A Marcus-type model for steric and electronic effects of ligands in atom transfer reactions of metal carbonyl radicals

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Abstract

The rate constants for reaction of a series of $Re(CO)_4L$ (L=CO, PR_3, $P(OR)_3$) radicals with various atom or functional group donors in hexane at room temperature have been measured using laser flash photolysis. The data in each series have been analyzed in terms of the linear free energy relationship, $\ln k = aE_i + bS_i + c$, where E_i represents a measure of the donor character of ligand L (the ^{13}C chemical shift of the CO groups in $LNi(CO)_3$), and S_i represents a measure of its steric requirement (the ligand repulsive energy parameter, E_R). Expressing the atom or group transfer process in terms of the Marcus model for atom transfer, the variation in electron donor–acceptor character of L is related to variation in the overall free energy change in the atom transfer step, $\Delta G^{\circ\prime}$. The variation in ligand steric requirement is related to variation in the intrinsic barrier for the process, $\Delta G^*(0)$. The model leads to a new prediction: for a group of related reaction sets, such as the atom transfer reactions of the $Re(CO)_4L$ radicals, the ratio a/b decreases monotonically with increasing exergonic character. That is, the relative sensitivity of the rate to variation in the electronic character of the ligand as compared with variation in its steric character decreases as the reaction becomes more exergonic. The predicted behavior is in good agreement with the experimental results for the large body of atom and group transfer data presented.

Introduction

Ligand effects have long been recognized as important in organometallic chemistry. The steric and electronic properties of phosphines, amines, sulfides, isocyanides and many other classes of ligands materially affect the reactivities of metal centers to which they are bound. Ligands play important roles in modifying the reactivities and selectivities of catalysts in many processes of commercial importance. The use of phosphines to modify the properties of cobalt carbonyl catalysts in hydroformylation provides one of the earliest examples [1]. More recently, the use of $P(C_6H_4SO_3)_3^{3-}$ as a ligand in rhodium-based hydroformylation catalysis has led to extremely effective and selective catalytic systems [2].

Despite the generally recognized importance of ligand effects, systematic treatments of the effects of ligands on reactivity and selectivity have been comparatively few. Linear free energy relationships involving ligand effects, analogous to those employed in treating substituent effects in organic chemistry, have been put forth only within the past 20 years [3–13], and still do not enjoy widespread use. In part this situation has arisen because ligand effects in organometallic chemistry are varied, and arise in many contexts which are difficult

to interrelate. Secondly, the basis for choosing appropriate ligand parameters has not been clear.

It is generally accepted that the effects of ligands and substituents can be considered to consist of separable electronic and steric parts [14]. Each of these in turn might be considered to embrace more than a single parameter [15, 16]. For example, the electronic term might be separated into σ and π components, and the π component in turn into π-donor and π-acceptor terms. Among the potential difficulties in defining multiple parameters is that the experimental data may not be extensive or accurate enough to justify their use. Further, the parameters themselves, however they are obtained, contain inherent uncertainties that limit their statistical significances.

The linear free energy approximation expressed in eqn. (1)

$$\ln k = aE_i + bS_i + c \tag{1}$$

affords the simplest and most widely applicable approach to treating ligand effects [3–13]. Ln k (or $\ln K_{eq}$), which is proportional to the free energy of activation (or free energy change), is expressed as the sum of contributions attributable to ligand electronic and steric properties. The quantities E_i and S_i represent the electronic and steric parameters for the ith ligand, respectively. The coefficients a and b represent the sensitivities of $\ln k$

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to variations in the electronic and steric parameters, respectively. The constant c can be thought of as $\ln k$ for a hypothetical ligand with zero values of the electronic and steric parameters. In the application of eqn. (1) to a reaction set, the ligands may be reagents, as in substitution process in which the ligand is the attacking reagent, or the displaced group. Alternatively, they may be involved as 'spectator' ligands; the ligand is bound to the metal center at which reaction occurs, or is a component of the attacking reagent.

Only recently has eqn. (1) (or extensions of it) been applied systematically to the treatment of kinetics and equilibrium data. Furthermore, there has not been general agreement on the choices of ligand parameters to be employed. We have recently developed a new measure of ligand steric requirements, the ligand repulsive energy, E_R, based on molecular mechanics calculations [17]. Using either E_R or Tolman's cone angle, Θ [18] as the S_i parameter, and Bodner's δ parameter (based on the ^{13}C chemical shift of the CO groups in $LNi(CO)_3$ compounds) as the electronic parameter [19], eqn. (1) has been applied to a large body of substitution and other kinetics data. The uniform application of a simple linear free energy relationship affords the opportunity to examine the variations in coefficients a, b and c among reactions to discern regularities that would otherwise not be evident.

In this contribution we discuss the effects of ligands L on atom transfer rates for metal carbonyl radicals, $M(CO)_mL_n$. Following a brief review of the overall trends in these reactions, we present an extensive body of data for the rates of atom transfer reactions of $Re(CO)_4L$ radicals, and apply eqn. (1) to their analysis and interpretation. The analysis reveals that the relative sensitivity of the reactions to ligand electronic and steric effects varies in a regular way with the ergonicity of the reaction for the reference compound in each series. This regular variation, which has heretofore not been noticed, can be understood in terms of a Marcus-type model for the atom transfer process.

Atom transfer reactions of metal carbonyl radicals

The extensive data accumulated to date on the atom transfer reactions of metal carbonyl radicals illustrate several important systematic effects of ligands [20]. By way of illustration, Table 1 lists the rate constants for the rates of chlorine atom transfer upon reaction of $Mn(CO)_{5-n}L_n$ ($n = 0, 1, 2$) with CCl_4 in hydrocarbon solution [21]. All these reactions were conducted under essentially equivalent reaction conditions. The results show that the atom transfer process is generally quite fast. The rate increases upon replacement of CO by the moderately bulky $P(n\text{-}Bu)_3$, indicating that the more

TABLE 1. Rate constants for chlorine atom transfer in reactions of $Mn(CO)_{5-n}L_n$ radicals with CCl_4 in hexane

Radical	k_T (M^{-1} s^{-1})
$Mn(CO)_5$	1.4×10^6
$Mn(CO)_4P(n\text{-}Bu)_3$	1.8×10^6
$Mn(CO)_4P(i\text{-}Bu)_3$	8.9×10^4
$Mn(CO)_4P(C_6H_{11})_3$	2.0×10^4
$Mn(CO)_4P(i\text{-}Pr)_3$	2.8×10^4
$Mn(CO)_4P(O\text{-}i\text{-}Pr)_3$	2.2×10^4
$Mn(CO)_3[P(i\text{-}Bu)_3]_2$	3.0×10^4
$Mn(CO)_3[P(i\text{-}Pr)_3]_2$	1.0×10^3

strongly donor character of the phosphine relative to CO results in an increased rate. On the other hand, the trend in rate constants among the phosphines in the $Mn(CO)_4L$ series clearly shows that increasing steric requirement of the ligand slows the reaction.

Table 2 lists the rate constants for the atom transfer reactions of a selected set of $Re(CO)_4L$ radicals with a wide range of atom donors in hexane solvent. The ligands in the series were chosen to provide a wide range of values for both the electronic and steric parameters of the ligands; the ligand parameter values are listed in Table 3. The atom transfer rate data shown in Table 2 are the most extensive body of related, ligand-dependent reaction rate data available. Each data set was subjected to multivariate least-squares analysis using eqn. (1), with δ as the electronic parameter and E_R as the steric parameter [17]. Figure 1 shows the correlation of the rate constants for bromine atom transfer for the $Re(CO)_4L$ set with benzyl bromide, using eqn. (1). The correlation coefficient $r = 0.95$, with $a = 0.50$ and $b = -0.059$. The positive value for a indicates that the reaction rate increases with increasing electron release from the ligand; the negative value for b indicates that increasing steric requirement of the ligand results in a lower rate constant. The results of linear least-squares analysis for all the data in Table 2 are given in Table 4. In carrying out the correlation analyses, atom transfer rate constant values 1×10^9 or greater were corrected for diffusion, to yield the activated rate constant, k_{act}, using the expression, $k_{act}^{-1} = k_T^{-1} - k_{diff}^{-1}$, where k_{diff} is estimated as 1.1×10^{10} [10]. The corrections have only minor effects on the resulting values of a and b.

A Marcus-type model for atom transfer

It is instructive to consider the atom transfer process in terms of a Marcus-type model, i.e. one in which the free energy of activation in the rate-determining elementary step is treated as a function of a thermodynamic component, the overall free energy change in the pro-

TABLE 2. Atom and group transfer rate constants[a] for reactions of $Re(CO)_4L$ radicals in hexane at 22 °C

Donor	Ligand							
	CO	PMe$_3$	P(OMe)$_3$	P(O-i-Pr)$_3$	P(n-Bu)$_3$	P(i-Bu)$_3$	P(i-Pr)$_3$	PCy$_3$
CH$_2$CHCH$_2$I[b]	66	66	40	30	37	15	16	
CCl$_4$[c]	0.49	32	3.3	2.0	7.6	0.8	0.9	0.7
CH$_2$Br$_2$[c]	0.48	21	1.5	0.81	3.9	0.27	0.14	0.15
C$_6$H$_5$I[d]	0.55	12	0.73	0.37	1.6	0.22	0.18	0.12
CH$_3$I[d]	6.3	36	7.4	3.3	18	1.6	0.75	0.49
CHCl$_3$[c]	4.4×10^{-3}	0.21	0.015	9.3×10^{-3}	0.054	4.5×10^{-3}	4.0×10^{-3}	3.0×10^{-3}
C$_6$H$_5$CHCl$_2$[d]	0.038	0.41	0.086	0.012	0.12	9.0×10^{-3}	0.011	4.8×10^{-3}
C$_6$H$_5$CH$_2$Br[d]	8.2	23	4.0	1.8	4.9	0.67	0.66	0.39
4-NCC$_6$H$_4$CH$_2$Br[d]	13	36	11	5.7	14	2.9	3.2	1.8
4-CH$_3$C$_6$H$_4$CH$_2$Br[d]	10	22	4.8	1.9	5.7	0.71	0.80	0.44
4-BrC$_6$H$_4$CH$_2$Br[d]	10	29	6.7	3.8	7.7	1.6	1.5	0.92
4-CF$_3$C$_6$H$_4$CH$_2$Br[d]	8.3	27	7.3	4.0	9.1	1.2	1.5	0.92
(n-Bu)SS(n-Bu)[e]	0.14	3.7	0.27	0.078	0.82	0.047	0.016	0.012
PhSSPh[d]	11	16	4.7	3.0	4.8	1.6	2.0	0.55
(p-tolyl)SS(p-tolyl)[d]	11	19	5.9	2.9	6.1	1.8	2.0	1.1
Me$_3$SiSMe[e]	6.0×10^{-3}	0.093	9.5×10^{-3}	4.7×10^{-3}	0.017	2.2×10^{-3}	1.0×10^{-3}	7.1×10^{-4}
HSnBu$_3$[c]	0.51	1.7	0.64	0.15	0.51	0.053	0.013	0.041
Benzylthiocyanate[d,f]	0.72	1.2	0.41	0.17	0.33	0.062	0.028	0.012

[a] ×10^8 M^{-1} s^{-1}. [b] R. Menon and T. L. Brown, unpublished results. [c] Ref. 10. [d] This work. [e] Ref. 13. [f] Toluene.

TABLE 3. Ligand parameters

Ligand	δ[a]	Θ[b]	E_R[c]
CO	0	95	7
PMe$_3$	5.05	118	39
P(OMe)$_3$	3.18	107	52
P(O-i-Pr)$_3$	3.90	130	74
P(n-Bu)$_3$	5.69	132	64
P(i-Bu)$_3$	5.40	143	83
P(i-Pr)$_3$	6.20	160	109
P(C$_6$H$_{11}$)$_3$	6.32	170	116

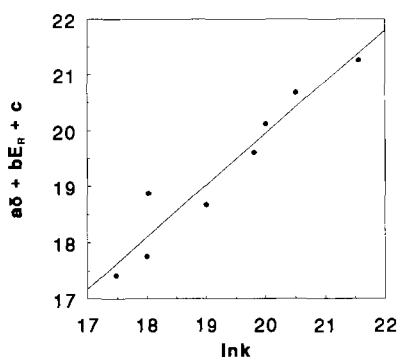[a] ^{13}C chemical shift in LNi(CO)$_3$ [19]. [b] Cone angle (°) [18]. [c] Ref. 17.

Fig. 1. Linear free energy correlation of the rate constants for bromine atom transfer in the reactions of $Re(CO)_4L$ radicals with benzyl bromide, based on eqn. (1).

cess, and a kinetic component, the intrinsic free energy barrier [22, 23]. Marcus developed a model for atom or proton transfer, based on a simplified bond en-ergy–bond order model for the reaction process [24]. Agmon and Levine showed later that the same expression arises from a general treatment in which a mixing function has a particular form, and depends smoothly on the degree of advancement of the reaction in proceeding from reactants to products [25–27].

Consider the atom transfer process described by eqn. (2).

$$A-B+C \rightleftharpoons \{A-B\cdots C\} \rightleftharpoons$$
$$\{A\cdots B-C\} \rightleftharpoons A+B-C \quad (2)$$
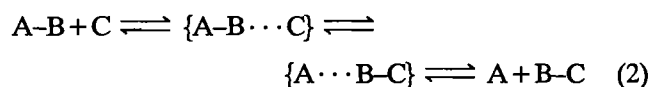
The first equilibrium involves formation of the encounter complex. The second involves the rate-determining atom transfer step. The third describes the encounter complex equilibrium involving the products. The following definitions apply:

ΔG^*_s is the free energy of activation for the atom transfer process in solution. $\Delta G^*_s = \Delta G^* + w_r$, where w_r is the work term associated with formation of the encounter complex of reactants, and ΔG^* is the free energy of activation for the atom transfer process in the encounter complex.

$\Delta G^*(0)$ is the intrinsic barrier for the hypothetical ergoneutral atom transfer process in the encounter complex. $\Delta G_{AA}^*(0)$ and $\Delta G_{CC}^*(0)$ refer to the free energies of activation for the identity reactions, $A-B+A \rightarrow A+B-A$, and $C-B+C \rightarrow C+B-C$, respectively.

$\Delta G^{o\prime}$ represents the overall free energy change in the atom transfer reaction, under the prevailing conditions of temperature, concentration and pressure.

TABLE 4. Linear free energy parameters for atom or group transfer reactions of $Re(CO)_4L$ radicals

Compound	a	$-b$	c	r[a]	$-E_{1/2}$[b]	a/b
CH_2CHCH_2I	0.14	0.028	23.4	0.93	0.23	5.0
CCl_4	1.10	0.066	18.8	0.89	0.78	16.6
CH_2Br_2	1.12	0.082	18.9	0.92	1.48	13.7
C_6H_5I	0.92	0.071	18.6	0.95	1.62	13.0
CH_3I	0.81	0.073	21.2	0.96	1.63	11.1
$CHCl_3$	1.07	0.069	13.9	0.93	1.67	15.5
$C_6H_5CHCl_2$	0.84	0.070	16.0	0.94	1.80	12.0
$C_6H_5CH_2Br$	0.50	0.059	21.1	0.95	1.36	8.5
$4\text{-}NCC_6H_4CH_2Br$	0.51	0.049	21.5	0.95	0.96	10.4
$4\text{-}CH_3C_6H_4CH_2Br$	0.49	0.059	21.3	0.96	1.34	8.3
$4\text{-}BrC_6H_4CH_2Br$	0.49	0.052	21.3	0.95	1.26	9.4
$4\text{-}CF_3C_6H_4CH_2Br$	0.52	0.053	21.2	0.93	1.24	9.8
$(n\text{-}Bu)SS(n\text{-}Bu)$	1.12	0.092	17.6	0.97	1.50	12.2
PhSSPh	0.29	0.042	21.3	0.95	1.18	6.9
(p-tolyl)SS(p-tolyl)	0.33	0.041	21.2	0.96	1.17	8.0
Me_3SiSMe	0.86	0.073	14.3	0.95		11.8
$HSnBu_3$	0.53	0.064	18.7	0.91		8.3
$C_6H_5CH_2SCN$	0.39	0.061	19.0	0.97		6.4

[a]Correlation coefficient.   [b]Volts, relative to SCE, 75% dioxane/25% water.

$\Delta G^\circ_R{}'$ represents the free energy change in the atom transfer process occurring in the encounter complex. $\Delta G^{\circ\prime} = \Delta G^\circ_R{}' + w_r - w_p$, where w_p is the work term associated with separation of products.

The reactions under consideration here occur in nonpolar solvents, and involve neutral reactants and products. It is therefore possible to neglect the work terms. Not only are they small, their variation with changes in ligand steric and electronic characteristics will be small with respect to other changes in the free energy terms [29]. Under these circumstances the Marcus expression for the free energy of activation in the atom transfer reaction is given by eqn. (3).

$$\Delta G^* = \Delta G^{\circ\prime} + \frac{\Delta G^*(0)}{\ln 2} \ln[1 + \exp(-\Delta G^{\circ\prime} \ln 2/\Delta G^*(0))]$$

(3)

Through eqn. (4) we can relate the rate constant to the components of the Marcus expression:

$$k = (k_B T/h) \exp(-\Delta G^*/RT)$$

(4)

$$\ln k = \ln(k_B T/h) - \Delta G^*/RT$$

(5)

$$\ln k = \frac{-\Delta G^{\circ\prime}}{RT}$$
$$- \frac{\Delta G^*(0)}{RT \ln 2} \ln\left[1 + \exp\left(\frac{-\Delta G^{\circ\prime} \ln 2}{\Delta G^*(0)}\right)\right] + \ln(k_B T/h)$$

(6)

Our task is now to relate the coefficients of eqn. (1) to the variables of eqn. (6). To do this we first consider

a simple, qualitative model for how ligand steric and electronic effects relate to the thermodynamic and kinetic components of the free energy of reaction. A schematic sketch of the atom transfer process is shown in Fig. 2. The center A to which B is initially bound, has other groups bound to it which interact with other groups bound to C, the center to which B is being transferred. One of the groups bound to A is the ligand L, which exerts both electronic and steric effects. The electronic effect is expressed in terms of the extent to which L affects the electronic charge on A, regardless of whether the effect is exerted through σ or π bonds. In general, the charge on A affects the energy of the A–B bond. A variation in the extent of electron donation from L will thus have an effect on the overall free energy change, $\Delta G^{\circ\prime}$, as shown in Fig. 3. It will not, however, substantially affect the intrinsic barrier, $\Delta G^*(0)$.
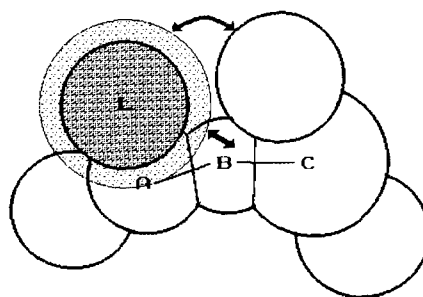

Fig. 2. A schematic illustration of the transition state in an atom transfer process. An increase in ligand steric requirement results in increased steric repulsive interactions with the atom acceptor, C, thus producing a looser transition state with higher $\Delta G^*(0)$.
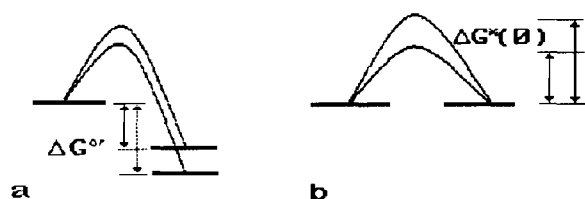
Fig. 3. Schematic of the energy profile for the atom transfer process. In (a), the variation in ligand donor character results in variation in the overall free energy change, $\Delta G^{o\prime}$. In (b), variation in ligand size results in variation in the intrinsic barrier, $\Delta G^*(0)$.

If one assumes that $\Delta G^*(0)$ can be expressed as $(\Delta G_{AA}{}^*(0) + \Delta G_{CC}{}^*(0))/2$ [23], a variation in the ligand donor character would affect only $\Delta G_{AA}{}^*(0)$. If, for example, an increase in electron donation from L resulted in a stronger A–B bond, $\Delta G_{AA}{}^*(0)$ might be expected to increased by about 10 to 15% of the increase in A–B bond energy [24, 28, 29]. Inasmuch as this increase is diluted by a factor of 2, the effect on $\Delta G^*(0)$ will clearly be small in comparison with the change in $\Delta G^{o\prime}$.

An increase in the steric requirement of L causes an increase in the steric repulsions between L and the groups bound to C. If we assume that the steric effects of L are more important in the crowded activated complex, the effects of an increase in the size of L on the energetics of formation of the activated complex will be larger than the effects on the reactant molecule A–B or product A. To the extent that an increase in steric requirement of L impedes formation of the activated complex, it contributes to a 'looser' transition state [30], and thus to an increase in the intrinsic barrier, $\Delta G^*(0)$, as illustrated in Fig. 3. Again, using the approximation that $\Delta G^*(0) = (\Delta G_{AA}{}^*(0) + \Delta G_{CC}{}^*(0))/2$, the increase in size of L would markedly affect the value of $\Delta G_{AA}{}^*(0)$, since L is present in both the atom donor and atom acceptor fragments. The effect of L on $\Delta G_{AA}{}^*(0)$ would, to first order, be about twice as large as the effect exerted on the cross-reaction.

Thus, in terms of this simple approach, a change in the donor–acceptor character of L affects the thermodynamic component of the free energy of activation, i.e. the overall free energy change in the reaction, $\Delta G^{o\prime}$. A change in the steric requirement of L affects the kinetic component of the free energy of activation, the intrinsic barrier, $\Delta G^*(0)$. The same arguments would apply if L were part of C, the atom acceptor in eqn. (2).

We next obtain the partial derivatives of $\ln k$ with respect to $\Delta G^{o\prime}$ and $\Delta G^*(0)$:

$$\frac{\partial \ln k}{\partial \Delta G^{o\prime}} = \frac{-1}{RT} + \frac{\exp(-\Delta G^{o\prime} \ln 2/\Delta G^*(0))}{RT[1 + \exp(-\Delta G^{o\prime} \ln 2/\Delta G^*(0))]} \quad (7)$$

$$\frac{\partial \ln k}{\partial \Delta G^*(0)} = \frac{-\ln}{RT \ln 2}[1 + \exp(-\Delta G^{o\prime} \ln 2/\Delta G^*(0))]$$

$$- \frac{\Delta G^{o\prime} \exp(-\Delta G^{o\prime} \ln 2/\Delta G^*(0))}{\Delta G^*(0)[1 + \exp(-\Delta G^{o\prime} \ln 2/\Delta G^*(0))]} \quad (8)$$

The partial derivatives of $\ln k$ in eqn. (1) with respect to $\Delta G^{o\prime}$ and $\Delta G^*(0)$ can be obtained similarly. The assumptions of the simple model described above lead to:

$$\frac{\partial \ln k}{\partial \Delta G^{o\prime}} = a\left(\frac{\partial E_i}{\partial \Delta G^{o\prime}}\right) \quad (9)$$

$$\frac{\partial \ln k}{\partial \Delta G^*(0)} = b\left(\frac{\partial S_i}{\partial \Delta G^*(0)}\right) \quad (10)$$

Thus, the coefficients of the linear free energy relationship (1) can be expressed in terms of the variables in the Marcus-type model for atom transfer:

$$a = \frac{\partial \Delta G^{o\prime}}{\partial E_i}$$
$$\times \left[\frac{-1}{RT} + \frac{\exp(-\Delta G^{o\prime} \ln 2/\Delta G^*(0))}{RT[1 + \exp(-\Delta G^{o\prime} \ln 2/\Delta G^*(0))]}\right] \quad (11)$$

$$b = \frac{\partial \Delta G^*(0)}{\partial S_i}\left[\frac{-\ln}{RT \ln 2}[1 + \exp(-\Delta G^{o\prime} \ln 2/\Delta G^*(0))]\right]$$

$$- \left[\frac{\Delta G^{o\prime} \exp(-\Delta G^{o\prime} \ln 2/\Delta G^*(0))}{\Delta G^*(0)[1 + \exp(-\Delta G^{o\prime} \ln 2/\Delta G^*(0))]}\right] \quad (12)$$

Assuming that E_i and S_i can be treated as continuous functions, the derivatives $\partial \Delta G^{o\prime}/\partial E_i$ and $\partial \Delta G^*(0)/\partial S_i$ should be continuous. Their values will be roughly constant for any particular reaction system, but will vary from one reaction type to another. For example, their values should be approximately constant for the atom transfer reactions of $Re(CO)_4L$ radicals with a variety of atom donors. However, we do not know what these values are, in the absence of a specific model for the atom transfer process that incorporates the steric and electronic effects of L.

Even when the specific values for $\partial \Delta G^{o\prime}/\partial E_i$ and $\partial \Delta G^*(0)/\partial S_i$ are not known, the model leads to an important prediction regarding the ratio a/b, given in eqn. (13).

$$\frac{a}{b} = \left(\frac{\partial \Delta G^{o\prime}}{\partial E_i}\right)\left(\frac{\partial \ln k}{\partial \Delta G^{o\prime}}\right)\bigg/\left(\frac{\partial \Delta G^*(0)}{\partial S_i}\right)\left(\frac{\partial \ln k}{\partial \Delta G^*(0)}\right) \quad (13)$$

Assuming that the ratio $(\partial \Delta G^{o\prime}/\partial E_i)/(\partial \Delta G^*(0)/\partial S_i)$ is a constant, κ, for a given class of related reactions, a/b takes the form
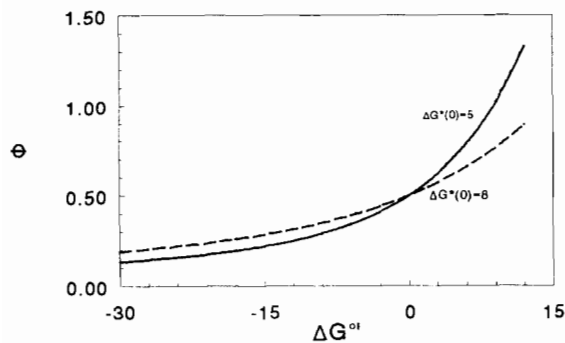
Fig. 4. Variation in Φ (see eqn. (15)), with $\Delta G^{\circ\prime}$ for constant values of $\Delta G^*(0)$ (kcal mol^{-1}).

$$\frac{a}{b} = \kappa\Phi \tag{14}$$

where Φ is the ratio $(\partial \ln k/\partial\Delta G^{\circ\prime})/(\partial \ln k/\partial\Delta G^*(0))$:

$$\Phi = \frac{2^y\Delta G^*(0)\ln 2}{\Delta G^*(0)\ln(2^y+1)-2^y(\Delta G^{\circ\prime}\ln 2 - \Delta G^*(0)\ln(2^y+1))} \tag{15}$$

where $y = \Delta G^{\circ\prime}/\Delta G^*(0)$.

Figure 4 shows the variation in Φ with $\Delta G^{\circ\prime}$ for constant values of $\Delta G^*(0) = 5$ and 8 kcal mol^{-1}. The smaller value is representative of the value for atom transfer reactions of Re(CO)$_4$L [28]. A value in the range of 8 to 11 kcal mol^{-1} has been measured for CpM(CO)$_3$ (M = Mo, W) halogen atom transfer reactions [31]. Although the value of Φ increases steeply in the endergonic regime, in the exergonic region it decreases more nearly linearly with increasingly negative values of $\Delta G^{\circ\prime}$.

Thus, the model described here leads to a remarkable generalization: for a group of related sets* of atom transfer reactions, the relative sensitivity of the rate to a change in the electronic characteristics of the ligand decreases relative to the sensitivity to a change in steric properties, as the reaction set becomes more exergonic. Put another way, for strongly exergonic reactions, variations in steric characteristics are most important in affecting changes in rate; in the endergonic regime, variations in electron donor–acceptor character are most important.

Comparison with experimental atom transfer rate data

The extensive body of atom transfer rate data summarized in Tables 2 and 4 affords an opportunity to

*The term *set* here refers to the reactions of several Re(CO)$_4$L radicals with a particular atom transfer reagent. In a set, both $\Delta G^{\circ\prime}$ and $\Delta G^*(0)$ may vary. By contrast, the term reaction *series* denotes several related reactions in which $\Delta G^*(0)$ is relatively constant [24, 26, 28].

test the Marcus-type model just described. However, there is some difficulty in establishing the appropriate scale of $\Delta G^{\circ\prime}$ values, since no thermodynamic data are available. Two possibilities present themselves. It was shown earlier that for the atom transfer reactions of Re(CO)$_4$L radicals with a large number of organic halides, a relationship in agreement with eqn. (6) was obtained when the variation in the irreversible electrochemical reduction potentials of the organic halides was employed as a measure of the variation in $\Delta G^{\circ\prime}$ [28]. Table 4 lists the irreversible half-wave reduction potentials known or measured in our laboratory for the atom transfer reagents studied. A graph of a/b versus $-E_{1/2}$ is shown in Fig. 5. A reasonably good fit to a second-order polynomial is seen; the form of the relationship is close to that predicted by the model (Fig. 4).

A second approach is to employ the constant c in eqn. (1) to obtain a measure of the overall driving force for the reaction. We have

$$\frac{-\Delta G^*}{RT} = aE_i + bS_i + c - \ln(k_B T/h) \tag{16}$$

For $E = S = 0$, $\Delta G^* = \Delta G_r^*$

$$c = -\frac{\Delta G_r^*}{RT} + \ln(k_B T/h) \tag{17}$$

$$= -\frac{\Delta G_r^{\circ\prime}}{RT} - \frac{\Delta G_r^*(0)}{RT\ln 2}$$

$$\ln[1 + \exp(-\Delta G_r^{\circ\prime}\ln 2/\Delta G_r^*(0))] + \ln(k_B T/h) \tag{18}$$

where the subscript r refer to the reference reaction, with $E = S = 0$. Given that the (hypothetical) reference ligand is the same in each case, $\Delta G^*(0)$ should be approximately constant from one set to the next. (That is, the $\Delta G_r^*(0)$ are values for a reaction series.) The
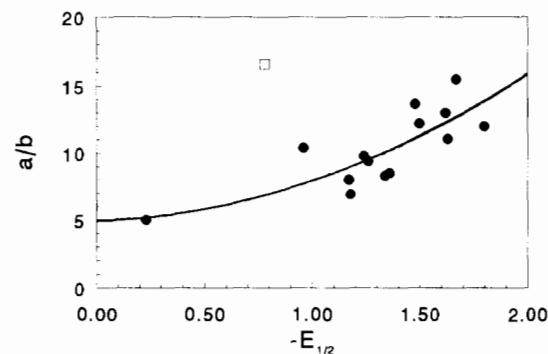

Fig. 5. Variation in a/b for Re(CO)$_4$L atom transfer reaction sets as a function of the irreversible half-wave reduction potentials for the atom or group donors.

variation in c from one reaction set to another is then due primarily to variation in $\Delta G_r^{\circ\prime}$. Figure 6 shows graphs of the variation in c with $\Delta G_r^{\circ\prime}$, assuming constant values of 5 and 8 kcal mol^{-1} for $\Delta G^*(0)$.

Figure 7 shows a graph of Φ versus c, assuming $\Delta G^*(0)$ values of 5 and 8 kcal mol^{-1}. The relationship between the two variables is nearly linear in the range of c values observed for the reactions tabulated in Table 4. Figure 8 shows a graph of the experimentally measured ratios a/b for all the reactions listed in Table 4, as a function of c. The relationship is linear, and shows that a/b decreases as c becomes larger; that is, as the reaction becomes increasingly exergonic.

The correlation coefficient for the linear relationship, r_{corr}, in Fig. 8 is 0.71 when the anomalous CCl_4 set is excluded. The quality of the correlation is reasonably good, considering that the atom transferred ranges from hydrogen to iodine, and that the reactions include even group transfers, as in the case of the disulfide or thiocyanate reaction sets. Some of the observed scatter is doubtless due also to variation in the steric requirements of the atom donors, which would produce variations in $\Delta G^*(0)$.
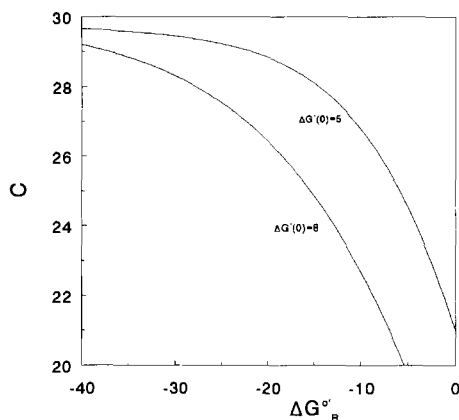

Fig. 8. Experimentally determined values of a/b vs. c (Table 4). The solid line represents the linear least-squares fit to the data (correlation coefficient = 0.71). The dotted line represents $\kappa\Phi$, with $\kappa = 18$. The open square represents the CCl_4 data.

Recall that a/b is related to Φ by the constant κ. A value of 18 for κ yields a variation in $\kappa\Phi$ shown by the dotted line in Fig. 8. Clearly, there is good agreement between the theoretical and observed variation in a/b throughout the group of reactions studied.

Conclusions

Using the Marcus-type model for atom transfer, we have related variations in the steric and electronic properties of ligands bound to the atom transfer center to variations in the intrinsic free energy barriers and overall free energy changes, respectively. The qualitative model thus developed makes it possible for the first time to relate the coefficients of ligand steric and electronic terms in a linear free energy equation to the thermodynamic and kinetic components of the free energy barrier to reaction. The model has been applied to a substantial body of atom transfer data for $Re(CO)_4L$ radicals. The ratio of the coefficients of the electronic and steric terms in the linear free energy relationship, a/b, is shown to vary with the overall free energy change in the reaction, in accord with the predictions of the model. The relationship seems to be robust; it applies to atom transfer data for a wide range of atom and group transfer agents in their reactions with $Re(CO)_4L$ radicals.

Fig. 6. Variation in c with $\Delta G_r^{\circ\prime}$ (kcal mol^{-1}) for two different constant values of $\Delta G^*(0)$.
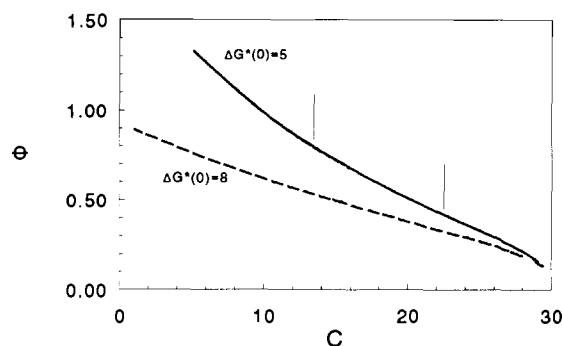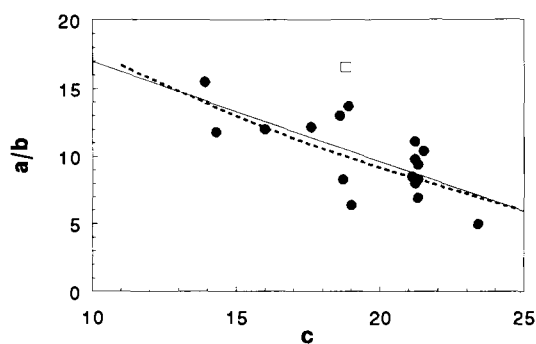

Fig. 7. Φ vs. c, assuming two different constant values for $\Delta G^*(0)$ (kcal mol^{-1}). The vertical marks indicate the range of values of c found for the atom transfer reactions of $Re(CO)_4L$ radicals.

The model described here should be applicable to the atom transfer reactions of organic free radicals, as well to other reaction types in which bond order is at least approximately conserved during reaction, e.g. associative substitution reactions and migratory insertions. All such reaction systems should obey the general rule that the relative sensitivity of the reaction to changes in ligand electronic parameter as compared with the sensitivity to changes in ligand steric parameter decreases as the reaction becomes more exergonic. A full

treatment of substitution reactions will be published elsewhere.

Experimental

The $Re_2(CO)_8L_2$ compounds were prepared by standard procedures [10, 32]. Their purities were monitored by careful examination of the IR spectra in the carbonyl stretching region. Solvents for both flash photolysis and electrochemical studies were carefully purified by drying and distillation under an inert atmosphere.

The flash photolysis measurements were carried out as described previously [10, 21]. Half-wave potentials of donor molecules for which the values were measured in 75% dioxane/25% water against SCE [28, 33] are listed in Table 4. The irreversible half-wave potentials for the disulfides and for 4-cyanobenzyl bromide were measured using a Bioanalytical Systems BAS-100A electrochemical analyzer operating in the cyclic voltammetry mode. A three-electrode electrochemical cell with platinum auxiliary electrode, Ag/AgCl reference electrode and a platinum disk working electrode was used in the measurements, with DMF as solvent and 0.1M tetraethylammonium bromide as supporting electrode, under an Ar atmosphere. The measured values were shifted to the values appropriate to the other values in Table 4 by adding 0.46 V. The shift value was determined by comparing the values obtained for four substituted benzyl bromides under the two sets of conditions and reference electrodes.

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