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Notes

Correlations between the Ligand Electrochemical Parameter, E_L(L), and the Hammett Substituent Parameter, σ

Hitoshi Masui* and A. B. P. Lever*

Department of Chemistry, York University, North York,
Toronto, Ontario, Canada M3J 1P3

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Recently, a ligand electrochemical parameter, E_L(L), based upon the Ru^{III}/Ru^{II} reduction potential as an electrochemical standard, was introduced[1-3] and developed.[4-14] This parameter allows one to predict the metal-centered redox potential of a variety of complexes on the basis of the additivity of the E_L(L) parameters. The prediction is made using the linear relationship

$$E_{obs} = S_M[\sum E_L(L_i)] + I_M \qquad (1)$$

where the slope, S_M, and the intercept, I_M, are constant for all derivatives of a given metal undergoing a defined redox process, i.e. having a defined initial and final oxidation state, coordination number, stereochemistry, and spin state.

Hammett σ parameters have been shown to correlate with, inter alia, metal-centered electrochemical potentials in a variety of substituted ligand complexes.[15-31] It follows that, in these cases, Hammett parameters must also linearly correlate with E_L(L) values, as briefly noted for substituted benzoquinone diimine species.[3,32]

In this exploratory paper, we consider possible relationships between Hammett or Taft parameters and E_L(L) parameters. The question of whether it is better to use σ_p, σ_m, σ^+, or σ^* is discussed briefly. From a pragmatic point of view, correlation with σ_p or σ_m is preferred since there is a large database of these parameters for a wide variety of substituents. For example, σ_m and σ_p values for some 530 substituents are listed in Table I of ref 33. However, when the substituent is closer to the metal and metal–substituent π interactions are possible, σ^* or σ^+ may be more appropriate.

It should be possible to use Hammett or Taft parameters to derive E_L(L) values for a large variety of ligands not covered in ref 1, thereby greatly expanding the utility of the electrochemical parameter analysis. In particular, the availability of Hammett parameters for a great number of organic functional groups should permit these E_L(L) parameters to be used to derive redox potentials in a variety of organometallic species. Their availability should spur the synthesis of more exotic complexes by defining a potential range for their isolation. Further, electrochemically generated E_L(L) values may then be used to obtain σ values for hitherto unreported substituents. This paper begins the exploration of such a correlation but is restricted to a single- rather than multiple-parameter correlation.

The relationship between the E_L(L) parameter and the σ parameter can be deduced from the mathematical definition of the E_L(L) parameter (eq 4b of ref 1), the Nernst equation,[34] and the equations expressing the Hammett free-energy relationship.[31,35,36] Thus, the E_L(L) parameter of a substituted ligand, LX (LH denotes a parent ligand substituted by X which may also generally represent a collection of substituents as in the case of polysubstituted ligands), is given by[37]

$$E_L(LX) = 2.303(RT/nF)\rho(L)_{Ru^{III/II}}\sum\sigma + E_L(LH) \qquad (2)$$

Here, $\rho(L)_{Ru^{III/II}}$, the reaction parameter, characterizes the sensitivity of the $Ru^{III/II}$ redox potential to substitution at L for the series, $\sum\sigma$ is the sum of the Hammett or Taft parameters of the substituent(s) attached to L, and E_L(LH) is the E_L(L) parameter of the unsubstituted ligand. The remaining constants retain their usual meanings.[1,33-36] The reaction parameter is the fitted parameter.

On the basis of previous literature,[15-31] a correlation can be expected between $\sum\sigma$ and E_L(L) for homologous series such as substituted pyridines R-Py, substituted bipyridines, 4-R,4′-R′,5-R″,5′-R‴-bpy, R,R′,R″-phosphines, diketones (RCOCHR′COR″), and benzoquinone diimines, R-BQDI, for which a significant E_L(L) database[1,32] is available. In the pyridine and bipyridine series, it is reasonable to use the σ_p and σ_m parameters for substituents on the aromatic rings which are para or meta to the coordinating atoms; regression data are shown in Table I. In the case of the phosphines and diketones, where the substituent

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Table I. Correlation Parameters for $E_L(L)$ vs $\sum\sigma$ Plots[a]

ligand	S'_M	$E_L(LH)$	ρ^b	R^c	sample size
benzoquinone dimines, σ_p	0.17	0.26	2.9	0.98	6
phosphines, σ^*	0.17	0.35	2.9	0.95	10
pyridines, $\Sigma\sigma^d$	0.13	0.24	2.2	0.95	17
bipyridines, $\Sigma\sigma$	0.07	0.25	1.2	0.99	18
diketones, σ^+	0.12	0.01	2.0	0.98	13
direct, $\sigma_p{}^e$	0.62	–0.37	10.5	0.95	20

[a] Solutions to eq 3. See text for details concerning parameter used. Values of σ_m and σ_p, of σ^*, and of σ^+ were taken from Tables I, II, and V, of ref 33, respectively. Actual data are listed in the Appendix. [b] Reaction parameter for $Ru^{III/II}L$. [c] The regression coefficient. [d] $\Sigma\sigma = \sigma_m + \sigma_p$ as appropriate for the species concerned. [e] Solution to eq 3; also see Tables II and III.

is closer to the reaction center, parameters such as σ^+, σ^*, or R,[33,39,40] which incorporate a resonance or π interaction may be more appropriate, given the importance of these interactions in determining the ligand's $E_L(L)$ value.[1] In the case of the phosphines (including phosphites), there are too few available σ^+ parameter values to be very useful. A good correlation was observed with σ^* (Table I), and fairly good correlations were also observed for σ_p and σ_m although they were statistically less well behaved than σ^*. Correlation with R, the resonance parameter, was very poor. One may question whether σ^* values are fully additive when dealing with several substituents on the same atom (phosphorus), and a more detailed analysis of such an assumption is left for future analysis. An excellent correlation is observed for the diketone species with σ^+ much better than with σ^*. Good correlations are also observed with both σ_p and σ_m, but the application of σ^+ is more appropriate in this case (Table I).

While good linear correlations were obtained for all the homologous series studied (Table I), one should note the narrow range of E_L parameters for each series (except perhaps the bipyridines) so that a good correlation, while useful, is not so surprising or dramatic.

Table II. Species Which Act as Ligands and Substituents

species (X)	$\sigma_p(X)^a$	$E_L(X^-)^b$	species (X)	$\sigma_p(X)^a$	$E_L(X^-)^b$
OH	–0.37	–0.59	NO_3	0.7	–0.11
SPh	0.07	–0.53	NCS	0.52	–0.06
F	0.06	–0.42	NO_2	0.78	0.02
N_3	0.08	–0.3	CN	0.66	0.02
H	0	–0.3	$NH_3{}^+$	0.6	0.07
NCO	0.19	–0.25	$SMe_2{}^+$	0.9	0.31
I	0.18	–0.24	$PMe_3{}^+$	0.73	0.33
Cl	0.23	–0.24	$PEt_3{}^+$	0.98	0.34
Br	0.23	–0.22	$PMePh_2{}^+$	1.18	0.37
$OCOCF_3$	0.46	–0.15	$N_2{}^+$	1.91	0.68

[a] Values obtained from ref 33. [b] Values obtained from ref 1.

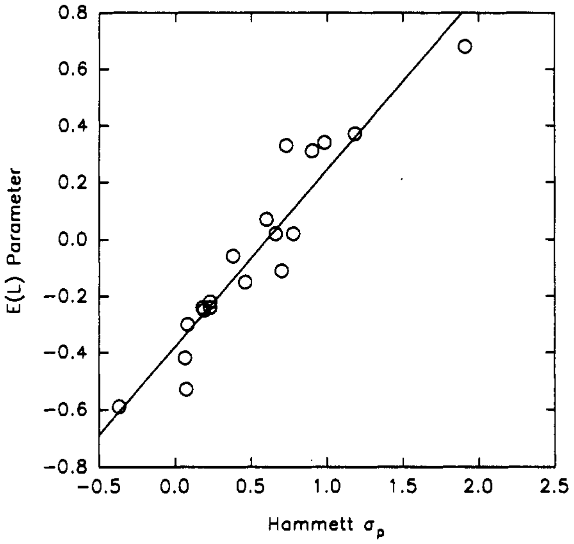

Figure 1. Plot of the $E_L(L)$ parameter versus the Hammett σ_p parameter for substituents capable of acting directly as ligands (data in Table II).

The $\rho(L)_{Ru^{III/II}}$ parameters do not vary greatly between these series and are largest for substituted benzoquinone diimines[32,41] and phosphines, where electronic coupling to the metal center is known to be very strong. Surprisingly, the reaction parameter for the pyridine series is twice that for the bipyridine series, showing that substituent effects are transmitted much more readily to ruthenium in the pyridine series than in the bipyridine series. This may be due to a steric effect.

Of more profound value, a correlation with σ_p was also noted between a large number of neutral and anionic ligands which may be regarded as substituents of a hydrido $M(L')_nH$ species. Thus if the substituent is attached directly to the metal

$$E_L(X^-) = 2.303(RT/nF)\rho_{Ru^{III/II}}\sum\sigma + E_L(H^-) \qquad (3)$$

For example (Table II), NH_3 and Cl^- ligands may replace the hydrido ligand on ruthenium just as $NH_3{}^+$ and Cl would replace the hydrogen of an organic molecule. Such analogies have been drawn previously between organic and inorganic fragments.[38]

The validity of eq 3 may be tested by plotting the $E_L(L)$ data listed in Table II against σ_p as in Figure 1. Indeed, quite a good linear correlation is observed between the two parameters with the y-intercept gratifyingly close to the $E_L(H^-)$ value of the hydride ligand. As expected, the sensitivity of the $Ru^{III/II}$ redox potential to direct substitution, as indicated by $\rho_{Ru^{III/II}}$, is much greater than that of the ligand substitutions in the homologous series identified above. Given the closeness of the interaction, the σ_p parameter is not necessarily the most appropriate parameter to use, but pragmatically it works, while parameters such as R[33] do not and σ^* and σ^+ cannot be adequately tested.

This direct correlation provides an exciting opportunity for greatly expanding the $E_L(L)$ database. Thus, the correlations shown in Tables I and II may now be used to derive $E_L(L)$ not only for many substituted ligands but also for a variety of exotic ligands chosen, for example, from Table I of ref 33, i.e. ligands which may be more common in organometallic chemistry. Some of these predicted $E_L(L)$ values are presented in Table III.

It remains to be seen if ligands such as $NH_2{}^-$, which are likely to be strongly π-bonded to ruthenium, can be treated in such a

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(37) Consider a series of complexes having the general form $M(L')_n(LH)$ (I) and $M(L')_n(LX)$ (II), where L′ represents spectator ligands which may be of one or more types, then the half-cell oxidation potentials of these species, referenced to NHE, E_0(I) and E_0(II), may be written as follows:

$$[M(L')_n(LH)]^n + e^- \rightleftarrows [M(L')_n(LH)]^{n-1} \quad K_{eq}(LH)$$

$$E_0(I) = \sum E_L(L') + E_L(LH) = (RT/nF)\ \ln(K_{eq}(LH))$$

$$[M(L')_n(LX)]^m + e^- \rightleftarrows [M(L')_n(LX)]^{m-1} \quad K_{eq}(LX)$$

$$E_0(II) = \sum E_L(L') + E_L(LX) = (RT/nF)\ \ln(K_{eq}(LX))$$

Thus

$$E_0(II) - E_0(I) = E_L(LX) - E_L(LH) = (RT/nF)[\ln(K_{eq}(LX)) - \ln(K_{eq}(LH))]$$

$$E_L(LX) - E_L(LH) = 2.303(RT/nF)\ \log[K_{eq}(LX)/K_{eq}(LH)]$$

But

$$\log[K_{eq}(LX)/K_{eq}(LH)] = \rho\sigma$$

Therefore

$$E_L(LX) = 2.303(RT/nF)\rho\sigma + E_L(LH)$$

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Table III. Predicted E_L(L) Values

species (X)	σ_p(X)^a	E_L(X$^-$)^b	species (X)	σ_p(X)^a	Ex_L(X$^-$)^b
NH_2	−0.66	−0.78	acetate	−0.16	−0.47
NHPh	−0.56	−0.71	$SiMe_3$	−0.07	−0.41
NMe_3^+	0.82	0.13	CMe_3	−0.2	−0.49
HS	0.15	−0.28	Ph	−0.01	−0.38
Me	−0.17	−0.47	C_6F_5	0.27	−0.20
CF_3	0.54	−0.04	$Si(NMe_2)_3$	−0.04	−0.39

^{a} Values obtained from ref 33. ^{b} Values obtained using eq 3 (see Table I, bottom entry).

simple fashion. One may also question in the future whether multiple substituents in the same ligand can be linearly treated with eq 2; this does appear to be possible to the extent that it has been tested in the species discussed here. Future work will also address how the reaction parameters change with other metal ions, to see how substituent effects are transmitted to couples other than Ru$^{III/II}$ and whether multiparameter fits[42] may offer advantages. One may also expect that careful analysis of Hammett or Taft parameters giving good correlations with E_L(L), compared with those that do not, will provide additional information about the factors determining such relationships.

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Appendix: Data Used To Determine the Regression Statistics in Table I

Benzoquinone diimines, E_L(L), $\Sigma\sigma = \Sigma\sigma_p$ (electrochemical data and hence E_L(L) values from ref 41): 4-NO_2BQDI, 0.38, 0.78; 4,5-Cl_2BQDI, 0.33, 0.46; BQDI, 0.28, 0; 4,5-$(CH_3)_2$BQDI, 0.25, −0.34; 4,5-$(OME)_2$BQDI, 0.16, −0.54; 4,5-$(NH_2)_2$BQDI, 0.01, −1.32.

Phosphines, E_L(L), $\Sigma\sigma^*$ (E_L(L) values from ref 1): Me_3P, 0.33, −0.15; Me_2HP, 0.34, −0.1; Me_2PhP, 0.34; 0; Pr_3P, 0.34, −0.15; Et_3P, 0.34, −0.15; $MePh_2P$, 0.37, 0.15; $(tolyl)_3P$, 0.37, 0.15; Ph_3P, 0.39, 0.3; $(PhO)_3P$, 0.58, 1.14; $(MeO)_3P$, 0.42, 0.69.

Pyridines, E_L(L), $\Sigma\sigma = \sigma_m + \sigma_p$ (E_L(L) values from ref 1): 4-ViPy, 0.2, −0.04; 3,5-Me_2Py, 0.21, −0.14; 4-PhPy, 0.23, −0.01; 4-MePy, 0.23, −0.17; 4-StPy, 0.23, −0.07; 4-*t*-BuPy, 0.23, −0.2; Py, 0.25, 0; 3-$CONH_2$Py, 0.26, 0.28; 4-ClPy, 0.26, 0.23; 4-$CONH_2$Py, 0.28, 0.36; 3-IPy, 0.29, 0.35; 4-COOHPy, 0.29, 0.45; 4-AcPy, 0.3, 0.5; 4-CHOPy, 0.31, 0.42; 4-CNPy, 0.32, 0.66; 4-CF_3Py, 0.32, 0.54; 3,5-Cl_2Py, 0.33, 0.74.

Bipyridines, E_L(L), $\Sigma\sigma = \sigma_m + \sigma_p$ (electrochemical data and hence E_L(L) values from refs 1 and 43–45): 4,4′-$(NEt_2)_2$bpy, 0.15, −1.44; 4,4′-$(Me)_2$bpy, 0.23, −0.34; 4,4′-$(CH{=}CHPh)_2$bpy, 0.24, −0.14; 5,5′-Me_2bpy, 0.24, −0.14; 4,4′-Ph_2bpy, 0.25, −0.02; bpy, 0.26, 0; 4-Cl-bpy, 0.27, 0.23; 4-Br-bpy, 0.27, 0.23; 4,4′-Cl_2bpy, 0.29, 0.46; 4,4′-Br_2bpy, 0.29, 0.46; 4,4′-$(CO_2Et)_2$bpy, 0.31, 0.9; 4-Me-4′-vinyl-bpy, 0.23, −0.21; 4-nitrobpy, 0.30, 0.78; 4,4′-$(CO_2Ph)_2$bpy, 0.31, 0.88; 5,5′-$(CO_2Et)_2$bpy, 0.32, 0.88; 4,4′,5,5′-Me_4bpy, 0.22, −0.48; 4,4′-$(CF_3)_2$bpy, 0.33, 1.08; 5,5′-$(CF_3)_2$bpy, 0.33, 0.86. Electrochemical data for the species 4,4′-$(OEt)_2$bpy, 4,4′-$(NHCOMe)_2$bpy, 4,4′-$(OPh)_2$bpy, and 5,5′-$(NHCOMe)_2$bpy, from ref 43 are excluded since they fit the correlation poorly; either the electrochemical or the Hammett data are suspect.

Diketones, E_L, σ^+ (electrochemical data and hence E_L(L) values from refs 1, 21, and 22) (listed as derivatives of RCOCR′COR″): CF_3,H,Ph, 0.05, 0.43; CF_3,H,CH_3, 0.03, 0.30; CF_3,H,CF_3, 0.17, 1.22; Ph,H,Ph, −0.04, −0.36; Ph,H,Me, −0.06, −0.49; Me,H,Me, −0.08, −0.62; Me,Br,Me, −0.03, −0.47; Me,Cl,Me, −0.03, −0.51; Me,I,Me, −0.03, −0.48; Me,Me,Me, −0.11, −0.93; Me,Ph,Me, −0.09, −0.80; CF_3,H,3-thienyl, 0.05, 0.23; CF_3,H,*t*-Bu, 0.02, 0.35.

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