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# Concurrent and Competitive Homolysis and Elimination Reactions of ($\alpha$-Phenylethyl)aquocobaloxime[1,2]

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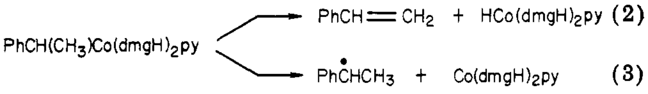
The kinetics of decomposition of $PhCH(CH_3)Co(dmgH)_2OH_2$ in aqueous methanol were studied in acidic solution and suggest parallel reactions of the parent complex ($k_{b,298} = 3.55 \times 10^{-3}$ s$^{-1}$, $\Delta H^\ddagger = 28.6 \pm 1.1$ kcal mol$^{-1}$, $\Delta S^\ddagger = 25.7 \pm 3.6$ cal mol$^{-1}$ K$^{-1}$) and its conjugate acid ($k_{a,298} = 1.48 \times 10^{-2}$ s$^{-1}$, $\Delta H^\ddagger = 23.2 \pm 0.2$ kcal mol$^{-1}$, $\Delta S^\ddagger = 11.1 \pm 0.7$ cal mol$^{-1}$ K$^{-1}$), the two reactants differing by the extent of protonation of the oxime oxygens and interrelated by an equilibrium constant $K_H = 8.1 \pm 0.4$ M$^{-1}$. The products consist of $Co^{2+}$, four "dimers" of $Ph\dot{C}HCH_3$ (including a quinoid from $\alpha$-to-para addition and 1,3-diphenylbutane as well as *meso*- and *rac*-2,3-diphenylbutanes) and styrene. The results suggest parallel homolytic (~72%) and $\beta$-elimination (~28%) pathways. The intermediacy of cobalt(II) cobaloxime was confirmed by experiments with added $H_2O_2$ and $Co(NH_3)_5Br^{2+}$. These reagents do not alter the rate constant but do produce mixtures of $Co^{2+}$ and $(H_2O)_2Co(dmgH)_2^+$ or $BrCo(dmgH)_2OH_2$, in ratios consistent with the rate constants determined independently for the Co(II) complex.

## Introduction

The study of the mechanisms by which organometallic compounds decompose has been a subject of much recent interest. Our attention was drawn to (1-phenylethyl)aquocobaloxime, $PhCH(CH_3)Co(dmgH)_2H_2O$, by results we had obtained[3] on the reactions of numerous organopentaaquochromium(III) cations which often react by homolytic cleavage of the chromium–carbon bond (eq 1).

$$(H_2O)_5CrR^{2+} \rightarrow Cr^{2+}(aq) + R\cdot \qquad (1)$$

Can the same mode of reaction be observed for other compounds such as the electronically saturated organocobaloximes? Alkylcobaloximes are, as a class, generally so stable toward thermal decomposition in solution, that the tendency of the $\alpha$-phenylethyl derivative to decompose is exceptional. Gaudemer et al. reported that the decomposition of ($\alpha$-phenylethyl)(pyridine)cobaloxime in methanol occurs by $\beta$-hydrogen elimination (eq 2) rather than



$$PhCH(CH_3)Co(dmgH)_2py \rightarrow PhCH{=}CH_2 + HCo(dmgH)_2py \qquad (2)$$

$$PhCH(CH_3)Co(dmgH)_2py \rightarrow Ph\dot{C}HCH_3 + Co(dmgH)_2py \qquad (3)$$

by homolysis (eq 3) on the basis of product analysis, deuterium labeling, and trapping of hydrido(pyridine)cobaloxime from eq 2 by its reaction with phenylacetylene.[4]

During the course of our work, Halpern, Ng, and Rempel[5] reported the results of kinetics and equilibrium determinations in toluene solution. They observed hydrogen and styrene were produced in an overall equilibrium reaction but suggested, on the other hand, a mechanism in which homolysis was the rate-limiting reaction. According to their proposal the products of the homolysis step undergo subsequent and rapid reactions to complete the sequence

$$Ph\dot{C}HCH_3 + Co(dmgH)_2py \xrightarrow{\text{fast}} PhCH{=}CH_2 + HCo(dmgH)_2py \qquad (4)$$

$$HCo(dmgH)_2py \xrightarrow{\text{fast}} Co(dmgH)_2py + {}^1/_2H_2 \qquad (5)$$

Our approach has been to do quantitative studies of the kinetics and products under several conditions, with particular emphasis on the detection and trapping of the likely reaction intermediates by suitable chemical reactions. We report here evidence that both of the pathways cited above do occur, but that conditions can readily be found wherein the course of the reaction can be directed largely along one pathway or the other.

## Experimental Section

**Materials.** ($\alpha$-Phenylethyl)(base)cobaloxime, with base = pyridine or water, was prepared under nitrogen in methanol from cobalt(II) acetate, dimethylglyoxime, styrene, and hydrogen by using published procedures.[6] The compound was recrystallized by dissolution in methylene chloride with reprecipitation by hexane. The crystalline, air-sensitive products were characterized by elemental analyses and $^1H$ NMR spectra which agreed with the published spectrum.[7] All experiments were conducted under rigorously deoxygenated solutions, using $Cr^{2+}$-scrubbed nitrogen, as rapid decay in the presence of $O_2$ was noted. The UV–visible spectrum in aqueous methanol shows absorption maxima at 464 nm ($\epsilon$ 850 M$^{-1}$ cm$^{-1}$) and 368 ($\epsilon$ $3.02 \times 10^3$).

Cobalt(II) cobaloxime was sometimes prepared and used as the solid material[8] $Co(dmgH)_2py_2$, which in neutral solution at the concentrations used is[9] $Co(dmgH)_2py$. More often, especially for experiments to determine its lifetime under various experimental conditions, $Co(dmgH)_2OH_2$ was produced directly in the quartz reaction cell in the desired reaction medium by visible light photodissociation[10] of $RCo(dmgH)_2OH_2$ for R = 2-propyl, $\alpha$-phenylethyl, and ethyl. The photolysis of the organocobaloxime was done by using a 100-J flash from fast extinguishing xenon flashlamps in the Xenon Corp. Model 710C flash photolysis system, using Pyrex filters to remove the UV radiation. Other

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(1) Based in part on the Ph.D. thesis of HBG, Iowa State University, 1981.

(2) Cobaloxime = $Co(dmgH)_2$, where $dmgH^-$ = monoanion of dimethylglyoxime (2,3-butanedione dioxime).

(3) (a) Kirker, G. W.; Bakač, A.; Espenson, J. H. *J. Am. Chem. Soc.*, in press. (b) Bakac, A.; Espenson, J. H. *Ibid.* **1981**, *103*, 2721. (c) Nohr, R. S.; Espenson, J. H. *Ibid.* **1975**, *97*, 3392. (d) Pohl, M. C.; Espenson, J. H. *Inorg. Chem.* **1980**, *19*, 235.

(4) Duong, K. N. V.; Ahond, A.; Merieene, C.; Gaudemer, A. *J. Organomet. Chem.* **1973**, *55*, 375. See also Nishinaga, A.; Nishizawa, K.; Nakayama, Y.; Matsuura, T. *Tetrahedron Lett.* **1977**, *1*, 85.

(5) Helpern, J.; Ng, F. J. J.; Rempel, G. J. *J. Am. Chem. Soc.* **1979**, *101*, 7124.

(6) Schrauzer, G. N.; Windgassen, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 143.

(7) Fontaine, C.; Duong, K. N. V.; Merienne, C.; Gaudemer, A.; Gianotti, C. *J. Organomet. Chem.* **1972**, *38*, 167.

(8) Schrauzer, G. N. *Inorg. Synth.* **1968**, *11*, 65.

(9) (a) Schneider, P. W.; Phelan, P. F.; Halpern, J. *J. Am. Chem. Soc.* **1969**, *91*, 71. (b) Rockenbauer, A.; Búdo-Záhonyi, E.; Simándi, L. I. *J. Coord. Chem.* **1972**, *2*, 53.

(10) Golding, B. T.; Kemp, T. J.; Sheena, H. H. *J. Chem. Res., Miniprint* **1981**, 334 and references therein.

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reagents were prepared by standard procedures or were purchased.

**Kinetics.** The kinetics of decomposition of ($\alpha$-phenylethyl)aquocobaloxime were determined in 40% aqueous methanol in solutions in which ionic strength was maintained at 1.00 M by lithium perchlorate. The progress of the reaction was monitored at the 368-nm absorption maximum of the reactant. The kinetic runs were conducted anaerobically in the presence of added perchloric acid and/or selected oxidizing agents, as described later.

Kinetic experiments to determine the rate of decomposition of cobalt(II) cobaloxime in acidic solution (eq 6) were conducted

$$Co(dmgH)_2H_2O + 2H^+ = 2H_2dmg + Co^{2+}(aq) \qquad (6)$$

at various [$H^+$]. The Co(II) complex was generated photolytically and its subsequent very fast decomposition recorded in the photolysis apparatus using a storage oscilloscope to record the transmittance change at 460 nm, an absorption maximum of $Co(dmgH)_2(H_2O)$ ($\epsilon$ $3.4 \times 10^3$ $M^{-1}$ $cm^{-1}$).

The kinetic data were analyzed by routine methods for pseudo-first-order kinetics, which all runs followed exactly.

**Products and Analyses.** The concentration of $Co^{2+}$ produced when the reaction was run under various conditions was determined spectrophotometrically as $Co(NCS)_4^{2-}$ in 50% acetone ($\epsilon_{623}$ = 1842 $M^{-1}$ $cm^{-1}$).[11] The same method was used to determine the total cobalt content of samples containing a mixture of species which were converted to $Co^{2+}$ by heating with a few milliliters of 70% perchloric acid almost to dryness after first vaporizing any organic material present. The concentration of $(H_2O)_2Co(dmgH)_2^+$, also produced from ($\alpha$-phenylethyl)cobaloxime under some conditions, was taken as the difference between the total cobalt and the concentration of $Co^{2+}$ directly determined. Under other conditions, some of the organocobaloxime was converted to $BrCo(dmgH)_2H_2O$. This yellow complex was washed through a column of SP Sephadex C-25 cation-exchange resin in the $H^+$ form, which retained $Co^{2+}$, $(H_2O)_2Co(dmgH)_2^+$, and excess $Co(NH_3)_5Br^{2+}$. It was identified by its characteristic UV spectrum, 250 nm ($\epsilon$ ~$2 \times 10^4$ $M^{-1}$ $cm^{-1}$) and 228 (~$2 \times 10^4$), and was determined[11] as $Co(NCS)_4^{2-}$ after conversion to $Co^{2+}$ by fuming with perchloric acid.

The organic products were analyzed by GC and GC–MS. After completion of the reaction, any free dimethylglyoxime was removed by filtration, and the organic products were extracted into methylene chloride. Those products which are dimers of the $Ph\dot{C}HCH_3$ radical were separated by using a Tracor 550 GC equipped with an OV-1-packed column with a FID at 150 °C using bibenzyl as an internal standard for quantitative analysis. Exact mass values of these products were obtained on the residue from evaporation of the original methylene chloride extract. Styrene was detected similarly by using a FFAP-packed column with a FID at 65 °C; its concentration was determined by the method of standard additions.

## Results and Interpretation

**Kinetics in Acidic Solution.** Studies of the kinetics of decomposition of $PhCH(CH_3)Co(dmgH)_2L$ were conducted for L = $H_2O$, with a smaller number of runs carried out on solutions prepared from the crystalline complex having L = pyridine. The results agreed for the two, as expected, since the latter is rapidly and completely converted to the aquo complex in acid solution.[12] The decomposition of the complex with $[PhCH(CH_3)Co(dmgH)_2OH_2]_0 = 1 \times 10^{-5}$ M followed a pseudo-first-order rate law at each [$H^+$] studied. The values of $k_{obsd}$ (eq 7) were determined at 25.0 °C over the concentration range [$H^+$] = $1.38 \times 10^{-3}$ to 1.00 M at a constant ionic strength of 1.00 M and are summarized in Table I.

$$-d[PhCH(CH_3)Co(dmgH)_2OH_2]/dt = k_{obsd}[PhCH(CH_3)Co(dmgH)_2OH_2] \qquad (7)$$

Table I. Pseudo-First-Order Rate Constants for Decomposition of $PhCH(CH_3)Co(dmgH)_2OH_2$ in Acidic Solution[a]

| [$H^+$]/M | $10^3k_{obsd}$/ $s^{-1}$ | [$H^+$]/M | $10^3k_{obsd}$/ $s^{-1}$ |
|---|---|---|---|
| 0.00138 | 3.65 | 0.170 | 10.2 |
| 0.00550 | 4.13 | 0.180 | 10.1 |
| 0.0083 | 4.22 | 0.200 | 10.5 |
| 0.0200 | 5.01 | 0.240 | 10.8 |
| 0.0300 | 5.90 | 0.300 | 11.3 |
| 0.0500 | 6.89 | 0.400 | 11.7 |
| 0.0600 | 7.53 | 0.500 | 12.4 |
| 0.0700 | 8.06 | 0.600 | 12.8 |
| 0.0900 | 8.37 | 0.700 | 13.0 |
| 0.100 | 8.56 | 0.800 | 13.4 |
| 0.120 | 9.01 | 0.900 | 13.9 |
| 0.130 | 9.25 | 1.00 | 14.3 |
| 0.150 | 9.81 | | |

[a] Conditions: 25.0 °C; 40% aqueous methanol; ionic strength 1.00 M (maintained by lithium perchlorate); initial [$RCo(dmgH)_2OH_2$] ≈ $1 \times 10^{-5}$ M.

The value of $k_{obsd}$ increases with [$H^+$] in this range, but not linearly. On the basis of the behavior of numerous other organoaquocobaloximes which are stable in acidic solution,[13] it seems reasonable to propose that a rapidly established protonation equilibrium is responsible for a portion of the effect seen. In that equilibrium one O–H···O link of the $(dmgH)_2$ pseudomacrocycle is converted, by protonation, to two OH groups (i.e., to the chelate $(dmg_2H_3)$). The equilibrium can be written as

$$RCo(dmgH)_2OH_2 + H^+ \overset{K_H}{\rightleftharpoons} RCo(dmg_2H_3)OH_2^+ \qquad (8)$$

where $K_H$ symbolizes the equilibrium constant for the reaction as written. If it is further assumed that each of the cobaloximes undergoes a unimolecular decomposition reaction, then the expression for $k_{obsd}$ as a function of [$H^+$] is

$$k_{obsd} = \frac{k_b + k_aK_H[H^+]}{1 + K_H[H^+]} \qquad (9)$$

where $k_b$ symbolizes the rate constant for the original unprotonated species (the "basic" form) and $k_a$ that for the protonated or "acidic" species. The assumption is being made that any intermediates generated in such steps are rapidly converted to the ultimate products, in which case the kinetic equations will reflect only the first reaction of the sequence. Values of $k_{obsd}$ were fit to eq 9, as illustrated in Figure 1. The least-squares parameters are $k_a = (1.48 \pm 0.06) \times 10^{-2}$ $s^{-1}$, $k_b = (3.55 \pm 0.07) \times 10^{-3}$ $s^{-1}$, and $K_H = 8.13 \pm 0.38$ $M^{-1}$. The satisfactory agreement between observed and calculated values substantiates this hypothesis. The value of $K_H$ is slightly larger than found for similar protonations: $pK_H = 0.91$ compared to the usual range[13] 0–0.6. This difference, as pointed out to us by a reviewer, may arise from the change in the usual aqueous solution to 40% aqueous methanol used in the present study for reasons of solubility.

Determinations of $k_{obsd}$ as a function of temperature (15–40 °C), also as a function of [$H^+$] at each temperature, yield the rate constants in Table II. The fit of the data was realized by using a nonlinear least-squares program for the fitting of $k_{obsd}$ as a simultaneous function of [$H^+$]

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[11] (a) Parker, O. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1968**, *90*, 3868. (b) Kitson, R. E. *Anal. Chem.* **1950**, *22*, 664.

[12] Brown, K. L.; Lyles, D.; Pencovici, M.; Kallen, R. G. *J. Am. Chem. Soc.* **1975**, *97*, 7338.

[13] (a) Adin, A.; Espenson, J. H. *J. Chem. Soc. D* **1971**, 653. (b) Abley, P.; Dockal, E. R.; Halpern, J. *J. Am. Chem. Soc.* **1973**, *95*, 3166. (c) Crumbliss, A. L.; Bowman, J. T.; Gaus, P. L.; McPhail, A. T. *J. Chem. Soc., Chem. Commun.* **1973**, 415. (d) Espenson, J. H.; Chao, T.-H. *Inorg. Chem.* **1977**, *16*, 2553.

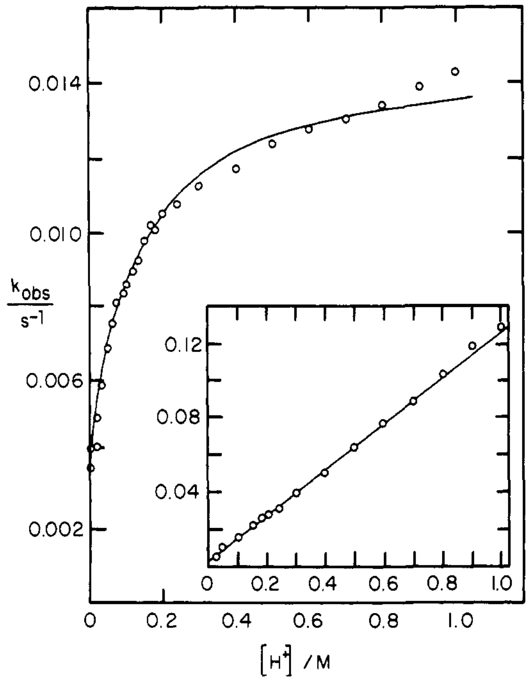

**Figure 1.** Illustrating the variation of the pseudo-first-order rate constant for decomposition of $PhCH(CH_3)Co(dmgH)_2OH_2$ (at 25.0 °C in 40% aqueous methanol at 1.00 M ionic strength with $[H^+]$). The solid line is that resulting from the least-squares fit according to eq 9. The inset shows $k_{obsd} \times (1 + K_H[H^+])$ vs. $[H^+]$ using $K_H = 8.33\ M^{-1}$.

Table II. Temperature Dependence of the Rate Constants[a] for the Decomposition of $PhCH(CH_3)Co(dmgH)_2OH_2$

| temp/°C | $10^3k_b/s^{-1}$ | $10^3k_a/s^{-1}$ |
|---|---|---|
| 15.0 | 0.75 ± 0.04 | 3.3 ± 0.3 |
| 25.0 | 3.55 ± 0.07 | 14.8 ± 0.6 |
| 35.0 | 14.67 ± 0.90 | 58.6 ± 5.2 |
| 40.0 | 31.06 ± 1.44 | 105 ± 9 |
| $\Delta H^‡$/kcal mol⁻¹ | 28.55 ± 1.1 | 23.23 ± 0.22 |
| $\Delta S^‡$/cal mol⁻¹ K⁻¹ | 25.65 ± 3.6 | 11.08 ± 0.70 |

[a] In 40% aqueous methanol at 1.00 M ionic strength. The value of $K_H$ is approximately invariant with temperature, the value obtained in the least-squares analysis is 8.1 ± 0.4 M⁻¹ (see also ref 14).

and T. The fit[14] gave $K_H = 8.1 \pm 0.4\ M^{-1}$ and the values of $\Delta H^‡$ and $\Delta S^‡$ given in Table II. The substantial values of $\Delta H^‡$ (23.2–28.6 kcal mol⁻¹) for both are similar to the value for the reaction in toluene[5] (21.2 ± 0.5 kcal mol⁻¹), but the values of $\Delta S^‡$ (11.1–25.7 cal mol⁻¹ K⁻¹) are much larger (1.4 ± 1.5 cal mol⁻¹ K⁻¹). It is subsequently noted that $k_a$ and $k_b$ are believed to represent the sum of two rate constants for concurrent elementary reactions; we return to this point later.

**Reactions with Oxidizing Agents.** The decomposition of $PhCH(CH_3)Co(dmgH)_2OH_2$ was also studied in the presence of $H_2O_2$ and $Co(NH_3)_5Br^{2+}$ in acidic solution. These reagents were chosen because they are known[15] to react with the products expected from homolysis and β elimination yet were thought likely to show no direct reaction with the organocobaloxime. That proved to be the case: the rate constant was independent of $[H_2O_2]$ and, in separate experiments, independent of $[Co(NH_3)_5Br^{2+}]$. The value of $k_{obsd}$ was the same within the experimental error at a given $[H^+]$ as when the oxidant was absent.

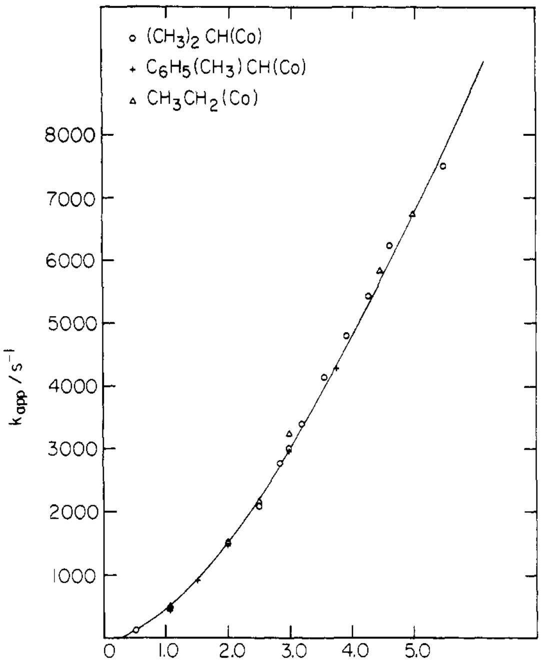

**Figure 2.** Illustrating the variation of the pseudo-first-order rate constant for the reaction of the Co(II) complex $Co(dmgH)_2OH_2$ with $H_3O^+$ as a function of hydrogen ion concentration. The same complex is produced in the photolytic decomposition of the 2-propyl (○), ethyl (△), and α-phenylethyl (+) complexes.

Yet it was shown, as reported in a later section, that different products were formed and systematically varying yields obtained. These findings substantiate our hypothesis, showing that the role of $H_2O_2$ or $Co(NH_3)_5Br^{2+}$ is to react with the intermediate(s) and not with the starting organocobaloxime.

**Kinetics of Decomposition of Cobalt(II) Cobaloxime.** The complex $Co(dmgH)_2OH_2$—or $Co(dmgH)_2(OH_2)_2$, the coordination number in solution is not known, although it is probably[9a] five—is rapidly converted to $Co^{2+}(aq)$ in acidic solution. Earlier studies[15b] were limited to determinations at lower $[H^+]$ owing to the upper limit of the stopped-flow method. In the present case we have extended the determinations to higher $[H^+]$, using flash photolysis to generate the cobalt(II) complex from any of three organocobaloximes. All three gave the same complex as judged by its absorption intensity and rate constants. Studies were carried out in the range $3.6 \times 10^{-4}$ to $5.35 \times 10^{-3}$ M $H^+$. The pseudo-first-order rate contant describing the decomposition of $Co(dmgH)_2$ in eq 6, $k_{app}{}^H$, increases sharply with $[H^+]$ as shown in Figure 2. Our interest is simply the value of $k_{app}{}^H$ at a particular $[H^+]$, rather than the algebraic expression of $k_{app}{}^H$ as a function of $[H^+]$ and the formulation of a mechanism for the reaction of eq 6. That is so because our purpose here is to consider by means of kinetic competition experiments and product ratios whether the Co(II) cobaloxime is an intermediate in the decomposition of $PhCH(CH_3)Co(dmgH)_2OH_2$. For that reason and also because the likely intervention of one or more protonation equilibria complicates a detailed understanding, we chose not to attempt a resolution other

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(14) A second approach was taken in which the values of the three parameters of eq 9 were adjusted in a separate least-squares calculation at each temperature and subsequently fit as a function of T. The values of $K_H$ so determined are 5.4, 8.3, 7.4, and 8.6 M⁻¹ at 15.0, 25.0, 35.0, and 45.0 °C, respectively. The rate constants and their activation parameters so calculated are within the experimental error of the values obtained by the method given in the text of the paper which was adopted as the preferable method since it better reflects the uncertainties in all of the parameters.

(15) (a) Heckman, R. A.; Espenson, J. H. *Inorg. Chem.* **1979**, *18*, 38. (b) Adin, A.; Espenson, J. H. *Ibid.* **1972**, *11*, 686.

Table III. Organic Products from Decomposition of $PhCH(CH_3)Co(dmgH)_2OH_2$ in Aqueous Methanol

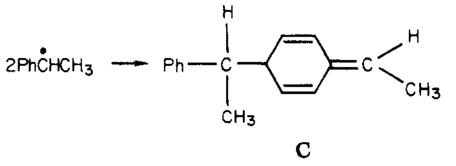
| $10^3[RCo]_0$/M | $[H^+]$/M | $10^5$[product]/M |  |  |  |  | % hom[a] | % elim[b] |
|---|---|---|---|---|---|---|---|---|
|  |  | A | B | C | D | styrene |  |  |
| 0.49 | 0.0050 | 8.6 | 7.8 | 1.9 | 3.9 | 7.1 | 71.1 | 28.9 |
| 1.54 | 1.00 | 32.2 | 22.2 | 5.8 | 11.4 | 22.7 | 72.6 | 27.4 |

[a] % homolysis = $2\{([A] + [B] + [C])/[RCo]_0\} \times 100$; [b] % elimination = $(2[D] + [styrene]/[RCo]_0) \times 100$. Percentages normalized to 100%.

than to note that an equation of the form $k_{app}{}^H = k_1[H^+] + k_2[H^+]^2$ does represent the results to fair accuracy.

**Products and Competition Experiments in Acidic Solutions.** Direct measurements in acidic solutions showed that $Co^{2+}$(aq) is formed quantitatively when the decomposition reaction of $PhCH(CH_3)Co(dmgH)_2OH_2$ is run in acidic solution in the absence of oxidizing agents.[16] Under the same conditions the organic products[17] consist of a mixture of dimers of the 1-phenylethyl radical (described below, total 86%) and of styrene (14%); no ethylbenzene was detected. The relative proportions of the two sets of products are invariant with $[H^+]$ in the range where the reaction proceeds nearly totally by one pathway or the other (15% by $k_a$ at $[H^+] = 5 \times 10^{-3}$ M, 97% at $[H^+] = 1.00$ M). The data cited mean that both species—$PhCH(CH_3)Co(dmgH)_2OH_2$ and $PhCH(CH_3)Co(dmg_2H_3)OH_2{}^+$—yield the same product ratios. The same results were found[18] for reactions of alkylcobaloximes with $Cr^{2+}$, where there is hardly any kinetic dependence on $[H^+]$ in the region where the protonation equilibrium is shifted. This reaction too involves transition states with substantial radical character, believed to proceed by the $S_H2$ mechanism. On the other hand the rates of electrophilic cleavage reactions, e.g. with $Hg^{2+}$ [13a] or $Tl^{3+}$ [13a,b] (which react by formal carbanion transfer), are strongly retarded by increasing $[H^+]$ since the protonated cobaloxime is completely unreactive. Both types of results are consistent with the very different inductive effects expected for the two groups of reactions.

Four different "dimers" of the α-phenylethyl radical (A–D) were separated and identified by the precise molecular mass (210.1409 ± 0.5 ppm) and where known (A and B) by comparison of the mass spectrometric fragmentation patterns[19] with those for the known materials. A and B are the expected *meso*- and *d,l*-2,3-diphenylbutanes. The di-α-phenylethyl quinoid structure was assigned to C (=ethylidene-4-(α-phenylethyl)cyclohexa-2,5-diene) and D is believed to be 1,3-diphenylbutane, again both on the basis of the mass spectrum (although now without comparison to knowns). The former product is believed to arise from α-to-para coupling of α-phenylethyl radicals (eq 10). Precedents for the formation of C (found

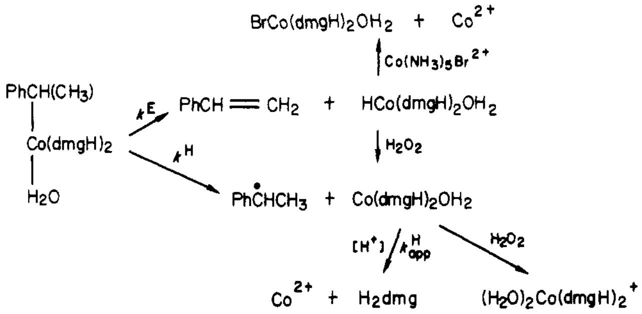


(10)

C

in ca. 7% yield and persisting in the solution for several days) are the analogous material formed (a) in ~2% yield from cumyl radicals[20] and (b) in high yield by dimerization of triphenylmethyl radicals.[21]

Scheme I



We suggest that D may arise from the reaction of $Ph\dot{C}HCH_3$ with (β-phenylethyl)cobaloxime. The latter may be produced in very small yield from styrene and hydridocobaloxime, products of the β-elimination pathway.

$$Ph\dot{C}HCH_3 + PhCH_2CH_2Co(dmgH)_2OH_2 \rightarrow \underset{D}{PhCH_2CH_2CH(CH_3)Ph} + Co(dmgH)_2OH_2$$

The dimers A, B, and C arise from coupling reactions of the α-phenylethyl radical. Their yields in sum represent the total amount of reaction proceeding by homolysis (~ 71–73%), whereas the yield of D and styrene (27–29%) affords a measure of the extent of β-elimination reaction occurring under the reaction conditions. The determinations referred to above are summarized in Table III.

On the basis of the kinetics and product determinations at 25 °C, the apparent rate constant $k_a$ and $k_b$ of eq 9 can be resolved into their respective components for homolysis and elimination. The values are $k_{a(H)} = 1.1 \times 10^{-2}$ s$^{-1}$, $k_{a(E)} = 4.1 \times 10^{-3}$ s$^{-1}$, $k_{b(H)} = 2.6 \times 10^{-3}$ s$^{-1}$, and $k_{b(E)} = 1.0 \times 10^{-3}$ s$^{-1}$.

Independently prepared α-phenylethyl radicals from the azo compounds[22] are known to produce A and B in roughly equal amounts, 88% in total. No C was detected in that study, and the remaining 12%, although not detected, was attributed to disproportionation products styrene and ethylbenzene. Our failure to detect ethylbenzene suggests that the styrene observed here is formed not from disproportionation of R but from a different process entirely, β elimination. Reduction of α-phenylethyl chloride and bromide by $Cr^{2+}$ leads to a rather different mixture of products,[23] 85–90% A and 10–15% B. This situation is not entirely comparable to ours, however, since it is probable that the (α-phenylethyl)chromium ion formed initially is responsible for products A and B by pathways other than free radical coupling reactions.

The inorganic products resulting from the decomposition of (α-phenylethyl)aquocobaloxime in the presence of $H^+$

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[16] In the absence of oxidant the balance of the $Co^{2+}$(aq) is formed via $Co(dmgH)_2OH_2$ from the slow[23] decomposition of the hydridocobaloxime (28%) formed in the elimination reaction $HCo(dmgH)_2OH_2 \rightarrow {}^1/_2H_2 + Co(dmgH)_2OH_2$.

[17] The yields are expressed as $(2[R_2]/[R(Co)]_0) \times 100\%$ and as $([styrene]/[R(Co)]_0) \times 100\%$ and sum to 105–108%. (The percentage cited are corrected to 100%.)

[18] Espenson, J. H.; Shveima, J. S. *J. Am. Chem. Soc.* 1973, *95*, 4568.

[19] The mass spectra are shown in the thesis cited.[1]

[20] Nelsen, S. F.; Barlett, P. D. *J. Am. Chem. Soc.* 1966, *88*, 137.

[21] Laukamp, H.; Nanta, W. Th.; MacLean, C. *Tetrahedron Lett.* 1968, 249.

[22] Greene, F. D.; Berwick, M.; Stowell, J. C. *J. Am. Chem. Soc.* 1970, *92*, 867.

[23] Castro, C. E.; Kray, Jr., W. C. *J. Am. Chem. Soc.* 1963, *85*, 2768.

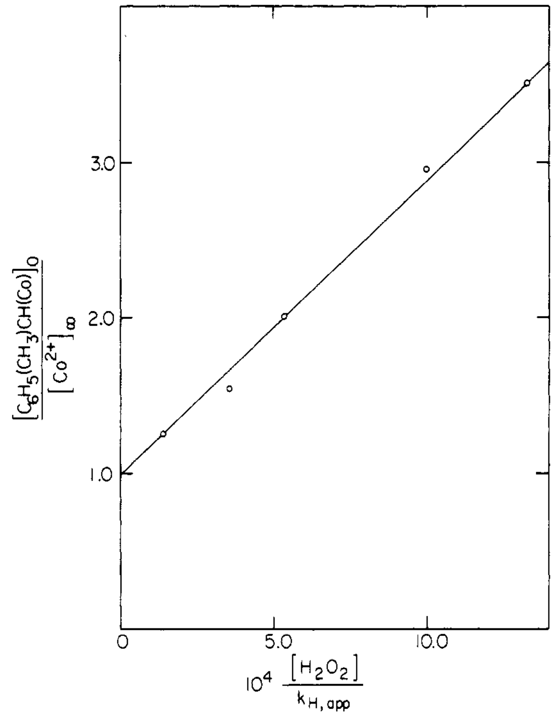

**Figure 3.** Illustrating the varying proportion of $Co^{2+}$ produced when decomposition of $PhCH(CH_3)Co(dmgH)_2OH_2$ is carried out in the presence of varying concentrations of $[H^+]$ and $[H_2O_2]$. The plot is that suggested by eq 15, using $k_{app}{}^H$ values at particular $[H^+]$ from Figure 2.

and $H_2O_2$ consisted of $Co^{2+}(aq)$ and $(H_2O)_2Co(dmgH)_2{}^+$. Their concentrations were determined in experiments having different $[H^+]$ and $[H_2O_2]$ and the results analyzed on the basis of the presumed competition of $Co(dmgH)_2OH_2$ for $H_3O^+$ (eq 6) and $H_2O_2$ (eq 11), the latter

$$2Co(dmgH)_2OH_2 + H_2O_2 + 2H^+ = 2(H_2O)_2Co(dmgH)_2{}^+ \tag{11}$$

$$d[(H_2O)_2Co(dmgH)_2{}^+]/dt = k_{H_2O_2}[Co(dmgH)_2OH_2][H_2O_2] \tag{12}$$

$$k_{H_2O_2} = (1.92 \pm 0.20) \times 10^3\ M^{-1}\ s^{-1}\ {}^{15a}$$

being a reaction also having a first-order dependence on $[Co(dmgH)_2OH_2]$ (eq 12). It is further assumed that $HCo(dmgH)_2OH_2$ from β elimination is very rapidly oxidized by hydrogen peroxide to cobalt(II) cobaloxime and enters the same competition.[16,24] The equations for the reaction rates based on Scheme I are

$$\frac{-d[RCo(dmgH)_2OH_2]}{dt} = k_{obsd}[RCo(dmgH)_2OH_2] \tag{13}$$

$$\frac{d[Co^{2+}]}{dt} = \frac{k_{obsd}k_{app}{}^H}{k_{app}{}^H + k_{H_2O_2}[H_2O_2]}[RCo(dmgH)_2OH_2] \tag{14}$$

where $k_{obsd}$ represents the total experimental rate constant for loss of organocobaloxime (eq 9), $k_{app}{}^H$ refers to the reaction of eq 6 (Figure 2), and $k_{H_2O_2}$ to the reaction of eq 11. Division of the two equations, and integration over the entire course of the reaction, gives, since $[H_2O_2]$ and $[H^+]$ are constant during every experiment

$$\frac{[RCo(dmgH)_2OH_2]_0}{[Co^{2+}(aq)]_\infty} = 1 + k_{H_2O_2}\frac{[H_2O_2]}{k_{app}{}^H} \tag{15}$$

Figure 3 depicts the results in a plot of the concentration ratio versus $[H_2O_2]/k_{app}{}^H$. The least-squares line has the expected intercept of unity (0.96 ± 0.05) and a slope of $(1.94 \pm 0.07) \times 10^3\ M^{-1}\ s^{-1}$ in excellent agreement with the accepted value[15a] of $k_{H_2O_2}$ (eq 12).

Two similar experiments were carried out based on a competition for $Co(dmgH)_2OH_2$ between $H^+$ and $Co(NH_3)_5Br^{2+}$ which reacts (eq 16) to produce $BrCo(dmgH)_2OH_2$.

$$Co(dmgH)_2OH_2 + Co(NH_3)_5Br^{2+} = BrCo(dmgH)_2OH_2 + Co^{2+} + 5NH_3 \tag{16}$$

$$k_{16} = 3.2 \times 10^5\ M^{-1}\ s^{-1}\ {}^{15b}$$

We further assumed that the hydridocobaloxime was quantitatively converted to $BrCo(dmgH)_2OH_2$. The observed yield of the bromocobalt(III) cobaloxime was 55–58% of the original $[PhCH(CH_3)Co(dmgH)_2OH_2]$, whereas some 41–43% was expected from Scheme I. Considering the experimental situation, this is not bad agreement; it serves to demonstrate formation of a substantial yield of $BrCo(dmgH)_2OH_2$, the most likely precursors of which are the cobalt(II) cobaloxime via eq 16 and hydridocobaloxime.

Experiments on the decomposition of the organocobaloxime in acidic solution were also done by using other oxidizing agents, $Fe^{3+}$ and $Cu^{2+}$. The spectral changes noted with $Fe^{3+}$ were complex, undoubtedly a reflection of the complexation of iron(III) by the oxime oxygens of the cobaloxime,[26] and possibly indicative of a pathway for direct reaction. Addition of $Cu^{2+}$ to acidic solutions of $PhCH(CH_3)Co(dmgH)_2OH_2$ caused a reaction to occur more rapidly than if the solution contained only $H_3O^+$. Instead of the large spectral change noted in all other cases corresponding to decomposition of the (α-phenylethyl)cobaloxime, however, the changes were small. The final UV–visible spectrum, now stable toward further change, was that of an alkylcobaloxime, all of which are quite similar. Clearly none of the very reactive α-phenylethyl complex remained at this point. It is proposed that $Cu^{2+}$ caused isomerization to the more stable (β-phenylethyl)cobaloxime, although the details of the process were not explored further.[27]

**Kinetics in Neutral Solutions.** The rate constant for decomposition of $PhCH(CH_3)Co(dmgH)_2OH_2$ was determined directly by adding an oxidizing agent which would draw the reaction to completion by reaction with the cobalt(II) cobaloxime and hydridocobaloxime produced. The decomposition followed first-order kinetics with $k_{obsd} = (3.27 \pm 0.21) \times 10^{-3}\ s^{-1}$ when carried out at 25.0 °C and $\mu = 1.00$ M in the presence of $Co(NH_3)_5Br^{2+}$, and $k_{obsd}$ was independent of its concentration. Similarly when the solution was saturated with $O_2$ ($\sim 1 \times 10^{-3}$ M), $k_{obsd}$ was (3.16 ± 0.01) × $10^{-3}\ s^{-1}$. These experiments establish the validity of the extrapolation of the kinetic data obtained in acidic solution and verify the correctness of the interpretation given to $k_b$ so obtained by a fit to the $[H^+]$ dependence

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[24] The basis for assuming the reaction occurs according to the equation $2HCo(dmgH)_2OH_2 + H_2O_2 = 2Co(dmgH)_2OH_2$ is the following. The hydrido complex reacts with $H_3O^+$ slowly[25] and clearly disappears by an oxidation process. The other two possibilities, that it is rapidly oxidized exclusively to $Co^{2+}(aq)$ or to $(H_2O)_2Co(dmgH)_2{}^+$, are untenable, since the observed yields of these two products are incompatible with either assumption.

[25] Chao, T.-H.; Espenson, J. H. *J. Am. Chem. Soc.* 1978, *100*, 129.

[26] Bakač, A.; Espenson, J. H. *Inorg. Chem.* 1980, *19*, 242.

[27] A scheme in which $CuCH(CH_3)Ph^{2+}$, formed from $Cu^{2+}$ + $\cdot CH(CH_3)Ph$ in the first step of radical oxidation, reacts with hydridocobaloxime to produce $PhCH_2CH_2Co(dmgH)_2OH_2$ can be suggested to rationalize this result, but no evidence in its support can be cited.

in eq 9, $(3.55 \pm 0.07) \times 10^{-3}$ $s^{-1}$.

Experiments were done on the decomposition of the organocobaloxime in the presence of $Co(en)_3^{3+}$. In acidic solution it was without effect on the rates or product yields. This is to be expected since $Co(en)_3^{3+}$ does not react with $Ph\dot{C}HCH_3$ in acid, and its reaction with $Co(dmgH)_2OH_2$ is so slow that reaction 6 occurs instead. The concentration of $Co^{2+}$ formed agreed exactly with $[PhCH(CH_3)Co(dmgH)_2OH_2]_0$.

In neutral solution, however, the rate constant when $Co(en)_3^{3+}$ was present was much smaller than $k_b$, and $[Co^{2+}]_\infty \approx (1.3–1.6) \times [PhCH(CH_3)Co(dmgH)_2OH_2]_0$. This suggests that the buildup of $Co(dmgH)_2OH_2$ suppresses at least partially the homolysis reaction, setting up a competition for the free radical. It may return to the starting complex by reaction with $Co(dmgH)_2OH_2$ or may be oxidized by $Co(en)_3^{3+}$. The effect is most pronounced when the reaction is run in the presence of added $Co(dmgH)_2OH_2$.

The relative yields of styrene are 1:22:7 in the following three experiments involving decomposition of ($\alpha$-phenylethyl)aquocobaloxime (a) in the presence of $Co(en)_3^{3+}$ in neutral solution, (b) alone in neutral solution over a longer period of time, and (c) with $Co(en)_3^{3+}$ in acidic solution. The much diminished yield of styrene in the first experiment is consistent with oxidation of the radical by $Co(en)_3^{3+}$ under these conditions. Only in c is a substantial quantity of dimers A–D produced; styrene is the only appreciable organic product of b.

**Conclusions.** The data obtained in this study support the occurrence of parallel homolysis and $\beta$-elimination pathways for decomposition of $PhCH(CH_3)Co(dmgH)_2OH_2$. The former is readily reversed, such that when $[Co(dmgH)_2OH_2]$ is allowed to accumulate as in neutral solution, the reaction occurs largely by $\beta$ elimination. This appears to have been the situation in Gaudemer's work,[4] and the conclusion that decomposition occurs only by $\beta$ elimination is the correct one *for the conditions employed.* On the other hand, homolytic Co–C cleavage becomes the major pathway under conditions in which a reagent which reacts rapidly with $Co(dmgH)_2OH_2$ is present. In that case the inorganic and organic products can be quantitatively attributed to these intermediates.

The question remains which is the predominant pathway in toluene.[5] Since $Co(dmgH)_2py$ is stable under those conditions, it seems likely that the contribution of homolysis is suppressed and that the major pathway is $\beta$ elimination. The small values of $\Delta S^\ddagger$ under those conditions[5] as compared to that when homolysis can be authenticated (1.4 vs. 25.7 cal $mol^{-1}$ $K^{-1}$) lends support to that argument.

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**Registry No.** A, 4613-11-0; B, 2726-21-8; C, 80326-00-7; D, 1520-44-1; styrene, 100-42-5; $PhCH(CH_3)Co(dmgH)_2(H_2O)$, 14783-95-0; $PhCH(CH_3)Co(dmgH)_2(py)$, 37824-58-1; $RCo(dmgH)_2OH_2$ (R = 2-propyl), 28132-41-4; $RCo(dmgH)_2OH_2$ (R = ethyl), 10210-55-6; $Co^{2+}$, 22541-53-3; $(H_2O)_2Co(dmgH)_2^+$, 46932-87-0; $HCo(dmgH)_2OH_2$, 80327-77-1; $Co(dmgH)_2OH_2$, 80327-78-2; $BrCo(dmgH)_2OH_2$, 51446-51-6.

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# Disproportionation of Monoorganothallium(III) Compounds Induced by Trimethyl Phosphite and Related Reagents: Evidence against a Spontaneous Disproportionation Mechanism

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The mechanism of the reaction between organothallium(III) diacetates ($RTl(OAc)_2$) and trimethyl phosphite, which gives $R_2TlOAc$ as the main product, was reexamined primarily on the basis of stereochemical and kinetic considerations. The reaction is suggested to proceed through an initial $RTl(OAc)_2–P(OMe)_3$ interaction rather than via spontaneous disproportionation of $RTl(OAc)_2$ into $R_2TlOAc$ and $Tl(OAc)_3$ as originally proposed, enhancing the reactivity of the compounds with respect to $R_2TlOAc$ formation. The implications of such disproportionation as a potential obstacle in the synthetic application of $RTlX_2$ are pointed out.

Redistribution of organic groups (disproportionation hereafter) of organometallic salts has received much attention, particularly in recent years, from an environmental chemical point of view.[1,2] The disproportionation of RHgX is believed[3] to proceed through the complexation of Lewis bases with either RHgX or $HgX_2$ formed in a preequilibrium and the electron transfer from reductants to RHgX. Recent studies[2,4] related to the biomethylation of $Tl^I$ suggested that disproportionation of $RTl(OAc)_2$ (R = Me, Ph) with $P(OMe)_3$ (eq 1)[5] proceeds through initial

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(1) Jarvie, A. W. P.; Markall, R. N.; Potter, H. R. *Nature* (*London*) **1975**, *255*, 217. Craig, P. J.; Bartlett, P. D. *Ibid.* **1978**, *275*, 635. Craig, P. J.; Ropsomanikis, S. "Abstracts of Papers", The 10th International Conference on Organometallic Chemistry, Toronto, 1981, p 57.

(2) Huber, F.; Schmidt, U.; Kirchmann, H. "Organometals and Organometalloids. Occurrence and Fate in the Environment"; Brinckman, F. E., Bellama, J. M., Eds.; American Chemical Society: Washington, D.C. *ACS Symp. Ser.* **1978**, p 65.

(3) Jensen, F. R.; Rickborn, B. "Electrophilic Substitution of Organomercurials"; McGraw-Hill: New York, 1968; p 120.

(4) Pohl, U.; Huber, F. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1188.

(5) This reaction is also useful for the synthesis of a variety of diarylthallium(III) compounds from readily accessible arylthallium(III) bis(trifluoroacetates).[6]