Thus, the overall disproportionation process is represented by the summation of two times eq 12 plus eq 8 and eq 13

$$2O_2^- + PhOH \rightleftharpoons HO_2^- + O_2 + PhO^- \qquad K_{14} = K_aK_8K_{H_2O_2}/K_7^2 = 10^{38}K_a = 10^{18} \quad (14)$$

Thus, the reaction is driven far to the right to yield stoichiometric amounts of HO_2^- and PhO^-.

Even weakly protic substrates such as 1-butanol (BuOH) and water induce the complete disproportionation of O_2^- in DMF, but at much reduced rates (Tables II and III). A previous study has determined the apparent pK_a values for BuOH and H_2O in DMF to be approximately equal ($pK_a = 33$).[7] Thus, the overall reactions can be expressed in a form analogous to eq 14,

$$2O_2^- + BuOH \rightleftharpoons HO_2^- + O_2 + BuO^- \qquad K_{15} = 10^5 \quad (15)$$

and

$$2O_2^- + H_2O \rightleftharpoons HO_2^- + O_2 + OH^- \qquad K_{16} = 10^5 \quad (16)$$

For weak acids such as water and alcohols, the overall decomposition of O_2^- is further complicated by the base-induced (A^-) decomposition of H_2O_2 in aprotic solvents.[13]

$$H_2O_2 + A^- \rightarrow HO_2^- + HA \quad (17)$$

$$HO_2^- + H_2O_2 \rightarrow O_2^- + \cdot OH + H_2O \quad (18)$$

The rate of protonation of O_2^- by moderate and weak protic substrates probably depends on the stability of a superoxy intermediate.[14]

$$O_2^- + HA \rightarrow [\cdot O_2{:}H{:}A]^- \rightarrow A^- + HO_2\cdot \quad (19)$$

Although this process is diffusion controlled for strong acids and slow for water and alcohols, with moderate substrates the relative rates appear to depend on steric and electrostatic factors as much as relative pK_a values (Table II).

The first-order dependence on HA concentration for the proton-induced disproportionation of the superoxide ion in aprotic media (eq 11) may be representative of a hydrophobic biological matrix.[12] If so, the effective rate for the nonenzymatically catalyzed disproportionation of superoxide in mitochondria and in erythrocytes would be much slower than the second-order process in bulk water (eq 2 and 3). Hence, the need for superoxide dismutases under such conditions is even more compelling. The latter maintain the free superoxide ion concentration at levels that are several orders of magnitude lower than would be possible if reaction 11 were rate limiting.

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Registry No. O_2^-, 11062-77-4; H_2O, 7732-18-5; NH_4ClO_4, 14452-39-2; H_2Asc, 50-81-7; $HAsc^-$, 299-36-5; $DTBCH_2$, 1020-31-1; $DTBCH^-$, 65767-25-1; phenol, 108-95-2; α-tocopherol, 59-02-9; 1-butanol, 71-36-3; *p*-chlorophenol, 106-48-9; *p*-*tert*-butylphenol, 98-54-4; *p*-ethoxyphenol, 622-62-8; *p*-cresol, 106-44-5; catechol, 120-80-9.

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Ligand Additivity: Applications to the Electrochemistry and Photoelectron Spectroscopy of d^6 Octahedral Complexes

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Abstract: It is proposed that the energies of the three MO's derived from the three metal d_π orbitals in d^6 $ML_nL'_{6-n}$ systems obey the simple additivity relationship $\epsilon = a + bn + cx$, where x is the number of ligands L which can interact with a given d_π orbital, and a, b, and c are empirically determined parameters. This relationship is used to investigate the electrochemical oxidation data for the compounds $M(CO)_n(CNR)_{6-n}$ (M = Mn(I), Cr(0); R = CH_3, C_6H_5). The model fits the data extremely well, and it also explains the different oxidation potentials observed for the isomers with $n = 2$ or 3. Two of the derived parameters are shown to be measures of the difference in the abilities of the ligands to electrostatically stabilize the metal center and the difference in the abilities of the ligands to stabilize d_π orbitals by π back-bonding. It is indicated that, as a ligand for Cr(0), phenyl isocyanide is both a poorer σ donor and poorer π acceptor than methyl isocyanide. The application of the model to the photoelectron spectroscopy of $ML_nL'_{6-n}$ systems is discussed and predictions are made concerning the trends in the ionization potentials of such systems.

The notion that ligand effects upon a transition-metal center are, in some sense, additive has been a cornerstone of intuitive inorganic chemistry. In recent years several groups have attempted to quantify ligand additivity relationships, especially in metal carbonyl complexes and their derivatives, for application to a variety of physical measurements. Timney[1] has extended the ideas of Haas and Sheline[2] to yield a marvelously simple empirical relationship for the prediction of CO stretching frequencies in a wide variety of metal carbonyl complexes. Other groups have attempted to obtain empirical ligand parameters for the correlation of ^{13}C NMR spectra of metal carbonyls.[3] With regard to the energetics of electrons in metal carbonyl complexes, many groups have attempted the quantitative correlation of electrochemical data. Pickett and Pletcher[4] proposed that the oxidation potentials

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of $[M(CO)_{6-x}L_x]^{y+}$ systems could be empirically fit to a three-parameter equation. The Pickett–Pletcher equation could not explain the differences in the oxidation potential of certain isomeric pairs, however, and it seemed necessary to account explicity for the sterochemistry of the ligands as well as their relative bonding capabilities. A qualitative bonding picture involving ligand stereochemistry had been proposed by Wimmer, Snow, and Bond[5] to explain the differences in the oxidation $E_{1/2}$ values of *cis*- and *trans*-$M(CO)_2(dppe)_2$.

In 1975, Sarapu and Fenske[6] demonstrated a remarkable linear correlation for the series $[Mn(CO)_n(CNCH_3)_{6-n}]^+$ between oxidation potential and the highest occupied molecular orbital (HOMO) energy as calculated by the nonempirical Fenske–Hall[7] method. Treichel, Mueh, and Bursten[8] have shown that this relationship can be used quantitatively to explain the difference in oxidation potentials for the isomeric pairs obtained for $n = 2$ or 3, and further proposed that the effects of the ligands upon the energetics of the principally 3d molecular orbitals obeyed a simple additive relationship

$$\epsilon_i = a + bn + cx_i \tag{1}$$

where n is the number of carbonyl ligands in the complex, x_i is the number of carbonyl ligands that may interact with a given d orbital, and a, b, and c are empirically determined parameters.[9]

In this paper, the above ligand additivity relationship is generalized for low spin octahedral d^6 systems $ML_nL'_{6-n}$. It will be demonstrated that the relationship is generally applicable to $M(CO)_n(CNR)_{6-n}$ systems and that it appears to be appropriate for other ligand combinations as well. Two of the empirically obtained parameters may be interpreted as measures of (a) the difference of the abilities the ligand to stabilize the metal electrostatically and (b) the difference of the π-back-bonding capabilities of ligands. For the systems investigated it is shown that this interpretation implies that phenyl isocyanide is both a weaker σ donor and a weaker π acceptor than methyl isocyanide. Finally it is proposed that the ligand additivity relationship should be quantitatively applicable to the photoelectron spectroscopy of d^6 $ML_nL'_{6-n}$ systems and predictions are made concerning the valence ionization potentials of such systems.

Postulates of Ligand Additivity

The low-spin d^6 octahedral complexes to be considered here are characterized by a filled set of three highest lying molecular orbitals comprised primarily of the d_π (xy, xz, or yz under the usual octahedral coordinate system) orbitals of the metal atom. These three orbitals would, of course, correspond to a t_{2g} orbital under strict O_h symmetry. It will be assumed that the d_π orbitals of the metal atom interact with the ligands predominantly via empty π^* orbitals, and that each ligand has an orthogonal pair of π^* orbitals, although these are not necessarily degenerate. Each of the d_π metal orbitals may therefore interact with four ligand π^* orbitals.

For a system $ML_nL'_{6-n}$ it is postulated that the energetic contribution by the ligands to each MO derived from one of the d_π orbitals depends only on the number of each type of ligand in the complex, and on the number of each type of ligand with which the d_π orbital can interact. It is further postulated that both of these dependencies are linear, so that

$$\epsilon_i = a_M{}^0 + nb_M{}^L + (6 - n)b_M{}^{L'} + x_i c_M{}^L + (4 - x_i)c_M{}^{L'} \tag{2}$$

where $a_M{}^0$ is a characteristic constant of the metal atom in its particular oxidation state, $b_M{}^L$ and $b_M{}^{L'}$ are constants describing the gross energetic effect upon the metal atom of binding to L and L′, respectively, and $c_M{}^L$ and $c_M{}^{L'}$ are constants describing the energetic effect upon the d_π metal orbital of interacting with L and L′, respectively. The correspondence between eq 1 and 2 is given by

$$\begin{aligned} a &= a_M{}^0 + 6b_M{}^{L'} + 4c_M{}^{L'} \\ b &= b_M{}^L - b_M{}^{L'} \\ c &= c_M{}^L - c_M{}^{L'} \end{aligned} \tag{3}$$

so that constants b and c of eq 1 each measure some difference in the effect of L and L′ upon M. The interpretation of these differences will be discussed later.

Equation 2 will form the basis of ligand additivity as discussed in this paper. Its simple linear form implies the following about the energetic effects in a $ML_nL'_{6-n}$ system:

(1) The gross ligand effects upon the metal atom must be isomer independent, i.e., the average orbital energy of the three d_π based MO's depends only upon n.

(2) The gross effect upon the metal atom of replacing L′ with L must be independent of n.

(3) The d_{xy}, d_{xz}, and d_{yz} orbitals do not rehybridize upon replacement of L′ with L, even though they may be allowed to do so by symmetry.

(4) The effect of allowing one of the d orbitals to interact with L instead of L′ is independent of n.

(5) The orbital energy of any of the primarily d_π molecular orbitals depends only on the number of each type of ligand available for bonding and is independent of the stereochemistry of the ligands about the orbital.

It is to be noted that eq 2 will be used here without any theoretical justification; it is based entirely on empirical observation. The investigation of the theoretical ramifications of eq 2 will be the subject of a subsequent publication.

Applications of Ligand Additivity

Electrochemistry as a Probe. For the series $[Mn(CO)_n(CNCH_3)_{6-n}]^+$, Sarapu and Fenske[6] found a linear correlation between the calculated HOMO energy and the $E_{1/2}$ value for oxidation.[10] A similar relationship had been noted earlier for a series of aromatic hydrocarbons by Peover.[12] A plot of HOMO energy vs. $E_{1/2}$ has a negative slope, indicating that the lower (more negative) the HOMO energy of a complex, the harder it is to oxidize. The implication of these observations is clear, namely for a series of similar complexes for which electrochemical oxidation is carried out under similar conditions there is a "scaled Koopmans' theorem"[13] wherein the $E_{1/2}$ value is directly proportional to the HOMO energy:

$$E_{1/2} = k_1(-\epsilon_{HOMO}) + k_2; \qquad k_1 > 0 \tag{4}$$

This relationship indicates that, under appropriate conditions, the

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[10] Most of the electrochemical data used here was obtained from reversible or quasi-reversible cyclic voltammetry. The values reported for these cases are actually $^1/_2(E_{p,a} + E_{p,c})$ which, for a reversible electron transfer reaction, will be equal to the polarographic $E_{1/2}$ value. These are related to the E^0 values by the equation[11]

$$E_{1/2} = E^0 - \frac{RT}{nF} \ln \frac{f_{red}D_{ox}{}^{1/2}}{f_{ox}D_{red}{}^{1/2}}$$

where f_{red} and f_{ox} and D_{red} and D_{ox} are the activity coefficients and diffusion coefficients of the reduced and oxidized species, respectively. For the molecular species considered here it is expected that the mass transport properties and activity coefficients of the reduced and oxidized species should be similar so the correction term will be small. Additionally, the correction term should be relatively constant for a given series and will therefore cancel upon taking differences. For notational convenience, $E_{1/2}$ will be used throughout the paper.

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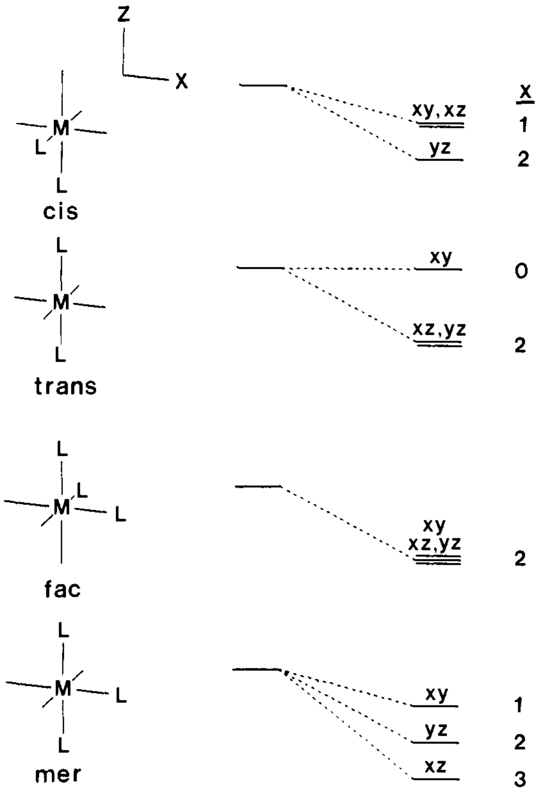

Figure 1. Qualitative diagram showing the energy levels of the d_π orbitals for isomers of $[MnL_nL'_{6-n}]^+$ (n = 2, 3), where L is a better π acceptor than L'. For clarity, only the L ligands are shown.

Table I. Predicted $E_{1/2}$ Values for a Series $ML_nL'_{6-n}$ (L' a Poorer π Acceptor than L)

compd	n	x_{HOMO}[a]	predicted $E_{1/2}$
ML'_6	0	0	A
MLL'_5	1	0	$A + B$
trans-$ML_2L'_4$	2	0	$A + 2B$
cis-$ML_2L'_4$	2	1	$A + 2B + C$
mer-$ML_3L'_3$	3	1	$A + 3B + C$
fac-$ML_3L'_3$	3	2	$A + 3B + 2C$
trans-$ML_4L'_2$	4	2	$A + 4B + 2C$
cis-$ML_4L'_2$	4	2	$A + 4B + 2C$
ML_5L'	5	3	$A + 5B + 3C$
ML_6	6	4	$A + 6B + 4C$

[a] x_{HOMO} is the number of L ligands contributing to the HOMO.

oxidation potential of a complex may be interpreted as a "solution ionization potential" and it provides a connection between the electrochemical experiment and electronic structural data, either calculated or measured.[14]

Based upon eq 2 and 4, the $E_{1/2}$ values for the series $ML_nL'_{6-n}$ should obey the relation

$$E_{1/2} = A_M{}^0 + nB_M{}^L + (6-n)B_M{}^{L'} + x_{HOMO}C_M{}^L + (4 - x_{HOMO})C_M{}^{L'} \quad (5)$$

where $A_M{}^0 = k_1a_M{}^0 + k_2$, $B_M{}^L = -k_1b_M{}^L$, $C_M{}^L = -k_1c_M{}^L$, and so on. x_{HOMO} is the number of ligands L that interact with the d_π orbital which comprises the HOMO of the complex. Eq 5 reduces to

$$E_{1/2} = A + Bn + Cx_{HOMO} \quad (6)$$

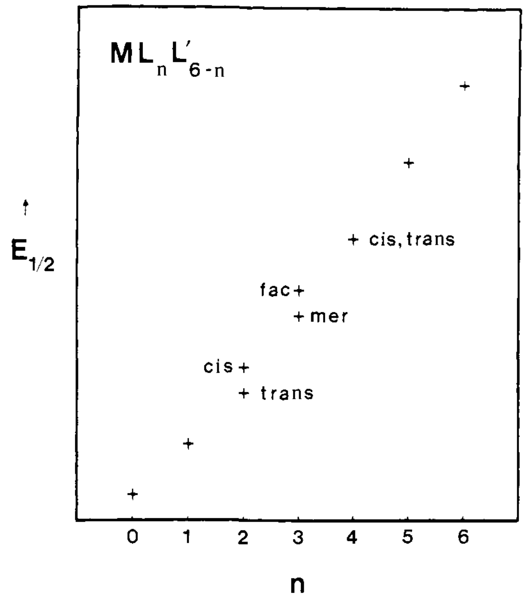

Figure 2. Predicted trend in $E_{1/2}$ value for $ML_nL'_{6-n}$ systems, where L is a better π acceptor than L'.

Table II. Cyclic Voltammetric Data for $M(CO)_n(CNR)_{6-n}$ Systems and $E_{1/2}$ Values (V vs. SCE)

M	Mn(l)	Mn(l)	Mn(l)	Cr(O)	Cr(O)
R	CH_3	CH_3	C_6H_5	CH_3	C_6H_5
process	+1 → +2	+1 → +2	+1 → +2	0 → +1	0 → +1
solvent	CH_3CN	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2
ref	16	8, 17	16, 18	19	18, 20
		$E_{1/2}$ Values			
n = 0	0.38	0.47	1.00		−0.32
1	0.79	0.88	1.28		−0.15
trans-2	1.12	1.28	1.54		
cis-2		1.44	1.70		0.14
mer-3	1.65	1.73	1.98		
fac-3		1.90	2.12	0.20[a]	0.56
trans-4					
cis-4	2.14		2.28	0.59	0.74
5	2.65			1.10	1.09
6					1.43

[a] Value reported is that for R = i-C_3H_7. The value for R = CH_3 is expected to be within 0.02 V of that for R = i-C_3H_7.

and the correspondence between eq 6 and 5 is the same as that between eq 1 and 2.

In order to use eq 6 it is necessary to know the value of x_{HOMO}, which will range from 0 to 4. This value may be easily determined if L and L' differ greatly in their π acidity, for if L' is a poorer π acceptor than L, it will stabilize a metal d_π orbital to a lesser degree.[15] Hence the HOMO will be derived from the d_π orbital which has the fewest interactions with ligands L. This reasoning may be used to explain the difference in $E_{1/2}$ values for the isomers of $ML_nL'_{6-n}$ (n = 2, 3) as shown in Figure 1.

For the series $ML_nL'_{6-n}$ where L' is a poorer π acceptor than L, the predicted $E_{1/2}$ values in terms of A, B, and C of eq 6 are given in Table I. Several interesting observations may be made from this tabulation. First, it is evident that although the $E_{1/2}$ values for n = 2 or 3 are expected to be isomer dependent, for n = 4 the cis and trans isomers should exhibit the same $E_{1/2}$ value. Second, even though the ligand effects are assumed to be additive, a plot of $E_{1/2}$ vs. n should not be linear, although portions of the plot will be. Thus $E_{1/2}$ vs. n for n = 0, 1, trans-2 should be linear with a slope of B while for n = trans-2, mer-3, 4, 5, 6 it should be linear with a slope of $B + C$. This situation is shown in Figure 2, a plot of expected $E_{1/2}$ vs. n for the series $ML_nL'_{6-n}$ where L'

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[14] An implicit assumption in the "scaled Koopmans' theorem" approach is that electron transfer rates for oxidation are much faster than those for electronic or nuclear rearrangement, i.e., that the oxidation potential may be determined by examining the reduced state only. Inasmuch as solution electron-transfer rates are much slower than those for gas-phase electron ionization, it seems likely that this approach will not be applicable to systems which undergo spin crossover or geometric rearrangement upon oxidation.

[15] For a general discussion of π acidity in ligands see: Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; Chapter 3 and references therein.

Table III. Least-Squares Fit of the Data for $M(CO)_n(CNR)_{6-n}$ Systems Given in Table II to the Equation $E_{1/2} = A + Bn + Cx_{HOMO}$ and Predicted $E_{1/2}$ Values[a]

M	Mn(I)	Mn(I)	Mn(I)	Cr(0)	Cr(0)
R	CH_3	CH_3	C_6H_5	CH_3	C_6H_5
solvent	CH_3CN	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2
A	0.39	0.49	1.02	−1.21	−0.34
B	0.37	0.38	0.26	0.39	0.18
C	0.13	0.13	0.14	0.12	0.18
			Predicted $E_{1/2}$ Values		
$n = 0$	0.39 (0.38)	0.49 (0.47)	1.02 (1.00)	−1.21	−0.34 (−0.32)
1	0.76 (0.79)	0.87 (0.88)	1.28 (1.28)	−0.82	−0.16 (−0.15)
trans-2	1.13 (1.12)	1.25 (1.28)	1.54 (1.54)	−0.43	0.02
cis-2	1.26	1.38 (1.44)	1.68 (1.70)	−0.31	0.20 (0.14)
mer-3	1.63 (1.65)	1.76 (1.73)	1.94 (1.98)	0.08	0.38
fac-3	1.76	1.89 (1.90)	2.08 (2.12)	0.20 (0.20)	0.56 (0.56)
cis-4	2.13 (2.14)	2.27	2.34 (2.28)	0.59 (0.59)	0.74 (0.74)
trans-4	2.13	2.27	2.34	0.59	0.74
5	2.63 (2.65)	2.78	2.74	1.10 (1.10)	1.10 (1.09)
6	3.13	3.29	3.14	1.61	1.46 (1.43)

[a] Experimental $E_{1/2}$ values, when known, are given in parentheses.

is a poorer π acceptor than L, and $C = B/3$. The degree to which these ideas may be applied to real systems will now be considered.

The $ML_nL'_{6-n}$ systems with M = Mn(I) or Cr(0), L = CO, and L′ = $CNCH_3$ or CNC_6H_5 are well-known and have been widely studied. Available electrochemical data are given in Table II. Least-squares fits of these data to the parameters A, B, and C of eq 6 are presented in Table III, along with the $E_{1/2}$ values predicted.

The fit of the data for the series $[Mn(CO)_n(CNCH_3)_{6-n}]^+$ is quite satisfactory and, as has been noted previously, accounts for the differences in the $E_{1/2}$ values for the isomeric pairs with n = 2 and 3. The value of A depends on the solvent used, whereas B and C are virtually independent of solvent. This is a reasonable expectation as will be shown later.

For the series $[Mn(CO)_n(CNC_6H_5)_{6-n}]^+$, the seven known $E_{1/2}$ values fit eq 6 remarkably well. The overall consistency of the fit for the Mn(I) systems can be checked by comparing the extrapolated $E_{1/2}$ value for $[Mn(CO)_6]^+$, which cannot be electrochemically oxidized in CH_2Cl_2 or CH_3CN due to solvent breakdown. There is reasonable agreement between the two series and $[Mn(CO)_6]^+$ would be expected to have an $E_{1/2}$ value of 3.15–3.25 V vs. SCE.

The data for the series $Cr(CO)_n(CNC_6H_5)_{6-n}$ also agree with the predicted values very well. This series provides a particularly stringent test of eq 6 since both $Cr(CO)_6$ and $Cr(CNC_6H_5)_6$ have been studied; thus the equation is tested for the extremes $n = 0$ and $n = 6$ as well as intermediate values of n. The worst agreement occurs for *cis*-$Cr(CO)_2(CNC_6H_5)_4$ but it is noted that the electrochemistry of this species is extremely complex,[18] involving several electrode processes in the range of −1.0 to +1.5 V. The nearness of the predicted value to the peak at $E_{1/2} = 0.14$ V substantiates the assignment of this peak as the oxidation of the parent compound, and portends the utility of this model of ligand additivity as a diagnostic tool for unraveling complex cyclic voltammograms.

The three available data points for the $Cr(CO)_n(CNCH_3)_{6-n}$ system minimially determine the parameters A, B, and C. The extrapolation to $Cr(CO)_6$, which was not used in the least-squares fit so as to allow a check of internal consistency, yields a predicted $E_{1/2}$ value of 1.61 V, nearly 0.2 V higher than that observed by Treichel et al.[18] This agreement is worse than expected. The studies of the $Cr(CO)_n(CNCH_3)_{6-n}$ and $Cr(CO)_n(CNC_6H_5)_{6-n}$ systems were performed by two different research groups, however, and it is difficult to gauge whether the apparent disagreement is due to a failure of the simple model proposed here, or whether it is due to a difference in experimental conditions or interpretation.

One prediction of the model which is not tested in Table III is that the $E_{1/2}$ values for the cis and trans isomers of $M(CO)_4(CNR)_2$ should be the same. For each system, only the cis isomer has been isolated. Recently, however, Bond, Darensbourg, and co-workers[21] have reported that the $E_{1/2}$ values for the oxidation of *cis*- and *trans*-$Mo(CO)_4[P(n\text{-}C_3H_7)_3]_2$ are essentially identical, as predicted by the model here.

Interpretation of the Constants A, B, and C. In the previous section the simple model of ligand additivity has been successfully applied to mixed carbonyl–isocyanide systems. The goal of any empirical model should be the attaining of chemically useful information and in this section the significance of the derived parameters A, B, and C and what may be gleaned from them will be discussed.

For the $M(CO)_n(CNR)_{6-n}$ system, the correspondence between eq 6 and 5 is

$$A = A_M^0 + 6B_M^{CNR} + 4C_M^{CNR}$$
$$B = B_M^{CO} - B_M^{CNR}$$
$$C = C_M^{CO} - C_M^{CNR} \qquad (7)$$

Parameter A is a constant which varies with solvent and will not be discussed further. Parameters B and C, on the other hand, both measure the difference in some quantity intrinsic to each ligand. The parameter B is isomer independent and reflects the change in the overall stabilization of the metal center due to replacing a CNR ligand with a CO ligand. Since the donation of charge to a metal center destabilizes all the metal orbitals, and the removal of charge from the center will stabilize all of them, B will be interpreted as an "electrostatic term" which measures the difference of the abilities of the ligands to electrostatically stabilize the metal atom. If it is assumed that CO and CNR each interact with the metal atom only by donating charge from its σ lone pair orbital and by accepting charge into its empty π^* orbitals, then it follows that $B_M^L \propto$ (π acceptance by L) − (σ donation from L). For all of the systems discussed here $B_M^{CO} - B_M^{CNR}$ is positive, indicating that CO more effectively depletes charge from a metal center than does CNR. This is in agreement with the generally accepted view that isocyanides are better σ donors and poorer π acceptors than carbonyls.[22]

The parameter C reflects the effect upon a given d_π orbital of replacing a CNR ligand with a CO ligand. It is this term which

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differentiates isomers of the same complex. C will be interpreted as a "bonding term" which measures the relative ability of each ligand to stabilize a given d_π orbital. If it is assumed that π donation from the ligand to the metal is negligible, then it follows that $C_M{}^L \propto$ (π acceptance by L). For all of the $M(CO)_n(CNR)_{6-n}$ systems, $C_M{}^{CO} - C_M{}^{CNR}$ is positive, indicating that CO is a better π acceptor than CNR, again in agreement with the generally accepted view.

Inspection of the B and C parameters in Table III leads to the following conclusions, based on the above discussion:

(1) For the $[Mn(CO)_n(CNCH_3)_{6-n}]^+$ system, B and C are essentially solvent independent. This is in accord with the interpretation of B and C as intrinsically molecular parameters.

(2) For the Mn(I) system it is seen that CNC_6H_5 depletes charge more effectively than does $CNCH_3$, but that the two isocyanides compete with CO for π acceptance to virtually the same degree. Thus it would seem that, for these systems, CNC_6H_5 and $CNCH_3$ are acting as equivalent π acceptors and the differences between the ligands is explained entirely by a greater σ donating ability of the latter.

(3) For the $Cr(CO)_n(CNCH_3)_{6-n}$ system, the values of B and C are effectively unchanged from the Mn(I) system. This result, which may be fortuitous, seems to indicate that the relative σ-dnor and π-acceptor capabilities of CO and $CNCH_3$ are the same for Mn(I) and Cr(0). It is of interest to note electrochemical measurements[23] on the Re(I) systems $[Re(CO)(CNCH_3)_5]^+$, *cis*-$[Re(CO)_2(CNCH_3)_4]^+$, and *fac*-$[Re(CO)_3(CNCH_3)_3]^+$, a series which does not allow the independent determination of B and C but which does indicate that $B + C = 0.51$, the same value as that in the Mn(I) and Cr(0) systems.

(4) For the $Cr(CO)_n(CNC_6H_5)_{6-n}$ system there is a marked difference in the B and C parameters from those of the corresponding Mn(I) system. The C parameter has decreased, indicating that CNC_6H_5 is less effectively competing with CO as a π acceptor in the Cr(0) system than in the Mn(I) system. The B parameter has decreased relative to the Mn(I) system, however, indicating that the difference in the ability of CO and CNC_6H_5 to electrostatically stabilize the metal center has decreased. The conclusion which must be reached is that upon changing from Mn(I) to Cr(0) both the σ-donating and π-accepting abilities of CNC_6H_5 have decreased relative to CO.

Although the C parameters for the two isocyanides are about the same for the Mn(I) systems, the C parameter for $Cr(CO)_n(CNC_6H_5)_{6-n}$ is larger than that for the $Cr(CO)_n(CNCH_3)_{6-n}$ systems. This leads to the rather surprising conclusion that phenyl isocyanide is a poorer π acceptor than methyl isocyanide in Cr(0) systems. Phenyl isocyanide clearly stabilizes Cr(0) more than methyl isocyanide so it must be concluded that this is entirely due to the stronger σ-donor abilities of the latter. This view is consistent with a delocalization of the important C–N orbitals onto the phenyl ring.[24]

The above conclusion could be easily tested by investigating the electrochemistry of the $Cr(CNC_6H_5)_n(CNCH_3)_{6-n}$ system. For this system the $E_{1/2}$ value should increase with n, indicating the greater stabilizing (or lesser destabilizing) ability of CNC_6H_5 relative to $CHCH_3$ ($B_{Cr}{}^{CNC_6H_5} - B_{Cr}{}^{CNCH_3} > 0$). It is predicted, however, that for $n = 2$ there would be no difference between $E_{1/2}$ values for the cis and trans isomers whereas for $n = 4$ the trans isomer should be easier to oxidize.

There have been previous attempts to measure the relative σ-donor and π-acceptor abilities of ligands empirically. As an example, Graham[25] has analyzed the influence of a variety of ligands upon the CO force constants in $M(CO)_5L$ complexes as calculated by the Cotton–Kraihanzel[26] method. Through the use of simple assumptions he was able to partition the ligand contributions into inductive (σ) and bonding (π) terms. The interpretation of B and C presented here provides a complementary technique for the measurement of relative ligand σ- and π-bonding capabilities.

Table IV. Predicted Ionization Potentials for the Series $ML_nL'_{6-n}$ in Terms of $b' \equiv b_M{}^L - b_M{}^L$ and $c' \equiv c_M{}^L - c_M{}^L$ [a]

compd	first IP	second IP	third IP
ML'_6	0 (3)		
MLL'_5	b' (1)	$b' + c'$ (2)	
trans-$ML_2L'_4$	$2b'$ (1)	$2b' + 2c'$ (2)	
cis-$ML_2L'_4$	$2b' + c'$ (2)	$2b' + 2c'$ (1)	
mer-$ML_3L'_3$	$3b' + c'$ (1)	$3b' + 2c'$ (1)	$3b' + 3c'$ (1)
fac-$ML_3L'_3$	$3b' + 2c'$ (3)		
cis-$ML_4L'_2$	$4b' + 2c'$ (1)	$4b' + 3c'$ (2)	
trans-$ML_4L'_2$	$4b' + 2c'$ (2)	$4b' + 4c'$ (1)	
ML_5L'	$5b' + 3c'$ (2)	$5b' + 4c'$ (1)	
ML_6	$6b' + 4c'$ (3)		

[a] Both b' and c' are assumed positive. The ionization potential of ML'_6 is chosen to be 0. Degeneracies are given in parentheses.

Photoelectron Spectroscopy as a Probe. The model of ligand additivity proposed here should pertain to all three d_π orbitals in $ML_nL'_{6-n}$ systems, not just the HOMO. Photoelectron spectroscopy (PES), through the use of Koopmans' theorem,[13] is the most direct probe of valence orbital energetics, and the predictions of the ligand additivity model with regard to PES will be discussed here.

As postulated in the model, each of the d_π orbitals in the octahedral systems is assumed independent; rehybridization or mixing of s and p orbitals does not occur even if allowed by symmetry. The orbital energy of d_π orbital is then given by eq 2.

Use of Koopmans' theorem leads to the predicted ionization potential

$$IP_i = -\epsilon_i = a' + b'n + c'x_i$$

where

$$a' = -a_M{}^0 - 6b_M{}^{L'} - b_M{}^L$$

$$b' = b_M{}^{L'} - b_M{}^L$$

$$c' = c_M{}^{L'} - c_M{}^L$$

and x_i is the number of ligands L with which the particular d_π is allowed to interact. If L is a better π acceptor and worse σ donor than L′, then a', b', and c' will all be positive. For this case the predicted trends in ionization potentials and their degeneracies are given in terms of b' and c' in Table IV.

If the model is appropriate for PE spectra, it is apparent that the following should be observed:

(1) A plot of the first IP's vs. n should exhibit the trends of Figure 2.

(2) The *cis*- and *trans*-$ML_2L'_4$ species, although having different first IP's, should have the same second IP and in the trans isomer it will be displaced twice as far from the first IP as in the cis isomer.

(3) The *mer*-$ML_3L'_3$ compound should have three equally spaced IP's, and the second IP will be the same value as the IP of the fac isomer.

(4) Although the *cis*- and *trans*- $ML_4L'_2$ species will have the same first IP, the second IP for the trans isomer will be displaced twice as far from the first IP as in the cis isomer.

Although there have been no detailed studies of the PE spectra of $ML_nL'_{6-n}$ systems, it is hoped that these predictions provide the impetus for such investigations. It will be of particular interest to see if the trends in the ionization potentials of isomeric pairs are as readily explained as are their oxidation potentials.

Registry No. $[Mn(CNCH_3)_6]^+$, 45228-39-5; $[Mn(CO)(CNCH_3)_5]^+$, 45211-82-3; *trans*-$[Mn(CO)_2(CNCH_3)_4]^+$, 62445-30-1; *cis*-$[Mn(CO)_2(CNCH_3)_4]^+$, 62445-29-8; *mer*-$[Mn(CO)_3(CNCH_3)_3]^+$, 54630-99-8; *fac*-$[Mn(CO)_3(CNCH_3)_3]^+$, 54631-01-5; *cis*-$[Mn(CO)_4(CNCH_3)_2]^+$, 54630-97-6; *trans*-$[Mn(CO)_4(CNCH_3)_2]^+$, 59598-79-7; $[Mn(CO)_5(CNCH_3)]^+$, 45113-87-9; $[Mn(CO)_6]^+$, 21331-06-6; $[Mn(CNC_6H_5)_6]^+$, 47873-92-7; $[Mn(CO)(CNC_6H_5)_5]^+$, 47840-66-4; *trans*-$[Mn(CO)_2(CNC_6H_5)_4]^+$, 70831-76-4; *cis*-$[Mn(CO)_2(CNC_6H_5)_4]^+$, 70800-86-1;

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mer-$[Mn(CO)_3(CNC_6H_5)_3]^+$, 70877-80-4; *fac*-$[Mn(CO)_3(CNC_6H_5)_3]^+$, 70800-84-9; *cis*-$[Mn(CO)_4(CNC_6H_5)_2]^+$, 70800-82-7; *trans*-$[Mn(CO)_4(CNC_6H_5)_2]^+$, 80695-81-4; $[Mn(CO)_5(CNC_6H_5)]^+$, 80642-45-1; $Cr(CNCH_3)_6$, 80642-46-2; $Cr(CO)(CNCH_3)_5$, 80658-41-9; *trans*-$[Cr(CO)_2(CNCH_3)_4]$, 80696-55-5; *cis*-$[Cr(CO)_2(CNCH_3)_4]$, 80642-47-3; *mer*-$[Cr(CO)_3(CNCH_3)_3]$, 80695-82-5; *fac*-$[Cr(CO)_3(CNCH_3)_3]$, 80695-83-6; *cis*-$[Cr(CO)_4(CNCH_3)_2]$, 37131-11-6; *trans*-$[Cr(CO)_4(CNCH_3)_2]$, 80695-84-7; $Cr(CO)_5(CNCH_3)$, 33726-04-4; $Cr(CO)_6$, 13007-92-6; $Cr(CNC_5H_6)_6$, 17375-15-4; $Cr(CO)(CNC_5H_6)_5$, 70800-89-4; *trans*-$[Cr(CO)_2(CNC_5H_6)_4]$, 80695-85-8; *cis*-$[Cr(CO)_2(CNC_5H_6)_4]$, 70800-88-3; *mer*-$[Cr(CO)_3(CNC_5H_6)_3]$, 80695-86-9; *fac*-$[Cr(CO)_3(CNC_5H_6)_3]$, 70831-80-0; *cis*-$[Cr(CO)_4(CNC_5H_6)]$, 70831-79-7; *trans*-$[Cr(CO)_4(CNC_5H_6)_2]$, 80695-87-0; $Cr(CO)_5(CNC_5H_6)$, 14782-94-6.

Direct Determination of Rate Constants of Slow Dynamic Processes by Two-Dimensional "Accordion" Spectroscopy in Nuclear Magnetic Resonance

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Abstract: A novel class of NMR experiments, based on the systematic variation of three time variables, permits both the identification of exchange networks and the direct measurement of the corresponding rate constants. Linear combinations of cross sections taken from two-dimensional spectra allow a straightforward analysis of nonexponential recovery behavior by identifying normal modes. The line widths of the resulting Lorentzian line shapes provide a direct measure of the rate constants of various dynamic processes, such as chemical exchange, transient Overhauser effects, and spin-lattice relaxation.

I. Introduction

The study of slow dynamic processes by nuclear magnetic resonance is of practical importance in numerous applications, including transient nuclear Overhauser effects[1-3] and polarization transfer associated with slow chemical exchange.[4] Both processes lead to very similar phenomena in NMR spectroscopy and can be studied by the same experimental techniques.

Nuclear Overhauser effects have proven to be of extraordinary importance for the determination of molecular structure of biomolecules in solution.[5-10] In particular, these effects allow the elucidation of amino acid sequences and tertiary structures in proteins.

The study of chemical processes by NMR has long been known to provide unique insight into molecular dynamics.[11,12] A particular virtue lies in the ability to study dynamic equilibria without the need for chemical perturbations. Very fast reactions can be studied through their effect on nuclear relaxation, since they contribute to the spectral densities at the Larmor frequency.[13] An intermediate regime, with reaction rates comparable to chemical shift differences, to spin couplings or quadrupolar splittings, can be studied by line-shape analysis.[12,14] Slow exchange processes, with rates smaller than typical line widths, may be characterized by monitoring the transfer of nuclear polarization between inequivalent sites. In selective magnetization transfer experiments,[4] the longitudinal magnetization of a specific site is labeled by selective saturation or inversion. The exchange process can be traced out by monitoring the migration of the nonequilibrium magnetization to other sites. This migration occurs in a mixing interval t_m which separates the initial perturbation and the observation by a nonselective pulse.

It has recently been shown that magnetization transfer experiments can be carried out much more efficiently by two-dimensional spectroscopy,[15] both for NOE studies of biomolecules[16-20] and for the investigation of chemical exchange.[21,22] All sites are labeled in a single experiment without previous knowledge of the spectrum, thus allowing all exchange pathways to be observed simultaneously. Thus the 2-D method greatly enhances the information obtained per unit of time. In addition, problems associated with selective irradiation in crowded spectra are completely avoided.

For a quantitative measurement of the exchange rates, it is normally not sufficient to record one 2-D spectrum with a single mixing time, t_m. Often, it is necessary to observe the magnetization transfer as a function of the mixing time by obtaining a set of 2-D spectra for different t_m delays. The recording of the buildup and decay of the transfer represents, in effect, an extension from

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