Multi-mechanism linear free energy relationships and isoequilibrium or isokinetic temperatures

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The equations that describe the temperature dependence of the various terms in multi-mechanism linear free energy relationships (MMLFERs) are outlined with respect to reactions of organometallics involving P-donors. Each MMLFER includes a term defining the free energy of a standard reaction characterized by a chosen standard P-donor. Other terms quantify the various mechanisms by which the free energy of the standard reaction is modified by the participation of other P-donors that have different electronic and steric properties. Several different electronic terms can be involved. The temperature dependence of the modifying terms can provide measurements of the separate enthalpic and entropic contributions to the modifying processes. For MMLFERs that involve equilibrium or rate constants, each modifying term is associated with its own isoequilibrium or isokinetic temperature (IET or IKT) which defines the temperature at which each term is reduced to zero. These temperatures are provided by the ratios of the enthalpic and entropic contributions and it is suggested that they have little or no theoretical significance in themselves, although they can of course be of practical importance. There can be no meaningful single IET or IKT for any single series of reactions that show MMLFERs. The equations defining the temperature dependence of the modifying terms are applied to an extensive set of published reduction potentials for the complexes $[(\eta^5\text{-}C_5H_5)(CO)LFe(COMe)]^+$, where L = a large selection of P-donor ligands. The main modifying terms involve opposing σ-donicity and π-acidity effects and the enthalpic and entropic contributions are examined.

Introduction

The occurrence of linear free energy relationships (LFERs) within sets of kinetic, equilibrium or other data for groups of organic reactions has been known for many years[1–4] and is still a matter of current interest, especially with regard to their relationships to the existence of isokinetic or isoequilibrium temperatures (IKTs or IETs, respectively).[5–12] The groups are generally defined by having a set of substituents attached to a common reaction centre as, classically, with hydrolysis of esters. The dependence of the rate or equilibrium constants on the nature of the substituents provides the basis for the LFERs. The LFERs have been very widely used to imply similar mechanisms for the members of those groups by comparison of rate data with data for standard reactions. The sensitivity of the rates to electronic and steric properties of substituents that define each group helps to reveal the intimate nature of the mechanisms in terms of differing extents of bond making or breaking *etc*. Solvent effects play an important part in such studies, especially for reactions involving ionic species.[9]

LFERs were also used some time ago in inorganic chemistry to infer the intimate mechanisms of aquation reactions of complexes such as $[Co(NH_3)_5X]^{n+}$, where X represents a variety of ligands such as halides, oxyanions *etc*.,[13] or substitution reactions of planar, four-coordinate d^8 platinum(II) complexes.[14,15] More recently, and following seminal work by Basolo and co-workers[16] and Tolman,[17] they have also been used to systematize data for reactions of organometallic complexes according to the electronic and steric properties of ligands involved as nucleophiles[18–20] or substituents.[20–23] This procedure is widely known as QALE, or the quantitative analysis of ligand effects.[20,24]

Another criterion that has been used to define groups of related and mechanistically similar reactions is the relationship between enthalpies and entropies of activation for the reactions in the groups. The values of the enthalpies are often linearly related to the entropy values, and the gradients of such plots were originally taken to define the isokinetic temperature (IKT or T_{iso}) at which all the reactions would occur at identical rates.[25] Corresponding relationships between the enthalpies and entropies of groups of equilibria provide the isoequilibrium temperature (IETs), at which all the equilibrium constants are the same. Unfortunately, a tendency to ignore the effects of the closely covariant uncertainties in the values of the enthalpies and entropies led to many cases where IKTs were incorrectly inferred,[26,27] and linear plots of enthalpies against entropies are now referred to simply as "compensation plots"[6] without the implication that there are precise values of T_{iso}. Nevertheless, alternative ways of relating parameters obtained from temperature dependence studies have been developed that avoid the problems of covariance. They

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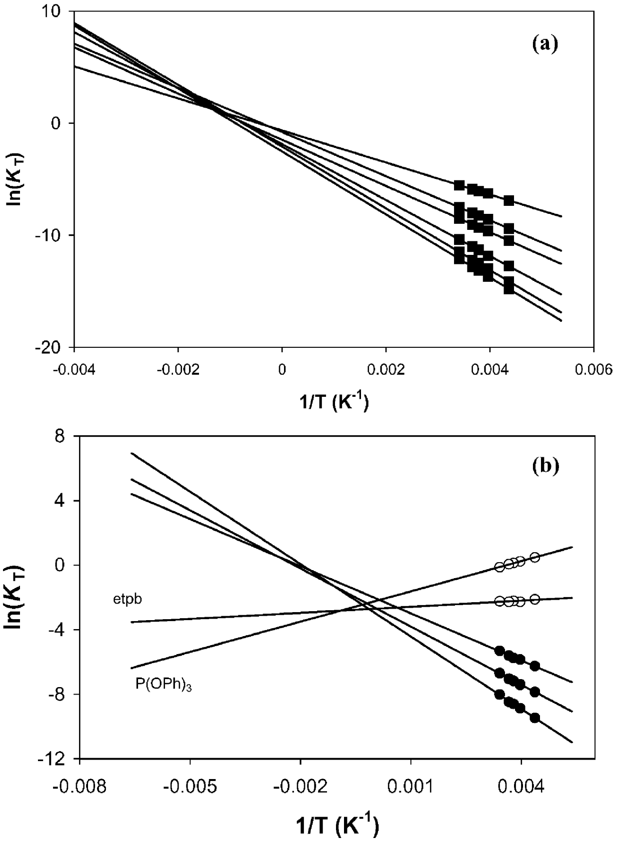

Fig. 1 van't Hoff "fan plots" (a) for PAr_3, and (b) for $P(OR)_3$ with data taken from refs. 30 and 31 for the reactions shown in eqn (15); etpb = $P\{(OCH_2)_3CEt\}$.

involve statistically rigorous criteria for demonstrating the existence of isokinetic or isoequilibrium behaviour, and can give quite precise values of the IKTs or IETs.[6,26,28,29]

Frequently, a group of reactions that is defined by having a common value of T_{iso} is simply revealed by the series of Eyring or van't Hoff plots for the reactions, plots that indicate an intersection at a common value of $1/T_{iso}$, and that can be called Linert–Exner or 'fan' diagrams. Examples are shown in Fig. 1. One plot shows quite a sharp IET and the other shows that some members of a group of phosphite ligands do not fit the trend shown by the others. (The data for these plots were based on the relative equilibrium constants derived from the reduction potentials for the reaction shown below in eqn (14)[30,31] and these data will be considered in greater detail later.)

Values of T_{iso} can be obtained[5,6,29] by a least squares analysis that minimizes the squares of all the deviations from the plots when they are constrained to go through a postulated $1/T_{iso}$. Programs to do this do not provide, in any simple way, values for the uncertainties in T_{iso}. However, statistical tests are available to indicate the degree of reliability of the postulates either that there is a low probability that there is *not* an IKT or IET or, a more rigorous test, that there is a high probability that there *is* one.

Alternatively, Krug *et al.*[27,28] showed that plots of ΔH° against ΔG° (the latter at a chosen temperature) for a group of reactions that is defined by having a common value of T_{iso} will be a straight line with a gradient of $(1 - T/T_{iso})$. This procedure will also be free of the statistical problems that arise when ΔH° values are plotted against ΔS°. A linear least squares analysis of the data, weighted if necessary, will provide the value of T_{iso} directly from the gradient, together with an estimate of its uncertainty.[7,27,28] Examples of such plots are shown in Fig. 2 where it can be seen that the data for the phosphite ligands give a poor fit to the expected behaviour, as they did in Fig. 1.

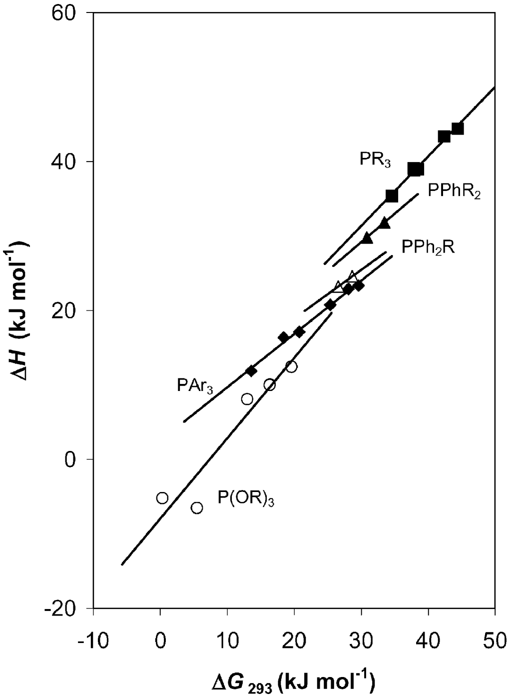

Fig. 2 Examples of Krug plots using data at 293 K for the reactions shown in eqn (15). (Data obtained from refs. 30 and 31.)

The connection between LFERs and isokinetic or equilibrium behaviour is, in fact, a very close one.[2,5] This can be seen intuitively from the Linert–Exner plots in Fig. 1(a). If the data at any one value of $1/T$ can be related to each other by an LFER then it follows, by geometry, that the data at all other temperatures must also follow the same form of LFER, albeit with a different gradient. However, a more rigorous and informative demonstration of the connection is shown by LFERs that are defined by a number, sometimes quite large, of different quantifiable ligand properties, *i.e.* a set of reactions with "multi-interaction mechanisms" where each property provides its own unique interaction mechanism with the reaction centre.

Linear free energy relationships (LFERs)

Multi-interaction mechanism LFERs (MMLFERs)

It is in organometallic chemistry that the development of more complicated equations relating equilibrium or kinetic behaviour to properties of ligands has occurred. It originated with the discovery by Basolo and co-workers[16] that the log of the second order rate constants for nucleophilic attack by P-donor nucleophiles on certain types of metal carbonyl could be proportional to the basicity of the P-donor as measured by its basicity towards the proton in solution. Deviations of larger nucleophiles from this behaviour were ascribed to steric effects that decreased the rates. This approach was developed in a more quantitative way in which the gradients of the LFERs were used as "dynamic characterizations" of the substrate metal carbonyls, and steric deviations were systematically collected.[32,33] However, with the advent of cone angles as a measure of the size of P-donor ligands,[17] a more quantitative representation of steric effects became possible[34–36] and a large number of kinetic data sets were found to fit well to equations such as eqn (1)[20,37] $\mathrm{p}K_\mathrm{a}'$ is a measure[37] of the proton basicity of the P-donor nucleophile in the non-polar solutions usually used for such studies, and θ is its cone angle.

$$\log k = \alpha + \beta(\mathrm{p}K_\mathrm{a}' + 4) + \gamma(\theta - \theta_\mathrm{th})\lambda \qquad (1)$$

θ_th is a steric threshold above which the "switching function", λ, is unity and a steric effect proportional to θ is operative. Below the threshold, λ is zero and no steric effect is evident. The term $+4$ in the second term ensures that the electronic effect, defined by that term, will be zero when $\mathrm{p}K_\mathrm{a}'$ corresponds to a very weakly basic P-donor with $\mathrm{p}K_\mathrm{a}' = -4$, *i.e.* one that is weaker than all other nucleophiles commonly used. This was chosen so that the standard reactivity, α, that is observed when $(\mathrm{p}K_\mathrm{a}' + 4)$ is zero and when there are no steric effects, is least affected by the P-donor's basicity and all other nucleophiles lead to faster reactions unless modulated by steric or other effects. The values of α and θ_th, and of the coefficients β and γ, are all characteristic of the substrate carbonyl. They can be used to provide a full dynamic characterization of the complex in a way that is complementary to its other physicochemical characteristics such as its molecular structure and spectroscopic properties.[37] The fact that these LFERs have terms corresponding to more than a single modulating factor characterizes them as multi-interaction mechanism linear free energy relationships, or MMLFERs.[38]

Although kinetic data for a large number of reactions were found to fit well to eqn (1), deviations of rate and other data from that predicted by equations similar to eqn (1), (but sometimes involving quite different physiochemical properties) were observed for ligands that had aryl groups attached to the P-donor atom, *i.e.* there was a so-called 'aryl effect'.[39,40] This led to the introduction of another term into such MMLFERs, *e.g.* δE_ar where E_ar[40] was equal (or close) to the number of pendant aryl groups on the phosphorus atom. Subsequently, the advent of parameters such as $\mathrm{p}K_\mathrm{a}'\pi$[41] that quantitatively measure the π-acidity of phosphite ligands enabled data for these P-donors to be included in the analyses so that kinetic data for attack by a wide variety of P-donors on the carbonyl clusters $\mathrm{Ru_3(CO)_{12}}$[42] and $\mathrm{Rh_4(CO)_{12}}$[43] could be fitted to eqn (2).

$$\log k = \alpha + \beta(\mathrm{p}K_\mathrm{a}' + 4) + \gamma(\theta - \theta_\mathrm{th})\lambda + \delta E_\mathrm{ar} + \phi(\mathrm{p}K_\mathrm{a}'\pi) \quad (2)$$

More recently,[44] an analysis of the energies of the σ → σ* transitions in the bis axially substituted complexes $\mathrm{Mn_2(CO)_8L_2}$ has suggested that, in addition to the "pendant group effects" (PGEs) shown by aryl ligands, there is probably another such effect shown by ligands that contain OR groups and previously also assigned to an "aryl effect" even when there were no aryl groups attached to the P-donor atoms.[31] This may be an example of a general PGE that extends to groups such as halides as well as alkoxy and aryl groups. It can be incorporated into equations such as eqn (2) so that they become as written in eqn (3). E_ox refers to the number of oxygen groups attached to the P-donor atoms, and $\log k$ has been replaced by the more general "Prop." that refers to a wide range of physicochemical parameters. Other physicochemical properties had also been shown to exhibit MMLFER behaviour.[39,40]

$$\begin{aligned}\text{Prop.} = {} & \alpha + \beta(\mathrm{p}K_\mathrm{a}' + 4) + \gamma(\theta - \theta_\mathrm{th})\lambda + \phi(\mathrm{p}K_\mathrm{a}'\pi) \\ & + \delta E_\mathrm{ar} + \Omega E_\mathrm{ox}\end{aligned} \qquad (3)$$

The temperature dependence of the coefficients in MMLFERs

In addition to the importance of these complex LFERs the temperature dependence of the derived constants α, β and γ *etc.*, and the way in which this dependence relates to the existence of T_iso values, is also of concern.

Consider the simple case where an equilibrium is affected only by the σ-donor and steric properties of a ligand. Similar considerations can be applied to rate constants. For generality let there be a σ-donor parameter B and a steric parameter Γ so that the LFER shown in eqn (4) is operative. The value of α is equivalent to $\log K^0$, where K^0 is

$$\log K = \alpha + \beta B + \gamma \Gamma \qquad (4)$$

the equilibrium constant involving the ligand with the standard values chosen for B and Γ (*e.g.* $B = \mathrm{p}K_\mathrm{a}' + 4$ and $\Gamma = 0^\circ = \theta$). The values of the coefficients β and γ are measures, respectively, of the modifying electronic and steric effects on $\log K^\circ$ due to each actual ligand. In this sense, eqn (4) can be replaced by eqn (5) where

$$K = K^0 f_B f_\Gamma \qquad (5)$$

f_B and f_Γ are ligand-dependent modifying *factors* that measure the electronic and steric effects of the given ligands compared with the standard ligand.[42]

Suppose[38] we also have the relationships shown in eqn (6) and (7) where α_H and α_S, together with the various coefficients, are temperature independent.

$$\Delta H^\circ = \alpha_H + \beta_H B + \gamma_H \Gamma \qquad (6)$$

$$\Delta S^\circ = \alpha_S + \beta_S B + \gamma_S \Gamma \qquad (7)$$

It can then be shown[30,38] that the LFER can be expressed as in eqn (8), where $x = -2.303R$, so that α, β and γ are given by eqn (9), (10) and (11), respectively.

$$\begin{aligned}x\log K = \Delta G^\circ/T = {} & \{(\alpha_H/T) - \alpha_S\} + \{(\beta_H/T) - (\beta_S)\}B \\ & + \{(\gamma_H/T) - \gamma_S\}\Gamma\end{aligned} \qquad (8)$$

$$x\alpha = \{(\alpha_H/T) - \alpha_S\} = \{(1/T) - (\alpha_S/\alpha_H)\}\alpha_H \qquad (9)$$

$$x\beta = \{(\beta_H/T) - \beta_S)\} = \{(1/T) - (\beta_S/\beta_H)\}\beta_H \qquad (10)$$

$$x\gamma = \{(\gamma_H/T) - \gamma_S)\} = \{(1/T) - (\gamma_S/\gamma_H)\}\gamma_H \qquad (11)$$

The temperature dependence of α will give values of α_H and α_S, the enthalpy and entropy for the standard reaction, while the temperature dependence of β and γ will give the enthalpy and entropy contributions associated with the electronic and steric modifying factors, respectively.

It is evident from eqn (10) that, if $1/T = \beta_S/\beta_H$, the electronic term is reduced to zero and the equilibrium constants will not depend on the basicity of the ligands. β_H/β_S can therefore be regarded as an isoequilibrium temperature, $(T_{\text{iso}})_\beta$, as far as the electronic modifying term is concerned. Similarly γ_H/γ_S can be taken as $(T_{\text{iso}})_\gamma$ so that no dependence on the size of the ligands will be observed at $T = (T_{\text{iso}})_\gamma$. Eqn (8) can therefore be transformed into eqn (12). This shows that the values of each of the modifying terms β and γ are dependent on how far the temperatures of measurements are from the

$$x \log K = \Delta G^\circ/T = \{(\alpha_H/T) - \alpha_S\} - \{(1/T) - (1/(T_{\text{iso}})_\beta)\}\beta_H B + \{(1/T) - 1/(T_{\text{iso}})_\gamma)\}\gamma_H \Gamma \qquad (12)$$

IETs $(T_{\text{iso}})_\beta$ and $(T_{\text{iso}})_\gamma$, whereas β_H and γ_H are independent of temperature. Since these IETs are not the same, except by coincidence, this means that some terms can disappear at certain temperatures while others are still significant. In general, the values of β and γ for one set of reactions at one temperature cannot be directly compared with those for another group of reactions at a different temperature. This is equivalent to the fact that equilibrium or rate constants for one reaction at one temperature cannot be compared with those for other reactions at different temperatures. In addition, however, there is the fact that, even at the same temperature, comparison of coefficients must allow for the differences between the actual temperatures of measurement and the relevant T_{iso} values. Thus, if by chance the temperature of measurement of one coefficient coincides with the related T_{iso} value the contribution of that parameter to the rates or equilibria will appear to be zero whereas, at other temperatures, it could be significant. This implies that the "dynamic characterization" of complexes that was referred to above cannot be considered complete without study of the temperature dependence of the LFERs.

Finally, the question has to be considered of whether a given set of reactions that depend on a multiplicity of interaction mechanisms can show isokinetic or isoequilibrium behaviour. The answer is that this can only occur when the parameters are linearly related to each other[39] so that there is effectively only one composite interaction. Otherwise the occurrence of distinct T_{iso} values for each parameter will ensure that there cannot, except by coincidence, be one characteristic of the whole group of reactions.

The physical significance of isokinetic and isoequilibrium temperatures

When isokinetic or isoequilibrium behaviour is considered *in isolation* the question of the physical meaning of the isokinetic or isoequilibrium temperatures arises. Linert and Jameson[5] have described a model involving a transfer of energy between the reacting systems and the medium, acting as a "heat bath", so that the isokinetic temperatures are related closely to vibrational frequencies characteristic of the media. Reis and co-workers[11] have shown that this relationship can be expressed by the remarkably simple eqn (13), where ν_{medium} is

$$\nu_{\text{medium}} = 0.695 T_{\text{iso}} \qquad (13)$$

the wave number of the characteristic vibration of the medium, and T_{iso} is the isokinetic temperature in Kelvin. Implicit in this is the fact that, if there are several interaction mechanisms and, therefore, individual T_{iso} values for each mechanism, each one will have to undergo its own individual interaction with the heat bath.

However, the fact that the T_{iso} values are given by the ratios of quite separate enthalpy and entropy terms, such as β_H/β_S, suggests a much simpler explanation for the existence of the temperatures themselves. Thus, consider the simple case where equilibrium data are involved and there is only one interaction mechanism. The van't Hoff plots in Fig. 3(a)–(e) show that there can be a steady progression of $1/T_{\text{iso}}$ values from *minus* infinity upwards, depending on the ratios of entropy to enthalpy values. If the enthalpies for a set of reactions are all the same then the plots never intersect until $1/T = -\infty$, and the different equilibria are completely "entropy controlled". However, if the enthalpies become different in the way indicated in Fig. 3(b), the values of $1/T_{\text{iso}}$ will become finite but still negative. In this region, as the slopes become larger, and the enthalpies more favourable, the entropies become larger, and also more favourable. In this region of negative T_{iso} values there is therefore "anti compensation" of the enthalpic and entropic contributions. As the values of $1/T_{\text{iso}}$ become less and less negative and approach zero, all the entropies become equal and the reactions become entirely "enthalpy controlled". When $1/T_{\text{iso}}$ values become positive, but still less than the values of $1/T$ at which measurements are made ($1/T_{\text{exp}}$), the reactions are increasingly controlled by the relative enthalpies, with the entropies acting in the opposite direction, but not to a degree that negates enthalpy control. Thus, as the enthalpies become more and more unfavourable so the entropies become more favourable, and the more common "compensation" behaviour is shown in which changes in enthalpies are offset by changes in the entropies. Eventually, this opposite influence of entropies and enthalpies becomes so pronounced that values of $1/T_{\text{iso}}$ are reached that are higher than $1/T_{\text{exp}}$ and the effects of entropy overcome those of the enthalpies and the reactions become mainly entropy controlled again, although still being in a region where enthalpy/entropy compensation is observed. Total entropy control is reached again when $1/T_{\text{iso}}$ is *plus* infinity. Thus the values of the isoequilibrium temperatures are determined entirely by the relative importance of entropy and enthalpy contributions, and have nothing fundamental to do with the intimate nature of the media involved, except to the extent that solvation or other specific medium effects play a part. In many cases solvent effects are minimal so that all the "normal" factors such as bond making and bond breaking, and vibrational changes within the *reactants etc.*, are dominant in determining isokinetic or isoequilibrium behaviour. Although Fig. 3(a)–(e) are appropriate for van't Hoff plots of equilibrium data the same conclusions can be drawn from Eyring plots, where all the slopes are necessarily negative, and from those van't Hoff plots where the slopes *can* be negative.

The fact that the temperature dependence of the electronic and steric parameters β and γ can give values for the *separate* entropic and enthalpic contributions of electronic and steric effects to modifying the equilibrium constants does not seem

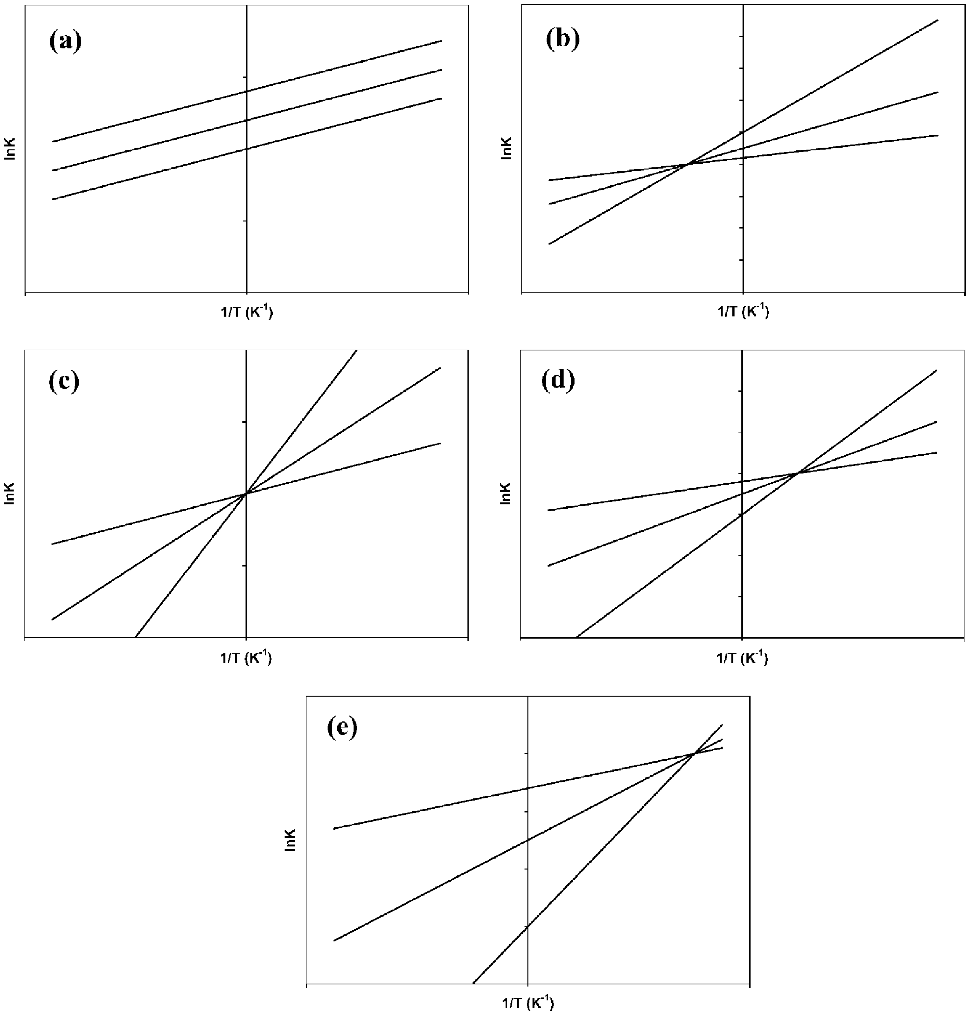

Fig. 3 Schematic plots indicating the various relationships between isoequilibrium temperatures and the corresponding relative enthalpy and entropy values. The central vertical line corresponds to $1/T = 0$ and values of $1/T_{\text{exp}}$ are, of course, all positive. (a) van't Hoff plots for $1/T_{\text{iso}} = -\infty$. (b) van't Hoff plots with intersection at $1/T_{\text{iso}} < 0 < 1/T_{\text{exp}}$. (c) van't Hoff plots with intersection at $1/T_{\text{iso}} = 0 < 1/T_{\text{exp}}$. (d) van't Hoff plots with intersection at $0 < 1/T_{\text{iso}} < 1/T_{\text{exp}}$. (e) van't Hoff plots with intersection at $0 < 1/T_{\text{exp}} < 1/T_{\text{iso}}$.

to have been recognized before. This is because too much attention has been paid to the T_{iso} values, *i.e.* the enthalpy/entropy *ratios*, and not enough to the separate enthalpic and entropic contributions that are actually available. It is, therefore, of interest to find sets of data that can be used both to derive values for the various coefficients contained in equations such as eqn (1)–(3), and to investigate their temperature dependence. Suitable data have been reported by Fernandez *et al.*[30,31,45] E° values for the reduction reactions shown in eqn (14) were measured to an excellent precision, estimated to be ±0.7 mV for a large selection of P-donor ligands, L, with reference to the reduction of $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4COMe)Fe]^+$.

$$[(\eta^5\text{-}C_5H_5)(CO)LFe(COMe)]^+ + 1\,e \rightarrow [(\eta^5\text{-}C_5H_5)(CO)LFe(COMe)]^0 \qquad (14)$$

The E° values can therefore provide equilibrium constants for the reactions in eqn (15).

$$[(\eta^5\text{-}C_5H_5)(CO)LFe(COMe)]^+ + [(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4COMe)Fe]^0 \rightarrow [(\eta^5\text{-}C_5H_5)(CO)LFe(COMe)]^0 + [(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4COMe)Fe]^+ \qquad (15)$$

We have therefore re-analyzed these data to determine the values of the various parameters that are necessary for a full description of the equilibrium constants, and to investigate the temperature dependence of the coefficients in terms of equations such as eqn (9)–(11). Table 1 shows the ligand properties and the values of $\log K$ at temperatures covering a range of 64 K, while Table 2 contains the corresponding values of the relevant enthalpies and entropies for the reactions.

Analysis of the reduction potential data for the complexes $[(\eta^5\text{-}C_5H_5)(CO)LFe(COMe)]^+$ (L = P-donor ligands)

Systematic development of LFER analyses

The data were analyzed by following well established protocols[35,36,46] which have been found to be very successful.[18–21,23,24,42,43] These involved initial graphical analyses, to establish the possible existence of the various terms in equations such as eqn (3), and subsequent derivation of values for the various coefficients by regression analysis. However,

Table 1 Physical parameters and log K_T values for the [(η^5-C_5H_5)(CO)(L)Fe(COMe)]$^{+/0}$ couple[a]

Name	pK_a'	θ/°	E_{ar}	p$K_a'\pi$	E_{ox}	log K (229 K)	log K (252 K)	log K (264 K)	log K (273 K)	log K (293 K)
P{$(OCH_2)_3$CEt}	−0.3	101	0	8.5	3	−0.920	−0.986	−0.962	−0.988	−0.972
$P(OMe)_3$	0.83	107	0	4.85	3	−2.718	−2.054	−2.499	−2.433	−2.304
$P(OEt)_3$	1.64	109	0	3.97	3	−3.414	−3.224	−3.118	−3.061	−2.909
$P(OBu)_3$	1.64	109	0	3.47	3	−3.407	−3.202	−3.112	−3.057	−2.902
PMe_3	6.4	118	0	0	0	−7.908	−7.158	−6.833	−6.604	−6.144
$PPhMe_2$	5.07	122	1	0	0	−6.977	−6.364	−6.092	−5.911	−5.479
$P(OPh)_3$	−2.79	128	0	5.33	3	0.207	0.100	0.053	0.022	−0.055
P(O-*i*-Pr)$_3$	3.38	130	0	4	3	−4.109	−3.852	−3.732	−3.676	−3.480
P(*p*-$MeOC_6H_4$)$_3$	5.13	145	3	0	0	−6.422	−5.938	−5.712	−5.570	−5.258
P(*p*-MeC_6H_4)$_3$	4.46	145	3	0	0	−6.141	−5.630	−5.437	−5.297	−4.992
PPh_3	3.28	145	3	0	0	−5.535	−5.138	−4.906	−4.782	−4.509
P(*p*-FC_6H_4)$_3$	1.63	145	3	0	0	−4.551	−4.182	−4.044	−3.936	−3.687
P(*p*-ClC_6H_4)$_3$	0.87	145	3	0	0	−4.089	−3.724	−3.576	−3.475	−3.274
P(*p*-$CF_3C_6H_4$)$_3$	−1.39	145	3	0	0	−3.009	−2.718	−2.635	−2.557	−2.412
PEt_3	7.96	132	0	0	0	−8.674	−7.892	−7.489	−7.265	−6.724
P(*n*-Bu)$_3$	8.67	132	0	0	0	−8.790	−7.960	−7.636	−7.359	−6.840
P(*i*-Bu)$_3$	8.36	143	0	0	0	−8.669	−7.832	−7.495	−7.239	−6.729
P(*i*-Pr)$_3$	9.88	160	0	0	0	−9.697	−8.798	−8.396	−8.110	−7.533
PCy_3	11.26	170	0	0	0	−10.118	−9.214	−8.805	−8.520	−7.983
$PMePh_2$	4.06	136	2	0	0	−5.885	−5.408	−5.195	−5.046	−4.723
PEt_2Ph	5.94	136	1	0	0	−7.540	−6.876	−6.600	−6.391	−5.943
$PEtPh_2$	4.6	140	2	0	0	−6.319	−5.824	−5.588	−5.426	−5.093

[a] Values of log K refer to the [(η^5-C_5H_5)(CO)(L)Fe(COMe)]$^{+/0}$ redox couple relative to [(η^5-C_5H_5)(η^5-C_5H_4COMe)Fe]$^{+/o}$ and were calculated from the $E°$ values given in refs. 30, 31 and 35. Each $E°$ value has an uncertainty of ±0.7 mV.

because we and Giering and Prock *et al.* formulate our equations in significantly different ways, we provide a comparison of the two formulations in the Appendix. This does not affect the protocols, which begin by considering data for the ligands PAr_3 which are isosteric, and will therefore not show any steric effects. They are also not π-acids, and all contain three aryl groups attached to the P-donor atom so they will show no π-acid or aryl effects. Having no oxygen atoms attached to the phosphorus the term ΩE_{ox} will also be zero. The only difference between them is their σ-basicity, measured by their pK_a' values, and values of the coefficient β can be obtained from the dependence of log K on pK_a'. In practice, an excellent linear plot of log K *vs.* (pK_a' + 4) is obtained and a linear least squares analysis provides the precise values of β shown by analysis 1 in Table 3. However, the values of α will be affected by any contributions, albeit constant ones, that might be made by steric or other electronic effects.

Table 2 Thermodynamic data[a] for the reduction of [C_5H_5)(CO)(L)-Fe(COMe)]$^+$ complexes

Ligand	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}
P{$(OCH_2)_3$CEt}	−1.1(6)	−21.7(21)
$P(OMe)_3$	8.10(47)	−16.8(18)
$P(OEt)_3$	10.08(31)	−21.5(12)
$P(OBu)_3$	9.99(28)	−21.7(11)
PMe_3	35.37(16)	3.1(6)
$PPhMe_2$	29.82(51)	−3.5(20)
$P(OPh)_3$	−5.20(11)	−18.7(12)
P(O-*i*-Pr)$_3$	12.44(38)	−24.4(15)
P(*p*-$MeOC_6H_4$)$_3$	23.34(12)	−21.0(5)
P(*p*-MeC_6H_4)$_3$	22.89(42)	−17.4(16)
PPh_3	20.74(45)	−15.6(17)
P(*p*-FC_6H_4)$_3$	17.12(37)	−12.4(14)
P(*p*-ClC_6H_4)$_3$	16.36(34)	−6.6(13)
P(*p*-$CF_3C_6H_4$)$_3$	11.87(52)	−5.4(20)
PEt_3	39.11(54)	4.5(21)
P(*n*-Bu)$_3$	38.96(50)	1.9(19)
P(*i*-Bu)$_3$	38.81(38)	3.7(15)
P(*i*-Pr)$_3$	43.38(18)	3.7(7)
PCy_3	44.42(63)	0.0(24)
$PMePh_2$	23.22(25)	−11.4(10)
PEt_2Ph	31.81(46)	−5.5(18)
$PEtPh_2$	24.58(25)	−13.8(10)

[a] Thermodynamic data calculated by converting $E°$ values to ln K and carrying out a Van't Hoff analysis.

A plot against (pK_a' + 4) of the data for the PR_3 ligands is found to deviate slightly but systematically from those predicted by the PAr_3 data. These ligands are different in size from the PAr_3 ligands, and from each other, and have no aryl effects. This suggests that small aryl and/or steric effects might be operative. A regression analysis of the data for the 10 PAr_nR_{3-n} ligands (n = 0–2) and six PAr_3 ligands was carried out, allowing for steric and aryl effects in addition to the already established sigma donor effect. This gives the coefficients listed as analysis 2 in Table 3 and suggests that the additional aryl effect is possibly significant at lower temperatures. The steric effect is very small at all temperatures although the coefficient γ could just as well be quite significant at 0.007 deg^{-1} as insignificant at 0.001 deg^{-1}. The values of both coefficients are all of the same sign, irrespective of the temperature, and this also suggests that their values are not randomly distributed around zero and it would not be appropriate at this stage to disregard them entirely. When the equilibrium data are adjusted for the steric and aryl effects an excellent linear plot against (pK_a' + 4) is obtained as shown in Fig. 4.

The situation becomes clearer when data for the π-acid ligands are considered as well. Fig. 4 includes the data for the phosphite ligands that have been adjusted for the small steric effects. These all deviate clearly from the line for the non-π-acid ligands in a way that suggests immediately that

Table 3 Summary of regression analyses at various values of T. (Coefficients are dimensionless, except for the values of γ which have the dimensions deg^{-1})

Anal. no.	Coeff.	n^a	229 K	252 K	264 K	273 K	293 K
1^b	α	6	−1.55(8)	−1.36(9)	−1.32(8)	−1.27(8)	−1.19(8)
	β	6	−0.54(1)	−0.51(1)	−0.48(1)	−0.47(1)	−0.45(1)
	R^2		0.998	0.997	0.997	0.997	0.997
2^c	α	16	−2.42(26)	−2.52(38)	−2.40(35)	−1.81(23)	−1.61(21)
	β	16	−0.53(2)	−0.50(2)	−0.48(2)	−0.47(2)	−0.44(2)
	γ	16	0.004(3)	0.005(3)	0.005(3)	0.005(3)	0.005(3)
	δ	16	0.21(6)	0.14(6)	0.11(5)	0.09(5)	0.04(5)
	R^2		0.996	0.996	0.996	0.996	0.996
3^d	α	22	−2.03(28)	−1.70(25)	−1.61(23)	−1.51(22)	−1.36(20)
	β	22	−0.58(2)	−0.54(2)	−0.52(2)	−0.51(2)	−0.47(2)
	γ	22	0.011(3)	0.010(3)	0.010(3)	0.010(3)	0.009(2)
	δ	22	0.10(6)	0.04(5)	0.02(5)	−0.00(5)	−0.03(4)
	ϕ	22	0.31(4)	0.27(4)	0.26(4)	0.25(3)	0.23(3)
	Ω	22	0.23(8)	0.16(7)	0.13(7)	0.10(7)	0.07(6)
	R^2		0.997	0.997	0.997	0.997	0.998
4^e	α	22	−1.18(17)	−1.13(15)	−1.13(14)	−1.13(13)	−1.13(11)
	β	22	−0.61(2)	−0.55(1)	−0.52(1)	−0.50(1)	−0.46(1)
	ϕ	22	0.32(3)	0.28(2)	0.27(2)	0.26(2)	0.24(2)
	R^2		0.993	0.994	0.994	0.994	0.995

[a] Number of ligands used in the analysis. [b] PAr_3 ligands only. [c] Non π-acid ligands. [d] All ligands, all effects. [e] All ligands, but with no steric effect, aryl effect, or "oxygen effect".

π-acidity must make an important positive contribution to the log K values. The deviations of the data for these π-acids can be plotted against the values of p$K_a'\pi$,[41] as in Fig. 5. The line through the data, not including the origin where p$K_a'\pi$ is zero, indicates that there is a positive gradient of *ca.* 0.3, and ϕ is therefore quite large. Although this conclusion depends heavily on the data for the ligand $P\{(OCH_2)_3CEt\}$, with the highest value of p$K_a'\pi$, this is exactly the ligand with the most reliable value of p$K_a'\pi$. This reliability arises from the fact that the values of p$K_a'\pi$ are derived[41] from differences in observed values of ν_{CO} (the C–O A_1 stretching frequency in $Ni(CO)_3L$) from those expected from trends observed for non-π-acid ligands. The difference is largest, and therefore most precise and reliable, for the $P\{(OCH_2)_3CEt\}$ ligand.

A possible positive intercept at p$K_a'\pi$ = 0 would correspond to a finite value of Ω, the PGE characteristic of ligands with pendant oxygen atoms attached to the P-donor atoms (see above), and a least squares analysis of the data in Fig. 4 shows that an intercept with a value of +0.7 would fall within 95% confidence limits. This term is therefore included in

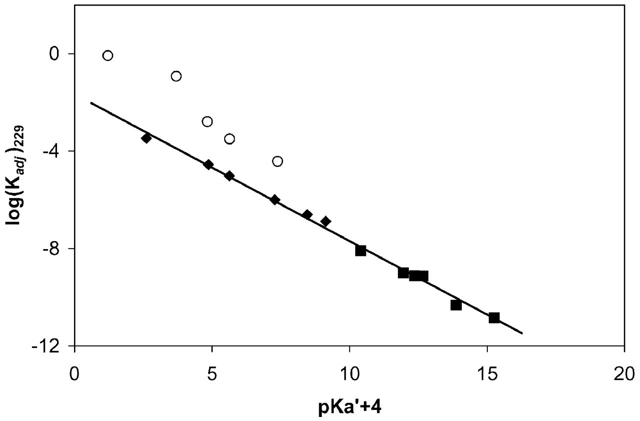

Fig. 4 log K *vs.* (pK_a' + 4) plot for PR_3 (solid squares) and PAr_3 (solid diamonds) ligands with log K values adjusted for the small steric effects relative to θ = 100°. T = 229 K. Data for phosphite ligands (open circles) are included (also with steric corrections). The phosphite ligands are, from left to right, $P(OPh)_3$, $P\{(OCH_2)_3CEt\}$, $P(OMe)_3$, $P(OEt)_3$ and $P(O\text{-}i\text{-}Pr)_3$.

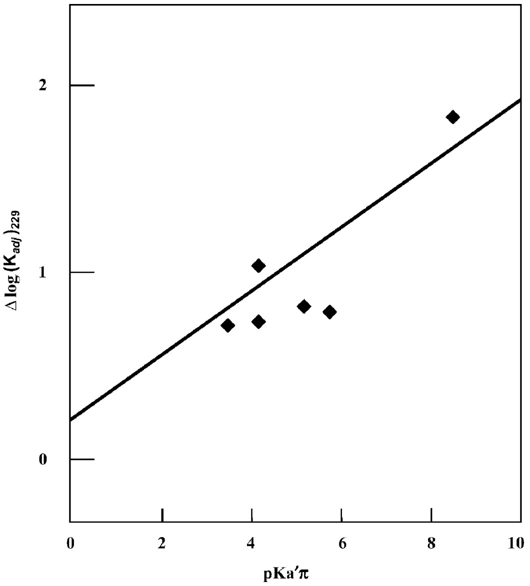

Fig. 5 Deviations of the data for the phosphite ligands from the line for the PAr_3 and PR_3 ligands in Fig. 4, plotted *vs.* their values of p$K_a'\pi$. The ligands are, from left to right, $P(OBu)_3$, $P(OEt)_3$ (lower point), $P(O\text{-}i\text{-}Pr)_3$ (upper point), $P(OMe)_3$, $P(OPh)_3$ and $P\{(OCH_2)_3CEt\}$.

Table 4 Enthalpy and entropy parameters calculated from the temperature dependence of the major coefficients from analyses in Table 3[a]

Anal. no.	α_H/kJ mol^{-1}	α_S/J K^{-1} mol^{-1}	β_H/kJ mol^{-1}	β_S/J K^{-1} mol^{-1}	ϕ_H/kJ mol^{-1}	ϕ_S/J K^{-1} mol^{-1}
1[b]	—	—	1.88 ± 0.15	−2.17 ± 0.57	—	—
2[c]	18 ± 8	+26 ± 30	1.79 ± 0.11	−2.38 ± 0.42	—	—
3[d]	13.4 ± 0.7	+20.1 ± 2.5	2.15 ± 0.14	−1.78 ± 0.56	−1.58 ± 0.08	−1.03 ± 0.32
4[e]	—	—	3.02 ± 0.04	1.48 ± 0.13	−1.58 ± 0.08	0.84 ± 0.32

[a] Analysis number from Table 3. [b] Only the 6 aryl ligands. [c] All 16 non π-acid ligands. [d] All 22 ligands, all effects. [e] All 22 ligands, but with no aryl, steric or oxygen effects.

analysis 3 in Table 3, where it can be seen to be probably significant at lower temperatures. Even at higher temperatures the chance that the pendant oxygen effect of the phosphites contributes as much as 0.4 to log K is equal to the chance that it contributes essentially nothing. The constant δ, however, now seems to be of less significance The significance or otherwise of these terms does not affect the fact that the contribution of the π-acidity to the equilibria is substantial, in the opposite direction to the σ-donicity effect, and of comparable magnitude. A regression analysis including only the σ-donor and π-acidity factors is shown in analysis 4. It is found to be quite adequate although less so than the other analyses in a way that suggests that minor contributions from the other factors could indeed be significant. Thus the values for α, which would include contributions from the possible minor effects, are quite different from those obtained in analyses 2 and 3. The data are therefore well represented by the full analysis according to eqn (16) where the contributions of the σ-donor and π-acidity terms are substantial and quite unambiguous. Thus, taking into account the range of values of the various parameters, the σ-donor and π-acidity contributions amount to *ca.* 7 and −3, respectively, to the values of log K at 229 K. Those of the other terms are considerably smaller and decrease in the order $\gamma\theta$ (0.7) $\approx$ ΩE_{ox} (0.7) > $\delta(E_{\mathrm{ar}})$ (0.3).

$$\log K = \alpha + \beta(\mathrm{p}K_{\mathrm{a}}' + 4) + \gamma\theta + \phi(\mathrm{p}K_{\mathrm{a}}'\pi) + \delta(E_{\mathrm{ar}}) + \Omega E_{\mathrm{ox}} \qquad (16)$$

The above analysis, as with all the analyses now known as the quantitative analysis of ligand effects or QALE, is based on the conclusion that alkyl and aryl phosphines are pure σ-donors. However, the situation has recently been reviewed[47] in the light of other studies and of density functional theoretical analyses that have suggested that $\mathrm{PMe_3}$ and $\mathrm{PH_3}$ do in fact show significant π-acidity that affects, particularly, the geometry of complexes that contain them. The energetic effects were not estimated, nor were the relative contributions of σ-basicity and π-acidity in the alkyl and aryl phosphines compared with those in the accepted π-acid phosphites or the possible effects of changing σ-basicity on the contribution of π-acidity to the bonding. It may well be that π-acidity contributions decrease systematically with decreasing basicity and, in this case, the observed π-acidity effects discussed above would be a measure of the greater effects shown by the phosphites compared with those operating in the alkyl and aryl phosphines. This argument resembles that put forward[39] in connection with the possible contribution of aryl effects to the values of χ derived[17] from the $\mathrm{A_1}$ C–O stretching frequencies in $\mathrm{LNi(CO)_3}$ complexes; *i.e.* any contributions of π-acidity (or aryl effects) that are detected are implicitly over and above those contributions that occur in these standard complexes.

Temperature dependence of the coefficients

Because $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -2.303 \log K$, eqn (16) can be rewritten as in eqn (17) to allow for the temperature dependence of the coefficients. As in eqn (8)–(11), $x = -2.303R$, and the temperature dependence of the less significant coefficients of E_{ar} and E_{ox} have been omitted.

$$x \log K = (\alpha_H/T - \alpha_S) + (\beta_H/T - \beta_S)(\mathrm{p}K_{\mathrm{a}}' + 4) + (\phi_H/T - \phi_S)\mathrm{p}K_{\mathrm{a}}'\pi + (\gamma_H/T - \gamma_S)\theta \qquad (17)$$

As is clear from eqn (17), plots of the coefficients α, β and ϕ against $1/T$ will give values of α_H and α_S, β_H and β_S, and ϕ_H and ϕ_S, respectively. These values are given in Table 4 using all the coefficients as derived in analysis 3, as described above. Since the contribution of the steric effect to log K is small, albeit probably significant, there is no point in deriving enthalpy and entropy contributions from its temperature dependence. However, it changes only very slightly with increasing temperature, and any contributions to the values of log K are therefore mainly entropic.

Discussion

The existence of quite complex multi-interaction LFERs is now well established, and simple equations show clearly that each individual mechanism of interaction is characterized by its own value of T_{iso}. Mechanisms that involve substituent ligands with different σ-basicity and π-acidity, different sizes, and different numbers of aryl or OR groups attached to donor phosphorus atoms, can be distinguished.[42–44] In the case of the thermodynamic data obtained for the reactions described in eqn (15) only two major contributions, σ-basicity and π-acidity, contribute to the values of the equilibrium constants. Judging by the uncertainties in the values of γ, analysis 3 in Table 3 shows that the steric effect is rather small but probably significant. The aryl and oxygen effects seem to be of less significance, although the trends with changing temperature are monotonic, and their significance cannot be rejected with any high degree of confidence.

The negative values of β show that the higher the σ-basicity the less facile is reduction, as would be expected. On the other hand, the positive values of ϕ show that the greater the π-acidity the more facile is reduction, also as expected, although β is numerically *ca.* twice that of ϕ. Also, because of the greater range of pK_{a}' values compared with those of p$K_{\mathrm{a}}'\pi$, σ-basicity decreases the tendency for reduction considerably more than the π-acidity increases it. Thus, the free energies are increased by up to *ca.* 40 kJ mol^{-1} (for PCy_3, compared with the standard reaction) while the maximum decrease due to π-acidity is only *ca.* 12 kJ mol^{-1} (for $P\{(OCH_2)_3CEt\}$). This direct comparison of the σ-donor and π-acidity effects is possible because of the origins and dimensionless nature of both $pK_a'$and $pK_a'\pi$, something that is not possible with the π-acidity parameters derived[31] by Giering, Prock *et al.* as shown in the Appendix.

More information can be obtained from the temperature dependence of the equilibrium constants and of the coefficients α, β and φ. Other than in exceptional circumstances such sets of reactions do not lead to a single value of T_{iso}. These circumstances include groups restricted to a single variable physical parameter, or cases where two such parameters are linearly related to each other. Thus the intersection of the Van't Hoff plots in Fig. 1(a) gives quite a sharp isoequilibrium temperature because the ligands involved differ only in their σ-basicity. However, the plots in Fig. 1(b) do not intersect sharply because the ligands differ in π-acidity as well as in their σ-basicity and size. Related groups of reactions are also clearly revealed by linear Krug plots as shown in Fig. 2, plotted for the same reactions. The different groups are distinguished by different values of ΔH° and by different slopes. The slopes provide values of the relevant isoequilibrium temperatures, where appropriate, and also provide estimates of their uncertainties. The IET for the PAr_3 ligands can be estimated to be −740 ± 150 K from the Krug plot, −786 K from the Linert–Exner plots, and −680 ± 120 K from the plot of ΔH° against ΔS°. The latter emphasizes the fact that *negative* T_{iso} values indicate that there is "*anti*-compensation" where the most unfavourable change in the enthalpy (biggest positive ΔH°) is accompanied by the most unfavourable change in the entropy (most negative ΔS°), *i.e.* the overall free energy is determined by the combination of enthalpic and entropic effects that operate in the same direction. This is also indicated by Fig. 3(b) and data in Table 2. The slope of the Krug plot for the PR_3 ligands is quite well defined, because of the correlation between the σ-basicities and sizes of the ligands, but no meaningful value of T_{iso} can be derived because the slope is a composite of $(1/T_{iso})_\beta$ and $(1/T_{iso})_\gamma$. The Krug plot for the $P(OR)_3$ ligands is not so well defined for the same reason that the lines in Fig. 1(b) have such an ill-defined intersection point. However, an incidentally useful aspect of the Krug plots is that information can be included, in one graph, for several groups of reactions whereas 'fan diagrams' occupy more space and cannot be combined so easily.

The temperature dependence of the coefficients α, β and φ can be used to derive the values of α_H and α_S, β_H and β_S, and ϕ_H and ϕ_S, that are given in Table 4. The various results are in quite good agreement with each other except for those where only the σ-basicity and π-acidity effects are included. This is another indication that, among the 'minor effects', the steric effect is indeed significant.

As is evident, the parameters that are obtained in the first place are the enthalpies and entropies for the standard equilibrium constant, and for the major terms that modify those standard values through the effects of different σ-basicities and π-acidities of the ligands. These modifying terms can be combined to give the ratios β_H/β_S and ϕ_H/ϕ_S that are equal, respectively, to $(T_{iso})_\beta$ and $(T_{iso})_\phi$. The value for $(T_{iso})_\beta$ from the data for the PAr_3 ligands is $(1880 \pm 150)/\{-(2.17 \pm 0.57)\} = -910 \pm 170$ K in reasonable agreement with the values derived above for the same data by analysis of the Linert, Krug and (anti)compensation plots. The value of $(T_{iso})_\phi$ obtained from the data in Table 4 for all the ligands and all the parameters is $(-1580 \pm 80)/\{-(1.03 \pm 0.32)\} = 1700 \pm 600$ K and this value can only be obtained from data of this kind. In these examples the values of the entropy contributions are relatively small and the modifying factors β and γ are essentially determined more by enthalpic contributions than by entropic ones. The latter can actually change sign when derived in different ways, thus leading to positive or negative IETs.

Negative values of T_{iso} present a problem for the Linert model of the origin of isokinetic or isoequilibrium behavior, and assumptions about pre-equilibria with unusually large negative enthalpy values were invoked to explain negative IKTs.[5] In the approach described here the existence of negative IETs or IKTs is determined solely by the *sign* of the entropy contribution to the factor that modifies the standard reaction. In the case of the electron-transfer equilibria described in eqn (15) negative entropic factors are not at all surprising. The activated intermediates $\{[(\eta^5\text{-}C_5H_5)(CO)LFe(COMe)]^+ \cdot [(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4COMe)Fe]\}^*$ and $\{[(\eta^5\text{-}C_5H_5)(CO)LFe(COMe)] \cdot [(\eta^5\text{-}C_5H_5)(\eta^5 \cdot C_5H_4COMe)Fe]^+\}^*$ have had to have their atomic configurations adjusted so that there are two energy levels of equal energy available for electron transfer between them.[48] This will have required enthalpy and entropy changes but the subsequent electron transfer between equally energetic levels could be subject to unfavourable probability/entropic factors (*i.e.* to *non*adiabaic behaviour) leading to negative overall entropy, and to negative entropy effects on the *modifying* factors as well. In addition, it is clear from the values of ϕ_H and ϕ_S that negative values of the entropy do not necessarily lead to negative T_{iso} values, and that positive values can arise when the enthalpy values are also negative.

The values of β_H and β_S, and of ϕ_H and ϕ_S, can be used to estimate the entropy and enthalpy contributions to the maximum modifying influences of σ-donicity (the unfavorable effect due to PCy_3), and π-acidity (the favorable effect due to $P\{(OCH_2)_3CEt\}$). Thus the 40 kJ mol^{-1} increase of the free energy at 229 K, caused by the high basicity of PCy_3, is a combination of an approximately 32 kJ mol^{-1} unfavourable increase in ΔH° and a reinforcing and unfavourable 7 kJ mol^{-1} decrease in $T\Delta S^\circ$. On the other hand, the 12 kJ mol^{-1} decrease in the free energy at 229 K, caused by the high π-acidity of $P\{(OCH_2)_3CEt\}$, is a combination of a favourable decrease of ~13 kJ mol^{-1} in the enthalpy offset by an unfavourable 2 kJ mol^{-1} decrease in $T\Delta S^\circ$. Thus in both cases the entropy effect is unfavorable and appreciably smaller than the enthalpy effect, so the enthalpy is dominant in determining the overall modifying effect. Also, if a ligand with a π-acidity comparable to the σ-donicity were available, the two enthalpy effects would also be comparable. Although enthalpy and entropy values can be obtained *via* α_H and α_S values in Table 4, for the standard reaction (with the ligand with a pK_a' of −4 and no π-acidity or size effects) they have no particular significance in this case because the values are merely relative to the reduction of the quite different complex $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4COMe)Fe]^+$.

However, the use of eqn (17) to describe the effects of temperature on the *relative* equilibrium constants allows a penetrating analysis to be made of the thermodynamics of the modifying effects of different physical properties of the ligands. Although, in this case, the steric effects are so small that a precise breakdown of those effects into entropy and enthalpy contributions cannot be obtained, it does seem that the contributions are mainly entropic. Entropy control of relative steric effects have also been observed for some CO-dissociative reactions of metal carbonyl complexes.[49] What is remarkable is that no information of any significance can be obtained from isoequilibrium or isokinetic temperatures themselves, data that have been the subject of so much effort to obtain. Where the values are validly derived, the same data could be used to provide measures of the enthalpy and entropy contributions separately, as has been done above. The use of the IKTs and IETs alone is comparable to the unprofitable use of entropy/enthalpy ratios alone to describe a reaction when each is known individually.

Summary

MMLFERs (multi-mechanism linear free energy relationships) can relate physicochemical parameters, such as rate or equilibrium constants, to a standard constant and a series of modifying factors. These quantify the electronic and steric effects of various substituents or nucleophiles such as P-donor ligands. Equations are provided which describe the temperature dependence of the standard constant and of the modifying factors. These can provide the separate enthalpic and entropic contributions to those factors while the enthalpy/entropy ratios can provide the individual isokinetic (IKT) or isoequilibrium (IET) temperatures that are characteristic of each factor, and at which the individual modifying terms are reduced to zero. There is no single IKT or IET that can characterize the group of reactions as a whole, and the individual IKTs or IETs have little or no theoretical significance in themselves.

The equations defining the temperature dependence of the standard reaction and of the modifying terms can be applied to an extensive set of published reduction potentials for the complexes $[(\eta^5\text{-}C_5H_5)(CO)LFe(COMe)]^+$, where L = a large selection of P-donor ligands. The potentials are reduced substantially by increasing the σ-donor capacity of L, and are increased by increasing its π-acceptor capacity. Small increases are probably associated with increasing size of L, but the aryl effect and other terms are probably unimportant. The decrease of the reduction potential due to increasing *P*-donor basicity is due to a large increase in enthalpy that is reinforced by a smaller but still unfavourable entropy contribution. This leads to *anti*-compensation behaviour, and a negative T_{iso} value. The increase in the reduction potential due to π-acids is due to a favourable, negative, enthalpic contribution offset by an entropic contribution that is unfavourable in this case as well. This results in a *positive* value of T_{iso} for this term so that the question of whether T_{iso} values are positive or negative relates in this case to whether the enthalpic contributions of the various terms are positive or negative.

Appendix

Equations for MMLFERs

These are formulated in terms of equilibrium constants but can easily be adapted for use with rate constants or other physicochemical properties. Eqn (A1) has been developed here at the University of Toronto,[50] while eqn (A2) has been developed by Fernandez, Giering, Prock *et al.* at Boston University.[51]

$$\log K = \alpha + \beta(pK_a' + 4) + \gamma(\theta - \theta_{\text{th}})\lambda + \phi(pK_a'\pi) + \delta(E_{\text{ar}}) + \Omega E_{\text{pge}} \qquad \text{(A1)}$$

$$\log K = \boldsymbol{a}\chi_{\text{d}} + \boldsymbol{b}(\theta - \theta_{\text{st}})\lambda + \boldsymbol{c}E_{\text{ar}} + \boldsymbol{d}\pi_{\text{p}} + \boldsymbol{e} \qquad \text{(A2)}$$

The σ-donicities of the ligands are measured either by the dimensionless values of pK_a' or by χ_d (in cm^{-1}). Values of pK_a' are closely related to χ_d values which are values of χ (the C–O stretching frequencies for the A_1 vibration of $LNi(CO)_3$[17,52]) that have been adjusted for contributions of π-acidity.[53] However, the coefficient β in eqn (A1) is dimensionless while ***a*** in eqn (A2) has the dimensions cm.

The constant α in eqn (A1) represents a standard or reference value of log *K* for the hypothetical, weakly basic σ-donor ligand with a pK_a' value of only −4, while ***e*** in eqn (A2) takes as a reference the value of log *K* for the most highly basic σ-donor $P(t\text{-}Bu)_3$ ligand with $\chi = \chi_d = 0$. Both assume that the ligands have no steric effect, *i.e.* $\theta < \theta_{\text{th}}$ or zero (see below). The term $\beta(pK_a' + 4)$ measures the extent to which a ligand with higher σ-basicity ($pK_a' > -4$) modifies the standard value α, while the term $\boldsymbol{a}\chi_d$ measures the extent to which a ligand with a lower σ-basicity than that of $P(t\text{-}Bu)_3$ modifies the standard value ***e***.

Values of θ are given simply by the cone angles,[17,41] and the units of γ and ***b*** are therefore both deg^{-1} and both measure the extent to which larger ligands modify the standard values. θ_{th} (and θ_{st}) represent the steric threshold below which the switching function λ is zero and there are no steric effects, and above which λ is unity and steric effects are present.

Values of $pK_a'\pi$ in eqn (A1) have been derived from deviations of values of χ for π-acidic ligands from the values expected for simple σ-donors.[41] As a result values of the coefficients β and φ, and the relative effects of σ-donicity and π-acidity, can be directly and quantitatively compared. Values of the π-acidity parameter π_p in eqn (A2) have been derived[51a] from deviations similar to those in Fig. 4, with the deviation for $P(OMe)_3$ being arbitrarily set to be a dimensionless 3.0. Other deviations were scaled accordingly to give values of π_p for other π-acids, so that coefficients ***a*** and ***d*** cannot be directly compared.

E_{ar} in eqn (A1) is the so-called aryl effect parameter but is simply given by the number: 1, 2 and 3 of pendant aryl groups on the P-donor atom.[50] Giering and Prock *et al.* derived the values for E_{ar} in such a way that the aryl parameters for

$PR_{3-n}Ar_n$ ligands are 0, 1, 2 and 2.7 for n = 0, 1, 2 and 3, respectively.[39] However, the value 2.7 is actually an average of values for Ar = p-XC_6H_4 with a range that extends above the value 3. A derivation that avoids this problem[54] shows clearly that the value is not distinguishably different from 3, the actual *number* of aryl groups. The coefficient δ in eqn (A1) is therefore a measure of the deviation *per aryl group* of data for ligands with pendant aryl groups from that expected if only σ-donicity, π-acidity and steric effects were operative. The parameter E_{ar} in eqn (A2) has a similar significance but has been extended to include phosphite and other ligands that also show such deviations.[51] Thus a value of E_{ar} of 1.3 was derived[51a] for $P(OBu)_3$ from appropriate deviations observed for reduction potentials for $[(\eta^5\text{-}C_5H_5)(CO)LFe(COMe)]^+$. It is not quite clear how this value of E_{ar}, which is not an integral number, relates to the numbers 1, 2 and 3 for what one might call E_{ar}(proper), which are integral. However, in eqn (A1), the use of E_{ar} is restricted only to ligands with pendant aryl groups. Deviations of ligands with other pendant groups are related to parameters E_{pge}, which have the values 1, 2 or 3 depending on how many of the pendant groups are present, and which are applied to each pendant group individually. The coefficients Ω will therefore provide a measure of the particular effect of a given type of pendant group. (Of course, E_{ar} is simply a particular example of E_{pge} but can for now be considered separately because of its 'primacy' among these pendant group effects). The procedure for determining pendant group effects generally will be described in detail elsewhere, and a particular example has already been described.[50]

It should be noticed that a new, very different, approach to the systemization of data for complexes containing P-donor ligands has recently been put forward.[47] Instead of using experimentally based properties, such as pK_a', p$K_a'\pi$ and θ, ligand "descriptors" are calculated *via* density functional theory, and used to model various experimental parameters.

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