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Reactions of Bis(dimethylglyoximato)cobalt(II) Complexes with Polyhalomethanes

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The stoichiometry and kinetics of the reactions of $\mathrm{Co(dmgH)_2L}$ and polyhalomethanes (RX) are reported. In both acetone and benzene the data are in accord with a two-step mechanism, the first and rate-limiting step being halogen atom abstraction by the cobalt complex and formation of a free radical. The existence and reactivity of the latter intermediate for the case $\mathrm{R\cdot = \cdot CCl_3}$ were examined by use of 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (4-HTMPO) in a kinetic competition mode. Numerical integration techniques (Gear's method) were used to simulate kinetic data with various choices of competitive rate constants, permitting an estimate of the relative rate constants for reaction of $\mathrm{\cdot CCl_3}$ with 4-HTMPO (k_6) vs. its reaction with $\mathrm{Co(dmgH)_2py}$ in benzene (k_2) as $k_6/k_2 = 1.8 \pm 0.1$ (25 °C).

Introduction

The general mechanism by which various cobalt(II) cobaloxime[1] complexes, $\mathrm{Co(dmgH)_2L}$ with L = pyridine, triphenylphosphine, etc., react with organic halides in solution is believed to be that given by the reactions in eq 1 and 2.[2,3] The net result is the overall process of eq 3 characterized by a 2:1 ratio of reactants and by the production of equimolar amounts of halocobalt(III) and organocobalt(III). A similar mechanism operates for other cobalt(II) and chromium(II) complexes.[4-8]

$$\mathrm{Co(dmgH)_2L + RX \xrightarrow{k_1} XCo(dmgH)_2L + R\cdot} \qquad (1)$$

$$\mathrm{Co(dmgH)_2L + R\cdot \xrightarrow{k_2} RCo(dmgH)_2L} \qquad (2)$$

$$\mathrm{2Co(dmgH)_2L + RX = XCo(dmgH)_2L + RCo(dmgH)_2L} \qquad (3)$$

An investigation of the previously unstudied reactions of $\mathrm{Co(dmgH)_2L}$ with polyhalomethanes was undertaken with several objectives in mind. This particular reaction has been implicated[9] as one of the two key steps in the catalytic chain reactions of RX with benzylcobaloximes, making it desirable to quantitate the kinetics of eq 3. It was also our intention to learn whether the values of k_1 correlate with a fundamental property of RX such as the carbon–halogen dissociation energy. Finally, the mechanism shown and the intervention of a free radical intermediate need to be demonstrated for polyhalomethanes. We thus sought to examine the effects of radical scavengers on the stoichiometry and kinetics, along with mathematical modeling of the effects expected when the two reactions of the free radical occur to comparable extents.

Results

Stoichiometry and Products. Only a few stoichiometric determinations were done for polyhalomethanes since previous work[2] had established the overall stoichiometry to be 2:1 Co(II)/RX, as expected from eq 3. The same results were found from spectrophotometric titrations of $\mathrm{Co(dmgH)_2L}$ with $\mathrm{BrCCl_3}$ in benzene (L = py, average ratio, Co(II)/RX = 2.06 ± 0.13, Figure 1A) and in acetone ($\mathrm{L = PPh_3}$, average ratio = 2.14 ± 0.10). The products in this case were not readily separated in pure form by using the usual chromatographic techniques successful for other mixtures of halocobaloximes and alkylcobaloximes. Both $\mathrm{BrCo(dmgH)_2L}$ and $\mathrm{Cl_3CCo(dmgH)_2L}$ were detected in roughly comparable quantities as expected from eq 1–3 by ^{1}H NMR spectrum of reactions run in various solvents (methane, acetone, benzene, tetrahydrofuran, methylene chloride, toluene, and ethanol). Singlets at δ 2.35 for $\mathrm{Cl_3CCo(dmgH)_2L}$ and at δ 2.25 for bromocobaloxime (relative to $\mathrm{Me_4Si}$) were observed. The latter is assigned in comparison with the known complexes. On exposure to aqueous base the peak at δ 2.35 is lost and that at δ 2.25 grows, consistent with the reported reaction of (trihaloalkyl)cobaloximes with alkali.[10] Reaction with bromoform in benzene, however, gave products which were readily purified and isolated as detailed in the Experimental Section.

Kinetics. Pseudo-first-order rate constants were determined in the presence of a large excess of organic halide and represent a quantity defined as

$$k_{\mathrm{obsd}} = -\mathrm{d} \ln [\mathrm{Co(dmgH)_2L}]/\mathrm{d}t \qquad (4)$$

Plots of k_{obsd} vs. [RX] are linear and pass through the

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(1) Cobaloxime is the trivial name for bis(dimethylglyoximato)cobalt complexes, $\mathrm{Co(dmgH)_2}$, in which $\mathrm{dmgH^-}$ represents the monoanion of dimethylglyoxime (2,3-butanedione dioxime): Schrauzer, G. N. *Acc. Chem. Res.* **1968**, *1*, 97.

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Table I. Values of the Second-Order Rate Constants k_1 for the Reaction of $\mathrm{Co(dmgH)_2L}$ with Polyhalomethanes

	$k_1/\mathrm{M^{-1}\ s^{-1}}$ (T/°C)			
	$\mathrm{Co(dmgH)_2py}$		$\mathrm{Co(dmgH)_2PPh_3}$	
RX	acetone	benzene	acetone	benzene
$\mathrm{CCl_4}$		0.199 (10.88)	0.161 (15.74)	0.0835 (19.67)
	1.90 (25.00)	0.558 (25.01)	0.304 (25.01)	0.106 (24.91)
		1.18 (34.77)	0.571 (34.61)	0.212 (34.44)
			[3.53 (25.00)][b]	[1.06 (25.00)][b]
$\mathrm{CHBr_3}$		0.274 (14.49)		
	1.12 (25.00)	0.515 (25.00)	0.231 (25.00)	0.0755 (25.00)
		0.814 (34.78)		
$\mathrm{BrCCl_3}$		614 (14.89)		
		938 (25.35)		
		1280 (34.56)		
$\mathrm{CBr_4}$		1900 (5.91)		
		2580 (14.21)		
		4580 (25.02)		

[a] Details of the kinetic results are given elsewhere.[11] [b] L = 4-methylpyridine.

Table II. Activation Parameters for the Reaction of $\mathrm{Co(dmgH)_2L}$ with Polyhalomethanes

RX	L	solvent	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}
$\mathrm{CCl_4}$	$\mathrm{PPh_3}$	acetone	11.26 ± 0.10	−23.13 ± 0.33
$\mathrm{CCl_4}$	$\mathrm{PPh_3}$	benzene	10.42 ± 0.90	−27.6 ± 3.0
$\mathrm{CCl_4}$	$\mathrm{C_5H_5N}$	benzene	12.01 ± 0.25	−19.33 ± 0.85
$\mathrm{CHBr_3}$	$\mathrm{C_5H_5N}$	benzene	8.87 ± 0.49	−30.16 ± 1.63
$\mathrm{BrCCl_3}$	$\mathrm{C_5H_5N}$	benzene	5.94 ± 0.23	−25.06 ± 0.76
$\mathrm{CBr_4}$	$\mathrm{C_5H_5N}$	benzene	6.97 ± 0.88	−18.5 ± 3.0

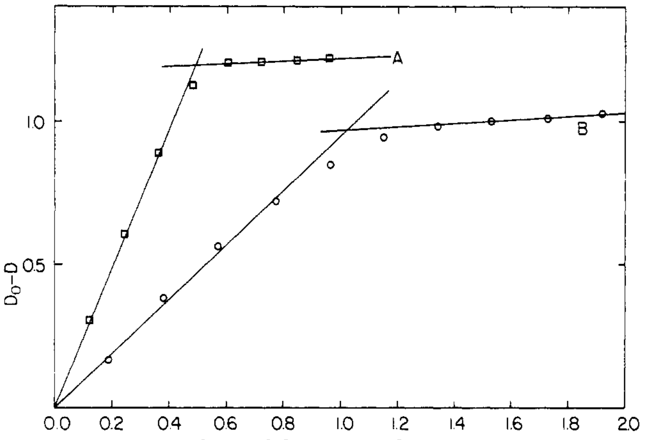


Figure 1. Illustrating the results of spectrophotometric titrations of $\mathrm{Co(dmgH)_2py}$ by $\mathrm{BrCCl_3}$: A, no added radical scavenger; B, in the presence of excess 4-HTMPO.

origin as illustrated in the typical set of experiments shown in Figure 2. The net rate of reaction according to eq 1–3, assuming the first step is rate limiting, is

$$\frac{-d[\mathrm{Co(dmgH)_2L}]}{dt} = \frac{-2d[\mathrm{RX}]}{dt} = 2k_1[\mathrm{Co(dmgH)_2L}][\mathrm{RX}] \qquad (5)$$

Values of k_1 are calculated as $k_{\mathrm{obsd}}/2[\mathrm{RX}]_{\mathrm{av}}$. Table I summarizes the rate constants for $\mathrm{CCl_4}$, $\mathrm{BrCCl_3}$, $\mathrm{CBr_4}$, and $\mathrm{CHBr_3}$ in acetone and benzene. Many reactions were examined at different temperatures, yielding the activation parameters given in Table II. Kinetic determinations were carried out only in these solvents. The Co(II) complexes are quite stable in them, whereas slow decomposition was noted in methanol and ethanol. Evidently the solvents $\mathrm{CH_2Cl_2}$ and $\mathrm{CHCl_3}$ themselves undergo reaction with the Co(II) complexes, albeit very slowly, rendering them also unsuitable for precise work.

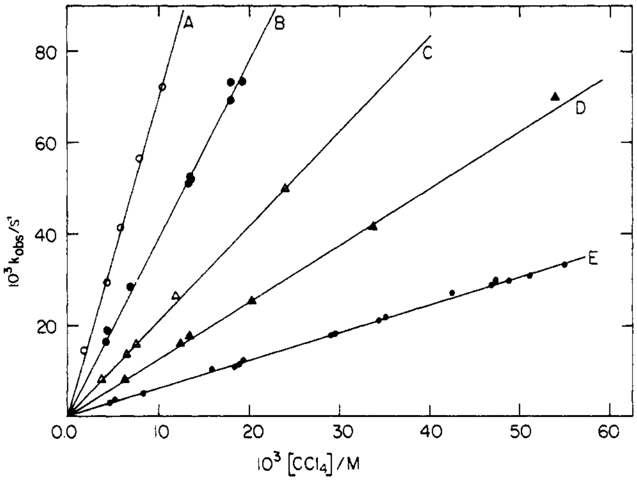
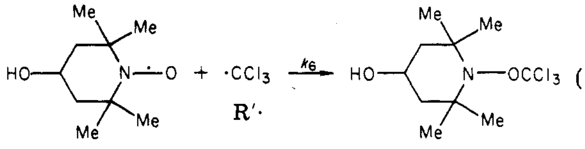


Figure 2. Plots of the pseudo-first-order rate constants at 25.0 °C vs. [$\mathrm{CCl_4}$] for its reaction with $\mathrm{Co(dmgH)_2L}$ in acetone (A, B, E) and benzene (C, D) for L = 4-picoline (A, C), pyridine (B, D), and triphenylphosphine (E).

Reactions in the Presence of Radical Scavengers. The substance which most successfully competes with $\mathrm{Co(dmgH)_2L}$ under conditions compatible with the other reagents is 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (4-HTMPO). It reacts with organic radicals such as $\cdot\mathrm{CCl_3}$ (eq 6)[12] but not with the Co(II) complex.



(6)

4-HTMPO ($\mathrm{R_2NO\cdot}$) $\mathrm{R_2NOR'}$

Titrations of benzene solutions of $\mathrm{BrCCl_3}$ with $\mathrm{Co(dmgH)_2py}$ in the presence of a substantial excess of 4-HTMPO were markedly different than in its absence, although blank experiments showed that either reactant separately was unaffected. The end point occurred at $\mathrm{BrCCl_3/Co(II)}$ ratios of 1.02, 1.00, and 1.00 (average 1.01 ± 0.01), as illustrated in Figure 1B. These results correspond to the overall stoichiometry expected if reactions 1 and 6 occur in sequence:

$$\mathrm{Co(dmgH)_2L + R'X + R_2NO\cdot = XCo(dmgH)_2L + R_2NOR'} \qquad (7)$$

Kinetic determinations with a large excess of 4-HTMPO resulted in a value of $k_{\mathrm{obsd}}[\mathrm{BrCCl_3}]$ which was lower than

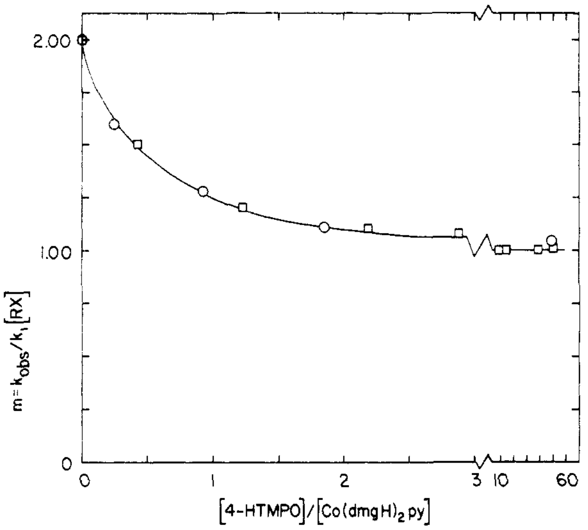


Figure 3. Competitive reactivity of 4-HTMPO and $Co(dmgH)_2py$ toward $\cdot CCl_3$, generated from $BrCCl_3$ (○) and from CCl_4 (□) as illustrated by the variation of m (eq 11) with the ratio of initial concentrations. The solid line shows the same quantity using kinetic data simulated by forward integration techniques for the ratio $k_6/k_2 = 1.8$.

in its absence by a factor of 2.0. For example, the reaction between $Co(dmgH)_2py$ and $BrCCl_3$ in benzene has $k_{obsd}/[BrCCl_3] = (1.88 \pm 0.06) \times 10^3\ M^{-1}\ s^{-1}$ at 25.35 °C without 4-HTMPO and $(9.13 \pm 0.09) \times 10^2\ M^{-1}\ s^{-1}$ at 25.0 °C with $(5-6) \times 10^{-3}$ M 4-HTMPO present, a ratio of 2.05 ± 0.09. These results are exactly consistent with what has gone before. In the former case $k_1 = k_{obsd}/2[BrCCl_3] = (9.38 \pm 0.03) \times 10^2\ M^{-1}\ s^{-1}$ (25.35 °C), and in the latter $k_1 = k_{obsd}/[BrCCl_3] = (9.13 \pm 0.09) \times 10^2\ M^{-1}\ s^{-1}$ (25.0 °C). The values of k_1 agree within acceptable limits, and with 4-HTMPO added in large excess the rate law is

$$\frac{-d[Co(dmgH)_2L]}{dt} = \frac{-d[RX]}{dt} = k_1[Co(dmgH)_2L][RX] \tag{8}$$

The situation at intermediate concentrations of 4-HTMPO is more complex, because of the competition between the reactions of eq 2 and eq 6. When the steady-state approximation is made for $[R\cdot]$, the rate of reaction by eq 1, 2, and 6 becomes

$$\frac{-d[Co(dmgH)_2L]}{dt} = k_1\left(\frac{2+\alpha}{1+\alpha}\right)[Co(dmgH)_2L][RX] \tag{9}$$

where α is given by

$$\alpha = k_6[4\text{-HTMPO}]/k_2[Co(dmgH)_2L] \tag{10}$$

At the two extreme concentrations of 4-HTMPO, these relations reduce to the correct limiting forms, eq 5 and 8. In the intermediate region, however, a more complicated analysis must be made. Consider a quantity m ($1 \leq m \leq 2$) calculated from k_{obsd} and the independently known value of k_1 according to the definition

$$m = \frac{k_{obsd}}{k_1[RX]} = \frac{2+\alpha}{1+\alpha} \tag{11}$$

Different compounds leading to the same free radical (e.g., $BrCCl_3$ and CCl_4) will have the same value of m at a given value of α since k_2 and k_6 are independent of the variation of X.

Figure 3 depicts the variation of m with the initial concentration ratio, [4-HTMPO]/[RX]. The shape of the curve is consistent with eq 11. The observation that conventional kinetic data for the slowly reacting CCl_4 ($k_1 = 0.56\ M^{-1}\ s^{-1}$) and flash photolytic data for the rapidly reacting $BrCCl_3$ ($k_1 = 9.4 \times 10^2\ M^{-1}\ s^{-1}$) lie on the same curve establishes the expected congruence for the case $R\cdot = \cdot CCl_3$.

Mathematical Stimulations. The previously given treatment of the kinetic data in the presence of a free radical scavenger is imprecise on two counts. First, the values of α and m (eq 10 and 11) were taken to be constant in any kinetic run. In fact, both should vary during the course of a kinetic run since the scavenger and the Co(II) complex are consumed at different rates. One of the consequences is that the reaction should not follow pseudo-first-order kinetics since the factor $(2 + \alpha)/(1 + \alpha)$ of eq 9 varies with time. Second, a description of m as a function of the initial concentration ratio [4-HTMPO]/[Co(II)] can be only approximate since the ratio changes during the course of each experiment.

To examine how these effects should be manifest and how seriously they need to be accounted for, the kinetic situation represented by eq 1, 2, and 6 was examined mathematically. The differential rate equations are

$$-d[Co(II)]/dt = k_1[Co(II)][RX] + k_2[Co(II)][R\cdot]$$

$$d[RCo^{III}]/dt = k_2[Co(II)][R\cdot]$$

$$d[XCo^{III}]/dt = k_1[Co(II)][RX]$$

$$d[R\cdot]/dt = k_1[Co(II)][RX] - k_2[Co(II)][R\cdot] - k_6[R_2NO\cdot][R\cdot]$$

$$d[R_2NOR]/dt = k_6[R_2NO\cdot][R\cdot]$$

Numerical integration techniques were applied to their solution. The Runge–Kutta method proved highly inefficient, however, since k_2 and k_6 are so much larger than k_1 that minute time increments were necessary making the computer calculations too lengthy and expensive. This case is referred to as involving "stiff" equations and is a situation to which Gear's predictor–corrector method[13] for numerical integration is well suited. Initial values of all reactant concentrations were chosen for each calculation corresponding to the different experimental conditions used, and values were set for the rate constants k_1 at its experimentally determined value ($0.558\ M^{-1}\ s^{-1}$ for CCl_4 in benzene at 25.0 °C) and k_2 and k_6 at large values (10^7–$10^9\ M^{-1}\ s^{-1}$). The latter choices, provided the values themselves are much greater than k_1, are important only relative to one another. The computer program[13b] used generated all concentrations at frequent time intervals and a simulated absorbance reading calculated by using the known molar absorptivities of every species. The results of numerous calculations are summarized as follows. (1) The concentration of the free radical intermediate $\cdot CCl_3$ does, in fact, remain at very low steady-state values throughout, $\sim 10^{-4}\%$ of [Co(II)]. (2) Without any 4-HTMPO or when a large excess is added, the simulated data follow a precise pseudo-first-order equation. Consistent with the chemical and rate equations and with our experimental findings, the values of k_{obsd} at a given $[CCl_4]$ differ by a factor of precisely 2.00 at these extremes. (3) At lower concentrations of 4-HTMPO the simulated data are not precisely pseudo first order, having values of k_{obsd} which decrease somewhat as the run progresses. The extent of curvature in the pseudo-first-order plots of such "data" is not large, however, and in experimental situations

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[13] (a) Gear, C. W. "Numerical Initial Value Problems in Ordinary Differential Equations"; Prentice-Hall: Englewood Cliffs, NJ, 1971. (b) Hindmarsh, A. C. "GEAR: Ordinary Differential Equation System Solver"; Lawrence Livermore Laboratory, Report UCID-30001(3), 1974.

would probably be compensated for by a relatively small adjustment of the final absorbance reading D_∞ in the pseudo-first-order kinetic equation, $\ln [(D_t - D_\infty)/(D_0 - D_\infty)] = -k_{obsd}t$. (4) Each simulation, after the adjustment of D_∞ to force a first-order fit, yields a value of k_{obsd} and (by eq 11) of m. The variation of m with the initial concentration ratio for the simulated data was compared to that found experimentally, as depicted in Figure 3. The best agreement occurred at the ratio $k_6/k_2 = 1.8 \pm 0.1$.

Interpretation and Discussion

Much work has gone before to establish the generality of the mechanism represented by eq 1 and 2 in the case of other halogenated compounds RX. The present results appear completely consistent with this formulation as well. The stoichiometry and products are in accord with eq 3, and the rate law establishes the bimolecularity of the rate-limiting step.

The question can be raised whether the reaction starts with halogen atom abstraction and formation of a carbon-centered free radical (as in eq 1) or with transfer of R and formation of a halogen atom X. The trapping experiments, including the change in stoichiometry and reaction rates, are clearly indicative of the former mechanism which also has been supported in earlier work.[2,4,5] The minor decrease in rate accompanying a large increase in solvent polarity from benzene to acetone is further proof of the nonionic character of the transition state, again consistent with eq 1 being the rate-limiting reaction.

The rate of reaction between a given halide RX and the compound $Co(dmgH)_2L$ depends upon the identity of the axial base L, increasing in the order PPh_3 < pyridine < 4-methylpyridine. Ligand basicity increases in the same order, at least as measured by the pK_a values, which are 2.7, 5.3 and 6.1, respectively.[14,15] The trend in reactivity is consistent with a transition state for eq 1 in which electron transfer from Co(II) is enhanced by electron donation from L onto the metal. The increases in rate along this series are not large—about a factor of 10 between the extreme members—and are comparable to the changes noted earlier[2] for analogous reactions of $PhCH_2Br$ with $Co(dmgH)_2L$.

Variation of the organic halide gives rise to pronounced differences in the rate constant k_1 and the associated value of $\Delta H^\ddagger$. For purposes of comparison, the rate constants must be statistically corrected for the number of equivalent reactive C–X bonds. On that basis the reactivity order (and k_1^{corr} values for reactions of $Co(dmgH)_2py$ in benzene) are CCl_4 ($0.14\ M^{-1}\ s^{-1}$) < $CHBr_3$ (0.17) ≪ $BrCCl_3$ (938) < CBr_4 (1145). The trend noted here is consistent with previous work[2,4,7b,c,16] on another point. Carbon–chlorine bond cleavage occurs more slowly than carbon–bromine cleavage in comparable compounds. The large difference between $CHBr_3$ and the two more reactive bromides appears to lie in the differences in carbon–bromine bond strength.

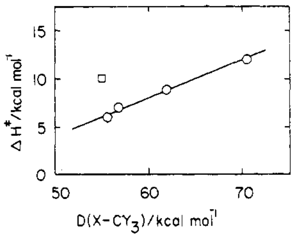

Figure 4. The enthalpy of activation associated with halogen atom abstraction reaction of eq 1 is linearly correlated with the bond dissociation enthalpy for the given polyhalomethane (○). The correlation does not extend to benzyl bromide, however (□).

One approach to examining variations such as these in a homologous series is to consider the variation of $\Delta H^\ddagger$ with the bond dissociation enthalpy of the reactive carbon-halogen bond. The latter values are well established.[17] As depicted in Figure 4, the two quantities show a good linear correlation. The point cannot be taken too far, however; if systems outside the group of polyhalomethanes are considered (e.g., $PhCH_2Br$), the correlation is lost. Presumably in such cases, the stability differences among the different carbon-centered free radicals being formed at the transition state now play a deciding role in influencing the activation and bond enthalpies.

The values of $\Delta S^\ddagger$ are quite negative, −19 to −30 cal mol^{-1} K^{-1} (Table II), as were values of $\Delta S^\ddagger$ reported previously[2b] for the analogous reaction of benzyl bromide with $Co(dmgH)_2PPh_3$ (−32 cal mol^{-1} K^{-1}) and $Co(dmgH_2)py$ (−29 cal mol^{-1} K^{-1}). These values are not explained by solvation effects, since reactants and products are uncharged and since the results were obtained in the relatively nonpolar solvents acetone and benzene. Instead, we suggest that the values of $\Delta S^\ddagger$ imply a highly ordered transition state. Of many possible collision complexes formed during encounter of $Co(dmgH)_2L$ and RX in the solvent cage, only a small proportion would be likely to occur with an orientation suitable for halogen atom transfer. In addition, the participants in a gas-phase association reaction experience a large loss of translational entropy in their combination.

The effect of 4-HTMPO on the stoichiometry and kinetics is accurately modeled as arising from the reactions of eq 2 and 6 and afford an estimate of the ratio $k_6/k_2 = 1.8$. The absolute value of each of these rate constants is not known, although an estimate $k_6 = 1.5 \times 10^8\ M^{-1}\ s^{-1}$ is based on the value[12] for addition of c-C_5H_9 and other carbon-centered radicals to 4-HTMPO can be made. On the basis of this estimate, $k_2 \approx 8 \times 10^7\ M^{-1}\ s^{-1}$. The latter can be compared to the rate constants for the capture of other aliphatic radicals by cobalt(II) complexes in Co–C bond-forming reactions: $R\cdot + Co(Me_6[14]4,11\text{-diene-}N_4)(OH_2)_2^{2+}$, $(1\text{–}7) \times 10^8\ M^{-1}\ s^{-1}$ ($R\cdot = CH_3$),[18] 8×10^7 ($R\cdot = \cdot CH_2CHO$),[19] 7×10^7 ($R\cdot = \cdot CH_2OH$),[19] 3×10^7 ($R\cdot = \cdot CH(CH_3)OH$),[19] 4×10^7 ($R\cdot = \cdot CH(CH_2NH_3^+)OH$),[19] and $\sim 1 \times 10^7$ ($R\cdot = \cdot CHOHCH_2OH$).[19] On the basis of these comparisons, we believe the estimates of k_2 and k_6 are at least roughly correct.

The lack of effect on k_{obsd} of 1-octene (to 135-fold excess using $Co(dmgH)_2PPh_3$ in benzene) is probably due to its inability to compete with $Co(dmgH)_2PPh_3$ for reaction with $\cdot CCl_3$. Considering the level of experimental uncertainty, we place a limit $\leq 6 \times 10^4\ M^{-1}\ s^{-1}$ on the second-order rate constant for addition of $\cdot CCl_3$ to the olefin. No values have been reported for this rate constant, but values in the range $(5\text{–}30) \times 10^3\ M^{-1}\ s^{-1}$ are found for $\cdot CH_3$ + olefins,[20] suggesting that the lack of kinetic effect of 1-octene merely reflects its low reactivity with $\cdot CCl_3$ as

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compared to the rate of the reaction of eq 2.

Experimental Section

Materials. The solvents used for quantitative work were acetone and benzene. Experimental results (spectra, kinetics) were identical with the reagent grade solvents as compared to purified samples. Acetone was purified by distillation from the sodium iodide complex and benzene by distillation from P_2O_5 after being washed with sulfuric acid and then with H_2O or by fractional crystallization from ethanol.

The organic halides were dried over anhydrous calcium chloride and distilled from P_2O_5 (CCl_4 and $BrCCl_3$) or under vacuum from $CaCl_2$ ($CHBr_3$), except for CBr_4, which was recrystallized three times from absolute ethanol and dried under vacuum. The purified materials were stored in the dark under nitrogen or argon. 4-Hydroxy-2,2,6,6-tetramethylpiperidinyloxy (Aldrich) was recrystallized twice from acetone. 1-Octene was dried over magnesium sulfate and distilled onto anhydrous calcium chloride.

The cobalt(II) cobaloximes, $Co(dmgH)_2{\cdot}2L$, and the organocobaloximes, $RCo(dmgH)_2L$—with R = CH_3, $CHBr_2$, and $CH(CH_3)_2$ and with L = 4-methylpyridine, triphenylphosphine, or pyridine—were prepared by standard methods.[3,21,22] Elemental analyses, UV-visible spectra, and ^1H NMR spectra agreed excellently with calculated or known values. For the reasons cited by Halpern,[2a,b] the major Co(II) species in benzene and acetone solutions is the five-coordinate complex $Co(dmgH)_2L$. This is consistent with the very low formation constant of $Co(dmgH)_2py_2$ in methanol.[23] We have not made allowance for formation of $Co(dmgH)_2(solv)$, although it is important in methanol at similar concentrations,[23] in view of the higher stability constants in the poorly coordinating solvents used in this work. Consistent with these assumptions, kinetic experiments using cobalt(II) solutions prepared from either the solid cobalt(II) derivative $Co(dmgH)_2L_2$ or by photolysis of $RCo(dmgH)_2L$ gave the same rate constants.

Stoichiometry and Kinetics. Spectrophotometric titrations were done by injecting successive 5-μL volumes of a standard solution of organic halide into a solution containing a known volume and concentration of $Co(dmgH)_2L$ in the desired solvent. The latter solution was contained in a cylindrical quartz spectrophotometer cell. All solutions were made up under rigorously anaerobic conditions, and transfers were made so as to exclude air. The absorbance was recorded after each addition of halide, at the maximum for the Co(II) complex, λ 420 nm (ϵ 3.55×10^3 M^{-1} cm^{-1}) for $Co(dmgH)_2py$ in benzene or λ 460 nm (ϵ 2.67×10^3 M^{-1} cm^{-1}) for $Co(dmgH)_2PPh_3$ in acetone.

The kinetic determinations, also strictly anaerobic, were done by using conventional methods or flash photolytic methods, as required by the particular system. The progress of the reaction was monitored spectrophotometrically, usually by recording the absorbance at a single wavelength with time, occasionally by intermittent spectral scans from 600 to 400 nm. In the former situation the monitoring wavelength was λ_{max} of the particular Co(II) complex in the given solvent, λ 420–460 nm.

In addition to using the independently synthetized cobalt(II) complex for kinetics, some experiments were done by generating it in situ with use of visible flash photolytic decomposition of $(CH_3)_2CHCo(dmgH)_2L$ in benzene solutions also containing RX. This method employed a Xenon Corporation Model 710 flash photolysis unit operated at 250 J according to procedures described previously.[23] This was particularly useful for rapidly reacting halides, $BrCCl_3$ and CBr_4. In such cases the temperature was adjusted to the desired value prior to photolysis, but the accurate value was measured with a thermistor thermometer immediately after the reaction was complete.

All of the kinetic runs were conducted by using a large stoichiometric excess of organic halide over cobalt(II) complex. The data for each run followed a pseudo-first-order rate law, $-d[Co(II)]/dt = k_{obsd}[Co(II)]$. The rate constants were calculated by using standard graphical or computer-implemented least-squares techniques.

Product Separations. The organocobaloximes are easily separated from the inorganic (halo) cobaloximes except in the case of the trihaloalkyls. With bromoform, for example, the reaction of 2.46 g of $Co(dmgH)_2{\cdot}2py$ (5.6 mmol) with 23 g of $CHBr_3$ (91 mmol) in 50 mL of benzene yielded 2.5 g of mixed product after precipitation with hexane. Chromatography of portions of the latter in 4% ethanol–carbon tetrachloride on silica gel caused yellow $Br_2CHCo(dmgH)_2py$ to separate cleanly, followed by brown $BrCo(dmgH)_2py$ which was eluted with 1:1 ethanol/carbon tetrachloride. The solids obtained after evaporation each gave correct ^1H NMR spectra and elemental analyses. For $Br_2CHCo(dmgH)_2py$: ^1H NMR ($CDCl_3$) δ 2.2 (s, 12 H), 5.75 (s, 1 H). Anal. Calcd for $CoC_{14}H_{20}N_5O_4Br_2$: C, 31.08; H, 3.73; N, 12.94. Found: C, 30.79; H, 3.74; N, 12.64. For $BrCo(dmgH)_2py$: ^1H NMR ($CDCl_3$) δ 2.41 (s, 12 H). Anal. Calcd for $CoC_{13}H_{19}N_5O_4Br$: C, 34.84; H, 4.27; N, 15.63. Found: C, 35.34; H, 4.54; N, 15.58.

Computer Simulations. The numerical computations using Gear's method used a standard program.[13b] The computations were performed on an IBM 3600 computer.

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Registry No. Co(dmgH)(py), 36451-60-2; Co(dmgH)(PPh_3), 36451-59-9; CCl_4, 56-23-5; CBr_4, 558-13-4; $CBrCl_3$, 75-62-7; $CHBr_3$, 75-25-2.

Supplementary Material Available: Tabulations of kinetic data for individual experiments (12 pages). Ordering information is given on any current masthead page.

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