

test. An advantage of this approach is that the arrangements of atoms can be determined regardless of the stereogenicities of the atoms involved. Control of the tether allows systematic variation of the possible geometries of transition structures, and variations in concentration and reactant groups may be used to probe the available modes of a reaction. It is to be noted that the conclusions which can be drawn from this approach are independent of the yield of the rearranged product.

We hope that this Account may help to stimulate applications of this approach to other atoms and other kinds of reactions.

*The experimental results from our laboratories were achieved by the colleagues cited in the references. They and many others in Urbana have made this work possible, and I am very grateful to them for their effort and accomplishments. We also very much appreciate support by the National Science Foundation and the National Institutes of Health for this work.*

## Chemistry of Organochromium(III) Complexes

JAMES H. ESPENSON

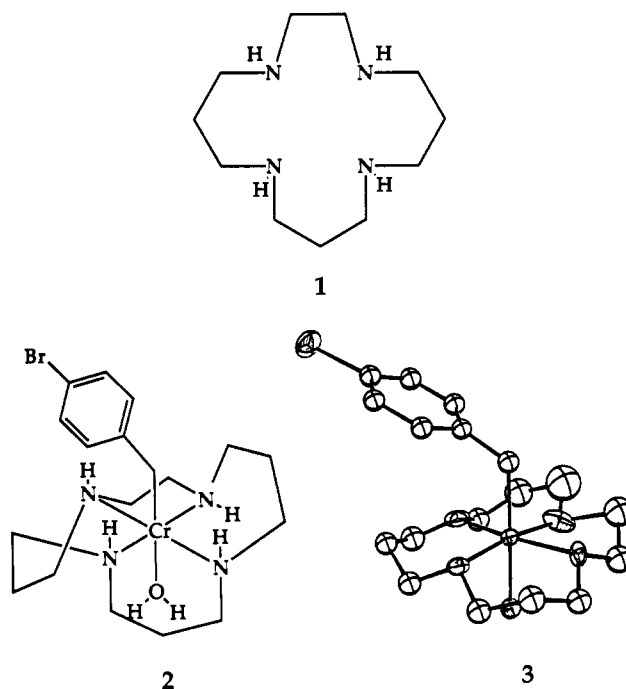
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Compounds with a bond between chromium and carbon are now reasonably common. Here we consider species containing trivalent chromium, which tend therefore to involve  $\sigma$  donor ligands rather than  $\pi$  acceptors. Their general formula is  $R_nCrL_m$ ; this includes such species as  $R_3Cr(THF)_3$ ,  $(H_2O)_5CrR^{2+}$ ,  $RCr(THF)_3Cl_2$ ,  $RCr(acac)_2(NC_5H_5)$ , etc. Only for the family with the general formula  $(H_2O)_5CrR^{2+}$  have reaction mechanisms been explored systematically, and in this Account I summarize these results. Earlier work was reviewed about a decade ago,<sup>1,2</sup> and the chemistry of other series such as  $[(\eta^5-C_5Me_5)CrRCl_2]_2$  has been reviewed with particular attention to applications as polymerization catalysts.<sup>3</sup> For mechanistic studies the existence of a single alkyl group is highly advantageous since it is difficult to deconvolute the sequential and similar reactions of a species like  $R_3Cr(THF)_3$ .

**Structures and Trans Effects.** As yet, not one member of the  $(H_2O)_5CrR^{2+}$  series has been isolated as a pure solid, or in a form suitable for crystallography. By coating the chromium with other ligands, however, so as to reduce hydrogen bonding to the solvent, crystal structures have been obtained<sup>4-6</sup> for derivatives, including *trans*- $RCr(acac)_2(NC_5H_5)$  with  $R = CHCl_2$  and  $CH_2Cl$  and  $[trans-RCrL(H_2O)](ClO_4)_2$  with  $L = 1,4,8,12$ -tetraazacyclopentadecane (1) and  $R = 4$ - $BrC_6H_4CH_2$  (2, 3). The crystallographic data substantiated the structures inferred from chemical and spectroscopic data (but not, of course, from NMR owing to paramagnetism).

A notable feature of the structures is the elongated bond between chromium and its *trans* ligand, compared to that in species lacking the chromium-carbon bond. For example, the complexes *trans*- $ClCH_2Cr(acac)_2B$  have trans distances as follows:  $d_{CrN} = 220.1$  pm ( $B = NC_5H_5$ ),  $d_{CrO} = 213.4$  pm ( $B = H_2O$ ), and  $d_{CrO} = 215.6$

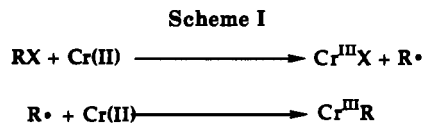


pm ( $B = CH_3OH$ ).<sup>4,5</sup> In comparison,  $d_{CrO}$  values are 210, 196.5, and 197.5–209.0 pm for *mer*- $Cr(CF_3CO_2)_3(NC_5H_5)_3$ ,<sup>7</sup> *trans*- $[CrCl_2(CH_3OH)_4]^+$ ,<sup>8</sup> and various other  $CrOH_2$  compounds.<sup>5</sup>

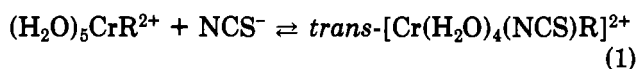
The discovery of the elongated *trans* distances confirms the kinetic measurements. The reactivity of  $(H_2O)_5CrR^{2+}$  and other metal-alkyl complexes, including organocobaloximes, toward ligands entering into the

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James H. Espenson was born in Los Angeles in 1937. He received a B.S. degree from Caltech in 1958 and a Ph.D. degree from the University of Wisconsin in 1962 under Edward L. King. He then was a postdoctoral fellow at Stanford University with Henry Taube. He joined Iowa State University as an instructor in 1963, where he is now distinguished professor and chairman of the Chemistry Department as well as senior chemist and program director at the Ames Laboratory. His research interests concern the mechanisms of inorganic and organometallic reactions.

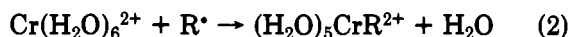


trans position is increased.<sup>4,9-14</sup> Compared to their purely inorganic counterparts, the organometallic species are much more labile, often by a factor of  $10^5$ . More specifically, the half-times for addition of one thiocyanate ion (at 25.0 °C, 0.200 M  $\text{H}^+$ , and 0.100 M  $\text{NCS}^-$ ) are 42, 128, and  $9.3 \times 10^6$  s for  $(\text{H}_2\text{O})_5\text{CrCH}_2\text{Cl}^{2+}$ ,<sup>9</sup>  $(\text{H}_2\text{O})_5\text{CrCHCl}_2^{2+}$ ,<sup>9</sup> and  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ .<sup>15</sup> This is a kinetic phenomenon, not a thermodynamic one, since the binding constants for thiocyanate ion by these three chromium complexes are (per molecule of replaceable water) 10.4, 12.7, and 12  $\text{L mol}^{-1}$ , respectively.

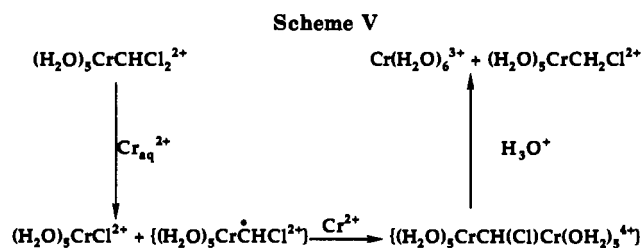
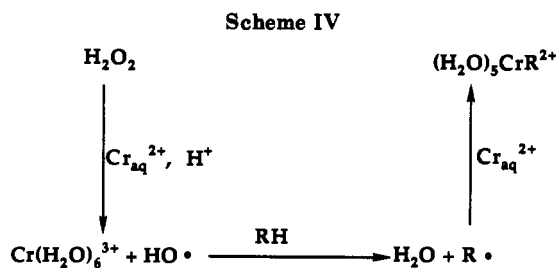
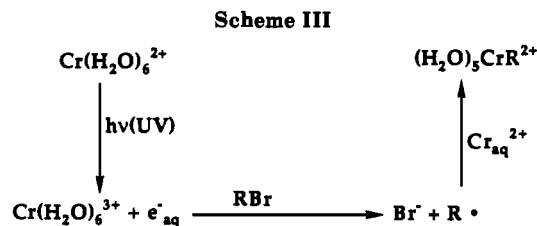
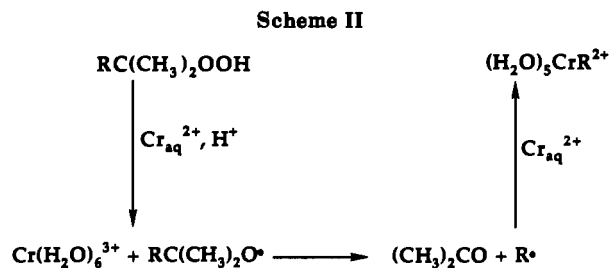


Experiments have also been carried out to show that only one of the water molecules in  $(\text{H}_2\text{O})_5\text{CrCH}_2\text{Cl}^{2+}$  is subject to rapid replacement. This was shown<sup>9</sup> by using  $\text{CH}_3\text{OH}$  as the entering ligand; even at very high mole fractions only one methanol was found to replace water within a few minutes, compared to four or five methanols that would become coordinated were the cis positions also equilibrated. The substitution inertness of ligands cis to the R group, too, is supported by the structural data, in that the cis Cr-O distances in  $\text{ClCH}_2\text{Cr}(\text{acac})_2\text{B}$  are "normal".

**Chromium-Carbon Bond Formation.** Virtually every one of the  $(\text{H}_2\text{O})_5\text{CrR}^{2+}$  ions is formed by a "colligation"<sup>16</sup> process, eq 2. Flash photolysis for alkyl radicals and pulse radiolysis for other aliphatic radicals give rate constants in the range  $10^{7.5}-10^{8.2}$   $\text{L mol}^{-1} \text{s}^{-1}$ .<sup>17-20</sup> The values vary relatively little over a wide range of R groups.



The reactions by which  $\text{R}\cdot$  is generated, allowing reaction 2 to occur, are quite varied. Among the methods used are chemical reaction, photolysis, and radiolysis. One radical source is an alkyl halide, but in the case of  $\text{Cr}(\text{H}_2\text{O})_6^{2+}$  itself, reaction is limited to "activated" molecules such as benzyl halides and polyhaloalkanes.<sup>21-24</sup> Simple alkyl halides, even iodides, fail to

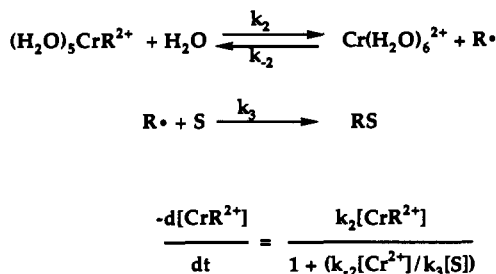


react with  $\text{Cr}(\text{H}_2\text{O})_6^{2+}$  in aqueous solution when complexing ligands are absent. One can bring about this reaction in other solvents (e.g.,  $\text{CrSO}_4$  in aqueous dimethylformamide or dimethyl sulfoxide). Also, addition of a ligand such as ethylenediamine<sup>25</sup> or a saturated tetraazamacrocyclic such as **1**<sup>26</sup> leads to ready reaction.<sup>26</sup> This results in  $\text{RCr}(\text{en})_2^{2+}$  and  $[\text{RCrL}(\text{H}_2\text{O})]^{2+}$ . The effect of solvent and ligands is a thermodynamic and kinetic one. The  $\text{CrL}_6^{3+/2+}$  potential becomes more negative when water is replaced. This adds to the driving force of the first step in Scheme I. Also, the reorganizational barrier between the two oxidation states appears to be less as more powerfully donating ligands are added, which provides a kinetic advantage. The alkyl and aralkyl halide reactions occur with two  $\text{Cr(II)}$ 's consumed per mole of halide, one to form the  $\text{Cr(III)}$  halide, the other, an organometallic complex. This mechanism, which was validated in early work,<sup>21-23,25,26</sup> is shown in Scheme I. It features an inner-sphere halogen atom abstraction reaction as its first and rate-controlling step. The isolation of the  $\text{Cr}^{\text{III}}\text{X}$  product confirms the inner-sphere nature of this reac-

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Scheme VI



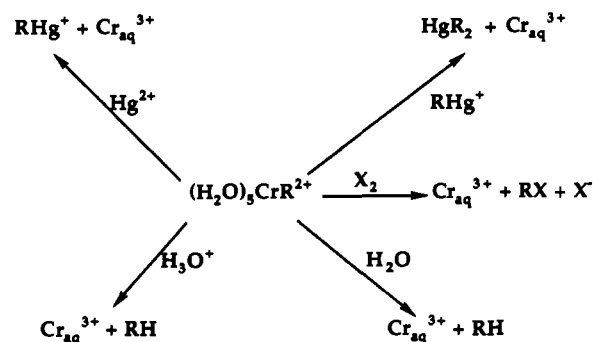
tion, since for both thermodynamic and kinetic reasons  $\text{Cr}^{3+}$  and  $\text{X}^-$  would not combine under these conditions.

The ions  $(\text{H}_2\text{O})_5\text{CrR}^{2+}$  in which R is a simple alkyl group can be prepared from hydroperoxides (Scheme II)<sup>27-30</sup> and by UV photolysis (Scheme III).<sup>31</sup> Still another route is a so-called modified Fenton reaction (Scheme IV), in which the reaction between  $\text{Cr}^{2+}$  and  $\text{H}_2\text{O}_2$  is conducted in the presence of hydrocarbon RH or  $(\text{CH}_3)_2\text{SO}$ . This utilizes the reactive  $\text{HO}\cdot$  intermediate. Complexes with  $\alpha\text{-OH}$ ,  $\text{-OR}$ , and  $\text{-CO}_2\text{H}$  substituents can thus be prepared from alcohols, ethers, and carboxylic acids, as can the cyclopentyl and methyl complexes.<sup>19,20,28,32,33</sup> Appropriate variants have allowed the preparation of bimetallic complexes<sup>34-37</sup> such as  $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CNC}(\text{NH}_3)_5^{3+}$ ,  $(\text{H}_2\text{O})_5\text{Cr}=\text{OC}(\text{NH}_2)\text{-CH}_2\text{Cr}(\text{OH})_2^{5+}$ , and  $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{C}_6\text{H}_4]_2\text{O}^{4+}$ . Related to this is the chlorine atom abstraction from  $\text{CrCHCl}_2^{2+}$  by  $\text{Cr}^{2+}$ , which yields  $\text{CrCH}_2\text{Cl}^{2+}$ , probably via  $\text{CrCHClCr}^{4+}$  (Scheme V).<sup>38</sup>

The long-lived  $\text{CrR}^{2+}$  derivatives can be purified and concentrated by chromatography on a cation-exchange resin. Shorter-lived species are often used as prepared. All of the  $(\text{H}_2\text{O})_5\text{CrR}^{2+}$  complexes are orange in color because of a fairly intense absorption near 390–405 nm, relatively insensitive to the nature of R. The molar absorptivities of this band are usually 200–400  $\text{L mol}^{-1} \text{cm}^{-1}$ , indicating some charge-transfer character to what is otherwise a weaker d–d band in the inorganic analogues  $(\text{H}_2\text{O})_5\text{CrX}^{2+}$ . A strong charge-transfer band at 270–290 nm ( $\epsilon$  2–4  $\times 10^3 \text{ L mol}^{-1} \text{cm}^{-1}$ ) is also noted. There is a weak d–d band at longer wavelengths, 520–570 nm ( $\epsilon$  10–40  $\text{L mol}^{-1} \text{cm}^{-1}$ ), typical of aquachromium(III) complexes.

**Homolysis.** One of the most important of the  $\text{CrR}^{2+}$  reactions is unimolecular homolysis, the reverse of the process in eq 2 by which it is formed. The chromium–carbon bond is moderately strong, however, and homolysis is an uphill reaction that occurs only upon addition of a scavenger for either of the fragments,  $\text{Cr}^{2+}$  or  $\text{R}\cdot$ . In confirmation of this mechanistic assignment, the first-order rate constant remains independent of the

Scheme VII



nature of the scavenger as well as its concentration.<sup>33,39,40</sup> Also, when the reaction is conducted with added  $\text{Cr}^{2+}$ , the rate is retarded. In the presence of a radical scavenger, a competition for  $\text{R}\cdot$  occurs, in accord with Scheme VI and the associated rate law.<sup>41-46</sup> The two terms in the denominator of the rate law show the retardation effect of added  $\text{Cr}^{2+}$ . In other words, this confirms that homolysis and colligation are the reverse of one another. In particular this shows that  $\text{Cr}^{2+}$  is the immediate product of the first step, which is thus confirmed to be a homolytic reaction.

The temperature dependence of  $k_2$  affords activation parameters for the homolysis of different  $\text{CrR}^{2+}$  complexes. Values of  $\Delta H^\ddagger$  are large, 100–140  $\text{kJ mol}^{-1}$ , reflecting the strength of the chromium–carbon bond. The value of  $\Delta H^\ddagger$  is a kinetic measure of the chromium–carbon bond enthalpy. Values of  $\Delta S^\ddagger$  are large and positive, 80–150  $\text{J mol}^{-1} \text{K}^{-1}$ . This reflects a contribution from the separation of two entities from one and (probably more important) the introduction of the aliphatic free radical into the aqueous medium.

The rates of homolysis vary sharply with the nature of R. Aralkyl and secondary complexes are the most labile: typical values of  $k_2$  are  $2.6 \times 10^{-3} \text{ s}^{-1}$  ( $\text{R} = \text{PhCH}_2$ ) and  $1.8 \times 10^{-4} \text{ s}^{-1}$  ( $\text{CH}(\text{CH}_3)_2$ ). Primary alkyl complexes do not homolyze to any appreciable extent. Another series reflecting this trend consists of  $\text{R} = \text{C}(\text{CH}_3)_2\text{OH}$  ( $k_2 = 1.3 \times 10^{-1} \text{ s}^{-1}$ ),  $\text{CH}(\text{CH}_3)\text{OH}$  ( $8.5 \times 10^{-4} \text{ s}^{-1}$ ), and  $\text{CH}_2\text{OH}$  ( $3.7 \times 10^{-5} \text{ s}^{-1}$ ). This trend in reactivity is largely a reflection of the change in the Cr–C dissociation enthalpy along the series.

The general reactions in Scheme VI can be used to evaluate  $k_3$  for reactions of a given radical with various substrates. This application has been termed the “method of stored free radicals”. This requires that  $k_2$  and  $k_{-2}$  be known, which is usually the case in that  $k_2$  can be obtained for a given  $\text{CrR}^{2+}$  complex from studies with the most reactive scavengers, and  $k_{-2}$ , the colligation rate constant, can be measured directly by flash photolysis or pulse radiolysis. This method has been used to evaluate  $k_3$  for a wide range of substrates that have values in the range  $10^3 < k_3 < 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ . The fast-reacting members, those with  $k_3 \geq 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ , are independently dealt with by pulse radiolysis or flash

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photolysis, and the stored free radical method is used only as a matter of convenience or to check a directly-determined value. Actually, this method becomes important when  $k_3$  lies in the range  $10^3$ – $10^7$  L mol<sup>-1</sup> s<sup>-1</sup>, which is below the usual limit for pulse radiolysis or flash photolysis. In those techniques, the radiation produces the radicals all at once, in a burst. Unless the substrate reacts rapidly ( $k_3 > 10^7$  L mol<sup>-1</sup> s<sup>-1</sup>, usually), the radical is wasted on the R· + R· self-reactions (dimerization or disproportionation). With the "stored free radicals", however, [R·]<sub>SS</sub> is always so low, by virtue of the competing reactions –2 and 3 in Scheme VI, that self-reactions are unimportant. The most studied radicals are those with α-OH or -OR groups, such as ·C(CH<sub>3</sub>)<sub>2</sub>OH and ·CH(CH<sub>3</sub>)OC<sub>2</sub>H<sub>5</sub>.<sup>41–46</sup>

**Heterolysis.** The (H<sub>2</sub>O)<sub>5</sub>CrR<sup>2+</sup> complexes react readily with electrophiles. Reagents and products are shown in Scheme VII.<sup>33,47–51</sup> It should be noted that X<sub>2</sub> gives RX and X<sup>-</sup>, not (H<sub>2</sub>O)<sub>5</sub>CrX<sup>2+</sup>. The failure of CrX<sup>2+</sup> to form, Cr<sub>aq</sub><sup>3+</sup> and X<sup>-</sup> resulting instead, shows that a four-centered transition state is not effective. The rate constants for all the electrophiles drop off sharply with substitution on the α carbon. For an illustration of this, consider one series: The rate constants for Hg<sup>2+</sup> reactions with different (H<sub>2</sub>O)<sub>5</sub>CrR<sup>2+</sup> complexes are 1.0 × 10<sup>7</sup> L mol<sup>-1</sup> s<sup>-1</sup> (R = CH<sub>3</sub>), 1.4 × 10<sup>5</sup> L mol<sup>-1</sup> s<sup>-1</sup> (C<sub>2</sub>H<sub>5</sub>), 3.5 × 10<sup>4</sup> L mol<sup>-1</sup> s<sup>-1</sup> (*n*-C<sub>3</sub>H<sub>7</sub>), and 1.56 × 10<sup>0</sup> L mol<sup>-1</sup> s<sup>-1</sup> (*i*-C<sub>3</sub>H<sub>7</sub>).<sup>47</sup> This trend indicates direct attack of the electrophile on the α-C atom.

These data suggest that the reactions occur with *inversion* of configuration at carbon. Not one of these reactions has been studied stereochemically, however, and I believe none can be. That is, no chiral CrR<sup>2+</sup> complex can be prepared since each is made from a free radical. One might argue that the formation of CrR<sup>2+</sup> from Cr<sup>2+</sup> + RCo(dmgh)<sub>2</sub>OH<sub>2</sub> offers such a possibility since these cobalt complexes are known in chiral form, e.g., with R = *sec*-butyl and 2-octyl. It is in just these cases, with bulky R groups, that alkyl transfer to chromium becomes so slow that CrR<sup>2+</sup> decomposition by homolysis or reaction with H<sub>2</sub>O would prevent product to accumulate. Were PhCHDCo(dmgh)<sub>2</sub>OH<sub>2</sub> made in chiral form, a chiral CrCHDPh<sup>2+</sup> ion could be made momentarily, but it seems likely to racemize rapidly by virtue of homolysis.<sup>39</sup>

In any event, the kinetic inference that inversion at carbon occurs in the Hg<sup>2+</sup> reaction is supported by comparing the rates of reactions between RCo(dmgh)<sub>2</sub>OH<sub>2</sub> complexes and Hg<sup>2+</sup>. These reactions are unequivocally known to proceed with inversion.<sup>52</sup> The pattern of rates with varying R is the same for cobalt and chromium. The kinetic parallel is complete, as it also is for the reactions of Br<sub>2</sub> with CrR<sup>2+</sup>.<sup>49–51</sup>

The proton is much less reactive than other electrophiles, as shown by the data for (H<sub>2</sub>O)<sub>5</sub>CrCH<sub>3</sub><sup>2+</sup>.<sup>28,33</sup> The rate constants for different electrophiles are as follows: Hg<sup>2+</sup>, 1.0 × 10<sup>7</sup> L mol<sup>-1</sup> s<sup>-1</sup>; Br<sub>2</sub>, 2.1 × 10<sup>6</sup> L mol<sup>-1</sup> s<sup>-1</sup>; I<sub>2</sub>, 8.5 × 10<sup>4</sup> L mol<sup>-1</sup> s<sup>-1</sup>; CH<sub>3</sub>Hg<sup>+</sup>, 1.0 × 10<sup>4</sup>

L mol<sup>-1</sup> s<sup>-1</sup>; H<sub>3</sub>O<sup>+</sup>, 4.9 × 10<sup>-3</sup> L mol<sup>-1</sup> s<sup>-1</sup>. The rate of CrR<sup>2+</sup> decomposition in acidic medium, in the absence of other reagents, is<sup>28,33</sup>

$$-d[\text{CrR}^{2+}]/dt = (k_{A1} + k_{A2}[\text{H}_3\text{O}^+])[\text{CrR}^{2+}] \quad (3)$$

The contribution of the two terms for a given group R depends upon [H<sub>3</sub>O<sup>+</sup>], but their relative contributions vary greatly with R. For example,<sup>30</sup>



$$v = (<5 \times 10^{-5} + 4.94 \times 10^{-3}[\text{H}^+]) \text{ mol L}^{-1} \text{ s}^{-1} \quad (4)$$

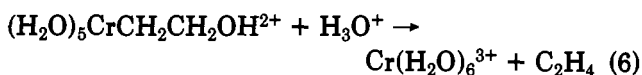


$$v = (2.2 \times 10^{-4} + 1.15 \times 10^{-4}[\text{H}^+]) \text{ mol L}^{-1} \text{ s}^{-1} \quad (5)$$

Clearly, the ethyl complex hydrolyzes much more rapidly than the methyl complex by the acid-independent pathway, yet more slowly when accelerated by acid. The *n*-propyl complex continues the trend.<sup>30</sup> At pH > 4, both OH<sup>-</sup> and OAc<sup>-</sup> ions accelerate the solvolysis.<sup>53–55</sup>

There is a sharp contrast between the acidolysis reactions of (H<sub>2</sub>O)<sub>5</sub>CrR<sup>2+</sup> and RCrL(H<sub>2</sub>O)<sup>2+</sup>. The macrocyclic complexes do not react at all with either H<sub>3</sub>O<sup>+</sup> or H<sub>2</sub>O,<sup>6,56</sup> even over long periods of time, although their reactions with Hg<sup>2+</sup> and Br<sub>2</sub> proceed like those of (H<sub>2</sub>O)<sub>5</sub>CrR<sup>2+</sup>.<sup>57</sup> This suggests that the very small electrophiles, H<sub>2</sub>O and H<sub>3</sub>O<sup>+</sup>, which must approach the Cr–C bond more closely than Hg<sup>2+</sup>, cannot do so easily owing to interactions with the macrocyclic rings and/or the amine protons.

Organochromium cations with a β-OH or β-halogen group on R are very short-lived. These complexes react by β-elimination, generating alkenes. An example is shown in eq 6 for one particular complex, which undergoes β-elimination in a reaction with a rate directly dependent upon [H<sup>+</sup>], eqs 6 and 7.<sup>58</sup> Related reactions,<sup>20,59</sup> including β-chloride elimination, are known.<sup>60–63</sup>



$$v_{298} = 1.5 \times 10^4 [\text{CrCH}_2\text{CH}_2\text{OH}^{2+}] [\text{H}^+] \text{ mol L}^{-1} \text{ s}^{-1} \quad (7)$$

**Reaction with Oxygen.** The reaction of (H<sub>2</sub>O)<sub>5</sub>CrR<sup>2+</sup> with oxygen has been studied only for (H<sub>2</sub>O)<sub>5</sub>CrCH(CH<sub>3</sub>)<sub>2</sub><sup>2+</sup>, but qualitative indications suggest that the result may be more general. This reaction (eq 8) follows a chain mechanism, as indicated by the unusual rate law (eq 9) and the inhibiting effect of Cu<sup>2+</sup>, which is expressed by an alternative rate law (eq 10)<sup>64</sup>

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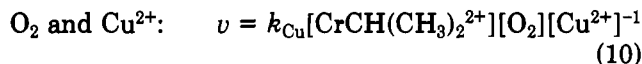
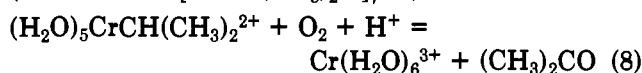
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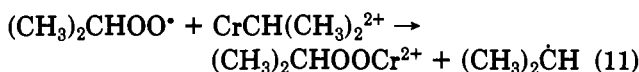
(where  $\nu = -d[\text{CrCH}(\text{CH}_3)_2^{2+}]/dt$ ):



A mechanism that accounts for these data is given in Scheme VIII, according to which the experimental rate constant is related to the elementary constants by  $k_{\text{O}_2} = k_c(k_a/2k_d)^{1/2}$ . Or, with  $\text{Cu}^{2+}$  present,  $k_{\text{Cu}} = k_a k_b/k_e$ .

The resolution of this mechanism actually occasioned the discovery of a new principle concerning the effect of ionic strength on the rates of "ill-behaved" chain reactions (i.e., those in which the initiation and termination steps are not the reverse of one another).<sup>65</sup> This small group of reactions includes that between  $\text{CrCH}(\text{CH}_3)_2^{2+}$  and  $\text{O}_2$ . In such cases, alternatives that lead to the same kinetic rate equations can be distinguished. Ordinarily (i.e., for nonchain reactions), any mechanism consistent with the form of the rate law will have an identical kinetic salt effect. In this case, we also considered a mechanism similar to that in Scheme VIII, except that  $\text{CrOO}^{2+}$  rather than  $(\text{CH}_3)_2\text{CHOO}^\bullet$  is a chain-carrying intermediate. The alternative was eliminated from consideration because its predicted salt effect was in disagreement with the experimental data.

One of the chain-propagating steps in Scheme VIII, labeled as c, is a reaction between  $\text{ROO}^\bullet$  and  $\text{CrR}^{2+}$ . One radical seems to displace another, and we suggest an  $\text{S}_{\text{H}}2$  mechanism. The first reaction step in c would be



The alkylperoxy complex of chromium is believed to be a metastable species. It then hydrolyzes to acetone and hexaaquachromium(III) ion, with only the net effect given as c in Scheme VIII. Hydrolysis of (alkylperoxy)cobalt complexes has been independently reported.<sup>66</sup>

If the alkylperoxy complex is indeed formed as in eq 11, then the overall sequence constitutes a mechanism for oxygen insertion into the chromium-carbon bond. Related to this is the reaction of  $\text{CrR}^{2+}$  with  $\text{SO}_2$ , which yields  $\text{CrOS}(\text{O})\text{R}^{2+}$  (20%), with the majority of the reaction forming  $\text{Cr}^{3+}$  and  $\text{RSO}_2^-$ .<sup>67</sup>

**Electron Transfer.** Strong oxidizing agents cause the chromium-carbon bond to be cleaved by an oxidative-homolysis sequence, Scheme IX. Reagents that have been used as acceptors (A) include  $\text{Ni}(\text{cyclam})^{3+}$ ,  ${}^2\text{E-Cr}(\text{bpy})_3^{3+}$  (a long-lived excited state),  $\text{HONO}$ , and  $\text{Ru}(\text{bpy})_3^{3+}$ .<sup>68-70</sup> Oxidizing inorganic radicals such as  $\text{Br}_2^{\bullet-}$ ,  $\text{I}_2^{\bullet-}$ , and  $(\text{SCN})_2^{\bullet-}$  also serve as A.<sup>71</sup> Substantiation of this scheme comes from trapping of  $\text{R}^\bullet$ ; addition of  $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ , for example, yields  $\text{RBr}$ . The

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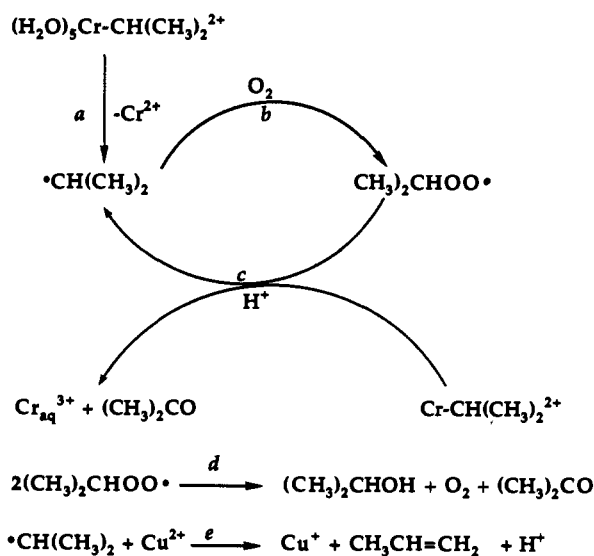
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## Scheme VIII

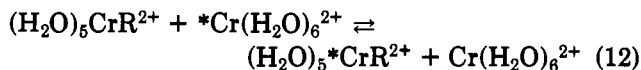
Scheme IX<sup>a</sup>

<sup>a</sup> A =  $\text{Ni}(\text{cyclam})^{3+}$ ,  $\text{HONO}$ ,  $\text{Ru}(\text{bpy})_3^{3+}$ , etc.

first step in Scheme IX is the rate-controlling one in all the systems examined. Attempts to measure the rate at which the free radical is released by the oxidized organometal have not been successful.

Oxidation of  $(\text{H}_2\text{O})_5\text{CrR}^{2+}$  complexes, with R containing an  $\alpha$ -OH or -OR group, also takes place with  $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{VO}^{2+}$ .<sup>72</sup> Here, the R group itself is oxidized. This is not entirely surprising in that these particular R groups, as free radicals, are strong reducing agents.<sup>73</sup>

**Radical Transfer.** Alkyl groups transfer to and from  $\text{Cr}^{2+}$ , as in eq 12.<sup>74</sup> This reaction is remarkable in that it represents an *inner-sphere reaction in which the bridging ligand lacks an electron pair*. It seems to follow an  $\text{S}_{\text{H}}2$  mechanism: bimolecular homolytic substitution. What is special about this is that it is a relatively rare example of  $\text{S}_{\text{H}}2$  substitution at saturated carbon. The rates drop off sharply with bulkier R groups, consistent with their bridging role and with metal attack at the  $\alpha$ -carbon. Transalkylation of  $\text{Cr}^{2+}$  by other organometals (e.g., cobalt, nickel) is a known and related phenomenon.<sup>75-78</sup>



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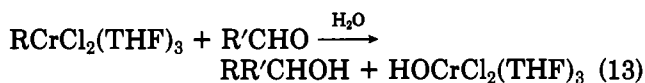
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**Applications.** Chromium compounds have found commercial use for the polymerization of ethylene and propylene.<sup>79-81</sup> In aqueous solutions, ethylene is polymerized upon addition of  $\text{ArCH}_2\text{CrL}(\text{H}_2\text{O})^{2+}$ , presumably by a chain reaction of  $\text{ArCH}_2^\bullet$ , formed by homolysis.<sup>82</sup> Other organochromium(III) compounds are also active catalysts for alkene polymerization, usually in organic solvents like  $\text{CH}_2\text{Cl}_2$  and THF. This includes  $[\text{Cp}^*\text{Cr}(\text{THF})_3\text{CH}_3](\text{BPh}_4)$  and  $[\text{Cp}^*\text{Cr}(\text{CH}_2\text{SiMe}_3)_2]$ .<sup>83</sup>

Under certain circumstances, organochromium(III) compounds react with aldehydes, as in eq 13. This occurs for  $\text{RCrCl}_2(\text{THF})_3$ , as shown.<sup>84</sup> Ketones are unreactive. The complexes  $\text{R}_2\text{CrCl}(\text{THF})_3$  also react, but  $(\text{H}_2\text{O})_5\text{CrR}^{2+}$  is unreactive.<sup>85</sup> The R groups used include  $\text{CH}_3$ ,  $n\text{-C}_3\text{H}_7$ ,  $n\text{-C}_4\text{H}_9$ ,  $\text{sec-C}_4\text{H}_9$ ,  $n\text{-C}_8\text{H}_{17}$ , and  $\text{PhCH}_2$ . Extensive tests were run for both heptanal and benzaldehyde.



Another application for organochromium(III) complexes is found in their use for selective coupling of free

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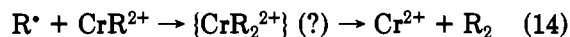
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radicals. Once some  $\text{CrR}^{2+}$  is formed, as in Scheme I, the radical may instead react with  $\text{CrR}^{2+}$ :



Reactant ratios must be chosen carefully, and conditions can even be arranged first to make  $\text{CrR}^{2+}$  and then, with a different alkyl halide,  $\text{RR}'$ . There is no evidence for the dialkylchromium(IV) intermediate pictured in eq 14. This reaction might also be viewed as an  $\text{S}_{\text{H}2}$  displacement, although its mechanism has not been studied.

**Concluding Remarks.** The family of  $(\text{H}_2\text{O})_5\text{CrR}^{2+}$  complexes has provided remarkably fertile ground for mechanistic study. Many reactions display a range of reactivity. As shown, the  $\text{CrR}^{2+}$  bond dissociates both heterolytically and homolytically, and the balance between them can be controlled. That is, for a given R, homolysis can be promoted by addition of a scavenger and retarded by added  $\text{Cr}^{2+}$ . Similarly, increasing steric bulk on the  $\alpha$ -carbon greatly increases the rate of homolysis but accelerates heterolysis only marginally. Because the proton and the solvent are kinetically inefficient electrophiles, the complexes survive in aqueous media. More reactive electrophiles, such as mercuric salts or halogens, react very rapidly.

These complexes, or closely related ones, have recently been shown to have promise in organic reactions.<sup>86</sup> They can initiate olefin polymerization and can add nucleophilically to aldehydes.

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## The Transient Grating: A Holographic Window to Dynamic Processes

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### Introduction

As laser technology progresses, nonlinear optical (NLO) techniques<sup>1</sup> are becoming increasingly important tools in chemistry. Most NLO techniques involve several laser beams and a distinct signal beam; however, the single defining characteristic of a NLO experiment is that the intensity of the observed signal is proportional to the  $n$ th power of the laser intensity, where  $n$

> 1. Examples of NLO techniques that have been used in chemistry include the photon echo,<sup>2</sup> second-harmonic generation,<sup>3</sup> and hole burning.<sup>4,5</sup> In this Account we discuss what has become perhaps the most widely used NLO technique in chemistry, the transient grating (TG).<sup>6,7</sup> TG experiments have been performed in all

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