The relevance of the phosphoryl bond is well-known in phosphorus chemistry. The free phosphite molecules are quite reactive and the formation of a stable P=O bond is assumed to be the driving force for most of the reactions of neutral phosphorus esters.[20,28] The tautomerization equilibrium constants of $10^{7.2}$ and $10^{10.3}$ in favor of the phosphonate tautomer,[25] for R = Et and H, respectively, provides a measure of such preference. However, when coordinated to Ru(II) centers, the phosphites exhibit remarkable resistance to hydrolysis[5-9] (1 M CF$_3$COOH) and to oxidation[5] (Ce^{4+}, Br$_2$, H$_2$O$_2$).

The great strength of the phosphoryl linkage is indicated by the almost universal preference for the phosphonate form when alternative tautomeric forms are possible. Nevertheless, as pointed out earlier in this section, in accordance with the accumulated experimental data[19] for the complexes dealt with in this study, the metal center is directly bonded to the phosphorus atom. In this aspect, the complexes *trans*-[Ru(NH$_3$)$_4$P(OR)$_2$-

(OH)(H$_2$O)]$^{2+,3+}$ and *trans*-[Ru(NH$_3$)$_4$P(OR)$_2$(O)(H$_2$O)]$^{+,2+}$ (R = H, Et), as far as we know, are the first examples of complexes where diethyl phosphite and phosphorous acid are not bonded to a metal center through oxygen atoms.

The ability of the Ru(II) center to stabilize the phosphite form through 4d$_\pi$ (Ru)···3d$_\pi$ (P) back-bonding, as the oxygen does in the 2p$_\pi$ (O)···3d$_\pi$ (P) bond, accounts for the chemical inertness of the coordinated phosphite and strongly suggests that the Ru(II)=P(III) bond is stronger than the O(II)=P(III) bond.

(28) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cool Publishing Company: Monterey, CA, 1985.
(29) Franco, D. W.; Nascimento Filho, J. C.; De Rezende, J. M.; Lima Neto, B. S. *Proceedings of the Sixth International Symposium on Homogeneous Catalysis*; Vancouver, Canada, 1988.

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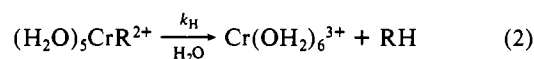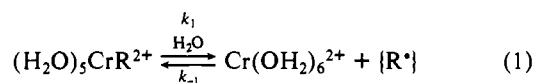# Kinetic Study of the Modes of Decomposition of Pentaaquabenzylchromium(III)

P. Kita[†] and R. B. Jordan*

The preparation of moderately concentrated solutions of (H$_2$O)$_5$CrCH$_2$C$_6$H$_5$$^{2+}$ has allowed its visible spectrum to be fully characterized with maxima (nm (molar absorptivities, M^{-1} cm^{-1})) at 533 (31.9) and 358 (2.15 × 10^3). The kinetics of acidolysis of (H$_2$O)$_5$CrCH$_2$C$_6$H$_5$$^{2+}$ have been studied between 56 and 74 °C in 1 M NaClO$_4$/HClO$_4$ and in the presence of chromium(II) to suppress homolysis. The rate law has terms independent of (k_0) and first order in [H$^+$] (k_a) with ΔH_0^* and ΔH_a^* values (kcal mol^{-1}) of 21.4 ± 0.4 and 20.3 ± 2.1 and ΔS_0^* and ΔS_a^* values (cal mol^{-1} deg^{-1}) of -11.7 ± 1.9 and -16.5 ± 8.7. Calculated values at 25 °C are $k_0 = 3.8 \times 10^{-6}$ s^{-1} and $k_a = 2.0 \times 10^{-6}$ M^{-1} s^{-1}. The homolysis reaction was studied at 41 °C and found to have apparent half-order kinetics in [(H$_2$O)$_5$CrCH$_2$C$_6$H$_5$$^{2+}$] with an inverse dependence on the hydrogen ion concentration. The products for the heterolysis, homolysis, and decomposition in the presence of ethanol and dioxygen have been characterized by ion-exchange separation and spectrophotometry for the inorganic species and by extraction and proton NMR spectroscopy for the organic products.

Introduction

The decomposition of pentaaqua(organo)chromium(III) complexes in aqueous solution has been observed to occur by homolysis of the Cr-C bond (eq 1) or by acidolysis, which may be viewed as aquation or heterolytic cleavage of the Cr-C bond with assistance from some proton source (eq 2).

$$(H_2O)_5CrR^{2+} \underset{k_{-1}}{\overset{k_1}{\underset{H_2O}{\rightleftarrows}}} Cr(OH_2)_6^{2+} + \{R^\bullet\} \qquad (1)$$

$$(H_2O)_5CrR^{2+} \xrightarrow[H_2O]{k_H} Cr(OH_2)_6^{3+} + RH \qquad (2)$$

The homolysis reaction can be studied by adding reagents that will react with either Cr^{2+} or the organic radical to drive the reaction to completion. In favorable cases, the homolysis can be suppressed by adding Cr^{2+} and then the acidolysis reaction can be studied. Work of this type has been summarized in a recent review.[1]

Previous studies on the benzyl complex have produced a somewhat confusing picture of its decomposition mechanism. The early work of Kochi and co-workers[2,3] indicates that this species undergoes relatively rapid acidolysis in ethanol-water mixtures

to produce toluene with half-order kinetics in [(H$_2$O)$_5$CrCH$_2$C$_6$H$_5$$^{2+}$]. Later, Nohr and Espenson[4] observed a much slower acidolysis in aqueous perchloric acid with an apparent first-order dependence on the chromium complex. Both groups observed that the reaction rate increases with increasing [H$^+$], with an apparent saturation effect at higher [H$^+$] in the data of Nohr and Espenson, who also found that the reaction is slowed by the addition of Cr(ClO$_4$)$_2$ in the 10^{-2}–10^{-3} M range. This could be interpreted to mean that acidolysis really was not being observed exclusively.

Nohr and Espenson also studied the homolysis reaction in the presence of various oxidizing agents, and this aspect seems to have been well characterized with $k_1 = 2.6 \times 10^{-3}$ s^{-1}. More recently Blau et al.[5] have measured the rate constant for the reaction of aqueous Cr^{2+} with the benzyl radical and found $k_{-1} = 8.5 \times 10^7$ M^{-1} s^{-1}. These results were combined to estimate a chromium–carbon bond energy of ~30 kcal mol^{-1} for this system.

In related work, Schmidt and Swaddle[6] studied the decomposition of (H$_2$O)$_5$CrCH$_2$C$_5$H$_4$NH^{3+}, which gave half-order kinetics in the absence of other reagents and first-order kinetics in the presence of dioxygen, in agreement with the previous work of

(1) Espenson, J. H. *Adv. Inorg. Bioinorg. Mech.* **1982**, *1*, 1.
(2) Kochi, J. K.; Davis, D. D. *J. Am. Chem. Soc.* **1964**, *86*, 5264.
(3) Kochi, J. K.; Buchanan, D. *J. Am. Chem. Soc.* **1965**, *87*, 853.
(4) Nohr, R. S.; Espenson, J. H. *J. Am. Chem. Soc.* **1975**, *97*, 3392.
(5) Blau, R. J.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1984**, *23*, 3526.
(6) Schmidt, A. R.; Swaddle, T. W. *J. Chem. Soc. A* **1970**, 1927.

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Table I. Products of the Decomposition of $(H_2O)_5CrCH_2C_6H_5^{2+}$ under Various Conditions

reacn	[HClO$_4$], M	other reagent	% org product[e]			% inorg product		
			bibenzyl	toluene	benzaldehyde	Cr^{2+}	Cr^{3+}	dimer
acidol[a]	0.02	Cr^{2+}	3–5	>95	0			
acidol[a]	0.50		3–5	>95	0			
homol[b]	0.02	5% EtOH	0–10	>90	0	65[f]	35	
homol[b]	0.50	5% EtOH	0–10	>90	0	10[f]	88	
homol[b]	0.02	9% EtOH	0–10	>90	0	37[f]	60	
homol[b]	0.50	9% EtOH	0–10	>90	0	10[f]	90	
homol[b]	0.50	20% EtOH				~5[f]	95	
homol[c]	0.02	O$_2$	10	30	60		30	70
homol[c]	0.50	O$_2$	10	30	60		80	20
homol[d]	0.02		75	25	0	40[f]	60	
homol[d]	0.50		85	15	0	27[f]	73	

[a] At 60 °C with (5–8) × 10^{-2} M Cr^{2+} under an argon atmosphere. [b] At 22 °C with the percentage of ethanol given by volume and under an argon atmosphere. [c] At 22 °C in air. [d] At 45 °C under an argon atmosphere; trace amounts of benzyltoluene(s) appear in the organic products. [e] Relative product distribution from NMR integration of CCl$_4$ extracts. [f] Determined as the dimer that originates from Cr^{2+} when the solution is exposed to air for analysis.

Coombes and Johnson.[7] Schmidt and Swaddle observed that the addition of Cr(ClO$_4$)$_2$ slowed the reaction with an inverse first-order dependence on [Cr^{2+}] and a first-order dependence on [(H$_2$O)$_5$CrCH$_2$C$_5$H$_4$NH^{3+}]. Although the latter authors suggested a mechanism to explain their observations, it was noted by Nohr and Espenson[4] that the explanation is not entirely satisfactory, and this problem is addressed in more detail later in this work.

The present study was undertaken to clarify the mechanism of decomposition of (H$_2$O)$_5$CrCH$_2$C$_6$H$_5^{2+}$ with the hope that inconsistencies could be explained and that some general insight into the decomposition mechanisms of these complexes might be obtained.

Results and Discussion

One significant result of this work, which is not immediately apparent, is that we have prepared solutions of (H$_2$O)$_5$CrCH$_2$C$_6$H$_5^{2+}$ at much higher concentrations ($\geq 1 \times 10^{-2}$ M) than in the previous studies. These solutions are stable for days if stored in the absence of dioxygen. We believe that earlier implications about the instability of the complex and the variability in its reactivity may relate to traces of dioxygen, which can be important if the complex concentration is $\leq 10^{-4}$ M. The more concentrated solutions scavenge initial traces of dioxygen without having a significant effect on the concentration of (H$_2$O)$_5$CrCH$_2$C$_6$H$_5^{2+}$.

Between 340 and 700 nm, the electronic spectrum of (H$_2$O)$_5$CrCH$_2$C$_6$H$_5^{2+}$ has maxima at 358 and 533 nm, with molar absorptivity coefficients of 2.15 × 10^3 and 31.9 M^{-1} cm^{-1}, respectively, in 0.5 M NaClO$_4$, 0.5 M HClO$_4$ under argon. The 358-nm peak agrees with the report of Nohr and Espenson[4] (356 nm, 2.2 × 10^3 M^{-1} cm^{-1}). The 533-nm peak has not been observed previously, presumably because of its low absorptivity coefficient. This result should correct any possible impression[1] that the usual visible peak is not present or is greatly shifted in these benzyl complexes.

In the following sections, the products and kinetics of the acidolysis and homolysis are described. The acidolysis has been studied by adding chromium(II) to the solution to suppress the homolysis. The major portion of the homolysis results are for conditions in which no other reagents have been added.

Acidolysis. The products of this reaction have been determined by allowing the reaction to proceed to greater than 95% completion at 60 °C in the presence of chromium(II) at concentrations of (5–8) × 10^{-2} M and (5–15) × 10^{-3} M (H$_2$O)$_5$CrCH$_2$C$_6$H$_5^{2+}$. The major product is toluene with traces of bibenzyl (see Table I). It is not possible to determine the inorganic product because of the large excess of chromium(II).

The kinetics of the acidolysis have been studied between 56.2 and 74.4 °C, and the results are summarized in Table II. The

(7) Coombes, R. G.; Johnson, M. D. *J. Chem. Soc. A* **1966**, 177.

Table II. Rate Constants for the Acidolysis of $(H_2O)_5CrCH_2C_6H_5^{2+}$ in 1 M NaClO$_4$/HClO$_4$

temp, °C	[H$^+$], M	10^{4}k, s^{-1}	
		obsd	calcd[a]
74.4	0.927	10.1	10.2
74.4	0.773	9.27	9.74
74.4	0.580	9.00	9.16
74.4	0.389	8.51	8.58
74.4	0.158	7.66	7.87
74.4	0.014	7.41	7.44
65.4	0.927	4.48	4.42
65.4	0.773	4.30	4.21
65.4	0.580	4.03	3.95
65.4	0.389	3.83	3.69
65.4	0.158	3.41	3.38
65.4	0.014	3.34	3.19
56.2	0.927	1.78	1.79
56.2	0.773	1.70	1.71
56.2	0.580	1.56	1.60
56.2	0.389	1.49	1.49
56.2	0.158	1.37	1.36
56.2	0.014	1.24	1.28

[a] Calculated from a least-squares fit by using the activation parameters given in the text.

time dependence of the absorbance change is consistent with a first-order dependence on [(H$_2$O)$_5$CrCH$_2$C$_6$H$_5^{2+}$]. The rate is independent of [Cr^{2+}] in the range (2–80) × 10^{-3} M but increases and becomes erratic if [Cr^{2+}] < 1 × 10^{-3} M. The acid dependence of the psuedo-first-order rate constant is given by eq 3. The values
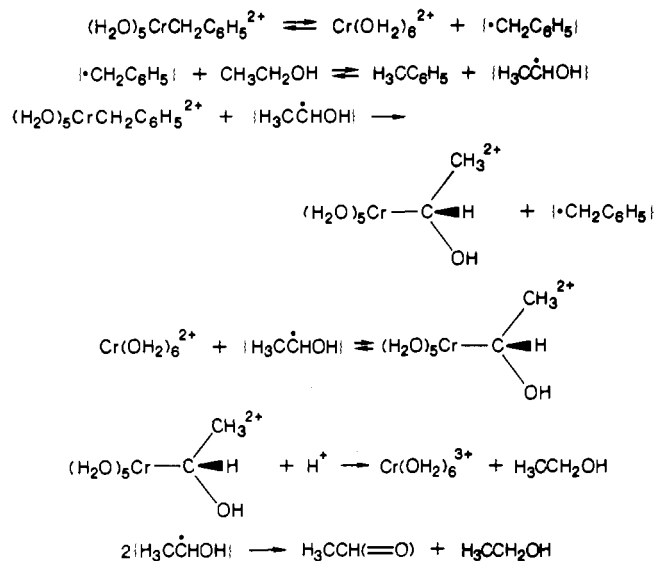
$$k_{obsd} = k_H = k_0 + k_a[H^+] \tag{3}$$

of the activation parameters ΔH^* (kcal mol^{-1}) and ΔS^* (cal mol^{-1} deg^{-1}) are 21.4 ± 0.4 and −11.7 ± 1.9 for k_0 and 20.3 ± 2.1 and −16.5 ± 8.7 for k_a. The experimental and calculated values of k_{obsd} are compared in Table II. The calculated values at 25 °C are $k_0 = 3.8 \times 10^{-6}$ s^{-1} and $k_a = 2.0 \times 10^{-6}$ M^{-1} s^{-1}. These values predict rate constants between 20 and 100 times smaller than those attributed to acidolysis by Nohr and Espenson[4] at various acidities but in the absence of chromium(II). The present results do not show the saturation effect in the [H$^+$] dependence that is apparent in the data of the latter authors.

Homolysis. The results of Nohr and Espenson[4] indicate that homolysis should be the dominant decomposition path if it is not suppressed by the addition of chromium(II).

The early work of Kochi and co-workers[2,3] was done in mixed ethanol–water solutions. Our observations confirm that (H$_2$O)$_5$CrCH$_2$C$_6$H$_5^{2+}$ is less stable in this medium than in water. The organic product (see Table I) is mainly toluene (>90%) with traces of bibenzyl (<10%) with no significant variation between 0.02 and 0.5 M H$^+$ or with ethanol between 5 and 9% by volume. Ethanol may decrease the stability because of the hydrogen atom abstraction reaction with the benzyl radical as shown in Scheme

Scheme I

$$(H_2O)_5CrCH_2C_6H_5{}^{2+} \rightleftharpoons Cr(OH_2)_6{}^{2+} + \{\cdot CH_2C_6H_5\}$$

$$\{\cdot CH_2C_6H_5\} + CH_3CH_2OH \rightleftharpoons H_3CC_6H_5 + \{H_3C\dot{C}HOH\}$$

$$(H_2O)_5CrCH_2C_6H_5{}^{2+} + \{H_3C\dot{C}HOH\} \longrightarrow$$

$$(H_2O)_5Cr-\overset{CH_3}{\underset{OH}{C}}H^{2+} + \{\cdot CH_2C_6H_5\}$$

$$Cr(OH_2)_6{}^{2+} + \{H_3C\dot{C}HOH\} \rightleftharpoons (H_2O)_5Cr-\overset{CH_3}{\underset{OH}{C}}H^{2+}$$

$$(H_2O)_5Cr-\overset{CH_3}{\underset{OH}{C}}H^{2+} + H^+ \longrightarrow Cr(OH_2)_6{}^{3+} + H_3CCH_2OH$$

$$2\{H_3C\dot{C}HOH\} \longrightarrow H_3CCH(=O) + H_3CCH_2OH$$

1. Gas-phase bond energies[8] indicate that this reaction is endothermic by ~2 kcal, but the reaction can be driven forward by consumption of the radical product in the next reaction. The chromium product does show a substantial variation with acidity and ethanol composition, being mainly chromium(II) in 0.02 M H^+ and 5% ethanol and almost all $Cr(OH_2)_6{}^{3+}$ in 0.5 M H^+ and 20% ethanol. This may be attributed to competing homolysis and acidolysis of $(H_2O)_5CrCH(OH)CH_3{}^{2+}$, as shown in Scheme I. Schmidt et al.[9] have shown that the decomposition of the latter complex does have an [H^+]-dependent path, but it must be more important in the mixed solvent than in water to be the sole explanation of the chromium(III) product.
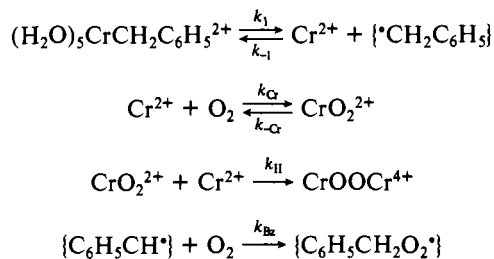
Reaction with Dioxygen. In the presence of dioxygen we have confirmed that the decomposition follows first-order kinetics with rate constants of $(2.32 \pm 0.05) \times 10^{-3}$ and $(2.40 \pm 0.04) \times 10^{-3}$ s^{-1} in 0.02 and 0.98 M perchloric acid, respectively (25 °C, 1.0 M $NaClO_4/HClO_4$, 3.0×10^{-5} M Cr), in agreement with Nohr and Espenson,[4] who found an acid-independent rate constant of 2.6×10^{-3} s^{-1}. The latter authors determined the decomposition products in an ethanol–water mixture at unspecified acidity as benzaldehyde and a chromium(III) dimer in agreement with earlier work.[3,10] Our observations of the products (Table I) are in qualitative agreement with the previous studies at least at 0.02 M H^+, with regard to the major products, except that we also observe significant amounts of toluene (30%) and traces of bibenzyl (10%). We also find that the chromium products vary substantially with acidity, from 70% bis(μ-hydroxo)chromium(III) dimer in 0.02 M H^+ to 80% $Cr(OH_2)_6{}^{3+}$ in 0.50 M H^+, while the organic product distribution remains unchanged. No $HCrO_4^-$ product could be detected spectrophotometrically at 350 nm, and an upper limit of <4% can be calculated from the known properties of $HCrO_4^-$.[11]

It is perhaps disappointing and somewhat confusing to note that the reactions of the isopropyl[11] and benzyl complexes with dioxygen are quite different. The rate is three-halves and first order, respectively, in the organochromium(III) species, and the isopropyl complex yields 9–13% Cr(VI) while the benzyl species gives no detectable Cr(VI) product. The organic products are about a 2:1 mixture of ketone and alcohol with more ketone at higher acidities in the isopropyl system, but no benzyl alcohol is observed. About 10% of the organic isopropyl product was not identified, and this could be hydrocarbon, which would be similar to the amount of bibenzyl found here. The reaction of $(H_2O)_5CrCH_2C_6H_5{}^{2+}$ with

dioxygen is more similar to that of benzylcobalamin studied by Blau and Espenson.[12] Both systems show first-order kinetics and yield benzaldehyde as the dominant product. The differences between the isopropyl and benzyl systems must be due to different reactivities of the organic radical species.

The known possible reactions in the presence of dioxygen are shown in Scheme II. The values of k_1 and k_{-1} are given above, while $k_{Cr} = 1.6 \times 10^8$ M^{-1} s^{-1},[13] $k_{-Cr} = 2.5 \times 10^{-4}$ s^{-1},[14] $k_{II} = 8 \times 10^8$ M^{-1} s^{-1},[14] and $k_{Bz} \approx 2.5 \times 10^9$ M^{-1} s^{-1}.[15]

Scheme II

$$(H_2O)_5CrCH_2C_6H_5{}^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cr^{2+} + \{\cdot CH_2C_6H_5\}$$

$$Cr^{2+} + O_2 \underset{k_{-Cr}}{\overset{k_{Cr}}{\rightleftharpoons}} CrO_2{}^{2+}$$

$$CrO_2{}^{2+} + Cr^{2+} \overset{k_{II}}{\longrightarrow} CrOOCr^{4+}$$

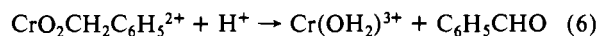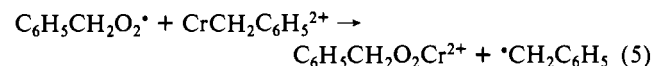$$\{C_6H_5CH^{\cdot}\} + O_2 \overset{k_{Bz}}{\longrightarrow} \{C_6H_5CH_2O_2{}^{\cdot}\}$$

Brynildson et al.[14] have shown that the decomposition of $CrO_2{}^{2+}$ is complex with competing routes that depend on whether there is excess Cr^{2+} (yielding Cr(III) dimer) or excess O_2 (yielding $HCrO_4^-$). In the present case, it appears that there is excess O_2 because the Cr^{2+} is produced by the relatively slow homolysis, but $CrO_2{}^{2+}$ is moderately persistent and may build up as the reaction proceeds to levels where it competes effectively with dioxygen for Cr^{2+} from the primary homolysis. This would account for the Cr(III) dimer product.

The results of Maillard et al.[15] imply that $C_6H_5CH_2O_2{}^{\cdot}$ decomposes by disproportionation to yield equal amounts of aldehyde and alcohol. The analysis of Nangia and Benson[16] on primary peroxy radicals indicates that the decomposition of these radicals can be a complex chain process but the products are generally those expected from disproportionation. In order to explain the absence of $HCrO_4^-$ and deficiency of benzyl alcohol, Blau and Espenson[12] have suggested that $CrO_2{}^{2+}$ is consumed by the oxidation of benzyl alcohol to benzaldehyde. It also seems possible that, as $CrO_2{}^{2+}$ accumulates, it may oxidize the benzyl radical to benzaldehyde as shown in eq 4.

$$CrO_2{}^{2+} + {}^{\cdot}CH_2C_6H_5 + H^+ \rightarrow CrOH_2{}^{3+} + C_6H_5CHO \qquad (4)$$
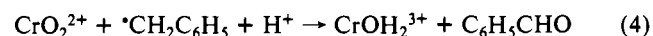
Since $C_6H_5CH_2O_2{}^{\cdot}$ is moderately persistent, it may react by a transfer process as shown in eq 5 to give a peroxy complex. This

$$C_6H_5CH_2O_2{}^{\cdot} + CrCH_2C_6H_5{}^{2+} \rightarrow$$
$$C_6H_5CH_2O_2Cr^{2+} + {}^{\cdot}CH_2C_6H_5 \qquad (5)$$

$$CrO_2CH_2C_6H_5{}^{2+} + H^+ \rightarrow Cr(OH_2)^{3+} + C_6H_5CHO \qquad (6)$$

is analogous to the proposal of Ryan and Espenson[11] for the isopropyl system. The peroxy complex may decompose in acidic solution to produce benzaldehyde according to eq 6.

The above discussion does not explain the formation of toluene. This might be produced by the reaction of the benzyl radical with the organochromium(III) reactant as proposed in the following section (eq 13 and 14). Since the reactant concentration is in the range of 0.01 M and the dioxygen is $\leq 1 \times 10^{-3}$ M, the benzyl radical has a reasonable chance of coupling with the reactant before being scavenged by dioxygen. Bibenzyl could form by a similar reaction as shown in eq 7.

$$CrCH_2C_6H_5{}^{2+} + {}^{\cdot}CH_2C_6H_5 \rightarrow Cr^{2+} + (C_6H_5CH_2)_2 \qquad (7)$$
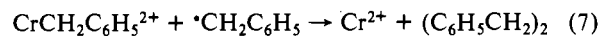
(8) Meot-Ner, M. *J. Am. Chem. Soc.* **1982**, *104*, 5. Holmes, J. L.; Lossing, F. P. *Int. J. Mass Spectrom. Ion. Processes* **1984**, *58*, 113.

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(16) Nangia, P. S.; Benson, S. W. *Int. J. Chem. Kinet.* **1980**, *12*, 43.

Table III. Apparent Half-Order Rate Constants for the Homolytic Decomposition of $(H_2O)_5CrCH_2C_6H_5{}^{2+}$ at 41.1 °C in 1 M $NaClO_4/HClO_4$

[H⁺], M	$10^5[(H_2O)_5Cr-CH_2C_6H_5{}^{2+}]$, M	10^6k, M$^{1/2}$ s^{-1} ^{a}	
		$k_{1/2}$(eq 8)	k_s(eq 9)
0.040	8.0	9.07	8.90
0.040	4.5	9.34	9.28
0.040	2.0	7.64	7.55
0.12	8.0	9.82	9.67
0.12	4.5	9.62	9.48
0.12	2.0	8.05	7.98
0.40	8.0	7.84	7.64
0.40	4.5	7.43	7.30
0.40	2.0	6.57	6.48
0.60	8.0	6.16	5.91
0.60	4.5	5.74	5.54
0.60	2.0	4.91	4.77
0.80	8.0	4.49	4.20
0.80	4.5	4.24	4.04
0.80	2.0	4.15	4.02
0.96	8.0	2.84	2.45
0.96	4.5	2.39	2.16
0.96	2.0	2.24	2.09

^{a} Calculated from the least-squares values of $k_{1/2}(\epsilon l)^{1/2}$ by dividing $(2.15 \times 10^3 \times 10)^{1/2}$. The least-squares parameters have 95% confidence limits of 2–7%.

Spontaneous Decomposition of $(H_2O)_5CrCH_2C_6H_5{}^{2+}$. The decomposition in the absence of added reagents other than sodium perchlorate and perchloric acid proves to be a more complex process, especially from the kinetic standpoint. The decrease of absorbance with time is faster than predicted by a first-order process and appears to follow half-order kinetics in $[(H_2O)_5CrCH_2C_6H_5{}^{2+}]$. The absorbance–time data were fitted to eq 8, which is a rearranged version of the half-order rate law

$$A_t = A_\infty + \left[\sqrt{A_0 - A_\infty} - \frac{k_{1/2}\sqrt{\epsilon l}}{2}t\right]^2 \quad (8)$$

given by Schmidt and Swaddle,[6] where A_t, A_0, and A_∞ are the absorbance at any time and the initial and final absorbances, respectively, ϵ is the molar absorptivity (M^{-1} cm^{-1}), and l is the cell path length (cm). This equation gives a satisfactory fit of the change of absorbance with time, but the half-order rate constants (see Table III) seem to decrease persistently at the lowest $[(H_2O)_5CrCH_2C_6H_5{}^{2+}]$, and the effect is especially apparent for $[H^+] \geq 0.6$ M. This problem at higher acidities suggests that heterolysis might be a competing and complicating factor since the spontaneous rate decreases with increasing $[H^+]$ while acidolysis is faster at higher $[H^+]$. Then the rate might be described by parallel first- and half-order terms. The integrated form of this rate law is given by eq 9, where k_H is the net heterolysis rate constant at a particular acidity as given by eq 3 and k_s is the rate constant for the half-order process.

$$A_t = A_\infty + \left[\frac{(k_s\sqrt{\epsilon l} + k_H\sqrt{A_0 - A_\infty})e^{-k_H t} - k_s\sqrt{\epsilon l}}{k_H}\right]^2 \quad (9)$$

The absorbance–time data were fitted to eq 9 with k_H fixed at values calculated from eq 3 with k_0 and k_a values of 2.5×10^{-5} s^{-1} and 1.2×10^{-5} M^{-1} s^{-1}, respectively, at 41.1 °C as calculated from the activation parameters. The resulting values of k_s are given in Table III. They are slightly changed, and k_s shows somewhat less variation with $[(H_2O)_5CrCH_2C_6H_5{}^{2+}]$ at the higher $[H^+]$, but there is still a significant decrease of k_s with increasing $[H^+]$. The adequacy of the absorbance–time fits and the variation of the rate with $[H^+]$ are shown by Figure 1.

The rate appears to show a half-order dependence on $[(H_2O)_5CrCH_2C_6H_5{}^{2+}]$ and an inverse dependence on $[H^+]$. The

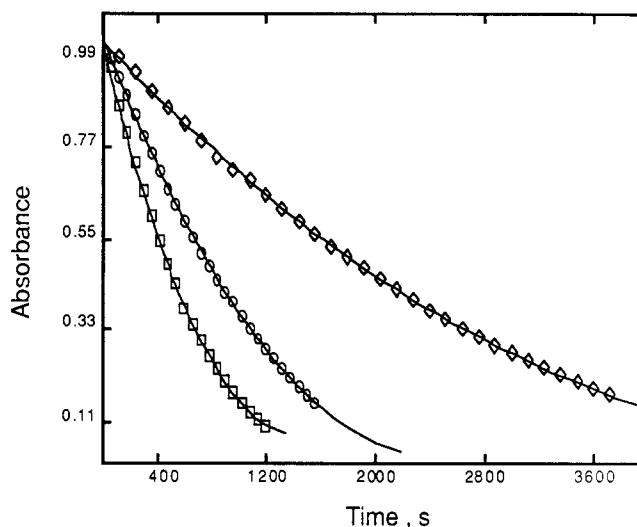**Figure 1.** Variation of the absorbance with time for the spontaneous decomposition of $(H_2O)_5CrCH_2C_6H_5{}^{2+}$ at 41.1 °C at 1 M ionic strength, 4.5×10^{-5} M $(H_2O)_5CrCH_2C_6H_5{}^{2+}$, and 0.96 (◊), 0.60 (○), and 0.040 M (□) $HClO_4$. The curves are based on the least-squares best-fit values to eq 9.
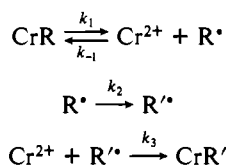
exact form of the latter dependence is somewhat ambiguous, but it appears to involve $[H^+]^2$ and can be reasonably reproduced by equations of the form $A/(1 + B[H^+]^2)$ or $(A/(1 + B[H^+]))^2$. However, it is difficult to envision species that will involve two protons in an inhibitory way given the fact that neither the chromium complexes nor the benzyl radical are thought to undergo significant proton equilibria under the acidic conditions of this study. It would seem safer to conclude that the decomposition kinetics are actually more complex than a simple half-order rate law and that the $[H^+]$ dependence is associated with some unresolved complexity in the rate law.

Before more complex alternatives are discussed, the simplest mechanism involving homolysis (eq 1) followed by radical combination to give bibenzyl can be examined. This is instructive because all the rate constants are known independently, and if this mechanism is not operative, it ought to predict a reaction half-time much longer than that observed, especially since it is inconsistent with the observed products. The rate constant values are $k_1 = 2.6 \times 10^{-3}$ s^{-1}, $k_{-1} = 8.5 \times 10^7$ M^{-1} s^{-1}, and $k_2 \approx 2 \times 10^9$ M^{-1} s^{-1} for bibenzyl formation. The first step (eq 1) can be considered as a rapid preequilibrium because the buildup of Cr(II) quickly makes $k_{-1}[Cr(II)] \gg k_2[{}^\bullet CH_2C_6H_5]$. Then the reaction half-time can be calculated to be in the range of 4000–5000 h at 25 °C for our initial concentration conditions. This is quite inconsistent with observed values of less than 1 h at 41 °C, even allowing for the 16 °C difference in temperature. The main difficulty with this mechanism is the very unfavorable initial equilibrium (eq 1), which is further suppressed as Cr(II) accumulates.

Schmidt and Swaddle[6] have suggested a mechanism that predicts the half-order kinetics for the decomposition of $(H_2O)_5CrCH_2C_5H_4NH^{3+}$, and one might hope that something analogous could apply to the benzyl complex. This reaction sequence is shown in a general way in Scheme III. In the 4-pyridylmethyl system the transformation of R$^\bullet$ to R$'^\bullet$ was proposed to be a tautomeric proton transfer from $-$NH to $-$CH$_2$ and the last step formed the Cr(III)–nitrogen-bonded product; however, there is a problem with the original analysis of this system. To explain the half-order kinetics, it was necessary to assume that $k_{-1}[Cr^{2+}] \gg k_2$, and the subsequent analysis gave $k_{-1} = 1.0 \times 10^{-2}$ M^{-1} s^{-1} and $k_2 = 3.9 \times 10^{-6}$ s^{-1}. To satisfy the inequality, one must have $[Cr^{2+}] \gg 3.9 \times 10^{-4}$ M, but the total chromium concentrations are in the range of 0.38×10^{-4}–15×10^{-4} M and the required $[Cr^{2+}]$ ranges from being impossible to being unreasonable, given that the reaction proceeds to completion in a monophasic fasion. Another anomaly in this analysis is the small k_{-1} value compared to values of $\sim 10^8$ M^{-1} s^{-1} found for many

other systems.[1,5] A much larger k_{-1} value would solve the inequality problem just mentioned and would yield $k_2 \approx 0.4$ M^{-1} s^{-1}, if k_1 is taken from the decomposition rate in the presence of dioxygen. The remaining problem is that the decomposition rate in the presence of added Cr^{2+} is too large to be due to homolysis as assumed by Schmidt and Swaddle and must contain a contribution from acidolysis.
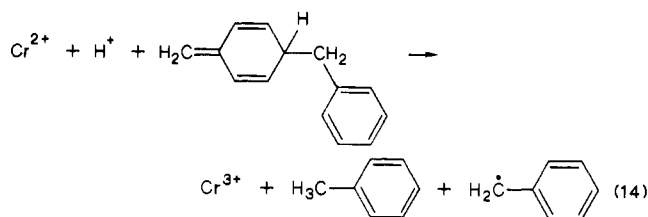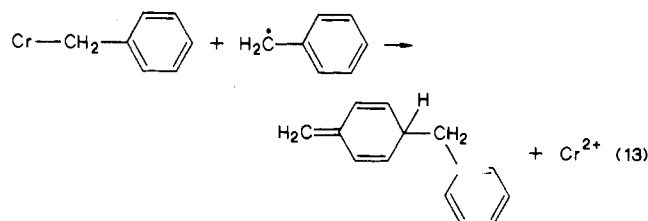
Scheme III

$$CrR \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cr^{2+} + R^{\bullet}$$

$$R^{\bullet} \overset{k_2}{\longrightarrow} R'^{\bullet}$$

$$Cr^{2+} + R'^{\bullet} \overset{k_3}{\longrightarrow} CrR'$$

Although Scheme III could account for the kinetics of the benzyl system, it is not clear how to assign the R$^{\bullet}$ to R'$^{\bullet}$ transformation for the benzyl radical. In addition, a good deal more must be happening because of the product distribution. In the final analysis it must be admitted that we have no closed solution to this question except to point out some possible reaction paths and the way that they can make the system very complex. One feature that is not widely acknowledged in the self-termination reactions of the benzyl radical is that semibenzenes are significant initial products, although they may rearrange to bibenzyl under many experimental conditions as shown in eq 10–12. Langhals

(10)

(11)

(12)
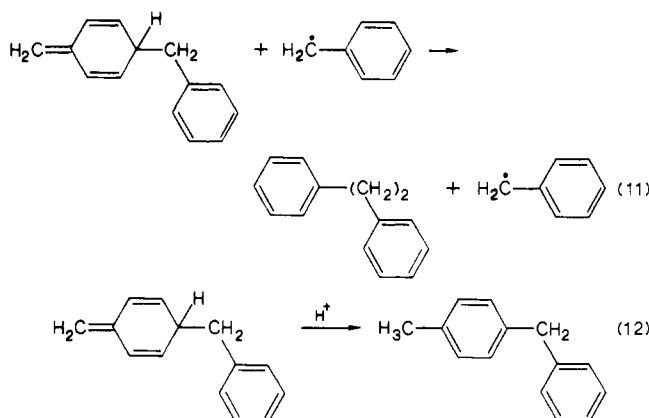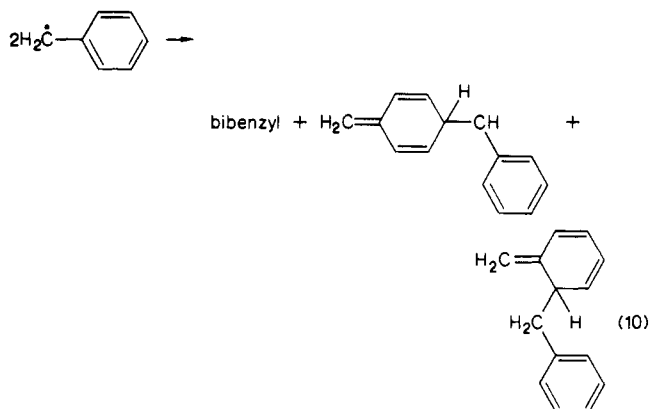
and Fischer[17] found about 20% semibenzene product as a nearly equal mixture of the ortho and para forms from the photochemical decomposition of dibenzyl ketone in cyclopentane at 25 °C. They also observed that HCl catalyzes the rearrangement of semibenzenes to benzyltoluene. Skinner et al.[18] found analogous products from α-substituted benzyl radicals. An analogous reaction may occur with the benzylchromium complex as shown in eq 13. The semibenzene product could rearrange as in eq 11 or 12. This is indicated by minor but persistent peaks in the product NMR spectra at $\sim$2.25 and 3.9 ppm, which could be

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(13)

(14)

assigned to the methyl and methylene protons of benzyltoluene.[17] The semibenzene also may be reduced by chromium(II) at the exocyclic double bond to produce toluene and another benzyl radical as in eq 14. These two reactions provide a potential chain-propagation pathway for the decomposition of the benzylchromium complex and explain the formation of toluene and chromium(III). As the bibenzyl product accumulates, it is also possible that the hydrogen atom abstraction shown in eq 15 may

(15)
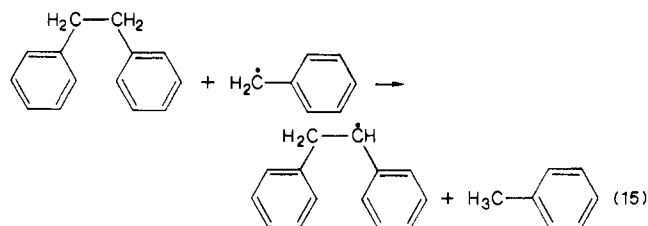
contribute to the formation of toluene. As the reaction proceeds, the fate of the benzyl radical is likely to shift between eq 13 and eq 15 because of the changing proportion of the benzylchromium complex and bibenzyl.

Our conclusion is that a full understanding of the homolytic decomposition of the benzyl chromium complex will require a detailed study of the time dependence of the product distribution. This is now much more feasible since the rate is known, and it is hoped that the above discussion has provided some guidance for a product study.

Experimental Section

Materials. The solutions of $(H_2O)_5CrCH_2C_6H_5{}^{2+}$ were prepared by the heterogeneous reaction of aqueous chromium(II) perchlorate (10 mmol, 0.25 M) in 0.10 M perchloric acid and benzyl bromide (4 mmol) under an argon atmosphere. The mixture was stirred vigorously for 2 h at ambient temperature, during which time the color changed from pale blue to yellow. The solution was charged onto a column (35 × 3 cm) of Sephadex SP-C25 (H$^+$) under an argon atmosphere. The column was washed with 0.01 M HClO$_4$ and then with 0.10 M NaClO$_4$ in 0.01 M HClO$_4$ to remove chromium(II). The desired product was eluted with 0.50 M NaClO$_4$ in 0.1 M HClO$_4$, which also separated $Cr(OH_2)_6{}^{3+}$ from small amounts ($\sim$5%) of higher charged polymers. The other expected product, $(H_2O)_5CrBr^{2+}$, was not present because of chromium(II)-catalyzed aquation under the preparative conditions, but it could be detected at lower initial ratios of Cr(II):C$_6$H$_5$CH$_2$Br. The separated yield of $(H_2O)_5CrCH_2C_6H_5{}^{2+}$ was 70% based on the initial C$_6$H$_5$CH$_2$Br, and the solutions typically contained 1.5 × 10^{-2} M $(H_2O)_5CrCH_2C_6H_5{}^{2+}$. The concentration can be increased by partial freezing of the solution at −15 °C and removal of the liquid phase with a syringe. Solutions of $(H_2O)_5CrCH_2C_6H_5{}^{2+}$ were stored under argon in the freezing compartment of a refrigerator at −10 to −15 °C.

Chromium(II) perchlorate solutions were prepared by reduction of aqueous chromium(III) perchlorate by amalgamated zinc under an argon atmosphere.

Product Analysis. Samples containing 0.3–1 mmol of $(H_2O)_5CrCH_2C_6H_5{}^{2+}$ ((5–15) × 10^{-3} M) were allowed to react to >95% completion. The organic products were determined by extraction of the aqueous reaction solution with three portions (5–10 mL) of carbon tetrachloride. The proton NMR spectra of the CCl$_4$ extracts were used to characterize the products and their relative amounts. Characteristic

resonances for bibenzyl, toluene, benzyl alcohol, and benzaldehyde are observed at 2.92 (CH$_2$), 2.34 (CH$_3$), 4.47 (CH$_2$), and 10.0 (CH) ppm, respectively, relative to internal TMS.

The inorganic products were separated on columns (8 × 1 cm) of Sephadex SP-C25 (H$^+$) after the reaction solution had been flushed with a stream of air for 1 min. Three chromium complexes were separated. A blue species is eluted with 0.5–0.6 M HClO$_4$ and was identified as Cr(OH$_2$)$_6$$^{3+}$ from its electronic spectrum. Two higher charged polymers, green-blue and green, are eluted in that order with 0.1 M HClO$_4$, and these two species also are formed as the major products in the air oxidation of aqueous Cr^{2+}. Total chromium was determined spectrophotometrically as chromate after oxidation by alkaline hydrogen peroxide.

The presence of chromium(II) in the reaction solutions was confirmed by comparison of the spectra of the solutions in the 570-nm region before and after exposure to air. If chromium(II) is present, there is a substantial increase in absorbance when it is oxidized.

Blank experiments, which relate to the homolysis product study in the absence of O$_2$, show that our procedure for the air oxidation of chromium(II) in 0.98 M NaClO$_4$ and 0.01 M HClO$_4$ yields ~15% Cr(OH$_2$)$_6$$^{3+}$ and 85% higher charged polymers. The amount of the blue-green polymer is about 35% under both conditions, and the main change is the production of more green polymer and less Cr(OH$_2$)$_6$$^{3+}$ at the higher acidity. These polymeric species are probably the bis(μ-hydroxo) and μ-hydroxo chromium(III) dimers of 4+ and 5+ charge, respectively.

Kinetic Methods. The reactions were followed by the decrease in absorbance at 358 nm recorded on a Cary 219 spectrophotometer equipped with a thermostated cell holder and standard water circulation and temperature control system. The concentrations of (H$_2$O)$_5$CrCH$_2$C$_6$H$_5$$^{2+}$ were in the range of (2–10) × 10^{-5} M, and the observations were made in 50 or 100 mm pathlength cells. An appropriate volume of the perchloric acid–sodium perchlorate reaction medium was placed in the cell, and the cell was closed with serum caps and purged for 30 min with a stream of argon that had been passed through a scrubber of aqueous chromium(II) perchlorate to remove dioxygen. Then Cr^{2+} was added if required, and the solution was equilibrated at the desired temperature before the addition of (H$_2$O)$_5$CrCH$_2$C$_6$H$_5$$^{2+}$. All reagents that are sensitive to dioxygen were handled by standard syringe techniques under an argon atmosphere.

Instrumentation. The electronic spectra were recorded on a Cary 219 spectrophotometer and the NMR spectra on a Bruker AM 300 system.

Registry No. (H$_2$O)$_5$CrCH$_2$C$_6$H$_5$$^{2+}$, 34788-74-4; chromium(II) perchlorate, 21359-99-9; benzyl bromide, 100-39-0.

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Kinetics and Mechanism of the Decomposition of Cobalt Dioxygen Complexes of the Binucleating Macrocyclic Ligand BISBAMP

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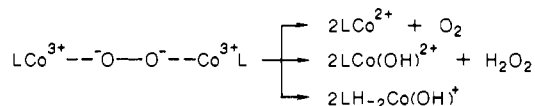
Received December 20, 1988

The kinetics of the decomposition of cobalt dioxygen complexes with the ligand 3,9,17,23,29,30-hexaaza-6,20-dioxatricyclo-[23.3.1.1^{11,15}]triaconta-1(28),11,13,15(30),25(29),26-hexaene, BISBAMP, has been studied at 50.0 °C between p[H] 9 and 12. Under these conditions, dioxygen complexes Co$_2$LO$_2$(OH)$_2$$^{2+}$ and Co$_2$LO$_2$(OH)$_3$$^+$ are present in solution and undergo irreversible metal-centered autoxidation to form Co(III) complexes. From the p[H] dependence of the observed rate constants, a mechanism is proposed in which both complexes decompose by two parallel pathways that correspond to direct aquation and base-catalyzed hydrolysis of a cobalt–dioxygen coordinate bond. Preliminary results are also described that indicate extensive dehydrogenation of BISBAMP upon reaction with Cu(I) in the presence of dioxygen.

Introduction

Cobalt dioxygen complexes have been shown to decompose according to the three processes illustrated in Scheme I for the case of a neutral pentadentate ligand L. The first process consists of the reversible decomposition of the dioxygen complex to dioxygen and the original Co(II) complex. This reaction occurs rapidly in acidic solutions for dioxygen complexes containing basic ligands, which are not usually stable at low pH. The proposed mechanism implies the formation of a mononuclear dioxygen complex intermediate, and it is essentially the inverse of the mechanism that operates for the formation of binuclear dioxygen complexes.[1,2]

Under neutral or basic conditions, cobalt dioxygen complexes are generally stable enough to be characterized, but they decompose slowly by either a metal-centered or a ligand-centered autoxidation process. Metal-centered autoxidation leads to the formation of Co(III) complexes with H$_2$O$_2$ release.[3–5] The reaction is base-catalyzed, and a mechanism has been proposed[5] in which deprotonation of a coordinated nitrogen activates the hydrolysis of the Co(III)–O$_2$ bond in a manner similar to that of the well-established dissociative conjugated-base mechanism for the base hydrolysis of Co(III) complexes. Although irreversible metal-centered autoxidation is the most common decomposition reaction of cobalt dioxygen complexes, ligand-centered oxidative

Scheme I

$$LCo^{3+}\text{---}^-O\text{---}O^-\text{---}Co^{3+}L \left\{ \begin{array}{l} 2LCo^{2+} + O_2 \\ 2LCo(OH)^{2+} + H_2O_2 \\ 2LH_{-2}Co(OH)^+ \end{array} \right.$$

dehydrogenation may occur when certain requirements are met. The process is essentially oxidative dehydrogenation of the ligand and leads to the formation of a binuclear Co(II) complex of the oxidized ligand, LH$_{-4}$ (**2**).[6] If this complex is stable it can reoxygenate to form a new dioxygen complex, but hydrolysis of the C=N bond formed in the previous step may occur to give an aldehyde with reduced complexing ability.[7,8] Ligand-centered autoxidation is also base-catalyzed, and the proposed mechanism implies the homolytic cleavage of the O–O bond. According to previous observations by Martell et al.,[5] in order that degradation occur as a ligand-centered dehydrogenation process, the C=N

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‡ Texas A&M University.