*J. Am. Chem. Soc.* **1987**, *109*, 3269–3275

2 H), 8.05–8.09 (m, 2 H). Anal. Calcd for $C_{44}H_{50}O_3$: C, 84.30; H, 8.04. Found: C, 84.11; H, 7.77.

Dicyanomethylation of **10(0,2)** (0.25 g, 0.4 mmol) was carried out as described above for the synthesis of **1(6)**. Recrystallization from EtOAc gave **1(12)** (0.26 g, 96%), mp 225–226 °C: IR (KBr, cm$^{-1}$) 2242 (CN); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.79 (s, 6 H, 2 × $CH_3$), 0.94 (s, 6 H, 2 × $CH_3$), 1.55–1.68 (overlapping multiplets, 6 H), 1.75 (t, $J$ = 2.1 Hz, 2 H), 1.84 (upfield half of partially obscured doublet, 1 H), 1.85 (s, 2 H), 1.87 (br s, 2 H), 1.90 (br s, 2 H), 1.93 (downfield half of partially obscured doublet, 1 H), 2.02 (d, $J$ = 7.8 Hz, 1 H), 2.03 (s, 2 H), 2.06 (d, $J$ = 7.8 Hz, 1 H), 2.16 (s, 2 H), 2.22 (s, 2 H), 2.96 (quintet, $J$ = 2.1 Hz, 2 H), 3.62 (s, 2 H), 3.97 (s, 6 H, 2 × $OCH_3$), 7.42–7.45 (m, 2 H), 8.06–8.09 (m, 2 H). Anal. Calcd for $C_{47}H_{50}N_2O_2$: C, 83.64; H, 7.47; N, 4.15. Found: C, 83.35; H, 7.47, N, 3.98.

## Measurements

Electrochemical measurements were performed by using a glassy carbon working electrode and an Ag/AgCl/KCl (saturated) reference electrode (−40 mV relative to the saturated calomel electrode (SCE)) in acetonitrile containing 0.1 M tetraethylammonium tetrafluoroborate as a supporting electrolyte. Static absorption and emission measurements were performed by using Hewlett-Packard 8451A and Spex Fluorolog instruments.

Fluorescence lifetimes have been obtained by time correlated single photon counting. The experimental setup is an improved version[56] of the one developed by de Vries et al.[57] Excitation pulses (7 ps fwhm) are created by synchronously pumping a Rh6G dye laser (Coherent 490 with extended cavity) with a mode-locked $Ar^+$ laser (Coherent CR8, repetition rate 94 MHz). The second harmonic of the dye laser is then generated by means of a 90° phase-matched ADA crystal, at exit of which the fundamental frequency is filtered off with a Schott UG5 filter. The wavelength of the UV pulses thus created was 303 nm.

Fluorescence of the samples was focussed onto the entrance slit of a Zeiss M20 monochromator by means of a quartz condensor and a Dove prism. Light detection was performed by means of a Hamamatsu R1564U-01 microchannel plate photomultiplier, with an optical time response of 47 ps at 273 nm.[56] The output of this photomultiplier was amplified by an ENI 500 LM amplifier. The amplified pulses were fed into a Tennelec 455 constant fraction discriminator producing the start pulses for a calibrated Ortec 457 time-to-amplitude-converter (TAC). Care was taken that the rate of start pulses did not exceed $10^{-4}$ of the laser repetition rate to ensure good statistics.

Stop pulses for the TAC were derived directly from the sync. output of the modelock driver. The output of the TAC (a voltage proportional to the time elapsed between start and stop pulse) was digitized and accumulated in an EG&G 918 multichannel buffer coupled to an IBM personal computer. The overall time response of the system was measured to be 70 ps fwhm by directly recording the stray light from a milky suspension of $Al_2O_3$ in water.

Recorded spectra were analyzed by means of a homewritten program based on iterative reconvolution. This allows for the presence of more than one exponential decay and automatically corrects for nonlinearity in the TAC time-base and for residual emission resulting from previous excitation pulses. The quality of a fit was judged from the normalized residuals and the $\chi^2$, the latter being always smaller than 1.6. Realistic simulations have shown that this program is capable of determining lifetimes as short as 20 ps to within 5 ps accuracy.

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# On the Nature of Halogen Atom Transfer Reactions of Re(CO$_4$)L$^\cdot$ Radicals[1]

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**Abstract:** Rhenium carbonyl radicals $Re(CO)_4L^\bullet$ (L = $P(CH_3)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$), generated by $N_2$ laser flash photolysis, react with organic halides in a bimolecular atom transfer reaction to form $XRe(CO)_4L$ (X = Cl, Br, I). Rate constants for reactions with 18 organic halogen atom donors were measured in toluene at 22 °C. The rate constants do not correlate well with available thermochemical C–X bond energies. Rate constants for bromine atom transfer for a series of benzyl bromides with $Re(CO)_4P(O\text{-}i\text{-}C_3H_7)_3^\bullet$ obey a Hammett equation correlation, with $\rho$ = 0.75. The data are well-fitted by the Marcus/Agmon–Levine equation for atom or electron transfer, when the half-wave reduction potentials for the organic halides are employed as a measure of relative overall free energy change in the rate-determining process. The data are similarly well accommodated by the Rehm–Weller equation. The estimated intrinsic barriers, $\Delta G^\ddagger(0)$, are 3.5 kcal mol$^{-1}$ for L = $P(CH_3)_3$ and 5.0 for L = $P(O\text{-}i\text{-}C_3H_7)_3$. The experimental results provide the first extensive test of the Marcus/Agmon–Levine or Rehm–Weller equation for halogen atom transfer. They suggest that atom transfer processes could be accommodated within such a theoretical framework when variations in electronic or steric properties are not so large as to markedly alter the equilibrium constant for formation of the encounter complex or the magnitude of the intrinsic barrier. They also provide an indication that electron transfer is a significant component in the reaction process and that configurational changes (C–X bond stretch and X–Re bond formation) in attaining the transition state are not large, or largely compensating.

Metal-centered radicals based on transition metal organometallic compounds have been the subject of much recent work.[2] Our interest has centered on metal carbonyl radicals. These can be produced by a variety of means, including atom abstraction,

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electron transfer, and photochemical bond homolysis. The radicals, once formed, undergo a variety of reactions, including recombination, electron transfer, atom transfer, and substitution. These reactions are of interest in themselves, but also because their relative rates under a given set of circumstances determine the roles the radicals might play as intermediates in radical chain processes such as substitution or disproportionation.

We have recently begun a systematic study of the atom transfer and electron transfer processes of metal carbonyl radicals.[3] In this paper we report the results of a study of the atom transfer reactions of Re(CO)$_4$L$^\bullet$ radicals (L = PMe$_3$, P(O-*i*-Pr)$_3$) with an extended series of organic halides

$$\mathrm{Re(CO)_4L^\bullet + RX \rightarrow Re(CO)_4LX + Re^\bullet} \qquad (1)$$

In these reactions, RX is present in excess; Re(CO)$_4$LX is the sole rhenium-containing product. Our aim in the study has been to understand more fully the nature of the atom transfer process; to determine the variability of reaction rate with changes in the halogen donor; and to assess the extent to which electron transfer plays a role in the reaction.

The halogen atom transfer reactions of the carbonyl radicals are formally analogous to those of other metal-centered radicals previously studied,[4] e.g., Co(CN)$_5^{2-}$,[5] Cr(en)$_2^{2+}$,[6] or any of several chelated Co(II) complexes.[7,8] However, the conditions of the experiment are different for the carbonyl radicals; they have comparatively short lifetimes because of recombination following their formation in a laser flash. The carbonyl radical reactions are formally analogous also to those of main group metal radicals, e.g., R$_3$Sn$^\bullet$, R$_3$Ge$^\bullet$, or R$_3$Si$^\bullet$.[9-11] In all these cases the issue of polarity in the transition state and the extent of electron transfer in the reaction have been discussed.

It is widely recognized that polar effects can operate in atom transfer reactions. Polar effects have been related qualitatively to some degree of electron transfer from metal to the organic halide. However, there has not as yet been an effort to relate the reactivity patterns in such reactions to prevailing theoretical models of atom or electron transfer. The mechanism for atom transfer can be viewed in terms of two extreme models. Equation 2 describes a classical "inner sphere" process in which there is concurrent M–X bond formation and R–X bond rupture. Equation 3 describes a process that might be described as more "outer-sphere" in character; there is a weaker degree of interaction between reactants in the transition state and a more clearly defined electron transfer process. This latter process might be referred to as a concerted electron transfer–bond rupture when $k_{30} \gg k_{32}$.

$$\mathrm{RX + {}^\bullet Re(CO)_4L \rightleftharpoons \{RX\cdots{}^\bullet Re(CO)_4L\} \rightleftharpoons}$$
$$\mathrm{\{R\cdots X\cdots{}^\bullet Re(CO)_4L\} \rightleftharpoons R^\bullet + XRe(CO)_4L} \qquad (2)$$

$$\mathrm{RX} +$$
$$\mathrm{{}^\bullet Re(CO)_4L \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \{RX\cdots{}^\bullet Re(CO)_4L\} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \{RX^{\bullet -}\ {}^{+}Re(CO)_4L\}}$$
$$\mathrm{\xrightarrow{k_{30}} R^\bullet + XRe(CO)_4L} \qquad (3)$$

For most metal-centered radicals and most halogen or hydrogen atom donors, the reaction coordinate may be somewhere between these extremes. The presence of a polar intermediate or transition state has been proposed on the basis of systematic studies of electronic and steric effects on reaction rate,[7,10,11] on the values of kinetic isotope effects,[10b] and on solvent effects.[7b] The results of all these studies are suggestive of the comparative degrees of polarity in such reactions from one metal center to another but do not in themselves clearly measure the characteristics of the reaction coordinate.

Our approach has been to collect experimental kinetics results that can be evaluated in terms of the Marcus[12] and related theoretical models[13] for atom transfer. To that end we have measured the rate constants for halogen atom transfer between 18 organic halogen atom donors and the Re(CO)$_4$P(O-*i*-Pr)$_3^\bullet$ and Re(CO)$_4$PMe$_3^\bullet$ radicals. The donor molecules were chosen to span a wide range in terms of half-wave reduction potentials and R–X bond dissociation energies. The reaction system chosen is in many ways ideal for investigation of the issues at hand. The Re(CO)$_4$L$^\bullet$ radicals can be readily formed by pulsed N$_2$ laser flash irradiation of Re$_2$(CO)$_8$L$_2$ compounds at 337 nm. The reactivity of the Re(CO)$_4$L$^\bullet$ radicals is the highest among the metal carbonyl radicals that have been studied, so we can anticipate covering a wide range of atom transfer rate constants. Finally, the atom transfer rate constants can be obtained directly with good accuracy by measurement of the disappearance of the absorption at about 550 nm due to Re(CO)$_4$L$^\bullet$ following the laser flash.

## Theoretical Aspects

During the past two decades there has been a considerable interest in formal treatments of free energy relationships in reactions that range from weak-overlap (outer-sphere) type electron transfer reactions to proton and atom transfers and strong-overlap (inner-sphere) electron transfer processes.[12-16] The most generally successful models are those based on the theoretical foundations established by Marcus,[12] or empirically related to the Marcus formalism.[13,15,17] In our application of these theoretical models to atom transfer processes we will employ the notation used by Scandola, Balzani, and Schuster,[16] who have summarized the relationships between several approaches. The halogen atom transfer process can be viewed in terms of either eq 2 or 3. These two quite distinct formulations lead to similar formal free energy relationships involving certain overall parameters of the reaction

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system (vide infra). However, for the purpose of bringing to the fore the important issue of the extent of electron transfer in the atom transfer process, we will employ the reaction model embodied in eq 3.

Application of the usual steady-state approximation to the concentration of the encounter complex {RX$\cdots{}^\bullet$Re(CO)$_4$L} and the intermediate (or transition state) resulting from electron transfer, {RX$^{\bullet-}$ $^+$Re(CO)$_4$L}, yields eq 4 for the experimental rate constant for disappearance of $^\bullet$Re(CO)$_4$L.[16]

$$k_T = \frac{k_{12}}{1 + (k_{21}/k_{23}) + (k_{32}/k_{23})(k_{21}/k_{30})} \qquad (4)$$

The rate constants for electron transfer and the ratio $k_{32}/k_{23}$ can be expressed as

$$k_{23} = k^\circ_{23} \exp(-\Delta G^\ddagger_{23}/RT) \qquad (5)$$

$$k_{32}/k_{23} = \exp(\Delta G_{23}/RT) \qquad (6)$$

where $k^\circ_{23}$, $\Delta G^\ddagger_{23}$, and $\Delta G_{23}$ are the frequency factor, the standard free energy of activation, and standard free energy change for the electron transfer step. For this we can obtain

$$k_T = \frac{k_{12}}{1 + \frac{k_{21}}{k^\circ_{23}} \exp(\Delta G^\ddagger_{23}/RT) + \frac{k_{21}}{k_{30}} \exp(\Delta G_{23}/RT)} \qquad (7)$$

$\Delta G^\ddagger_{23}$ can be expressed as a function of $\Delta G_{23}$; we employ the formulation first proposed by Marcus[12a] and later developed on somewhat different grounds by Agmon and Levine.[13]

$$\Delta G^\ddagger_{23} = \Delta G_{23} + \frac{\Delta G^\ddagger(0)}{\ln 2} \ln \left\{ 1 + \exp\left[ \frac{-\Delta G_{23} \ln 2}{\Delta G^\ddagger(0)} \right] \right\} \qquad (8)$$

$\Delta G^\ddagger(0)$ in eq 8 represents an intrinsic barrier; it is defined as the free energy of activation for the electron transfer process with overall $\Delta G_{23} = 0$. By using eq 7 and 8, $k_T$ can be expressed as a function of $\Delta G_{23}$. Let $A = k_{21}/k^\circ_{23}$ and $B = k_{21}/k_{30}$. Then

$$\log k_T = \log k_{12} - \log \left[ 1 + A \exp(\Delta G_{23}/RT) \exp\left\{ \frac{\Delta G^\ddagger(0)}{RT \ln 2} \ln\left[1 + \exp(-\Delta G_{23} \ln 2/\Delta G^\ddagger(0))\right] \right\} + B \exp(\Delta G_{23}/RT) \right] \qquad (9)$$

$k_{12}$ is the diffusion rate constant, estimated to be on the order of $6 \times 10^9$ M$^{-1}$ s$^{-1}$.[18] For a series of similar reactions, $A$, $B$, and $\Delta G^\ddagger(0)$ are taken to be constants. Figure 1a shows the general shape of the relationship between $k_T$ and $\Delta G_{23}$. As noted previously,[16] the shape of the curve depends on the magnitude of $\Delta G^\ddagger(0)$, the intrinsic barrier to the electron transfer process. The value for $A$ determines the vertical placement of the curve (Figure 1b); the value of $B$ affects the shape of the curve only in the endoergic region (Figure 1c). For $B$ values smaller than 2, a condition that almost certainly obtains in the reactions that concern us, the value of $B$ has no impact on the overall curve shape in any region of interest.

To apply eq 9 to the rate data we have obtained, certain assumptions must be made. We are attempting to test the relationship of $k_T$ to $\Delta G_{23}$, with the assumption that $A$, $B$, and $\Delta G^\ddagger(0)$ are constant. This constancy is assumed to hold for a series of reactions of organic halogen donors with a given Re(CO)$_4$L$^\bullet$ radical. As indicated above, there is little problem in assuming constancy of $B$. However, the value for $A$ might vary as the halogen is altered; further, as the steric requirements of the organic donor vary, the intrinsic barrier might also change. Thus, it is by no means clear that eq 9 will hold for the series studied.

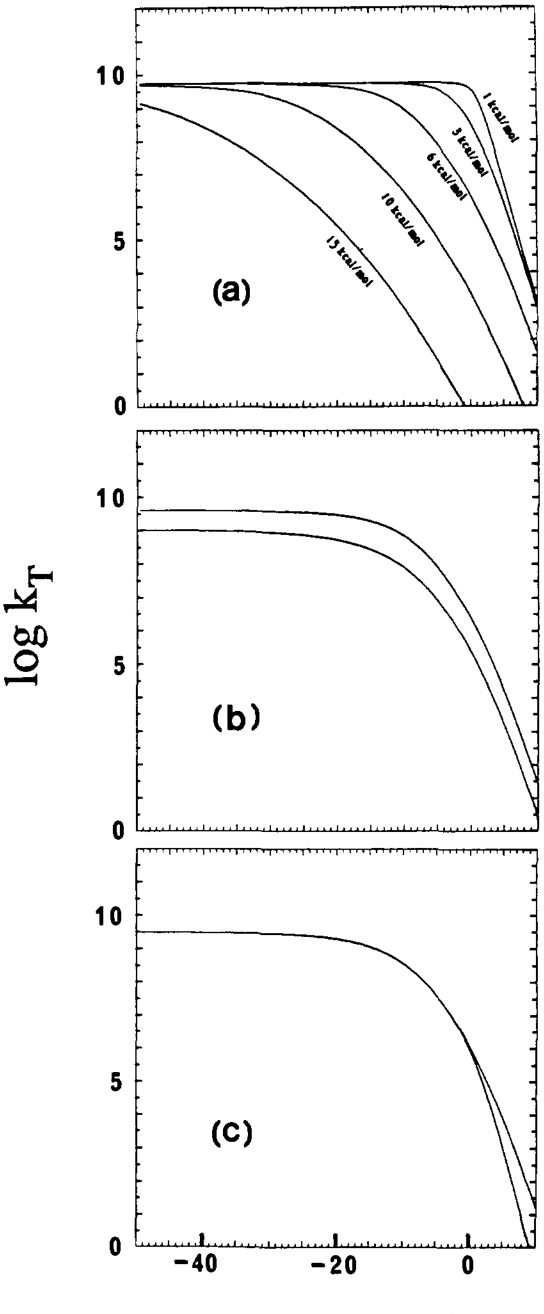

**Figure 1.** log $k_T$ vs. $\Delta G_{23}$ based on eq 9: (a) $A = B = 0.1$; $\Delta G^\ddagger(0) = 1, 3, 6, 10, 15$ kcal mol$^{-1}$; (b) $A = 0.5, 5.0$; $B = 1.0$; $\Delta G^\ddagger(0) = 5$ kcal mol$^{-1}$; (c) $A = 1.0$; $B = 10^3$ (left), $10^{-4}$ (right); $\Delta G^\ddagger(0) = 5$ kcal mol$^{-1}$.

Assuming that the reaction series chosen for study are appropriate in the sense just discussed, i.e., constancy of $A$, $B$, and $\Delta G^\ddagger_{23}(0)$ within each series, the question arises as to the meaning of the variable against which variations in $k_T$ are measured. In terms of the model embodied in eq 3 $\Delta G_{23}$ represents the free energy change upon electron transfer, assuming that the immediate products of the electron transfer are in equilibrium states. If the RX$^{\bullet-}$ radical anion formed in the electron transfer step is bound, then the overall free energy change could be discussed in terms of the thermodynamic energies of RX$^{\bullet-}$ and $^+$Re(CO)$_4$L and the coulombic work term for separation of these products. However, halide radical ions are either only weakly bound or dissociative;[19] thus, halide ion transfer is likely to occur as a concerted process

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with electron transfer. Whether or not $RX^{\bullet -}$ is bound under the reaction conditions, the overall free energy change in the process can be expressed in terms of the potential for oxidation of the radical and the half-wave reduction potential for the organic halide

$$\Delta G_{23} = -23.06E_{1/2} + C \tag{10}$$

where $C$ is a constant that reflects the potential for oxidation of $Re(CO)_4L^{\bullet}$ and other energy terms that should be constant in the series. Substitution of this expression into eq 9 yields a relationship between $k_T$ and $E_{1/2}$ of the same form as eq 9

$$\log k_T = \log k_{12} - \log \left[ 1 + A \exp\left( -\frac{23.06E_{1/2}}{RT} + \frac{C}{RT} \right) \exp\left\{ \frac{\Delta G^{\ddagger}(0)}{RT \ln 2} \ln \left[ 1 + \exp\left( \frac{23.06(\ln 2)E_{1/2}}{\Delta G^{\ddagger}(0)} - \frac{C \ln 2}{\Delta G^{\ddagger}(0)} \right) \right] \right\} + B \exp\left( -\frac{23.06E_{1/2}}{RT} + \frac{C}{RT} \right) \right] \tag{11}$$

Before going on to test a relationship between $k_T$ and $E_{1/2}$ for the organic halides, it must be noted that it is possible to impute a substantially different meaning to $\Delta G_{23}$ in eq 8. This equation can be just as well associated with the reaction model expressed by eq 2. Agmon and Levine have shown how the equation follows from a simple atom transfer mechanism, with no assumption whatever regarding polarity of transition state or electron transfer content.[13] Rather, the emphasis is on the energetics of bond rupture and bond formation processes. In this formulation, as before, the intrinsic barrier, $\Delta G^{\ddagger}(0)$, is the important empirical parameter, assumed to be more or less constant for a series of reactions. The overall free energy barrier, $\Delta G_{23}$, is associated with the difference in bond energies of bonds formed and broken, and other less important contributions to overall energetics. In this formulation, based on the simple BEBO model for atom transfer, as is the Marcus formulation,[12a] the Hammond principle[20] enters naturally; i.e., the loss in bond order in the bond being broken and the gain in bond order in the bond being formed are not large for a strongly exoergic process. Conversely, for strongly endoergic processes, the transition state is late; the atom donor bond is largely broken and the new bond is largely formed.

Given the shift in character of the transition state in proceeding from exoergic to endoergic reactions, what observable property of the reactants should one associate with $\Delta G_{23}$ in correlating $k_T$ in a series of reactions? The bond dissociation energy for the atom donor might be the best single quantity to employ. This is likely to be an imperfect measure, in the sense that the extent of atom donor bond rupture varies as a function of the overall energy change, but the variation should at least be continuous in a series.

## Experimental Section

The preparation of materials and the techniques for use of the $N_2$ laser flash photolysis apparatus have been described previously.[3] It is worth noting that the experimental method employed here is limited in the range of measurable rate constants by the diffusion limit on the upper end and by the competing recombination of the metal-centered radicals on the other. The concentration of halogen donor is varied over the range from $2 \times 10^{-3}$ to 1.5 M to cause the observed rate to fall into the appropriate range. The SHAZAM program was employed for the multivariable, nonlinear regression analysis.[21]

## Results

**Rate Law and Rate Constants.** The reactions of $Re(CO)_4PMe_3^{\bullet}$ and $Re(CO)_4P(O\text{-}i\text{-}Pr)_3^{\bullet}$ with a series of organic halides were carried out in toluene at 22 °C. The halides chosen span a range of C–X bond dissociation energies from 43 to 78 kcal/mol[22] and half-wave potentials from 0.23 to 1.96 V in dioxane/water solvent.[23] Knowledge of the electronic spectra of the $Re(CO)_4L^{\bullet}$ radicals ($\lambda_{max}$ at 550 ± 20 nm)[3a,24] provides a means for following their reactions. The experiments were arranged so that reaction of the radical dominated over recombination. Thus, the halogen atom transfer process determines the character of the transient decay. We have shown elsewhere that the reactions are pseudo-first-order in radical.[3a] A plot of the pseudo-first-order rate constant, $k_{obsd}$, for reaction of a typical radical, $Re(CO)_4PPh_3^{\bullet}$, with $CH_2Br_2$ vs. the $CH_2Br_2$ concentration is linear over the 0.05–1.0 M range, with zero intercept within the error limits, as shown in Figure 2. From the slope of such a graph the bimolecular rate constant is readily calculated. On the basis of these and other results we assume that reactions of the $Re(CO)_4L^{\bullet}$ with all the organic halides studied are first order each in metal carbonyl radical and organic halide. The measured rate constants, listed in Table I, span the range from $7.0 \times 10^4$ to $4.6 \times 10^9$ $M^{-1}$ $s^{-1}$.

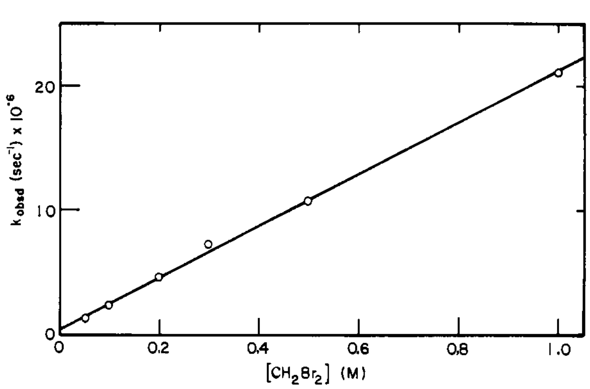

Figure 2. Observed pseudo-first-order rate constants vs. $CH_2Br_2$ concentration in reaction of $Re(CO)_4PPh_3^{\bullet}$ with $CH_2Br_2$ in toluene at 22 °C.

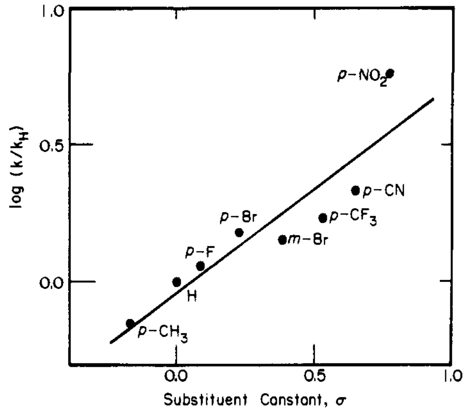

Figure 3. Hammett free energy relationship, $\log (k_X/k_H) = \rho\sigma_X$, for reactions of the $Re(CO)_4P(O\text{-}i\text{-}Pr)_3^{\bullet}$ radical with meta- and para-substituted benzyl bromides in toluene at 22 °C (Table I).

**Reactions with Benzyl Bromide.** A series of meta- and para-substituted benzyl bromides form a subset of the organic halides reacted with $Re(CO)_4P(O\text{-}i\text{-}Pr)_3^{\bullet}$. As shown in Table I, electron-withdrawing groups enhance the rate. The Hammett relationship, $\log k_X/k_H = \rho\sigma_X$, shown in Figure 3, yields a slope $\rho$ of 0.75. The positive sign of the slope is consistent with electron release to the halogen donor in the transition state. It is consistent also with the results of earlier studies that show an enchanced rate constant as the electron-donor properties of L in $Re(CO)_4L^{\bullet}$ increase.[3a] The slope $\rho$ obtained here is somewhat smaller than

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(20) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

(21) SHAZAM, a regression analysis program, was developed by K. J. White, University of British Columbia, Vancouver, B.C., Canada.

(22) *CRC Handbook of Chemistry and Physics*; West, R. C., Ed.; CRC Press, Inc.: Boca Raton, FL, 1985, or the dissociation energies are calculated from $D_{R-X} = \Delta H_f^\circ(R^{\bullet}) + \Delta H_f^\circ(X^{\bullet}) - \Delta H_f^\circ(RX)$. The $\Delta H_f^\circ$ values are taken from the above reference, and references cited therein.

(23) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Marcel Dekker, Inc.: New York, 1970. Half-wave potentials were measured in 75% dioxane/25% water against SCE. The half-wave potentials of substituted benzyl bromides, measured in DMF against Ag/AgBr, were normalized to the other halide values by adding the shift value (−0.54 V) that is based on the comparisons of five organic halides in the two different standard electrodes and media.

(24) Meckstroth, W. K.; Walters, R. T.; Waltz, W. L.; Wojcicki, A.; Dorfman, L. M. *J. Am. Chem. Soc.* **1982**, *104*, 1842.

**Table I.** Halogen Atom Transfer Rate Constants for Reactions of Various Organic Halides and $^\bullet$Re(CO)$_4$L (Units for $k_T$ and [RX] are M$^{-1}$ s$^{-1}$ and M, respectively)

| RX | $-E_{1/2}$ of RX[a] | C–X Bond dissociation energy (kcal/mol)[b] | L = PMe$_3$ | | | L = P(O-*i*-Pr)$_3$ | | |
|---|---|---|---|---|---|---|---|---|
| | | | [RX] | $kT \times 10^{-7}$ | log $k_T$ | [RX] | $k_T \times 10^{-7}$ | log $k_T$ |
| allyl iodide | 0.23 | 43 | 0.0020 | 390 ± 10 | 9.59 | 0.0020 | 200 ± 10 | 9.30 |
| $CBr_4$ | 0.30 | 56 | 0.0020 | 460 ± 10 | 9.66 | 0.0037 | 410 ± 20 | 9.61 |
| $C_2Cl_6$ | 0.62 | 72 | 0.0020 | 200 ± 10 | 9.30 | 0.0020 | 23 ± 1 | 8.36 |
| $CHBr_3$ | 0.64 | 56 | 0.0032 | 470 ± 20 | 9.67 | 0.0092 | 220 ± 20 | 9.34 |
| $\alpha,\alpha,\alpha$-trichlorotoluene | 0.68 | | | | | 0.070 | 4.3 ± 0.1 | 7.63 |
| $CCl_4$ | 0.78 | 70 | 0.0052 | 160 ± 10 | 9.20 | 0.020 | 16 ± 1 | 8.20 |
| 4-nitrobenzyl bromide | 0.80 | | | | | 0.0050 | 71 ± 4 | 8.85 |
| 4-cyanobenzyl bromide | 0.96 | | 0.0098 | 140 ± 10 | 9.15 | 0.020 | 26 ± 1 | 8.41 |
| 4-(trifluoromethyl)benzyl bromide | | | | | | 0.095 | 20 ± 1 | 8.30 |
| 3-bromobenzyl bromide | 1.16 | | 0.0058 | 100 ± 10 | 9.00 | 0.027 | 17 ± 1 | 8.23 |
| 4-bromobenzyl bromide | 1.26 | | | | | 0.031 | 18 ± 1 | 8.26 |
| 4-methylbenzyl bromide | 1.34 | | | | | 0.033 | 8.3 ± 0.3 | 7.92 |
| benzyl bromide | 1.36 | 55 | 0.0084 | 110 ± 10 | 9.04 | 0.030 | 12 ± 1 | 8.08 |
| 4-fluorobenzyl bromide | 1.38 | | | | | 0.050 | 13 ± 1 | 8.11 |
| allyl bromide | 1.21 | 55 | 0.010 | 93 ± 4 | 8.97 | 0.010 | 9.4 ± 0.2 | 7.97 |
| $CH_2Br_2$ | 1.48 | 60 | 0.0070 | 85 ± 4 | 8.93 | 0.050 | 4.7 ± 0.1 | 7.67 |
| $BrCH_2CH_2Br$ | 1.52 | | 0.040 | 11 ± 1 | 8.04 | 0.50 | 0.51 ± 0.03 | 6.71 |
| $CH_3CHBr_2$ | 1.62 | | 0.010 | 51 ± 3 | 8.71 | 0.10 | 0.86 ± 0.03 | 6.93 |
| $CHCl_3$ | 1.67 | 78 | 0.50 | 1.4 ± 0.1 | 7.15 | 0.50 | 0.073 ± 0.002 | 5.86 |
| $\alpha,\alpha$-dichlorotoluene | 1.80 | | 0.31 | 1.9 ± 0.1 | 7.28 | 1.1 | 0.11 ± 0.01 | 6.04 |
| 4-bromobenzonitrile | 1.80 | | 0.50 | 0.058 ± 0.005 | 5.76 | | | |
| allyl chloride | 1.91 | | 1.5 | 0.038 ± 0.002 | 5.58 | | | |
| benzyl chloride | 1.94 | 69 | 0.52 | 0.14 ± 0.01 | 6.15 | 1.5 | 0.0070 ± 0.001[c] | 4.85 |
| 1-bromonaphthalene | 1.96 | | 1.5 | 0.021 ± 0.001 | 5.32 | | | |

[a] Reference 23. [b] Reference 22. [c] Transient decay shows that there is a slight competition from recombination in the transient decay in this system so the real atom transfer rate constant is probably smaller by at most 10%.

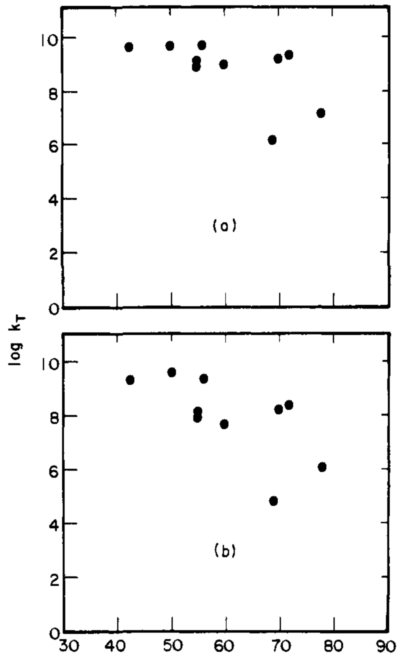

**Figure 4.** log $k_T$ for reactions of Re(CO)$_4$PMe$_3^\bullet$ (a) and Re(Co)$_4$P(O-*i*-Pr)$_3^\bullet$ (b) with organic halides vs. the C–X thermochemical bond energies.

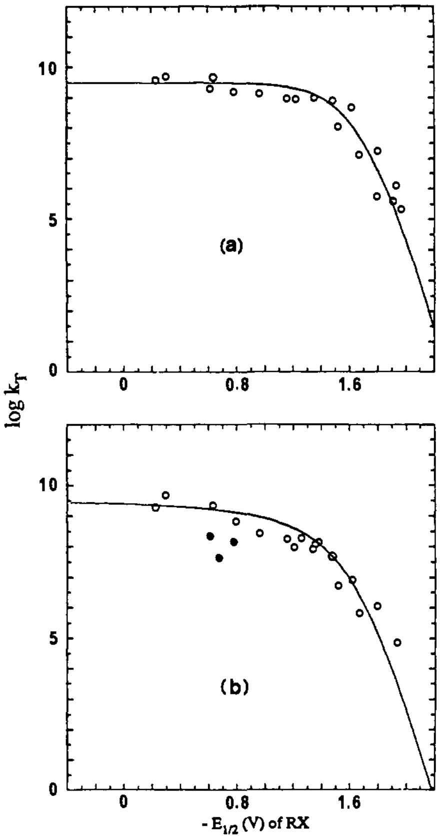

**Figure 5.** log $k_T$ for reactions of Re(CO)$_4$PMe$_3^\bullet$ (a) and Re(CO)$_4$P(O-*i*-Pr)$_3^\bullet$ (b) with organic halides vs. the $E_{1/2}$ values for the halides in 75% dioxane/25% water.[23] The curves through the data are based on eq 11: (a) $A = 1.0$, $B = 2.0$, $C = -40.5$ kcal mol$^{-1}$, $\Delta G^\ddagger(0) = 3.5$ kcal mol$^{-1}$; (b) $A = 1.5$, $B = 2.0$, $C = -38.5$ kcal mol$^{-1}$, $\Delta G^\ddagger(0) = 5.0$ kcal mol$^{-1}$. The closed circles in part b represent data for $CCl_4$, $C_2Cl_6$, and $C_6H_5CCl_3$.

the value of 1.4 for reaction of Co(dimethylglyoximato)$_2$PPh$_3$ in benzene with substituted benzyl bromides.[7b] Hammett correlations of halogen atom transfer reactions of main group metal-centered radicals also exhibit positive $\rho$ values,[10a,25] as does polarographic reduction.[26]

**Tests of the Marcus/Agmon–Levine Equation.** We now consider the relationship of the data to eq 8. If the reaction proceeds as described by eq 2, then there might be a correlation of $k_T$ with the C–X bond dissociation energy, $D$. Bond energy data are not available for all the organic halides studied; the graphs of log $k_T$

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(25) Sakurai, H.; Mochida, K. *J. Organomet. Chem.* **1972**, *42*, 339.

(26) Streitweiser, A., Jr.; Perrin, C. *J. Am. Chem. Soc.* **1964**, *86*, 4938.

vs. $D$ for the available data for both radicals are shown in Figure 4. The correlation is not very good, although there is a generally downward drift in $k_T$ with increasing C–X bond energy.

We next test eq 11, using tabulated values of $E_{1/2}$ for the organic halides in dioxane/water solvent.[23] Figure 5a shows the data for Re(CO)$_4$PMe$_3^\bullet$. The data were fit to eq 11 with use of a nonlinear regression analysis.[21] The line of Figure 5a corresponds to $A$ = 1.0, $B \leq 2$, $C$ = −40.5 kcal mol$^{-1}$, and $\Delta G^{\ddagger}(0)$ = 3.5 kcal mol$^{-1}$. A similar fit of the data for Re(CO)$_4$P(O-*i*-Pr)$_3^\bullet$, shown in Figure 5b, corresponds to $A$ = 1.5, $B \leq 2$, $C$ = −38.5 kcal mol$^{-1}$, and $\Delta G^{\ddagger}(0)$ = 5.0 kcal mol$^{-1}$. The values for $C$ of +1.8 V for Re(CO)$_4$PMe$_3^\bullet$ and +1.7 V for Re(CO)$_4$P(O-*i*-Pr)$_3^\bullet$ are made up largely of the irreversible oxidation potentials for the radicals, but they contain other energy terms as well. Their absolute values mean little; their relative values are in the expected sense, in that the radical with the more electron releasing ligand, PMe$_3$, is oxidized more readily. It is important to note that the values obtained for $\Delta G^{\ddagger}(0)$ are not affected by the fact that we employ irreversible $E_{1/2}$ potentials, so long as all the $E_{1/2}$ potentials are shifted from the reversible values by the same amount. That is, what counts is the *variation* in potentials in the reaction series, rather than the absolute values.

The fit to eq 11 is generally good, particularly for Re(CO)$_4$PMe$_3^\bullet$. The three points in Figure 5b denoted by solid circles correspond to CCl$_4$, CCl$_3$CCl$_3$, and C$_6$H$_5$CCl$_3$, all fully substituted carbon–chlorine centers. We attribute the lower than expected rates in these three cases to steric hindrance, reflected in a lower value for $A$ and perhaps a greater value for $\Delta G^{\ddagger}(0)$. The same effect is presumably not observed in the Re(CO)$_4$PMe$_3^\bullet$ series because the PMe$_3$ ligand is smaller (cone angle 118° vs. 130° for P(O-*i*-Pr)$_3$).[27]

We also tested the experimental data in terms of the Rehm–Weller eq 12[17] as an alternative to eq 8. Not surprisingly, the results are essentially identical in terms of the optimal values for $\Delta G^{\ddagger}(0)$ and $C$, with slightly different values for $A$ and $B$.[16]

$$\Delta G^{\ddagger}_{23} = \frac{\Delta G_{23}}{2} + \left\{\left[\frac{\Delta G_{23}}{2}\right]^2 + [\Delta G^{\ddagger}(0)]^2\right\}^{1/2} \qquad (12)$$

## Discussion

The data of Table I represent the most extensive set of results of which we are aware for testing eq 9 in terms of an atom transfer reaction series. (The approach has, however, been applied to other reaction series with large $\Delta G_{23}$ ranges.[13]) Therefore the fact that the fits shown in Figure 5 are as good as they are is of considerable interest. Several points are worthy of note. First, the quality of the correlations in Figure 5, especially for Re(CO)$_4$PMe$_3^\bullet$, suggests that the assumptions of relative constancy of $\Delta G^{\ddagger}(0)$, $A$, and $B$ are reasonably good ones. Indeed, the departures from the fit in Figure 5b are just those to be expected when variations in steric factors become significant.

The rate constant data reporeted here, coupled with those previously reported for atom transfer reactions of Re(CO)$_4$L$^\bullet$ radicals,[3a] make it evident that there is some measure of polarity in the atom transfer reaction, in the sense that there is a flow of charge from the metal center to the halogen atom donor in the transition state. Beyond this expected result there is a question of whether the reaction is best viewed as a continuous shift in charge with extent of reaction, reflected in eq 2, or as involving a more discrete electron transfer, as described by eq 3. The Marcus/Agmon–Levine equation is equally applicable to either mechanism. The correlations of Figure 5 show that variations in the energetics of the irreversible electrochemical reductions of organic halides parallel variations in the energetics of the atom transfer reaction. One may ask, however, whether this tells us anything about the importance of electron transfer in the process. Saveant and co-workers have recently made important contributions to an understanding of the reduction of aliphatic halides.[19] Their work establishes that heterogeneous electrochemical reduction (a highly irreversible process), or homogeneous reduction by an organic anion, is characterized by intrinsic free energy barriers on the order of 16–24 kcal/mol. In either case the reduction, which can be viewed as a concerted electron transfer–bond breaking process,[19] proceeds without the involvement of an agent that acts as a halogen atom or halogen ion acceptor. In such a situation the transition state is likely to involve a considerable stretching of the C–X bond.[28] Saveant and co-workders note that formally analogous processes involving low-valent metals are in many cases several orders of magnitude faster than more clearly outer-sphere electron-transfer reactions (e.g., reduction by aromatic radical anion) of comparable driving force.[29] The results presented here clearly reinforce the distinction in the two types of processes; we observe intrinsic free energy barriers on the order of 3.5–5 kcal/mol, as contrasted with values in the range 16–24 kcal/mol for the reductions via organic anions. The fit of the data by the Marcus/Agmon–Levine equation, using $E_{1/2}$(red) values, suggests that the atom transfer reaction involving Re(CO)$_4$L$^\bullet$ radicals can be viewed as a facilitated electron transfer–bond cleavage process. The involvement of the rhenium center in bond formation with the halogen may provide free energy stabilization and promote early electron transfer, with a resulting substantial reduction in the overall free energy barrier. It is significant that $\Delta G^{\ddagger}(0)$ is not large for either reaction series, suggesting that configurational changes in reactants required to attain the transition state are not large, or that they largely compensate. The fact that $\Delta G^{\ddagger}(0)$ is larger for Re(CO)$_4$P(O-*i*-Pr)$_3^\bullet$ than for ReCO)$_4$PMe$_3^\bullet$ can be ascribed to the larger size of P(O-*i*-Pr)$_3$ as compared with PMe$_3$.[27] The presence of the large substituent on Re would increase the free energy barrier to attainment of the optimal arrangement of atom donor and acceptor in the transition state.

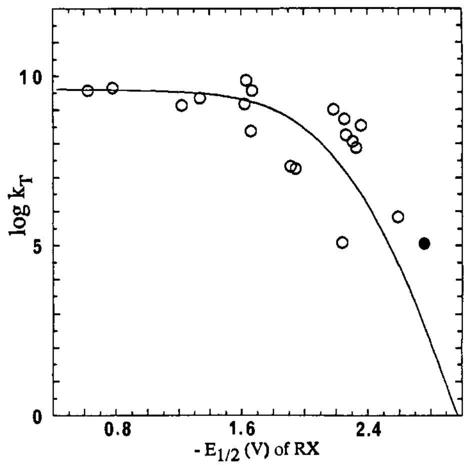

**Figure 6.** log $k_T$ for reactions of Et$_3$Si$^\bullet$ radicals[11a] with organic halides vs. $E_{1/2}$ values for the halides in 75% dioxane/25% water.[23] The closed circle and the matching point at the same value of log $k_T$ represent alternative values for the reduction potential of CH$_3$Cl. (Reference 23 and the following: Meites, L.; Zuman, P.; Rupp, E. *CRC Handbook Series in Organic Electrochemistry*; CRC Press, Inc.: Boca Raton, FL, Vol. III.)

The successful application of eq 9 to the atom transfer reactions of the rhenium radicals suggests that it might be applicable to the halogen and hydrogen atom transfer reactions of other metal-centered radicals, including both main group as well as transition metals, and including other metal carbonyl radicals.[3b,24,30] Unfortunately, the requisite data are not generally available to

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(27) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(28) Eberson, L. *Acta Chem. Scand.* **1982**, *B36*, 533.

(29) Reference 19a, footnote 20.

(30) (a) Waltz, W. L.; Hackelberg, O.; Dorfman, L. M.; Wojcicki, A. *J. Am. Chem. Soc.* 1978, *100*, 7259. (b) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 1258. (c) Fox, A.; Malito, J.; Poe, A. *J. Chem. Soc., Chem. Commun.* **1981**, 1052. (d) Laine, R. M.; Ford, P. *Inorg. Chem.* **1977**, *16*, 388. (e) Yesaka, H.; Kobayashi, T.; Yasufuku, K.; Nagakura, S. *J. Am. Chem. Soc.* **1983**, *105*, 6249. (f) Hughey, J. L.; Bock, C. B.; Meyer, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 4440. (g) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065. (h) Abrahamson, H. B.; Wrighton, M. S. *J. Am. Chem. Soc.* **1977**, *99*, 5510; *Inorg. Chem.* **1978**, *17*, 1003.

evaluate the intrinsic barriers for a properly chosen reaction series. Ingold and co-workers have reported the rate constants for reactions for $Et_3Si^\bullet$ radicals with several organic halides.[11a] Figure 6 shows a graph of log $k_T$ vs. the half-wave potenials of the halides. The curve through the data is drawn by using eq 11, with $A$ = 0.5, $B$ = 0.5, C = −57 kcal mol$^{-1}$ (−2.5 V), and $\Delta G^{*}(0)$ = 6.0 kcal mol$^{-1}$. Although the fit to the experimental results is not as good as that for the metal carbonyl radicals, it looks promising. It is noteworthy that the Arrhenius parameters (log $A$) vary in the order $CCl_4$, 10.2 ($E_{1/2}$ = −0.78 V); $C_6H_5CH_2Cl$, 8.9 ($E_{1/2}$ = −1.94 V); and $CH_3Cl$, 8.0 ($E_{1/2}$ = −2.76 V). The relationship suggests a tighter and more restricted transition state as the reaction becomes more endoergic, consistent with increased C–Cl bond rupture and Si–Cl bond formation.

## Conclusions

The results reported here provide the first opportunity to test the applicability of the Marcus/Agmon–Levine equation, eq 8, or the Rehm–Weller equation, eq 12, with a significant body of experimental data for halogen atom transfer. For two reaction series involving rhenium carbonyl radicals the results are quite good. This suggests that the atom transfer processes under study conform to the assumptions of the model, most notably, that the intrinsic barrier for the reaction is comparatively constant as the halogen donor is varied. Second, the fact that log $k_T$ correlates with the irreversible half-wave reduction potentials for the organic halides suggests that electron transfer plays a significant role in the reaction. The fit of the data to eq 11 suggests also that a single value of $\Delta G^{*}(0)$ applies to reactions that range from strongly exoergic (−25 kcal mol$^{-1}$) to mildly endoergic (+5 kcal mol$^{-1}$).

Aside from the extent to which electron transfer is important in the atom transfer process, the fact that the data can be fitted by eq 11 is important. The basic assumptions regarding atom transfer processes embodied in eq 8 provide a useful basis on which to understand the effect of variations in both atom donor and metal carbonyl radical on the atom transfer rate constant. Further, eq 8 provides a means for relating the atom transfer reactions of the radicals to other, more obviously outer-sphere type electron transfer reactions of the radicals.[31]

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[31] Rushman, P.; Brown, T. L. *J. Am. Chem. Soc.*, in press.

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# Photochemistry of $Fe(CO)_5$ Adsorbed onto Porous Vycor Glass

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**Abstract:** $Fe(CO)_5$ physisorbs onto porous Vycor glass without disruption of its primary coordination sphere. The spectral properties of the adsorbed complex mirror those found in fluid solution, and UV photolysis in vacuo leads to formation of the tetracarbonyl with a quantum yield of unity. The tetracarbonyl rapidly reacts with the PVG surface and chemisorbed water to form the spectrally distinct, oxidative addition products H–$Fe(CO)_4$–OSi and H–$Fe(CO)_4$–OH. These undergo secondary photolysis to form, depending on the initial loading, either elemental iron or the trimeric cluster $Fe_3(CO)_{12}$. Diffuse reflectance FTIR spectra, recorded after CW or pulsed laser excitation, establish the presence of dimeric and trimeric intermediates. Trapping experiments with CO and trimethylphosphine indicate a photochemically driven, stepwise reaction sequence in which the so-called "mobile intermediate", principally $Fe(CO)_3$, reacts with H–$Fe(CO)_4$–OH and $Fe(CO)_5$(ads) to form dimeric and trimeric products.

Hybrid catalysts composed of supported transition-metal carbonyls offer advantages of both homogeneous and heterogeneous catalysts.[1] Iron carbonyl, for example, has been examined on a number of supports[1] because of its catalytic activity in homogeneous solution.[2,3] Whether in solution or confined to a support, catalytic activity of the complex requires vacant or labile reaction sites where the substrate can bind and undergo chemical transformation.[4–6] In most cases, but particularly those involving hybrid systems, the complex is thermally activated.

$Fe(CO)_5$ physisorbs onto HY zeolite with a heat of adsorption of 2 kcal/mol.[7] Changes in the $^{13}C$ chemical shift and line width indicate that thermal decomposition of the complex, which occurs stepwise with an increasing, but weak interaction with the surface, leads to highly dispersed, atomic iron.[7] Adsorption of mono- and polynuclear iron carbonyls onto dehydrated HY zeolites, however, differs.[8] Adsorption of $Fe(CO)_5$ and $Fe_2(CO)_9$ occurs with the evolution of CO and results in identical adsorbate IR spectra, the latter being superimposed spectra of $Fe(CO)_5$ and $Fe(CO)_4Q$ where Q represents a lattice oxygen of the support.[8] Evacuation at 60 °C causes further CO evolution and formation of $Fe_3(CO)_{12}$.[8] Adsorption of $Fe_3(CO)_{12}$, on the other hand, occurs without CO evolution, and the IR spectrum of the adsorbed trimer is similar to that in fluid solution.[8] Nevertheless, changes in the spectrum of the zeolite and low-frequency shifts of the bridging $\nu_{CO}$ bands suggest the formation of a Lewis acid adduct where the bridging CO's interact with surface hydroxyls of the zeolite supercage. Thermal activation of the adsorbed trimer leads to decarbonylation. $H_2$ and $CO_2$ evolution, which occurs at 200 °C, is followed by $CH_4$ evolution at 250 °C.[8]

Thermal activation $Fe(CO)_5$ adsorbed onto Grafoil, a high surface area, oriented graphite support, causes CO evolution and formation of metallic iron preferentially at the edges or other dislocations in the graphite structure.[9] $Fe(CO)_5$ and $Fe_3(CO)_{12}$ reversibly adsorb onto hydroxylated silicas, whereas adsorption onto alumina, magnesia, and zinc oxide is irreversible due to

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[1] Bailey, D. C.; Langer, S. H. *Chem. Rev.* **1981**, *81*, 109–148.

[2] Wender, I.; Pino, P. *Organic Synthesis Via Metal Carbonyls*; Interscience: New York, 1968.

[3] Taqui Khan, M. M.; Martell, A. E. *Homogeneous Catalysis in Metal Complexes*; Academic: New York, 1974; Vols. 1 and 2.

[4] Nakamura, A.; Tsutsui, M. *Principles and Applications of Homogeneous Catalysis*, Wiley: New York, 1980; pp 24–25.

[5] Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980; pp 5–21.

[6] Slocum, D. W.; Hughes, O. R. *Ann. N.Y. Acad. Sci.* **1980**, *53*.

[7] Nagy, N. B.; Eenoo, M. V.; Derouane, E. G. *J. Catal.* **1979**, *58*, 230–7.

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[‡] Dow Chemical Company.

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