

# Kinetics of Homolysis of Substituted Benzyl Complexes of Pentaquachromium(III) and Product Variation with Substituent and Scavenger

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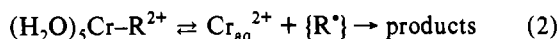
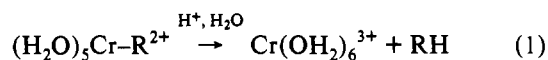
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The kinetics of homolysis have been studied for  $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{C}_6\text{H}_5^{2+}$  and derivatives with the following substituents: 4- $\text{CH}_3$ , 4-fluoro, 2,4-difluoro, 3,5-difluoro, 2-cyano, 3-cyano, and 4-cyano. The reactions have been studied in the general temperature range 20–35 °C in 0.01–0.90 M  $\text{HClO}_4$  at ionic strength 1.00 M ( $\text{NaClO}_4/\text{HClO}_4$ ). The reactions were done in the presence of several oxidizing scavengers, dioxygen, aqueous iron(III),  $(\text{NH}_3)_5\text{CoCl}^{2+}$ , and  $(\text{NH}_3)_5\text{CoBr}^{2+}$ . The homolysis rate is independent of the nature and concentration of the scavenger, and the rate constant (25 °C) changes from  $4 \times 10^{-3}$  to  $0.23 \times 10^{-3} \text{ s}^{-1}$  from the most reactive 4-methyl to the least reactive 3-cyano. This change is primarily due to a change in  $\Delta H^\ddagger$  from 26 to 30 kcal mol $^{-1}$ , while  $\Delta S^\ddagger$  is typically in the range 22–24 cal mol $^{-1} \text{ K}^{-1}$ . The organic products, identified by  $^1\text{H NMR}$ , vary considerably with the nature of the scavenger and the substituent on the benzyl ligand. With aqueous iron(III) in several systems, the products show competition between oxidation to form the alcohol and radical dimerization to give the bibenzyl derivative. From the dependence of the product distribution on the iron(III) concentration, the rate constant for oxidation of  $^{\bullet}\text{CH}_2\text{C}_6\text{H}_5$  by  $\text{Fe}(\text{OH})_2^{3+}$  is calculated to be  $1.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . With  $(\text{NH}_3)_5\text{CoBr}^{2+}$ , the more easily oxidized radicals give the alcohol, while others give a mixture of alcohol and bromide or exclusively bromide for the least oxidizable systems. However,  $(\text{NH}_3)_5\text{CoCl}^{2+}$  is different and gives only the bibenzyl derivative for all the systems.

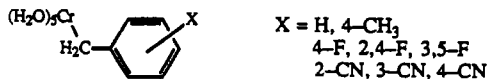
## Introduction

There is a wide range of  $\eta^1$  organometallic derivatives of pentaquachromium(III)<sup>1</sup> with the general formula  $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$ . They decompose in aqueous acid by either heterolytic (eq 1) or homolytic (eq 2) cleavage of the chromium–carbon bond,



and the rates and relative importance of these processes vary greatly with the nature of the R group. The homolysis process can be inhibited by the addition of aqueous chromium(II) which reacts rapidly with the  $\text{R}^{\bullet}$  radical to re-form the reactant. Then decomposition proceeds exclusively by the heterolytic pathway. On the other hand, scavengers can be added to irreversibly react with chromium(II) and/or  $\text{R}^{\bullet}$ . Then decomposition proceeds by both heterolysis and homolysis, and the homolytic reactivity can be determined if it is at least competitive with heterolysis.

The heterolysis of the following series of substituted benzyl derivatives of  $(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}$  has been the subject of a previous publication:<sup>2</sup>



Homolysis of the H, 4- $\text{CH}_3$ , and 4-CN complexes was studied by Nohr and Espenson,<sup>3</sup> but the kinetics were not corrected for heterolysis, and a peculiar acid dependence was suggested for the parent benzyl complex. Kita and Jordan<sup>4</sup> studied the heterolysis and spontaneous decomposition kinetics of the benzyl complex.

In the present work, the homolysis of the above series of compounds is studied, the acid dependence and activation

parameters have been determined, and organic product studies have been performed. The observation that the organic products depend on the nature of both the scavenger and the substituent on the benzyl ligand provides interesting information about the redox activity of these ligands. The interpretation of these results is aided greatly by recent electrochemical studies<sup>5</sup> of substituted benzyl radicals. In two systems, two products are formed in competitive pathways in amounts which depend on the iron(III) scavenger concentration, and this allows us to calculate rate constants for reaction of the radicals with aqueous iron(III).

## Results and Discussion

The observations from this study concern both the kinetics and the organic products of the homolysis reaction. The kinetic results are described first, because the organic products result from reactions subsequent to the rate-controlling Cr–C bond breaking.

**Kinetics.** The decomposition of the various substituted benzyl derivatives of  $(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}$  have been studied in the presence of several scavengers, dioxygen,  $(\text{NH}_3)_5\text{CoCl}^{2+}$ , aqueous iron(III), and  $(\text{NH}_3)_5\text{CoBr}^{2+}$ , with the latter two used mainly for the kinetic studies because of interferences arising from products with the other two. The temperature and acid dependence of the rate have been studied in the general range 20–35 °C and 0.01–0.9 M  $\text{H}^+$  in 1.00 M  $\text{NaClO}_4/\text{HClO}_4$ , with the chromium(III) reactant at  $(1-3) \times 10^{-5} \text{ M}$ . The decomposition was monitored spectrophotometrically at an appropriate maximum for the reactant in the 300–350-nm region. The full kinetic results are given in the supplementary material.

For all of the systems for which kinetic data are given, the decrease of absorbance with time in the presence of scavenger is first order and least-squares analysis gave the rate constant  $k_{\text{obsd}}$ . These values were corrected for heterolysis ( $k_{\text{het}}$ ) to obtain the rate constant for homolysis (eq 3). The  $k_{\text{het}}$  values were obtained

$$k_{\text{homo}} = k_{\text{obsd}} - k_{\text{het}} \quad (3)$$

by extrapolation from the activation parameters previously determined<sup>2</sup> in the 55–75 °C temperature range. This correction

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- (2) Zhang, Z.; Jordan, R. B. *Inorg. Chem.* **1993**, *32*, 5472.
- (3) Nohr, R. S.; Espenson, J. H. *J. Am. Chem. Soc.* **1975**, *97*, 3392.
- (4) Kita, P.; Jordan, R. B. *Inorg. Chem.* **1989**, *28*, 3489.

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**Table 1.** Kinetic Results for the Homolysis of (4-Cyanobenzyl)pentaquachromium(III) at 25 °C in 1.00 M HClO<sub>4</sub>/NaClO<sub>4</sub>

scavenger	[H <sup>+</sup> ], M	10 <sup>4</sup> k <sub>obsd</sub> , s <sup>-1</sup>	10 <sup>4</sup> k <sub>homo</sub> , s <sup>-1</sup>		
			obsd <sup>a</sup>	calcd <sup>b</sup>	
O <sub>2</sub> (air)	0.010	5.170	4.17	4.08	
	0.020	5.260	4.03	3.96	
	0.0298	5.225	3.85	3.88	
	0.0398	5.330	3.85	3.82	
	0.0596	5.345	3.72	3.75	
	0.0990	5.300	3.51	3.66	
	0.248	5.660	3.68	3.55	
	0.346	5.450	3.43	3.53	
	0.595	5.690	3.62	3.60	
	0.573	5.730	3.63	3.49	
	Fe(III)	0.0230	5.349	4.07	3.94
		0.0420	5.368	3.86	3.81
		0.0610	5.517	3.88	3.74
0.100		5.571	3.78	3.66	
0.241		5.742	3.77	3.56	
0.336		5.731	3.71	3.53	
0.573		5.734	3.66	3.50	
0.857		5.765	3.67	3.49	
(NH <sub>3</sub> ) <sub>5</sub> CoBr <sup>2+</sup>		0.0230	4.758	3.48	3.94
		0.0424	5.053	3.55	3.81
	0.0610	4.952	3.32	3.74	
	0.100	5.045	3.26	3.66	
	0.336	5.117	3.10	3.53	
	0.573	5.327	3.26	3.50	
0.857	5.475	3.38	3.49		

<sup>a</sup> Calculated by subtraction of the heterolysis rate constant from k<sub>obsd</sub>.

<sup>b</sup> Calculated from the rate law described in the text and ΔH<sup>\*</sup> and ΔS<sup>\*</sup> determined from the full data set and given in Table 2.

is small (<2%) for all systems except the more heterolytically reactive 2-cyano complex where it is <6% and the 4-cyano complex where it is 30 to 50%, depending on the acidity. The kinetics of the latter system are discussed separately below. For all the systems, k<sub>homo</sub> is essentially independent of the nature of the scavenger and independent of the concentration of H<sup>+</sup> except for the 4-cyano complex.

The 4-cyano complex is somewhat different because the rate law for heterolysis shows a saturation effect with [H<sup>+</sup>] described by eq 4. This rate law is consistent with pre-equilibrium

$$k_{\text{het}} = \frac{K_a k_0 + k_1 [\text{H}^+]}{K_a + [\text{H}^+]} \quad (4)$$

protonation of the complex with an acid dissociation constant (K<sub>a</sub>) and specific rate constants k<sub>0</sub> and k<sub>1</sub> for heterolysis of the unprotonated and protonated forms, respectively. The temperature dependence of these values was determined<sup>2</sup> between 25 and 43 °C, and K<sub>a</sub> = 3.15 × 10<sup>-2</sup> M at 25 °C. Then one would expect the homolysis to show a similar saturation effect with [H<sup>+</sup>], but k<sub>homo</sub> appears to be almost independent of [H<sup>+</sup>] as can be seen from representative results at 25 °C in Table 1. The kinetic observations for the heterolysis and homolysis seem to be internally consistent only if the rate constants for homolysis of the unprotonated (k<sub>0</sub><sup>o</sup>) and protonated (k<sub>1</sub><sup>o</sup>) forms are almost identical. Inspection of all of the data reveals that there is a small trend to higher values of k<sub>homo</sub> at lower acidity. The temperature and [H<sup>+</sup>] dependencies of k<sub>homo</sub> have been fitted to the form of eq 4 with k<sub>0</sub><sup>o</sup> and k<sub>1</sub><sup>o</sup> replacing k<sub>0</sub> and k<sub>1</sub>, respectively, and K<sub>a</sub> fixed at values determined from the heterolysis study. It has been possible to extract values of k<sub>0</sub><sup>o</sup> and k<sub>1</sub><sup>o</sup> and their temperature dependence as given in Table 2.

The rate constants and activation parameters for all the systems are summarized in Table 2. The values are given independently for the two scavengers, Fe(III) and (NH<sub>3</sub>)<sub>5</sub>CoBr<sup>2+</sup>, to show that there are no substantial or persistent differences. The rate constants at 25 °C change by about a factor of 20 from the most

reactive 4-methyl to the least reactive 3-cyano system, and this is largely due to a small increase in ΔH<sup>\*</sup> from about 26 to 30 kcal mol<sup>-1</sup> with ΔS<sup>\*</sup> values of ~22 cal mol<sup>-1</sup> K<sup>-1</sup>. Large positive ΔS<sup>\*</sup> values are typical of homolysis reactions<sup>1</sup> of (H<sub>2</sub>O)<sub>5</sub>Cr-R<sup>2+</sup> complexes. The rate constants for the 4-methyl and benzyl complexes are in reasonable agreement with the values of 3.7 × 10<sup>-3</sup> and 2.6 × 10<sup>-3</sup> s<sup>-1</sup> determined by Nohr and Espenson.<sup>3</sup> Their value of 5.56 × 10<sup>-4</sup> s<sup>-1</sup> for the 4-cyano complex is consistent with our k<sub>obsd</sub> values (Table 1), but they were unaware of the substantial heterolysis correction so that the true homolysis rate constants are smaller.

Nohr and Espenson noted a correlation of k<sub>homo</sub> and the Hammett substituent constant σ. The latter are also given in Table 2, and the correlation now is not as good with the expanded and corrected data base and the inclusion of ortho- and meta-substituted systems. If the results of Nohr and Espenson for the 4-bromo and 4-(trifluoromethyl) complexes are included, it appears that the 3-cyano and 3,5-difluoro complexes are reacting too slowly and the 2-cyano complex reacts too fast. If the latter three systems are excluded, one finds log(k<sub>homo</sub>) = -2.62 - 1.06σ (r = 0.985). For the three deviant systems, the predicted and observed rate constants differ by about a factor of 2.

It is interesting to note that the stability of the benzyl radical does not seem to be a determining factor in the homolysis rate. Various measures of substituted benzyl radical stability<sup>6,7</sup> (σ\* values)<sup>8</sup> indicate that, relative to the benzyl radical, the 3-cyano should be less stable and the 4-cyano more stable. If the stability of the radical were contributing significantly to the stability of the transition state, one would expect the 4-cyano complex to homolyze more rapidly and the 3-cyano complex less rapidly than the benzyl. This is certainly not true.

There is a reasonable correlation of the rate constants for heterolysis and homolysis of these benzyl systems. For six of the eight systems in Table 2, log(k<sub>homo</sub>) = 5.46 + 1.51 log(k<sub>het</sub>) (r = 0.985; k<sub>het</sub> is the H<sup>+</sup> independent value; rate constants at 25 °C). This implies that the strength of the Cr-C bond is important for both processes. The two exceptions to this correlation are the 2-cyano and 4-cyano complexes which undergo heterolysis faster than predicted by 10 and 50 times, respectively. The larger heterolysis rates were attributed<sup>2</sup> to delocalization of negative charge from CH<sub>2</sub> onto the CN substituent thereby weakening the Cr-C bond. For homolysis, this effect may be attenuated if homolysis is viewed as also involving electron transfer from the R- ligand to Cr<sup>III</sup>. The electron transfer would be disfavored by delocalization.

It was noted above that dioxygen and (NH<sub>3</sub>)<sub>5</sub>CoCl<sup>2+</sup> were not used regularly as scavengers for the kinetic studies because of product interference. For (NH<sub>3</sub>)<sub>5</sub>CoCl<sup>2+</sup>, the bibenzyl product tends to precipitate during the kinetic runs, and this scavenger could only be used with the cyano derivatives. With dioxygen, we often observed that the first-order rate constant appeared to be somewhat wavelength dependent in the 280–320-nm region. This was especially a problem for the cyano systems whose absorbance maxima<sup>2</sup> are below 320 nm. The problem is due to a second process which is clearly manifested by observations in the 240–260-nm region, which show an initial increase in absorbance followed by a decrease. We have made some attempt to deconvolute these processes by fitting absorbance-time data at four wavelengths (typically 244, 256, 284, and 316 nm) to a biphasic model. The general conclusion is that the faster process is homolysis as judged from the correspondence of the rate constant to that with other scavengers (see Table 1) and from wavelengths

(6) Dust, J. M.; Arnold, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 1221.

(7) Fisher, T. H.; Meierhoefer, A. W. *J. Org. Chem.* **1978**, *43*, 224. Fisher, T. H.; Dershem, S. M.; Prewitt, M. L. *J. Org. Chem.* **1990**, *55*, 1040.

(8) Tokumura, K.; Ozaki, T.; Nosaka, H.; Saigusa, Y.; Itoh, M. *J. Am. Chem. Soc.* **1991**, *113*, 4974. These authors found that the reactivity of substituted benzyl radicals with O<sub>2</sub> is correlated by the σ\* values of ref 7.

**Table 2.** Summary of the Rate Constants and Activation Parameters for the Homolysis of Substituted Benzyl Complexes of Pentaquachromium(III)

substituent	scavenger	Hammett $\sigma$	$10^3 k_{\text{homo}}$ , s <sup>-1</sup> (25 °C) <sup>a</sup>	$\Delta H^\ddagger$ , kcal mol <sup>-1</sup> <sup>b</sup>	$\Delta S^\ddagger$ , cal mol <sup>-1</sup> K <sup>-1</sup> <sup>b</sup>
4-methyl	(NH <sub>3</sub> ) <sub>5</sub> CoBr <sup>2+</sup>	-0.14	4.05	27.1 ± 1.0	21.5 ± 3.3
	Fe(III)		4.15	25.9 ± 0.6	17.3 ± 2.0
-H	(NH <sub>3</sub> ) <sub>5</sub> CoBr <sup>2+</sup>	0	2.07	27.3 ± 1.2	20.6 ± 4.0
	Fe(III)		2.03	26.9 ± 0.5	19.3 ± 1.6
4-fluoro	(NH <sub>3</sub> ) <sub>5</sub> CoBr <sup>2+</sup>	0.06	1.87	27.6 ± 1.1	21.6 ± 3.7
	Fe(III)		1.78	27.3 ± 0.9	20.4 ± 3.1
2,4-difluoro	(NH <sub>3</sub> ) <sub>5</sub> CoBr <sup>2+</sup>	0.60	0.516	28.3 ± 0.5	21.2 ± 1.7
	Fe(III)		0.498	28.9 ± 1.4	23.4 ± 4.5
3,5-difluoro	(NH <sub>3</sub> ) <sub>5</sub> CoBr <sup>2+</sup>	0.68	0.278	28.7 ± 1.0	21.6 ± 3.2
3-cyano	(NH <sub>3</sub> ) <sub>5</sub> CoBr <sup>2+</sup>	0.62	0.223	30.0 ± 1.2	25.5 ± 4.0
	Fe(III)		0.249	29.3 ± 1.4	23.1 ± 4.6
2-cyano	(NH <sub>3</sub> ) <sub>5</sub> CoBr <sup>2+</sup>	1.06	0.346	29.1 ± 0.7	23.2 ± 2.4
	Fe(III)		0.377	29.3 ± 1.3	23.9 ± 4.3
4-cyano <sup>c</sup>	(NH <sub>3</sub> ) <sub>5</sub> CoCl <sup>2+</sup>	0.70	0.369	29.0 ± 0.6	23.1 ± 2.0
	Fe(III), (NH <sub>3</sub> ) <sub>5</sub> CoBr <sup>2+</sup>		0.428 ( <i>k</i> <sub>0</sub> <sup>o</sup> )	30.6 ± 0.4	28.6 ± 3.2
	Fe(III), (NH <sub>3</sub> ) <sub>5</sub> CoBr <sup>2+</sup>		0.346 ( <i>k</i> <sub>1</sub> <sup>o</sup> )	30.1 ± 0.3	26.6 ± 2.0

<sup>a</sup> Calculated from the  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for each scavenger. <sup>b</sup> Calculated for each scavenger; errors are 95% confidence limits. <sup>c</sup> The data for the two scavengers were analyzed together to determine *k*<sub>0</sub><sup>o</sup> and *k*<sub>1</sub><sup>o</sup>.

**Table 3.** Chemical Shifts of Diagnostic Proton Resonances in the Organic Reaction Products

reactant substituent	product functional group <sup>a</sup>				
	CH <sub>3</sub>	C <sub>2</sub> H <sub>4</sub>	HCO	CH <sub>2</sub> OH <sup>d</sup>	CH <sub>2</sub> Br
4-methyl	2.31 <sup>b</sup>	2.87	9.96 <sup>b</sup>	4.60 (2.16)	4.52 <sup>c</sup>
H	2.35 <sup>c</sup>	2.95 <sup>c</sup>	10.03 <sup>c</sup>	4.70 (1.77) <sup>c</sup>	4.51 <sup>c</sup>
4-fluoro	2.35	2.87	9.96	4.65 (1.93)	4.48 <sup>c</sup>
2,4-difluoro	2.24	2.88	10.28 <sup>c</sup>	4.72 (1.70)	4.49 <sup>c</sup>
3,5-difluoro	2.35	2.89	9.95 <sup>c</sup>	4.67 (2.07) <sup>c</sup>	4.40 <sup>c</sup>
2-cyano	2.58 <sup>b</sup>	3.17	10.34 <sup>b</sup>		4.64 <sup>c</sup>
3-cyano	2.39 <sup>b</sup>	2.97	10.05 <sup>b</sup>		4.47 <sup>c</sup>
4-cyano	2.41 <sup>b</sup>	3.00	10.11 <sup>b</sup>		4.48 <sup>c</sup>

<sup>a</sup> Chemical shifts in ppm relative to internal TMS in CDCl<sub>3</sub>. <sup>b</sup> Identified by comparison to data for the compound in the Aldrich compilation. <sup>c</sup> Identified by comparison to spectra of commercial samples. <sup>d</sup> OH values in parentheses.

in the 350–360 range. The second process has  $k \approx 2 \times 10^{-4}$  s<sup>-1</sup> at 25 °C for both the 2- and 4-cyano complexes, and we suspect that this process involves decomposition of CrO<sub>2</sub><sup>2+</sup> (formed from Cr<sup>2+</sup> + O<sub>2</sub>; see below), because the rates we observe are quite similar to those indicated by the absorbance–time curves reported by Brynildson, Bakac, and Espenson<sup>9</sup> for the decomposition of CrO<sub>2</sub><sup>2+</sup> in the presence of dioxygen. In addition, CrO<sub>2</sub><sup>2+</sup> has significant absorbance at the  $2 \times 10^{-5}$  M concentrations of this study and in the 240–300-nm range where we observe these complications. These are not ideal systems for studying CrO<sub>2</sub><sup>2+</sup> because of the absorbance of the aromatic products, but homolysis of other Cr–R complexes could be adapted to the preparation of CrO<sub>2</sub><sup>2+</sup> because it avoids the presence of excess Cr(II) which leads to decomposition of CrO<sub>2</sub><sup>2+</sup>.

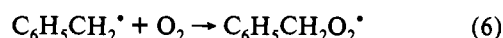
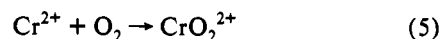
**Organic Products.** These products have been identified by <sup>1</sup>H NMR after extraction into chloroform, as described in the Experimental Section, and relative amounts have been determined from the integrated NMR intensities. The chemical shifts of the most diagnostic protons for each product are given in Table 3. The reactions were done in 0.10 M HClO<sub>4</sub> with (1.8–3.2) × 10<sup>-3</sup> M chromium and the oxidant concentration varied typically in the range 3–15 times the chromium, except for the air-saturated solutions with an O<sub>2</sub> concentration of  $\sim 3 \times 10^{-4}$  M. The stoichiometry with respect to the oxidant scavenger has been determined for (NH<sub>3</sub>)<sub>5</sub>CoCl<sup>2+</sup>, aqueous iron(III), and (NH<sub>3</sub>)<sub>5</sub>CoBr<sup>2+</sup>.

The product results are summarized in Table 4, and the stoichiometry results are given in the supplementary material. The stoichiometries are consistent with the product results and are close to 2 mol of scavenger/mol of chromium, unless bibenzyl

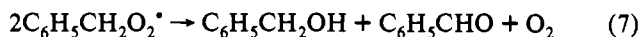
is formed when the ratio reduces to 1:1 in the limit of 100% bibenzyl formation. The results are ordered in Table 4 in such a way as to show trends in the type and percentage of products.

Scavenging with dioxygen is the simplest experiment to carry out, but there are problems because of the limited solubility of O<sub>2</sub> in water<sup>10</sup> ( $\sim 1.6 \times 10^{-3}$  M at 1 atm O<sub>2</sub>). This may make dissolved dioxygen in deficiency at chromium concentrations and solution volumes compatible with product recovery. Bubbling O<sub>2</sub> or air through the solution risks removal of volatile products such as benzaldehyde.

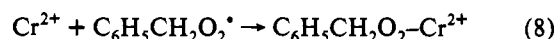
Dioxygen gives the aldehyde as the major product in all cases, but there is a substantial amount of alcohol with the 4-methyl complex, equal amounts (9%) of bibenzyl and alcohol from the benzyl complex, and small amounts (5–10%) alcohol in three other systems. The potential diversity of reactions makes an explanation of the products problematic. The primary homolysis products are expected to react with O<sub>2</sub> via reactions 5 and 6, with  $k > 1 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup>.<sup>8,11,12</sup> The CrO<sub>2</sub><sup>2+</sup> species is relatively stable<sup>9</sup>



at modest concentrations, and the benzyl peroxy radical is much more reactive. The standard chemistry of the peroxy radical<sup>12,13</sup> suggests that it would undergo the equivalent of disproportionation (eq 7). The formation of small amounts of alcohol relative to aldehyde, rather than equal amounts, implies that disproportionation is generally a minor pathway.



Direct reaction of Cr<sup>2+</sup> and the peroxy radical (eq 8) appears unlikely because it involves a bimolecular reaction between



transient intermediates. However, at the rather low O<sub>2</sub> concentrations, this reaction could be competitive with eq 5, since the peroxy radical might recombine with its parent Cr<sup>2+</sup> before the latter reacts with a second O<sub>2</sub>. The chromium(III) organoperoxy

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

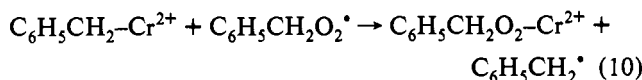
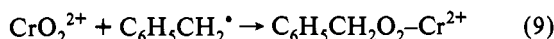
(9) Brynildson, M. E.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 4579.

**Table 4.** Summary of Products with Various Scavengers for Homolysis of Substituted Benzylpentaquachromium(III) Complexes in 0.10 M HClO<sub>4</sub> at Ambient Temperature Where Products Are the Corresponding Bibenzyl ((PhCH<sub>2</sub>)<sub>2</sub>), Alcohol (PhCH<sub>2</sub>OH), Aldehyde (PhCHCO), Bromide (PhCH<sub>2</sub>Br), and Methyl (PhCH<sub>3</sub>) Derivatives, with Percentages Given in Parentheses

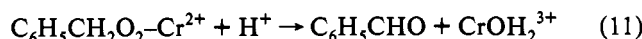
substituent	scavenger			
	(NH <sub>3</sub> ) <sub>5</sub> CoCl <sup>2+</sup>	(NH <sub>3</sub> ) <sub>5</sub> CoBr <sup>2+</sup>	Fe(III)	O <sub>2</sub> (~700 mm)
4-methyl	(PhCH <sub>2</sub> ) <sub>2</sub> (100)	PhCH <sub>2</sub> OH (100)	PhCH <sub>2</sub> OH (100)	PhCHCO (70) PhCH <sub>2</sub> OH (30)
4-fluoro	(PhCH <sub>2</sub> ) <sub>2</sub> (100)	PhCH <sub>2</sub> OH (100)	PhCH <sub>2</sub> OH (100)	PhCHCO (95) PhCH <sub>2</sub> OH (5)
-H	(PhCH <sub>2</sub> ) <sub>2</sub> (100)	PhCH <sub>2</sub> OH (>98) <sup>a</sup> (PhCH <sub>2</sub> ) <sub>2</sub> (<2)	PhCH <sub>2</sub> OH (70-98) <sup>b</sup> (PhCH <sub>2</sub> ) <sub>2</sub> (30-2)	PhCH <sub>2</sub> OH (9) PhCHCO (82) (PhCH <sub>2</sub> ) <sub>2</sub> (9)
2,4-difluoro	(PhCH <sub>2</sub> ) <sub>2</sub> (100)	PhCH <sub>2</sub> OH (100)	PhCH <sub>2</sub> OH (51-85) <sup>b</sup> (PhCH <sub>2</sub> ) <sub>2</sub> (49-15)	PhCHCO (92) PhCH <sub>2</sub> OH (8) PhCHCO (91)
3,5-difluoro	(PhCH <sub>2</sub> ) <sub>2</sub> (100)	PhCH <sub>2</sub> OH (52-47) <sup>b</sup> PhCH <sub>2</sub> Br (45-53) (PhCH <sub>2</sub> ) <sub>2</sub> (3-0)		PhCH <sub>2</sub> OH (9) PhCHCO (>98) <sup>a</sup> (PhCH <sub>2</sub> ) <sub>2</sub> (<2)
2-cyano	(PhCH <sub>2</sub> ) <sub>2</sub> (100)	PhCH <sub>2</sub> Br (>97) <sup>a</sup> (PhCH <sub>2</sub> ) <sub>2</sub> (<2)	(PhCH <sub>2</sub> ) <sub>2</sub> (100)	PhCHCO (>98) <sup>a</sup> (PhCH <sub>2</sub> ) <sub>2</sub> (<2)
3-cyano	(PhCH <sub>2</sub> ) <sub>2</sub> (100)	PhCH <sub>2</sub> Br (96) (PhCH <sub>2</sub> ) <sub>2</sub> (4)	(PhCH <sub>2</sub> ) <sub>2</sub> (100)	PhCHCO (>98) <sup>a</sup> (PhCH <sub>2</sub> ) <sub>2</sub> (<2)
4-cyano	(PhCH <sub>2</sub> ) <sub>2</sub> (92) PhCH <sub>3</sub> (8)	PhCH <sub>2</sub> Br (92) PhCH <sub>3</sub> (8)	(PhCH <sub>2</sub> ) <sub>2</sub> (76-80) PhCH <sub>3</sub> (24-20)	PhCHCO (95) PhCH <sub>3</sub> (5)

<sup>a</sup> Small amounts of the minor product could not be quantified. <sup>b</sup> The product distribution varies with increasing oxidant concentration in the direction given.

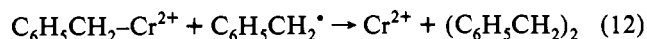
complex product of eq 8 could form in other ways, such as eq 9.



But this does not seem to be highly important because our observations indicate that CrO<sub>2</sub><sup>2+</sup> is decomposing at its normal spontaneous rate as a product of the homolysis. Another pathway for producing this complex is given by eq 10, which is analogous to that proposed by Ryan and Espenson<sup>14</sup> for the Cr-(isopropyl)<sup>2+</sup> + O<sub>2</sub> system. In any event, the peroxy complex could decompose to aldehyde via eq 11. These reactions can account for the aldehyde and alcohol products.



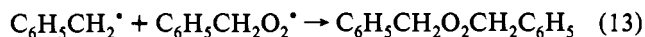
The formation of 9% bibenzyl by the parent benzyl complex and the traces of analogous products with the 2- and 3-cyano complexes requires further explanation. This would normally be explained by dimerization of two benzyl radicals, but the low concentrations and short lifetimes of these radicals in the presence of dioxygen makes dimerization unlikely. Although Nohr and Espenson<sup>3</sup> reported no bibenzyl from this reaction, Kita and Jordan<sup>4</sup> found 10%, in agreement with the 9% found in this study. Kita and Jordan suggested that the bibenzyl might form by eq 12 in competition with scavenging by O<sub>2</sub>. However, we must



withdraw this possibility because it has untenable implications for other scavengers. For example, (NH<sub>3</sub>)<sub>5</sub>CoCl<sup>2+</sup> gives exclusively bibenzyl, but if this were formed exclusively by reaction 12, then the homolysis rate constant should be twice that with other oxidants which do not yield bibenzyl because eq 12 results in the loss of 2 mol of reactant per homolysis event. In fact, Nohr and Espenson found the same rate constant for the benzyl complex with (NH<sub>3</sub>)<sub>5</sub>CoCl<sup>2+</sup> and iron(III), and we observe the same result with several substituted benzyl complexes. We now suspect that the bibenzyl may form at very low O<sub>2</sub> concentrations, such as

toward the end of the reaction, or trace amounts are introduced during handling of the stock reactant solutions.

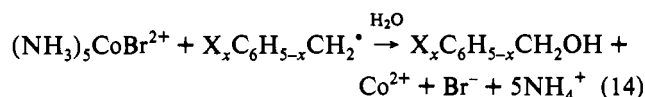
It should be noted that we also observed small (<5%) and variable amounts of a product with an <sup>1</sup>H resonance near 4.9 ppm. This is tentatively assigned to the dibenzyl peroxide derivative, for which the parent benzyl compound has the CH<sub>2</sub> resonance at 4.83 ppm in CCl<sub>4</sub>.<sup>15</sup> This could form by reaction 13. More of this product, relative to bibenzyl, is formed with air



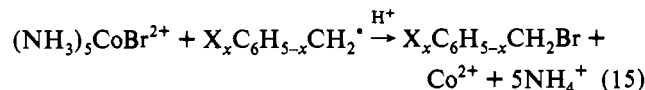
compared to pure O<sub>2</sub> as the scavenger source. This indicates that dimerization of the benzyl radical is competitive with reaction 6 at typical O<sub>2</sub> concentrations.

Homolysis in the presence of (NH<sub>3</sub>)<sub>5</sub>CoCl<sup>2+</sup> always proceeds with production of one cobalt(II) per chromium and produces only the bibenzyl derivative. The latter must form by dimerization of two X<sub>x</sub>C<sub>6</sub>H<sub>5-x</sub>CH<sub>2</sub><sup>\*</sup> radicals, and this process must be more efficient than oxidation of the radical by (NH<sub>3</sub>)<sub>5</sub>CoCl<sup>2+</sup>. Nohr and Espenson also found only bibenzyl from the reaction of (NH<sub>3</sub>)<sub>5</sub>CoCl<sup>2+</sup> and Cr-CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub><sup>2+</sup>.

Rather surprisingly, just changing the oxidant to (NH<sub>3</sub>)<sub>5</sub>CoBr<sup>2+</sup> gives entirely different products, and the stoichiometry is always two cobalt(II) produced per chromium. The first four complexes in Table 4 give >98% alcohol, indicating that (NH<sub>3</sub>)<sub>5</sub>CoBr<sup>2+</sup> oxidizes these radicals effectively in competition with dimerization. The oxidized radical, X<sub>x</sub>C<sub>6</sub>H<sub>5-x</sub>CH<sub>2</sub><sup>\*</sup> will react with water to give the alcohol, with the overall reaction of eq 14.



With the 3,5-difluoro complex, the situation becomes more complex and the products are on average 50% alcohol and 50% organic bromide. This implies that outer-sphere (eq 14) and inner-sphere (eq 15) oxidations are competitive processes for the



3,5-difluorobenzyl radical. The cyano-substituted benzyis all give

(14) Ryan, D. A.; Espenson, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 704.

(15) Ward, G. A.; Mair, R. D. *Anal. Chem.* **1969**, *41*, 538.

**Table 5.** Summary of Products and Stoichiometry for Systems Where Product Distribution Depends on the Iron(III) Oxidant Concentration in 0.10 M HClO<sub>4</sub> at Ambient Temperature

substituent	10 <sup>3</sup> [Cr-R <sup>2+</sup> ], M	10 <sup>3</sup> [Fe(III)], M	[Fe(II)]/[Cr] <sup>a</sup>	% ROH <sup>b</sup>	
				obsd <sup>c</sup>	calcd <sup>d</sup>
-H	3.10	9.30	1.72 <sup>e</sup>	70 (72)	73.3
	3.10	18.6	1.90	88 (90)	88.8
	3.10	27.9	2.02	>98 (100)	94.1
2,4-difluoro	3.20	9.60	1.50	51 (50)	50.7
	3.20	19.2	1.68	f (68)	71.4
	3.20	28.8	1.80	85 (80)	81.9

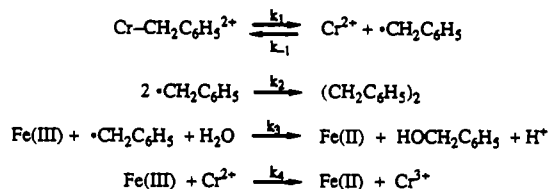
<sup>a</sup> Stoichiometry ratio of Fe(II) produced to initial Cr-R. <sup>b</sup> The other product is the bibenzyl derivative as given in Table 4. <sup>c</sup> Values from NMR integration of CHCl<sub>3</sub> extracts and values predicted from the stoichiometry ratio in parentheses. <sup>d</sup> Calculated from Scheme 1 with rate constants given in the text. <sup>e</sup> Experiments in 0.44 and 0.94 M HClO<sub>4</sub> gave only slightly different ratios of 1.71 and 1.68, respectively. <sup>f</sup> Products were not determined by NMR.

the bromide as the dominant product. Espenson and co-workers have reported that the cyclopentyl<sup>16</sup> and isopropyl<sup>14</sup> radicals also react with (NH<sub>3</sub>)<sub>5</sub>CoBr<sup>2+</sup> by an inner-sphere mechanism, and the ethyl radical<sup>17</sup> reacts with both (NH<sub>3</sub>)<sub>5</sub>CoBr<sup>2+</sup> and (NH<sub>3</sub>)<sub>5</sub>-CoCl<sup>2+</sup> by this mechanism. The ethyl radical reacts 6.4 × 10<sup>-3</sup> more slowly with (NH<sub>3</sub>)<sub>5</sub>CoCl<sup>2+</sup> than with (NH<sub>3</sub>)<sub>5</sub>CoBr<sup>2+</sup>, and this reactivity difference might explain the lack of an inner-sphere product with (NH<sub>3</sub>)<sub>5</sub>CoCl<sup>2+</sup>.

The lack of outer-sphere reactivity of (NH<sub>3</sub>)<sub>5</sub>CoCl<sup>2+</sup> is more difficult to rationalize. With typical outer-sphere reductants such as Cr(bipy)<sub>3</sub><sup>2+</sup> and Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>, (NH<sub>3</sub>)<sub>5</sub>CoCl<sup>2+</sup> has about a 7 times smaller rate constant than (NH<sub>3</sub>)<sub>5</sub>CoBr<sup>2+</sup>. Simple Marcus theory<sup>18</sup> implies that a similar reactivity difference would be expected for reducing agents, such as the benzyl radicals. However, the more detailed analysis described below indicates that (NH<sub>3</sub>)<sub>5</sub>CoCl<sup>2+</sup> is at least 10<sup>3</sup> times less reactive than (NH<sub>3</sub>)<sub>5</sub>-CoBr<sup>2+</sup> with the benzyl radicals.

With aqueous iron(III) as the oxidant, the products indicate that the first two radicals in Table 4 undergo outer-sphere oxidation. For the benzyl and 2,4-difluorobenzyl radicals, oxidation and dimerization are competitive processes and product distribution varies with the oxidant concentration. These results are analyzed further below. The last four species in Table 4 give only dimerization. This pattern seems consistent with the thermodynamic oxidizability trends of the radicals, based on the polarographic data in acetonitrile.<sup>5</sup> However, these data give the reduction potential of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub><sup>•</sup> as 0.73 V (in acetonitrile vs SCE), which can be converted<sup>19</sup> to ~0.98 V vs the NHE. On this basis, Fe(OH<sub>2</sub>)<sub>6</sub><sup>3+</sup>, with an E° ≈ 0.75 V, should not be able to oxidize C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub><sup>•</sup>. The same argument applies to the 4-fluoro system for which E° = 0.73 V (in acetonitrile vs SCE). The E° values for the 3- and 4-cyano systems<sup>5</sup> are > 1 V, and these radicals should not be oxidized by Fe(OH<sub>2</sub>)<sub>6</sub><sup>3+</sup>, consistent with the products. A more realistic analysis should take into account that solvation will make the carbocations less reducible in water than in acetonitrile, so that the E° values in acetonitrile, corrected to the NHE scale, are all too positive. In fact, it appears that this correction (~0.25 V) is about the magnitude which the solvation contribution makes, so that E° vs SCE in acetonitrile may be about the correct value in water vs NHE.

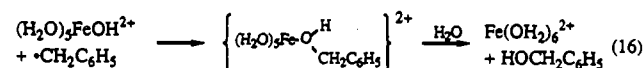
For the reaction of iron(III) with the benzyl and 2,4-difluorobenzyl complexes, the product distribution depends on the iron(III) concentration, and further details are given in Table 5. It should be noted that the isolated product ratio agrees with that predicted from the stoichiometry also given in Table 5. These

**Scheme 1**

observations can be understood from Scheme 1 as due to competition between dimerization ( $k_2$ ) and oxidation ( $k_3$ ) since higher iron(III) concentrations give more of the alcohol oxidation product and the thermodynamically more oxidizable benzyl gives more oxidation. To quantitatively analyze the system, we have used numerical integration based on the reactions in Scheme 1. The known rate constants are  $k_1 = k_{\text{homol}}$ , determined in this work and  $k_4$ , determined by Dulz and Sutin.<sup>20</sup> The colligation rate constant  $k_{-1}$  is  $8.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>21</sup> The rate constant  $k_2$  for the benzyl radical ( $-\text{d}[R^{\bullet}]/\text{dt} = 2k_2[R^{\bullet}]^2$ ) has been determined as  $1.5 \times 10^9$  (aqueous 0.1 M *tert*-butyl alcohol),<sup>22</sup>  $2.5 \times 10^9$  (aqueous *tert*-butyl alcohol, pH 7.5),<sup>23</sup> and  $1.35 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (aqueous 0.2 M *tert*-butyl alcohol, pH 7.0).<sup>24</sup> We have used  $1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  as a reasonable estimate for  $k_2$ .

The product distributions have been calculated for the various concentration conditions with the assumption that  $k_2$  and  $k_{-1}$  are the same for the benzyl and 2,4-difluorobenzyl radicals and that only  $k_3$  is different. Reasonable agreement of calculated and experimental values can be obtained, as shown by the results in Table 5, with  $k_3$  values of  $1.8 \times 10^4$  and  $2.9 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  for the benzyl and 2,4-difluorobenzyl radicals, respectively.

It seems likely that oxidation of a radical by aqueous iron(III) to give an alcohol is an outer-sphere reaction. However, there is a potential inner-sphere pathway involving hydrolyzed iron(III) with OH<sup>-</sup> acting as the bridging ligand, as shown in eq 16.



If alcohol is the only product, it is difficult to test this possibility because one needs to measure directly the rate of reaction 16 as a function of [H<sup>+</sup>]. However, with oxidation and dimerization in competition, as for the benzyl radical, the fraction of alcohol product should decrease with increasing acidity if the inner-sphere pathway (eq 16) is operative. We find that the products, as judged

(16) Espenson, J. H.; Connolly, P.; Meyerstein, D.; Cohen, H. *Inorg. Chem.* **1983**, *22*, 1009.

(17) Kelley, D. G.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1990**, *29*, 4996.

(18) Marcus, R. A. *Ann. Rev. Phys. Chem.* **1964**, *15*, 155.  $k_{12} = (k_{11}k_{22}K_{12})^{1/2}$ , where  $\log f = (\log K_{12})/(4 \log(k_{11}k_{22}Z^{-2}))$  and the symbols have the usual meaning. We have assumed  $Z = 2 \times 10^{10}$  and  $k_{11} = 6 \times 10^{-3}$  for the Fe<sup>III</sup>/Fe<sup>II</sup> reactions, based on the correlation found by Bernhard, P.; Sargeson, A. M. *Inorg. Chem.* **1987**, *22*, 2557.

(19) Andrieux, C. P.; Le Gorand, A.; Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 6892.

(20) Dulz, G.; Sutin, N. *J. Am. Chem. Soc.* **1964**, *86*, 829.  $k_4 = 2.3 \times 10^3 + 5.6 \times 10^3[\text{H}^+]^{-1}$ .

(21) Blau, R. J.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1984**, *23*, 3526.

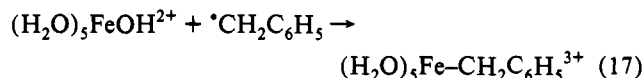
(22) Christensen, H. C.; Schested, K.; Hart, E. J. *J. Phys. Chem.* **1973**, *77*, 983.

(23) Mittal, J. P.; Hayon, E. *J. Phys. Chem.* **1974**, *78*, 1790. The rate constant from this study may be too large because the molar extinction coefficient of the benzyl radical was taken as almost two times larger than in refs 22 and 24.

(24) Horii, H.; Fujita, S.; Mori, T.; Satsuo, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3099.

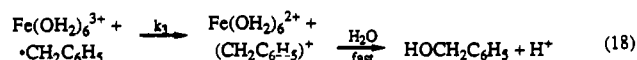
from the stoichiometry, do not vary when the  $[H^+]$  is changed from 0.10 to 0.94 M (see footnote to Table 5). Therefore eq 16 is not operative for these systems.

Another possible inner-sphere mechanism is shown by eq 17. This is an example of what Espenson<sup>25</sup> has called a colligation



reaction, although it has aspects of an oxidative addition and formally gives an Fe(IV) complex of the benzyl anion. Such reactions are observed for M(II) ions (Cr(II),<sup>1</sup> V(II),<sup>26</sup> Co(II) complexes,<sup>27,28</sup> Fe(II)-NTA complexes,<sup>28</sup> Ni(II) complexes<sup>25</sup>) which have a normally accessible M(III) oxidation state. They also have been observed for aqueous Cu(II)<sup>29,30</sup> and some of its complexes.<sup>31</sup> The reaction of aqueous Cu(II) with the benzyl radical<sup>30</sup> has  $k = 2.1 \times 10^7 M^{-1} s^{-1}$ , and the  $(Cu^{III}-CH_2C_6H_5)^{2+}$  product decomposes to benzyl alcohol and Cu(I), rather than Cu(III) and toluene. Cohen and Meyerstein<sup>28</sup> have suggested that the NTA ligand is necessary in the Fe(II) system, for example, because it labilizes the coordinated water for substitution and reduces the oxidation potential for the M(III)/M(II) couple. The modest water exchange rate of  $Fe(OH_2)_6^{3+}$  ( $k_{ex} = 1.6 \times 10^2 s^{-1}$ , 25 °C)<sup>32</sup> and the fact that  $Fe(OH_2)_6^{4+}$  is unknown make eq 17 an unattractive alternative. One would have expected this pathway to show an  $[H^+]^{-1}$  dependence because of the greater lability of  $(H_2O)_5FeOH^{2+}$  ( $k_{ex} = 1.2 \times 10^5 s^{-1}$ , 25 °C),<sup>32</sup> but the amount of alcohol formed from the decomposition of the product of eq 17 shows no  $[H^+]$  dependence, as already noted. Furthermore, the more oxidizing radicals, such as 4-cyanobenzyl compared to 4-fluorobenzyl,<sup>5</sup> should favor eq 17 and produce more alcohol, but the opposite is actually observed.

One is left with the outer-sphere oxidation mechanism of eq 18 as the most probable source of the alcohol product. This can be tested by using Marcus theory<sup>18</sup> to estimate the rate constant  $k_3$ , which will be the rate-controlling process in eq 18. If one



assumes that  $k_{22}$ , the electron exchange rate constant for  $PhCH_2^{\cdot} + PhCH_2^+$ , is  $1 \times 10^9 M^{-1} s^{-1}$  and that the  $E^\circ$  values in acetonitrile (vs SCE) are equal to the values in water (vs NHE), then  $k_3$  ( $=k_{12}$ )<sup>18</sup> is calculated to be  $0.4 \times 10^4 M^{-1} s^{-1}$ , in reasonable agreement with  $1.8 \times 10^4$  calculated from the product distribution. Similar calculations for the 4-methyl and 3-CN radicals give  $k_3$  values of  $2.6 \times 10^5$  and  $2.7 M^{-1} s^{-1}$ , respectively. These are consistent with >99% oxidation of the former and >99% bibenzyl formation in the latter.

If the outer-sphere mechanism is also operative for  $Co(NH_3)_5Br^{2+}$ , then the dominant or substantial formation of alcohol compared to bibenzyl for the first four substituents in Table 4 implies that it oxidizes these radicals with  $k_3 > 1 \times 10^5 M^{-1} s^{-1}$ , assuming that the rate constant for bibenzyl formation is essentially independent of the substituent. The situation changes at the 3,5-difluoro complex which yields similar amounts of alcohol and bromide and small to negligible amounts of bibenzyl

derivative. This requires that the rate constants for the outer-sphere and inner-sphere reactions are  $\sim 3 \times 10^4 M^{-1} s^{-1}$ . Then for the more difficult to oxidize cyano systems, only the inner-sphere product is observed.

The same analysis applied to the results with  $Co(NH_3)_5Cl^{2+}$  indicates that  $k_3 \leq 10^2 M^{-1} s^{-1}$  in order to explain the absence of oxidation product, and the inner-sphere rate constant must be of the same or smaller magnitude to explain the absence of inner-sphere product. Therefore, for the most easily oxidized 4-methylbenzyl radical,  $Co(NH_3)_5Cl^{2+}$  is at least  $10^3$  times less reactive than  $Co(NH_3)_5Br^{2+}$ . This may be contrasted with the normal outer-sphere reactivity difference of  $\sim 7$  for these complexes with  $Cr(bipy)_3^{2+}$  and  $Ru(NH_3)_6^{2+}$  and with the strongly reducing radical  $\cdot C(CH_3)_2OH$ .<sup>33</sup> On the basis of reasonable success of the simple Marcus equation to predict the radical reactivity with  $Fe(OH_2)_6^{3+}$ , one is encouraged, perhaps naively, to extend this to the cobalt(III) oxidants. If the  $E^\circ$  for  $C_6H_5CH_2^+$  is  $\sim 0.7 V$ , a value consistent with the reactivity and pathway changeover with  $Fe(OH_2)_6^{3+}$ , then no set of self-exchange rate constants and  $E^\circ$  values for the  $Co(NH_3)_5X^{2+}$  complexes will predict the reduction rate constants with  $Ru(NH_3)_6^{2+}$  and the values with the benzyl radical. The essential problem is that the  $E^\circ$  difference of the reductants (0.051 vs 0.7 V) gives  $\sim 10^{11}$  times smaller  $K_{12}$  for the radicals, which cannot be compensated by a radical self-exchange rate constant of  $1 \times 10^9$  compared to  $6.7 \times 10^3 M^{-1} s^{-1}$ <sup>34</sup> for  $Ru(NH_3)_6^{2+/3+}$ . Therefore the predicted radical reduction rate constants are  $\sim 10^3$  times smaller than the values<sup>35</sup> with  $Ru(NH_3)_6^{2+}$ , which are  $2.6 \times 10^2$  and  $1.6 \times 10^3 M^{-1} s^{-1}$  for  $Co(NH_3)_5Cl^{2+}$  and  $Co(NH_3)_5Br^{2+}$ , respectively.

In summary, it is apparent that the wide range of oxidizability of the substituted benzyl radicals presents some interesting possibilities for measuring their reactivity with different oxidizing agents. As yet it is unclear whether these rates will conform to Marcus theory, as seems to be the case with  $Fe(OH_2)_6^{3+}$ , or if there are special factors affecting the reactivity as for the halopentaamincobalt(III) complexes.

## Experimental Section

**Materials.** Solutions of the benzyl complexes of pentaquachromium(III) were prepared by mixing 2 mmol of the appropriate benzyl bromide (Aldrich) in 40 mL of methanol with 20 mL of aqueous 0.30 M chromium(II) perchlorate, prepared by reduction of chromium(III) perchlorate over amalgamated zinc. Each product complex was separated by ion-exchange chromatography as described previously,<sup>2</sup> where the electronic spectra are also given.

Aqueous iron(III) perchlorate was prepared from iron wire as described by Xu and Jordan.<sup>36</sup>  $[(NH_3)_5CoCl](ClO_4)_2$  and  $[(NH_3)_5CoBr](ClO_4)_2$  were prepared from  $[(NH_3)_5CoCl](Cl)_2$ <sup>37</sup> and  $[(NH_3)_5CoBr](Br)_2$ <sup>38</sup> by dissolving either 2 g of chloride or 1 g of bromide in 100 mL of 3.0 M  $NaClO_4$  in 0.1 M  $HClO_4$  at 50 °C, filtering the solution, and cooling in an ice bath. The crystalline solid was collected by filtration and washed three times with cold methanol and twice with diethyl ether. The product was dried for 2 h at 45 °C.

**Kinetic Measurements.** The absorbance decrease was followed on a Hewlett Packard 8451 diode array spectrophotometer at an appropriate wavelength in the 310–360-nm region. The absorbance–time data (80 points over 5–6 half-lives) were analyzed by least-squares to obtain the first-order rate constants. As noted in the discussion, some systems with dioxygen as the scavenger showed biphasic behavior and were followed at four wavelengths. These data were fitted simultaneously to a biphasic model to obtain the first-order rate constants.

Solutions for kinetic runs were prepared by adding the required amounts of standardized sodium perchlorate, perchloric acid, and scavenger to a 50-mm cylindrical spectrophotometer cell. For scavengers other than

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dioxygen, the cell was closed with a serum cap, degassed with argon, and brought to the required temperature and then enough of the benzylchromium(III) complex solution was added by syringe to give a chromium concentration of  $\sim 2 \times 10^{-5}$  M. With dioxygen as the scavenger, the reaction was simply open to the air.

**Product Analysis.** Solutions of 0.12–0.2 mmol ( $(1.8\text{--}3.2) \times 10^{-3}$  M) of the benzylchromium(III) complex in 0.1 M HClO<sub>4</sub> were prepared as for the kinetic runs. After being stirred for about 4 h, the solution was extracted with 10 mL of chloroform. The solvent was evaporated and the extract redissolved in CDCl<sub>3</sub>, and the <sup>1</sup>H NMR spectrum was recorded on a Bruker AM 300 spectrometer. When appropriate, the aqueous phase was analyzed for iron(II) or cobalt(II). The iron(II) produced was determined by titration with standardized potassium dichromate. The

cobalt(II) was determined spectrophotometrically as Co(SCN)<sub>4</sub><sup>2-</sup> in aqueous acetone by the method of Kitson.<sup>39</sup>

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**Supplementary Material Available:** Tables of temperatures, H<sup>+</sup> concentrations, and experimental and calculated rate constants (Tables S1–S15) and stoichiometry results (Table S16) (10 pages). Ordering information is given on any current masthead page.

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