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

Oxidant	$k_{Cr(II)}$, M^{-1} sec^{-1}	$k_{V(II)}$, M^{-1} sec^{-1}	$k_{Cr(II)}/k_{V(II)}$	Ref
$Co(NH_3)_6^{3+}$	8.9×10^{-5}	3.7×10^{-3}	0.024	13, 14
$Co(en)_3^{3+}$	$\cong 2 \times 10^{-5}$	2.0×10^{-4}	$\simeq 0.10$	15
$Co(NH_3)_5py^{3+}$	4.3×10^{-3}	2.4×10^{-1}	0.018	16–18
$[Co(NH_3)_5]_2NH_2^{5+}$	3.1×10^{-3}	1.5×10^{-1}	0.021	19, 20
$Ru(NH_3)_5py^{3+}$	3.4×10^{3}	1.2×10^{5}	0.028	21
$Co(NH_3)_5OH_2^{3+}$	$\leq 0.1^{a,b}$	5.3×10^{-1}	≤ 0.2	This work, 14
$Fe(H_2O)_6^{3+}$	$\leq 5.7 \times 10^{2\,a}$	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 $Co(NH_3)_5OH_2^{3+}$. Their conclusion that this result implies an inner-sphere path for $Co(NH_3)_5OH_2^{3+}$ as well as for the transition state of composition $Co(NH_3)_5OHCr^{4+}$ rests upon the conclusion that a finite H^+-independent term in the rate law for reduction of $Co(NH_3)_5OH_2^{3+}$ exists.[5] Our evidence indicates that this term is most likely a medium effect. (2) Consideration of the precursor complex formed in reduction of $Co(NH_3)_5OH_2^{3+}$ with Cr^{2+} leads to the conclusion that it is unlikely that a $[H^+]$-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 $[H^+]$ 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 equation[12]

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

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 II[13–25] 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 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 $Co(NH_3)_5OH_2^{3+}$ (isotopic fractionation experiments[26]) and Fe^{3+} (the rate constant is greater than the rate of substitution on the V^{2+} center[23]) 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 $MnRe(CO)_{10}$ and $(C_5H_5)(CO)_3WMn(CO)_5$ 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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(1) A. N. Nesmeyanov, G. G. Dvoryantseva, Yu-N Sheinker, N. E. Kolobova, and K. N. Anisimov, *Dokl. Akad. Nauk SSSR, Ser. Khim.*, **169**, 843 (1966).

metal carbonyl $MnRe(CO)_{10}$ five intense absorptions in the carbonyl stretching region of the infrared spectrum (2064 (m), 2039 (m), 2006 (s), 1974 (m), and 1968 (m) cm^{-1}; CCl_4 solution). While it is true that the strict application of symmetry rules requires that there be six infrared-active fundamental modes for this carbonyl, in fact we[2a] and others[2b] had earlier observed that it exhibits only three principal absorptions (2054 (m), 2017 (s), and 1978 (m) cm^{-1}; cyclohexane solution) which resemble those of the symmetrical dimetal decacarbonyls. Whatever differences may arise concerning the assignment of the modes, however, it is apparent that there must be some additional problem if two groups of workers report a different number of bands for the same species. A similar discrepancy was brought to our attention recently when we had occasion to record the spectrum of $(C_5H_5)(CO)_3WMn(CO)_5$, for which we obtained in cyclohexane solution fewer principal absorptions (2088 (m), 2028 (w), 1996 (s), 1979 (s), 1915 (w), and 1899 (m) cm^{-1}) than reported[1] by Nesmeyanov, *et al.*, in carbon tetrachloride solution (2081 (m), 2049 (m), 2021 (w), 1988 (s), 1971 (s), 1905 (w), and 1888 (m) cm^{-1}). In both this case and that for $MnRe(CO)_{10}$ our suspicions were aroused that the differences might be due to chemical impurities arising from reaction with solvent. One of us had earlier noted during spectroscopic studies that $Mn_2(CO)_{10}$ reacts with carbon tetrachloride under mild conditions.[3]

Dealing first with the case of $(C_5H_5)(CO)_3WMn(CO)_5$, we note that an infrared spectrum of the complex in carbon tetrachloride, recorded as quickly as possible after preparation of the solution, does indeed show one additional band (2055 cm^{-1}) over that noted in cyclohexane solution. We observe, in addition, that this band continues to grow rapidly, until it becomes apparent that it is one of the strong bands of $Mn(CO)_5Cl$, the other of which (2000 cm^{-1}) is initially obscured by a genuine absorption of $(C_5H_5)(CO)_3WMn(CO)_5$. After 3 hr the entire sample is converted to a mixture of $Mn(CO)_5Cl$ and its decomposition product $[Mn(CO)_4Cl]_2$.[3] No attempt was made to determine the fate of the tungsten and no $(C_5H_5)(CO)_3WCl$ or other soluble carbonyl-containing species was observed. The rhenium analogs $(C_5H_5)(CO)_3MRe(CO)_5$ (M = Mo, W) are apparently more resistant, and in carbon tetrachloride a pattern of six carbonyl bands is reported[1] similar to that observed by us for $(C_5H_5)(CO)_3WMn(CO)_5$ in cyclohexane.

In the case of $MnRe(CO)_{10}$ the discrepancy arises from a different source; this carbonyl does *not* react with carbon tetrachloride even within 24 hr. The sample used to record the spectrum reported by Nesmeyanov, *et al.*,[1] is perfectly fitted by a mixture of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ both in our laboratory and also by taking the peaks reported in that paper for these derivatives. As we have formerly reported,[2] the published[4] synthesis of $MnRe(CO)_{10}$ leads to a product mixed with some of the symmetrical dimetal decacarbonyls. In fact, from the combination of $NaRe(CO)_5$ and $Mn(CO)_5Br$ we obtain principally a mixture of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. A high yield of $MnRe(CO)_{10}$ with only traces of the symmetrical decacarbonyls is obtained from $NaMn(CO)_5$ and $Re(CO)_5Br$.

One last point needs to be made concerning a footnote in the paper by Nesmeyanov, *et al.*, namely:[1] "Weak bands in the 1800–2100 cm^{-1} region, which have intensities 1–2 orders lower than the intensities of ν_{CO} cannot be assigned to fundamental vibrations, and are not considered further." This is a misleading assumption. It has already been demonstrated in the case of the pentacarbonyl halides[5] and hydrides[6] of Mn, Tc, and Re that a fundamental mode can be quite weak and this is undoubtedly also true for $MnRe(CO)_{10}$. Following the study of the Raman spectrum of $Re_2(CO)_{10}$ by Cotton and Wing,[7] we can now assign the weak band of $MnRe(CO)_{10}$ at 2124 cm^{-1} (band E in Figure 1 of ref 2a) as the A_1 mode, which has only weakly gained infrared activity compared to that of the corresponding A_1 mode of the symmetrical decacarbonyls, which is strictly only Raman active. This is no doubt the result of only a small departure from D_{4d} to C_{4v} symmetry for the *effective* electron density available to the ten terminal carbonyls from the dimetal core in going from $M_2(CO)_{10}$ to $MM'(CO)_{10}$.

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The Presence of $H_5O_2^+$ in Erbium and Yttrium Oxalate–"Hydrogen Oxalate" Trihydrate[1]

Sir:

The X-ray crystal structure of $Er(C_2O_4)(HC_2O_4)\cdot 3H_2O$ was recently reported by Steinfink and Brunton.[2] These authors undertook the study because the compound was thought to contain both the anion $C_2O_4^{2-}$ and the acid anion $HC_2O_4^-$. They found the space group to be $P_{4/n}$ with two molecules per unit cell and interpreted their results in terms of a disorder between the oxalate and the acid oxalate ions. The six waters occupy two crystallographically distinct positions in the cell. Two of the waters are in the twofold positions 2c and each occupies one of the nine coordination positions about the erbium. The remaining four waters caused some difficulty, being statistically distributed among the eightfold positions 8g, and had very short O–O distances. The two shortest distances between these disordered water oxygens were observed to be 2.43 and 1.87 Å.[2]

We wish to point out that the thermal ellipsoids for the oxalate oxygens are normal for a completely ordered oxalate ion and show no elongation along the C–O bond as one might expect for a disorder between

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