ring size (13, 14, 15, and 16 membered) as dichlorides. Hence, in each case the metal ion has the same six donor atoms. The reduction potentials vary by about 0.5 V, and there is no obvious correlation between $E_{1/2}$ and the splitting parameter in the *xy* plane, $Dq^{xy}$. The values reported in ref 3 are given in Table II.

A related study by Endicott and co-workers,[2] in which the macrocyclic ligand was held constant and the axial ligands were varied, does show a nearly linear correlation between $E_{1/2}$ for $Co^{III}/Co^{II}$ and the axial splitting parameter $Dq^z$. This system may be unique in that the most probable acceptor orbital, $d_{z^2}$, is the orbital affected by the ligand changes. In addition, the Co(II) product is low spin[2] so that the electron added most likely remains localized in the $d_{z^2}$ orbital.

In each of the systems we have investigated that exhibit no correlation between $E_{1/2}$ and $10Dq$ (or one observed under only the most closely controlled conditions) there is, however, a strong correlation between appropriate Hammett substituent constants and $E_{1/2}$.[3-5] This is true even though substitutent changes may take place several bonds removed from the electroactive metal center. Interestingly, these correlations often parallel correlations between the Hammett substitutent constants and ligand properties such as $pK_a$.[18] Thus, although the splitting parameter, $Dq$, is not a predictor of $E_{1/2}$, one does have the strong indication from these linear free-energy-type relationships that changes in bonding parameters are responsible for $E_{1/2}$ variations within a given series. The following discussion is an attempt to identify these parameters within the scope of existing, useful bonding approaches in transition-metal-complex chemistry.

A general reaction defining $E_{1/2}$ for a $d^n \rightarrow d^{n+1}$ system can be written

$$\mathrm{Ref_{red}} + \mathrm{ML_6}^{3+} \rightleftharpoons \mathrm{Ref_{ox}} + \mathrm{ML_6}^{2+} \quad (1)$$

The $E_{1/2}$ for the reaction can be expressed as

$$-FE_{1/2} = \Delta G^\circ = G(\mathrm{prod}) - G(\mathrm{react}) = \Delta G(\mathrm{Ref}) + \Delta G(\mathrm{ML_6}^{3+} \rightarrow \mathrm{ML_6}^{2+}) \quad (2)$$

$\Delta G(\mathrm{Ref})$ for a particular reference electrode is a constant and

$$\Delta G(\mathrm{ML_6}^{3+} \rightarrow \mathrm{ML_6}^{2+}) = \Delta H(\mathrm{ML_6}^{3+} \rightarrow \mathrm{ML_6}^{2+}) - T\Delta S(\mathrm{ML_6}^{3+} \rightarrow \mathrm{ML_6}^{2+}) \quad (3)$$

The entropic term for the electron transfer can vary widely from compound to compound. However, if the entire range of about 1.5 V observed for the 1,3-diketonates was attributed to changes in $\Delta S$, then the $\Delta S$ term for the series would have to vary by 118 eu which would be unreasonably large. There is, in fact, good reason to believe that the $\Delta S$ term is small in such complexes and that the variation of $\Delta S$ within the series is also small. The $\Delta S$ term is often considered to be the sum of a solvent reorganization entropy, $\Delta S_s$, and an internal reorganization entropy, $\Delta S_i$. The $\Delta S_i$ term is dependent upon ligand rearrangements, and since the redox couples for the compounds in Table I are reversible, ligand rearrangements must be extremely facile and relatively unimportant in the $\Delta S$ term. The $\Delta S_s$ term which is often the major contributor can also be expected to be small since these compounds are neutral and the studies carried out in nonaqueous media. Born model calculations[19,20] for a spherical species of 5-Å radius in DMF going from charge 0 to 1– indicate that $\Delta S_s$ should be ~4 eu. The general assumption that $\Delta S_s$ is small in these bulky, neutral complexes is supported by the conclusions of Hanania et al.[21] and by the recent work of Weaver et al.[22]

Since the large variation in $E_{1/2}$ for the tris(diketonate) systems does not arise from differences in the $Dq$ term nor apparently from $\Delta S$ terms, it must arise mainly from the $\Delta H$ term. Inasmuch as $P\Delta V$ is negligible, $\Delta H$ may be equated to $\Delta E$ and is, therefore, equal to the difference in the sum of the energies of the electrons in the oxidized and reduced forms. For the purposes of this discussion it will be assumed that the most significant energy changes occur in the metal–ligand interactive electrons. The most important point to consider in this regard is what factors determine the energy of the acceptor orbital. In complexes of the type discussed herein, the acceptor orbital is considered to be antibonding with a large amount of d character. In ligand field terms, the energies of the antibonding d electrons are determined by the spherical potential term, $V_s$, and the $Dq$ term. Since $Dq$ variations do not seem to be a major contributor to $E_{1/2}$ variations, one is left, within the context of ligand field theory, with $V_s$ as a major contributor.

Qualitatively, one can predict that the repulsive $V_s$ term should be sensitive to changes in the substituent groups; i.e., an electron-supplying group that increases electron density on the donor atoms will increase $V_s$, while an electron-withdrawing group will decrease $V_s$. Thus, one would expect that the partially filled antibonding "d" orbitals are higher in energy in a complex containing electron-supplying substituents than in a complex containing electron-withdrawing substituents. This prediction is in agreement with the often observed linear dependence between the reduction potentials and the Hammett substituent constants in series of closely related complexes. Similar qualitative arguments can be developed for complexes in which donor atoms are changed, macrocyclic ring size is varied, etc.

In summary, there are several studies in which the redox potentials vary significantly (1–2 V) in a series of closely related complexes containing the same metal ion. Within these series $Dq$ may or may not change by an appreciable amount, thereby casting considerable doubt on the concept that changes in $Dq$ are responsible for changes in $E_{1/2}$. Other bonding parameters such as the repulsive spherical ligand field term, $V_s$, are potentially much more important and are expected to be sensitive to subtle changes in the ligands.

**Acknowledgment.** This work was supported by the Office of Basic Energy Sciences of the Department of Energy.

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(18) R. L. Lintvedt, H. D. Russell, and H. F. Holtzclaw, Jr., *Inorg. Chem.*, **5**, 1603 (1966).

(19) K. J. Laidler, *Can. J. Chem.*, **34**, 1107 (1956).

(20) R. M. Noyes, *J. Am. Chem. Soc.*, **84**, 513 (1962).

(21) G. I. H. Hanania, D. H. Irvine, W. A. Eaton, and P. George, *J. Phys. Chem.*, **71**, 2022 (1967).

(22) E. L. Yee, R. J. Cave, K. L. Guyer, P. D. Tyma, and M. J. Weaver, *J. Am. Chem. Soc.*, **101**, 1131 (1979).

Department of Chemistry
Wayne State University
Detroit, Michigan 48202

**Richard L. Lintvedt***
**D. Earl Fenton**

*Received July 13, 1978*

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## Oxidative Addition: An Alternative View

*Sir:*

"Oxidative addition" is a useful general term for reactions of type 1, in which both the formal oxidation state and co-

$$\mathrm{ML}_m + \mathrm{X}_2 \rightarrow \mathrm{ML}_m\mathrm{X}_2 \quad (1)$$

ordination number of the metal increase by 2 units.[1]

Unfortunately, ambiguities and contradictions attach to the use of the term. These arise from two sources: (i) our inability

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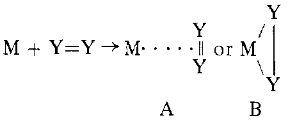
(1) J. K. Stille and K. S. Y. Lau, *Acc. Chem. Res.*, **10**, 434 (1977).

0020-1669/80/1319-0571$01.00/0

to define unambiguously the formal oxidation state of a complex in all cases and (ii) the recent discovery of new reactions of type 1 that are not oxidative in character.

For example, the addition of ethylene to a metal (eq 2,



$$\mathrm{M + Y{=}Y \rightarrow M\cdots\cdots\overset{Y}{\underset{Y}{\|}} \text{ or } M\Big\langle\begin{matrix}Y\\ |\\ Y\end{matrix}} \qquad (2)$$

$Y = CH_2$) can be described as a ligand addition (eq 3) if the

$$\mathrm{M + L \rightarrow ML} \qquad (3)$$

structure of the adduct is considered as A or as an oxidative addition if the adduct is considered as B. For ethylene, structure A is often a better model, but for $C_2F_4$ ($Y = CF_2$) or the analogous oxygen adducts ($Y = O$), structure B is more appropriate.[2] The terms "oxidative addition" and "ligand addition" therefore merely express different ways of looking at the single process described by eq 2. The two terms, consequently, cannot be unambiguously defined and distinguished.

Jonas,[3] in very elegant work, has observed additions of electropositive elements to various nickel complexes (eq 4).

$$\mathrm{LNi} \xrightarrow[\text{TMEDA}]{\text{Li, THF}} trans\text{-}[\mathrm{LNi(Li(TMEDA))_2}] \qquad (4)$$

$$\mathrm{L = 1,5,9\text{-}cyclododecatriene;\ TMEDA = \{Me_2NCH_2\}_2}$$

This author has called these processes "reductive additions", because they are analogous to eq 1 and since they cannot be oxidative in character.

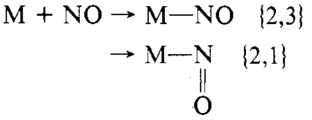
Our own work in the addition of $H_2$ to certain cationic cyclooctadiene complexes of iridium leads us to believe that this addition, too, is reductive in character; the additions are favored by electron-acceptor ligands and inhibited by electron-donor ligands.[4]

Clearly, the reductive or oxidative character of the addition depends on the electronegativity of the groups X in eq 1. Electronegative groups such as X = Cl lead to an addition that is largely oxidative in character, less electronegative groups (X = H) lead to additions that are less oxidative and may even be reductive in character, and electropositive groups [X = Li(TMEDA)] lead to additions that can only be described as reductive in character.

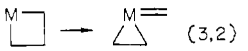
The terms "oxidative addition" and "ligand addition" will no doubt continue to be used where no ambiguity arises. It may, however, be useful to develop new frameworks in which these examples can be discussed. We suggest that additions of type 1, 2, or 4 might be termed three-center, two-electron {3,2} additions. New bonds are formed by the metal to two X atoms (three-center), and the electron count of the metal rises by 2 units (two-electron) in each case. An addition of type 3 (L = CO), in contrast, would be a two-center, two-electron {2,2} addition. A large variety of processes could be described similarly, e.g.

$$\mathrm{M + H^+ \rightarrow MH^+} \quad \{2,0\} \qquad (5)$$

$$\mathrm{M + e^- \rightarrow M^-} \quad \{1,1\} \qquad (6)$$



$$\begin{aligned}\mathrm{M + NO} &\rightarrow \mathrm{M{-}NO} \quad \{2,3\}\\ &\rightarrow \mathrm{M{-}\underset{\underset{O}{\|}}{N}} \quad \{2,1\}\end{aligned} \qquad (7)$$



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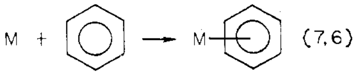

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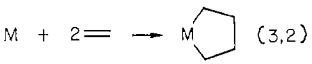
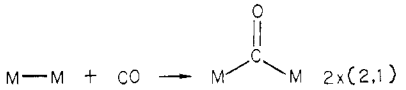


(10)

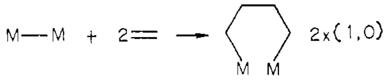
This system describes only what happens to the metal. Equation 10 is globally a 2 + 2 + 2 cycloaddition but a {3,2} process at the metal.

Multimetallic systems pose problems where a simple VB picture of the molecule cannot be used and electron counting becomes ambiguous. Some cases, however, are amenable to description:



(11)

$$\mathrm{M\ M + H_2 \rightarrow H{-}M{-}M{-}H} \quad 2 \times \{3,2\} \qquad (12)$$



(13)

This nomenclature describes the changes in the metal coordination number and electron count on reaction, both of which are relatively free from ambiguity. In contrast, the classical nomenclature relies on the often ambiguous concept of oxidation state and on assumptions, sometimes unjustified, as to the polarity of metal–ligand bonds.

Workers in the field are well aware of these shortcomings in our jargon, but perhaps by developing more logical terminology, we can make our ideas more accessible to fellow scientists in related disciplines.

Sterling Chemistry Laboratory
Yale University
New Haven, Connecticut 06520

**Robert H. Crabtree***
**Gregory G. Hlatky**

*Received March 29, 1979*

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[2] B. L. Shaw and N. I. Tucker in "Comprehensive Inorganic Chemistry", Vol. 4, Pergamon Press, Elmsford, N.Y., 1975, p 834; L. Vaska, *Acc. Chem. Res.*, **1**, 335 (1968).

[3] K. Jonas, *Angew. Chem., Int. Ed. Engl.*, **14**, 752 (1975). The structure of the Ni–Li complex was determined by X-ray crystallography.

[4] R. H. Crabtree, H. Felkin, T. Khan, and G. E. Morris, *J. Organomet. Chem.*, **168**, 183 (1979); R. H. Crabtree, *Acc. Chem. Res.*, **12**, 331 (1979). New $^{13}C$ NMR evidence also supports the reductive character of the addition: an upfield shift, observed in the vinyl carbon resonances of $Ir(cod)_2{}^+$ on addition of $H_2$, suggests that the electron density at Ir increases (R. H. Crabtree and J. M. Quirk, unpublished results, 1979).

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## Application of the Edwards Equation to Formation of Adducts of Copper(II) Macrocyclic Tetraamine Complexes with Anions

*Sir:*

Edwards[1] has shown that equilibrium constants for various acid–base reactions can be quantitatively correlated by means of the equation

$$\log (K/K_0) = \alpha E_n + \beta H \qquad (1)$$

In this equation, $K$ is the equilibrium constant for the acid–base reaction, $K_0$ is the constant for a reference base (say, water) reacting with the same acid, $H$ is a proton basicity factor defined by $H = 1.74 + pK_a$, and $E_n$ is a redox factor defined by $E_n = E° + 2.60$, where $E°$ is the standard oxidation potential for the process, $2X^- \rightleftarrows X_2 + 2e^-$. The parameters $\alpha$ and $\beta$ are constants characteristic of the acid. The terms $\alpha$, $\beta$, and $\alpha/\beta$ are of value and can be used as a measure of the

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(1) Edwards, John O. *J. Am. Chem. Soc.* **1954**, *76*, 1540.