

the reactions⁴ of $\text{Br}_2(\text{aq})$ with $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+}$.

Only for the alkylcobaloximes has a stereochemical determination proved feasible,^{4a} since it is only here that a chiral organometallic complex can be made. We believe that in the chromium complexes the reaction probably proceeds with the same stereochemistry, namely, inversion of configuration at the α -carbon; aside from similar changes in reactivity with changes in R, however, direct evidence is lacking.

The 1-adamantyl complex, which is one of the more stable of the present group toward acidolysis or other decomposition, also reacts with mercury(II) ion. Its rate constant is comparable to that found for the secondary alkyls, yet it cannot react by an inversion process. It is thus questionable whether the 1-adamantyl complex follows the same mechanism; its rate is directly proportional to $[\text{Hg}^{2+}]$, however, and if direct attack at the α -carbon occurs, the process cannot involve inversion.

Another trend apparent from Table I is the marked change in rate among the primary alkyls. Models show that the α -carbon becomes more shielded with chain length, at least up to some three or four carbon atoms; beyond that, little increased shielding of the chromium-carbon bond toward attack by mercury(II) ion is noted.

The activation parameters given in Table I show rather wide ranges, considering the relatively narrow spread in values of k_{Hg} at 25 °C. The differences are well beyond experimental error, and it may be that variations in $\Delta S^\ddagger$ arise from different degrees of solvent participation in the transition state and not from any fundamental changes of mechanism.

It is of interest to compare the reactivity of $\text{R}-\text{Cr}([\text{15}] \text{aneN}_4)(\text{H}_2\text{O})^{2+}$ and $(\text{H}_2\text{O})_5\text{Cr}-\text{R}^{2+3}$ toward Hg^{2+} . At least

two factors appear to govern the differences. First, the saturated macrocyclic ligand adds considerable steric bulk around the chromium-carbon bond, the site of reactivity. This steric bulk could cause a lowering of rate if the mechanism does involve, as suggested, attack of Hg^{2+} at the α -carbon leading to inversion of configuration at this carbon. In addition, replacement of four water molecules by the stronger-field nitrogen donor ligand will serve to increase the electron density on chromium and, in turn, on the α -carbon atom of R. These factors act in opposite direction, the former expected to lower the reactivity of the 15-aneN₄ complex, the latter to increase it, relative to the aquo complex. The data³ actually show that the pentaquo complex is always the more rapidly reacting, by factors ranging from ~ 3 ($\text{R} = \text{CH}_3$) to $\sim 4 \times 10^2$ ($\text{R} = n\text{-C}_3\text{H}_7$ and $i\text{-C}_3\text{H}_7$). We conclude that a compromise between the opposing influences is at work, with the steric factor always the dominant consideration, the more so the greater the further steric barrier posed by the group R.

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Registry No. $\text{CH}_3\text{Cr}([\text{15}] \text{aneN}_4)(\text{H}_2\text{O})^{2+}$, 70832-96-1; $\text{CH}_3\text{CH}_2\text{Cr}([\text{15}] \text{aneN}_4)(\text{H}_2\text{O})^{2+}$, 70832-97-2; $n\text{-C}_3\text{H}_7\text{Cr}([\text{15}] \text{aneN}_4)(\text{H}_2\text{O})^{2+}$, 70832-98-3; $n\text{-C}_4\text{H}_9\text{Cr}([\text{15}] \text{aneN}_4)(\text{H}_2\text{O})^{2+}$, 70832-99-4; $n\text{-C}_5\text{H}_{11}\text{Cr}([\text{15}] \text{aneN}_4)(\text{H}_2\text{O})^{2+}$, 71818-69-4; $\text{C}_6\text{H}_5\text{CH}_2\text{Cr}([\text{15}] \text{aneN}_4)(\text{H}_2\text{O})^{2+}$, 70833-03-3; $i\text{-C}_3\text{H}_7\text{Cr}([\text{15}] \text{aneN}_4)(\text{H}_2\text{O})^{2+}$, 70833-00-0; $c\text{-C}_6\text{H}_{11}\text{Cr}([\text{15}] \text{aneN}_4)(\text{H}_2\text{O})^{2+}$, 70833-01-1; (1-adamantyl) $\text{Cr}([\text{15}] \text{aneN}_4)(\text{H}_2\text{O})^{2+}$, 70833-02-2; Hg^{2+} , 14302-87-5; CH_3Hg^+ , 22967-92-6; $(\text{H}_2\text{O})_2\text{Cr}([\text{15}] \text{aneN}_4)^{3+}$, 70832-95-0.

Contribution from the Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011

Preparation, Reactions, and Reaction Mechanisms of a Family of Difunctional Complexes of Bis(benzylchromium) Cations¹

MICHAEL C. POHL and JAMES H. ESPENSON*

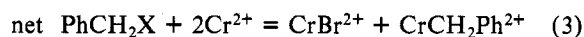
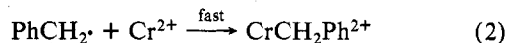
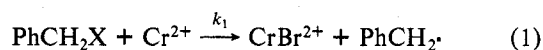
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Six new dimetallic organochromium cations, each containing two benzylchromium-like units per molecule, were prepared from selected dibromides and chromium(II). These tetrapositive complexes (and certain related monochromium analogues) were isolated and purified by ion-exchange chromatography in aqueous solution. The complexes were characterized by their UV-visible absorption spectra and by the stoichiometry and composition of the products obtained from reactions with chloropentaamminecobalt(III) ion, with sodium carbonate, and with mercury(II) chloride. These complexes react with oxidizing agents such as iron(III) ion, copper(II) ion, and halopentaamminecobalt(III) ion in reactions that are first order in the concentration of organochromium ion, but independent of the identity as well as the concentration of oxidizing agent (except for iron(III) ion which shows, for some complexes, a small contribution of an Fe^{3+} -dependent pathway). These data, and comparisons with mononuclear, substituted benzylchromium cations, suggest that the rate-limiting step is unimolecular homolysis of a chromium-carbon bond. The dichromium cations produce only polymer. The monochromium cation $[\text{p-CrCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH}]^{2+}$ also polymerizes upon oxidation and has $k_h = 1.66 \times 10^{-3} \text{ s}^{-1}$ at 25 °C, consistent with other rates and leading to a Hammett substituent constant for $p\text{-CH}_2\text{OH}$ of $\sigma_p = +0.19$. The mechanism of homolysis and of the polymerization initiation step are discussed in light of the kinetic data which give no evidence of a biphasic or stepwise loss of the benzylchromium absorption bands used to monitor the reaction rate.

Introduction

Benzyl halides are sufficiently reactive toward chromium(II) that a halogen abstraction reaction occurs in aqueous or semiaqueous media. The radical so formed combines with a second chromium(II) ion in a rapid reaction, leading to the formation of the cationic organometallic benzyl(pentaquo)-chromium(III) ion.^{2,3} These reactions occur as follows (omitting coordinated water or other solvent molecules; all the

chromium ions are six-coordinate):



By analogy, if the benzyl halide were one containing two aralkyl halide (ArCH_2X) functional groups, it is to be expected that a tetrapositive dichromium complex will be formed provided an excess of chromium(II) is used in the reaction. For the sake of a brief notation for a number of such complexes,

(1) Based on the Ph.D. Thesis of M.C.P., Iowa State University, 1979.

(2) Anet, F. A. L.; LeBlanc, E. L. *J. Am. Chem. Soc.* **1957**, *79*, 2649.

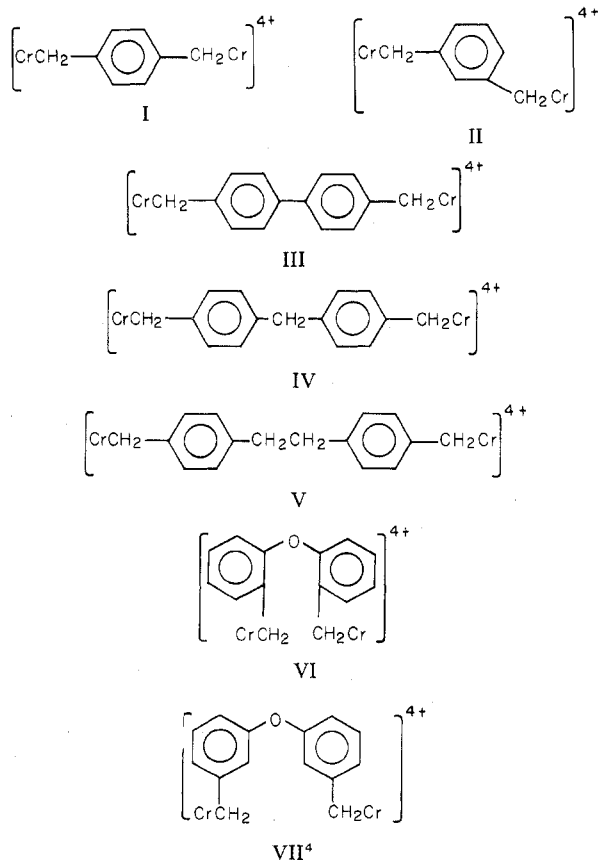
(3) Kochi, J. K.; Davis, D. D. *J. Am. Chem. Soc.* **1964**, *86*, 5264.

Table I. Analyses and Properties of the Starting Materials

compd	mp, °C (lit. value)	¹ H NMR spectrum, δ	elemental anal. found (calcd)
α,α'-dibromo- <i>m</i> -xylene	75-77 (75-77) ^a	7.35 (8, m), 4.50 (4, m) ^b	
α,α'-dibromo- <i>p</i> -xylene	142-143 (142-143) ^a	7.42 (8, s), 4.50 (4, s) ^b	
4,4'-bis(bromomethyl)biphenyl	167.5-170.5 (170) ^c	<i>d</i>	C 49.65 (49.41), H 3.58 (3.53)
4,4'-bis(bromomethyl)diphenylmethane	151.5-153.5 (153.5) ^e	<i>d</i>	C 50.88 (50.88), H 3.94 (3.98)
4,4'-bis(bromomethyl)1,2-diphenylethane	116-119.5 (117-120) ^e	<i>d</i>	C 52.18 (52.20), H 4.38 (4.38)
4,4'-bis(bromomethyl)diphenyl ether	94-95 (93-95) ^f	7.1 (8, AA'BB'), 4.52 (4, s) ^g	
2,4-bis(bromomethyl)toluene	96.5-97.0 (97.0) ^h	<i>d</i>	C 38.58 (38.88), H 3.72 (3.63)
<i>p</i> -phenylbenzyl bromide	83-84 (84-85) ⁱ	7.40-7.60 (9, m), 4.50 (2, s) ^j	C 63.18 (63.18), H 4.52 (4.49)
<i>p</i> -(bromomethyl)benzyl alcohol	82.5-83.0 (84.0) ^k	<i>d, l</i>	C 48.23 (47.79), H 4.51 (4.51)
<i>p</i> -pyCo(dmgH) ₂ CH ₂ C ₆ H ₄ CH ₂ OH		<i>d</i>	C 51.18 (51.53), H 5.73 (5.76), N 14.19 (14.30)
<i>p</i> -[pyCo(dmgH) ₂ CH ₂] ₂ C ₆ H ₄		6.8 (4, s), 2.8 (4, s), 1.9 (24, s) ^m	C 48.61 (48.68), H 5.80 (5.51), N 15.36 (16.66)

^a "Handbook of Organic and Biochemicals"; Aldrich Chemical Co.: Milwaukee, 1978. ^b Agrees with reported NMR spectrum: "Aldrich Library of NMR Spectra"; Aldrich Chemical Co.: Milwaukee, 1974. ^c Braun, C. V. *Chem. Ber.* **1937**, *70*, 993. ^d The ¹H NMR spectra, while too complex to be easily summarized here, agree with published values; the spectra are depicted in the thesis referenced.¹ ^e Reference 12. ^f Buhts, R. E.; Chesney, K. K.; Handly, J. R.; Popp, F. D.; Smith, D. C. *Org. Prep. Proc. Int.* **1975**, *7*, 193. ^g Lit.^f nmr: 7.05-8.45 (8), 4.56 (4). The reported spectrum was run in CCl₄ with internal Me₄Si standard. ^h Hjelt, E.; Gadd, M. *Chem. Ber.* **1886**, *19*, 867. ⁱ Reference 8. ^j Lit.ⁱ nmr: 7.40-7.60, 4.48. ^k Charpentier, M.; Tchoubar, B. C. R. *Hebd. Seances Acad. Sci.* **1951**, *233*, 1621. ^l The high-resolution mass spectrum shows a major peak at 199.98367 (calcd for ¹²C₈¹H₉⁷⁹Br¹⁶O 199.98368. ^m Agrees with ref 14.

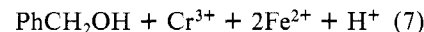
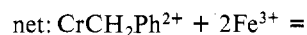
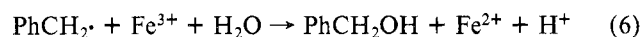
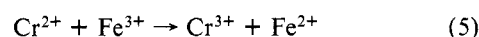
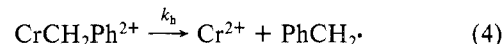
we represent any of the dichromium cations as [CrCH₂PhCH₂Cr]⁴⁺, prepared from the dihalide XCH₂PhCH₂X, undoubtedly formed in a stepwise fashion by way of the monochromium complex [CrCH₂PhCH₂X]²⁺. The specific organochromium complexes studied in the course of this work are shown (I-VI); a similar complex (VII) prepared



earlier⁴ is also shown. In addition to the tetrapositive dichromium complexes shown, certain related monofunctional benzylchromium cations were also examined.

This paper reports the preparation, isolation, and characterization of these complexes. In addition we have carried out a thorough study of the kinetics and mechanisms of selected

reactions. In particular, we have been interested in examining the homolytic cleavage process, the reverse of reaction 2 by which such complexes are formed. Earlier studies⁵ of the reactions of the parent benzylchromium cation have provided several lines of evidence in support of our contention that "oxidative" cleavage (with such oxidants as Fe³⁺, Cu²⁺, H₂O₂, O₂, and Co(NH₃)₅X²⁺) proceeds in a sequence of two steps, the first and rate limiting being the homolysis process (S_H1 mechanism) referred to and the second the rapid oxidation of either or both of the resulting radicals (i.e., Cr²⁺ and PhCH₂·) by the oxidant. The occurrence of this second step interferes with recombination and draws the oxidation to completion. To be more specific, the homolysis mechanism for oxidative cleavage is that shown in eq 4-7, where, for illustrative purposes, the specific oxidant chemistry shown, which is different for each, is that for Fe³⁺.



Related to the question of how the difunctional benzylchromium cations contrast with this in their homolytic chemistry is the question of possible polymer formation. Lunk and Youngman^{6a} found that difunctional benzyl halides such as α,α'-dibromo-*p*-xylene undergo coupling reactions in the presence of chromium(II) salts forming poly(*p*-xylylene). These authors did not attempt mechanistic work, yet the formation of monofunctional benzylchromium cations and the radicals formed upon their homolysis suggested to us that they were probably involved in this chemistry. Accordingly, we set out to use this reaction to form the dichromium complexes shown above and to undertake a study of their chemical reactions, particularly those involving radical formation through homolysis in the presence of oxidizing agents.

Experimental Section

Materials. The organic halides were purchased or prepared and purified as described below. Data giving elemental analysis, melting

(4) Marty, W.; Espenson, J. H. *Inorg. Chem.* **1979**, *18*, 1246.

(5) Nohr, R. S.; Espenson, J. H. *J. Am. Chem. Soc.* **1975**, *97*, 3392.
(6) (a) Lunk, H. E.; Youngman, E. A. *J. Polym. Sci. Part A-1* **1965**, *3*, 2983. (b) Hoyt, J. M.; Koch, K.; Sprang, C. A.; Stregovsky, S.; Frank, C. E. *Am. Chem. Soc., Div. Polym. Chem., Prepr.* **1964**, *5*, 680.

point, and ^1H NMR spectra are summarized in Table I. Specific details are as follows.⁷ These reagents were purchased (Aldrich Chemical Co.) and purified as indicated: α,α' -dibromo-*m*-xylene by sublimation (0.5 mm, 60–65 °C), α,α' -dibromo-*p*-xylene by recrystallization from chloroform. Literature procedures were used for *p*-phenylbenzyl bromide,⁸ which was first sublimed (0.5 mm, 65–70 °C) and then recrystallized from petroleum ether, and for *p*-(bromomethyl)benzyl alcohol, which was prepared from α -bromo-*p*-toluic acid via the methyl ester⁹ by lithium aluminum hydride reduction¹⁰ using an exactly stoichiometric quantity (1:2 LAH/substrate), giving a mixture of products which were separated by chromatography on silica gel with methylene chloride as eluent and further purified by recrystallization from hot petroleum ether, yielding a pure but unstable substance which had to be used promptly. Different isomers of bis(bromomethyl)diphenyl ether were prepared¹¹ and recrystallized from hot benzene. The three dibromides used to prepare complexes III, IV, and V were synthesized by the same procedure modified from the published method.¹² The parent hydrocarbon (0.137 mol) was added to a mixture of 21.0 g of paraformaldehyde, 54.0 cm³ of 48% hydrobromic acid, 48.5 cm³ of 85% phosphoric acid, and 66.0 cm³ of glacial acetic acid. The solution was stirred and warmed; at 95 °C gaseous hydrogen bromide¹³ was bubbled into the solution through a frit for 5 h while the temperature was maintained at 95–110 °C. The mixture was cooled overnight and then poured into 600 cm³ of water yielding a pasty precipitate of the impure dibromide. The individual products were purified as follows. The biphenyl was reprecipitated three times from acetone upon addition of water; the diphenylmethane was recrystallized three times from hot benzene, the first benzene solution being washed with water; the diphenylethane was chromatographed on silica gel with carbon tetrachloride eluent to obtain pale yellow crystals which were further purified by extracting the impurities into a porous plate¹¹ with hexane, yielding a pure product after recrystallization from ether. The reaction of 1,2,4-trimethylbenzene and *N*-bromosuccinamide was carried out as for the ethers,¹¹ yielding an impure sample of 2,4-bis(bromomethyl)toluene; the impurities in oily yellow crystals were extracted into a porous plate¹¹ with hexane yielding a compound which was then recrystallized from chloroform.

The desired organobis(dimethylglyoximate)cobalt(III) complexes (so-called "cobaloximes") were prepared as their pyridine complexes by standard methods^{14,15} and purified by reprecipitation from methylene chloride upon addition of hexane. The particular compounds prepared are *p*-pyCo(dmgH)₂CH₂C₆H₄CH₂OH and *p*-[pyCo(dmgH)₂CH₂]₂C₆H₄.

All of the tetrapositive organodichromium complexes were prepared in roughly the same manner, so only one example will be given. All operations in the preparation, isolation, and storage are conducted in oxygen-free conditions under chromium(II)-scrubbed nitrogen. A deaerated acetone¹⁶ solution of α,α' -dibromo-*p*-xylene (39.6 mg, 0.15 mmol) was reacted at room temperature with aqueous chromium(II) perchlorate (5.0 cm³ of 0.2 M solution prepared by zinc amalgam reduction of the chromium(III) salt). After about 20 min, during which the solution had changed from pale blue to dark yellow-green, it was cooled to 0 °C and loaded onto a water-jacketed column (10 × 1.5 cm) of Sephadex SP-C25 ion-exchange resin in the hydrogen ion form. Excess Cr²⁺ was eluted with 0.1 M perchloric acid, followed

by Cr³⁺.¹⁷ The desired [(CrCH₂)₂Ph]⁴⁺ cation was easily eluted with 1 M electrolyte, usually 0.9 M NaClO₄, 0.1 M HClO₄. This band was collected under nitrogen and stored at 5 °C for further use. Any dimeric Cr(III) complex from oxidation of Cr²⁺ was eluted with 2 M sodium perchlorate. This particular resin is useful for the separation of complexes of high charge using reasonable concentrations of eluents. Various species eluted in distinct, compact bands clearly separated from one another. The white resin color constitutes a considerable advantage in effecting clean separations.

A similar procedure is used for monochromium complexes such as *p*-CrCH₂C₆H₄CH₂OH²⁺, except that only half the amount of Cr²⁺ was used. The dipositive complexes appear after Cr²⁺ but before Cr³⁺ and are readily removed from the resin by elution with 0.1 M perchloric acid. The synthesis of monochromium cations from organic dibromides requires special considerations⁴ to prevent further reaction to the tetrapositive complex. In these cases a deficiency of chromium(II) was used and the reaction interrupted with only partial conversion. For example, *m*-CrCH₂C₆H₄CH₂Br²⁺ was obtained by reaction of the dibromide (0.3 mmol) with chromium(II) (0.6 mmol) in aqueous acetone for 15 min, precipitation of the unreacted dibromide with aqueous 0.1 M perchloric acid, rapid aeration to oxidize Cr²⁺, filtration, and deaeration. The resulting solution was chromatographed as before, the desired dipositive product being eluted with 0.1 M perchloric acid.

Reaction Products. The reaction of mercury(II) salts with the various organochromium cations is expected¹⁸ to yield cationic organomercurials, in general [HgCH₂PhCH₂Hg]²⁺, when the dichromium analogues are used. To obtain reasonable quantities, we usually conducted the reaction on the same solution in which the organochromium cation had been prepared without its isolation. The expected organomercurials proved difficult to isolate with mercury(II) perchlorate,¹⁸ and an alternative procedure¹⁹ was used. The methanol-water solution was bubbled with air for 1 min to destroy chromium(II) and then immediately added to a 25% stoichiometric excess of mercury(II) chloride in methanol. An immediate white precipitate was formed along with the characteristic blue color of Cr(H₂O)₆³⁺. Addition to an equal volume of water precipitated an additional quantity of the impure organomercury chloride, which was filtered, washed with water, and dried. To free the solid of any mercury(I) chloride, we dissolved it in pyridine and filtered this solution into 0.01 M aqueous hydrochloric acid. The resulting white material was dried in a vacuum desiccator overnight prior to elemental and NMR analysis. In some instances, the sample was recrystallized from dimethyl sulfoxide.

Reaction with mild base²⁰ proved to be a valuable means of confirming the identity of the organochromium complexes, many of which are converted to the parent hydrocarbon (i.e., to the substituted toluene). To avoid incorporation of paramagnetic chromium(III) in the material isolated and the accompanying broadening of the NMR signals, we found prompt reacidification proved important. The specific procedure used is as follows. The sample of the organochromium cation (typically 30–40 cm³ of the 0.05 M complex, freshly prepared in acetone-water and not isolated by ion exchange) was added to 30 cm³ of deaerated, saturated sodium carbonate. After some 15–20 min under nitrogen, concentrated perchloric acid was added dropwise until the solid brown residue formed during the carbonate treatment had dissolved and a clear blue solution of Cr(H₂O)₆³⁺ was formed. This faintly acidic solution is then extracted with four 125-cm³ portions of carbon tetrachloride. The combined extracts are dried over magnesium sulfate and evaporated to dryness yielding crystals which may or may not require recrystallization prior to analysis.

Reaction of some complexes with certain oxidizing agents as well as thermal decomposition produced polymeric materials, poly(*p*-xylylene) and analogues; other reactions gave discrete molecular products. Much of the former tended to form in a film which tightly coated the glassware, but some floated in the solution and could be filtered, washed with water, and dried in a vacuum desiccator. The mono-

(7) Further details are provided in the thesis referenced.¹

(8) Bullpitt, M.; Kitching, W.; Doddrell, D.; Adcock, W. *J. Org. Chem.* **1976**, *41*, 760.

(9) Codington, J. T.; Mosettig, E. *J. Org. Chem.* **1952**, *17*, 1035.

(10) Felkin, M. H. C. *R. Hebd. Seances Acad. Sci.* **1950**, *230*, 304.

(11) Kagi, S.; Marty, W., unpublished results. We are grateful to Dr. Marty for access to this work prior to publication and for a sample of the 2,2' isomer used in these studies to prepare complex VI.

(12) Goodson, J. A.; Goodwin, L. J.; Garwin, J. H.; Goss, M. D.; Kirby, K. S.; Lock, J. A.; Neal, R. A.; Sharp, T. M.; Salomon, W. *Brit. J. Pharmacol.* **1945**, *3*, 62.

(13) From a lecture cylinder or from the reaction of bromine with tetralin: Schmeiser, M. In "Handbook of Preparative Inorganic Chemistry", G. Brauer, Ed., Academic Press: New York, 1963; Vol. I, p 282.

(14) Anderson, S. N.; Ballard, D. H.; Johnson, M. D. *J. Chem. Soc., Perkin Trans. 2*, **1972**, 311.

(15) Schrauzer, G. N. *Inorg. Synth.* **1970**, *11*, 65.

(16) Acetone is distilled as an acetone-water azeotrope from aqueous potassium permanganate solution to remove impurities which react with chromium(II) and interfere with the ion-exchange chromatography. Methanol was used in place of acetone in some instances without difficulty.

(17) One does not usually isolate the CrBr²⁺ expected from eq 3, presumably owing to its Cr²⁺-catalyzed aquation under these conditions. Runs at higher [H⁺] and lower [Cr²⁺] clearly showed CrBr²⁺ in place of Cr³⁺, as expected.

(18) Leslie, J. P.; Espenson, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4839.

(19) Coombes, R. G.; Johnson, M. D., unpublished results; we are grateful to Dr. Johnson for making these results available to us prior to publication.

(20) Coombes, R. G.; Johnson, M. D.; Winterton, M. *J. Chem. Soc.* **1965**, 7029.

chromium complexes especially yielded more tractable products, usually isolated by extraction. For example, an acetone–water solution containing the *p*-phenylbenzylchromium cation was added to a twofold stoichiometric excess of iron(III) and allowed to stand while being bubbled out with nitrogen for 2 h during which time the acetone was largely volatilized. The remaining aqueous solution, ~50 cm³, was extracted with four 50-cm³ portions of 90:10 pentane/ether. The combined extracts were dried over magnesium sulfate and evaporated to yield white crystals shown by analysis in this case to be *p*-phenylbenzyl alcohol.

Kinetics. A spectrophotometric method was used, usually following the change in absorption at 360 nm. All of the benzylic organochromium cations have a maximum at 355–360 nm, in every case with a molar absorptivity near $2.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ per chromium–carbon bond (i.e., ϵ for complexes I–VII is near $4.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). The rate of formation by reaction of a large excess of Cr²⁺ with aralkyl bromides was monitored in oxygen-free aqueous ethanol or acetone with the reaction conducted in a quartz spectrophotometer cuvet maintained at the reaction temperature, usually 25 °C, in a thermostated holder positioned in the light beam of a Cary Model 14 spectrophotometer. Similar experiments were conducted on the decomposition reactions which were studied in aqueous solution in the presence of a large excess of oxidant.

Most reactions followed a first-order rate equation with the value of the rate constant obtained from the slope of a plot of $\ln |D_t - D_\infty|$ vs. time (D = absorbance). In certain cases, it proved difficult to obtain a reliable value of D_∞ and the method of Guggenheim was used. Only rarely was a more complicated situation encountered, corresponding to biphasic kinetics; in those instances standard methods were applied.^{4,21}

Analyses. Concentrations of chromium(II) ion were determined from the yield of cobalt(II) ion upon reaction²² with $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ and total chromium spectrophotometrically as CrO_4^{2-} after oxidation with hydrogen peroxide in base.²³ Iron(II), produced in the reaction of iron(III) with the organochromium complexes, was determined as its tris(1,10-phenanthroline) complex;²⁴ erroneous high values were found until metal syringe needles were replaced by Teflon ones. Most elemental analyses for C, H, and N were done locally by the Ames Laboratory analytical services groups, although some polymer samples were sent to commercial firms.

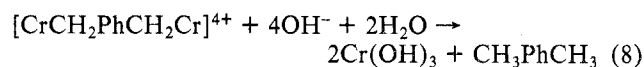
Instrumentation. Cary spectrophotometers, Models 14 and 219, were used extensively. A Princeton Applied Research Model 173 potentiostat/galvanostat was used for the electrochemical generation²⁵ of poly(*p*-xylylene). A Sorenson xenon lamp was used for photolyses which were done in Pyrex vessels to reduce ultraviolet exposure. A number of computer simulation experiments²⁶ were done by using an EAI TR-20 analog computer.

Results

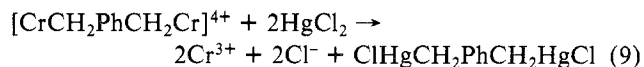
Organodichromium Cations. Several experimental results support our contention that a major product of reaction of the dihalide $\text{XCH}_2\text{PhCH}_2\text{X}$ with chromium(II) ion is the difunctional aralkylchromium cation having a general formula given as $[\text{CrCH}_2\text{PhCH}_2\text{Cr}]^{4+}$, with the specific complexes studied here shown as structures I–VII. These species elute as tetrapositive cations from the column of Sephadex ion-exchange resin, eluting after $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and requiring a higher electrolyte concentration, whereas monofunctional complexes such as $\text{CrCH}_2\text{Ph}^{2+}$ elute as dipositive ion ahead of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ at lower electrolyte concentrations. The dichromium complexes have absorption spectra qualitatively similar to the benzylchromium cation and its substituted analogues, which differ but little from one to the other. The complexes are characterized by peaks at 355–360, 300, and 265 nm except

complex III for which the long wavelength band is shifted to 330 nm. The agreement is even more convincing in that the molar absorptivities of the tetrapositive cations, calculated under the assumption of two chromiums/complex, are almost exactly a factor of 2 higher than for the monochromium cations. The spectral values are based on a chromium concentration determined under the assumption that the dichromium cations react with $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ in an analogous fashion to the monobenzylchromium ions. That is, we assume that each of the two chromium–carbon bonds present in $[\text{CrCH}_2\text{PhCH}_2\text{Cr}]^{4+}$ produces one Co^{2+} . This particular reaction was chosen as the analytical standard because this is the one oxidant of those studied earlier⁵ which reacts only with the Cr^{2+} product of homolysis (eq 4) and not with the carbon-centered radicals. On this basis the molar absorptivities at the 358–360-nm peak are as follows: I, 4980 $\text{M}^{-1} \text{ cm}^{-1}$; II, 4430; V, 4790; VII, 4200; *m*- $\text{CrCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{Br}^{2+}$, 2190; and *p*- $\text{CrCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH}^{2+}$, 2290.

The most convincing proof that the dichromium cations I–VII have been correctly formulated arises when the products of its reactions can be identified unambiguously. The reactions of most use are hydrolysis with mild base and reaction with mercury(II) chloride. Many other reactions yield organic polymer and are much less useful in identification. The base hydrolysis procedure used gives a good yield of methyl-substituted aralkyl, i.e., that expected from reaction 8 for complexes III–VII (but not for I and II where polymer is found).



This was verified for complexes III, IV, V, VI, and VII as well as for the monochromium complexes *p*- $\text{CrCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH}^{2+}$ and *m*- $\text{CrCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{Br}^{2+}$. The resulting hydrocarbons were characterized by proton NMR and in two cases also by their high-resolution mass spectrum. Since the products are well-known compounds, the data need not be given in detail.⁷ Repeated attempts to use this reaction for cations I and II under a variety of reaction conditions gave only polymeric products. The latter complex was identified by reaction with mercury(II) chloride, as described subsequently, and the only arguments for I as formulated are based on its analogy to the other complexes, its chromatographic characteristics, and its UV–visible absorption spectrum. A second reaction useful for characterization was that with mercury(II) chloride. Ideally the reaction should occur according to eq 9, but it often



happens that the organomercury chloride is unstable on standing and darkens in a short time even in the dark under nitrogen. The best results were obtained for II, which gave a stable crystalline product identified^{20,27} as *m*-(ClHgCH_2)₂ C_6H_4 . ¹H NMR: δ 2.97 [CH_2 , $J(^1\text{H}-^{199}\text{Hg}) = 296 \text{ Hz}$ (adjacent Hg), $J(^1\text{H}-^{199}\text{Hg}) = 11 \text{ Hz}$ (meta Hg)], δ 7.06 [$\text{C}_6\text{H}_4(\text{m})$]. Attempts to stabilize other diorganomercurials were unsuccessful.

Polymeric material such as poly(*p*-xylylene) was isolated in copious quantities from several reactions. This material did not melt or decompose significantly up to 310 °C and was very insoluble in common solvents. Some of the polymeric material did dissolve in hot (>200 °C) benzyl benzoate, but it did not become crystalline upon cooling. The best characterization was made on the basis of the infrared spectrum. That obtained from I upon slow thermal decomposition, base hydrolysis, and reaction with oxidants has an IR spectrum⁷ which agrees

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Table II. Kinetic Data for the Reactions of Substituted Monofunctional Benzylchromium Cations with Oxidizing Agents^a

complex	copper(II)		cobalt(III)		iron(III)	
	$10^3[\text{Cu}^{2+}]/\text{M}$	$10^3k/\text{s}^{-1}$	$10^3[\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}]/\text{M}$	$10^3k/\text{s}^{-1}$	$10^3[\text{Fe}^{3+}]/\text{M}$	$10^3k/\text{s}^{-1}$
<i>p</i> -CrCH ₂ C ₆ H ₄ CH ₂ OH ²⁺			0.7 ^b	1.65 (1)	(0)	(1.65) ^c
	2.50	1.66 (1)	1.0	1.69 (1)	9.0	1.9 (4)
			1.3 ^b	1.67 (3)		
	5.00	1.65 (7)	2.0	1.68 (5)	18.0	2.14 (5)
			2.6 ^b	1.64 (1)		
<i>m</i> -CrCH ₂ C ₆ H ₄ CH ₂ Br ²⁺	10.0	1.69 (2)	4.0	1.71 (1)	(0)	(1.21) ^c
	16.5	1.22 (1)	5.0	1.21 (1)	1.60	1.32 (3)
	33.0	1.24 (6)	10.0	1.22 (4)	3.30	1.48 (5)
	66.0	1.27 (1)	20.0	1.25 (1)	6.60	1.70 (4)
					(0)	(3.2) ^{c,e}
<i>p</i> -CrCH ₂ C ₆ H ₄ Ph ²⁺ ^d	8.3	3.19 (2)			13.0	4.5
	16.6	3.28 (6)			31.7	5.5
	33.2	3.19 (2)			63.3	9.2

^a In aqueous perchlorate solution at 25.0 °C with $[\text{H}^+] = 0.1 \text{ M}$ and ionic strength (maintained with sodium perchlorate) = 0.4 M. The number in parentheses following each rate constant is the number of replicate determinations. The initial concentration of chromium complex was usually 0.1–0.7 mM. Other than the magnitude of the iron(III)-dependent contribution, the rate constant is invariant from $\mu = 0.1$ to 0.4 M. ^b These values refer to $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$. ^c The rate shows a slight dependence on $[\text{Fe}^{3+}]$, as described in the text; the value given is the rate constant extrapolated to zero concentration, representing the oxidant-independent pathway. ^d The rate constants for this complex should be regarded as approximate owing to the precipitation of organic products during the runs. ^e The dependence on $[\text{Fe}^{3+}]$ is sufficiently steep and the data sufficiently scattered that the concentration-independent term is given as the value in the copper(II) runs.

closely with authentic samples (prepared by electrolysis in DMF²⁵ and purchased from ICN Pharmaceuticals, Inc.), save for OH bands from entrapped water. Elemental analysis of any of these materials proved quite unsatisfactory, apparently because the materials are impure. Attempts were made to purify the polymers by prolonged Soxhlet extraction with acetone as described by Hoyt et al.^{6b} This improved the results considerably, giving a product containing 88.4% C and 7.45% H (calcd for poly(CH₂C₆H₄CH₂): 92.3% C, 7.74% H). The use of the dichloride rather than the dibromide gave a material with still better analysis after only one Soxhlet extraction step showing 90.7% C and 7.80% H. The former polymer was found by microprobe analysis to contain traces of bromine, which would serve to lower the C,H content. On the basis of earlier characterization,^{6a} however, we find little reason to doubt its identity.

In contrast to the production of a polymer upon reaction of the dichromium cations with oxidizing agents, the few additional monochromium complexes examined here gave a monomeric, molecular product. Thus the reaction of [*p*-CrCH₂C₆H₄Ph]²⁺ with Cu²⁺ or Fe³⁺ gave an easily isolable crystalline product having a ¹H nmr spectrum in agreement with that of commercial *p*-phenylbenzyl alcohol. This result is just that anticipated based on earlier studies^{5,28} of oxidizing agents and benzylchromium cations.

Kinetics. A thorough study of the kinetics of formation rates of the [CrCH₂PhCH₂Cr]⁴⁺ complexes from the parent bromide and chromium(II) was not undertaken, largely because earlier studies of monochromium complexes³ provided an understanding of the mechanism (eq 1–3) and data⁴ for one of the dichromium complexes, VII, indicated little in the way of unusual reactivity. The reaction appeared to occur in a single stage under some conditions but in two stages (as if, as expected, CrCH₂PhCH₂X²⁺ occurs as an intermediate) under others, but studies to provide a more precise description were not carried out.

Reactions of oxidizing agents with these new organochromium cations were studied extensively. The reagents studied most thoroughly were the same ones found in the earlier work with the benzylchromium cation and its substituted analogues to react by the oxidant-independent homolysis

mechanism (see eq 4–7). Much of this work employed Cu²⁺ and Fe³⁺, with lesser efforts devoted to (NH₃)₅CoX²⁺ (X = Cl, Br), H₂O₂, and O₂.

For purposes of comparison it was desirable to study certain monochromium complexes also, and we begin with a consideration of these cases, which constitute the simpler group of reactions. One of the more interesting monochromium complexes is *p*-CrCH₂C₆H₄CH₂OH²⁺, the product which would be expected from the homolysis of a single chromium–carbon bond of complex I in the presence of iron(III), by analogy to reactions 4–7. This monochromium complex does, indeed, react with these oxidants. The reaction rate is independent of the concentration of the oxidizing agents, as summarized in Table II, except for iron(III) where this complex and certain others show a small contribution from an iron-dependent term; $k_{\text{obsd}} = k_h + k_{\text{Fe}}[\text{Fe}^{3+}]$. Extrapolation to $[\text{Fe}^{3+}] = 0$ gives for this and other complexes the same value of k_h as found for Cu²⁺ and Co(NH₃)₅Cl²⁺ for the same complex. Data for *m*-CrCH₂C₆H₄CH₂Br²⁺ and *p*-CrCH₂C₆H₄Ph²⁺ are also summarized in Table II. These complexes can be considered as substituted benzylchromium ions and as with other substituted derivatives their rates might be expected to correlate with the Hammett linear free-energy relationship. This point will be explored in the Discussion.

One very surprising result is the organic product formed upon oxidation of *p*-CrCH₂C₆H₄CH₂OH²⁺. This complex produced only an organic polymer, unlike any of the other monochromium complexes. It is definitely not the case, however, that the identity of the parent complex can be doubted, in that its reaction with carbonate gave only *p*-CH₃C₆H₄CH₂OH, a known and easily identified material. The polymeric material is presumed to be poly(*p*-xylylene), although it cannot be definitely shown that a polymeric ether such as (–OCH₂C₆H₄CH₂O–)_n was not formed instead. Elemental analysis proved of relatively little help, however, in view of the difficulties encountered; similar C,H content was found for this sample, for that from I, prepared electrochemically²⁵ from α,α'-dibromo-*p*-xylylene and purchased. The electrolysis of *p*-(bromomethyl)benzyl alcohol failed to produce any polymer. The photolysis of *p*-CrCH₂C₆H₄CH₂OH²⁺ was ineffective; in 4 h only slight decomposition had occurred. Although some polymer was formed, the unphotolyzed blank gave the same amount of polymer. Solutions of the cobaloxime analogue, Co(dmgH)₂CH₂C₆H₄CH₂OH, readily underwent

Table III. Kinetic Data for the Reaction of Benzylic Dichromium Complexes with Oxidizing Agents^a

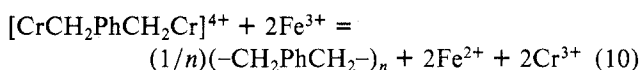
complex	copper(II)		cobalt(III)		iron(III)	
	$10^3[\text{Cu}^{2+}]/\text{M}$	$10^3k/\text{s}^{-1}$	$10^3[\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}]/\text{M}$	$10^3k/\text{s}^{-1}$	$10^3[\text{Fe}^{3+}]/\text{M}$	$10^3k/\text{s}^{-1}$
I	6.75	2.47 (2)	4.5	2.51 (1)	(0)	(2.50) ^b
	13.5	2.48 (2)	9.0	2.58 (5)	9.0	2.56 (1)
	27.0	2.56 (2)	18.0	2.45 (1)	18.0	2.65 (7)
II	16.5	2.09 (1)	5.0	2.09 (1)	2.20	2.16 (2)
	33.0	2.15 (5)	10.0	2.11 (4)	3.30	2.10 (2)
	66.0	2.20 (1)	20.0	2.01 (1)	6.60	2.19 (1)
IV	10.0	2.63 (2)	--	--	(0)	(2.55) ^b
	20.0	2.61 (11)			9.0	2.56 (1)
	40.0	2.71 (1)			18.0	2.67 (4)
V	16.5	2.18 (1)	5.0	3.17 (1)	36.0	2.80 (1)
	33.0	3.12 (8)	10.0	3.11 (6)	(0)	(3.05) ^b
	66.0	3.17 (1)	20.0	3.07 (1)	3.20	3.19
					4.10	3.25
					6.60	3.36

^a In aqueous perchlorate solution at 25.0 °C with $[\text{H}^+] = 0.1 \text{ M}$ and ionic strength (maintained with sodium perchlorate) = 1.0 M. The number in parentheses following each rate constant is the number of replicate determinations. The initial concentration of chromium complex was usually 0.1–0.7 mM. ^b The rate shows a slight dependence on $[\text{Fe}^{3+}]$, as described in the text; the value given is the rate constant extrapolated to zero concentration, representing the oxidant-independent pathway.

photolysis within 30–60 min, but the organic product was methanol soluble and not polymeric.

Photolysis of $p\text{-Co}(\text{dmgH})_2\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{Co}(\text{dmgH})_2$ produced poly(p -xylylene) within 20–30 min. This dicobaloxime is so unstable that it can be readily decomposed in room light. The photolysis of the analogous chromium complex, I, also produced poly(p -xylylene), but it required 1–2 h for complete photodecomposition. In all of the photochemical tests, reactions were conducted under nitrogen with a Pyrex-filtered xenon lamp.

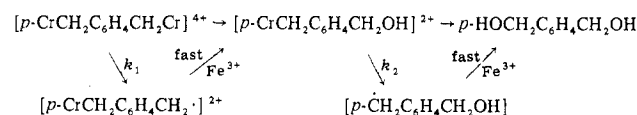
The dichromium cations react with Fe^{3+} in a reaction having the stoichiometry $[\text{Fe}^{2+}]_\infty/[\text{Cr}-\text{C bond}]_0 \sim 1$, compared to a 2:1 stoichiometry found earlier⁵ and confirmed here for the benzylchromium ion. In particular this stoichiometric ratio for complex I is 1.05:1.00 and 1.00:1.00 for II. (Note that these values are expressed per chromium–carbon bond.) This change is consistent with an altered stoichiometry here as compared to the benzylchromium cation which reacts with iron(III) on a 2:1 basis as shown in eq 7. Consistent with this change, the dichromium complexes produce polymer; both observations are accounted for by the following net reaction:



That the iron(III) reaction should change stoichiometry on going from monochromium to dichromium complexes and the halopentaamminecobalt(III) reaction should not is also consistent with the overall scheme proposed: the former oxidant is believed to oxidize the organic radical in one case but not the other, whereas the cobalt(III) oxidant does so in neither instance, leading to the coupling product (bibenzyl) in one case and extended coupling products (polymer) in the other.

Kinetics measurements were made on several of these reactions. The rate constants are summarized in Table III. The same features are noted here as for monochromium complexes: the rate of reaction is independent of the concentration and nature of the oxidizing agent (except for iron(III) where, as before, some reactions show a slight dependence and require extrapolation to zero concentration). The striking aspect of the results is that each run followed an exact first-order kinetic equation, whereas a biphasic sequence of reactions might have been expected. That is to say, if the homolyses of the two chromium–carbon bonds proceed at comparable but not identical rates, a supposition easily supported by the results shown in Tables II and III as well as by earlier work,^{4,5} then a monochromium cation is expected to be formed during the course of a reaction starting with a dichromium complex. This

Scheme I



sequence of events is shown in Scheme I, using complex I for illustrative purposes. In this scheme the materials on the top horizontal line are the ones envisaged to occur as bulk species (i.e., substances which would attain substantial concentrations) and highly reactive intermediates on the second. The particular products shown are those expected when iron(III) is the oxidizing agent if the chemistry of the dichromium complexes were analogous to that of the benzylchromium cation (eq 4–7). The kinetic data probably provide the weakest test of the correctness of this scheme. The reason is that this biphasic pattern, which corresponds to a simple sequence of two first-order reactions as in $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, can, under certain conditions,^{4,21a,29,30} appear to occur in a single step. One of these conditions which should be considered in the present case is the one we term “statistical”: suppose that the rate constant for homolysis of the dichromium complex were just twice that for the monochromium ($k_1/k_2 = 2.000$) and also that the molar absorptivity of the former were just twice that of the latter ($\epsilon_1/\epsilon_2 = 2.000$). This constitutes one situation in which a biphasic reaction reduces exactly to the single exponential expected for a single-stage reaction; under these conditions the general expression for the absorbance change, $D_t - D_\infty$, simplifies to a single exponential. The actual ratios, k_2 being directly and independently evaluated (Table II), are $k_1/k_2 = 1.50$ and $\epsilon_1/\epsilon_2 = 2.27$. As Chipperfield²⁹ has shown, however, it is not necessary that the ratios be exactly the statistical ones to give rise to this result. These ratios are close enough that, to within quite good error limits, correlation coefficient >0.999 , a first-order kinetic expression will fit the data in each run. This was confirmed through the use of extensive analog computer calculations⁷ to confirm the applicability of monophasic kinetics as one deviates from the precise statistical case. In any event, and despite its mathematical applicability, we argue against the mechanism shown in Scheme I. (See Discussion.)

The biphenyl dichromium complex, III, constitutes a special case, in that this cation was markedly less stable than any of the others. When prepared with excess Cr^{2+} , it could be isolated by ion-exchange chromatography, but as soon as it

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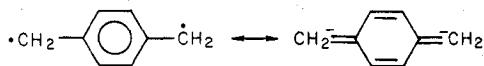
(30) Vanderheiden, D. B.; King, E. L. *J. Am. Chem. Soc.* **1973**, *95*, 3860.

was eluted from the resin it began to decompose to polymer and Cr^{3+} . This decomposition was inhibited by addition of a small concentration of Cr^{2+} (all of the benzylchromium cations are so stabilized against spontaneous decay,⁵ but except for this complex the latter process occurs slowly). For this reason studies of the oxidation reactions of III were not possible. One notes that the *p*-phenylbenzylchromium cation, Table II, shows no unusual properties.

Discussion

The mathematical acceptability of the biphasic mechanism of Scheme I has been shown, and on this basis it would seem to be a possibility—one that is, moreover, to be expected on the basis of earlier results with monofunctional benzylchromium cations. It is, in fact, on quite a different basis that we argue *against* the mechanism of Scheme I. If the monochromium cation of this mechanism were a key species, then it should have been isolable by the ion-exchange separation applied to solutions of I reacted with a stoichiometric deficiency of Fe^{3+} . Instead, such solutions yielded only Cr^{3+} and unreacted dichromium cation I. The strength of this argument rests on our ability to isolate this very monochromium cation in a direct synthesis from *p*- $\text{BrCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH}$ and on the direct measurement of its rate of reaction with Fe^{3+} . The latter is at the lower end of the spectrum of reactivity we have seen; had this complex been formed it should easily have been isolated. The argument is further supported by the isolation of such monochromium cations from reactions where the kinetic pattern is, in fact, known to be a biphasic one with "statistical" (or nearly statistical) values of the kinetic and spectral parameters, these examples being the reactions of Cr^{2+} with $(m\text{-BrCH}_2)_2\text{C}_6\text{H}_4$ and $(m\text{-BrCH}_2\text{C}_6\text{H}_4)_2\text{O}$.⁴

It is our contention that the reaction of the dichromium complexes with oxidants does, indeed, proceed by rate-limiting homolysis (ignoring for the moment the minor pathway showing a direct dependence on $[\text{Fe}^{3+}]$). The similarities between all aspects of the kinetic data for these complexes and the parent benzylchromium cations are so great as to lead us to no other tenable conclusion. The monophasic reaction is believed to arise in these cases simply because the immediate product of this homolysis, $[\text{CrCH}_2\text{PhCH}_2]^{2+}$, evidently undergoes reactions which (a) are very rapid compared to the rate at which it is formed, (b) do not lead to monochromium cations such as $[\text{CrCH}_2\text{PhCH}_2\text{OH}]^{2+}$ or $[\text{CrCH}_2\text{PhCH}_3]^{2+}$, and (c) lead to the production of polymer. The nature of this chemistry cannot be described with certainty. Formation of a diradical by a second homolysis step is possible, although we might argue against this because there is no evident basis for this homolysis being so much more rapid than that of every other benzylchromium cation. Second, homolysis would be required to occur in a special fashion not only for the radical product formed from such complexes such as I, for which a second and rapid homolysis produces a *p*-xylylene intermediate which can be resonance stabilized



but also from the meta complex II, where similar effects are not possible. This leads us to suggest that polymer growth may be effected by direct radical displacement reactions at the benzylchromium species; there is no evidence for or against the presence of chromium-containing polyorganics such as $[\text{CrCH}_2\text{PhCH}_2(-\text{CH}_2\text{PhCH}_2)_n]^{2+}$. The mechanism, eq 1–3, by which the dichromium complexes are formed from the dibromides, is regarded as well established and supported further in our work by the isolation of the half-substituted monochromium precursor of II, $[m\text{-CrCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{Br}]^{2+}$. The next species formed is the monochromium radical cation formed by reaction of this species with Cr^{2+} , namely, $[m\text{-}$

$\text{CrCH}_2\text{C}_6\text{H}_4\text{CH}_2]^{2+}$. Clearly this, once formed, then reacts rapidly with Cr^{2+} to form II. But this radical is identical with the species formed by homolysis of II. One must account for its conversion to II in the one case, yet its failure (in the mechanism we are proposing) to survive for a sufficiently long time to be oxidized by Fe^{3+} . The Cr^{2+} reaction is very rapid; on the basis of the formation rates,³¹ one estimates $k \sim 10^7 \text{ M}^{-1} \text{ s}^{-1}$. The reactions leading to polymer growth, on the other hand, evidently occur much more rapidly than reaction of this radical with iron(III).

One notes that the one dichromium complex which is different from all the others, much more reactive toward polymer formation, is the biphenyl-based cation III, which, like I, is a complex having a structure which should afford the readiest electronic communication between metal centers. These results bring to mind the results of Harriman and Maki³² on the rate of intramolecular electron transfer in the species *p*- $\text{NO}_2\text{C}_6\text{H}_4(-\text{CH}_2)_n\text{C}_6\text{H}_4\text{NO}_2-p'$ ($n = 0-2$). Higher rates were obtained for these radical anions when $n = 0$ compared to $n = 2$. Other than in complex III, however, such intramolecular charge-transfer processes are clearly unimportant for the species we have studied. Their homolysis reactions are all very similar to monochromium analogues. The small variations of the rate constant from one complex to the next appear to reflect little more than the usual effects of meta and para substituents.

The rate constant for homolysis of *p*- $\text{CrCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH}^{2+}$ ($k = 1.66 \times 10^{-3} \text{ s}^{-1}$) can be combined with the earlier Hammett correlation⁵ to derive a substituent constant for *p*- CH_2OH of $\sigma_p = +0.19$, for which a reliable value does not appear to be available. This value is quite close to that for *p*- CH_2Br ($\sigma_p = +0.14$) and suggests that *p*- CH_2OH is just slightly more electron withdrawing than the latter substituent. The only monochromium complex which fails to fit into this correlation is that with *m*- CH_2Br ($k = 1.22 \times 10^{-3} \text{ s}^{-1}$; expected from correlation for $\sigma_m = +0.12$, $1.93 \times 10^{-3} \text{ s}^{-1}$). This is the only meta-substituted derivative and suggests a direct stabilizing influence (through-space interaction between *m*- CH_2Br and the trans coordination site of chromium?); the data do not permit further comment. One is tempted to ask whether the rate constants for the dichromium cations should be considered in the same light. If one did so, these rate constants, after division by 2.00 to correct for the presence of the two identical $\text{CH}_2\text{Cr}^{2+}$ substituents, correspond to $\sigma_p = +0.31$ and $\sigma_m = +0.38$. The former value we view with confidence, but the latter is questionable since the *m*- CH_2Br , the only other meta-substituted complex examined, deviates considerably.

It was found that some of the complexes react with iron(III) ions at a rate which increases somewhat with increasing $[\text{Fe}^{3+}]$. The magnitude of the effect was generally rather small, although for a few of the runs the dependence was clearly outside of the experimental error. There was some indication that the rate of reaction by this pathway may also be proportional to $1/[\text{H}^+]$, but in no run does the iron(III)-dependent pathway assume sufficient importance to permit a meaningful study of the term. We suggest that this corresponds to a contribution from a minor pathway in which FeOH^{2+} or Fe^{3+} attacks directly the chromium complex; we infer this from studies³³ of other systems in which direct attack is the major (or sole) pathway and unimolecular homolysis relatively unimportant.

Finally, we remark on the unexpected finding that reaction of any of the dichromium complexes with aqueous bromine leads to formation of organic polymer. This stands in marked contrast to our results on the benzylchromium ion and on its substituted monochromium analogues.³⁴ These complexes

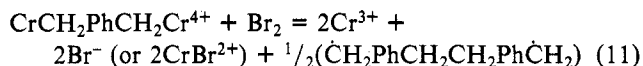
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react with aqueous bromine, iodine, and iodine monobromide in a reaction of straightforward stoichiometry and kinetics ($\text{CrCH}_2\text{Ph}^{2+} + \text{X}_2 \rightarrow \text{Cr}^{3+} + \text{PhCH}_2\text{X} + \text{X}^-$), for which kinetic comparisons suggest an $\text{S}_\text{E}2$ mechanism, like that between organochromium cations and mercury(II) ion.¹⁸ One might thus have expected that the dichromium complexes would also have reacted sequentially, as they appear to do⁴ with mercury(II), first forming a monochromium cation and then the dibromide: $[\text{CrCH}_2\text{PhCH}_2\text{Cr}]^{4+} \rightarrow [\text{CrCH}_2\text{PhCH}_2\text{Br}]^{2+} \rightarrow \text{BrCH}_2\text{PhCH}_2\text{Br}$. The middle member has been made for the two complexes II and VII,⁴ but from reaction of the appropriate dibromide with chromium(II) and not via bromine. It proves to be a stable species, however, typical of other monochromium cations. We did not perform kinetic determinations, but the reactions between the dichromium cations and aqueous bromine occur very rapidly, appearing complete upon mixing. This establishes that the mechanism is direct attack and not unimolecular homolysis. Two possible explanations come to mind. Reaction may occur by an oxidative pathway in which an organochromium complex capable of initiating polymerization is produced. Or a low concentration of atomic bromine may prove sufficient to function similarly. Further resolution does not appear possible at this point, although we note the recent report³⁵ of reductive

coupling induced by oxidation. Similar chemistry applied to the systems at hand would lead to a reaction, eq 11, which would result ultimately in polymer formation.



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Registry No. I, 71837-75-7; II, 71886-74-3; III, 71837-76-8; IV, 71837-77-9; V, 71837-78-0; VI, 71837-79-1; VII, 69493-83-0; *m*- $\text{CrCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{Br}^{2+}$, 71886-75-4; *p*- $\text{CrCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH}^{2+}$, 71837-80-4; *p*- $\text{CrCH}_2\text{C}_6\text{H}_4\text{Ph}^{2+}$, 71886-76-5; Cu(II), 15721-63-8; Co(III), 22541-63-5; Fe(III), 20074-52-6; α, α' -dibromo-*m*-xylene, 626-15-3; α, α' -dibromo-*p*-xylene, 623-24-5; 4,4'-bis(bromomethyl)-biphenyl, 20248-86-6; 4,4'-bis(bromomethyl)diphenylmethane, 16980-01-1; 4,4'-bis(bromomethyl)-1,2-diphenylethane, 6337-67-3; 4,4'-bis(bromomethyl)diphenyl ether, 4542-75-0; 2,4-bis(bromomethyl)toluene, 56752-76-2; *p*-phenylbenzyl bromide, 2567-29-5; *p*-(bromomethyl)benzyl alcohol, 71831-21-5; *p*-pyCo-(dmgH) $_2\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH}$, 71837-81-5; *p*-[pyCo(dmgh) $_2\text{CH}_2\text{C}_6\text{H}_4$], 36425-45-3.

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Contribution from the Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011

Kinetics and Mechanism of Adduct Formation between Iron(III) and Bis(dimethylglyoximate)cobalt(III) Complexes

ANDREJA BAKAČ¹ and JAMES H. ESPENSON*

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Iron(III) ion undergoes a reversible association with methyl(aquo)cobaloxime and with diaquocobaloxime in which it replaces the hydrogen-bonded proton in one O-H...O group of the parent cobaloxime. Equilibrium constants for the reaction $\text{Fe}^{3+} + [\text{XCo}^{\text{III}}(\text{dmgH})_2\text{H}_2\text{O}]^n = [\text{XCo}(\text{dmg}_2\text{HFe})\text{H}_2\text{O}]^{n+2} + \text{H}^+$ were evaluated at 25 °C, the values for $\text{X} = \text{CH}_3^-$ being 16.2 ± 0.5 ($\mu = 0.10$ M) and 15.3 ± 0.8 ($\mu = 1.0$ M) and for $\text{X} = \text{H}_2\text{O}$, 2.55 ± 0.055 ($\mu = 1.0$ M). The rates of both reactions were determined at various concentrations of iron(III) and hydrogen ion, with results consistent with the equilibrium nature of the reactions. The rate laws and rate constants determined are consistent with the mechanism being a process of ligand substitution on iron(III) but are perhaps better explained by a mechanism common to every pathway in which the rate-limiting step is neutralization of the hydrogen-bonded proton of O-H...O by $(\text{H}_2\text{O})_5\text{FeOH}^{2+}$ with concurrent incorporation of iron into the oxime bridging position.

Introduction

Some metal complexes with planar, tetradentate chelating ligands are able to form adducts with a second metal ion. Most such adducts reported are formed between the bis(salicylalimine) complexes of divalent transition metals and a variety of metal ions.²⁻⁶ Shifts in the ^1H NMR spectrum and changes in the visible spectrum which occur when various metal ions are added to the organometallic complex $\text{CH}_3\text{Co}(\text{salen})\text{H}_2\text{O}$ (salen = *N,N'*-ethylenebis(salicylideneiminato)) have been ascribed to similar adduct formations⁷ whereby cobalt(III) and

the second metal ion are bridged by the two oxygen atoms of the macrocyclic salen ligand.

The possibility of bis(dimethylglyoximate)metal complexes forming similar Lewis acid-base adducts is less obvious owing to intramolecular hydrogen bonding in the pseudomacrocycle. However, replacement of hydrogen in such an O-H...O group takes place readily when $\text{RCo}(\text{dmgH})_2\text{B}$ (R = alkyl group, $\text{B} = \text{H}_2\text{O}$ or organic base such as pyridine or phosphine, and dmgH = the monoanion of dimethylglyoxime) reacts with boron trifluoride etherate forming $\text{RCo}(\text{dmgBF}_2)_2\text{B}$ containing two O-BF₂-O units.⁸ Compounds such as $\text{ClCo}(\text{dmgBF}_2)_2\text{PBu}_3^9$ and $\text{ClCo}(\text{dmg}_2\text{HBF}_2)\text{PBu}_3^{10}$ the latter

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