resulting in no net observed $[H^+]$ dependence. Since H_2SeO_3 is a reasonably strong acid ($pK_a = 2.51$ at 25 °C, $\mu = 1.00$ M ($NaClO_4$)[18]) and since Se(IV) can readily expand its coordination shell to accept the neptunium "yl" oxygen as a ligand, all the requirements of the "tautomeric" transition state are satisfied by the Se(IV)–Np(VII) system.

The lack of an inverse acid-dependent path in the Se(IV)–Np(VII) reaction is in marked contrast to the presence of this path in the HCOOH–Np(VII) reaction.[11] However, the HCOOH–Np(VII) system is distinct from all of the Np(VII) oxidations of aquometal ions (including H_2SeO_3) studied to date [9–13] in that HCOOH cannot readily function as a Lewis acid toward the neptunium "yl" oxygen. It is therefore not unreasonable to expect that the HCOOH–Np(VII) reaction proceeds by an entirely different mechanism, and indeed strong evidence has been presented[11] indicating that C–H bond fission is predominant in the rate-determining step of this reaction. The disparate nature of the mechanisms of the H_2SeO_3–Np(VII) and HCOOH–Np(VII) reactions is further reflected in the considerably different entropies of the two activated complexes. The standard entropy of the activated complex, relative to that of Np(VII), can be calculated as $S^* - S^\circ_{Np(VII)} = \Delta S^* + S^\circ_{reductant}$;[13,19] using ΔS^* values of $[H^+]$-independent terms for HCOOH and H_2SeO_3, $S^\circ_{HCOOH} = 39.0$ eu and $S^\circ_{H_2SeO_3} = 49.7$ eu,[20] the relative entropies of the activated complexes for H_2SeO_3 and HCOOH oxidation are respectively +30 and −2.5 eu (no account has been taken of the moles of water involved in these activated complexes). These values for neutral reductants are greater than or equal to those observed for Np(VII) oxidation of positively charged reductants,[13] consistent with the proposition that Np(VII) bears a formal positive charge in aqueous acidic media.[13,19] The relatively small enthalpies of activation for both the HCOOH–Np(VII) and H_2SeO_3–Np(VII) reactions (5.8 and 7.4 kcal/mol, respectively) are characteristic of Np(VII) oxidations in acidic media.[9–13]

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Registry No. H_2SeO_3, 7783-00-8; Np(VII), 20826-07-7.

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(1) (a) A portion of this investigation was conducted under the auspices of the U.S. Energy Research and Development Administration. (b) Bucknell University. (c) Rosary College. (d) Argonne National Laboratory. (e) University of Cincinnati.

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Contribution from the Chemistry Division,
Argonne National Laboratory, Argonne, Illinois 60439

Pulse Radiolysis Studies on the OH-Induced Oxidation of Thiolatometal Complexes[1]

J. C. SULLIVAN,* E. DEUTSCH, G. E. ADAMS,[2] S. GORDON, W. A. MULAC, and K. H. SCHMIDT

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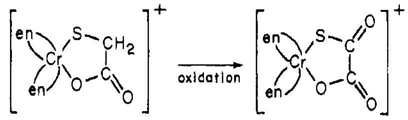
Pulse radiolysis of an N_2O-saturated solution of (mercaptoacetato-*O,S*)bis(ethylenediamine)chromium(III) perchlorate using the streak-camera method shows two intense transient absorption bands centered at 345 and 410 nm. The absorption bands are due to the oxidation of the compound by OH radicals, the absorption at 345 nm being due to attack at the S atom and the one at 410 nm being due to reaction at the α-carbon atom. The results differ from those obtained by the use of strong chemical one-electron oxidants such as neptunium(VI) and cerium(IV). An explanation is offered for this difference.

Introduction

Several enzymes such as hepatic aldehyde dehydrogenase and xanthine oxidase are capable of catalyzing the dehydrogenation of aldehyde to carboxylic acids. A new class of thiolato–transition metal complexes may represent useful models for the active sites of these enzymes.[3] The oxidation of one of these compounds, (mercaptoacetato-*O,S*)bis(ethylenediamine)chromium(III) perchlorate, by one-electron oxidants such as neptunium(VI) and cerium(IV), has been studied by both conventional and stopped-flow methods.[4] These studies showed an unexpected result in that the α-carbon atom was oxidized rather than the sulfur atom, i.e.



There is some interest, therefore, in studying the initial steps in the oxidation of the above compound and other model complexes of this type. This paper describes the use of microsecond pulse radiolysis for observation of the one-electron oxidation products of these complexes.

Experimental Section

Preparation of Complexes. All thiolato complexes except that of α-mercaptoisobutyric acid were available from previous studies.[4b-6] This complex, (2-mercapto-2-methylpropionato-*O,S*)bis(ethylenediamine)chromium(III) perchlorate, was prepared from 2,2-dithiobis(isobutyric acid)[3a] in a manner analogous to that reported for the preparation of the mercaptoacetato complex.[5,7]

Anal. Calcd for $(en)_2Cr(SC(CH_3)_2COO)[ClO_4]\cdot H_2O$: C, 23.56; H, 5.93; N, 13.74; S, 7.86; Cl, 8.69; Cr, 12.75. Found: C, 23.90; H, 6.04; N, 13.89; S, 7.69; Cl, 8.80; Cr, 12.71.

Pulse Radiolysis. Absorption spectra of the transient species, following irradiation of the solutions with single pulses of high-energy electrons, were obtained by the streak camera–TV scanning method described previously.[8-10] Some spectra and all of the kinetic data were obtained by the conventional photomultiplier techniques.[11] The kinetic data were photographed on Polaroid film as oscilloscope traces. The smoothed traces were scanned by an automatic line follower (Hewlett-Packard type F3B). The signals were converted to digital form in a 400-channel analyzer and processed by a Xerox Σ 5 computer. The computer data were treated by a three-parameter least-squares program which calculated the best kinetic fit to the data as well as the standard deviations of three parameters: rate constant, I_0, and I_∞.

Preparation of Solutions. All solutions were made up in triply distilled water and degassed by the syringe technique as described previously.[12] When the solutions were to be irradiated in the presence of nitrous oxide, the gas was purified by freeze-pumping before equilibration with the solutions. The pH's of the solutions were adjusted, where appropriate, with carbonate-free lithium hydroxide or perchloric acid.

Results

Spectral Data. The streak-camera method was used to observe and characterize transient absorption spectra from N_2O-saturated solutions of (mercaptoacetato-*O,S*)bis(ethylenediamine)chromium(III) perchlorate (complex **1**) for a range of concentrations and pH. In dilute solutions, essentially all of the energy absorption processes occur in the aqueous component leading to the formation of the oxidizing radical, OH, the reducing species H·, and the hydrated electron e_{aq}^-. The respective initial yields of these three species, expressed as the "*G* values", i.e., the number of radicals produced per 100 eV of energy absorbed, are $G(OH) \simeq 2.8$, $G(e_{aq}^-) \simeq 2.8$, and $G(H) \simeq 0.55$. In N_2O-saturated solutions hydrated electrons react rapidly with N_2O to give a stoichiometrically equivalent yield of OH radicals according to the reaction

$$N_2O + e_{aq}^- \rightarrow N_2 + OH^- + OH\cdot \qquad (1)$$

for which the rate constant[13] is $8.7 \times 10^9\ M^{-1}\ s^{-1}$.

Therefore, about 10^{-7} s after pulse irradiation, the solution is an approximately one-radical system since OH will constitute approximately 90% of the total radical concentration. Subsequent oxidative reactions of OH with a solute can be studied under fairly ideal conditions.

Figure 1 shows four transient streak spectra from N_2O-saturated solutions of complex **1** (Figure 1a) and three other related chromium complexes (Figure 1b–d) (see later) each irradiated with an electron pulse of 1.0-μs duration. The three-dimensional computer traces show the spectra recorded immediately after the irradiation pulse and at intervals up to 180–200 μs thereafter. For complex **1**, Figure 1a, the spectrum shows two maxima at 345 and 410 nm which, apparently, decay at different rates. Both maxima appear to be formed either within, or immediately after, the electron pulse indicating that one peak does not arise as a consequence of the decay of the other.

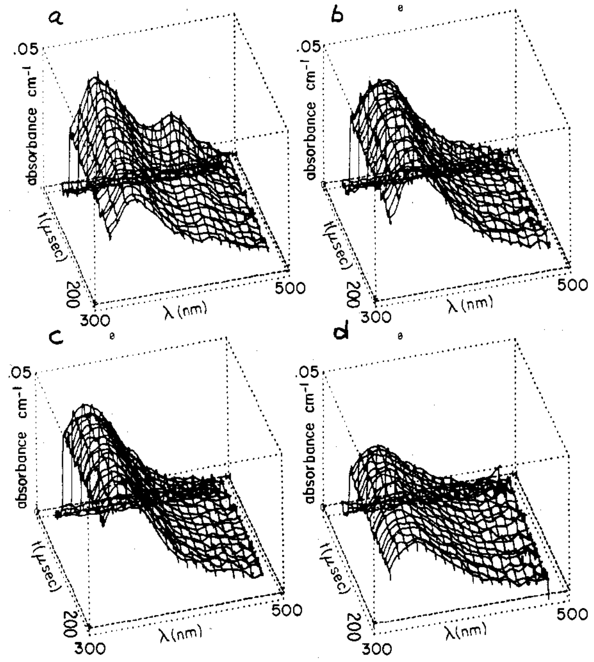


Figure 1. Time-dependent transient spectra obtained by the streak-camera method for neutral N_2O-saturated solutions of (a) complex **1** (2.27×10^{-4} M), (b) dimethylthioglycolato complex (2.33×10^{-4} M), (c) thiopropionato complex (3.05×10^{-4} M), and (d) 2-aminoethanethiolato complex (2.72×10^{-4} M) (for structures see text).

The relative intensities of the two maxima were measured over the pH range 5.3–10.1 and for concentrations of the complex from 0.3 to 1.3 mM. The ratio of absorptivities remained unchanged.

In irradiated aqueous solutions, there is a small yield of H atoms formed directly by water radiolysis ($G = 0.55$). An experiment was conducted to test the possibility that one of the maxima in Figure 1a, with initial complex concentration of 0.307 mM, was due to a product of reductive attack by H atoms. It would follow, therefore, that the rate constant for reaction of H atoms would have to be nearly diffusion controlled since the spectra appeared to be formed within a few microseconds of the irradiation pulse. This possibility was investigated by irradiating a deaerated N_2O-free solution containing 0.5 mM complex **1** and 0.1 mM *tert*-butyl alcohol. This alcohol reacts with OH radicals with a rate constant of $5.2 \times 10^8\ M^{-1}\ s^{-1}$.[14] In contrast, the rate constant for the corresponding reaction with H atoms is only $10^5\ M^{-1}\ s^{-1}$.[15] Thus, under these conditions, the alcohol would be an effective scavenger for all OH radicals but would not compete efficiently with the complex for H atoms if the rate constant for the latter reaction is nearly diffusion controlled. It was found that alcohol completely suppressed the transient absorption. It follows, therefore, that one-electron reduction is not responsible for either of the maxima and that both must arise from the reaction of OH radicals.

Rate of Reaction of OH with Complex 1. The overall rate constant for reaction of OH with complex **1** was obtained by direct observation of the rate of formation of the transient spectra using the photomultiplier technique. Concentrations of the solute in N_2O-saturated solution ranged from 0.047 to 0.28 mM and the dose per pulse was kept below 1000 rads. At this dose, the OH radical concentration present immediately after the pulse was about 6 μM. Since the bimolecular rate constant for reaction of OH with complex **1** is very large, kinetic complications arising from radical–radical reactions are negligible under these conditions. The rate for formation of the absorption was found to be exponential and first order

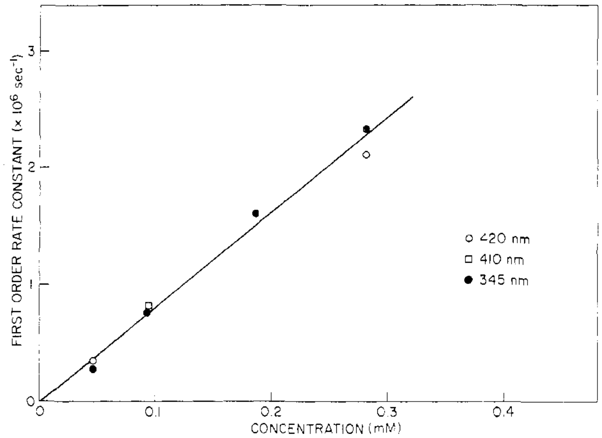


Figure 2. Rate of reaction of OH with complex **1**, showing first-order dependence on solute concentration of the rate of formation of the transient absorption in N_2O-saturated solutions of complex **1** at neutral pH.

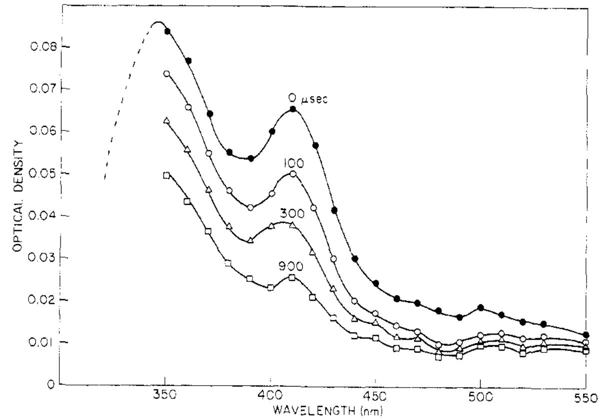


Figure 3. Transient spectra, obtained by the photomultiplier method, from an N_2O-saturated solution containing 0.2 mM complex **1** irradiated with a pulse of 1 krad. Spectra were measured immediately after the pulse and for delays of 100, 300, and 900 μs thereafter.

in solute concentration as is shown in Figure 2. The bimolecular rate constant was found to be $8.2 \times 10^9\ M^{-1}\ s^{-1}$. The figure also shows that the rate of formation is the same irrespective of which absorption maximum is used to monitor the reactions. This confirms, therefore, that the two reaction products responsible for the maxima must be formed in simultaneous rather than in sequential reactions.

The Reaction Sites for OH. Several complexes structurally related to complex **1** were irradiated in order to provide information on the site, or sites, of reactions of OH with complex **1**.

i. Tris(ethylenediamine)chromium(III) Perchlorate. This complex, of formula $(en)_3Cr(ClO_4)_3$, was investigated in order to measure the transient spectra formed on reaction of OH either with the central chromium atom or with the ethylenediamine ligands. Irradiation of a neutral N_2O-saturated solution containing 0.5 mM tris complex showed only a weak transient absorption rising into the uv region below 300 nm. No absorption bands were seen in the region of the maxima found with complex **1**, from which it can be concluded that these maxima are not associated with products of reaction of OH with either the central atom or the ethylenediamine ligands.

ii. Substituted Thiolatochromium Complexes. The above results led to the hypothesis that probable sites for OH radical reaction are the sulfur atom and the α-carbon atom of the thioglycolate ligand. This would imply that the two maxima in the transient spectra are due to reactions at each of these sites. The relative intensities of these maxima would be expected to vary with changes in the structure of the thiolato ligand. To test this interpretation, streak spectra were measured for the following related complexes; Figure 1b shows the transient spectrum obtained by irradiating dimethylthioglycolatochromium(III)

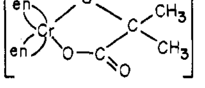
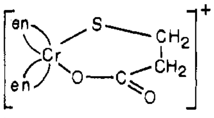
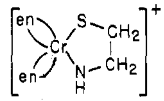


Figure 1c shows the transient spectrum obtained by irradiating thiopropionatochromium(III)



and Figure 1d shows the transient spectrum obtained by irradiating 2-aminoethanethiolatochromium(III)



Comparison of the spectra with those measured from solutions of complex **1** irradiated under similar conditions shows that, whereas the maximum at 345 nm is present, that at 410 nm is absent in all three derivatives.

In the complex depicted in Figure 1b, OH attack at the α-carbon atom is prevented by the two substitutent methyl groups. In the other two complexes, the lability of the hydrogen atoms on this carbon atom is reduced relative to those at the corresponding position in the parent complex. These results indicate, therefore, that the maximum at 410 nm in the spectrum from complex **1** is associated with a radical species formed by direct OH attack at the α-carbon atom. It would follow, therefore, that since the maximum at 345 nm is present in the transient spectra from all four complexes irrespective of the structure of the ligand, this peak is due to a radical species formed by OH attack at the sulfur atom.

iii. (Mercaptoacetato-*O,S*)bis(ethylenediamine)cobalt(III). To determine the effect of a change in the metal ion on the reactivity of the coordinated mercaptoacetato ligand, an N_2O-saturated solution 0.48 mM in the above cobalt complex was irradiated using the streak-camera method. A weak transient absorption was present immediately after the pulse, rising from about 350 nm into the uv region. The two maxima at 345 and 410 nm were not observed.

Resolution of the Transient Spectra. The photomultiplier method was used to make a more accurate measurement of the relative absorbances of the two absorption maxima in the transient spectra from complex **1**. A neutral N_2O-saturated solution 0.2 mM in complex **1** was irradiated with a pulse of 1.6 krads and the resultant optical absorptions were measured over the wavelength range 350–550 nm at intervals of 10 nm. The transient spectra recorded were those present immediately after the radiation pulse and after delays of 100, 300, and 900 μs. The spectra were corrected for minor pulse-to-pulse fluctuations in radiation dose and are shown in Figure 3. The dotted line in the figure represents the absorption below 350 nm and was obtained from the data taken by the streak-camera method and normalized to the optical density at 350 nm. The spectra clearly illustrate the different decay rates of the two maxima.

The two components in the spectra in Figure 3 were extracted by the following normalization procedure. Oscillo-

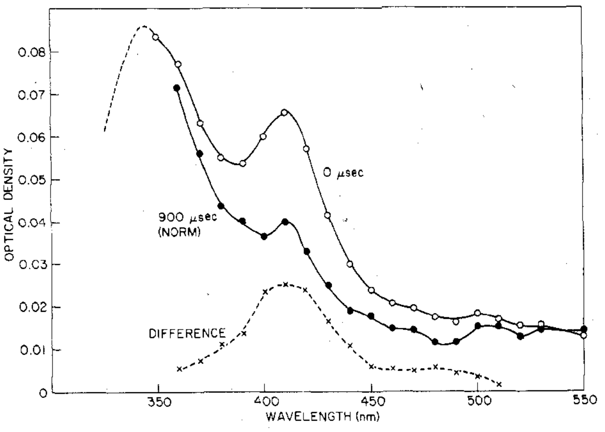


Figure 4. Resolution of the two components in the transient spectra from Figure 3 (see text).

grams taken at 350 nm showed a fast initial decay of the absorption and this was followed by a much slower decay process. Kinetic analysis showed that this slower decay was second order, decaying to a lower limiting absorption.

The spectrum at 900 μs was taken to be that of the transient species responsible for the absorption maximum at 345 nm. This spectrum was used to extract from the spectrum at time zero the absorption spectrum of the faster decaying component. At 345 nm, there is a small but significant contribution from the absorption spectrum of this component and analysis showed that this was 7% of the total initial absorption at this wavelength. In the normalization, therefore, the 900-μs spectrum was adjusted so that the absorptivity at 345 nm was 93% of that at zero time. Subtraction of the two spectra gave the spectrum of the fast component present immediately after the pulse. The normalized and difference spectra are shown in Figure 4.

Extinction Coefficients. Since the proportions of the initial yield of hydroxyl radicals which react at the two sites are not known, the individual extinction coefficients of each species cannot be calculated. However, apparent overall extinction coefficients for the two maxima in the composite spectrum were obtained from the data by using the radical $(SCN)_2^-$ as a dosimeter. An N_2O-saturated solution of 1.2 mM KSCN was irradiated and the absorption of the $(SCN)_2^-$ radical formed by OH-induced oxidation of SCN^- was compared with that of the transient from complex **1** formed under isodose conditions. The extinction coefficient of the $(SCN)_2^-$ radical used for the calculation was ϵ_{500} 7250 M^{-1} cm^{-1}.[16,17] From the data the apparent extinction coefficients of the two maxima from complex **1** were found to be ϵ_{410} 870 M^{-1} cm^{-1} and ϵ_{345} 1150 M^{-1} cm^{-1}.

Decay Kinetics. The decay of the transient responsible for the maximum at 345 nm was analyzed and was found to be second order. For six determinations carried out at low ionic strength (0.0005–0.010) k was found to be $(9.3 \pm 2.5) \times 10^7$ M^{-1} s^{-1}.

The variation of this rate parameter as a function of ionic strength maintained with $LiClO_4$ was studied over a concentration range of 5×10^{-4} to 0.976 M. The value of the apparent rate constant increased to $(14 \pm 1) \times 10^7$ M^{-1} s^{-1} at $\mu = 0.98$. The extended Debye–Hückel equation in the form

$$\log k = k_0 + \frac{A \Delta Z^2 \mu^{1/2}}{1 + B\mu^{1/2}} + C\mu$$

was used to adjust the data in terms of three parameters, k_0, A, and B, for various combinations of $A\Delta Z^2$ using a computer program developed by Newton.[18] The weighted variance from the least-squares adjustment suggested no reasons for rejecting either of the hypotheses $\Delta Z^2 = 0$ or $\Delta Z^2 = 1$ but was not consistent with a value of $\Delta Z^2 = 4$.

It is most improbable that the radical product has zero charge since this would imply that the reaction with the OH radical leads to a one-electron reduction of the chromium complex.

Discussion

The conclusions from the data can be summarized as follows.

(1) Hydroxyl radicals react at a nearly diffusion-controlled rate with complex **1** to produce a transient absorption spectrum with maxima at 345 and 410 nm.

(2) The two maxima are associated with two separate transients which appear to be formed simultaneously rather than consecutively.

(3) The relative intensities of these two maxima are independent of pH over the range 5.3–10.1 and of solute concentration in the range 0.3–1.3 mM.

(4) The site of OH attack is not the central chromium atom or the ethylenediamine ligands.

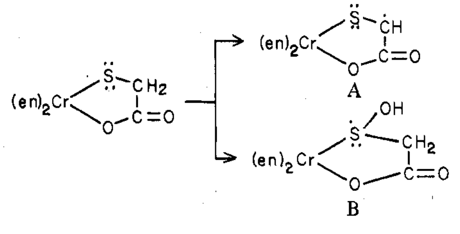
(5) Studies with related complexes indicate that OH attack occurs at both the S atom and the α-carbon atom. Reduction of, or elimination of, reactivity at the α-carbon atom leads to loss of the absorption at 410 nm. This absorption band is associated, therefore, with a radical centered at this carbon atom which implies that the maximum at 345 nm is due to a sulfur-centered radical. Since the disappearance of the 410-nm band is not accompanied by a significant change in the intensity of the other band, we conclude that the sulfur atom is the major site for the reaction of OH.

(6) The sulfur-centered radical probably carries unit charge and decays to form an unstable product.

(7) The reaction of the cobalt analogue of complex **1** with the OH radical results in a markedly different transient species from that observed with complex **1**.

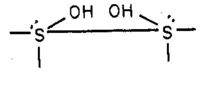
Previous studies of the oxidation of complex **1** and the cobalt analogue by Np(VI)[4b] have also indicated a marked difference in the reactivity patterns. For the cobalt complex, three separate products were noted and the rate of the reaction was slower than with the chromium species. The comparative kinetic behavior of OH as an oxidant of the same substrates is consistent with the results obtained using Np(VI) as an oxidant. These observations may be rationalized as a reflection of the significantly shorter bond lengths in the Co(III) complexes as compared to those in the Cr(III) species.

From conclusions 1–6 it would follow, therefore, that the initial one-electron oxidation is the branched reaction



where A results from H· abstraction from the carbon atom and B results from OH radical addition to the sulfur atom.

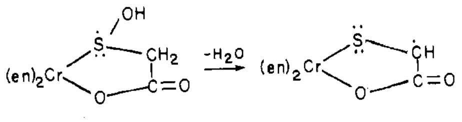
We propose that the species B is the transient with a maximum at 345 nm. This decays by a bimolecular process to form a product which is probably the dimeric species



This product is likely to be relatively long-lived on the time scale of pulse radiolysis and could be responsible, therefore, for the absorption present at 345 nm after the decay of B is complete. However, the expanded valence shell of sulfur in the formulation of the dimer would make it likely that this product would not be very stable and would decay to other products over a longer time scale.

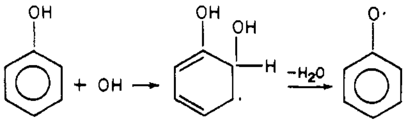
Oxidation of complex **1** by Np(VI) leads to the formation of the monothiooxalato product; i.e., oxidation occurs only at the α-carbon atom.

If the monothiooxalato product is also produced from species B, there must be a pathway for converting species B to a structure which can undergo a net oxidation at the α-carbon atom. This would occur through a unimolecular water elimination reaction



B A

However, this reaction cannot occur to any extent under the conditions of pulse radiolysis since the transient products A and B are formed simultaneously and decay independently. A similar type of water elimination reaction has been observed in substituted hydroxycyclohexadienyl radicals following pulse radiolysis of aqueous solution of hydroxybenzenes, e.g., phenol[19] and hydroquinone.[20]



For hydroquinone, semibenzoquinone is the final radical product. In these studies, it was found that the elimination reactions were sufficiently slow to allow appreciable competition from the bimolecular reaction between two of the intermediate OH adduct radicals. This competition was so marked in the case of the phenol system that the relatively slow water elimination reaction could only be measured quantitatively for very low pulse doses (<30 rads) which gave end-of-pulse radical concentrations of <0.2 μM. Water elimination from these hydroxycyclohexadienyl radicals must be very exothermic in view of the high resonance energy of the aromatic radicals thereby produced. With regard to the present work, it is reasonable that water elimination from the sulfur radical B would not be as exothermic and might be considerably slower. If so, it could not occur under the conditions used in these pulse radiolysis experiments.

In the chemical study where the monothiooxalato product was observed,[3] the stationary-state concentration of radical species formed during the overall oxidation process would be many orders of magnitude lower than the radical concentration present immediately after pulse radiolysis. Therefore, in the chemical system bimolecular reactions between two radical species B would be correspondingly slower and this would favor unimolecular water elimination leading to the formation of species A, the precursor of the monothiooxalato product. In addition, it is known that this type of elimination reaction is strongly acid catalyzed. Since the earlier study[4] was carried out at low pH, acid catalysis would further cause the elimination reaction to predominate and thus lead preferentially to oxidation at the α-carbon atom.

Acknowledgment. We are indebted to C. Jonah and E. Hamilton for the computer program used for the kinetic analysis of the transient decays and to T. W. Newton of Los Alamos Scientific Laboratory for treating the ionic strength data by his computer program. E.D. gratefully acknowledges financial support from the National Science Foundation (Grant No. MPS74-01540-A01) and the Argonne National Laboratory Summer Faculty Participation Program.

Registry No. **1**, 41212-24-2; $(en)_2Cr(SC(CH_3)_2COO)[ClO_4]$, 60195-76-8; $[(en)_2Cr(S(CH_2)_2COO)]^+$, 51911-42-3; $[(en)_2Cr(S(CH_2)_2NH)]^+$, 60195-77-9; OH (radical), 3352-57-6.

References and Notes

(1) Based on work performed under the auspices of the U.S. Energy Research and Development Administration.
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