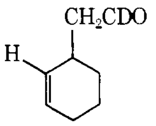
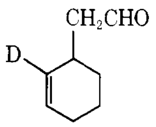
transfer of axial and equatorial hydrogen in **2e** are identical. This calculation leads to an isotope effect (k_H/k_D) of ~2[11] and an inherent stereoselectivity of ~20:1 favoring transfer of axial hydrogen in intermediate **2e**.

The calculated isotope effect is unexceptional. Quantitative data on intermolecular gas phase radical disproportionations suggest a value of ~1.5,[12] and qualitative agreement comes from observation of small isotope effects in intramolecular disproportionations in solution.[13] The calculated stereoselectivity indicates that in disproportionation of **2e** axial hydrogen is transferred ~95% of the time. In part this selectivity may be steric in origin; although the acyl radical can approach the axial and equatorial hydrogens equally closely, there may well be small energy differences in the favorable geometry for each transfer. We suggest, however, that the most important factor leading to the observed selectivity is stereoelectronic control arising from interaction of the bond being broken with the adjacent p orbital of the unpaired electron. Several investigations indicate that, in homolytic cleavage of a carbon-carbon bond adjacent to a radical center, the bond preferentially broken is the one lying closest to the plane of the p-orbital bearing free spin.[14] Such a requirement applied to cleavage of a carbon-hydrogen bond adjacent to a radical center would lead to preferential transfer of axial hydrogen in **2e**. Stereoelectronic control in radical fragmentations and in the reverse addition of radicals to olefins has been discussed for several years,[14,15] but to our knowledge there is no prior experimental evidence implicating such control in a hydrogen transfer reaction.



13



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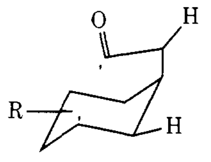
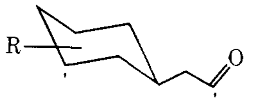
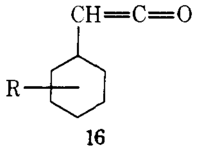


15a



15e



16

We previously showed that in photolysis of substituted bicyclo[3.2.1]octan-6-ones for which **15a** and not **15e** is the stable conformer of the biradical, all disproportionation occurs from **15a** and leads preferentially to ketene **16** through hydrogen transfer from side chain to ring.[1] We established the importance of steric factors in this preferential formation of ketene rather than aldehyde from **15a** and suggested that a stereoelectronic effect might also operate here.[1] The present findings support this suggestion. Disproportionation of **15a** to form aldehyde necessarily involves transfer of equatorial hydrogen to the side chain, and this transfer cannot conform to the stereoelectronic requirement discussed above.[16]

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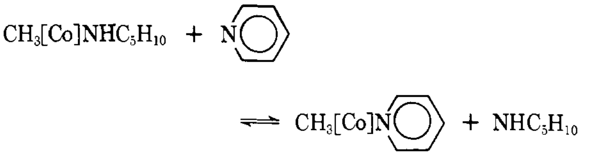
Kinetic Ambiguity between the I_d and D Mechanisms in Ligand Substitution Reactions. The Intimate Mechanism for Axial Base-Ligand Exchange Reactions in Alkyl(base)cobaloximes and Related Species

Sir:

Recently Jensen and Kiskis have proposed a kinetic differentiation between I_d and D mechanisms for axial base-ligand exchange in alkyl(base)cobaloximes in noncoordinating solvents.[1] These workers concluded that this exchange (eq 1) occurs via a purely dissociative (D) process.



(1)

The proposed mechanism for a dissociative interchange (I_d) ligand substitution proceeding to completion is given below (eq 2, 3, and 4).[2]

$$\mathrm{M(L)}_n\mathrm{A} + \mathrm{B} \overset{K_1}{\rightleftharpoons} \mathrm{M(L)}_n\mathrm{A}\cdot\mathrm{B}\ \text{(rapid)} \tag{2}$$

$$\mathrm{M(L)}_n\mathrm{A}\cdot\mathrm{B} \xrightarrow{k_2} \mathrm{M(L)}_n\mathrm{B}\cdot\mathrm{A} \tag{3}$$

$$\mathrm{M(L)}_n\mathrm{B}\cdot\mathrm{A} \xrightarrow{\text{fast}} \mathrm{M(L)}_n\mathrm{B} + \mathrm{A} \tag{4}$$

The rate constant expressions (eq 5 and 6)[3] are:

$$k_{\text{obsd}} = \frac{k_2K_1[\mathrm{B}]}{1 + K_1[\mathrm{B}]} \tag{5}$$

$$\frac{1}{k_{\text{obsd}}} = \frac{1}{k_2} + \frac{1}{k_2K_1[\mathrm{B}]} \tag{6}$$

On the other hand a purely dissociative (D) mechanism (eq 7 and 8) obeys the rate constant expressions given by eq 9 and 10.[2]

$$\mathrm{M(L)}_n\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{M(L)}_n + \mathrm{A} \tag{7}$$

$$\mathrm{M(L)}_n + \mathrm{B} \xrightarrow{k_2} \mathrm{M(L)}_n\mathrm{B}\ \text{(rapid)} \tag{8}$$

$$k_{\text{obsd}} = \frac{k_1k_2[\mathrm{B}]}{k_{-1}[\mathrm{A}] + k_2[\mathrm{B}]} \tag{9}$$

$$\frac{1}{k_{\text{obsd}}} = \frac{1}{k_1} + \frac{k_1[\mathrm{A}]}{k_1k_2[\mathrm{B}]} \tag{10}$$

Table I. Frequency Shifts of ν_{NH} in $CH_3Co(dmgH)_2$piperidine in the Presence of Lewis Bases[a]

Base	ν_{NH} (cm^{-1})	$\Delta\nu_{NH}$ (cm^{-1})
—	3254	—
C_6D_6	3251	3
THF	3230	24
CS_2	3224	30
$(MeO)_3PO$	3219	35
$(n\text{-}Bu)_3PO$	3204	50
NC_5H_5	3152	102
NDC_5H_{10}	3146	108

[a] Spectra observed in $CDCl_3$ in 1-mm solution cells.

Jensen and Kiskis[1] proposed that since eq 6 does not show a concentration dependence on the departing ligand (A) whereas eq 10 does, a variation of k_{obsd} with the concentration of A proved a D mechanism was operative.

However, inclusion of the equilibrium process involving outer-sphere complex formation with A in the interchange process (eq 11)

$$M(L)_nA + A \overset{K_2}{\rightleftharpoons} M(L)_nA \cdot A \tag{11}$$

yields the rate constant expressions (eq 12 and 13),

$$k_{obsd} = \frac{k_2K_1[B]}{1 + K_1[B] + K_2[A]} \tag{12}$$

$$\frac{1}{k_{obsd}} = \frac{1}{k_2} + \frac{1 + K_2[A]}{k_2K_1[B]} \tag{13}$$

Equations 13 and 10 have equivalent algebraic forms. If $K_2[A] \gg 1$ the slopes computed by eq 10 and 13 will vary identically with [A].[4,5] In other words, the overall rate can be equally affected by the competition of A and B for the highly reactive coordinatively unsaturated intermediate, $[M(L)_n]$, as well as by competition of A and B to form outer-sphere complexes with $M(L)_nA$. Similar considerations (eq 14–21) explain the "delicate balance" between I_d and D mechanisms when changing solvents, where S is a solvent with an accessible lone pair (e.g., THF) and S′ is a π-base (e.g., benzene). Solvents thus may act as catalysts or inhibitors in these substitution reactions through specific solvent effects.[6] The polarity of the solvents otherwise has little effect.[7]

$$M(L)_nA + S \rightleftharpoons M(L)_nA \cdot S \tag{14}$$

$$M(L)_nA \cdot S \rightarrow M(L)_nS \cdot A \tag{15}$$

$$M(L)_nS \cdot A \rightarrow M(L)_nS + A \tag{16}$$

$$M(L)_nS \rightleftharpoons M(L)_n + S \tag{17}$$

$$M(L)_n + B \rightarrow M(L)_nB \tag{18}$$

or

$$M(L)_nA + S' \rightleftharpoons M(L)_nA \cdot S' \tag{19}$$

$$M(L)_nA \rightleftharpoons M(L)_n + A \tag{20}$$

$$M(L)_n + B \rightarrow M(L)_nB \tag{21}$$

In order to better understand the axial base–ligand exchange process in alkyl(base)cobaloximes, we have investigated the infrared spectra of these complexes in the ν(NH) region in the presence of excess Lewis bases (Table I).[8] Spectroscopically identifiable outer-sphere hydrogen-bonded adduct formation was observed analogous to the type previously reported by us in $M(CO)_5$(piperidine) species under similar conditions.[4] At piperidine concentrations far less than the 100-fold excess employed by Jensen and Kiskis[1] in their kinetic study, complete reduction of the ν(NH) absorbance in the free complex was observed. The bridging intramolecular hydrogen bonds between the dimethylglyoxime ligands are disrupted as well upon the addition of Lewis bases to the solutions of the cobaloximes in chloroform with concomitant formation of new hydrogen bonds. For example, the ν(OH···O) value of 3410 cm^{-1} in the free complex has a corresponding value in THF of ν(OH···THF) 3510 cm^{-1}. Similarly the half-band width of ν(OH···O) in the free complex changes from about 210 to 370 cm^{-1} (ν(OH···N)) when pyridine is added to methyl(pyridine)cobaloxime.[9-12]

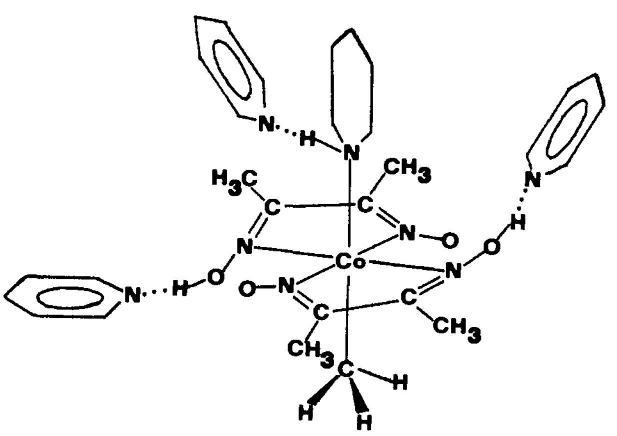


Figure 1. Possible reaction intermediate for piperidine substitution with a nitrogen base in the (methyl)cobaloxime piperidine derivative. All sites for hydrogen-bonding interactions are shown.

A number of reaction intermediates can be visualized (see Figure 1) particularly during competition experiments, making an unambiguous interpretation of the data unlikely.[13]

The results listed in Table I show that considerable steric interaction exists between the hydrogen-bonded bases and the cobalt complex, e.g., CS_2 vs. THF. Similarly, addition of excess piperidine (ΔHNP = −47)[14] results in only a 6 cm^{-1} greater shift in ν(NH) when compared with the planar pyridine base (ΔHNP = 286).[14,15] Electronic factors are also important, as $\Delta\nu$(NH) for $(n\text{-}Bu)_3PO$ is greater than the corresponding change for $(MeO)_3PO$.

These steric repulsions in the outer-sphere complex may dissociatively activate the substitution processes and add to the catalytic effect of the rapid exothermic preequilibria.[4,5,16] More importantly, the rapid reversible association process serves as an "entropy trap". Thus considerable rate enhancements result from the increase in the effective concentration or activity of the incoming ligand at the reaction center. On the other hand, inductive effects that would increase the cobalt-nitrogen bond strength in the outer-sphere complex are probably weak as ν(CN) is impervious to this hydrogen-bonding interaction.[17]

The process for dissociation of H_2O from the ethyl- and methyl(aquo)cobaloxime complexes followed by substitution with benzimidazole[18] or $M(CN)_6^{3-}$ (M = Co, Fe, or Cr)[19] has also been interpreted in terms of a preequilibrium between the aquocobaloxime complex and the incoming ligand. Indeed Espenson and Russell[19] pointed out that a possible mode for this interaction involves hydrogen bonding between the coordinated water molecule and the nitrogen of a cyanide ligand. In addition, Guschl and Brown's[20] interesting result that the observed rate of 86.5 s^{-1} at −2° for the exchange of coordinated CH_3OH in a 1:1 solvent mixture of $CH_2Cl_2/C_6H_5NO_2$ was unexpectedly fast, compared with Costa and co-workers' [18] rate of 6.9 s^{-1} at 25° for H_2O substitution with benzimidazole in aqueous solution, can readily be understood in terms of the proposed outer-sphere hydrogen-bonded complexes. In the aqueous solution, competition by the strongly hydrogen-bonding water molecules result in no net reaction, whereas in the mixed organic solvents, displacement of the methanol will be assisted by the nitrobenzene solvent as outlined in eq 14–

18.[21-23] Nitrobenzene has been found to have a similar catalytic effect in substitution reactions of group 6b metal carbonyl amine derivatives.[5,6]

In ligand exchange reactions where coordinated water in aquocobalamin is displaced by other ligands, the kinetic data are consistent with a transition state in which both entering and leaving groups are loosely bound (I_d process).[24-29] If we extrapolate from the more inert model systems,[30] to aquocobalamins obeying the same rate law, it is logical to assume that the incoming ligand will compete with the solvent for the acidic protons of axially coordinated water in aquocobalamin.[31-33]

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Photochemistry of Alkyl Halides. 3. Generation of Vinyl Cations[1]

Sir:

Recent reports from these laboratories have shown that irradiation of alkyl bromides and, particularly, iodides in solution is a convenient, powerful method for the generation of carbocations.[1,2] The available data support a process involving initial homolytic cleavage of the carbon–halogen bond followed by electron transfer within the resulting radical pair to generate an ion pair.[1] We wish now to report that irradiation of vinyl iodides is a particularly facile route to the corresponding vinyl cations.

$$\begin{tikzcd}
R\text{—}I \arrow[r, "h\nu"] & {[R^{\cdot}\ I^{\cdot}]} \arrow[r, "\text{electron}", "\text{transfer}"'] \arrow[d] & {[R^+\ I^-]} \arrow[d] \\
 & \text{radical products} & \text{ionic products}
\end{tikzcd}$$

Thus irradiation of 1-iodocyclohexene (**1a**) in methanol or methylene chloride solution at 40° in the presence of zinc as an iodine scavenger afforded principally the nucleophilic substitution product **2** or **5**, respectively, in 65% yield, each accompanied by minor amounts (19–27%) of the radical-derived reduction product cyclohexene.[3,4] In ethylene glycol the ketal **6** was obtained (77% yield), presumably via cyclization of the initially formed enol ether **4**. When the irradiation of **1a** in methanol was conducted in the absence of zinc, the ketal **3** was obtained as the principal product (70%), apparently via acid-catalyzed addition of methanol to the enol ether **2.** Similar behavior was exhibited by the bromide **1b,** which afforded ketal **3** (26%) and cyclohexene (62%); as noted previously in saturated alkyl systems,[1,2] bromides display less ionic behavior than the corresponding iodides. Reducing the temperature resulted in a significant increase in the amount of ionic product formed from **1a.** Thus at −20° the yields of ketal **3** and chloride **5** rose to 87 and 76%, respectively.[5]

From these results it is clear that irradiation of **1a** or **b** results in formation of the 1-cyclohexenyl cation—in contrast to previous reports on the photochemical behavior of vinyl iodides,[6] in which it is concluded that only radical behavior is displayed. The results are of even more interest in that cyclic vinyl cations are difficult to form via the usual solvolytic methods because of the preferred linear geometry of vinyl cations.[7] Attempts to extend the photochemical method to generation of the even more highly strained 1-cyclopentenyl cation were initially unsuccessful. Irradiation of 1-iodocyclo-