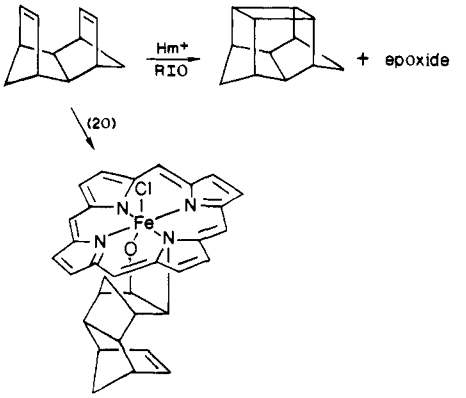

(19)

alkenes such as norbornene, cyclohexene, etc. This pathway, with the accompanying catalysis by *N*-alkylhemin, is summarized in Scheme I.

The products and the mechanism of decomposition of the *N*-alkylhemin are not known but are under investigation as is the possible use of stable *N*-alkylhemins as oxidation catalysts.[43]

Conclusions

The transient green species that accumulates under some conditions during hemin-catalyzed epoxidation is an *N*-alkylhemin of the type that formed during suicide inhibition of cytochrome P-450.[42] The *N*-alkylhemin is a catalyst for epoxidation and therefore does not result in inhibition. It is not an intermediate in the epoxidation reaction. The proposed mechanism of rate-limiting metallacycle decomposition is shown not to occur since no intermediate accumulates. All of the data reported to date seem to be best accommodated by the electron-transfer mechanism for hemin-catalyzed epoxidation.

Acknowledgment. We are grateful to the National Science Foundation for support of this research (Grant CHE 84-20612) and the National Institutes of Health Training Grant AM07233.

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(42) The term "suicide labeling" applied to the formation of *N*-alkylhemin in cytochrome P-450[3] cannot be used with model systems for two reasons. Unlike the enzyme, this species is an efficient catalyst and it is also reversibly formed with internal alkenes. The *N*-alkylhemin becomes more stable toward return to hemin when the alkene is less substituted or when the porphyrin is more electron-rich.

(43) **Note Added in Proof.** The iron(III) porphyrin *N*-oxide recently reported (Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7836) has some spectral characteristics that are similar to those of our transient. However, the EPR and UV-visible spectra of the transients are identical with those of **6**$^+$Cl$^-$ and differ significantly from those reported by Groves. Furthermore, the transients require alkenes and do not occur with some alkenes such as cyclohexene or cyclooctene. Even if the transients were the *N*-oxides rather than *N*-alkylhemins, the mechanistic conclusions would be the same. Additional verification of structures is in progress.

Kinetics of the Electron-Transfer Reactions of Re(CO)$_4$L$^\bullet$ Radicals: Ligand, Ion Pairing, and Solvent Effects

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Abstract: Re(CO)$_4$L$^\bullet$ radicals (L = CO, PR$_3$, P(OR)$_3$, AsEt$_3$), generated from the corresponding Re$_2$(CO)$_8$L$_2$ compound by laser flash photolysis, undergo fast electron-transfer reactions with *N*-methyl-4-cyanopyridinium tetrafluoroborate in CH$_3$CN solution, and with maleic anhydride. The reactions follow a bimolecular rate expression, and rate constants for each series were determined ($k_T \geq 3 \times 10^6$ M^{-1} s^{-1}). For reaction of Re(CO)$_4$(P(*i*-Bu)$_3$)$^\bullet$ with MCP$^+$BF$_4^-$, a nonlinear dependence of k_{obsd} on [MCP$^+$BF$_4^-$] is observed that is explained in terms of ionic association of the pyridinium salt. Ion pair and ion triplet dissociation constants were determined from conductivity measurements. k_{obsd} varies linearly with free cation concentration. A model is proposed in which Re radicals react selectively with the free MCP$^+$ cation. Rate constants for each series of reactions show a dependence on both the steric and electronic properties of L which are evaluated with a two parameter free energy relationship. On the basis of the relative steric dependencies, it is proposed that reactions with MCP$^+$ are outer sphere in nature, whereas reactions with MA show inner sphere character. The MA reactions show only a small solvent dependence.

Metal carbonyl radicals are known to undergo reactions of several general types, including recombination,[2,4d] ligand substitution,[3] atom transfer,[3a,4] and electron transfer.[4a,5,6] In contrast to the recombination, substitution, and atom-transfer processes, the electron-transfer reactions have not been studied in much detail as yet, and kinetic data for such reactions are scarce.

The tendency for organometallic radicals to undergo both oxidative and reductive electron transfer is thought to be a consequence of the fact that the singly occupied radical HOMO is intermediate in energy between the filled σ and unfilled σ^* levels of the M–M bonded dimer, thus providing both a relatively high energy electron for oxidation and a low energy hole for reduction, with respect to the parent dimer. Electron-transfer reactions are

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(1) This work was supported by the National Science Foundation through Research Grant CHE-8312331.

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evident in the thermal and photochemical reactivities of metal carbonyl dimers where homolysis of the metal–metal bond occurs. For example, in the base-promoted thermal disproportionation of $Co_2(CO)_8$[7] an electron transfer is involved. The rate of such a reaction depends greatly on the nature of the base and on the other ligands corrodinated to the metal center. The photochemical disproportionation of $Cp_2Mo_2(CO)_6$[8] in the presence of added ligands is another example, which occurs only with certain ligands. Evidently, both the steric and electronic characteristics of the ligands coordinated to the metal center play decisive roles in the electron-transfer chemistry of metal carbonyl radicals. However, there is no quantitative study of these effects in the current literature.

Hepp and Wrighton[4a] deduced rates of oxidative electron transfer relative to Cl atom transfer for $CpW(CO)_3^\bullet$, $Mn(CO)_5^\bullet$, and $Re(CO)_5^\bullet$ with several electron acceptors. Their experiments consisted of continuous photolysis of the corresponding dimer to produce the radical in the presence of both the electron acceptor, and CCl_4, a Cl atom donor (eq 1 and 2). From the ratio of

$$L_nM^\bullet + A \rightarrow L_nM^+ + A^- \qquad (1)$$

$$L_nM^\bullet + CCl_4 \rightarrow L_nMCl + {}^\bullet CCl_3 \qquad (2)$$

cationic to chlorinated products, they derived a ratio of rate constants; where the halogen atom transfer rate constant was known the electron transfer rate constant could be calculated. A more versatile approach entails the direct observation of a photochemically generated radical and its quenching by an electron acceptor in a flash-photolysis experiment. Meyer and Caspar[5] have reported rate constants for oxidation of $Mn(CO)_5^\bullet$ with four different pyridinium cations. The one-electron oxidation of $Pd(CNMe)_3^+$ radicals with several viologen type oxidants and dichlorobenzoquinone has also been studied by flash photolysis.[6]

Herein, we present the results of our kinetic studies of the oxidation of rhenium-centered radicals, $Re(CO)_4L^\bullet$ (L = phosphine, phosphite, arsine, CO), with the electron acceptors *N*-methyl-4-cyanopyridinium tetrafluoroborate (henceforth abbreviated as $MCP^+BF_4^-$) or maleic anhydride (MA), eq 3, using the laser flash photolysis technique.

$$Re(CO)_4L + A \rightarrow Re(CO)_4L^+ + A^{\bullet -} \xrightarrow{S\,=\,\text{solvent}} Re(CO)_4LS^+ \qquad (3)$$

Experimental Section

All solvents and Re dimers were obtained and purified as described in detail elsewhere.[4f] Maleic anhydride and triphenylphosphine (Aldrich) were used as supplied.

$MCP^+BF_4^-$ was prepared by the reaction of 4-cyanopyridine (Aldrich) with an equimolar quantity of $Me_3O^+BF_4^-$ (Alfa) in 1,2-dichloroethane. The slurry was stirred under Ar at 0 °C for 2 h and then allowed to warm to room temperature and further stirred overnight. The precipitate was filtered and recrystallized twice from CH_3CN/THF solution. The resultant white crystals were filtered, washed with diethyl ether, and dried in vacuo. Yield: 55%. Anal. Calcd for $C_7H_7N_2BF_4$: C, 40.82; H, 3.45; N, 13.60. Found: C, 40.70; H, 3.53; N, 13.69. Mass spectrum (F.A.B.), *m/e* 119 (cation).

[*cis*-$Re(CO)_4(PMe_3)(CH_3CN)]^+(ClO_4]$ was synthesized as follows. A CH_2Cl_2 solution of *cis*-$Re(CO)_4(PMe_3)Cl$ (200 mg) was stirred with a slight excess of anhydrous $AgClO_4$ at room temperature for ca. 2 h during which time the IR bands of the starting material were replaced by a new pattern ($\nu_{CO}(CH_2Cl_2)$ 2118 (w), 2015 (s), 1960 (m), 1915 (w)). This intermediate, probably *cis*-$Re(CO)_4(PMe_3)(ClO_4)$, was not isolated. The mixture was filtered, and an excess of CH_3CN added to the filtrate, whereupon a rapid reaction took place to give [*cis*-$Re(CO)_4(PMe_3)(CH_3CN)]^+(ClO_4]^-$. The solvent was removed, and the resultant oil was purified by separation from CH_3CN solution with ether and by thick-layer chromatography (silica, CH_3CN/ether, 2:1 eluant). The oil did not crystallize. IR (CH_3CN): ν_{CO} 2120 (w), 2020 (s), 2000 (sh), 1986 (m). Mass spectrum (F.A.B., high resolution) *m/e* 416.0077. Calcd for $C_9H_{12}O_4NPRe^+$: 416.0264. $^{13}C\{^1H\}$ NMR (CH_2Cl_2/CD_2Cl_2, 1:1): δ 4.4 (s), 17.0 (d, J_{PC} = 35.2 Hz), 127.0 (s), 181.7 (d, J_{PC} = 46.1 Hz, 1CO), 183.4 (d, J_{PC} = 9.2 Hz, 2CO), 184.4 (d, J_{PC} = 6.8 Hz, 1CO).

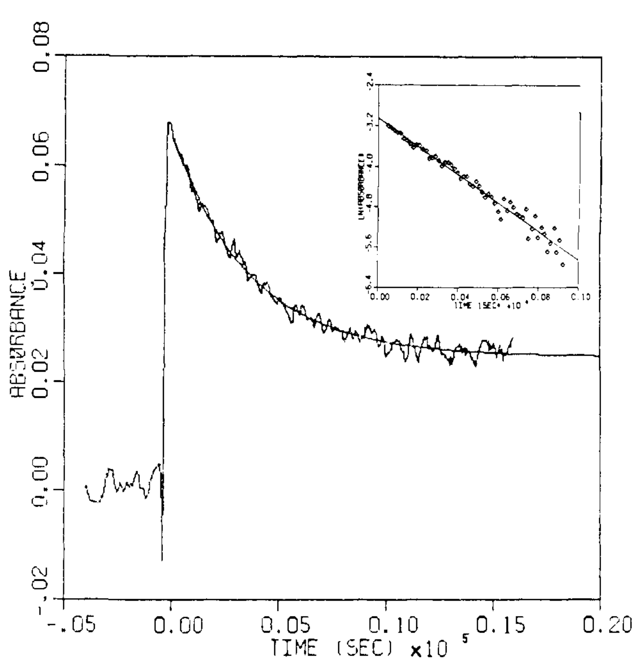

Figure 1. Transient observed at 540 nm upon flash photolysis of $Re_2(CO)_8(PMe_3)_2$ ($\sim 10^{-1}$ M) and $MCP^+BF_4^-$ (0.05 M) in CH_3CN solution. The line through the trace is the first-order least-squares fit of the data. The insert shows the linear least-squares fit of the data to a first-order rate expression over ca. 2.5 half-lives.

The laser flash photolysis apparatus and the data aquisition system used throughout this work for the kinetics studies have been described previously.[9] Solutions ca. 10^{-4} M in Re dimer were prepared in an N_2 atmosphere drybox and sealed in 1 cm quartz cuvettes.

Conductivity measurements were made on a Beckman RC-19 conductivity bridge and a Fischer Scientific 3403 cell. The cell constant was determined to be 1.037 cm^{-1} by measurement of the conductivity of KCl solutions of known molarity. All measurements were made at 22 °C.

Continuous photolysis experiments were carried out under an N_2 atmosphere at room temperature in an immersion well type reactor, solution volume ca. 10 mL, using an Oriel Corp. Hg pen lamp.

Results

Reaction of $Re(CO)_4L^\bullet$ with $MCP^+BF_4^-$. Laser flash photolysis (337 nm) of acetonitrile solutions of $Re_2(CO)_8L_2$ produces transient absorptions in the 540-nm region due to $Re(CO)_4L^\bullet$ radicals that rapidly recombine. Addition of $MCP^+BF_4^-$ to the solution results in a more rapid disappearance of these absorptions. All experiments with this reagent were carried out under pseudo-first-order conditions, at a concentration of $MCP^+BF_4^-$ such that radical recombination made an insignificant contribution to the transient decay. A typical decay trace and the corresponding ln (abs) vs. time plot for the reaction of $Re(CO)_4(PMe_3)^\bullet$ with $MCP^+BF_4^-$ are shown in Figure 1. After reaction, the absorbance did not return to its preflash level because of an absorbance due to the relatively stable $MCP^\bullet$ radical which persists over a much longer time scale. Thus, the observed decay trace is a superposition of the absorbance of the decaying $Re(CO)_4L^\bullet$ radical and the forming $MCP^\bullet$ radical. Since both absorbances have the same time dependence, the ln (abs) vs. time plot is linear and the observed rate constant k_{obsd} is readily obtained from the gradient of this plot. In some cases, e.g., L = P(*n*-Bu)$_3$, the absorbance of the $Re(CO)_4L^\bullet$ radical is relatively weak. The rather flat decay trace that results gives rise to poorer signal-to-noise ratios and a larger uncertainty in k_{obsd}. Monitoring the decay at λ = 540 nm was found to be acceptable for each radical, and all reported data were obtained at this wavelength. At shorter wavelengths, the absorption of $MCP^\bullet$ predominates, and the observed transients have the form of an increasing absorbance following the flash.

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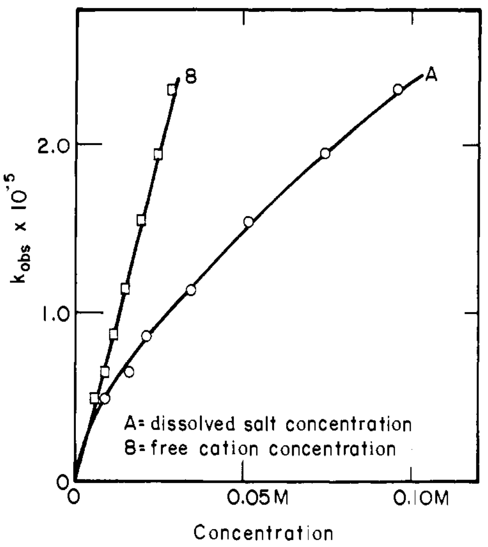

Figure 2. Curve A: variation of k_{obsd} with $[MCP^+BF_4^-]$ for the reaction of $Re(CO)_4(P(i\text{-}Bu)_3)^\bullet$ with $MCP^+BF_4^-$. Curve B: variation of k_{obsd} with α, the free cation concentration, for this reaction.

Table I. Electron-Transfer Rate Constants for Reactions of $[CHCHC(CN)(CH)_2NMe][BF_4]$ with $Re(CO)_4L^\bullet$ in CH_3CN Solution

L	δ_{CO}[a]	θ,[b] deg	$[MCP^+BF_4^-]$, M	α,[c] M	$10^{-7}k_T$, $M^{-1}\ s^{-1}$
CO	0.00	95	0.064	0.022	16.9 ± 1.5
PMe_3	5.05	118	0.053	0.020	9.0 ± 0.6
$P(OMe)_3$	3.18	107	0.052	0.020	14.9 ± 0.6
$P(O\text{-}i\text{-}Pr)_3$	3.90	130	0.055	0.021	5.1 ± 0.7
$P(n\text{-}Bu)_3$	5.69	132	0.049	0.019	6.4 ± 1.2
$P(i\text{-}Bu)_3$	5.40	143	0.052	0.020	0.81 ± 0.05
$P(i\text{-}Pr)_3$	6.20	160	0.051	0.020	1.3 ± 0.2
$AsEt_3$	5.33	128[d]	0.051	0.020	11.1 ± 1.6

[a] δ_{CO} is the downfield ^{13}C chemical shift of $Ni(CO)_3L$ vs. $Ni(CO)_4$, as reported in ref 25. [b] Cone angle of L from ref 26. [c] α is the concentration of free MCP^+, see text. [d] Approximate cone angle, see ref 4f.

The reaction of $Re(CO)_4(P(i\text{-}Bu)_3)^\bullet$ was studied with varying concentrations of $MCP^+BF_4^-$. A plot of k_{obsd} vs. $[MCP^+BF_4^-]$ is distinctly nonlinear as shown in Figure 2 (curve A). This behavior is attributed to ionic association of the pyridinium salt in solution. The ion pair dissociation constant, K_D, and the triple ion dissociation constant, K_T, for the equilibria

$$MCP^+|BF_4^- \overset{K_D}{\rightleftharpoons} MCP^+ + BF_4^- \tag{4}$$

$$MCP^+|(BF_4^-)_2 \overset{K_T}{\rightleftharpoons} MCP^+|BF_4 + BF_4^- \tag{5}$$

where $MCP^+|BF_4^-$ and $MCP^+|(BF_4^-)_2$ represent the ion pair and the ion triplet, respectively, were determined from conductivity measurements ($K_D = 1.22 \times 10^{-2}$M, $K_T = 0.15$ M). The concentration of free MCP^+, α, could then be calculated at each concentration of dissolved salt (vide infra). A plot of k_{obsd} vs. α is linear, with zero y intercept (Figure 2, curve B). Thus, the electron-transfer reaction is first order in $Re(CO)_4(P(i\text{-}Bu)_3)^\bullet$ and first order in free cation. A value of $k_T = 9.0 \times 10^6\ M^{-1}\ s^{-1}$ was derived from the gradient of the k_{obsd} vs. α plot. There is no evidence in our results for a measureable electron transfer to either the ion pair or ion triplet. Accordingly, we have treated all kinetic data assuming that electron transfer occurs only to the free cation.

Table II. Equivalent Conductances of $[CHCHC(CN)(CH)_2NMe][BF_4]$ in CH_3CN Solution at 22 °C

$10^3[MCP^+BF_4^-]$, M	Λ, $cm^2\ \Omega^{-1}\ equiv^{-1}$	$10^3[MCP^+BF_4^-]$, M	Λ, $cm^2\ \Omega^{-1}\ equiv^{-1}$
0.494	165	20.3	117
1.01	160	35.1	108
1.15	159	49.6	101
1.65	156	67.2	93.7
3.15	149	89.6	88.4
4.12	146	218	69.4
5.92	141	436	52.3
9.77	129	872	36.0

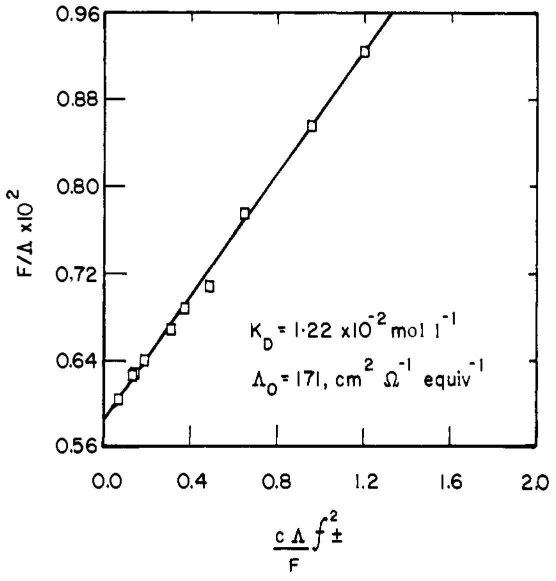

Figure 3. Fuoss plot for $MCP^+BF_4^-$ in CH_3CN solution at 22 °C.

Similar results were obtained when the faster reaction of $Re(CO)_4(PMe_3)^\bullet$ with varying concentrations of $MCP^+BF_4^-$ was studied. A plot of k_{obsd} vs. α was again linear; the gradient of this plot yielded a value of $k_T = 0.92 \times 10^8\ M^{-1}\ s^{-1}$. In this case, a non-zero y intercept of $0.76 \pm 0.21 \times 10^6\ s^{-1}$ (95% confidence level) was observed. This value is 33% of k_{obsd} at $[MCP^+BF_4^-] = 0.05$ M; we ascribe it to accumulated experimental inaccuracies resulting from the steep dependence of R_{obsd} on α. (A positive intercept is *not* the expected result of a contribution from electron transfer to the ion pair or triplet).

Other $Re(CO)_4L^\bullet$ radicals were assumed to follow the same rate law. Values of k_T and α are collected in Table I, where $k_T = k_{obsd}/\alpha$.

Conductivity Measurements. The conductivities of CH_3CN solutions of $MCP^+BF_4^-$ (Table II) were analyzed according to Fuoss' method for solution of eq 6,[10] where Λ, Λ_0, c, $f_\pm$, and K_D

$$\frac{F}{\Lambda} = \frac{1}{\Lambda_0} + \frac{c\Lambda f_\pm^2}{\Lambda_0^2 F K_D} \tag{6}$$

represent the equivalent conductance at concentration c, the limiting conductance, the concentration, the mean activity, and the ion pair dissociation constant (eq 4), respectively, and F is a function defined elsewhere.[10] This treatment yielded a linear relationship between F/Λ and $c\Lambda f_\pm^2/F$ (Figure 3) at concentrations below ca. 3.5×10^{-2} M. However, the estimated upper limit of concentration for applicability of eq 6, C_0, is about 1.5×10^{-2} M in acetonitrile.[11] Above this concentration the Fuoss equation is not applicable, due to the onset of higher association. The y intercept and gradient yield values of $\Lambda_0 = 171\ cm^2\ \Omega^{-1}\ equiv^{-1}$ and $K_D = 1.22 \times 10^{-2}$ M, respectively. Solutions used in the flash-photolysis studies were in general a little more concentrated than the C_0 value (typical concentration ca. 5×10^{-2} M). We therefore attempted to fit the higher concentration data to the Fouss equation for triple ion association[12]

$$\Lambda c^{1/2} g(c) = \frac{\Lambda_0}{K_D^{1/2}} + \left(\frac{\lambda_0 K_D^{1/2}}{K_T}\right)\left(1 - \frac{\Omega}{\Lambda_0}\right)c \tag{7}$$

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(10) Fuoss, R. M. *J. Am. Chem. Soc.* **1935**, *57*, 488.

(11) Fuoss, R. M.; Accascina, F. *Electrolytic Conductance*; Interscience: New York, 1959; p 253.

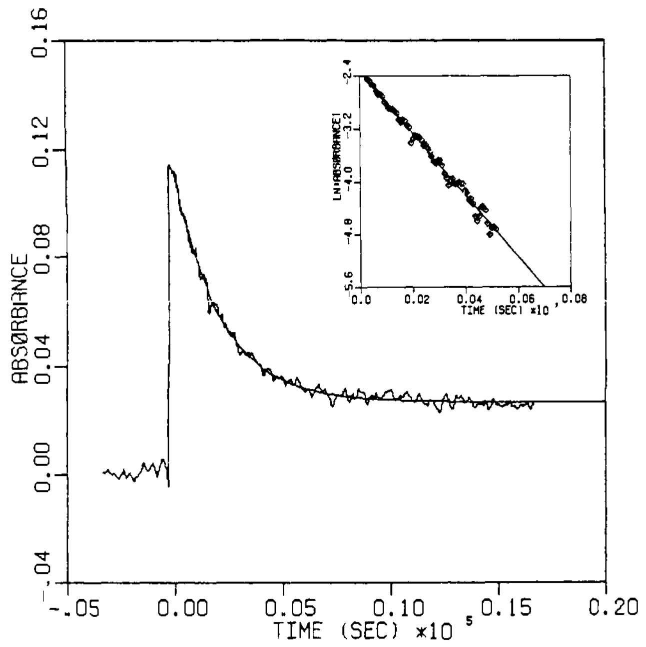

Figure 4. Transient observed at 600 nm upon flash photolysis of $Re_2(CO)_8(P(O\text{-}i\text{-}Pr)_3)_2$ (~10^{-4} M) and MA (0.034 M) in toluene solution. The line through the trace is the first-order least-quares fit of the data. The insert shows the linear least-squares fit of the data to a first-order rate expression over ca. 3 half-lives.

where $g(c)$ represents a function defined elsewhere,[12] and K_T and λ_0 are the triple ion dissociation constant and the limiting conductance of the triple ion, respectively. Since λ_0 cannot be determined, we have assumed $\lambda_0/\Lambda_0 = 1/3$.[12] A plot of $\Lambda c^{1/2}g(c)$ vs. $(1 - \Lambda/\Lambda_0)c$ is linear. The gradient and y intercept provide values of $K_T = 0.15$ M and $K_D = 2.5 \times 10^{-2}$ M. The latter value is approximately a factor of 2 different from that calculated from eq 6. The discrepancy is not considered serious in view of the approximations made in the analysis

The concentration of free cation, α, was calculated at each concentration as follows. An initial estimate was obtained assuming no triple ion association from the relationship $\alpha^2 + K_D\alpha - cK_D = 0$. With use of these values of α and c, the concentration of ion triplets, β, was calculated from $\beta = \alpha(c - \alpha)/K_T$. A second value of α was then determined by using an adjusted concentration $c' = c - \beta$, and the process was repeated. This method of successive approximation converged to within experimental error after two cycles and resulted in a corrected α value roughly 4% less than that calculated by ignoring triple ion association.

Reaction of Re(CO)₄L• with Maleic Anhydride. The transient absorptions attributed to $Re(CO)_4L^\bullet$ radicals following flash photolysis of $Re_2(CO)_8L_2$ in toluene disappear more rapidly when maleic anhydride is added. To obtain the electron transfer rate constant, maleic anhydride was employed at concentrations such that radical recombination made an insignificant contribution to the decay of $Re(CO)_4L^\bullet$. It was found that at monitoring wavelengths around 540 nm, the rate of decay of $Re(CO)_4L^\bullet$ (L = PMe_3, $P(O\text{-}i\text{-}Pr)_3$) was wavelength dependent, probably because of underlying transient absorptions produced by reactions of the maleic anhydride radical anion. There is no detectable wavelength dependence between 585 and 620 nm; in all cases, reactions were monitored at 600 nm. A typical decay curve for the reaction of $Re(CO)_4(P(O\text{-}i\text{-}Pr)_3)^\bullet$ and MA is shown in Figure 4 along with the corresponding ln (abs) vs. time plot (inset). Again, the absorbance did not return to its preflash level, due to the weak absorbance of $MA^{\bullet-}$ at this wavelength.[13] This reaction was studied at varying MA concentrations. A plot of k_{obsd} vs. [MA] was linear with zero y intercept within experimental error (Figure 5). The gradient of this plot yielded a value of $k_T = 1.03 \times 10^8$ M^{-1} s^{-1}. Thus, the reaction is first order in both MA and Re radical; the other $Re(CO)_4L$ studied were assumed to behave similarly.

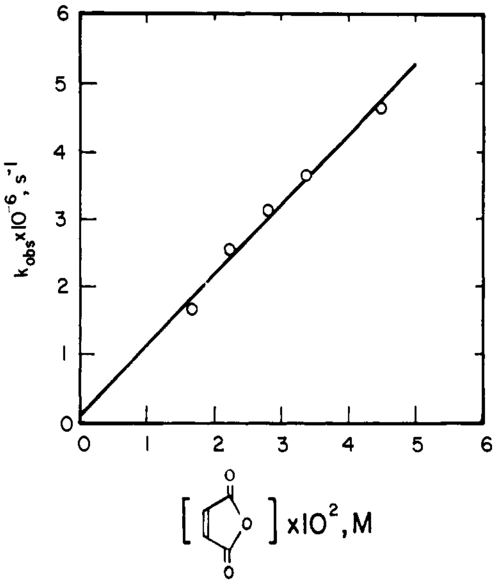

Figure 5. Variation of k_{3bsd} with [MA] for the reaction of $Re(CO)_4(P(O\text{-}i\text{-}Pr)_3)^\bullet$ with MA.

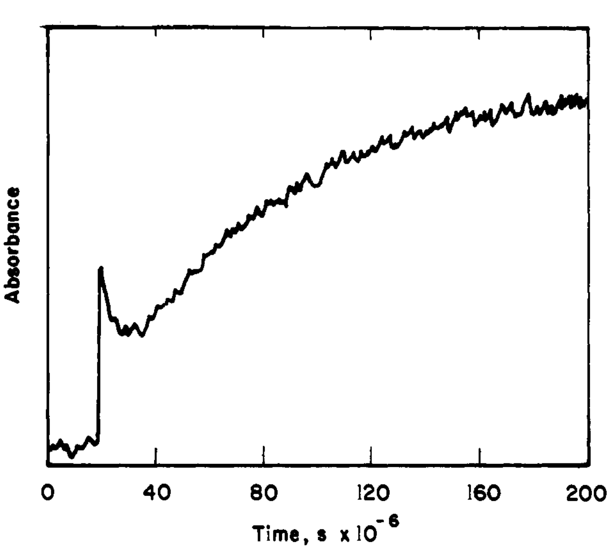

Figure 6. Absorbance vs. time curve upon flash photolysis of a toluene solution of $Re_2(CO)_{10}$ and MA.

In two cases, L = CO, $P(OMe)_3$, the transients were complicated by an increase in absorption after the radical had decayed. Figure 6 shows the absorption vs. time plot for the reaction of $Re(CO)_5^\bullet$ with MA. The transient radical absorption decays within 10 μs following the flash. This is then followed by a steady growth in absorption over a longer time scale which had leveled off after ca. 200 μs when [MA] = 0.013 M. we could not be certain that the rate constant could be reliably evaluated from the initial decay. However, it was noted that added CH_3CN entirely prevented the additional absorptions, and good data were readily obtained in CH_3CN, 7:3 (v/v) CH_3CN/toluene, and 3:7 (v/v) CH_3CN/toluene solutions. Plots of k_T vs. solution composition (Figure 7) were extrapolated to a composition of 100% toluene, and the reported values of k_T for L = CO, $P(OMe)_3$ were derived in this manner. The error margin in these k_T values was estimated to be ±10%. All values of k_T are collected in Table III.

Discussion

In designing experiments to probe the electron-transfer reactions of $Re(CO)_4L^\bullet$ radicals, several experimental limitations have to be taken into consideration. The electron acceptor must react

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[12] Reference 11, pp 256, 257, 258.

[13] Shida, T.; Iwata, S.; Imamura, M. *J. Phys. Chem.* **1974**, *78*, 741.

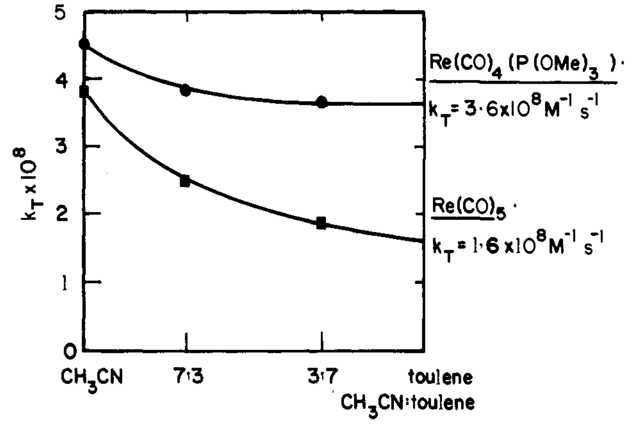

Figure 7. Variation in k_T with solvent composition in CH_3CN/toluene mixtures: (●) $Re_2(CO)_8(P(OMe)_3)_2$ + MA, (■) $Re_2(CO)_{10}$ + MA.

Table III. Electron-Transfer Rate Constants for Reactions of Maleic Anhydride with $Re(CO)_4L^\bullet$

L	δ_{CO}[a]	θ,[b] deg	solvent	$10^2[C_4H_2O_3]$, M	$10^{-6}k_T$, $M^{-1} s^{-1}$
CO	0.00	95	toluene		160 ± 16[d]
PMe_3	5.05	118	toluene	0.66	287 ± 18
$P(OMe)_3$	3.18	107	toluene		360 ± 36[d]
$P(O\text{-}i\text{-}Pr)_3$	3.90	130	toluene	3.4	107 ± 3
			CH_3CN	4.2	189 ± 16
			THF	6.4	59 ± 2
			pyridine	7.1	140 ± 8
$P(n\text{-}Bu)_3$	5.69	132	toluene	2.4	141 ± 6
$P(i\text{-}Bu)_3$	5.40	143	toluene	1.7	3.1 ± 0.2
$P(i\text{-}Pr)_3$	6.20	160	toluene	1.3	16 ± 2
$AsEt_3$	5.33	128[c]	toluene	3.9	239 ± 39

[a] See Table I, footnote *a*. [b] See Table I, footnote *b*. [c] See Table I, footnote *d*. [d] These rate constants were determined by extrapolation of results in mixed solvents, see text. Uncertainty estimated to be ±10%.

with the Re radical within a time window bounded on the slow side by radical recombination and on the fast side by the duration of the laser pulse (~10 ns at half-maximum intensity). Within limits, the concentration of acceptor can be adjusted accordingly, but the reduction potential of the acceptor must fall within a certain range. Second, the acceptor must not absorb strongly in the region of the laser pulse (337 nm), otherwise, the Re dimer, which is present in smaller concentrations in a pseudo-first-order experiment, will not be extensively homolyzed. Neither may it absorb strongly in the 540-nm region, otherwise the direct observation of the Re radical is hampered. Further, the acceptor should not give rise to transient absorptions independently of the Re radicals. These restrictions have proven to be quite stringent, and experiments with various pyridinium salts, quinones, substituted nitro and cyano aromatics, benzophenone, tropylium cation, trityl cation, TCNQ, TCNE, and others have failed for one or another reason. Good results were obtained with $MCP^+BF_4^-$ and MA.

The values of k_T for both series of reactions are collected in Tables I and III. At first sight, the most striking feature is that the reactions are all very fast, having k_T values of 3×10^6 M^{-1} s^{-1} or greater. A rate constant of 5.5×10^5 M^{-1} s^{-1} for the reaction of $Mn(CO)_5^\bullet$ with $MCP^+BF_4^-$ has been reported.[5] For $Re(CO)_5^\bullet$ the value is 1.7×10^8 M^{-1} s^{-1}, more than two orders of magnitude greater. However, the $Mn(CO)_5^\bullet$ value was not corrected for ion pairing effects.[14] A correction for ion pairing would not in any case increase the value to that for $Re(CO)_5^\bullet$. Thus these comparative values echo the trend found in atom-transfer reactions, in which the Re-centered radicals are more reactive than their Mn congeners.

Reactions of $Re(CO)_4L^\bullet$ with $MCP^+BF_4^-$. Continuous photolysis of $Re_2(CO)_8(PMe_3)_2$ and $MCP^+BF_4^-$ in CH_3CN solution gives rise to a mixture of carbonyl-containing products, among which is the cation $[cis\text{-}Re(CO)_4(PMe_3)(CH_3CN)]^+$, identified by comparison of its IR bands with those of an authentic sample. This cation is stable to further photolytic substitution by CH_3CN under the conditions employed, ruling out secondary photolysis as the origin of the other products. However, it is known that the $MCP^\bullet$ radical disproportionates quickly in polar medium to yield the methyl viologen dication, MV^{2+}, and CN^-, eq 8.[15]

$$2MCP^\bullet \rightarrow MV^{2+} + 2CN^- \tag{8}$$

Further experiments showed that a CH_3CN solution of the Re cation reacts with solid NaCN under photolysis within minutes and thermally within hours to give a mixture of products. The IR spectrum consists of several broad features and resembles the pattern observed for the products of the continuous photolysis of $Re_2(CO)_8(PMe_3)_2$ with $MCP^+BF_4^-$. Pure samples of isolated products were not obtained. These results, while not conclusive, suggest that the complex product mixture is derived from secondary reactons of the $MCP^\bullet$ radical and that the primary reaction is oxidation of the $Re(CO)_4(PMe_3)^\bullet$ radical through simple electron transfer.

It is conventional to picture electron-transfer reactions in terms of an initial equilibrium between the free reactants and an association or precursor complex, followed by a nonradiative or Frank–Condon electronic transition within the precursor complex.[16] In the reactions of $Re(CO)_4L^\bullet$ with $MCP^+BF_4^-$, the precursor complex may be composed of the Re radical and either the MCP^+ cation or the $MCP^+BF_4^-$ ion pair. (We do not distinguish between tight ion pairs and solvent-separated ion pairs.) These two situations are represented by eq 9 and 10, in which the ion pair is represented by $MCP^+|BF_4^-$. For the process represented by eq 9, $k_{obsd} \propto \alpha$. We assume the equilibrium rates of ion pair dissociation and formation are very rapid and that the presence of Re radicals does not interfere with the equilibrium. The excellent linearity of the k_{obsd} vs. α plot (Figure 2, curve B) over all concentrations studied provides strong evidence that electron transfer occurs to the free ion only, as represented by eq 9. There is no necessity to invoke competitive electron transfer to the ion pair. the accuracy of our data is such that we would probably detect a competitive reaction which accounted for ca. 10% or more of the total reaction. Given the predominance of the ion pair at the higher concentrations, k_T must be at least an order of magnitude greater than k_{IP}, the rate constant for electron transfer to the ion pair.

$$Re(CO)_4L^\bullet + MCP^+ \rightleftharpoons \underset{\text{precursor complex}}{[Re(CO)_4L^\bullet|MCP^+]} \rightarrow Re(CO)_4L^+ + MCP^\bullet \tag{9}$$

$$Re(CO)_4L^\bullet + MCP^+|BF_4^- \rightleftharpoons \underset{\text{precursor complex}}{[Re(CO)_4L|MCP^+|BF_4^-]} \rightarrow Re(CO)_4L^+ + MCP^\bullet + BF_4^- \tag{10}$$

Precedents for this behavior are found in the self-exchange reactions of anthracene$^{0/-}$,[17a] naphthalene$^{0/-}$,[17a,b] $Cp_2Fe^{+/0}$,[18] and $MnL_6^{2+/+}$ (L = cyclohexyl isocyanide, $CN{\cdot}C_6H_{11}$)[19] and in the reaction of Cp_2Fe with $[Co(dmg)_3(BF)_2]^+[BF_4]^-$ (dmg = doubly deprotonated ion of dimethylglyoxime).[20] In each of these reactions, the rate of electron exchange is dependent upon the extent of ion pairing, usually becoming less as ion pairing becomes more prevalent, although the opposite dependence has been noted.[19] Quite large differences have been reported; for example, in the

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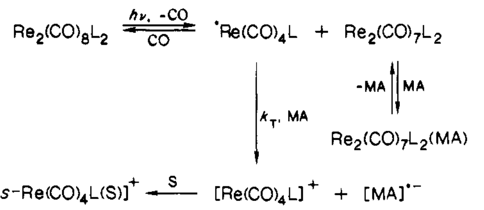
Scheme I



naphthalene/naphthalene$^{•-}$ self-exchange reaction (THF solution, K$^+$ counterion), the rate of free anion/naphthalene electron exchange is $k = 3 \times 10^9$ M^{-1} s^{-1}, whereas the rate of ion pair–naphthalene exchange is $k = 6 \times 10^7$ M^{-1} s^{-1}, a 50-fold difference.[17b] Qualitatively this accords with our results. There may be several reasons why k_T and k_{IP} differ: The electrostatic effect exerted by BF$_4^-$ on the MCP$^+$ cation in the ion pair should reduce its electron affinity, as compared with the free cation. Further, the anion in the Re radical ion pair precursor complex might intrude to some extent between the Re center and MCP$^+$ in the precursor complex, increasing the distance over which the electron has to be transferred. Finally, there will be a required geometry which must be achieved before electron transfer occurs. An entropic barrier can be envisaged which would be more significant with the ion pair.

Reactions of Re(CO)$_4$L$^•$ with MA. Continuous photolysis of CH$_3$CN solutions of Re$_2$(CO)$_8$(PMe$_3$)$_2$ and excess MA produces [*cis*-Re(CO)$_4$(PMe$_3$)(CH$_3$CN)]$^+$ in low yield in addition to other unidentified carbonyl-containing products that probably arise from secondary photolytic reactions of the cationic product. We assume that in toluene solutions the initial product of electron transfer is the unsolvated, five-coordinate, 16-electron cation. The fate of this 16-electron species is dependent upon the ligation at the metal center. When L = CO, P(OMe)$_3$, the decay of the radical is followed by the growth of a new absorption (Figure 6) on the flash photolysis time scale. There are several possible origins for this additional absorption. We can discount the idea that a radical anion dimer of MA, i.e., (MA)$_2^{•-}$ [21a] or a solvent–MA$^{•-}$ adduct,[21b] gives rise to this behavior since it is clearly dependent upon the specific Re radical. Immediately following electron transfer, an ion pair exists (Scheme I), which may collapse to give a directly bonded Re–MA radical adduct that might have an absorption in the visible region. This possibility can also be ruled out since the rate of growth of the absorption was found to be directly proportional to [MA], and this is inconsistent with this suggestion. Two further possibilities can be envisaged. The ion pair formed by electron transfer may separate, and then the Re cation may form an adduct with MA, [Re(CO)$_5$(MA)]$^+$. Alternatively, Re$_2$(CO)$_9$ which is also formed upon 337-nm irradiation may react with MA to give Re$_2$(CO)$_9$(MA). In either case, the visible absorption might arise from an intramolecular charge-transfer band. These two possibilities were distinguished in the following way. A competition experiment was carried out in which MA and CCl$_4$ were added to a solution of Re$_2$(CO)$_{10}$ such that 50% of the •Re(CO)$_5$ reacted with CCl$_4$ to give Re(CO)$_5$Cl.[4f] The ratio of the absorbance immediately following the flash (due to •Re(CO)$_5$) to the constant absorbance observed after about 200 μs (Figure 6) was found to be closely similar to that ratio found for an otherwise identical solution containing no CCl$_4$.[22] This result rules out •Re(CO)$_5$ as giving rise to the final absorbing product because half would have reacted with CCl$_4$ and thus produced a decreased final absorption. This leaves us with Re$_2$(CO)$_9$(MA). There is ample precedent for such a complex; MA is known to form stable mononuclear complexes with a variety of low oxidation state metal centers by replacement of weakly bound donors, where it is thought to bond as an η^2 olefin.[23a,b] The reactions are summarized in Scheme I.

Table IV. Coefficients for the Free Energy Relationship $\ln k_T = a\delta + b\theta + c$

electron acceptor	solvent	a	b	c	correl coeff
MCP$^+$BF$_4^-$	CH$_3$CN	0.24	−0.068	25	0.90
maleic anhydride	toluene	0.62	−0.109	29	0.81

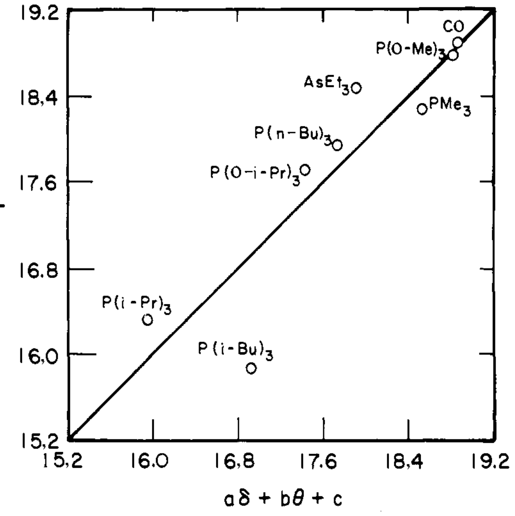


Figure 8. Correlation between ln k_T and the combined steric and electronic effects of various ligands L for the reactions of Re(CO)$_4$L$^•$ with MCP$^+$.

The proposal that Re$_2$(CO)$_7$L$_2$(MA) is involved is further corroborated by the observation that on addition of CH$_3$CN to the flash solutions, the new absorption was completely absent, a result consistent with involvement of a coordinatively unsaturated metal center. It is known that the amount of CO loss observed upon 337-nm irradiation is critically dependent upon the nature and stereochemistry of the L substituent.[24] For 1,2-*dieq*-Re$_2$(CO)$_8$L$_2$, CO loss is a minor photochemical pathway; this explains why no MA adduct was observed with any of these complexes. CO loss is a more significant process for 1,2-*diax*-Re$_2$(CO)$_8$L$_2$ complexes, but of these, only the P(OMe)$_3$ complex formed an adduct with MA upon photolysis. Clearly, the steric and electronic influences of L play a role in determining the subsequent reactions of Re$_2$(CO)$_7$L$_2$. The MA molecule would occupy a position cis to the L substituent on the unsaturated metal center. Thus, a steric impediment to the formation of Re$_2$(CO)$_7$L$_2$(MA) is expected when L is bulky. Furthermore, the unsaturated metal center will be most electron deficient when L is a weak σ donor/strong π acid. These steric and electronic predictions lead us to the conclusion that an Re$_2$(CO)$_7$L$_2$(MA) adduct will be most favored with small π acid ligands, i.e., L = CO, P(OMe)$_3$, and progressively disfavored as the steric bulk and σ basicity of L increase. This is in accord with the observation that adduct formation occurs only with L = CO and P(OMe)$_3$. It was also noted that Re$_2$(CO)$_7$(P(OMe)$_3$)(MA) is not as stable as Re$_2$(CO)$_9$(MA); over 500 μs, its absorption has significantly decayed and the decay is accelerated by the addition of 1 atm of CO. This can be explained if the reaction of Re$_2$(CO)$_7$(P(OMe)$_3$)$_2$ with MA is reversible and the subsequent slow reaction with CO yields the thermodynamically more stable product Re$_2$(CO)$_8$(P(OMe)$_3$)$_2$.

Ligand Effects on k_T. Both steric and electronic properties of the substituent L influence the electron transfer rate constant, k_T. To account for both the steric and electronic characteristics of ligands, we have analyzed the rate data in terms of a two-

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(22) Control experiments in which the absorption of Re$_2$(CO)$_9$ at $\lambda_{max} \simeq$ 400 nm was monitored showed that Re$_2$(CO)$_9$ was stable to CCl$_4$ under the conditions employed and that recombination with CO was a much slower process. It was not possible to directly observe the decay of Re$_2$(CO)$_9$ as it reacted with MA due to the superimposed absorptions of the radical and Re$_2$(CO)$_9$(MA) which are still relatively strong at this wavelength.

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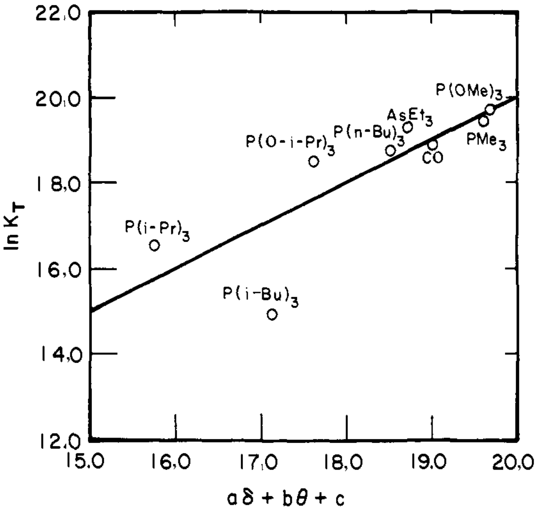

Figure 9. Correlation between ln k_T and the combined steric and electronic effects of various ligands L for the reactions of $Re(CO)_4L^{\bullet}$ with MA.

parameter free energy relationship, eq 11, in which δ, as defined by Bodner,[25] represents the electronic characteristics of L, and

$$\ln k_T = a\delta + b\theta + c \qquad (11)$$

θ, as defined by Tolman,[26] represents a measure of the steric requirements of L. Multiple linear regression analyses of the data for each series of reactions yield the values of a, b, and c given in Table IV; the distribution of points for each series is shown in Figures 8 (MCP^+) and 9 (MA). In general there is a good correlation between calculated and experimental values of ln k_T. However, the points for a given L show a consistent deviation from the line of identity when the two series are compared. In most instances this probably reflects an inaccuracy in the θ value. In both series, the reactions of $Re(CO)_4(P(i\text{-}Bu)_3)^{\bullet}$ were substantially slower than predicted from the δ and θ values of $P(i\text{-}Bu)_3$. In the atom-transfer reactions, this radical also reacts more slowly than predicted.[4f] It appears that β-branching in the alkyl groups of the phosphine results in hindrance at the metal center which is not adequately represented by its θ value.

It is noteworthy that the a values of 0.24 and 0.62 for the reaction series involving MCP^+ and MA, respectively, are small in comparison with values in the range 1.1 to 1.4 for halogen atom transfer reactions.[4f]

We have presented evidence elsewhere that the halogen atom transfer reactions are electron demanding at the metal center in the transition state. One would expect that the reactions presented here, more clearly involving obligatory electron transfer, would exhibit an even larger sensitivity to variations in electron availability at the metal center, as reflected in the value for a. However, these reactions are highly exergonic. We have shown that the Marcus/Agmon–Levine equation[27] accounts very well for the halogen atom transfer reactions of rhenium carbonyl radicals.[28] Unfortunately, the limitations described earlier on our choice of suitable acceptors have to date precluded a test of the Marcus/Agmon–Levine equation in the same manner for electron-transfer processes. However, there is every reason to suppose that, in principle, the electron-transfer reactions should also follow a similar pattern of dependence. In this case, because the reactions are highly exergonic, the dependence of k_T on modifications in structure of the rhenium carbonyl donor are expected to be small. To put it another way, the selectivity of the reaction is low. While the forgoing remarks account in a general way for the low value for a, they do not provide a rationale for the fact that a is considerably smaller for the electron-transfer reactions than for atom-transfer reactions of comparable overall ergonicity. This matter will be addressed in a separate contribution.

The b value for the MCP^+ reactions, −0.068, is less negative than that for the MA reactions, −0.11. This indicates that the bulk of L is of less relative importance in the reactions of the pyridinium salt. The result is consistent with a greater interaction of MA with the metal center in the transition state than for the pyridinium salt. That is, the reactions of the pyridinium cation are more outer sphere in character. The b value for the MA reactions, −0.11, is in the range found for halogen atom transfer reactions,[4f] which involve substantial interaction between the metal center and the halogen in the transition state.[28] Hence, an appropriate model for the MA reactions in toluene may be an inner sphere electron transfer in which one of the oxygen atoms of MA interacts directly with Re.

On the basis of a knowledge of a and b parameters, we can explain why only certain phosphines effectively induce disproportionation reactions of organometallic radicals. A general chain mechanism for the disproportionation of dimers is shown in eq 12–14. (We defer the question of whether the 17-electron or 19-electron radical is the reducing agent in eq 13.) For disproportionation to occur, the electron-transfer step, eq 13, and the preceding substitutions, eq 12, must occur rapidly and dominate over the radical recombination reactions which lead to substituted dimers.

$$^{\bullet}ML_n + xL' \rightarrow {}^{\bullet}ML_{n-x}L'_x + xL \qquad (12)$$

$$^{\bullet}ML_{n-x}L'_x + (ML_n)_2 \rightarrow [ML_{n-x}L_x']^+ + [(ML_n)_2]^{\bullet -} \qquad (13)$$

$$[(ML_n)_2]^{\bullet -} \rightarrow ML_n^- + {}^{\bullet}ML_n \qquad (14)$$

The rates of these reactions are influenced by the steric and electronic properties of the ligands to a greater or lesser degree, as repesented by the a and b parameters. In order that ligand substituent effects manifest themselves, there must exist substantial a and b values for recombination, corresponding to a large spread in k_R. We know that such a spread exists in the $Mn_2(CO)_8L_2$ series.[2c] Rhenium-centered radicals are comparatively insensitive to the steric and electronic effects of L (small a and b, and a small spread in k_T) in electron-transfer reactions; thus, the occurrence of disproportionation will be largely dependent upon the specific recombination rates of the radicals involved. For $^{\bullet}Re(CO)_5$, $k_R = 3.7 \times 10^9$ M^{-1} s^{-1};[2g] for substituted Re radicals, k_R values are not known but are expected to be very large also. This no doubt is the reason why disproportionation is not observed in the substitution chemistry of $Re_2(CO)_{10}$. At the other extreme, $V(CO)_6$ and its substituted derivatives do not dimerize at ambient temperature; here the disproportionation will be limited only by the feasibility of the substitution and electron-transfer steps.[29] These will be most favored when L is small and basic. Disproportionation reactions in other metal carbonyl systems will correspond to situations intermediate between these two extremes.

Solvent Effects. The solvent dependence of k_T for the reaction of $Re(CO)_4P(O\text{-}i\text{-}Pr)_3^{\bullet}$ and MA is not large: CH_3CN, 1.9×10^8 M^{-1} s^{-1} > pyridine, 1.4×10^8 M^{-1} s^{-1} > toluene, 1.1 10^8 M^{-1} s^{-1} > THF, 0.59×10^8 M^{-1} s^{-1}. These variations are qualitatively the same and quantitatively similar to the solvent dependence of the rate constant for reactions of $Re(CO)_4(PMe_3)^{\bullet}$ with CH_2Br_2, which also possesses electron-transfer character[4f,28] and also involves two neutral reactants giving rise to a more polar transition state. The relationship of k_T to solvent dielectric constant is not regular. In all likelihood, the nucleophilic character of the solvent is of more importance than solvent polarity in producing the modest solvent dependence observed.

Unfortunately, a similar study of solvent effects on the reactions with MCP^+ is not feasible, because of the limited solubility of the electron acceptor in various solvents. Further, the ion pair dissociation constant will be different in each solvent, and not

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always measurable. For a given rhenium radical, reaction with MA ($E^{1/2} = -0.84$ V vs. SCE[30]) is slightly faster than that with MCP$^+$ ($E_{1/2} = -0.66$V vs. SCE[5]). The relative rates are in the opposite sense from what we expect, namely that the rate will be faster for the more exergonic process.[27,31] However, it is difficult to make meaningful comparisons of the results, because the two series of reactions were studied in different solvents and involve different charge types.[32]

17-Electron vs. 19-Electron Radicals? The metal carbonyl radicals studied to date have been found to undergo associative ligand substitutions, giving rise to 19-electron intermediates or transition states.[3] Whether 17-electron or 19-electron species are responsible for electron transfer is less clear. In the absence of evidence to the contrary, it has been assumed that 17-electron radicals are capable of acting as reducing agents.[4a,5-7] On the other hand, Tyler and co-workers have favored reduction by 19-electron species in the photochemical disproportionations of dinuclear carbonyl compounds with Lewis bases.[8,33] A Lewis base substituted radical, being more electron-rich than its 17-electron counterpart, should be the more powerful reducing agent, but the question of whether such 19-electron species are kinetically significant remains to be answered. There have been no direct observations of 19-electron radical intermediates by transient techniques, and the kinetic evidence for their existence does not discriminate between a 19-electron transition state or intermediate. It is then questionable whether the equilibrium $ML_n^\bullet + L' \rightleftharpoons ML_nL'^\bullet$ favors the 19-electron species enough to make its bimolecular electron transfer reactions competitive with those of the 17-electron radical.

Our results suggest that 17-electron radicals undergo rapid electron-transfer reactions. Reaction of $Re(CO)_4L^\bullet$ with MA in toluene solution is rapid. There is no possibility of the Re radical reacting initially with a basic solvent molecule, although it might be argued that the base is MA itself; i.e., the reaction may have some inner-sphere character as discussed above. In any case, addition of MA to a rhenium-centered radical is unlikely to enhance the reducing capability of the radical since MA is expected to be a weak nucleophile as a σ-base and is thought to be a stronger π acid ligand than CO.[23a,b] Second, reaction of $Re(CO)_4(P(O\text{-}i\text{-}Pr)_3)^\bullet$ with MA exhibits small solvent effects; the rate in toluene ($k_T = 1.1 \times 10^8$ M^{-1} s^{-1}) is marginally less than that in the Lewis base solvents CH_3CN ($k_T = 1.9 \times 10^8$ M^{-1} s^{-1}) and pyridine ($k_T = 1.4 \times 10^8$ M^{-1} s^{-1}). If association to form a 19-electron species occurred to enhance the rate of electron transfer, a much faster rate should be observed in the more nucleophilic solvents. Finally, k_T was determined for the reaction of $Re(CO)_4(PMe_3)^\bullet$ with a constant concentration of $MCP^+BF_4^-$ in the presence of varying quantities of added $P(C_6H_5)_3$ in CH_3CN solution. The added phosphine had no effect on k_T at concentrations of up to 0.05 M. The experiment, while interesting, is not conclusive in ruling out a 19-electron intermediate in other cases. Unfortunately, use of a more nucleophilic phosphine is precluded by a direct reaction of phosphine with MCP$^+$.

Acknowledgment. We are grateful to James A. Wehmer for assistance with the laser flash experiments.

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Structural-Electronic Relationships in Inorganic Solids: Powder Neutron Diffraction Studies of the Rutile and Anatase Polymorphs of Titanium Dioxide at 15 and 295 K

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James W. Richardson, Jr.,[‡,⊥] and Joseph V. Smith[‡,§]**

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Abstract: Rietveld analysis of time-of-flight pulsed neutron diffraction of powders shows a nearly isotropic shrinkage of the structures of both the rutile and anatase polymorphs of TiO_2 upon cooling from 295 to 15 K and no change in the sense of the distortion of the TiO_6 octahedra (two long and four short Ti–O distances in both): rutile at 295 (first) and 15 K (second), a_0 4.593 08 (4), 4.586 66 (4), c_0, 2.958 89 (3), 2.954 07 (3), x_{oxygen}, 0.304 76 (6), 0.304 69 (6), Ti–O(4×), 1.9486 (3), 1.9459 (3), Ti–O(2×), 1.9796 (4), 1.9764 (4); anatase at 295 and 15 K, a_0, 3.784 79 (3), 3.782 16 (3), c_0, 9.502 26 (12), 0.504 65 (12), x_{oxygen}, 0.166 86 (5), 0.166 75 (4), Ti–O(4×), 1.9338 (1), 1.9322 (1), Ti–O(2×), 1.9799 (5), 1.9788 (4): all distances (Å) referenced to silicon (a = 5.430 88 Å). Both tight-binding calculations on the crystalline solids and molecular mechanics computations on the oxide lattice alone lead to a model in which the balance of attractive Ti–O and repulsive O–O interactions control the details of the overall structures. The relative bond lengths around metal centers in some other systems are predicted.

Rutile and anatase are two polymorphs of TiO_2 based on distorted close-packed, or eutactic,[1] anion arrays. Accurate crystallographic data have been obtained by powder[2-4] and single-crystal[5-8] X-ray diffraction and single-crystal[9] and powder[10] neutron diffraction; some were obtained at elevated temperatures.[7,8] It is still not clear how the details of the solid-state structure are controlled by the electronic properties of Ti and

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