

with only spins in the t_2 orbitals participating in the delocalization.²²

Thus the relative A is a direct index of relative covalency only if all complexes being compared have all of their spins in the same orbital subset [*i.e.*, Ni(II) and Cu(II)]. The relative spin density, ρ , is an index of the relative covalency only among members of a series of complexes where the spin occupation probability of the orbital subset is constant [*i.e.*, Mn(II), Fe(II), and Ni(II) in Table I]. In all other cases, eq 9 must be used. Though this analysis is given only for σ bonding in O_h symmetry, a similar analysis can easily be carried out for π bonding or for other symmetries. However, it may be difficult to determine the spin occupation probabilities of the d electrons in low-symmetry fields.²³ This latter problem is not serious as long as the distortion is not too severe and the covalencies being compared differ significantly.

(22) If the e spins also participate significantly in the delocalization, the relative covalencies of the Mn(II) and Fe(II) complexes cannot be unambiguously determined.

(23) See ref 16, pp 99-106.

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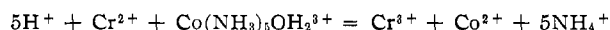
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On the Role of Coordinated Water as a Bridging Ligand in Oxidation-Reduction Reactions

Sir:

The role that water coordinated to the oxidant plays in oxidation-reduction reactions has been much discussed.¹⁻⁴ The general observation has been that reductants that utilize the inner-sphere mechanism react with such oxidants by a rate law that features a strong term inverse in $[H^+]$. This observation has led to the postulate that inner-sphere reactants will exhibit a large rate ratio for the inverse $[H^+]$ path to the path that is independent of $[H^+]$. In an attempt to obtain detailed information about the nature of the reaction of Cr(II) with $Co(NH_3)_5OH_2^{3+}$, we were led to reexamine⁵ the rate of this oxidation-reduction reaction



In this report we present the results of these studies and examine the ramifications of those results on redox reactions involving water coordinated to the oxidant.

The reduction of $[Co(NH_3)_5OH_2](ClO_4)_3$ by Cr(II) was carried out in ClO_4^- medium at $I = 1.0 M$ and 25° . Solutions were prepared from doubly distilled water and distilled $HClO_4$. The $[H^+]$ was varied over a range of 0.096-0.79 M , with the ionic medium held constant with $LiClO_4$. Individual rate constants were computed with a nonlinear least-squares program.

TABLE I
RATE CONSTANTS FOR THE REDUCTION OF $Co(NH_3)_5OH_2^{3+}$ BY Cr^{2+} AS A FUNCTION OF $[H^+]$ AT 25.1°

$[H^+]$, M	$10^3[Cr^{2+}]_0$, M	$10^3[Co(III)]_0$, M	k_{obsd} , $M^{-1} sec^{-1}$	k_{calcd}^a , $M^{-1} sec^{-1}$
0.794	7.13	2.58	3.39 ± 0.03	3.22
0.654	17.8	2.09	4.06 ± 0.04	4.12
0.560	7.13	2.58	4.83 ± 0.03	4.85
0.494	7.13	2.09	5.43 ± 0.02	5.59
0.438	3.56	2.09	6.53 ± 0.04	6.39
0.411	3.56	2.58	7.51 ± 0.16	6.86
0.386	14.3	2.09	6.72 ± 0.21	7.35
0.271	3.56	2.58	10.9 ± 0.1	10.8
0.202	3.56	2.58	14.9 ± 0.1	14.8
0.131	3.56	2.58	23.3 ± 0.2	23.0
0.114	3.58	2.60	27.1 ± 0.3	26.1
0.0965	3.56	2.58	31.6 ± 2.5	31.7

^a Calculated using the expression $k_{calcd} = c[H^+]^{-1} \exp(-d/[H^+])$, where c and d were obtained by nonlinear weighted least-squares analysis of these data. Weights were obtained from the standard deviations of the individual data points.

The individual points are listed in Table I. We have chosen two ways to fit these data. The first is

$$k_{obsd} = a + b[H^+]^{-1} \quad (1)$$

Least-squares analysis of this equation yields the values $a = -0.72 \pm 0.14 M^{-1} sec^{-1}$ and $b = 3.12 \pm 0.05 sec^{-1}$. The second equation tested was a single-term rate law with a medium effect given by a Harned-type equation⁶

$$k_{obsd} = c[H^+]^{-1} e^{-d/[H^+]} \quad (2)$$

The values of the parameters for this equation obtained by nonlinear least-squares analysis are $c = 3.13 \pm 0.05 sec^{-1}$ and $d = 0.25 \pm 0.05 M^{-1}$. The fit of the observed rate constants to eq 2 is illustrated by comparison of column 5 and column 4 of Table I. Although the value for d is somewhat large for medium effects,^{7,8} we believe that eq 2 is a considerably more satisfactory way to represent the variation in observed rate constant with a change in ionic medium. Certainly the negative value for a makes eq 1 unlikely. We conclude that the $[H^+]$ -independent term reported earlier is most likely a medium effect also. For instance, it has been reported by Butler and Taube⁹ that the change from Na^+ to Li^+ has a significant effect on the measured H^+ dependence of several oxidation-reduction reactions involving Cr(II) and Co(III).

If it is accepted that the hydrogen ion independent term in the Cr(II) reduction of $Co(NH_3)_5OH_2^{3+}$ is too small to measure directly, a self-consistent picture of oxidation-reduction reactions involving oxidants with coordinated water emerges. We present the hypothesis that the hydrogen ion independent path for all reactions of Cr^{2+} (and perhaps other reductants) with oxidants containing coordinated water as the only bridging ligand proceeds by an outer-sphere mechanism. This hypothesis is based on three lines of evidence. (1) The only experimentally relevant data in favor of an inner-sphere path for reduction of a water-containing oxidant is that of Kruse and Taube,¹⁰ who observed that 1.01 ± 0.01 water mole-

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TABLE II
 COMPARISON OF RATE REDUCTIONS BY Cr(II) AND V(II)

Oxidant	$k_{Cr(II)}, M^{-1} \text{ sec}^{-1}$	$k_{V(II)}, M^{-1} \text{ sec}^{-1}$	$k_{Cr(II)}/k_{V(II)}$	Ref
$\text{Co}(\text{NH}_3)_6^{3+}$	8.9×10^{-5}	3.7×10^{-3}	0.024	13, 14
$\text{Co}(\text{en})_3^{3+}$	$\cong 2 \times 10^{-5}$	2.0×10^{-4}	$\cong 0.10$	15
$\text{Co}(\text{NH}_3)_5\text{py}^{3+}$	4.3×10^{-3}	2.4×10^{-1}	0.018	16-18
$[\text{Co}(\text{NH}_3)_5]_2\text{NH}_2^{5+}$	3.1×10^{-3}	1.5×10^{-1}	0.021	19, 20
$\text{Ru}(\text{NH}_3)_5\text{py}^{3+}$	3.4×10^3	1.2×10^5	0.028	21
$\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$	$\leq 0.1^a, b$	5.3×10^{-1}	≤ 0.2	This work, 14
$\text{Fe}(\text{H}_2\text{O})_6^{3+}$	$\leq 5.7 \times 10^{2a}$	1.8×10^4	≤ 0.032	22, 23
Hg^{2+}	5.7×10^{-2}	1.3^c	0.044	24, 25

^a The value is an upper limit because medium effects are reported to be significant. ^b Calculated as the maximum allowable rate constant consistent with the values of the standard deviations obtained for *c* and *d* in eq 2. ^c This is the path that produces 2 mol of V^{3+} .²⁵

cules were transferred from Co(III) to Cr(II) in the reduction of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$. Their conclusion that this result implies an inner-sphere path for $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ as well as for the transition state of composition $\text{Co}(\text{NH}_3)_5\text{OHCr}^{4+}$ rests upon the conclusion that a finite H^+ -independent term in the rate law for reduction of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ exists.⁵ Our evidence indicates that this term is most likely a medium effect. (2) Consideration of the precursor complex formed in reduction of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ with Cr^{2+} leads to the conclusion that it is unlikely that a $[\text{H}^+]$ -independent term exists. This precursor complex contains an oxygen bonded to a Co(III) center, a Cr(II) center, and two protons; it is likely that such an oxygen would be highly acidic. Since the rate of deprotonation of this acid would be expected to be very large, it seems unlikely that the energy necessary to change the bond lengths and angles in order to satisfy the Franck-Condon principle for electron transfer could be lower than the energy to deprotonate the precursor complex. Such deprotonations as precursor complexes are formed are consistent with recent reports on $[\text{H}^+]$ dependence in other reactions.^{4, 11} (3) A positive argument that supports the hypothesis that water does not serve as a bridging ligand in reductions with Cr^{2+} can be made by consideration of the Marcus cross-reaction equation¹²

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}$$

If this equation is compared for reductants 1 and 1', say chromous and vanadous ions, and a common oxidant 2, a rate ratio results that is dependent only upon the properties of the pair of reductants (their rate of self-exchange, difference in oxidation-reduction potentials), if the *f* terms are neglected. In Table II¹³⁻²⁵ are listed the values of this ratio for several oxidation-reduction reactions of Cr^{2+} and V^{2+} with oxidants in which the mechanism is surely outer sphere and for several oxidants in which the only possible

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bridging ligand is a water molecule coordinated to the oxidant. Of the three cases listed in which a coordinated water molecule on the oxidant is available for an inner-sphere path, there is independent evidence that the V^{2+} reductions of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ (isotopic fractionation experiments²⁶) and Fe^{3+} (the rate constant is greater than the rate of substitution on the V^{2+} center²⁸) are outer sphere. In both cases the limit on the observed values for Cr^{2+} reduction fit the rate ratio values determined by the first five reactions, reactions in which the mechanism of both the V^{2+} and Cr^{2+} reductions must be outer sphere. For the reduction of Hg^{2+} by V^{2+} and Cr^{2+} , it has also been suggested that the V^{2+} reaction proceeds by an outer-sphere path; the rate data for the ratio are compatible with this suggestion. The available data are consistent with reductions of oxidants containing coordinated water as a possible bridging group proceeding by the outer-sphere mechanism. It would appear that the large rate ratio found for the rate by the inverse H^+ path compared to the H^+ -independent path in Cr^{2+} reductions is largely a result of the extraordinary preference for Cr^{2+} reductions to proceed by the inner-sphere path. It remains to be proven whether other metal ion reductants utilize coordinated water as an effective bridge in the absence of loss of a proton from the activated complex.

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On the Question of the Carbonyl Stretching Absorptions in $\text{MnRe}(\text{CO})_{10}$ and $(\text{C}_6\text{H}_5)_3(\text{CO})_3\text{WMn}(\text{CO})_5$ and the Cleavage of the Tungsten-Manganese Bond by Carbon Tetrachloride

Sir:

Nesmeyanov, *et al.*,¹ have reported for the mixed-

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