metal–ligand bonds in the $[Ru(2,2'\text{-bpy})_2Cl]_2L^{3+}$ species are assumed, average Δr values of nearly 0.1 Å/bond are required to account for the magnitude of the observed intercepts. Such large distortions do not appear compatible with the data for the $Fe(2,2'\text{-bpy})_3^{2+/3+}$ complexes. As suggested earlier, electronic factors introduced by the low symmetry of these mixed-valence ions may be responsible for contributions to the intercept. In any case, it is clear that the intercepts may conceal many complicating factors.

It is evident that the spectral properties of mixed-valence ions are proving of value in assessing some of the parameters for thermal electron-transfer reactions. The solvent dependence expected from eq 2 has been found for several systems[4,18,19] and lends support to the solvent model for thermal reactions. In a different kind of application of the spectral data, Taube and co-workers have used the intensities of IT transitions in mixed-valence diruthenium complexes as a criterion for adiabaticity of intramolecular electron transfer in ruthenium(II)–cobalt(III) complexes.[20] For the ion $(NH_3)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5^{5+}$ both the observed solvent-dependent and -independent behaviors of the IT band are in good agreement with theory. The calculated values $E_{in} = 4.0$ kcal mol^{-1} and $E_{out} = 22.4$ kcal mol^{-1} (in D_2O) lead to $E_{op} =$ 26.4 kcal mol^{-1} (in D_2O). Thus the calculated value of E_{th} is 6.8 kcal mol^{-1} in D_2O. From E_{th} a first-order rate constant for intramolecular electron transfer (k_{th}) within this mixed-valence ion in D_2O at 25 °C is calculated to be 1.1×10^8 s^{-1}. This value should probably be regarded as a low estimate since the thermal barrier may be lowered if $H_{ab} \neq 0$ (see Figure 1) or it may be lowered by other factors (for example see ref 21). Experiments designed to determine k_{th} directly in this and related ions are presently in progress.[22]

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Registry No. $(NH_3)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5^{5+}$, 54065-65-5.

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Electron Transfer between Cobalt(I) and Cobalt(III) in Vitamin B_{12}[1a]

Sir:

The rate of electron transfer between the Co(I) and Co(III) derivatives of vitamin B_{12} (B_{12s} and B_{12a}, respectively) has recently been determined by two different groups. Although conditions appeared comparable, the use of quite different experimental techniques led to distinctly different rate constants for the reaction

$$(Co^{I})^- + (Co^{III})^+ \rightarrow 2Co^{II} \quad (1)$$

Kaufmann and Espenson[2] used chemical production of B_{12s} and stopped-flow kinetics to evaluate second-order rate constants on the order of 10^4 dm^3 mol^{-1} s^{-1}. The values varied with pH according to[3]

$$-d[B_{12s}]/dt = k[B_{12s}][B_{12b}] \quad (2)$$

$$k/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1} = 5.8 \times 10^3 + 70.7/[OH^-] \quad (3)$$
$$(25\ °C, \mu = 0.1\ M)$$

Alternatively, B_{12s} was generated by pulse radiolysis[4] using reactions 4–5. These studies were carried out in buffer

$$e_{aq}^- + CO_2 \rightarrow CO_2^{-}\cdot \quad (4a)$$

$$CO_2^{-}\cdot + (Co^{II}) \rightarrow CO_2 + (Co^{I})^- \quad (4b)$$

$$\dot{O}H \text{ (or } \dot{H}) + (CH_3)_2CHOH \rightarrow (CH_3)_2\dot{C}OH + H_2O \text{ (or } H_2) \quad (5a)$$

$$(CH_3)_2\dot{C}OH + (Co^{II}) \rightarrow (CH_3)_2CO + H^+ + (Co^{I})^- \quad (5b)$$

solutions (5.8 < pH < 11.0) *saturated with CO_2*. They reported a pH-independent reaction with a rate constant 3.2×10^7 dm^3 mol^{-1} s^{-1}.

To resolve this discrepancy, we have carried out pulse radiolysis experiments under a variety of conditions. We first confirmed[5] by spectroscopic detection the production of B_{12s} in solutions of B_{12r} (2×10^{-5} M) in the following combinations: (1) by e_{aq}^- and $(CH_3)_2\dot{C}OH$ in He-saturated solutions containing 0.1 M 2-propanol, (2) by e_{aq}^- and $CO_2^{-}\cdot$ in He-saturated solutions containing 0.1 M sodium formate, (3) by $CO_2^{-}\cdot$ in CO_2-saturated solutions containing 0.1 M sodium formate, and (4) by $CO_2^{-}\cdot$ and $(CH_3)_2\dot{C}OH$ in CO_2-saturated solutions containing 0.1 M 2-propanol. In solutions containing formate, reaction 6 replaces reaction 5a.

$$\dot{O}H \text{ (or } \dot{H}) + HCO_2^- \rightarrow CO_2^{-}\cdot + H_2O \text{ (or } H_2) \quad (6)$$

A second set of pulse radiolysis experiments consisted of pulsing a mixture of B_{12r} and B_{12a} containing 0.1 M 2-propanol (formate solutions of B_{12a} developed yellow coloration on standing and thus were not used in the kinetic experiments). The former is preferentially reduced to B_{12s},[5] following which the electron-transfer reaction of interest (eq 1) occurs. The pulse is such that about 3×10^{-6} M B_{12s} is formed in the presence of excess B_{12a} at pH 4–12. Many solutions were free of buffers to avoid possible complications from side reactions,

Table I. Rates of Reaction of B_{12s} with B_{12a}[a]

additives	pH	k/dm^3 mol^{-1} s^{-1}
	4.0	1.5×10^7
CO_2 saturated[b]	~4.0	1.2×10^7
	7.8	1.0×10^7
	8.8	7.8×10^5
10^{-2} M borate buffer	9.1	9.0×10^5
10^{-2} M borate buffer	9.7	1.8×10^5
	10.35	7.7×10^4
	11.1	2.9×10^4

[a] All solutions contained 0.1 M 2-propanol, 6×10^{-5} M B_{12r}, and (0.6–2.4) $\times 10^{-5}$ M B_{12a} and were He saturated; accuracy ± 20%, temperature 22 ± 2 °C. Rates were measured at 390 and 460 nm. [b] CO_2 and not He was used as saturating gas.

although we have no evidence of these; these solutions thus had $\mu \approx 0$.

The results can be summarized as follows. (1) In the acidic range, pH 3.9–4.2, in the presence of 0.1 M 2-propanol, under either He or CO_2, the second-order rate constant is $(1.5 \pm 0.3) \times 10^7$ dm^3 mol^{-1} s^{-1}, in substantial agreement with that reported in the earlier radiolysis study[4] in the acidic range. These results also agree with those from the chemical study when the latter are extrapolated to acidic pH. The rate constant for the term in which eq 3 shows a dependence on $[OH^-]^{-1}$ can, with inclusion[3] of K_a and K_w, be written in the kinetically equivalent form $k[B_{12s}][B_{12a}]$, giving $k = 1 \times 10^8$ dm^3 mol^{-1} s^{-1}. Considering the extrapolations involved and the different ionic strengths, these results too can be considered comparable. (2) At higher pHs, especially pH > pK_a = 7.8, the rate constants decrease markedly as summarized in Table I. In this respect the results agree with the chemical result but not the earlier pulse radiolysis studies. Furthermore, the earlier radiolysis workers[4] who used buffer solutions of nominal pH (5.8–11.0) also saturated them with CO_2; thus they also really worked in comparably acidic solutions (i.e., saturation with excess CO_2 simply caused neutralization of the basic buffering components, and the solutions likely had pHs <7), and all their data refer to conditions where the major species is aquocobalamin, B_{12a}.

Thus these new pulse radiolysis experiments (a) affirm the kinetics results of the chemical study,[2] (b) establish by direct measurement that B_{12s} is much more reactive (by a factor of 10^3) toward B_{12a} than toward B_{12b} (perhaps for the reasons alluded to earlier[2]), in contradiction to the claim[4] that the two react at essentially the same rate, and (c) establish that a simple error in pH control was the likely reason for the published differences.[8]

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Registry No. B_{12s}, 13422-51-0; B_{12a}, 13422-52-1; B_{12b}, 18534-66-2.

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Base Catalysis of Ligand Substitution in Metal Carbonyls[1,2]

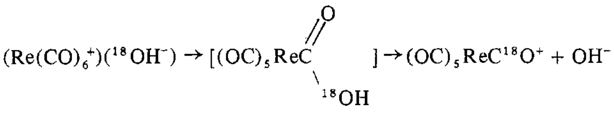
Sir:

Nucleophilic attack at carbon in metal carbonyls has been demonstrated in several different chemical situations. Examples include reaction of metal carbonyls with organolithium compounds[3,4] or Grignard reagents,[5] with amines to form carbamoyl compounds,[6,7] and with azide[8] and ^{18}O exchange of metal carbonyl cations with aqueous base.[9,10] The formation of hydridometal carbonyl species via hydroxide attack at carbonyl carbon is apparently an important pathway in homogeneous Reppe-type catalysis.[11] Nucleophilic attack of hydrides at carbon leads to formation of formyl complexes.[12]

In earlier work we have described the evidence that many ligands, L, in six-coordinate metal carbonyl compounds are capable of labilizing the metal center toward dissociative loss of CO as compared with L = CO.[13,14] This labilization is, for most ligands, specific to the cis position. The purpose of this correspondence is to point out that the ideas of cis labilization and nucleophilic attack at carbon together account for several interesting and important aspects of metal carbonyl reactivities.

As an illustration of the concept involved, consider Scheme I. The parent $Mn(CO)_6^+$ is, from all indications, quite inert with respect to CO dissociation.[13] The attack of CH_3^- at the carbonyl carbon to form the stable compound $Mn(CO)_5C(O)CH_3$ converts the relatively inert metal carbonyl species into one in which the rate of CO dissociation is increased by many orders of magnitude. That is, acetyl is a cis-labilizing ligand relative to CO.

Bases might interact with the carbon atoms of a metal carbonyl to form weak acid–base adducts, without forming a stable product. Such an interaction is presumably involved in the base-catalyzed exchange of ^{18}O between water and metal carbonyls.[9,10]



$$(Re(CO)_6^+)(^{18}OH^-) \rightarrow [(OC)_5ReC(=O)(^{18}OH)] \rightarrow (OC)_5ReC^{18}O^+ + OH^-$$

There are several indications from literature reports that base interaction with metal carbonyls may play a role in ligand substitution processes. The second-order term in the rate law for substitution of CO by another ligand L could be interpreted in terms of an associative interaction between L and carbonyl carbon.[15] In a somewhat different vein, Morris and Basolo interpreted the effect of bases on ligand substitution reactions of $Fe(CO)_2(NO)_2$ in terms of base interaction at carbon.[16] Drew, Darensbourg, and Darensbourg[7] report that $CH_3CNMn(CO)_5^+$ reacts with pyridine to give *fac*-$Mn(CO)_3(py)_3^+$ in several minutes at room temperature, whereas

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