that an adjacent heteroatom can decrease the rate of nitrogen inversion in cyclic systems. The increased pyramidal stability has been attributed to increased repulsion between the lone pairs on nitrogen and on the heteroatom in the transition state for inversion and to the electronegativity of the heteroatom.

Alternatively, in acyclic compounds, such as **1**, lone-pair repulsion might also lead to a barrier to rotation around the nitrogen–heteroatom bond like that which obtains in disulfides.[9] This explanation, too, can account for the nmr data presented for **1**, as well as those observed for other sulfenamides,[1] trialkylhydroxylamines,[10] and other acyclic compounds, and has been used to explain the nmr spectral data of N,O-diacyl-N-alkylhydroxylamines[11] as well as substituted hydrazines.[12] The results of further experiments designed to distinguish between these two alternatives will be reported subsequently.

In an effort to determine whether the substantial electronegativity of the trichloromethyl group plays an important role in raising the barrier, the nmr spectra of N-(*p*-toluenesulfenyl)-N-(1-phenylethyl)benzenesulfonamide ($C_6H_5SO_2N(SC_6H_4CH_3)CH(CH_3)C_6H_5$, **2**) have also been examined. In contrast to **1**, the room-temperature spectrum of **2** features a single doublet at δ 1.44 and a single *p*-toluene methyl singlet at δ 2.28. That this is the result of rapid epimerization rather than accidental equivalence or the presence of a single diastereomer is indicated by the low-temperature spectra. As the temperature is lowered the spectrum broadens, and at $-60°$ the spectrum features two doublets at δ 1.22 and 1.57 and two *p*-tolyl methyl singlets at δ 2.23 and 2.39, in both cases of nearly equal intensity. The free energy of activation at the coalescence temperature was calculated using the *p*-toluene signals ($\Delta\nu_{\max}$ 9.4 Hz, T_c $-38°$, $\Delta G \approx 12.3$ kcal/mol; solvent, deuteriochloroform). The large differences in the free energies of activation for the epimerization of **1** and **2** support the suggestion[1] that the trichloromethyl group plays an important role in raising the barrier and serves to bring into clearer perspective the observations that N,N-dimethyltrichloromethanesulfinamides exhibit nonequivalence at low temperatures while other sulfinamides do not.[13,14]

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The Role of Chromium(IV) in Oxidations by Chromic Acid. The Oxidative Cleavage of Cyclobutanol

Sir:

Two-thirds of the products formed in a chromic acid oxidation[1] originate not from a direct action of hexavalent chromium but from reactions with tetra- and/or pentavalent chromium compounds.[2] Scheme I

Scheme I

$$\begin{aligned}
&\mathrm{Cr(VI)} + \mathrm{S} \longrightarrow \mathrm{Cr(IV)} + \mathrm{P_6}\\
&\mathrm{Cr(IV)} + \mathrm{Cr(VI)} \longrightarrow 2\mathrm{Cr(V)}\\
&2\mathrm{Cr(V)} + 2\mathrm{S} \longrightarrow 2\mathrm{Cr(III)} + 2\mathrm{P_5}
\end{aligned}$$

represents the simplest and by far more popular reaction mechanism which can be written.

According to this mechanism the substrate can be oxidized in principle to two different products.[3] This mechanism is characterized by the absence of any reaction between chromium(IV) and the organic substrate, implying that such a reaction must be slow compared with the rapid reaction between chromium(IV) and chromium(VI). The mechanism further requires chromium(V) to be an effective oxidant for organic substrates.

A mechanism involving both chromium(IV) and chromium(V) oxidation of the organic compound has been considered by Westheimer[2] (Scheme II), where

Scheme II

$$\begin{aligned}
&\mathrm{Cr(VI)} + \mathrm{S} \longrightarrow \mathrm{Cr(IV)} + \mathrm{P_6}\\
&\mathrm{Cr(IV)} + \mathrm{S} \longrightarrow \mathrm{R}\cdot + \mathrm{Cr(III)}\\
&\mathrm{Cr(VI)} + \mathrm{R}\cdot \longrightarrow \mathrm{Cr(V)} + \mathrm{P_4}\\
&\mathrm{Cr(V)} + \mathrm{S} \longrightarrow \mathrm{Cr(III)} + \mathrm{P_5}
\end{aligned}$$

$R\cdot$ is an intermediate free radical and P_6, P_5, and P_4 the products originating from reactions of the substrate S with a hexa-, penta-, and tetravalent chromium species, respectively.

Several mechanisms involving only chromium(VI) and chromium(IV) oxidation of the substrate can also be written. One example postulating a disproportionation of chromium(V) is given in Scheme III.

Scheme III

$$\begin{aligned}
&\mathrm{Cr(VI)} + \mathrm{S} &&\longrightarrow \mathrm{Cr(IV)} + \mathrm{P_6}\\
&2\mathrm{Cr(IV)} + 2\mathrm{S} &&\longrightarrow 2\mathrm{Cr(III)} + 2\mathrm{R}\cdot\\
&2\mathrm{Cr(VI)} + 2\mathrm{R}\cdot &&\longrightarrow 2\mathrm{Cr(V)} + 2\mathrm{P_4}\\
&2\mathrm{Cr(V)} &&\longrightarrow \mathrm{Cr(IV)} + \mathrm{Cr(VI)}
\end{aligned}$$

The question of chromium(IV) reactivity, formulated almost 20 years ago,[2] thus still remains crucial to any further exploration of chromic acid oxidations. In this communication we wish to present evidence for a rapid reaction between chromium(IV) and an organic substrate, cyclobutanol, thus ruling mechanism I out at least for this particular compound.

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[1] For recent excellent reviews of chromic acid oxidations see: K. B. Wiberg, "Oxidation in Organic Chemistry," Part A, Academic Press Inc., New York, N. Y., 1965; R. Stewart, "Oxidation Mechanisms: Application to Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964.

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[3] The formation of chromium(V) and its accumulation in the reaction mixture to a measurable concentration has recently been demonstrated by Wiberg.[4]

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Our approach is based on Espenson's work[5] on the oxidation of vanadium(IV) by chromium(V) for which a mechanism has been established (Scheme IV), according to which pentavalent chromium is formed in a rapid reversible reaction whereas chromium(IV) is produced in the rate-limiting step. The chromic acid oxidation of vanadium(IV) proceeds under conditions which are mild enough to make any reaction of hexavalent chromium or pentavalent vanadium with organic compounds negligibly slow.

Scheme IV

$$\mathrm{Cr(VI)} + \mathrm{V(IV)} \underset{}{\overset{\text{fast}}{\rightleftharpoons}} \mathrm{Cr(V)} + \mathrm{V(V)}$$

$$\mathrm{Cr(V)} + \mathrm{V(IV)} \xrightarrow[\text{limiting}]{\text{rate}} \mathrm{Cr(IV)} + \mathrm{V(V)}$$

$$\mathrm{Cr(IV)} + \mathrm{V(IV)} \longrightarrow \mathrm{Cr(III)} + \mathrm{V(V)}$$

We have recently shown[6] that the chromic acid oxidation of cyclobutanol leads to the formation of basically two products, cyclobutanone and γ-hydroxybutyraldehyde. The existence of a sizable kinetic isotope effect in the oxidation of 1-deuteriocyclobutanol leads us to conclude that cyclobutanone is formed in the rate-limiting step by chromium(VI) oxidation (hence, cyclobutanone = P_6), whereas the hydroxyaldehyde must originate from a reaction of cyclobutanol with either chromium(IV) or chromium(V).

When cyclobutanol is introduced into the system vanadium(IV)–chromium(VI), the yield of vanadium(V) is decreased as part of the oxidant is used up for the oxidation of the alcohol (Figure 1). The only organic oxidation product which can be isolated from the reaction mixture (as a dinitrophenylhydrazone) is the cleavage product, γ-hydroxybutyraldehyde. This proves that cyclobutanol can intercept the intermediate chromium valence states formed during the reduction of chromium(VI) by vanadium(IV).

Table I. Effect of Cyclobutanol on the Rate of Consumption of Chromium(VI) in the Oxidation of Vanadium(IV) at 25°[a]

[Cyclobutanol] / [Vanadium(IV)]	Initial rate, $10^6 M$ sec^{-1}	% chromium(VI) consumed after 50 sec	100 sec
0	0.55	33.5	47.5
3.0	0.60	34.3	47.7
4.3	0.66	34.7	47.0
9.5	0.68	31.8	48.0
12.9	0.70	33.3	48.0
25.6	0.67	31.7	47.5
45.8	0.70	32.1	47.0
84.1	0.70	30.3	46.0

[a] Concentrations: vanadium(IV) 2.58×10^{-3} M, vanadium(V) 1.95×10^{-3} M, chromium(VI) $0.470\text{–}0.490 \times 10^{-3}$ M, $HClO_4$ 0.0628 M.

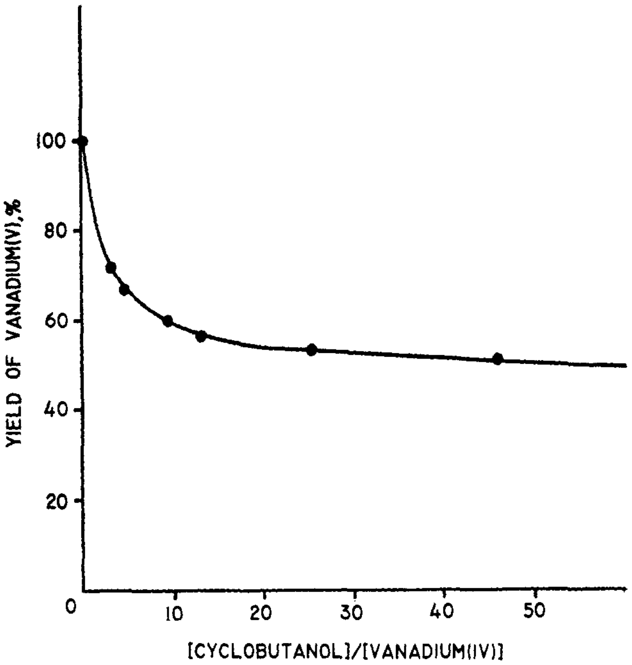

Figure 1. Effect of added cyclobutanol on the yield of V(V) in the oxidation of vanadium(IV) by chromium(VI) at 25°. Initial concentrations: $[VO^{2+}] = 2.58 \times 10^{-3}$ M, $[VO_2^{+}] = 1.95 \times 10^{-3}$ M, $[CrO_3] = 0.48 \times 10^{-3}$ M, $[HClO_4] = 6.3 \times 10^{-2}$ M.

Table I shows that, despite the extensive oxidation of cyclobutanol taking place, the over-all rate of chromic acid reduction is basically unaffected by the introduction of cyclobutanol.[7] As chromium(V) is formed in a rapid preequilibrium, the oxidation of cyclobutanol by chromium(V) would lead to a rate increase proportional to the concentration of the alcohol. As, on the other hand, chromium(IV) is formed only in the rate-limiting step, a reaction of this valence state of chromium with the organic substrate can affect only the product composition, but not the reaction rate.

We conclude therefore that chromium(V) is relatively unreactive toward cyclobutanol. Cyclobutanol is unable to compete successfully with vanadium(IV) for the chromium(V) species, even though the reduction of chromium(V) by vanadium(IV) represents the relatively slow rate-limiting step. On the other hand, *cyclobutanol exhibits an excellent reactivity toward chromium(IV)* for which it competes very successfully with vanadium(IV) even though the reaction between vanadium(IV) and chromium(IV) is considered to be a very rapid one.[5]

The oxidative cleavage of cyclobutanol in the system vanadium(IV)–chromium(VI) can be best summarized as shown in Scheme V, where R· stands for a free-radical intermediate.

Scheme V

$$\mathrm{Cr(VI)} + \mathrm{V(IV)} \overset{\text{fast}}{\rightleftharpoons} \mathrm{Cr(V)} + \mathrm{V(V)}$$

$$\mathrm{Cr(V)} + \mathrm{V(IV)} \xrightarrow[\text{limiting}]{\text{rate}} \mathrm{Cr(IV)} + \mathrm{V(V)}$$

$$\mathrm{Cr(IV)} + n\text{-}\mathrm{C_4H_7OH} \longrightarrow \mathrm{Cr(III)} + \mathrm{R\cdot}$$

$$\mathrm{R\cdot} + \mathrm{V(V)} \longrightarrow \mathrm{HOCH_2CH_2CH_2CHO} + \mathrm{V(IV)}$$

This scheme would predict that in the presence of a large excess of cyclobutanol the yield of vanadium(V) should reach a limiting value of one-third of the amount produced in the absence of cyclobutanol. As this limit is not quite reached (Figure 1), it is possible that a reaction interfering with the reduction of 1 equiv of vana-

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[5] J. H. Espenson, *J. Am. Chem. Soc.*, **86**, 5101 (1964).

[6] A. Radkowsky, Ph.D., The Catholic University of America, Washington, D. C., 1967.

[7] The negative first order in vanadium(V) is unchanged by the addition of the organic substrate. This demonstrates that no change in mechanism or in the rate-limiting step took place; particularly it rules out the possibility that the first step of Scheme IV (formation of chromium(V)) would have become rate limiting.

dium(V) in the last step of Scheme V takes place. A reaction between two radicals (*e.g.*, disproportionation) would offer a plausible explanation.

Our results thus rule out Scheme I for the chromic acid oxidation of cyclobutanol. Furthermore, preliminary experiments[8] *show that isopropyl alcohol and a number of primary alcohols as well as aldehydes exhibit similar behavior, making it unlikely that Scheme I is correct for any alcohol or related compound.*

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the U. S. Army Research Office, Durham, for generous support of this research.

[8] M. Rahman and J. Roček, unpublished results.

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A New Type of Intramolecular Antiferromagnetism[1]

Sir:

The lanthanide metals are thought to consist of magnetic ion cores surrounded by conduction electrons derived from 6s and 5d orbitals. The ferro- and antiferromagnetic magnetic properties of these substances are attributed to the interion coupling of the metal ion core 4f electrons *via* conduction electron polarization which results from direct exchange interaction of the 4f electrons and the 6s and 5d conduction electrons.[2]

We wish to report evidence for a new type of intramolecular antiferromagnetism in a formally low-valent complex of europium with bipyridyl and suggest this type of complex as a model for studying the interactions of core 4f electrons with conduction electrons.

Europium and ytterbium dissolve in liquid ammonia to give blue solutions.[3] We have found that Eu(bipy)$_4$, Yb(bipy)$_4$, and Yb(*o*-phen)$_4$ can be prepared by the reaction of bipyridyl or *o*-phenanthroline with the appropriate metal in liquid ammonia using the method reported for the preparation[4] of Ba(bipy)$_4$. After removal of the ammonia, the complex was dissolved in tetrahydrofuran and filtered. Removal of the tetrahydrofuran under high vacuum gave the unsolvated complex. *Anal.* Calcd for Yb(bipy)$_4$: Yb, 21.69; N, 14.05. Found: Yb, 21.7; N, 14.0. Calcd for Eu(bipy)$_4$: Eu, 19.57; N, 14.43. Found: Eu, 19.5; N, 14.4. Calcd for Yb(*o*-phen)$_4$: Yb, 19.36; N, 12.54. Found: Yb, 19.4; N, 12.6. The magnetic susceptibilities of the above complexes were measured in tetrahydrofuran by an nmr method.[5,6] TMS was used as the internal and external reference.[7] The magnetic moments of Yb(bipy)$_4$ and Yb(*o*-phen)$_4$ at 34° were found to be 2.79 and 2.78 BM, respectively.

These magnetic moments correspond to two unpaired electrons based on the spin-only formula for $J = 1$, $\mu = g\sqrt{J(J + 1)} = 2.83$ BM. Similar results[4] have been obtained by Herzog for Ba(bipy)$_4$. The triplet-state electron spin resonance[8] of complexes of the alkaline earths with bipyridyl and similar ligands indicates that formally low-valent metal complexes of electropositive metals are to be viewed as dipositive metal ions coordinated to radical anion-like ligands. Accordingly the presence of two unpaired electrons in Yb(bipy)$_4$ and Yb(*o*-phen)$_4$ suggests that the two 6s electrons of ytterbium metal have been transferred to the ligands.

The known close similarity of europium, ytterbium, and the heavier alkaline earths[9] indicates that Eu(bipy)$_4$ would have nine unpaired electrons, two on the radical anion-like ligands and seven in the shielded 4f subshell of the Eu^{2+} ion. The magnetic moments at different temperatures which we found for Eu(bipy)$_4$ are given in Table I. The magnetic moments calculated from the spin-only formula for five, seven, and nine unpaired electrons are 5.92, 7.94, and 9.95, respectively. We attribute the low magnetic moment of the europium complex to an antiferromagnetic exchange coupling between the $4f^7$ electrons of Eu^{2+} and the two unpaired electrons on the ligands. A simple bonding explanation for the low magnetic moment is not plausible in that it is known that the 4f electrons are well shielded from the ligands by the $5s^25p^6$ shell. Our observation is apparently the first case of intramolecular antiferromagnetism where the exchange is between metal nonbonding electrons and unpaired electrons on the ligands. A useful analogy may be to view the electrons on the ligands as localized conduction electrons.

Table I. Magnetic Moments of Eu(bipy)$_4$

Temp, °K	μ_{eff}, BM[a]	Temp, °K	μ_{eff}, BM[a]
211	5.68	269	5.67
218	5.70	273	5.67
234	5.65	294	5.70
253	5.69	304	5.74
261	5.64	317	5.80

[a] Calculated from $\mu = 2.84\sqrt{X_{\mathrm{m}}T}$ BM.

In the coupling of the two systems of electrons, J, the total angular momentum quantum number may take on all half-integral values[10] between $|J_{\mathrm{Eu}^{2+}} + J_{\mathrm{ligand}}|$ and $|J_{\mathrm{Eu}^{2+}} - J_{\mathrm{ligand}}|$, namely $^9/_2$, $^7/_2$, and $^5/_2$. In the antiferromagnetic scheme, the $^5/_2$ state will lie lowest. The near-constancy of the magnetic moments in Table I suggests that the $^7/_2$ and $^9/_2$ states are relatively unimportant at these temperatures. Therefore the exchange coupling must be strong and the Néel temperature must be well above room temperature. However, the results in Table I are related to the experimental observable

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[1] We wish to thank Research Corporation for partial support of this work.

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