on Marcus/Agmon–Levine equation (present work). [d] $d\pi \rightarrow \pi^*$ MLCT excited state. [e] Based on Rehm–Weller equation; in these systems the metal center serves as *oxidant*.

$Ru(bpy)_3^{2+}$[13] (Figure 4) and $Re(CO)_3Cl(phen)$[7a] (Figure 5) occur in both instances from excited states of the reductants in which the electron is localized in a ligand π^* orbital. Little configurational change is expected in such cases, and the values of $\Delta G^\ddagger(0)$ are correspondingly small. The value of C for the $Re(CO_3)Cl(phen)$ series, −27 kcal mol^{-1}, is in good accord with the estimated potential of −1.3 V (−30 kcal mol^{-1}) for oxidation of the excited state of $Re(CO)_3Cl(phen)$, on the basis of spectroscopic and electrochemical data.[7a]

We are left with the question of whether the values for C and $\Delta G^\ddagger(0)$ reliably represent the electron-transfer reactions of the rhenium carbonyl systems. We believe that the correct values are likely to be close to those obtained from both the MAL and quadratic Marcus equation. While it is difficult to justify this belief on the basis of the quality of fit of the data alone, electrochemical evidence also supports this conclusion. The reaction between the $Re(CO)_4L^\bullet$ radicals and the pyridinium salts can be viewed as a simple outer-sphere electron-transfer process. Because the reaction involves a neutral molecule reacting with a cation, the work terms involving both reactants and products should be comparatively small. Thus, the overall free energy change is, to a good approximation, the sum of the free energy changes for oxidation of the carbonyl radical and reduction of the pyridinium cation, i.e.

$$\Delta G_{23} = -nFE = -nF(-E_{1/2}(\text{red}) + E(\text{ox}))$$

Thus, assuming a value of about −16 kcal mol^{-1} for C, the oxidation potential of **2a** or **2b** determined from the fits is in the vicinity of −0.7 V[20] vs SCE. Unfortunately, there are no direct electrochemical measurements of the oxidation potential of $Re(CO)_5^\bullet$ or related phosphine-substituted radicals. However, oxidation of $Re(CO)_5^-$ is reported[28] to be a one-electron process occurring irreversibly on the time scale of the cyclic voltammetric experiment at about −0.1 V. The process is irreversible due to the rapid dimerization of resultant $Re(CO)_5^\bullet$ to form $Re_2(CO)_{10}$. We do not know the potential at which the radical undergoes oxidation, but it is unlikely to be much more negative than that for the anion. Thus, although oxidation of the radical is not directly observable under the conditions of the electrochemical or electron-transfer experiments, what is known of the electrochemistry of the rhenium and the related manganese system[29] suggests that the oxidation of $Re(CO)_5^\bullet$ is likely to occur at a potential in the vicinity of −0.1 V. Replacement of a CO by an electron-donating ligand such as trimethylphosphine should shift the potential perhaps 0.5 V more cathodic,[29a,30] to the vicinity of about −0.6 V, in reasonable consistency with the value of about −0.7 V (−16 kcal mol^{-1}) imputed from the fits of the kinetics data for **2**a by using eq 1 and 2.

Several other electron-transfer reaction series have been analyzed in terms of the Rehm–Weller equation,[11] which is functionally equivalent to the MAL equation. The results of such analyses, along with results from analysis of literature data from Table III, are gathered in Table IV; note that several low values of $\Delta G^\ddagger(0)$ are associated with electron transfer to or from an excited-state species in which the electron is localized in a ligand π^* orbital. The configurational changes required for electron transfer in all such cases are clearly small, as expected. Balzani and co-workers account for the small $\Delta G^\ddagger(0)$ values obtained for the reduction of the excited states of $Ru(bpy)_3^{2+}$, $Cr(bpy_3)^{3+}$, and $Ir(Me_2phen)_2Cl_2^+$ by noting the small Stokes shifts associated with their emissions.[14] All of these reaction systems involve neutral–cation interactions for the reactants, suggesting that the work term associated with formation of the precursor complex should be small. For all of the other systems in Table IV, the $\Delta G^\ddagger(0)$ values fall in the range of 8–12 kcal mol^{-1}. These larger values are associated with significant configurational changes at the metal center attendant upon electron transfer.

They presumably also reflect a work term associated with cation–cation interactions in the approach of the reactants. In spite of the rather poor fits obtained with the rhenium carbonyl radicals, the indications are that the $\Delta G^\ddagger(0)$ values associated with electron transfer to the pyridinium salts are small, on the order of perhaps 3 kcal mol^{-1} (Table III). Presumably loss of the electron from the radical does not occasion very large changes in configuration at the metal center. This is not surprising, considering that the HOMO, in which the transferred electron initially resides, possesses substantial nonbonding metal d orbital character, as evidenced from ESR analyses of $Mn(CO)_5^\bullet$[31] and $M(CO)_3(PR_3)_2^\bullet$ radicals (M = Mn,[32] Re[33]).

A major focus of this work was to compare the parameters of the Marcus-type relations for electron-transfer reactions of the $Re(CO)_4L^\bullet$ radicals with those derived from analysis of the rate constants for halogen atom transfer reactions with organic halides.[4g] Both reaction series appear to have comparatively low intrinsic barriers, $\Delta G^\ddagger(0)$, in the range of 3–5 kcal mol^{-1}. On the other hand, the value of C is much more negative for the halogen atom transfer series. The potentials for reduction of the alkyl halides are much more irreversible in character than those for reduction of the pyridinium ions, which in many cases are reversible. The high degree of irreversibility of the halide reductions arises from the fact that the resultant anion is not bound or is at most only weakly bound.[34] Thus, there is more than a full volt difference between $-E_{p,c}$ and the calculated standard reduction potential for the process $RX + e^- \rightarrow R^\bullet + X^-$. This factor and the existence of a direct interaction between the halogen and the metal center in the atom transfer process could account for the large difference in C parameters between the electron- and atom-transfer processes.

Acknowledgment. We are indebted to Professor R. A. Marcus for helpful correspondence regarding an early draft. This research was supported by the National Science Foundation through research Grant NSF CHE 86-08839.

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