$$\frac{-d[PQ^{\bullet+}]}{dt} = \frac{k_{10}k_{11}[CrCH_2Ph^{2+}][PQ^{\bullet+}]}{k_{-10}[Cr^{2+}] + k_{11}[PQ^{\bullet+}]} \qquad (12)$$

Other checks were also performed to trace the possible source of the deviations at high $[V^{2+}]$ either to a fault in a reagent or to side reactions. Using only glass and Teflon fittings throughout did not alter the situation nor did using V^{2+} prepared from ion-exchanged VO^{2+} or $PQ^{\bullet+}$ prepared electrochemically rather than by zinc reduction. Identical rate constants were obtained in chloride and perchlorate media, and the values were independent of $[H^+]$ and ionic strength. The same increase in the apparent rate constant at high $[V^{2+}]$ was observed when barium perchlorate was used to maintain constant ionic strength and reaction medium by maintaining $[V^{2+}] + [Ba^{2+}] = 2.60$ mM. Because of that, we continued to use the literature values of k_3 and k_{-3}, determined at $\mu = [H_3O^+] = 1.0$ M, even though the present experiments were run at $9 \leqslant [H_3O^+] \leqslant 27$ mM. At most, these reactions cause but a minor correction to the form for R_{PQ} given in eq 4; as such, any revisions in the values are of secondary importance.

Direct spectrophotometric measurements showed that negligible association between V^{2+} and $PQ^{\bullet+}$ occurs. Although association of $PQ^{\bullet+}$ pairs has been reported,[22] that equilibrium is not the problem here.[23] The product of eq 9a is a modified methyl viologen, which can be independently prepared by oxidation of $PQ^{\bullet+}$ with alkyl hydroperoxides:

$$2PQ^{\bullet+} + RC(CH_3)_2OOH + 2H^+ = PQ^{2+} + PQRH^{2+} + (CH_3)_2CO + H_2O \qquad (13)$$

The reduction of $PQRH^{2+}$ (prepared in situ according to eq 13) with V^{2+} produces an intensely blue monocation, which decomposes within a few minutes in weakly acidic solutions.[24] The formation and subsequent decomposition of small amounts of these reduced species in the alkyl hydroperoxide reactions with V^{2+} may be responsible for the deviations from pseudo-zeroth-order kinetics and the erroneous rate constants at high $[V^{2+}]$. The chemistry of $PQ^{\bullet+}$ and related species has recently been reviewed.[25]

In the final analysis, we failed to eliminate completely the kinetic deviations at high $[V^{2+}]$ for the ROOH reaction. The data are otherwise in such good conformity to the rate law of eq 4 that, despite this difficulty, we feel this method gives a correct evaluation of k_1, the second-order rate constant for the rate-limiting step of the sequence.

Discussion

Kinetic Data. The rate constant for the hydrogen peroxide reaction, 15.4 M^{-1} s^{-1} at 25.0 °C, is in good agreement with the value given by Rush and Bielski,[4] 17.2 M^{-1} s^{-1} at 21 °C. The small difference might be ascribed to systematic errors inherent in the use of the very different experimental methods or to the difference in reaction medium (low and variable ionic strength here, versus 0.12 M perchloric acid in the reported data[4]).

Another area of agreement in the two studies concerns the lack of VO^{2+} formation. VO^{2+} would have been very evident in the UV method used earlier, yet it was not seen. There was also no evidence for VO^{2+} formation in the present series of experiments. This also contradicts an earlier report.[3]

Inner-Sphere Mechanism. The rate constants for all of the peroxides lie within the range generally attributed to ligand substitution in the primary coordination sphere of the hexaaquavanadium(II) ion.[26] Since outer-sphere reductions of peroxides are rare and are perhaps without precedent,[27] it seems likely that rate-limiting inner-sphere substitution precedes the electron-transfer step.

The options for the immediate products of the inner-sphere reaction are several. The precursor complex might yield $\{VO^{2+} + ROH\}$ or $\{VOH^{2+} + RO^{\bullet}\}$. The first set is inconsistent with both inorganic and organic products obtained, whereas the latter is in good agreement. This has been detailed in eq 5 and 6 and is supported by the methanol trapping experiment represented by eq 7 and 8.

Acknowledgement is made to the National Science Foundation for support from Grant CHE-84-18084. Some of this work was accomplished with facilities of Ames Laboratory, operated by Iowa State University for the U.S. Department of Energy under Contract W-7405-Eng-82.

Registry No. V^{2+}, 15121-26-3; H_2O_2, 7722-84-1; $PQ^{\bullet+}$, 25239-55-8; *tert*-butyl hydroperoxide, 75-91-2; *tert*-amyl hydroperoxide, 3425-61-4; α,α-dimethyl-β-phenethyl hydroperoxide, 1944-83-8.

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(22) Kosower, E. M. In *Free Radicals in Biology*; Pryor, W. A., Ed.; Academic: New York, 1978; Vol. II. This author gives $K = 4 \times 10^3$ M^{-1} for $2PQ^{\bullet+} = (PQ_2)^{2+}$.

(23) Association of $PQ^{\bullet+}$ pairs is not of a magnitude to cause the effect noted at the concentrations of $PQ^{\bullet+}$ used. This association reaction is very rapid (we could not observe it by stopped-flow dilution with solvent), and the small difference in molar absorptivity between PQ^+ and its dimer cannot cause the problem in calculation of R_{PQ}.

(24) These features suggest a bipyridyl radical cation $(PQ\dot{R}H)^{\bullet+}$, a species we would expect to be very similar to $PQ^{\bullet+}$. It could participate in eq 3 and other reactions, and give rise to the effects noted.

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Kinetics and Mechanism of the Reactions of Alkylchromium Complexes with Aqueous Sulfur Dioxide

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The organopentaaquochromium(III) complexes, $(H_2O)_5CrR^{2+}$ (R = alkyl, substituted alkyl, benzyl, and substituted benzyl), react with SO_2 in aqueous perchloric acid solutions to yield $(H_2O)_6Cr^{3+}$ (~80%), $(H_2O)_5Cr(SO_2)R^{2+}$ (~20%), and alkanesulfinic acids. The reactivity pattern within the series ($CH_3 > 1° \sim$ benzyl $\gg 2°$) closely matches that observed earlier in electrophilic substitution reactions of these and other organometallic complexes. The competition between the solvent water and the oxygen or sulfur of the leaving RSO_2^- group is responsible for the formation of the two chromium products.

Introduction

Several mechanistic pathways have been identified in the reactions of SO_2 with organometallic species.[1-3] Coordinatively saturated complexes usually react by electrophilic substitution or a radical mechanism to yield sulfur- or oxygen-bonded insertion products. Electrophilic substitution is typified by the lack of the

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(2) Crease, A. E.; Johnson, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 8013.

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0020-1669/87/1326-4093$01.50/0

effect of radical scavengers and by a reactivity pattern[1,4] that reflects the retarding effect of steric crowding and the acceleration by electron-donating substituents. These reactions take place by inversion of configuration at the α-carbon.[1,5,6] Radical mechanisms, on the other hand, have been demonstrated only for certain organocobalt and organorhodium complexes that are known to undergo homolytic cleavage of the metal–carbon bond.[2,3] As expected, these reactions take place with a complete loss of stereochemistry at the α-carbon.[3]

The pentaaquoorganochromium(III) complexes, $(H_2O)_5CrR^{2+}$, constitute a unique series that is reactive in both electrophilic and homolytic cleavage reactions of the metal–carbon bond.[7,8] This group of complexes thus seems to have the potential to react with SO_2 by either mechanism. A rapid reaction of SO_2 with $(H_2O)_5CrCH_2C_6H_5^{2+}$ has been noted earlier,[9] but no kinetic or mechanistic data were reported.

This paper reports the results of our study of the reactions of SO_2 with the organochromium complexes $(H_2O)_5CrR^{2+}$. The kinetic data and the nature of the products strongly suggest that these reactions take place by electrophilic substitution.

Experimental Section

Reagents. The organochromium complexes were prepared as reported previously[7] and purified on a column of Sephadex SP-C25 cation-exchange resin. The ion-exchange step was omitted in the case of the short-lived methyl and hydroxymethyl complexes. Stock solutions of SO_2 were prepared by dissolving the SO_2 gas (Matheson) in deaerated aqueous perchloric acid. The concentrations of SO_2 in these solutions were initially determined by a standard procedure[10] based on the oxidation of SO_2 by I_3^- and titration of excess I_3^- by thiosulfate. The UV spectra of the SO_2 solutions in 1.2 M $HClO_4$ exhibit a maximum at 280 nm, $\epsilon = 449 \pm 22$ M^{-1} cm^{-1} (average of 21 determinations in the concentration range 0.001–0.1 M SO_2). This value of the molar absorptivity is somewhat higher than those previously reported ($\epsilon_{280} = 367 \pm 18$ M^{-1} cm^{-1} in 5.8 M $HClO_4$,[11] $\epsilon_{276} = 388$ M^{-1} cm^{-1} in 0.1 M H_2SO_4[12]). Subsequent determinations of $[SO_2]$ were done spectrophotometrically by use of the molar absorptivity determined in this work.

Product Analysis. Organic products were analyzed by HPLC on a column of homemade anion-exchange resin (20–26 μm XAD-1) coated with a proprietary weak-base anion-exchange material.[13] The instrument was equipped with a Wescan conductivity detector and a Hitachi D-2000 Chromato-Integrator. In a typical experiment, gaseous SO_2 was passed through a 0.05 M solution of an organochromium complex (not ion exchanged to avoid dilution) for several minutes. After the completion of the reaction, the excess SO_2 was removed by a stream of argon and the solution was diluted 100-fold to reduce the concentration of $HClO_4$ and analyzed by HPLC with 1.5 mM succinic acid as eluant. In several cases the experiments were performed in D_2O, the product mixture was extracted with $CDCl_3$, and the ^1H NMR spectrum was recorded by use of a Nicolet NT-300 NMR spectrometer. Inorganic products were separated by ion exchange on Sephadex SP-C25.

Kinetics and Stoichiometry. A pseudo-first-order excess of SO_2 was used in all the kinetic experiments. The progress of the reaction was monitored spectrophotometrically (Cary 219) at the wavelengths of maximum absorbance of the organochromium complexes (350–410 nm). Most of the experiments were run in 1.0 M $HClO_4$ under air-free conditions (Ar or N_2 atmosphere). A few blank experiments were conducted which showed that the variation of $[H^+]$ in the range 0.1–1.0 M and the presence of air have no effect on the kinetics. The kinetic parameters were evaluated by standard procedures.

The decomposition of the organochromium complexes by acidolysis, and in some cases homolysis, is the dominant reaction in the absence of a large excess of SO_2. This precluded the direct determination of the reaction stoichiometry, which was assumed to be 1.0 in all the reactions.

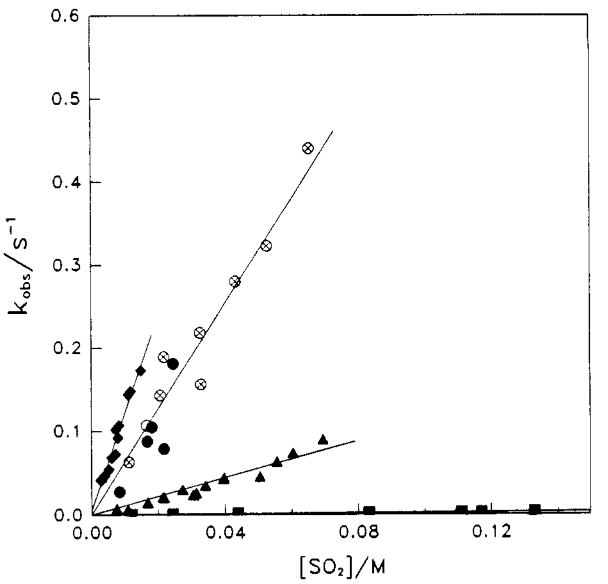

Figure 1. Linear plots of k_{obsd} vs the concentration of SO_2 for R = CH_3 (◆), C_2H_5 (●), n-C_3H_7 (▲), and i-C_3H_7 (■), illustrating the first-order dependence on $[SO_2]$. The kinetics for R = C_2H_5 are unaffected by the presence of O_2 (⊗) or $(NH_3)_5CoCl^{2+}$ (○).

Table I. Summary of the Kinetic Data for the Reactions of SO_2 with $(H_2O)_5CrR^{2+}$ in 1.0 M $HClO_4$ at 25 °C

R	$10^2k_{SO_2}$/ M^{-1} s^{-1}	R	$10^2k_{SO_2}$/ M^{-1} s^{-1}
CH_3	1100	p-CH_3-$C_6H_4CH_2$	670
C_2H_5	520	$C_6H_5CH_2$	250[a]
n-C_3H_7	94		350[b]
i-C_3H_7	2.2		520
c-C_5H_9	0.975		800[c]
CH_2OH	19.2	p-Br-$C_6H_4CH_2$	280
CH_2OCH_3	0.125	p-CF_3-$C_6H_4CH_2$	180
CH_2CH_2CN	0.079	$(CH_3)_5C_6CH_2$	2300
CH_2Cl	0.000848	2,4,6-$(CH_3)_3$-$C_6H_2CH_2$	590
p-CH_3O-$C_6H_4CH_2$	780		

[a] 1.9 °C. [b] 11.4 °C. [c] 39.9 °C.

The kinetics of the reactions of $(H_2O)_5CrR^{2+}$ (R = n-C_3H_7, CH_2OH, and CH_2CH_2CN) with Br_2 in 1.0 M $HClO_4$ were measured at 25 °C by use of a Durrum stopped-flow spectrophotometer, as described earlier.[14]

Results

Kinetics. The disappearance of the organochromium complexes in the presence of SO_2 followed the rate law of eq 1, where k_0

$$-d[(H_2O)_5CrR^{2+}]/dt = (k_0 + k_{SO_2}[SO_2])[(H_2O)_5CrR^{2+}] \quad (1)$$

represents the sum of all the first-order rate constants for the spontaneous decomposition of $(H_2O)_5CrR^{2+}$ (acidolysis and/or homolysis) and k_{SO_2} is the second-order rate constant for the reaction with SO_2.

The k_0 term was negligibly small in most of the experiments, typically contributing <10% to the observed rate constants at the lowest $[SO_2]$ employed (Figure 1). Only in the case of the isopropyl and cyclopentyl complexes, which decompose by both acidolysis and homolysis yet react with SO_2 extremely slowly, were the k_0 terms significant: 10% and 50% of $(H_2O)_5CrCH(CH_3)_2^{2+}$ and 40% and 75% of $(H_2O)_5Cr$-c-$C_5H_9^{2+}$ decomposed by the k_0 path at the highest and lowest $[SO_2]$, respectively. The invariance of the rate constant k_{SO_2} with $[H^+]$ was confirmed for $(H_2O)_5CrCH_2C_6H_5^{2+}$ and $(H_2O)_5CrC_2H_5^{2+}$ in the range 0.10–1.0 M $HClO_4$, and assumed for all the other complexes. Similarly, the kinetics were unaffected by the presence of air or by addition of 0.8 mM $(NH_3)_5CoCl^{2+}$. The kinetic data are summarized in Table I.

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(14) Espenson, J. H.; Williams, D. A. *J. Am. Chem. Soc.* **1974**, *96*, 1008.

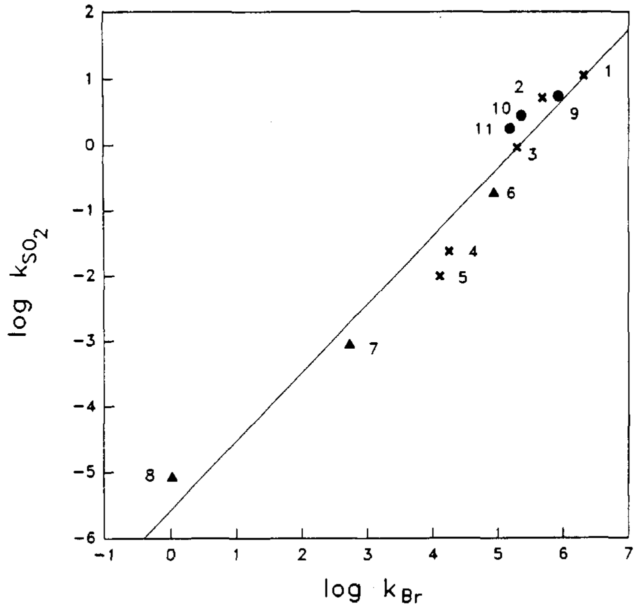


Figure 2. Plot of log k_{SO_2} vs log k_{Br} for the reactions with $(H_2O)_5CrR^{2+}$, R = CH_3 (1), C_2H_5 (2), n-C_3H_7 (3), i-C_3H_7 (4), c-C_5H_9 (5), CH_2OH (6), CH_2OCH_3 (7), CH_2Cl (8), $C_6H_5CH_2$ (9), p-Br-$C_6H_4CH_2$ (10), and p-CF_3-$C_6H_4CH_2$ (11).

The activation parameters were evaluated from the data for $(H_2O)_5CrCH_2C_6H_5^{2+}$ in the temperature range 1.9–39.9 °C. The values of $\Delta H^‡$ and $\Delta S^‡$ are 4.8 ± 0.2 kcal/mol and −39.1 ± 0.8 cal/(mol K), respectively.

Products. Two major peaks of comparable size are found in the HPLC chromatograms of all the product solutions analyzed. The species with the longer retention time is the sulfonic acid, RSO_3H. The yields of RSO_3H, determined by comparison to authentic samples of known concentrations, were 35 ± 10% of the $[(H_2O)_5CrR^{2+}]$ consumed. The other peak is possibly due to $RSSO_3H$. The assignment is based on the known chemistry of sulfinic acids and was not confirmed directly, since neither sulfinic acids nor $RSSO_3H$ acids are readily available.

The chromium-containing products of the reactions of SO_2 with $(H_2O)_5CrR^{2+}$ (R = C_2H_5, i-C_3H_7, CH_2OCH_3, and $CH_2C_6H_5$) were separated by cation exchange. In all the cases two bands were observed. The major band was identified as $Cr(H_2O)_6^{3+}$, formed in 80 ± 20% yield. The minor green band of 1+ or 2+ charge contained 20 ± 10% of the total chromium. The green complexes obtained in the reactions of the three alkyls examined (CH_2CH_3, $CH(CH_3)_2$, and CH_2OCH_3) all exhibit maxima in their UV–visible spectra at 590 nm (ϵ = 20 M^{-1} cm^{-1}), 420 (23), and 260 (~1000). The green complex obtained in the reaction of the benzylchromium cation exhibits a weak maximum at 415 nm and a strong one at 220 nm, ϵ ~7500 M^{-1} cm^{-1}. All of these green species persist for several days in acidic solutions but hydrolyze rapidly at pH 10. The HPLC chromatograms of the hydrolyzed solutions show only one peak, which corresponds to alkanesulfonic acid. The green complexes are thus identified as $(H_2O)_5Cr(SO_2)R^{2+}$.

Reactions with Bromine. The kinetics of the reactions of Br_2 with several $(H_2O)_5CrR^{2+}$ complexes were determined. The values of the rate constants are 2.0×10^5 (n-C_3H_7), 8.7×10^4 (CH_2OH), and 5.4×10^2 M^{-1} s^{-1} (CH_2CH_2CN).

Discussion

The reactivity pattern observed in the reaction of $(H_2O)_5CrR^{2+}$ ($CH_3 > 1° \sim CH_2C_6H_5 \gg 2°$) parallels closely that observed in electrophilic substitutions in these complexes,[7] notably reactions with Br_2, Hg^{2+}, IBr, Tl^{3+}, etc. This point is illustrated by the linearity of the plot log k_{SO_2} versus log k_{Br_2}, shown in Figure 2. The close correspondence of the data for the alkyl, substituted alkyl, and benzyl complexes is evident. This reactivity pattern is quite different from that for unimolecular homolysis ($CH_2C_6H_5 \gg 2° \gg 1°$),[7] which would be the key step in any radical mechanism for the reaction with SO_2.

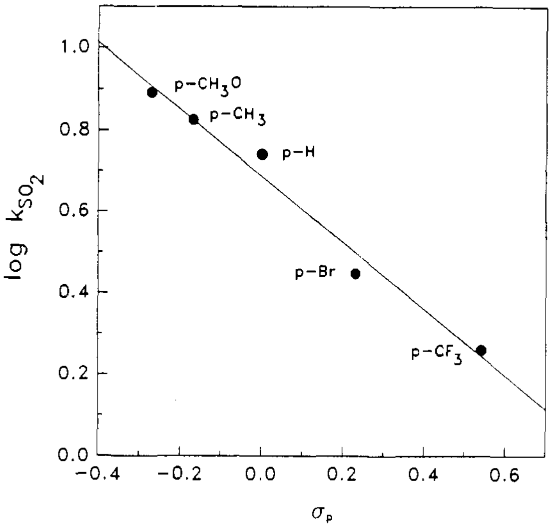
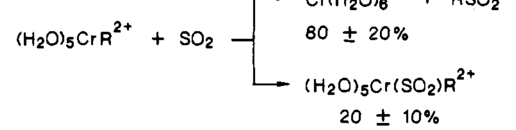


Figure 3. Plot of log k_{SO_2} vs the Hammett substituent constant σ_p for the reaction of $(H_2O)_5CrCH_2$-p-X-$C_6H_4^{2+}$ with SO_2.

The Hammett plot for the series of para-substituted benzylchromium complexes, Figure 3, is linear and yields a ρ value of −0.79. This reaction constant is consistent with electrophilic substitution and indicates the development of partial positive charge in the transition state. The reaction of Br_2 with substituted benzylchromium complexes has $\rho = -1.29$.[15]

The lack of the kinetic effect of oxygen strongly indicates that neither Cr^{2+} nor C-centered radicals play important roles in the mechanism, since both would be effectively scavenged by O_2 under the reaction conditions. Similarly, $(NH_3)_5CoCl^{2+}$ was without effect. This finding has, however, a less definite significance, owing to the possible competition of SO_2 and $(NH_3)_5CoCl^{2+}$ for Cr^{2+}.[16]

All the data presented, including the activation parameters for the reaction of $(H_2O)_5CrCH_2C_6H_5^{2+}$, are consistent with the mechanism of eq 2–4. The electrophilic substitution step, eq 2,



$$(H_2O)_5CrR^{2+} + SO_2 \rightarrow \begin{cases} \xrightarrow{H_2O} Cr(H_2O)_6^{3+} + RSO_2^- \quad 80 \pm 20\% \\ \rightarrow (H_2O)_5Cr(SO_2)R^{2+} \quad 20 \pm 10\% \end{cases} \qquad (2)$$

$$RSO_2^- + H^+ \rightleftharpoons RSO_2H \quad pK_a \sim 2^{17} \qquad (3)$$

$$3RSO_2H \rightarrow RSO_3H + RSSO_2R + H_2O \qquad (4)$$

produces mainly $Cr(H_2O)_6^{3+}$ and the alkanesulfinate. The protonation of the latter, eq 3, yields the unstable alkanesulfinic acid, which disproportionates to alkanesulfonic acid and alkyl alkanethiosulfonate,[17,18] eq 4. The HPLC analysis of the reaction products has indeed confirmed the presence of alkanesulfonic acids. The alkyl alkanethiosulfonates, on the other hand, were not detected in the NMR experiments,[19] presumably owing to the subsequent nucleophilic attack of HSO_3^-,[20] eq 5. The analogous

$$RSSO_2R + HSO_3^- \rightarrow RSSO_3H + RSO_2^- \qquad (5)$$

reaction of $C_6H_5SSO_2C_6H_5$ with a number of nucleophiles, including SO_3^{2-}, has been reported.[18] The other major peak in the

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(15) Chang, J. C.; Espenson, J. H. *J. Chem. Soc., Chem. Commun.* **1974**, 233.

(16) SO_2 reacts rapidly with Cr^{2+} to yield an intensely colored green species that decomposes within several hours. The kinetics of this reaction were not studied, and the efficiency of $(NH_3)_5CoCl^{2+}$ as a scavenger for Cr^{2+} in the presence of SO_2 is uncertain.

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(18) Kice, J. L. *Adv. Phys. Org. Chem.* **1980**, *17*, 65.

(19) This nonionizable species is not expected to give rise to a HPLC peak.

(20) Small amounts of the latter are always present in equilibrium with SO_2: $SO_2 + H_2O \rightleftharpoons HSO_3^- + H^+$, $K = 0.0126$ (van Eldik, R.; Harris, G. M. *Inorg. Chem.* **1980**, *19*, 880).

HPLC chromatogram has thus been assigned to $RSSO_3H$.

On the basis of eq 2-5, the calculated yields of RSO_3H, $RSSO_3H$, and unhydrolyzed $(H_2O)_5Cr(SO_2)R^{2+}$ are 40%, 40%, and 20%, respectively. The satisfactory agreement between the observed (25-45%) and calculated (~40%) yields of both RSO_3H and $RSSO_3H$ and, in particular, the formation of comparable amounts of the two products strongly support the proposed mechanism.

We assign the formula $(H_2O)_5Cr(SO_2)R^{2+}$ to the green species produced in 20 ± 10% yield in the reaction of $(H_2O)_5CrR^{2+}$ with SO_2. The visible spectra of these complexes show only low-intensity bands typical of inorganic complexes of chromium(III). The UV region indicates the presence of bound SO_2 (the band at 260 nm) and the alkyl group (strong absorption for R = benzyl). Base hydrolysis at pH 10 of the ion-exchanged complex formed in the reaction of SO_2 with the 2-propylchromium yields 2-propanesulfonic acid, probably by the sequence of reactions 6, 3,

$$(H_2O)_5Cr(SO_2)CH(CH_3)_2^{2+} \xrightarrow{H_2O} (H_2O)_6Cr^{3+} + (CH_3)_2CHSO_2^- \quad (6)$$

and 4. As expected, the decomposition of 2-propanesulfinic acid in the absence of SO_2/HSO_3^- yielded no $(CH_3)_2CHSSO_3H$. The concentrations were too low, however, to attempt the identification of $(CH_3)_2CHSSO_2CH(CH_3)_2$ by NMR.

Reaction according to eq 2 gives rise to two distinctly different chromium(III) products, $Cr(H_2O)_6^{3+}$ and the insertion product, $(H_2O)_5Cr(SO_2)R^{2+}$. The relative amounts of the two are apparently determined by the competition between a molecule of solvent and the nucleophilic site on the leaving ligand for the coordination site on the metal center. A similar situation occurs in the reactions of several functionalized alkylchromium complexes with Hg^{2+}.[21] In the alternative scheme[1] the transition state collapses to the contact ion pair $\{(H_2O)_5Cr^{3+},RSO_2^-\}$. The recombination of the fragments within the ion pair to yield the Cr-O or Cr-S product and their escape into the solvent are then responsible for the formation of the two products.

The insertion of SO_2 into the metal-carbon bonds by electrophilic substitution often yields the O-bonded product, which subsequently isomerizes. The data available in the present case are insufficient to distinguish between the O- and S-bonded species. If the initial product is indeed O-bonded, the isomerization might not take place, given the hard/soft properties of the pentaaquochromium(III) entity, sulfur, and oxygen. On the other hand, the isomerization to the S-bonded isomers has been observed for a number of related cobalt(III) and chromium(III) complexes of the type $L_5MOSO_2^+$.[22-24]

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Registry No. $(H_2O)_5CrCH_3^{2+}$, 32108-96-6; $(H_2O)_5CrC_2H_5^{2+}$, 52653-39-1; $(H_2O)_5Cr\text{-}n\text{-}C_3H_7^{2+}$, 52653-40-4; $(H_2O)_5Cr\text{-}i\text{-}C_3H_7^{2+}$, 60764-48-9; $(H_2O)_5Cr\text{-c-}C_5H_9^{2+}$, 84559-49-9; $(H_2O)_5CrCH_2OH^{2+}$, 32108-95-5; $(H_2O)_5CrCH_2OCH_3^{2+}$, 78402-17-2; $(H_2O)_5CrCH_2CH_2CN^{2+}$, 76068-69-4; $(H_2O)_5CrCH_2Cl^{2+}$, 17477-09-7; $(H_2O)_5CrCH_2C_6H_4\text{-}p\text{-}OCH_3$, 71605-13-5; $(H_2O)_5CrCH_2C_6H_4\text{-}p\text{-}CH_3$, 53150-36-0; $(H_2O)_5CrCH_2Ph^{2+}$, 34788-74-4; $(H_2O)_5CrCH_2C_6H_4\text{-}p\text{-}Br$, 53150-37-1; $(H_2O)_5CrCH_2C_6H_4\text{-}p\text{-}CF_3^{2+}$, 53150-38-2; $(H_2O)_5CrCH_2C_6(CH_3)_5^{2+}$, 110903-70-3; $(H_2O)_5CrCH_2C_6H_2\text{-}2,4,6\text{-}(CH_3)_3^{2+}$, 110903-71-4; $(H_2O)_5Cr(SO_2)C_2H_5^{2+}$, 110934-38-8; $(H_2O)_5Cr(SO_2)\text{-}i\text{-}C_3H_7^{2+}$, 110934-39-9; $(H_2O)_5Cr(SO_2)CH_2OCH_3^{2+}$, 110934-40-2; $(H_2O)_5Cr(SO_2)CH_2Ph^{2+}$, 110934-41-3; CH_3SO_3H, 75-75-2; $C_2H_5SO_3H$, 594-45-6; $n\text{-}C_3H_7SO_3H$, 5284-66-2; $i\text{-}C_3H_7SO_3H$, 14159-48-9; $c\text{-}C_5H_9SO_3H$, 19247-73-5; $HOCH_2SO_3H$, 75-92-3; $CH_3OCH_2SO_3H$, 110874-69-6; $NCCH_2CH_2SO_3H$, 107-67-5; $ClCH_2SO_3H$, 40104-07-2; $CH_3O\text{-}p\text{-}C_6H_4CH_2SO_3H$, 110874-70-9; $CH_3\text{-}p\text{-}C_6H_4CH_2SO_3H$, 110874-71-0; $C_6H_5CH_2SO_3H$, 100-87-8; $Br\text{-}p\text{-}C_6H_4CH_2SO_3H$, 110874-72-1; $CF_3\text{-}p\text{-}C_6H_4CH_2SO_3H$, 110874-73-2; $(CH_3)_5C_6CH_2SO_3H$, 110874-74-3; $2,4,6\text{-}(CH_3)_3C_6H_2CH_2SO_3H$, 4496-98-4; $Cr(H_2O)_6^{3+}$, 14873-01-9; SO_2, 7446-09-5.

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Reduction of Titanium(IV) and Oxidation of Titanium(III) by 1-Hydroxy-1-methylethyl Radicals

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Kinetic competition between TiO^{2+} and $Co(NH_3)_6^{3+}$ was used to study the reduction of titanium(IV) by the indicated aliphatic radical. The second-order rate constant is $(1.1 \pm 0.1) \times 10^6\ M^{-1}\ s^{-1}$ at 25 °C and 1.0 M ionic strength in aqueous 1 M 2-propanol. The rate constant is independent of $[H^+]$ over the range 0.03-0.08 M. The method of "stored free radicals", based on the homolysis of $CrC(CH_3)_2OH^{2+}$, was used to study the oxidation of titanium(III) by the same radical. The apparent second-order rate constant increases markedly with decreasing $[H^+]$. The inverse $[H^+]$ dependence, unprecedented for oxidations by this radical, suggests that a transient intermediate is stabilized by the incipient formation of titanium(IV) already partly deprotonated, thus assisting in the formation of the species TiO^{2+}. Schemes by which this can be accomplished are suggested.

Introduction

Reactions in which aliphatic radicals reduce and oxidize transition-metal aquo cations proceed by a diversity of mechanisms. Reduction reactions appear to occur by "simple" electron transfer, with metal-carbon bond formation known but rare.[2] The mechanisms for oxidation include, for example, metal-carbon bond formation (eq 1) and hydrogen atom abstraction from a coordinated water molecule (eq 2). The intervention of an organometallic intermediate has been verified for Cr^{2+} [3-5] and Cu^+,[6,7]

$$M(H_2O)_n^{x+} + {}^{\bullet}R \rightarrow \{(H_2O)_mM\text{-}R^{x+}\} \xrightarrow{H_3O^+} M(H_2O)_n^{x+1} + RH \quad (1)$$

$$M(H_2O)_n^{x+} + {}^{\bullet}R \rightarrow (H_2O)_mM\text{-}OH^{x+} + RH \quad (2)$$

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