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Kinetics and Mechanism of the Oxidation of Thiocyanate Ion by Chromium(VI)

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Received October 20, 1972

Chromium(VI) reacts with thiocyanate ions in acid to give cyanide (CN^-) and sulfate (SO_4^{2-}) ions and small amounts of polythiocyanogen $(NCS)_x$. The reaction proceeds *via* an O_3CrNCS^- and $O_2Cr(NCS)_2$ intermediate and activated state, respectively. All chromium(III) products are coordinated to SCN^-. The reaction is unusual for a chromium(VI) oxidation in that manganese(II) affects neither the stoichiometry nor rate, and Cr(V) intermediates are not observed.

Introduction

Chromium(VI) has been observed to form complexes with several sulfur-containing oxyanions.[1-3] Acid sulfate,[3] HSO_4^-, and acid sulfite,[2] HSO_3^-, form 1:1 complexes with formation constants in the range ($K_f = 4$–100) characteristic of O-bridged esters or anhydrides.[2,3] Acid thiosulfate,[1] on the other hand, forms a complex which exhibits a very high formation constant (10^5) and a red shift of the charge-transfer band in the near-uv, which have been interpreted as evidence for chromium-sulfur bonding ($O_3Cr\text{-}S\text{-}SO_3^{2-}$).[1,4]

The kinetics of oxidation of $HS_2O_3^-$ and HSO_3^- by chromium(VI) both include terms second order in reducing agent. This effect has been interpreted to be due to the formation of six-coordinate chromium(VI) in the activated state.[5]

The above findings make the present study of the kinetics and mechanism of the chromium(VI)-thiocyanate (SCN^-) reaction of interest for several reasons. First, a Cr(VI)-SCN^- complex is formed, which may be either sulfur or nitrogen bonded to chromium. Its formation constant and spectrum may extend correlations of stabilities and spectra with bond types.[1,4]

Second, it is of interest to compare the rate law for the Cr(VI)-SCN^- reaction with that for Cr(VI) with other sulfur-containing ligands. Third, since SCN^- shows many chemical similarities to I^-, a comparison with the rate laws and mechanisms proposed for the oxidation of iodide by chromium(VI) is of interest.[6,7]

Experimental Section

Reagent grade sodium dichromate, sodium thiocyanate, sodium perchlorate, perchloric acid, nickel sulfate, disodium ethylenediaminetetraacetic acid, ammonium hydroxide, sodium sulfate, manganous sulfate, and manganous perchlorate were used without further purification. All solutions were prepared with deionized water.

Stoichiometry. The stoichiometry of the reaction in excess Cr(VI) was determined both spectrophotometrically and iodometrically in the presence and absence of Mn^{2+}. Experiments with added Mn^{2+} were done in both perchloric acid and sulfuric acid media. Reactant solutions were $(1.0\text{–}2.0) \times 10^{-2}$ *M* in Cr(VI), 5.0×10^{-3} *M* in SCN^-, 0.4–0.5 *M* in acid, and 0.10–0.20 *M* in Mn^{2+}, and the ionic strength was maintained at 0.7–0.8 *M* with $NaClO_4$. Periodically aliquots were withdrawn, made basic with NaOH, and diluted 100-fold, and the Cr(VI) concentration was determined from the measured absorbance at 372 nm ($\epsilon_{CrO_4^{2-}} = 4.81 \times 10^3\ M^{-1}\ cm^{-1}$ at 372 nm). The reaction was assumed to be complete when the Cr(VI) concentration remained constant for several successive determinations. It was also assumed that all the SCN^- initially present had reacted to completion. Excess Cr(VI) was also determined iodometrically. The concentrations of solutions containing only Cr(VI), acid, and sometimes Mn^{2+} were determined in parallel with reactant solutions to be sure that no reaction of Cr(VI) other than with SCN^- occurred in the acid solutions. It was found that Mn^{2+} did not interfere with iodometric determination and excellent agreement was obtained between the spectrophotometric and iodometric methods.

Attempts to determine the reaction stoichiometry in the presence of a large excess of SCN^- were less successful. The reaction products were believed to be SO_4^{2-} and CN^- on the basis of the results in excess Cr(VI), but the amount of SO_4^{2-} formed was too small to be determined gravimetrically and SCN^- interference precluded potentiometric titration of CN^- with Ag^+. Analysis for CN^-, by addition of excess Ni^{2+} to reaction solutions buffered at pH 10 followed by back titration of remaining Ni^{2+} with EDTA using murexide indicator, was also tried without success.

The Cr(III) reaction products were separated using anion- and cation-exchange column chromatography. Cations were separated by the method of King and Dismukes.[8] Reaction mixtures containing 1.0×10^{-3}–1.0×10^{-2} *M* Cr(VI), 0.20 *M* SCN^-, and 0.10 *M* H^+ were diluted tenfold after reaction was complete and used to charge columns of Dowex 50 1-X8 cation-exchange resin. The column was then rinsed successively with water, 0.15 *M* $NaClO_4$, 1.0 *M* $HClO_4$, and 2.0 *M* $HClO_4$ at a flow rate of 1–2 ml/min. A diphenylcarbazide spot test for chromium[9] was made periodically during each wash and when the spot test became negative for one eluting solution the solution of next higher concentration was started. Anionic complexes were separated in similar fashion using Amberlite IRA-400 resin and 1.0–4.0 *M* NaCl as eluting solutions. The concentration of chromium in the various column fractions was determined spectrophotometrically as before.

Kinetics. All kinetic studies were done by following the decrease in absorbance at 380 nm using cells with a 1-cm optical path length in a Beckman DU-2 spectrophotometer. The cell compartment was thermostated at 25.0 ± 0.1° by means of a constant temperature water bath. Solutions for all kinetic runs contained a large excess of H^+ and SCN^- with ionic strength maintained constant at 0.70 ± 0.02 *M* by addition of $NaClO_4$. All of the reagents except Cr(VI) were mixed in a test tube, to which Cr(VI) was rapidly added by means of a syringe to start the reaction. The reaction mixture was inverted three times and quickly transferred to a Pyrex cuvette to observe the absorbance change. Using this technique, mixing times were less than 5 sec and absorbance readings could be obtained within 30–45 sec after mixing, while half times for the reaction were greater than 100 sec even at the highest concentrations used. Concentrations used were $(1.00\text{–}3.00) \times 10^{-4}$ *M* Cr(VI), 0.010–0.100 *M* SCN^-, 0.020–0.200 *M* H^+ as $HClO_4$, and $NaClO_4$ to give $\mu = 0.7$. The absorbance of a blank solution containing no SCN^- but the same concentrations of Cr(VI) and H^+ as the reactant solution was determined for each set of reactant concentrations.

Stock solutions of 1.00 or 0.100 *M* NaSCN were standardized by potentiometric titration with $AgNO_3$, using a Radiometer Type TTT 11b titrator with a silver billet sensing electrode and a mercurous sulfate reference electrode. These solutions were found to be stable for periods of up to 1–2 months.

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[1] I. Baldea and G. Niac, *Inorg. Chem.*, 7, 1232 (1968); 9, 110 (1970).

[2] G. P. Haight, Jr., E. Perchonock, F. Emmenegger, and G. Gordon, *J. Amer. Chem. Soc.*, 87, 3835 (1965).

[3] G. P. Haight, Jr., D. C. Richardson, and N. H. Coburn, *Inorg. Chem.*, 3, 1777 (1964).

[4] K. A. Muirhead, G. P. Haight, Jr., and J. K. Beattie, *J. Amer. Chem. Soc.*, 94, 3006 (1972).

[5] G. P. Haight, Jr., and J. K. Beattie in "Mechanisms of Inorganic Reactions," J. O. Edwards, Ed., Wiley, New York, N. Y., 1972.

[6] D. C. Gaswick and J. H. Krueger, *J. Amer. Chem. Soc.*, 91, 2240 (1969).

[7] K. E. Howlett and S. Sarsfield, *J. Chem. Soc. A*, 683 (1968).

[8] E. L. King and E. B. Dismukes, *J. Amer. Chem. Soc.*, 74, 1674 (1952).

[9] A. I. Vogel, "Macro and Semimicro Qualitative Analysis," Wiley, New York, N. Y., 1954, p 275.

All product analyses were performed by Mr. Josef Nemeth and the staff of the School of Chemical Sciences Microanalytical Laboratory.

Intermediate Complex. Although the decrease in absorbance at 380 nm was used to follow the redox kinetics, it was found that the initial effect of mixing Cr(VI) and SCN^- was an increase in the absorbance at 380 nm, presumably due to formation of an intermediate. The stoichiometry of the intermediate was determined by observing the difference between initial absorbances of reactant solutions with and without SCN^- at reactant concentrations low enough that only a small amount of Cr(VI) was converted to complex. The differences, ΔA_0, obtained by extrapolating to the time of mixing, were attributed to the rapid formation of the intermediate. The spectra were obtained using a Beckman Acta V spectrophotometer. Concentrations used were 1.99×10^{-4} *M* Cr(VI), 2.5×10^{-3}–1.0×10^{-2} *M* SCN^-, and 0.010–0.20 *M* H^+ with the ionic strength maintained at 0.71 *M* as before.

The spectrum of the intermediate was obtained by a continuous flow method. Two 500-ml round-bottomed flasks with stopcocks attached were used as constant flow rate vessels, following the method of Allen and Shelden,[10] and the flow rate was regulated by the bore of the syringe needle used. Solutions of Cr(VI) and SCN^- were mixed by passing into a Y-tube and the spectrum of the mixture was recorded in a 10-cm cylindrical Pyrex cell on a Beckman Acta V spectrophotometer. Preliminary experiments with colored solutions indicated that the flow of solution in the 10-cm cell gave complete displacement of all the solution in the cell within 30–60 sec, depending somewhat on the flow rate. The mixing ratio, determined by mixing 1×10^{-4} *M* Cr(VI) with water and observing the absorbance change, was found to be Cr(VI)/water = 0.90 ± 0.02. Concentrations used were 4.75×10^{-5} *M* Cr(VI), 0.010–0.100 *M* SCN^-, and 0.025–0.100 *M* H^+ (after mixing). The ionic strength was maintained at 0.71 *M*. At these concentrations the half-life of the redox reaction is greater than 50 min. At the 90–100 ml/min total flow rate used, the time elapsed between the solutions mixing and their leaving the spectrophotometer cell was about 30 sec. The reference cell contained a solution with no SCN^- but with Cr(VI) and H^+ concentrations identical with those in the mixed solution. Hence, the spectrum of the intermediate was obtained directly. Multiple scans of a given mixture gave spectra repeatable to within 5% of maximum absorbance.

Results and Discussion

A. Formation of $O_3Cr(NCS)^-$. The degree of dissociation of HSCN is of key importance to interpretation of results. Values for the acid dissociation constant of HSCN are numerous in the literature and vary from 0.1 to 100 *M*.[11] The value $K_a = 5$ *M* is the one for which there is most agreement. Since at the highest concentrations of H^+ and SCN^- used for kinetics in this study, the maximum deviations in the concentrations of H^+ and SCN^- from the formal values were 5% (assuming $K_a = 5$) and since the most consistent analysis of data is obtained if it is assumed that HSCN is a strong acid, we make the latter assumption in analyzing our results.

Analysis of preliminary kinetic experiments repeatedly gave initial absorbances for reactant solution larger than those expected for solutions containing only $HCrO_4^-$, as determined from the blank solutions. (Under kinetic conditions more than 95% of the uncomplexed chromium initially present is $HCrO_4^-$.) The magnitude of the absorbance enhancement was found to depend on the first power each of concentrations of hydrogen ion and thiocyanate ion present. These results imply the existence of a Cr(VI)-SCN^- complex, the kinetics of formation of which have since been reported.[11] The formation rate law contains a term first order in $HCrO_4^-$, first order in SCN^-, and first order in H^+, implying that the complex formation reaction is probably

$$HCrO_4^- + H^+ + SCN^- \rightleftarrows CrO_3(NCS)^- + H_2O \qquad (1)$$

The absorbance enhancement was too small for effective use of Job plots[11] to determine the stoichiometry. An approximate determination of the stoichiometry of the complex was obtained by us from the slope of plots of log (ΔA_0) *vs.* log $[H^+]$ at constant $[SCN^-]$ and log (ΔA_0) *vs.* log $[SCN^-]$ at constant $[H^+]$. The slope of such plots gives the H^+:Cr(VI) or SCN^-:Cr(VI) ratio in the complex. Analysis of the data in Table I gives a SCN^-/Cr(VI) ratio of 0.96 ± 0.15 and a H^+:Cr(VI) ratio of 0.77 ± 0.15. Considering the small absorbance differences measured, this is in reasonable agreement with the kinetic results and the complex is formulated as $CrO_3(NCS)^-$. The spectrum of $O_3Cr(NCS)^-$ appears in Figure 1.

A previous kinetic determination of K_{eq} for reaction 1 using *T*-jump apparatus has been reported to be 220 ± 25 M^{-1}.[11] This value permits a simple interpretation for our rate data and will be used, although it must be noted that ionic strength in the T-jump study was 0.3 compared with 0.7 used in this study.

N or S Bonding by CNS^-. The above results show that formation of a Cr(VI)–SCN^- complex is the first step in the Cr(VI) oxidation of SCN^-, similar to the cases of $S_2O_3^{2-}$ and SO_3^{2-}. The charge-transfer maximum for $O_3Cr(NCS)^-$ occurs at lower energy (380 nm) than that in $HCrO_4^-$ (350 nm), as is expected since there must be either a Cr–N or a Cr–S bond in the complex and since both sulfur and nitrogen are less electronegative than oxygen. If the complex is assumed to be nitrogen bonded, it might be expected that the charge-transfer maximum would fall closer to that for CrO_3Cl^- (360 nm) than to that for $CrS_2O_6^{2-}$ (390 nm) since nitrogen is closer to chlorine than to sulfur in electronegativity. Since Cr(VI) is a hard acid and nitrogen is a harder base than sulfur, it is tempting to postulate Cr–N rather than Cr–S bonding, and the relatively small equilibrium constant for the complex is not inconsistent with this. However, since no other Cr(VI) complexes of this type with Cr–N bonds are known, such an assumption must be tentative.

B. Oxidation of Thiocyanate. 1. Stoichiometry and Products. We infer that the stoichiometry of the Cr(VI)–SCN^- redox reaction is

$$2Cr(VI) + SCN^- \rightarrow SO_4^{2-} + CN^- + 2Cr(III) \qquad (2)$$

consistent with the value of 2.0 ± 0.1 for the Cr(VI):SCN^- reactant ratio determined in excess Cr(VI). Separate experiments showed no further reaction between Cr(VI) and CN^- even upon long standing in quite acidic solution. The addition of up to 0.2 *M* Mn^{2+} did not affect the stoichiometry in either perchloric or sulfuric acid, and there was no evidence for formation of MnO_2 upon addition of Mn^{2+} to reaction mixtures. The odor of HCN was apparent soon after mixing but attempts to determine CN^- by Ni^{2+}-EDTA titrations of reaction mixtures containing either excess Cr(VI) or excess SCN^- invariably gave Cr(VI):CN^- ratios greater than 2 and as high as 10. There are several possible explanations for this. One is that the stoichiometry of the reaction is different in the presence of excess SCN^- than with excess Cr(VI), as is the case in the Cr(VI)–SO_3^{2-} reaction.[2] However, a small number of titrations of mixtures containing excess SCN^- with $AgNO_3$ argue indirectly against this possibility. In these experiments the reaction was allowed to proceed to completion and an aliquot made basic to hydrolyze any Cr(III) complexes and, when reacidified, was titrated potentiometrically with Ag^+. This required the same amount of Ag^+ as was required to titrate a blank mixture containing the same amount of SCN^- as was originally present in the reaction mixture but no Cr(VI). This is consistent with the formation of CN^- as a SCN^- oxidation product since one CN^- would be produced for each SCN^- reacted. Also, it is

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[10] W. M. Allen and H. R. Shelden, *J. Chem. Educ.*, **47**, 841 (1970).

[11] C. T. Lin and J. K. Beattie, *J. Amer. Chem. Soc.*, **94**, 3011 (1972).

Table I. Stoichiometry of Cr(VI)-SCN$^-$ Complex at 380 nm, 25.0°, $[\mathrm{Cr(VI)}]_0 = 1.99 \times 10^{-4}$ *M*, $\mu = 0.71$ *M*

$[\mathrm{SCN^-}]_0$, $M \times 10^2$	$[\mathrm{H^+}]_0$, $M \times 10^2$	ΔA_0 (2-cm path length)
1.01	10.0	0.069 ± 0.006
1.01	10.0	0.058 ± 0.006
1.01	8.0	0.055 ± 0.006
1.01	6.0	0.043 ± 0.006
1.01	4.0	0.032 ± 0.006
1.01	2.0	0.020 ± 0.006
1.01	1.0	0.012 ± 0.006
2.50	20.0	0.282 ± 0.010
0.25	20.0	0.032 ± 0.006

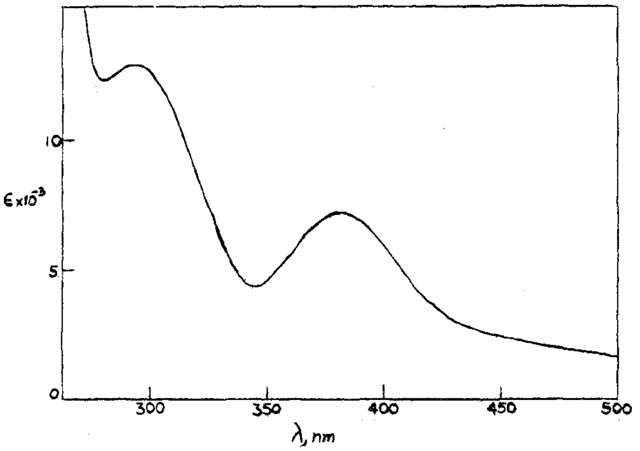

Figure 1. Spectrum of the intermediate, $\mathrm{O_3Cr(NCS)^-}$.

difficult to imagine other SCN$^-$ oxidation products which would give this behavior. A second possibility is that, despite efforts to prevent it, some HCN may have escaped from the acidic reaction mixtures, giving a Cr(VI):CN$^-$ ratio larger than 2. In the absence of evidence to the contrary, it is assumed that the stoichiometry is the same in both excess Cr(VI) and excess SCN$^-$ and that $\mathrm{SO_4^{2-}}$ and CN$^-$ are the oxidation products of SCN$^-$.

At least two thiocyanate-containing Cr(III) species were found as reaction products in analysis of reaction mixtures containing excess SCN$^-$ by cation ion-exchange chromatography. Within experimental error all of the chromium originally put on the column could be recovered by elution with water, 0.15 *M* $\mathrm{HClO_4}$ (which elutes $\mathrm{Cr(NCS)^+_2}$ but not $\mathrm{CrNCS^{2+}}$), and 1.0 *M* $\mathrm{HClO_4}$ (which elutes $\mathrm{CrNCS^{2+}}$ but not $\mathrm{Cr(H_2O)_6^{3+}}$ or any more highly charged species).[8] Varying amounts of chromium were found in the water wash, less at lower concentrations of inert electrolyte. Although only 84% of the chromium initially put on the anion column could be recovered by washing with water, no more chromium could be recovered even by washing with up to 4.0 *M* NaCl.[12] If it is assumed that all of the chromium in the cation column water wash was present as $\mathrm{Cr(NCS)}_n^{3-n}$ with $n > 2$, then 65.4% of the Cr(III) products were found to contain two or more thiocyanate ions coordinated to Cr(III) in each of two experiments, and 30.3 and 31.4% were found to be $\mathrm{CrNCS^{2+}}$ in the same experiments although the initial concentrations of Cr(VI) differed by a factor of 10. Decreasing [SCN$^-$] by a factor of 2 increased the ratio $[\mathrm{Cr(NCS)^{2+}}]/[\mathrm{Cr(NCS)_2^+}]$. Only traces of $\mathrm{Cr(H_2O)_6^{3+}}$ are found in all cases where reactions are fast enough that anation and aquation of products can reasonably be ignored. A maximum of 50% of the Cr(III) could be coordinated to CN$^-$. This is deemed unlikely since $\mathrm{Cr^{III}CN}$ complexes are not observed when Cr(VI) is reduced by hydrazine in the presence of HCN,[12] and $\mathrm{Cr(CN)^{2+}}$ aquates completely in the time needed to perform the experiment.[13] Detection of the odor of HCN indicates that at least a part of the CN$^-$ is formed as free CN$^-$ and not incorporated in Cr(III) products. $\mathrm{Cr^{III}SO_2^+}$ probably is labile and $\mathrm{Cr^{III}SO_3^+}$ is known to be so.[2] Since the time elapsed between mixing of reactants and elution of the various species from the column was about 3 hr in one case and 6 hr in the other, the quite constant percentage of the different products formed argues against the occurrence of any significant amount of aquation during this time. Half times for aquation of Cr(III) complexes with inert ligands are typically quite a bit longer. There is no evidence for formation of any $\mathrm{Cr(H_2O)_6^{3+}}$ or dimeric Cr(III) species as reaction products.

It should be noted that the results presented here may not distinguish between $\mathrm{CrSO_4^+}$ and $\mathrm{Cr(NCS)_2^+}$. Attempts to precipitate the Cr(III) species for elemental analysis were unsuccessful. However, the spectra of reaction products correspond very well to a mixture of $\mathrm{Cr(NCS)_2^+}$ and $\mathrm{CrNCS^{2+}}$, showing maxima at 416 and 566 nm and apparent extinction coefficients of approximately 30 M^{-1} cm^{-1} for both peaks. $\mathrm{CrNCS^{2+}}$ has maxima at approximately 410 and 572 nm,[8] while $\mathrm{Cr(NCS)_2^+}$ has maxima at approximately 417 and 570 nm for a mixture of geometrical isomers.[14] These differences cannot be due to significant amounts of $\mathrm{Cr(CN)}_x^{3-x}$ or $\mathrm{Cr(SO_4)^+}$ complexes.[13]

At very high concentrations of both H$^+$ and SCN$^-$ (about 0.5 *M* H$^+$ and 0.8 *M* SCN$^-$) and relatively high Cr(VI) concentrations ($\sim 10^{-2}$ *M*), formation of small crystals of bright yellow-orange substance occurred along with formation of the blue-purple Cr(III) products. This material was filtered, washed with water, dried, and found to contain 20.50-20.57% C, 23.87-23.96% N, and 48.78-50.55% S expected for polythiocyanogen, $\mathrm{(SCN)}_n$, which is known to be readily formed by polymerization of $\mathrm{(SCN)_2}$.[15] Long needle-like crystals of the same material also formed more slowly upon standing in reaction mixtures with high concentrations of H$^+$ and SCN$^-$ but lower Cr(VI) concentrations ($\sim 10^{-3}$-10^{-4} *M*).

2. Rate Law. Repeated spectral scans of relatively slowly reacting mixtures of Cr(VI) and SCN$^-$ show an isosbestic point at 328 nm. This is consistent with the only significant absorbing species being $\mathrm{HCrO_4^-}$, $\mathrm{O_3Cr(NCS)^-}$, and Cr(III) products since $\mathrm{HCrO_4^-}$ and $\mathrm{O_3Cr(NCS)^-}$ are assumed to be in rapid equilibrium. Plots of $\log(A_t - A_0)$ *vs.* time at 380 nm gave good linearity for at least 3 half-lives in the presence of large excesses of H$^+$ and SCN$^-$, and pseudo-first-order rate constants, k_{obsd}, were determined from their slopes. Several experiments showed that neither deoxygenation of reagents prior to mixing nor running the reaction under inert atmosphere affected the rate of reaction. Also, added CN$^-$ in concentrations up to 10^{-4} *M* did not affect the reaction rate nor did added $\mathrm{Mn^{2+}}$ in concentrations up to 10^{-2} *M* in either sulfuric or perchloric acid.

Some representative kinetic data are shown in Table II. It appears that the [SCN$^-$] dependence of k_{obsd} is slightly less than second order and the [H$^+$] dependence slightly less than third order. If $\mathrm{O_3Cr(NCS)^-}$ is a kinetically important species, a significant denominator term might be expected since up to 40% of the total chromium was present as complex at the

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(12) Cooper has since detected small amounts of neutral $\mathrm{Cr(NCS)_3}$ and various anions as products of this reaction: J. Cooper, private communication.

(13) D. K. Wakefield and Ward B. Schaap, *Inorg. Chem.*, 8, 512 (1969).

(14) J. T. Houzen, K. Schug, and E. L. King, *J. Amer. Chem. Soc.*, 79, 520 (1957).

(15) J. L. Wood, *Org. React.* 3, 240 (1946).

Table II. Cr(VI)–SCN^- Kinetics, 380 nm, 25.0 ± 0.1°, $\mu = 0.71\ M$

$[Cr(VI)]_0$, $M \times 10^4$	$[SCN^-]_0$, $M \times 10^2$	$[H^+]_0$, $M \times 10^2$	k_{obsd}, $sec^{-1} \times 10^3$	k_{calcd}, $sec^{-1} \times 10^3$ (eq 2)
2.00	1.01	10.0	0.194	0.190
2.00	2.53	20.0	5.25	5.50
2.00	5.07	4.99	0.379	0.475
2.00	5.07	10.0	2.45	2.79
2.00	5.07	15.0	7.46	7.46
2.00	5.07	20.0	15.7	14.8
2.00	10.1	2.50	0.228	0.23
2.00	10.1	4.99	1.39	1.36
2.00	10.1	7.49	4.01	3.70
2.00	10.1	10.0	8.06	7.25
1.00	2.53	20.0	5.34	5.60
1.00	5.07	4.99	0.420	0.475
1.00	5.07	10.0	2.31	2.79
1.00	5.07	15.0	7.79	7.46
1.00	5.07	20.0	15.7	14.8
1.00	10.1	10.0	8.35	7.25

higher concentrations used. Such a denominator term would account for the $[SCN^-]$ and $[H^+]$ dependences being somewhat less than second and third order, respectively. A least-squares analysis of the data gives the rate law

$$d[Cr(VI)]/dt = k^{11}[Cr(VI)][SCN^-]^2[H^+]^3/(1 + K_f[SCN^-][H^+]) \tag{3}$$

where $k^{11} = (2.30 \pm 0.30) \times 10^3\ M^{-5}\ sec^{-1}$ and $K_f = 220$, the formation constant for O_3CrSCN^-.[11]

The rate law given by eq 3 suggests that the activated complex for redox may be $CrO_2(NCS)_2$ analogous to known compounds such as CrO_2Cl_2 and CrO_2F_2. Alternatively, thiocyanate ion may attack O_3CrNCS^- to give the reaction

$$2H^+ + O_3Cr(NCS)^- + SCN^- \rightarrow Cr(IV) + (SCN)_2 \tag{4}$$

At high [Cr(VI)] and (SCN^-), polythiocyanogen is observed. This reaction is, however, considered to be a minor side reaction under the conditions of our kinetic studies.

The kinetics of this process invite comparisons with iodide and thiosulfate. Both iodide and thiosulfate have terms in the rate law which are second order in reducing agent.[6,7,16] Reactions like eq 4 have been suggested for both I^- and $S_2O_3^{2-}$. Neither I^- nor $S_2O_3^{2-}$ appears coordinated to Cr(III) products, whereas SCN^- does so appear. However, CrI^{2+} aquates rapidly[17] and no information on $CrS_2O_3^+$ aquation is available. Mn^{2+} inhibits the $S_2O_3^{2-}$ reaction but not the SCN^- reaction, indicating a different fate for Cr(IV) intermediates in the two cases.

3. Chromium(V) and Chromium(IV) Intermediates. Three esr spectra were run on reaction mixtures. Two of the spectra were run on aliquots which had been taken periodically from slowly reacting mixtures ($10^{-4}\ M$ Cr(VI), 0.05 M SCN^-, and 0.02 M H^+, half time greater than 3 hr), quickly frozen at −78° in an isopropyl alcohol–Dry Ice bath, and the spectra were run at liquid nitrogen temperature. In one case no attempt was made to deoxygenate the reactants and in the other the reactant solutions were deoxygenated for 1 hr before mixing, and aliquots of reaction mixture were transferred under inert atmosphere to the esr sample tubes. In the third experiment reactant solutions were deoxygenated, mixed, and transferred under an inert atmosphere into a liquid esr cell, and the spectrum was scanned repeatedly at room temperature. In this case the concentrations after mixing were $1.0 \times 10^{-3}\ M$ Cr(VI), 0.20 M SCN^-, and 0.020 M H^+, and the half time for the reaction was slightly greater than 20 min. In none of these experiments were any esr signals observed except a weak one due to Cr(III). There was no evidence for any Cr(V) species or radicals. The Cr(III) signal was somewhat weaker than was expected on the basis of its approximate concentration.

Mechanism. The following mechanism is suggested by the rate law and other observations above.

$$CrO_2(NCS)_2 \xrightarrow{k_1} Cr(IV) + SO + CN^- + SCN^- \quad (slow) \tag{5}$$

$$Cr(IV) + nSCN \xrightarrow{k_2} Cr(NCS)_n{}^{4-n} \tag{6}$$

$$Cr(NCS)_n{}^{4-n} \xrightarrow{k_3} Cr^{III}(NCS\cdot)(NCS)_{n-1} \tag{7}$$

$$CrO_3NCS^- + Cr^{III}(NCS\cdot) \xrightarrow{k_4} 2Cr(NCS)_m{}^{3-m} + SO_2 + CN^- \tag{8}$$

$$SO + Cr(VI) \xrightarrow{k_5} SO_2 + Cr(IV) \tag{9}$$

$$SO_2 + Cr(VI) \xrightarrow{k_6} SO_4{}^{2-} + Cr(IV) \tag{10}$$

Reactions 3 and 5 are deduced from the rate law. Reactions 6–10 are conjectural but satisfy the requirements that (a) no path involving Cr(V) is observed, (b) trapping of Cr(IV) by Mn^{2+} does not affect the rate, and (c) at most, traces of $Cr(H_2O)_6{}^{3+}$ are observed.

If facile reduction of SCN^- to a radical, $SCN\cdot$, which is coordinated to Cr(III), occurs, the esr signal of the radical as well as that of Cr(III) should be quenched. Only a diminished Cr(III) signal is observed.

Inability to detect Cr(V) does not exclude it as a kinetically active intermediate. However, since Cr(V), thought to be H_3CrO_4,[5] usually follows similar reaction patterns to Cr(VI) or $HCrO_4^-$ in terms of activated complexes and rates of reduction, especially when Cr(VI) reactions are slow, it should decay slowly enough to be detected in this system. Thiocyanate appears to be unique among reducing agents studied thus far in forming an efficient trap for chromium(IV) but not producing one-electron oxidation products.

Alternatively, the recent observations of three equivalent reductions of Cr(VI)[2,18] suggest that the complex $CrO_2(NCS)_2$ might be reduced in one step to Cr(III) complexes.

$$CrO_2(NCS)_2 \xrightarrow{H^+} Cr(NCS)^{2+} + SO\cdot^- + CN^- \tag{11}$$

$$SO_2\cdot^- + CrO_3NCS^- \xrightarrow{2H^+} SO_4{}^{2-} + CrNCS^{2+} + H_2O \tag{12}$$

Analyses showing more than one coordinated SCN^- in two-thirds of the product Cr(III) complexes argue for a path involving Cr(IV) as the major path.[19]

In summary, the Cr(VI)–SCN^- reaction shows activated complexes similar to those found in Cr(VI) oxidations of I^-, $S_2O_3^{2-}$, and HSO_3^-, all of which are characterized by formation of a Cr(VI) complex with reducing agent and a term in the rate law second order in reducing agent. However, product patterns are very different from those found with I^-, $S_2O_3^{2-}$, and HSO_3^-. One-electron oxidation and dimerization, $2X^- \rightarrow X_2 + 2e^-$, is a side reaction at most in the SCN^- case. $Cr(H_2O)_6{}^{3+}$ is the only Cr(III) product when I^- and $S_2O_3^{2-}$ are oxidized and $CrSO_4^+$ is formed when HSO_3^- is oxidized, whereas $Cr(NCS)_n{}^{3-n}$ complexes dominate products in the present case.

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(19) Note Added in Proof. Cooper has recently observed that azide ion, N_3^-, is both captured as a ligand and oxidized by Cr(IV), arguing strongly for steps 6 and 7 in this system: J. N. Cooper, private communication.

Registry No. Cr, 7440-47-3; HSCN, 463-56-9.

Acknowledgment. The authors wish to thank Professor James Beattie for valuable discussions, the National Science Foundation for a graduate fellowship (K. A. M.), and the National Institutes of Health for a supporting grant.

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Kinetics of the Boric Acid Catalyzed Decomposition of the *N*-Nitrosohydroxylamine-*N*-sulfonate Ion

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Received June 15, 1972

The decomposition of the *N*-nitrosohydroxylamine-*N*-sulfonate ion, $ON(SO_3^-)NO^-$, to nitrous oxide and sulfate ion follows the rate law, $-d[ON(SO_3^-)NO^-]/dt = k_1K_1[ON(SO_3^-)NO^-][H^+]$, in the pH range 6–10. K_1 is the equilibrium constant for protonation of $ON(SO_3^-)NO^-$ and k_1 is the rate constant for decomposition of the $ON(SO_3^-)NOH$ ion. Values of k_1K_1 are $4.9 \pm 1.0 \times 10^3$, $9.0 \pm 1.6 \times 10^3$, and $18.9 \pm 4.3 \times 10^3\ M^{-1}\ \text{sec}^{-1}$ at 15, 25, and 35°, respectively. Activation parameters are $\Delta H^\ddagger = 11.4 \pm 1.0$ kcal mol^{-1} and $\Delta S^\ddagger = -2 \pm 3$ eu. *cis*-Hyponitrite is proposed as an intermediate in the decomposition. At pH >13 and temperatures above 35° the decomposition rate increases markedly with increasing hydroxide ion concentration but no simple rate expression was found. The decomposition of $ON(SO_3^-)NO^-$ is specifically catalyzed by boric acid. In the pH range 6–10 the boric acid pathway follows the rate law, $-d[ON(SO_3^-)NO^-]/dt = k_3K_1[H^+]^2[ON(SO_3^-)NO^-][B(OH)_3]/(K_B + [H^+])$, where K_B is the ionization constant of boric acid and k_3 is the rate constant for the reaction of $B(OH)_3$ with $ON(SO_3^-)NOH$. Values of k_3K_1 are $4.2 \pm 0.2 \times 10^7$, $6.2 \pm 0.4 \times 10^7$, and $8.0 \pm 0.2 \times 10^7\ M^{-2}\ \text{sec}^{-1}$ at 15, 25, and 35°, respectively. $K_B = 6.8 \pm 1.2 \times 10^{-10}\ M$ at 25°. Activation parameters are $\Delta H^\ddagger = 5 \pm 1$ kcal mol^{-1} and $\Delta S^\ddagger = -6 \pm 2$ eu. A mechanism is proposed in which $B(OH)_3$ coordinates to one of the SO_3 group oxygen atoms of $ON(SO_3^-)NOH$ to promote N–S bond cleavage. $B(OH)_4^-$, lacking additional coordinating ability, does not enhance the rate of $ON(SO_3^-)NO^-$ decomposition.

Introduction

The decomposition of *N*-nitrosohydroxylamine-*N*-sulfonate ion, $ON(SO_3^-)NO^-$, has been studied by Seel and Winkler in the pH range 7–8 at very low ionic strength.[1] Their work in phosphate buffers demonstrated that the decomposition to nitrous oxide and sulfate was specifically catalyzed by hydrogen ion. These authors also reported a specific catalytic effect by borate buffers on $ON(SO_3^-)NO^-$ decomposition but did not investigate this effect. This specific borate buffer catalysis was also noted in the characterization of $ON(SO_3^-)NO^-$ as the product arising from air oxidation of hydroxylamine-*N*-sulfonate ion, $HONHSO_3^-$, in alkaline solution.[2] We now report the results of a study of the kinetics of the decomposition of $ON(SO_3^-)NO^-$ over a broad pH range in the presence of added boric acid. In the course of this study we have had occasion to examine the decomposition of $ON(SO_3^-)NO^-$ in the absence of boric acid over a more extended pH range than was previously studied and report this work as well.

Experimental Section

Materials. Dipotassium *N*-nitrosohydroxylamine-*N*-sulfonate, $K_2N_2O_2SO_3$, was prepared and stored as described.[3] It assayed spectrophotometrically at 99% purity.[2] All other chemicals were reagent grade and used without further purification.

Stoichiometry. Under all conditions studied the reaction stoichiometry for $ON(SO_3^-)NO^-$ decomposition corresponds to the equation

$$N_2O_2SO_3^{2-} \rightarrow N_2O + SO_4^{2-}$$

The gaseous product was analyzed by infrared spectrometry and gas chromatography. For the chromatographic analysis a 2-m column of 40-50 mesh 5A Molecular Sieve (Varian Aerograph) was used with hydrogen carrier gas. Sulfate was determined gravimetrically as barium sulfate.

Kinetic Procedure. Buffer solutions were prepared from sodium hydroxide, sodium hydrogen carbonate, sodium carbonate, sodium dihydrogen phosphate, sodium hydrogen phosphate, and sodium phosphate. The desired ionic strength was achieved by adjusting the concentrations of the reagents used to prepare the buffer. The pH was measured with a glass electrode on a Beckman Expandomatic pH meter or was calculated from the sodium hydroxide concentration and the ion product of water at the temperature of the kinetic run. The initial concentration of $ON(SO_3^-)NO^-$ was $2\text{-}3.5 \times 10^{-4}\ M$. Since heavy-metal ions are known to catalyze the decomposition of $ON(SO_3^-)NO^-$,[1] ethylenediaminetetraacetic acid was added to all runs. Concentrations of 10^{-3}–$10^{-5}\ M$ were employed and gave reproducible kinetics in this range.

The decomposition of $ON(SO_3^-)NO^-$ was followed spectrophotometrically at 2580 Å (ϵ 7140)[2] on a Gilford-modified Beckman DU spectrophotometer which was thermostated at the desired reaction temperature. For reactions at pH less than 9.5, kinetics were followed continuously in the thermostated spectrophotometer. Reactions at higher pH were carried out in thermostated flasks under a nitrogen atmosphere to prevent oxidation of $ON(SO_3^-)NO^-$ by atmospheric oxygen.[2] Aliquots were withdrawn periodically for spectrophotometric measurements. Runs were extended to at least 2 half-lives except for the slowest ones at high pH and low temperatures. All runs gave good first-order fits for $ON(SO_3^-)NO^-$ decomposition kinetics as determined by graphical analysis.

Results and Discussion

Studies in the Absence of Boric Acid. All kinetic runs for the decomposition of $ON(SO_3^-)NO^-$ fit the simple first-order relationship

$$\text{rate} = k_{\text{obsd}}[ON(SO_3^-)NO^-]$$

Values obtained for k_{obsd} are plotted in Figure 1 as a function of pH. These plots suggest that $ON(SO_3^-)NO^-$ decomposes by at least two different pathways.

In solutions more acidic than pH 9, k_{obsd} is directly proportional to the hydrogen ion concentration and the rate law has the form

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