An analysis of cobaloxime chemistry with the electrostatic–covalent model [1]

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Abstract

The ECW model is used to interpret the chemistry of $XCo(DH)_2 \cdot B$ complexes as B is varied. The ΔE–ΔC parameters provide a means of determining the influence of variation of X. Compared with the emphasis on steric effects in the literature explanation of this chemistry, these effects are seen to be minimal when a proper estimate of the covalency in the interaction is made. More electron-releasing substituents–X–are seen to decrease the tendency of cobalt to undergo electrostatic interaction with B, but to increase its tendency for covalent bonding. Electron-withdrawing substituents have the opposite effect. An entropic effect associated with rotational degrees of freedom of the X group is reported to cause deviations in free energy rate and equilibrium constant correlations. This effect is supported by its absence in bond distance and $E_{1/2}$ correlations. The cobalt center has significant tendencies to bind covalently to ligands and to undergo π-backbonding into phosphites and nitriles.

Keywords: Cobalt; Oximes; Electrostatic–covalent model

1. Introduction

The impact of the dual concept charge-frontier, hard-soft or electrostatic–covalent (E–C) models has been substantial. However, one-parameter basicity scales are used in many articles involved with analyzing the influence of structure on reactivity tacitly ignoring these ideas. In a recent article [1] it was shown that whenever a measured physicochemical property is plotted vs. a single parameter scale of basicity or acidity the assumption is being made that the property has the same ratio of the charge-frontier, hard–soft or E–C contributions as the scale. Recently, it has been shown [2] that the diversity of one parameter substituent constant scales (Hammett, Taft, etc.) correspond to scales in which the electrostatic–covalent properties are different. Deviations from one-parameter plots can arise from steric, entropic or π-backbond effects or they can arise because the scale has a different ratio for the electrostatic–covalent contributions. Thus, the interpretations are ambiguous when one parameter scales are used.

Two related approaches have been offered for the analysis of reactivity with the electrostatic–covalent model. The first [3] correlates sigma bond strengths and analyzes the sigma bond strength contribution to chemical reactivity with Eq. (1)

$$\Delta\chi = E_A^* E_B + C_A^* C_B + W \qquad (1)$$

Here the measured physicochemical property $\Delta\chi$ (in energy units) for a series of measurements in which the base, B, is varied toward a given acceptor, A, are correlated to reported electrostatic, E_B, and covalent, C_B, properties for the base. A series of equations, one for each measurement, is solved for the acceptor parameters E_A^*, C_A^* and W. Good agreement between the $\Delta\chi$ values calculated by substituting the best fit E_A^*, C_A^* and W into Eq. (1) with those measured indicates that the series of measurements is dominated by the same factors that influence sigma-bond strength. The asterisk is used to denote an acceptor parameter that is not a solvation minimized enthalpy measurement. These enthalpies are the basis for the E_B and C_B parameters.

The same approach is used to analyze physicochemical data in which the donor is held constant as a series of acceptors are studied. Reported E_A and C_A parameters are used and asterisks placed on the E_B^* and C_B^* for

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[1] Dedicated to Professor Marvin Rausch on the occasion of his 65th birthday.

the physicochemical base property. This procedure is offered as a replacement for plots of physicochemical data versus pK_B or other one parameter scales of basicity or acidity.

The second approach [2] is basically the same E–C approach for a series of measurements that are restricted to substituent changes in a family of compounds. Eq. (2) is employed.

$$\Delta\chi^X = d^E\Delta E^X + d^C\Delta C^X + \Delta\chi^H \tag{2}$$

$\Delta\chi^H$ is the physicochemical measurement of the parent hydrogen compound, $\Delta\chi^X$ the measurement for the X-substituted derivative, ΔE^X and ΔC^X are proportional changes made in the E and C values by the substituent i.e. they are dual parameter counterparts of Hammett σ values. Data are analyzed as described for Eq. (1).

Inorganic and organometallic systems often do not respond well to analyses with the organic-based substituent constants. This has led to a diversity of substituent constants. Recent work has shown that the ΔE^X and the ΔC^X parameters not only work well for the organic systems, but can also be applied to a variety of inorganic systems [4]. They have also been used to provide a new interpretation of phosphine reactivity in organometallic systems [5].

In this article our attention will be focused on the physicochemical properties of cobaloxime derivatives [XCo(DMGH)$_2$]. The attempts to understand B$_{12}$ chemistry via understanding the reactivity of model compounds has motivated a very considerable amount of work in this area. The effort up to 1989 has been summarized [6].

The interpretation of cobaloxime chemistry is described as having had a checkered past [7a]. The recent approaches have attempted analysis using the classical dual substituent constant equation. Marzilli and co-workers [6b] redefined the zero point of the substituent constant scale to CH$_3$ equal zero and renormalized the scales to make the parameters work. The resulting parameters were not even of general applicability to cobaloximes, but could only be used for X substituents on XCH$_2$Co(DH)$_2$ derivatives i.e. XCo(DH)$_2$ systems were excluded. Brown [7a] reported that the renormalization of the scale led to bizarre effects on the resonance substituent constants, and criticized the Marzilli parameters. The reader is referred to Ref. [7a] for details. A new approach was offered [7a] in which a steric term was added and a choice of σ_R^0, σ_R^+, σ_R^- parameter used in addition to σ_I in the equation

$$\Delta\chi = \rho_I\sigma_I + \rho_R\sigma_R + \rho_S\sigma_S + C \tag{3}$$

Added flexibility was provided by offering a choice of steric parameters, σ_S. Again, the analyses are limited to XCH$_2$Co(DH)$_2$ complexes and the resonance contribu-

tion is reported not to involve cobalt, but arises because of the non-orthogonality of X and CH$_2$.

The influence of the cobalt–ligand L interaction in XCo(DH)$_2$L on various physicochemical properties have also been treated with single parameter basicity scales, often pK_B, and is thus assumed to have a constant covalent/electrostatic ratio in all of the chemistry analyzed. The poor correlations expected from single parameter correlations [1] are explained by a variety of electronic effects or steric effects which are concluded to play a dominant role in much of the chemistry [6].

Several physicochemical properties of these compounds can be treated [4] by ΔE^X and ΔC^X. Eq. (2) affords a very different interpretation of the reactivity of cobaloximes than that reported in the literature. Steric effects were found to play a greatly diminished role. In addition to better understanding of the reactivity of this important class of compounds, the increased general applicability of this model further establishes our claim [4] that the electrostatic–covalent model is the energy counterpart of the Woodward–Hoffman symmetry rules for interpreting chemical reactivity. The ability of the electrostatic–covalent model to fit much of this chemistry with two parameters instead of three and the ability to include XCo(DH)$_2$ in the analyses as well as XCH$_2$Co(DH)$_2$ complexes has prompted a more detailed analysis of this chemistry. The systems treated will involve variation of L with X constant in XCo(DH)$_2$L and variation of X with L constant.

2. Results and discussion

2.1. Variation of B in XCo(DH)$_2$B

Compared to studies in which X is varied, relatively few studies have involved variation of the donor molecule B. Enthalpies for the reaction in Eq. (4) were measured in poorly solvating solvents [8] for various donors.

$$[CH_3Co(DH)_2]_2 + 2B \rightleftharpoons 2CH_3Co(DH)_2B \tag{4}$$
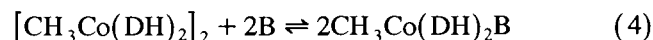
Using the reported E_B and C_B values [3a] the enthalpies are fit to Eq. (1) with $E_A = 4.70$, $C_A = 3.24$ and $W = -5.84$. The $\Delta\chi$ of Eq. (1) is $-\Delta H$ in this fit. The W value corresponds to an enthalpy of dissociation of 11.7 kcal mol^{-1} of dimer. The data fit is shown in Table 1 where the enthalpies correspond to the reaction in Eq. (4) in units of kcal mol^{-1} of product (i.e. one half the enthalpy for the equation written). The C_A/E_A ratio of 0.7 is compared to 0.5 for zinc tetraphenylporphyrin and 1.0 for [Rh(CO)$_2$Cl]$_2$. Triethylphosphite deviates from the fit in a direction corresponding to π-backbond stabilization providing a measure of the magnitude of this effect.

Table 1
ECW fits of physicochemical data for $XCo(DH)_2$ systems [a]

Donor	$-\Delta H$ $CH_3Co(DH)_2 \cdot B$		$\Delta H_D Co-C$		log K in DMSO		log k_r $CH_3Co(DH)_2L$		Donor	$\delta CH_3 - \delta CH_2$		$\delta^{59}Co$	
	Exp.	Calc.[b]	Exp.	Calc.[c]	Exp.	Calc.[d]	Exp.	Calc.[e]		Exp.	Calc.[f]	Exp.	Calc.[g]
C_5H_5N	14.1	14.0	19.5	19.6	2.96	2.90	−2.10	−2.15	C_5H_5N	1.40	1.36	4490	4515
$(CH_3)_3N$					1.24	(2.67)			$(CH_3)_3N$			4360	4362
Quinuclidine					2.25	2.25	−1.80	(−5.68)	NH_3	1.35	1.39		
$4\text{-}CNC_5H_4N$					1.73	1.74	−1.38	−1.32	CH_3NH_2	1.30	1.32		
$4\text{-}(CH_3)_3CC_5H_4N$			17.9	12.8	3.13	3.18	−2.88	−2.37	$(CH_2)_5NH$	1.30	1.30		
$RC(CH_2O)_3P$	13.0	(8.6)							$3\text{-}CNC_5H_4N$	1.52	1.49		
N-CH_3 imid	15.4	15.6	20.8	20.8	2.13	(−0.32)	−1.30	(−1.59)	$(C_2H_5)_2S$	1.63	1.65		
$4\text{-}(CH_3)_2NC_5H_4N$							−3.60	−3.61	H_2O	1.60	1.59		
$(CH_2)_4O$	9.1	8.9					−3.36	−3.30	$(CH_3)_2S$			4960	4958
$(CH_3)_2NCN$	6.0	6.2							CH_3CN			5470	(5010)
$(CH_2)_4S$	8.6	8.6							$4\text{-}CH_3C_5H_4N$			4490	4469
$4\text{-}CH_3C_5H_4N$			20.1	20.2					$3\text{-}CH_3C_5H_4N$			4490	4485

[a] The substituted pyridine E_B and C_B parameters are from Ref. [6]. n-values of 0.2 which refer to 1/weight given a measurement are used for all donors used in the fits. Those systems in parentheses are omitted from the fit and calculated from the parameters obtained by fitting the rest of the data set.

[b] Solvation minimized enthalpies. The enthalpies calculated are those for Eq. (4) in units of kcal mol^{-1} adduct. The W value of −5.84 represents minus one half the enthalpy of dissociating the dimer $[CH_3Co(DH)_2]_2$ and is entered as the negative number in Eq. (1) to give the calculated enthalpy values in this table. In this way dimer dissociation makes an endothermic contribution to the reaction enthalpy.

[c] Cobalt–carbon bond dissociation energies for $(C_6H_5)CH_3CHCo(DH)_2 \cdot B$ calculated with $E_A^* = 2.57$, $C_A^* = 1.99$, $W = 8.04$. N-Methyl imidazole parameters were used for imidazole. $4\text{-}NH_2C_5H_4$ was also fit; exp. 21.2; calc. 21.1.

[d] Log of the formation constants of $CH_3Co(DH)_2 \cdot B$ from $CH_3Co(DH) \cdot (CD_3)_2SO$ in $(CD_3)_2SO$ solvent at 32°C. Calculated with $W = -4.0$, $E_A^* = 2.9$ and $C_A^* = 0.70$. An n-value of 0.6 was used for 4-t-butylpyridine.

[e] Log of the pseudo first-order rate constants (s^{-1}) for the dissociation of donor from $CH_3Co(DH)_2 \cdot B$ by $(n\text{-}C_4H_9)_3P$ in CH_2Cl_2 at 25°C. Calculated with $W = 3.31$, $E_A^* = -0.59$ and $C_A^* = -1.27$. $4\text{-}CNC_5H_4N$ and $4\text{-}(CH_3)_2NC_5H_4N$ given n-values of 0.3.

[f] The difference in the proton chemical shift of the CH_3 and CH_2 groups of $C_2H_5Co(DH)_2 \cdot B$. Calculated with $W = 2.08$, $E_A^* = -0.21$, $C_A^* = -0.10$. The H_2O adduct was fit with gas phase, monomer water parameters.

[g] ^{59}Co chemical shift in $CH_3Co(DH)_2 \cdot B$ adducts referenced to external aqueous $Co(NH_3)_6Cl$. Calculated with $W = 5635$, $E_A^* = -312$, $C_A^* = -160$.

Substituting values for other physicochemical measurements, $\Delta\chi$, into Eq. (1), along with reported E_B and C_B values, corresponds to analyzing $\Delta\chi$ with the enthalpy based dual parameter E_B, C_B donor scale. The value of $\Delta\chi$ when $C_B = E_B = 0$ is given by W. A successful data fit indicates that the measured property is dependent on some combination of the same electrostatic and covalent properties that determine sigma bond strength when these donors react.

The limited data on cobalt–carbon bond energies for $(C_6H_5)(CH_3)CHCo(DH_2 \cdot B)$ are fit to Eq. (1) and the fit is shown in Table 1. The bond is seen to be stabilized by base binding. Both the covalent and electrostatic donor properties of the ligands contribute. The W value in this case is the enthalpy of dissociation of the cobalt–carbon bond when a base with E_B and C_B equal to zero is attached (i.e. only dispersion forces of cobalt with the non-basic solvent exist).

The next set of data to be analyzed with Eq. (1) is the difference in CH_3 and CH_2, proton chemical shifts of the ethyl group for donor, B, adducts of $C_2H_5Co(DH)_2 \cdot B$ (where DH is dimethylglyoximate monoanion) [9]. The difference in the methyl and methylene shifts is analyzed because the difference will compensate for the neighbour anisotropic contribution to the proton shift. The experimental values and results of the least squares fit of the data to Eq. (1) are listed in the first two data columns of Table 1. The average deviation of calculated and experimental values, $\bar{x}$, is 0.023, an excellent result in view of possible remaining variations in neighbor anisotropic contributions to the proton shift. The per cent fit ($100 \times \bar{x}$/high–low calc. value) of 6.5% is a satisfactory value for the small range of the measured values.

The E_A^* and C_A^* values show that increasing the covalent and electrostatic bond forming properties of the donor decreases the magnitude of the shift from the W value of 2.08 predicted for $\delta CH_3 - \delta CH_2$ in $C_2H_5Co(DH)_2$ with no donor attached. Increasing both the covalent and electrostatic bonding properties of the donors increases electron density on the ethyl group which shields the CH_2 resonance more than the CH_3 making the CH_2 and CH_3 resonances less different. This produces negative E_A^* and C_A^* values. The $\Delta C^*/\Delta E^*$ ratio for this data set is 0.45 and can be compared with the values of ~ 0.7 for the enthalpy fit of $CH_3Co(DH)_2 \cdot B$. This does not imply that the metal–ligand interaction is more electrostatic in the ethyl derivative. The lower ratio indicates that the sensitivity of the chemical shift difference is more dependent on the electrostatic bond forming tendencies of the donor [1] in these adducts than is the enthalpy in the methyl derivative.

The CH_3-CH_2 differences in chemical shift of the ethyl group in adducts of $C_2H_5Co(DH)_2$ are determined by the same donor properties (E_B and C_B) that deter-

mine σ-bond strengths for the donors studied. A minor contribution from metal to ligand π-back bonding may exist in the pyridine and 3-cyanopyridine adducts, but more donors would have to be studied to be confident of this conclusion. This interpretation differs from the literature analysis of the nmr shift difference [9] where $\delta CH_3 - \delta CH_2$ gave a poor plot vs the donor pK_B. Accordingly, two plots are made [9] to correlate the data. One plot consists of aliphatic donors and, the other of aromatic nitrogen donors. This division of the data often limits the donor C_B/E_B values for each set so straight lines can be obtained. Linear correlations of uncertain meaning and limited utility [1] result. Since all seven of the donors studied whose E_B and C_B values (including water and a sulfur donor) are known to fit the ECW model (Table 1), the deviations of the measurements from a single-line pK_B plot result because pK_B values provide a poor indication of the covalent properties of the donor that determine the shift difference. More important than fitting data, the electrostatic–covalent model has provided a much simpler, more rational explanation of this data set than that in the literature.

The chemical shifts of a much more extensive range of donors have been reported for $(CH_3)_2CHCo(DH)_2 \cdot B$ adducts [6a]. However, the range of shifts for donors with established E_B and C_B parameters is only 0.1 ppm, precluding a meaningful analysis.

Limited data are available [10] on the ^{59}Co chemical shift of $CH_3Co(DH)_2B$ adducts. The data fit very well ($\bar{x} = 11$ and % fit = 2) when the acetonitrile adduct is eliminated from the fit. The acetonitrile exception is attributed to π-backbonding and is consistent with the enthalpy fit proposal for the phosphite deviation. Back donation from cobalt into the π^* orbital of CH_3CN decreases the electron density on cobalt and increases the shift. Only five enthalpies are solved for three unknowns leading to a tentative C_A^*/E_A^* ratio of ~ 0.5 from the limited data set. The problem with misses in any limited data set involves determining which system to eliminate. In this data set, no one donor besides CH_3CN can be eliminated to produce as good a fit.

The ECW fit of the equilibrium constant for the formation of donor adducts [6a] by displacing $DMSO-d^6$ from $CH_3Co(DH)_2 \cdot DMSO-d^6$ in $DMSO-d^6$ solvent is shown in Table 1. Since phosphites undergo π-back bond stabilization, this donor is eliminated from the data fit. If $(CH_3)_3N$ is given low weight and the phosphite eliminated, a good fit results. With only four data points solved for three unknowns, the parameters are tentative. The tentative C_A^*/E_A^* ratio of 0.2 indicates that log K is more dependent on the electrostatic properties of the base than $-\Delta H$ is. Even with the limited data set, the inconsistency of the $(CH_3)_3N$ data point is observed. Since quinuclidine is fit and has steric requirements similar to $(CH_3)_3N$, the deviations of the latter donor are attributed to problems in working with a

gaseous donor and determining solution base concentrations. The greater tendency of pyridine to undergo electrostatic bonding than quinuclidine leads to a larger K for pyridine.

When the C_B and E_B parameters for dimethyl sulfoxide are substituted into Eq. (1) along with E_A^*, C_A^* and W, a value of zero should result. Instead of zero, a value of 4 kcal mol^{-1} results. This suggests the existence of S-bonded sulfoxide or a mixture of S and O bonded sulfoxide which gives rise to a larger W value corresponding to a stronger interaction than that predicted for oxygen coordination to dimethyl sulfoxide. This has no influence on the fit. Again, this result indicates the significance of an ECW analysis to an investigator not interested in correlations. When ECW analyses are employed while carrying out experimental measurements, the inconsistencies can be investigated by spectroscopic measurements. In this case, the mode of dimethylsulfoxide coordination could have been determined by IR spectroscopy.

Pseudo first-order rate constants [6a] for the dissociation of donors from $CH_3Co(DH)_2 \cdot B$ by $(n\text{-}C_4H_9)_3P$ in CH_2Cl_2 are fit next. A poor fit results. Since the reaction is first-order dissociative, those donors that gave a satisfactory fit to the enthalpies of adduct formation and $4\text{-}CNC_4H_5N$ and $4(CH_3)_3NC_5H_4N$ gave a good fit, with an $\bar{x}$ of 0.05 and a % fit of 2. Increased metal–ligand bond strength leads to an increase in the activation energy for ligand dissociation and a slower reaction. This gives rise to negative E_A^* and C_A^* values for the acceptor. The tentative C_A^*/E_A^* ratio of 3 for this system would suggest, if verified, a very substantial contribution to the cobalt–donor interaction from covalency compared with 0.7 for the enthalpies of adduct formation. The fit of the phosphite donor is surprising for an SN-1 (lim) mechanism. Steric interactions in the transition state are proposed for both this donor and quinuclidine leading to a faster reaction than calculated for quinuclidine and compensating for the expected π-contribution in the phosphite. It is proposed that rotational degrees of freedom are more restrictive in the adduct for pyramidal donors. This provides an entropic driving force for ligand dissociation. All of the donors that are well behaved in the fit are planar. Again, with only four donors used in the data fit, these conclusions must be regarded as tentative, but indicative of the insights that can be obtained from analyses with the electrostatic–covalent model.

The rate constants for the reduction of a series of $XC_5H_4NCo(DH)_2N_3$ adducts by Fe^{2+} in aqueous 2M ClO_4^- were measured [6a] at 25°C. Eight substituted pyridines were studied with C_B/E_B ratios varying from 1.64 (3-$NO_2C_5H_4N$) to 2.04 (4-$CH_3C_5H_4N$). The parameters $E_A^* = -0.597$, $C_A^* = 0.935$ and $W = 2.23$ lead to an excellent data fit of all reported systems; $\bar{x} = 0.08$ and the percent fit is 5.8.

A study of the kinetics [11] for the reaction of $Co(DH)_2 \cdot B$ with benzyl bromide provides an example of several studies of cobaloximes in which experimental design precludes any meaningful interpretation. The donors selected for study were C_5H_5N, $4\text{-}CH_3C_5H_4N$, N-methylimidazole, piperidine, $(CH_3)_3P$ and RCH $(CH_2O)_3P$. Benzene was employed as the solvent. With hydrogen bonding of coordinated piperidine to the solvent and π-backbonding into phosphorus complicating the interpretation of the measurements [8] only three systems remain to determine what normal sigma bond interactions are. If one accepts that at least two factors influence sigma bond strength, (electrostatic–covalent, hard–soft or charge–frontier control) the remaining donors are too similar to determine these contributions and no meaningful interpretation of these data are possible. This example illustrates the point that the electrostatic–covalent model is useful in experiment design as well as analysis.

2.2. Variation of the X group in $XCo(DH)_2B$

The successful correlation of cobalt–phosphorus bond distances in a series of $X\text{-}Co(DH)_2P(C_6H_5)_3$ complexes and the cobalt–nitrogen distances in a series of $X\text{-}Co(DH)_2C_5H_5N$ complexes have been reported [4]. The former series were fit to Eq. (2) with $d_B^E = 3.339$, $d_B^C = -0.723$ and $\Delta\chi^H = 2.057$ with an average derivation of 0.008. The d_B^E and d_B^C values like p-values have contributions from the demand reflected in the physicochemical property E_B^* and C_B^* as well as the sensitivity of the system to which the substituent is attached s_A^E and s_A^C

$$d_B^E = s_A^E E_B^*$$

$$d_B^C = s_A^C C_B^*$$

The sign reversal in d was attributed to a sign reversal in s, for both E_B^* and C_B^* are expected to be negative corresponding to a decrease in bond distance from strong electrostatic and covalent bonding. The sign of s_A^E is negative and that of s_A^C is positive. As a result, an electron-releasing substituent (e.g. methyl) with a positive ΔE and ΔC, decreases the acceptor strength for the electrostatic interaction, but increases the acceptor strength for the covalent interaction. The former is expected from the decreased partial positive charge on the cobalt, but the latter is unexpected from HOMO–LUMO energy considerations. The increased covalency is attributed to changes induced by the substituent in the s, p, d character of the cobalt acceptor orbital changing the polarizability of cobalt.

A total of 17 physicochemical properties were fit to Eq. (2) with few or no exceptions that could be attributed to front strain steric effects in the properties studied. This stands in sharp contrast to the major role

steric effects play in the literature interpretations of these different sets of measurements [6,7].

Table 2 summarizes the ΔE–ΔC data fits of cobaloxime systems that in the past were interpreted [6,7] with different sets of substituent constant parameters. It is important to emphasize that in contrast to past treatments, the electrostatic–covalent ΔE–ΔC data fit is not restricted to $XCH_2Co(DH)_2B$ systems. In the fits reported here, $XCo(DH)_2B$ complexes are treated and the ΔE–ΔC substituent constants employed are those for the entire CH_2X group. Literature reports that limit analyses to X substituents bound to CH_2 increase the chances for a successful correlation by limiting the E/C ratio of the cobalt complexes correlated and by decreasing the magnitude of the experimental changes with substituent changes.

The equilibrium constants, for formation of $XCH_2Co(DH)_2CN^-$ from $XCH_2Co(DH)_2H_2O$ in aqueous solution, determined [7a] from spectroscopic equilibrium measurements, are fit very well by ΔE–ΔC if the systems indicated by parentheses in the calculated column of Table 2 are omitted. Apparently an unusual solvation component contributes to the measured free

energies in the omitted substituents. The literature interpretation fits all the data points by using σ_R^- and invoking a steric component for every substituent based on Charton's parameters. In view of the absence of steric effects in bulkier systems than this one [4], this interpretation is discounted. The reported [7a] successful data fit illustrates the wide latitude offered in data analysis by the variety of electronic and steric scales in the literature. Unusual solvation or other effects can be masked by efforts to get good data fits by judicious selection of parameters.

The ^{13}C chemical shift is fit fairly well considering that π-backbonding into cyanide would influence different carbon orbital populations and have a very complex influence on the ^{13}C chemical shift. X-substituents containing donor groups deviate the most and may be hydrogen bonding to water. The literature interpretation fits all the ^{13}C data points very well using σ_R and invoking a steric component based on Taft's steric parameters. It is difficult to appreciate why different steric effect and substituent parameters are used [7a] to fit ^{13}C and ΔG values for the same complex. The excellent fit of the 4-t-butylpyridine and phosphite

Table 2

Physicochemical properties of $XCo(DH)_2 \cdot B$ where X is varied [a]

X	log K CN Exp.	Calc. [b]	^{13}C XCo^{13}CN$^-$ Exp.	Calc. [c]	log k XCoB Exp.	Calc. [d]	log k XCoB' Exp.	Calc. [e]	K XCoC5H5N Exp.	Calc. [f]	pK XCo·H2O Exp.	Calc. [g]	$E_{1/2}$ XCoH2O Exp.	Calc. [g]
CH$_3$	8.0	7.9	160.0	159.1	−0.32	(0.60)	−1.39	(−0.26)	3.4	(2.9)	12.7	(12.9)	0.79	0.77
C$_2$H$_5$	7.7	7.8	159.1	159.7	0.89	0.85	−0.02	−0.02	2.9	2.9	13.0	13.0	0.75	0.75
n-C$_3$H$_7$	7.6	7.7	160.1	159.8	0.93	0.87	0.08	0.01					0.75	0.75
n-C$_4$H$_9$	7.6	7.7	160.1	160.2									0.75	0.74
i-C$_4$H$_9$	7.5	7.6	159.9	160.2	1.11	1.18	0.15	0.29					0.75	0.75
CH$_2$C(CH$_3$)$_3$	7.3	(7.8)	160.2	(159.8)	1.54	(0.73)	1.04	(−0.12)					0.73	0.75
CH$_2$C$_6$H$_5$	8.3	8.2	156.9	157.3	0.45	(−0.04)	−0.48	(−0.89)					0.76	0.82
CH$_2$Si(CH$_3$)$_3$	7.9	7.9	158.3	159.5	−2.96	−2.61	−0.37	−0.55					—	
CH$_2$Cl	8.8	8.9	154.2	153.2	−1.47	−1.54	−2.51	−2.36	3.4	3.5	11.9	11.8	—	
CH$_2$Br	9.1	9.0	152.9	152.7	−1.76	−2.01	−2.59	−2.79					—	
CH$_2$I	9.1	9.2	151.1	152.1	−2.03	−2.25	−2.80	−3.02	3.4	3.5	11.7	11.8	—	
CH$_2$CN	10.0	9.9	144.0	(149.0)	−3.77	−3.68	−4.52	−4.38	3.7	3.7	10.6	(11.4)	—	
CH$_2$NO$_2$	9.9	(10.5)	144.2	145.6			−5.37	−5.65					—	
CH$_2$CF$_3$	10.1	(9.3)	149.4	152.2	−2.96	−2.61	−3.57	−3.31	3.4	3.3	11.0	11.0	0.90	0.92
CH$_2$OCH$_3$	7.3	7.2	160.0	160.8	2.18	2.54	1.38	1.47					—	
CH$_2$CO$_2$CH$_3$	9.8	(9.3)	149.9	(152.1)	−2.62	−2.49	−3.57	−3.22					—	
i-C$_3$H$_7$	—	—							2.7	2.7	13.3	13.3	0.71	0.72

[a] The d^E, d^C and $\Delta\chi^H$ values reported in this table for some systems differ from those reported earlier [4]. In the earlier fit the objective was to obtain substituent ΔE^X and ΔC^X values so all substituents were given equal weight. In this article, the objective is to obtain an understanding of the cobaloxime chemistry and substituents were assigned weights corresponding to the n-values reported in the literature [4].

[b] Formation constants at 25°C for $XCo(DH)_2CN^-$ from the aquo complex in water. Calculated with $d^E = -76.4$, $d^C = 13.2$, $\Delta\chi^H = 8.7$; $\bar{x} = 0.09$, % fit $= 2.2$.

[c] ^{13}C chemical shift of the coordinated cyanide of $XCo(DH)_2CN^-$. Calculated with $d^E = 317.8$, $d^C = -51.1$, $\Delta\chi^H = 155.0$; $\bar{x} = 0.7$, % fit $= 5$.

[d] Log first-order (SN-1 (lim)) rate constants in CH_2Cl_2 at 25°C for $XCo(DH)_2$ 4-$CH_3OC_6H_4NH_2$. Calculated with $d^E = 190.5$, $d^C = -34.3$, $\Delta\chi^H = -1.41$; $\bar{x} = 0.16$, % fit $= 2.6$.

[e] Log first order (SN-1 (lim)) rate constants in CH_2Cl_2 at 25°C for $XCo(DH)_2 \cdot 4$-CNC_5H_4N. Calculated with $d^E = 176.9$, $d^C = -31.6$, $\Delta\chi^H = -2.17$; $\bar{x} = 0.17$, % fit $= 2.4$.

[f] Log of spectrophotometric equilibrium constant for formation of $XCo(DH)_2C_5H_5N$ from the aquo complex in water. Calculated with $d^E = -6.78$, $d^C = -0.01$, $\Delta\chi^H = 3.15$; $\bar{x} = 0.06$, % fit $= 6.5$.

[g] pK_A of $XCo(DH)_2 \cdot H_2O$. Calculated with $d^E = 14.68$, $d^C = -0.22$, $\Delta\chi^H = 12.45$; $\bar{x} = 0.05$, % fit $= 2.2$.

[h] Reversible oxidation [12] of $XCo(DH)_2H_2O$. $E_{1/2}$ vs. SCE in CH_3CN. The C_6H_5 derivative has an exp. value of 0.86 and a calc. value of 0.84. Calculated with $d^E = -5.44$, $d^C = 0.733$, $\Delta\chi^H = 0.86$; $\bar{x} = 0.016$, % fit $= 8$.

adducts [6] to ΔE–ΔC would make the existence of a steric effect unlikely for the cyano complex. The ^{13}C data set analysis supports the suggestion that various choices of electronic scales and different steric scales provide such latitude in data fitting that obtaining a good fit may be meaningless.

The first order (SN-1 lim) rate constants for ligand exchange of XCo(DH)$_2$B where B is 4-CH$_3$OC$_6$H$_4$NH$_2$ and XCo(DH)$_2$B′ where B′ is 4-CN-C$_5$H$_4$N have been studied in CH$_2$Cl$_2$. Excellent fits are obtained using the ΔE and ΔC parameters for X. The CH$_3$, CH$_2$C(CH$_3$)$_3$ and CH$_2$C$_6$H$_5$ substituents deviate by comparable amounts in both data sets. It is proposed that in all the well-behaved substituents rotation of the CH$_2$X group around the cobalt–carbon bond is easier in the transition state than in the ground state. This freer rotation gives rise to an entropy effect that enhances the rate. The CH$_3$ group rotates freely in the ground state so no rate enhancement occurs for this derivative in the transition state. This entropic difference explains the difficulty encountered [6,7] when linear [13] free energy fits are attempted on cobaloxime free energy measurements with the methyl substituent. The deviations for –CH$_2$C(CH$_3$)$_3$ and –CH$_2$C$_6$H$_5$ are in the opposite direction to CH$_3$ and suggest even a larger entropic contribution from metal–X rotational constraints in the ground state of these adducts than what exists in those substituents that fit the correlation. For –CH$_2$C(CH$_3$)$_3$ the effect is entropic and not enthalpic because this substituent is well behaved [4] in the pyridine adduct bond distance fit, the ^{13}C fits of 4-t-butyl pyridine and P(OMe)$_3$ adducts and the $E_{1/2}$ for XCo(DH)$_2$H$_2$O. Contributions to the free energies of reactions from the entropy changes accompanying metal–ligand rotation are very common in the reactions of trisubstituted phosphines [5]. The entropic effect can be distinguished from a cone angle or front strain steric effect by being absent in the enthalpy of the reaction or in a physicochemical measurement where rotational conformation energies do not contribute.

It is interesting to note that, contrary to the CH$_2$C(CH$_3$)$_3$ substituent, the –CH$_2$Si(CH$_3$)$_3$ substituent fits the correlation. The longer C–Si bond gives rise to lower rotational constraints in the ground state than in CH$_2$C(CH$_3$)$_3$. The C$_6$H$_5$CH$_2$ derivative deviates slightly in most of these data sets suggesting a possible enthalpic interaction with the equatorial ligands. It is interesting to note that in the fit of log K for forming XCo(DH)$_2$ · 4-CNC$_5$H$_4$ from XCo(DH)$_2$ · (CH$_3$)$_2$SO, the CH$_3$ group is well behaved. The rotational barriers for CH$_2$X groups are similar in both the reactant and product adducts and do not contribute to the reaction free energy.

If the ΔE, ΔC interpretation is accepted, the claimed successes of other analyses [6,7] illustrate an important point. If one limits the physicochemical property to

similar derivatives (in this case –CH$_2$X), accommodating parameters can be constructed or found that will provide good fits that are lacking in meaning. It should be emphasized that the enthalpy basis for E and C and its carry-over to ΔE and ΔC make these parameters uniquely related to sigma bond strength. Accordingly, the most successful fit of data by these or other parameters is not judged solely by the average deviation of calculated and experimental values. Instead, finding effects in a data set that are not related to bond strength is important. These effects must show a consistent pattern when all the substituents and physicochemical measurements are considered.

The three remaining data sets in Table 2 support the entropic explanation for the –CH$_3$ substituent. As expected, log K for displacing the small aquo ligand by pyridine is larger than predicted for the methyl substituent. The other CH$_2$X groups and isopropyl lose rotational freedom when the aquo adduct is converted to the pyridine adduct giving a negative entropy contribution to K. This contribution is absent or smaller in the methyl derivative so the experimental value is larger than that calculated with parameters that include a negative entropy contribution.

Loss of a proton from XCo(DH)$_2$H$_2$O is expected to have little influence on the rotational properties of the CH$_2$X group. Thus, even though –CH$_3$ was omitted from the data fit, its value is predicted. The deviation of the CH$_2$CN derivative is in the direction of more extensive hydrogen bonding of water to the nitrile group in the anion.

The –CH$_3$ group and CH$_2$C(CH$_3$)$_3$ groups are seen to both be well behaved in the $E_{1/2}$ XCo(DH)$_2$H$_2$O data fit. An excellent correlation results with the major contribution arising from the electrostatic term. The literature interpretation claims [12] the data reflects the importance of steric interactions on the oxidation potentials. Based on the correlation shown in Table 1, there are no steric contributions in the $E_{1/2}$ data set.

3. Conclusion

The analysis of the $-\Delta H$ values, δCH$_3$–δCH$_2$ shifts, and limited data on the ^{59}Co NMR shifts as the base B is varied indicate that the XCo(DH)$_2$ systems are well behaved acceptors with most Lewis bases. The oxime and alkyl ligands give rise to a cobalt center that has a low positive charge. As a result, the covalent properties of the donor have an influence in between that of C$_6$H$_5$OH ($C_A/E_A = 0.5$) and [Rh(CO)$_2$Cl]$_2$ ($C_A/E_A = 1.0$) on the bond strengths ($-\Delta H$) of adducts. Characteristic of metals with a low partial positive charge, metal to ligand π-back bonding into good π-acceptor ligands is observed. This bonding interaction is minor or absent in pyridine donors but clearly present in

phosphites. Except for donors with inherent steric problems toward most Lewis acids, e.g. 2-methyl-pyridine and 2,6-dimethylpyridine, there is no indication of a front strain (cone angle) type of steric inhibition to coordination in the systems in Table 1.

The $\Delta E-\Delta C$ parameters have been shown to have a wide range of applicability and have changed the nature of substituent effect correlations. Instead of emphasis on which of the many sets of parameters give the best correlation coefficients, the emphasis is on using a given set of parameters to spot unusual behavior and consistently finding these deviations in the measured chemical properties of the reactant. Reactivity concepts of general utility result that enhance the understanding of the chemistry.

In the cobaloxime area, the $\Delta E-\Delta C$ analysis has led to a greatly diminished role for the front strain type of steric effect. A metal–X group entropic rotational effect explains substituent deviations in rate data. SN-1 LIM reactions have increased rates from more facile rotation of the CH_2X group in the transition state than in the ground state. This effect is absent for the $-CH_3$ substituent and explains the inconsistency in fitting rate and equilibrium data for this substituent. This entropic effect is absent in enthalpy measurements, $E_{1/2}$, bond distance and spectral shift correlations.

4. Calculations

Data are fit to Eqs. (1) and (2) using a previously described least squares minimization program. The E_B and C_B parameters for use in the data fits to Eq. (1) are from Ref. [3a]. All systems are entered into the initial data fits. If a poor fit results, one system is omitted to see if a good fit results. This is repeated omitting each system in the data fit to determine if a unique exception can be found. Since π-backbonding is established in the enthalpy fit by this procedure, π-acceptor donors are omitted in subsequent data fits. If the data still do not fit omitting one donor, a second system is omitted.

Data are fit to Eq. (2) using the refined set of substituent constants [5]. The procedure is the same as that described above for fits to Eq. (1).

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