$(Ta_6Br_{12})^{3+}X^-$ by Cr^{2+} or of the cluster ion by the Cr(II) complex CrX^+. Since the latter for chromium(II) thiocyanate would almost certainly involve the $Cr-NCS^+$ isomer, production of substantial quantities of $Cr-SCN^{2+}$, far in excess of the equilibrium values, suggests at least partial involvement of $(Ta_6Br_{12})^{3+}-NCS^- + Cr^{2+}$. In such a reaction the ion-paired thiocyanate ion would serve as a bridging group,[26] and the less stable $CrSCN^{2+}$ linkage isomer would result solely from the stereochemistry of such a transition state. Whether the $CrNCS^{2+}$ which is produced results from a parallel path or from isomerization of the S-bonded product could not be determined.

[26] D. W. Carlyle and J. H. Espenson, *Inorg. Chem.*, **8**, 575 (1969).

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The Mechanism of Inhibition of the Vanadium(IV)–Chlorate Reaction by Chloride Ion

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The reduction of chlorate ion by oxovanadium(IV) was studied at 25° and an ionic strength of 2.0 M under a variety of hydrogen ion concentrations from 0.40 to 1.9 M and chloride ion concentrations from 3.4×10^{-3} to 1.50 M. When the concentration of oxovanadium(IV) is in excess relative to the concentration of chlorate ion in the presence of initially added chloride ion, the stoichiometry is 4. In the absence of initially added chloride ion, the stoichiometry is 5. The kinetics of the reduction of chlorate ion by oxovanadium(IV) in the presence and absence of chloride ion are consistent with the following rate law: rate $= \{(k_1 + k_2[H^+])/(1 + K[Cl^-])\}[VO^{2+}][ClO_3^-]$. The parameters k_1 and K are independent of the hydrogen ion concentration and correspond to the values $(9.47 \pm 0.10) \times 10^{-3}\ M^{-1}\ sec^{-1}$ and $0.235 \pm 0.010\ M^{-1}$, respectively. The rate constant, k_2, for the hydrogen ion dependent term is calculated to be $(3.21 \pm 0.090) \times 10^{-3}\ M^{-2}\ sec^{-1}$. The change in stoichiometry, as a function of the chloride ion concentration, is due to differences in the rate of reaction between hypochlorous acid and chloride ion to form chlorine or hypochlorous acid and vanadium(IV) to form vanadium(V). The moderate inhibition of the vanadium(IV)–chlorate reaction by added chloride ion is discussed in terms of complex ion formation between vanadium(IV) and chloride ion.

Introduction

The reactions between various oxychlorine species and transition metal ions have been shown[1–6] to undergo both one- and two-electron-transfer processes. In an attempt to obtain more meaningful comparisons between one- and two-electron-transfer reactions, several kinetic studies of the reaction between vanadium(IV)[7] and chlorate ion were initiated[8–11] since vanadium(IV) is limited to a single electron oxidation. These investigations were complicated by the lack of availability of exact stoichiometric data. This complication arose in that the rates of reaction between vanadium(IV) and hypochlorous acid and chlorine were unknown. A recent report[12] indicates chlorine oxidizes vanadium(IV) only slowly but that the hypochlorous acid–vanadium(IV) reaction is relatively fast. A number of inherent kinetic complications were noted in the vanadium(IV)–chlorate reaction by Rosseinsky and Zlotnick[8] but the preliminary nature of their report precluded the possibility of a complete mechanistic interpretation. The kinetic data reported here are now sufficient to suggest a detailed rate law and reaction mechanism.

Experimental Section

Reagents.—Vanadium(IV) perchlorate solutions were prepared by electrolytic reduction of vanadium(V) oxide suspensions at platinum electrodes in perchloric acid media.[13] The vanadium(V) oxide was Fisher Certified reagent grade vanadium pentoxide. The electrolytic reduction was terminated when all of the vanadium(V) was reduced. Oxygen was bubbled through the vanadium(IV) solution to oxidize small amounts of vanadium(III). The purity of a vanadium(IV) solution was checked[14] by spot testing for vanadium(III) and vanadium(V). This procedure was sensitive to $10^{-5}M$ vanadium(III) and 10^{-4} M vandium(V) in 0.2 M vanadium(IV). Chloride ion[15] concentrations were below the 10^{-5} M level in the vanadium(IV) solutions as detected by the addition of aqueous silver nitrate. The vanadium(IV) solutions were standardized by using potassium permanganate.[16] The hydrogen ion concentration of the vanadium(IV) solutions was determined by the method described earlier.[4]

Sodium perchlorate was prepared by neutralizing reagent grade sodium carbonate with perchloric acid. Solid sodium perchlorate was obtained[4] by precipitation of sodium perchlorate, followed by three recrystallizations. J. T. Baker reagent grade sodium chlorate was used without further purification.

Chlorine dioxide was generated from the oxalic acid reduction of potassium chlorate in a method similar to that reported by Bray.[17] The chlorine dioxide was collected in water after being passed through a 2 M sodium carbonate wash solution. The vessel which contained the chlorine dioxide was sealed tightly

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[2] (a) R. Thompson and G. Gordon, *ibid.*, **5**, 562 (1966); (b) B. Z. Shakhashiri and G. Gordon, *J. Amer. Chem. Soc.*, **91**, 1103 (1969).

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[6] A. M. Azzam and I. A. W. Shimi, *Z. Phys. Chem. (Frankfurt am Main)*, **33**, 190 (1962).

[7] The vanadium(IV) species present in aqueous perchloric acid solution is the $[(H_2O)_4VO^{2+}]$ species which will be termed vanadium(IV) in this paper.

[8] D. R. Rosseinsky and J. Zlotnick, *J. Chem. Soc.*, 1200 (1970).

[9] C. W. Fuller and J. M. Ottaway, *Analyst*, **95**, 791 (1970).

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[16] H. H. Willard and P. Young, *Ind. Eng. Chem., Anal. Ed.*, **6**, 48 (1934).

[17] W. C. Bray, *Z. Phys. Chem.*, **54**, 569 (1906).

and maintained at 0° prior to use. The concentration of chlorine dioxide was determined spectrophotometrically[18,19] at 358.5 nm where chlorine dioxide has a molar extinction coefficient of 1250 ± 2 M^{-1} cm^{-1}.

Kinetic Measurements.—The rate of the vanadium(IV)–chlorate ion reaction was determined by following the disappearance of vanadium(IV) at 760 nm with a Cary 14 recording spectrophotometer. At this wavelength, in the range of hydrogen and chloride ion concentrations used, the molar extinction coefficient of vanadium(IV) is 17.2 ± 0.1 M^{-1} cm^{-1} at 25°. This extinction coefficient is in good agreement with reported values.[4,13] The ionic strength for each kinetic experiment was initially adjusted to 2.00 ± 0.03 M with sodium perchlorate. Except for the oxidizing agent, the reactants were added in the appropriate amounts to a 2.00-cm quartz cell and placed in the cell compartment which was thermostated to 25.0 ± 0.1°. The reaction was initiated manually by injecting the oxidizing agent into the reaction cell with a calibrated glass syringe which was equipped with a polyethylene tip. The injection of the final solution resulted in complete mixing. As a check on total concentration of oxidizing agent, the final absorbance of the reaction mixture was recorded after a period of at least 40 hr.

The kinetic data for the disappearance of vanadium(IV) was analyzed according to the rate law $-d[VO^{2+}]/n\,dt = k[VO^{2+}]\cdot[ClO_3^-]$, where k is the apparent second-order rate constant and n is the stoichiometric coefficient under the conditions of the kinetic experiment. In the absence of initially added chloride ion, the stoichiometric factor is 5 since the hypochlorous acid which is produced reacts rapidly with excess vanadium(IV) as can be seen from the data in Table I. The overall reaction is

$$5VO^{2+} + ClO_3^- + 2H_2O \longrightarrow 5VO_2^+ + 0.5Cl_2 + 4H^+ \quad (1)$$

TABLE I

SECOND-ORDER RATE CONSTANTS FOR VARIOUS REACTIONS IN 1.0 M PERCHLORIC ACID AT 25°

Reaction	k, M^{-1} sec^{-1}	Ref	Reaction	k, M^{-1} sec^{-1}	Ref
$HOCl–VO^{2+}$	5.6	12	$HOCl–Cl^-$	1.8 × 10^4	20
$Cl_2–VO^{2+}$	0.007[a]	12	$Cl_2–HClO_2$[b]	1.1 × 10^4	1a

[a] 0.1–1.0 M Cl^-. [b] 0.8 M $HClO_4$.

In the presence of initially added chloride ion, the hypochlorous acid preferentially reacts[20] with chloride ion to form chlorine rather than to oxidize vanadium(IV) rapidly. Thus, the stoichiometric factor becomes 4 as is shown by

$$4VO^{2+} + ClO_3^- + Cl^- + H_2O \longrightarrow 4VO_2^+ + Cl_2 + 2H^+ \quad (2)$$

In both reactions, chlorine is formed as a product. As can be seen from the data in Table I, chlorine oxidizes vanadium(IV) only slowly.

The time *vs.* absorbance data for each kinetic experiment were analyzed by means of a nonlinear least-squares computer program.[21] The best nonlinear least-squares fit of the data was found by minimizing the square of the difference between the measured and computed absorbances for the first 35–40% of the reaction. Under these conditions, the residual absorbances[22] were randomly scattered as a function of time and never exceeded ±0.0015 absorbance unit. Moreover, rate constants calculated for shorter periods of reaction agreed to better than one standard deviation with those calculated for 35–40% reaction.

On the other hand, inclusion of more of the reaction in the calculation resulted in smaller rate constants with distinct trending effects as would be expected on the basis of the slow but continuing vanadium(IV)–chlorine reaction.[12] Finally, detailed analysis of the latter portions of the vanadium(IV)–chlorate reaction, after correction for the appropriate stoichiometry, gave apparent second-order rate constants consistent with available data[12] for the vanadium(IV)–chlorine reaction.

The overall stoichiometry of the vanadium(IV)–chlorate ion reaction, including the slow chlorine reaction, was determined in the presence of excess vanadium(IV) in order to make direct comparisons with the results reported previously.[8,23] The stoichiometric coefficient was determined from the initial and final absorbance readings at 760 nm and the reactant concentrations. These results are shown in Table II.

TABLE II

TYPICAL OVERALL STOICHIOMETRIC DATA AT THE END OF THE VANADIUM(IV)–CHLORATE ION REACTION IN THE PRESENCE OF CHLORIDE ION

$[H^+]$, M	$[Cl^-]$, M	10^2 × $[VO^{2+}]$, M	10^3 × $[ClO_3^-]$, M	A_0	A_∞	Overall stoichiometric coeff
0.40	1.20	2.80	4.26	0.967	0.105	5.9 ± 0.10
1.00	0.08	2.80	4.26	0.963	0.100	5.9 ± 0.10
1.00	0.75	2.69	4.26	0.945	0.070	5.9 ± 0.10
1.30	0.10	5.60	4.26	1.922	1.084	5.8 ± 0.15
1.30	0.10	5.60	2.13	1.914	1.497	5.8 ± 0.15
1.30	0.60	4.20	4.26	1.454	0.598	5.9 ± 0.15
1.85	0.08	2.80	4.26	0.961	0.095	5.7 ± 0.20

When chloride dioxide was the oxidant, the reaction rates were determined by following the disappearance of chlorine dioxide at 358.5 nm under pseudo-first-order conditions with vanadium(IV) in excess. Because the reaction is relatively rapid, a rapid-mixing, spring-powered syringe[24] was employed to mix the reactants. The second-order rate constants were calculated from the pseudo-first-order rate constant and the average concentration of vanadium(IV) in each experiment.

The stoichiometric measurements on the vanadium(IV)–chlorine dioxide reaction were made at 358.5 nm where the initial concentration of chlorine dioxide in the reaction vessel could be determined reliably.[18] Vanadium(IV) was always present in excess in an attempt to obtain quantitative removal of chlorine dioxide. The initial concentration of vanadium(IV) was determined from a blank experiment at 760 nm. Since vanadium(IV) was the only absorbing species at this wavelength, the concentration of vanadium(IV) remaining at the end of the reaction could be estimated directly. The concentration of vanadium(V) produced in the reaction was estimated spectrophotometrically at 358.5 nm where the molar extinction coefficient in 1 M $HClO_4$ at 25° was found to be 83.9 ± 0.4 M^{-1} cm^{-1}. The molar extinction coefficient of vanadium(IV) at this wavelength was observed to 0.331 ± 0.005 M^{-1} cm^{-1}. The stoichiometry was calculated from the amounts of vanadium(V) produced and chlorine dioxide consumed.

Results

Kinetics of the Vanadium(IV)–Chlorate Ion Reaction.—During the total reduction of chlorate ion to form chloride ion, several chlorine-containing intermediates are formed. These intermediates include chlorine dioxide, chlorous acid, hypochlorous acid, and chlorine. The relative rates of the corresponding vanadium(IV)–chlorine-containing intermediate reactions determine the instantaneous stoichiometry. Fuller and Ottaway reported[9] that in the presence of excess chlorate ion and in the absence of added chloride ion, the stoichiometric factor is 5 and that chlorine is formed as is shown in eq 1. This is true only if chlorate ion is in large excess[9] and only in the initial stages of the reaction.

A further complication arises in the presence of excess vanadium(IV) in the absence of initially added chloride ion in that as chloride ion is formed *via* the relatively

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[18] R. G. Kieffer and G. Gordon, *Inorg. Chem.*, **7**, 235, 239 (1968).

[19] C. C. Hong, F. Lenzi, and W. H. Ragson, *Can. J. Chem. Eng.*, **45**, 349 (1967).

[20] M. Eigen and K. Kustin, *J. Amer. Chem. Soc.*, **84**, 1355 (1962).

[21] A description of the algorithm of the computer program is given in the Los Alamos publication LA-2367 and addenda. A modified version of this program is presently available from G. Gordon at the University of Iowa.

[22] The residual absorbance is defined as the difference between the calculated and the measured absorbance.

[23] In the presence of excess chlorate ion, Rosseinsky and Zlotnick reported[8] a stoichiometric coefficient of 6.39 ± 0.44. On the assumption that small amounts of ClO_2 and Cl_2 remain as unreacted by-products of the vanadium(V)–chlorate ion reaction, they applied a correction in order to obtain a final value of 5.82 ± 0.30.

[24] R. C. Thompson and G. Gordon, *J. Sci. Instrum.*, **41**, 480 (1964).

slow chlorine–vanadium(IV) reaction or *via* the self-interaction of various chlorine-containing intermediates, some chlorine is formed. The chlorine is formed appropriate to the reaction

$$\mathrm{HOCl} + \mathrm{Cl^-} + \mathrm{H^+} \rightleftharpoons \mathrm{Cl_2} + \mathrm{H_2O} \qquad (3)$$

Under these conditions, as chloride ion is slowly formed, the stoichiometry will change from 5 to 4. This change will be reflected by somewhat inconsistent rate constants and trends in the residual absorbances with increasing time. Clearly, however, a detailed analysis of the kinetic data alone will be insufficient to determine accurately the stoichiometric coefficients.

The results of a series of experiments designed to determine the order of the vanadium(IV)–chlorate reaction in the absence of initially added chloride ion confirmed the earlier reports[8-10] that the reaction is first order[25] with respect to both vanadium(IV) and chlorate ion. The deviations from second-order behavior reported[8,9,26] previously in the absence of initially added chloride ion are minimized by treatment of the data appropriate to the stoichiometry reported here.

The effect of hydrogen ion on the rate of the reaction in the absence of initially added chloride ion was determined by analysis of the kinetic data by using the method of initial rates.[26] The rates were obtained from the change in absorbance as a function of time during the first 35–40% of the reaction. For the purposes of these calculations, a stoichiometric factor of 5 was used appropriate to eq 1. At constant ionic strength and in the absence of initially added chloride ion, the observed second-order rate constants were found to be linearly dependent on the hydrogen ion concentration[27] according to

$$k_{\mathrm{obsd}} = k_1 + k_2[\mathrm{H^+}] \qquad (4)$$

These results are summarized in Table III and are compared with the values calculated from a least-squares analysis (*vide infra*).

TABLE III

APPARENT SECOND-ORDER RATE CONSTANTS[a] FOR THE VANADIUM(IV)–CHLORATE REACTION AS A FUNCTION OF HYDROGEN ION IN THE ABSENCE OF CHLORIDE ION AT 25°

$[\mathrm{HClO_4}]$, M	10^2k_{obsd}	10^2k_{calcd}	$[\mathrm{HClO_4}]$, M	10^2k_{obsd}	10^2k_{calcd}
0.25	1.06 ± 0.003	1.03	1.20	1.37 ± 0.003	1.33
0.50	1.12 ± 0.004	1.11	1.40	1.40 ± 0.002	1.40
0.75	1.21 ± 0.002	1.19	1.90	1.58 ± 0.005	1.56
1.00	1.28 ± 0.005	1.27			

[a] Initial rate analysis. Initial concentrations: $[\mathrm{V(IV)}] = 2.8 \times 10^{-2}\ M$, $[\mathrm{ClO_3^-}] = 3.31 \times 10^{-3}\ M$, $I = 2.00\ M$ ($\mathrm{NaClO_4}$). Rate constants given in $M^{-1}\ \mathrm{sec}^{-1}$.

At constant chloride ion concentrations a linear relationship is also observed between the second-order rate constant and the hydrogen ion concentration. These results for four different hydrogen ion concentrations and $0.00342 < \mathrm{Cl^-} < 1.50\ M$ are summarized in Table IV.

TABLE IV

APPARENT SECOND-ORDER RATE CONSTANTS[a] AT VARIOUS HYDROGEN ION AND CHLORIDE ION CONCENTRATIONS

$[\mathrm{Cl^-}]$, M	$[\mathrm{H^+}]$, M	10^2k_{obsd}[b]	10^2k_{calcd}
0.00342	0.50	1.21 ± 0.004	1.11
0.00342	1.00	1.34 ± 0.003	1.27
0.00342	1.40	1.44 ± 0.003	1.39
0.00342	1.90	1.58 ± 0.006	1.55
0.0050	0.50	1.17 ± 0.003	1.11
0.0050	1.00	1.31 ± 0.003	1.27
0.0050	1.40	1.43 ± 0.005	1.39
0.0050	1.90	1.57 ± 0.006	1.55
0.01026	0.50	1.12 ± 0.003	1.10
0.01026	1.00	1.26 ± 0.004	1.26
0.01026	1.40	1.41 ± 0.003	1.39
0.01026	1.90	1.57 ± 0.005	1.55
0.03079	0.50	1.06 ± 0.003	1.10
0.03079	1.00	1.20 ± 0.003	1.26
0.03079	1.40	1.36 ± 0.004	1.39
0.03079	1.90	1.51 ± 0.005	1.54
0.060	0.50	1.05 ± 0.002	1.09
0.060	1.00	1.19 ± 0.002	1.25
0.060	1.40	1.32 ± 0.004	1.38
0.060	1.90	1.49 ± 0.003	1.53
0.080	0.40	1.06 ± 0.003	1.06
0.080	1.00	1.24 ± 0.002	1.24
0.080	1.30	1.33 ± 0.005	1.34
0.080	1.85	1.51 ± 0.004	1.51
0.10	0.40	1.04 ± 0.004	1.05
0.10	1.00	1.19 ± 0.003	1.24
0.10	1.30	1.30 ± 0.005	1.33
0.10	1.85	1.49 ± 0.004	1.50
0.15	1.00	1.17 ± 0.004	1.22
0.30	0.40	0.988 ± 0.002	1.00
0.30	1.00	1.13 ± 0.003	1.18
0.30	1.30	1.25 ± 0.005	1.27
0.30	1.85	1.43 ± 0.002	1.44
0.60	0.40	0.918 ± 0.003	0.942
0.60	1.00	1.09 ± 0.002	1.11
0.60	1.30	1.20 ± 0.002	1.20
0.60	1.85	1.36 ± 0.003	1.35
0.65	1.00	1.09 ± 0.002	1.10
0.75	0.40	0.915 ± 0.003	0.914
0.75	1.00	1.07 ± 0.004[c]	1.08
0.75	1.30	1.13 ± 0.003	1.16
0.75	1.85	1.33 ± 0.002	1.31
0.825	1.00	1.04 ± 0.002	1.06
0.916	1.00	1.02 ± 0.002	1.04
1.20	0.40	0.826 ± 0.005	0.839
1.20	1.00	0.981 ± 0.002	0.989
1.20	1.30	1.10 ± 0.002	1.06
1.20	1.85	1.23 ± 0.003	1.20
1.50	0.40	0.819 ± 0.003	0.795
1.50	1.00	0.949 ± 0.002	0.937
1.50	1.30	1.03 ± 0.002	1.00
1.50	1.85	1.18 ± 0.004	1.14

[a] Second-order rate constants are in units of $M^{-1}\ \mathrm{sec}^{-1}$; the following conditions were maintained unless otherwise specified: temperature 25°, ionic strength 2.00 M, $[\mathrm{V(IV)}] = 2.80 \times 10^{-2}\ M$, $[\mathrm{ClO_3^-}] = 4.26 \times 10^{-3}\ M$; the calculated rate constants are based on the rate equation with a stoichiometry of 4.0 in the presence of initially added chloride ion. The assumption that chloride ion complexes other than mono(chloro)vanadium(IV) can be neglected appears to be justified on the basis of the agreement between the observed and calculated rate constants. [b] The uncertainties represent standard deviations in the fitted second-order rate constant as calculated directly from the absorbance *vs.* time data. [c] $[\mathrm{V(IV)}] = 0.0269\ M$.

The values obtained for the observed rate constants shown in Table IV are observed to decrease with in-

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(25) In the absence of chloride ion, Fuller and Ottaway[9] reported inhibition of the vanadium(IV)–chlorate reaction by chlorate ion. This gives rise to a rate law of the form $k_0K_1[\mathrm{ClO_3^-}][\mathrm{VO^{2+}}]/[1 + K_1[\mathrm{ClO_3^-}]]$. The data in Table III do not cover a sufficiently wide variation in chlorate ion concentration to allow the denominator term to be distinguished. Moreover, the inherent scatter in the data reported here in the presence of chloride ion and the variations possible in the stoichiometric coefficients owing to possible oxychlorine intermediate–chloride ion interactions to form chlorine precludes the possibility of discerning the existence of this chlorate ion inhibition.

(26) C. W. Fuller and J. M. Ottaway, *Analyst*, **94**, 32 (1969).

(27) In ref 8, the reaction is reported to be independent of hydrogen ion at an ionic strength of 0.50 M and to have only a marginal dependence on hydrogen ion concentration at 1.50 M ionic strength.

creasing chloride ion concentration. A graph of the logarithm of the observed rate constant at constant hydrogen ion concentration as a function of the logarithm of the corresponding chloride ion concentration is not linear. The order of the reaction[28] with respect to the chloride ion concentration varies from a value of about -0.06 in the concentration range $0.003 < \mathrm{Cl}^- < 0.060\ M$ to a value of -0.16 in the chloride ion concentration range $0.60 < \mathrm{Cl}^- < 1.5\ M$. Thus, the order with respect to chloride ion is decreasing as the chloride ion concentration is increasing. The type of behavior is good evidence for the formation of a complex which takes the form of an inhibiting denominator term in the rate law.

A variety of equations which relate k_{obsd} to various functions of hydrogen ion and chloride ion concentrations were tested by determining the equation which best reproduced the experimental data given in Tables III and IV. A comparison of the weighted variance for each of the mathematical models was used to determine which equation best reproduced the experimental observations. A nonlinear least-squares program[21] was used to compute the rate constants associated with various functions of k_{obsd}, hydrogen ion, and chloride ion. The data were weighted by the inverse of the square of the dependent variable which minimizes the per cent error of each data point.

The form of the rate law which best reproduced the experimental data is

$$k_{\mathrm{obsd}} = \frac{k_1 + k_2[\mathrm{H}^+]}{1 + K[\mathrm{Cl}^-]} \qquad (5)$$

The calculated constants at 25° and the corresponding standard deviations are $k_1 = (9.47 \pm 0.10) \times 10^{-3}\ M^{-1}\ \mathrm{sec}^{-1}$, $k_2 = (3.21 \pm 0.090) \times 10^{-3}\ M^{-2}\ \mathrm{sec}^{-1}$, and $K = 0.235 \pm 0.010\ M^{-1}$. The important test of the proposed rate law is the consistency of the observed and calculated second-order rate constants. A comparison of these values is given in both Tables III and IV. The parameters k_1, k_2, and K reproduce the experimentally observed values with a mean deviation of 2.8% and a maximum deviation of 5.8%. Because k_1 is the predominant term and k_2 is sensitive to changes in hydrogen ion concentration, the precision to which these terms are known is high. The precision with which K is determined is less. This originates from the moderate inhibition of the overall rate of the reaction by chloride ion.

By using absolute rate theory[29] and the nonlinear least-squares computer program,[21] the enthalpies and entropies of activation for the terms k_1 and k_2 in eq 5 were estimated simultaneously from the temperature data in Table V. The assumption was made that small concentrations of chloride ion do not significantly affect these activation processes.[30] The activation parameters for k_1 are $\Delta H^{\ddagger} = 19.26 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = -3.2 \pm 0.9$ eu while those for k_2 are $\Delta H^{\ddagger} = 17.4 \pm 0.7$ kcal/mol and $\Delta S^{\ddagger} = -11.6 \pm 1.3$ eu.

TABLE V

TEMPERATURE DEPENDENCE FOR THE VANADIUM(IV)–CHLORATE ION REACTION[a] AT VARIOUS HYDROGEN ION CONCENTRATIONS

$[\mathrm{H}^+]$, M	Temp, °C	10^2k_{obsd}, $M^{-1}\ \mathrm{sec}^{-1}$	10^2k_{calcd}, $M^{-1}\ \mathrm{sec}^{-1}$
0.40	10.6	0.189 ± 0.001	0.191
	25.0	1.06 ± 0.003	1.03
	35.0	3.00 ± 0.016	3.00
1.00	10.6	0.225 ± 0.001	0.230
	25.0	1.24 ± 0.002	1.21
	35.0	3.44 ± 0.015	3.49
	40.0	5.70 ± 0.042	5.81
1.85	10.6	0.285 ± 0.005	0.286
	25.0	1.51 ± 0.004	1.47
	35.0	4.15 ± 0.023	4.19

[a] Initial concentrations: $[\mathrm{VO}^{2+}] = 2.80 \times 10^{-2}\ M$, $[\mathrm{ClO}_3^-] = 4.26 \times 10^{-3}\ M$, $[\mathrm{Cl}^-] = 8.0 \times 10^{-2}\ M$. Ionic strength 2.00 M.

The Vanadium(IV)–Chlorine Dioxide Reaction.—In that chlorine dioxide was observed to be a reduction product[31] of chlorate ion as was expected, the reaction between vanadium(IV) and chlorine dioxide was briefly investigated. The reaction comprises two main reaction sequences.[32] The first sequence occurs rapidly and corresponds to the direct reduction of chlorine dioxide by vanadium(IV). This initial, fast reaction is followed by a much slower reaction. The slow reaction corresponds to an additional reaction which consumes vanadium(IV) and originates from another chlorine-containing oxidizing agent which is kinetically less reactive[33,34] than chlorine dioxide or chlorine(III). This slowly reacting oxidizing agent appears[1a,35] to be a mixture of chlorate ion and chlorine which is formed *via* interoxychloride interactions.[32]

Rapid reduction of chlorine dioxide by vanadium(IV) occurs with a variable stoichiometry which is dependent on the absence or presence of chloride ion. The stoichiometric coefficient for the rapid reaction shown by eq 6 was determined from the molar ratio of the amount of vanadium(V) produced to the amount of chlorine dioxide consumed. The results of these stoichiometric

$$m\mathrm{VO}^{2+} + \mathrm{ClO}_2 \xrightarrow{\text{fast}} m\mathrm{VO}_2^{+} + \text{products} \qquad (6)$$

measurements are listed in Table VI. In the absence of added chloride ion and in 0.20–2.0 M perchloric acid, $m \approx 1.7 \pm 0.05$. In the chloride ion range $0.003 < \mathrm{Cl}^- < 0.050\ M$ and in 1 M perchloric acid, $m \approx 1.3 \pm 0.1$.

The rate of reduction of chlorine dioxide was investigated in order to demonstrate that it oxidizes vanadium(IV) much more rapidly than does chlorate ion. The results of these experiments are listed in Table VII. It is important to note that chlorine dioxide reacts

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[28] A decrease in rate was also reported in ref 8 and was atrributed to either ion pairing with vanadium(IV) or a minor side path consuming an oxychlorine intermediate which might otherwise rapidly oxidize vanadium(IV).

[29] S. Glasstone, K. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, N. Y., 1941, p 199.

[30] This assumption appears to be valid in that chloride ion only moderately inhibits the overall rate of reaction. Additional support is found in the comparison of the overall activation parameters obtained from k_{obsd} with the temperature data in Table V at $[\mathrm{H}^+] = 1.00\ M$ and $[\mathrm{Cl}^-] = 0.08\ M$, $\Delta H^{\ddagger} = 18.8 \pm 0.4$ kcal/mol and $\Delta S^{\ddagger} = -5.0 \pm 1.1$ eu, with those obtained with a similar set of data at a much higher concentration of chloride ion. For example, at $[\mathrm{H}^+] = 1.00\ M$ and $[\mathrm{Cl}^-] = 0.575\ M$, $\Delta H^{\ddagger} = 18.8 \pm 0.5$ kcal/mol and $\Delta S^{\ddagger} = -4.5 \pm 1.2$ eu.

[31] Chlorine dioxide is easily extracted into an ethereal layer and characterized spectrophotometrically.[18]

[32] This is not entirely unexpected in that competitive interoxychlorine reactions are possible. For example see H. Taube and H. Dodgen, *J. Amer. Chem. Soc.*, **71**, 3330 (1949); G. Gordon and F. Emmenegger, *Inorg. Nucl. Chem. Lett.*, **2**, 395 (1966); F. Emmenegger and G. Gordon, *Inorg. Chem.*, **6**, 633 (1967); G. Gordon, R. G. Kieffer, and D. Rosenblatt, *Progr. Inorg. Chem.*, **15**, 201 (1972).

[33] The chlorine(III)–vanadium(IV) reaction has also been shown in this laboratory and by Thompson[34] to be relatively fast—but complicated. Some chlorate ion and chlorine are clearly formed in this reaction.

[34] R. C. Thompson, private communication, University of Missouri, 1971.

[35] This is similar in some aspects to the reaction between uranium(IV) and chlorite which produces, in addition to uranium(VI), chlorate and chloride ions.

TABLE VI

STOICHIOMETRY OF THE VANADIUM(IV)–CHLORINE DIOXIDE REACTION[a]

$[H^+]$, *M*	$[Cl^-]$, *M*	$[VO_2^+]_{produced}/[ClO_2]_{consumed}$	$[H^+]$, *M*	$[Cl^-]$, *M*	$[VO_2^+]_{produced}/[ClO_2]_{consumed}$
0.09	0.0	1.7 ± 0.1	1.00	0.010	1.2 ± 0.05
0.20	0.0	1.7 ± 0.1	1.00	0.050	1.2 ± 0.05
1.00	0.0	1.6 ± 0.1	1.00	0.20	1.3 ± 0.1[b]
2.00	0.0	1.6 ± 0.1	1.00	0.50	1.3 ± 0.1[b]
1.00	0.003	1.2 ± 0.05	1.00	1.00	1.4 ± 0.1[b]

[a] The uncertainty represents the average deviation for replicate experiments. [b] The vanadium(V) molar extinction coefficient increases slightly with increasing chloride ion concentration. No corrections have been applied to account for this increase or for the small amounts of chlorine formed.

TABLE VII

KINETIC DATA[a] FOR THE VANADIUM(IV)–CHLORINE DIOXIDE REACTION IN PERCHLORIC ACID AT 25°

$[Cl^-]$, *M*	k_3, sec^{-1}	k_2, M^{-1} sec^{-1}	$[Cl^-]$, *M*	k_3, sec^{-1}	k_2, M^{-1} sec^{-1}
0.0	0.076	6.8 ± 0.2	0.30	0.058	5.2 ± 0.1
0.01	0.065	5.9 ± 0.2	0.50	0.069	6.2 ± 0.2
0.10	0.052	4.7 ± 0.2			

[a] Initial concentrations: $[VO^{2+}] = 1.11 \times 10^{-2}$ *M*, $[ClO_2] = (5.0\text{–}7.6) \times 10^{-4}$ *M*, average ionic strength 2.2 ± 0.3 *M* ($NaClO_4$). The uncertainties represent the average deviations for replicate experiments.

approximately 100 times more rapidly than does chlorate ion with vanadium(IV). The chlorine(III)–vanadium(IV) reaction is also correspondingly fast.[34]

Discussion

The best nonlinear least-squares fit of data for the reaction between vanadium(IV) and chlorate ion in the absence of initially added chloride ion ($<10^{-5}$ *M*) and in range $0.003 < Cl^- < 1.50$ *M* and $0.25 < H^+ < 1.90$ *M* is given by eq 5. This rate law suggests two parallel pathways and also indicates that both these pathways are somewhat inhibited by the addition of chloride ion. The effect of chloride ion is most probably associated with the formation of a vanadium(IV)–chloride complex as shown by

$$VO^{2+} + Cl^- \overset{K}{\rightleftarrows} VOCl^+ \qquad (7)$$

A reliable value for the complex formation constant between vanadium(IV) and chloride ion is not available in the literature although some estimates are reported.[36–39] Arhland, for instance, reported[36] a value of 1.1 M^{-1} which sets the order of magnitude for complex formation between chloride ion and vanadium(IV). The results reported here on the effect which chloride ion has on the rate of the oxidation–reduction reaction between vanadium(V) and chlorate ion are consistent with chloride ion complexation by vanadium(IV). Analysis of the kinetic data under this assumption and in terms of eq 5 results in a formation constant of 0.235 ± 0.010 M^{-1} at 25°.

This treatment of the data assumes that the resulting inhibition in rate is due to the fact that the concentration of the more reactive tetraaquovanadium(IV) species is decreased relative to the concentration of the unreactive chloroaquovanadium(IV) species. It should be noted in this context, that in the presence of 0.1 *M* chloride ion with 0.03 *M* vanadium(IV), less than 3% of the vanadium(IV) would be tied up as the less reactive chloro complex. With 1.0 *M* chloride ion, less than 18% of the complex would be formed and a corresponding decrease in overall rate of about 20% would be expected.

The two parallel pathways which are suggested by eq 5 can be described most easily in terms of the net activation process formulation suggested by Newton and Rabideau.[40] These two processes would be

$$VO^{2+} + ClO_3^- \overset{k_1}{\rightleftarrows} [OVClO_3^+]^{\ddagger} \qquad (8)$$

$$VO^{2+} + ClO_3^- + H^+ \overset{k_2}{\rightleftarrows} [OVClO_3H^{2+}]^{\ddagger} \qquad (9)$$

At negligible concentrations of chloride ion the rate expression defined by eq 5 reduces to the limiting form shown in eq 4. This predicts that in 1 *M* perchloric acid and in the absence of chloride ion the overall second-order rate constant will be equal to $(1.27 \pm 0.02) \times 10^{-2}$ M^{-1} sec^{-1} at 25° as compared with the observed value of 1.28×10^{-2} M^{-1} sec^{-1}. It is also of particular interest to compare the results reported here with those reported previously.[8–10] In order to make this comparison, we have converted our data to 21.2° by means of our activation parameters and obtain a value of 0.82×10^{-2} M^{-1} sec^{-1}. Rosseinsky and Zlotnick[8] reported a second-order rate constant[41] of 0.86×10^{-2} M^{-1} sec^{-1} at an ionic strength of 2.5 *M* at 21.2°. Fuller and Ottaway reported[9,25] $k_0 = 0.074$ sec^{-1} at an ionic strength of 0.5 *M* and a corresponding value of K_1 of 0.75 M^{-1} which results in a second-order rate constant of 1.11×10^{-2} M^{-1} sec^{-1} at 25°. This should be compared with our value of 1.28×10^{-2} M^{-1} sec^{-1}. The results of Bontschev and Mladenowa[10] are considerably lower than any of the values presented here. They reported a rate constant of 1.4×10^{-4} M^{-1} sec^{-1} in a phthalate buffer in the pH 2.0–3.6 range. From our data, we would predict a rate constant of 95×10^{-4} M^{-1} sec^{-1}. On this basis, we conclude that the phthalate ion is coordinated to vanadium(IV) which results in a marked decrease in rate.[42]

The small apparent ionic strength dependence shown above[8,9] is not surprising in view of the possible involvement of both chlorate ion and chloride ion in prerate-determining equilibria with vanadium(IV). It should be expected that the associated equilibrium constants also would be sensitive to ionic strength changes.

At this point, it might be interesting to speculate on the nature of the apparent inhibition by chlorate ion reported by Fuller and Ottaway.[9] Two simple monodentate complexes can be envisioned:[26] one which would be chlorine bonded to vanadium(IV) and the other which could be oxygen bonded. It has been suggested recently,[1b] that chlorine bonding by chlorine-containing oxidizing agents in the first coordination sphere of reducing agents will most probably result

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(36) S. Arhland and B. Noren, *Acta Chem. Scand.*, **12**, 1595 (1958).

(37) J. C. Evans, *Inorg. Chem.*, **2**, 372 (1963).

(38) C. R. Giuliano and H. M. McConnell, *J. Inorg. Nucl. Chem.*, **9**, 171 (1959).

(39) An experimental value of 1.7 M^{-1} was assigned to the overall competition between vanadium(II) and vanadium(IV) for chloride ion by Newton and Baker.[15]

(40) T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, **63**, 365 (1959).

(41) Estimated from initial rates, where the effects of changes in stoichiometry are minimal.

(42) Similar complexes are formed between vanadium(IV) and glycine or tartrate as reported by H. Tomiyasu and G. Gordon, unpublished results, and by K. Kustin and R. Pizer, *Inorg. Chem.*, **9**, 1536 (1970).

in a one-electron-transfer process whereas oxygen bonding is a necessary and sufficient condition for two-electron transfer. Since each vanadium(IV) can transfer *only* one electron, we suggest that only the chlorine-bonded species would result in the formation of vanadium(V). We also wish to suggest that at high vanadium concentrations an additional term second order in vanadium(IV) would become important and this species would involve the oxygen-bonded complex.

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Microwave Spectrum, Structure, Dipole Moment, and Nuclear Quadrupole Coupling Constants of Cyanodifluorophosphine[1]

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The microwave spectra of the ground and some excited vibrational states of PF_2CN, $PF_2{}^{13}CN$, and $PF_2C^{15}N$ have been analyzed. From the moments of inertia, structural parameters have been derived as follows: $d(PF) = 1.566 \pm 0.007$ Å, $d(PC) = 1.815 \pm 0.005$ Å, $d(CN) = 1.157 \pm 0.003$ Å, $\angle FPF = 99.2 \pm 0.2°$, $\angle FPC = 96.9 \pm 0.2°$, and $\angle PCN = 171.2 \pm 0.8°$. The tilt of the CN group is away from the fluorine atoms. The nitrogen quadrupole coupling constants are $\chi_{aa} = -4.66 \pm 0.12$ MHz, $\chi_{bb} = 5.08 \pm 1.0$ MHz, and $\chi_{cc} = -0.42 \pm 1.0$ MHz. The dipole moments are $\mu_a = 2.03 \pm 0.01$ D, $\mu_c = 1.27 \pm 0.03$ D, and $\mu = 2.39 \pm 0.02$ D.

Introduction

An investigation of the microwave spectrum of cyanodifluorophosphine, PF_2CN, was undertaken as a result of the current interest in the structure and bonding in substituted fluorophosphines.[2] Of particular interest in this study were the PC bond distance and the PCN angle. The results of a determination of the crystal structure of phosphorus tricyanide, $P(CN)_3$, by X-ray diffraction[3] indicated that the average PCN angle is about 171 ± 3°, rather than the 180° that would be predicted by simple bonding theory. It has been suggested that this nonlinearity is due to the close packing in the crystal lattice and that it would not occur in the free molecule.[4]

Experimental Section

Samples of PF_2CN, $PF_2{}^{13}CN$, and $PF_2C^{15}N$ were prepared by the interaction of PF_2I with CuCN as reported by Rudolph, *et al.*[5] For the ^{13}C and ^{15}N species, the corresponding cuprous cyanides were obtained from appropriately enriched KCN by the use of the procedure of Barber.[6] The enriched samples contained 15% $PF_2{}^{13}CN$ and 25% $PF_2C^{15}N$, respectively. All samples were purified by trap-to-trap distillation, and their presence was confirmed by mass spectroscopy. In each case, the mass spectrum also revealed the presence of PF_2I as the major impurity, apparently because PF_2CN and PF_2I have about the same volatility.[5] Although PF_2I has a fairly rich spectrum, its interference in the study of the spectrum of PF_2CN has been minimal.

The spectra, all taken at Dry Ice temperature, were obtained with conventional Stark-modulated spectrometers of our own construction and a Hewlett-Packard R8460A MRR spectrometer. The uncertainty in the observed frequencies reported here is ±0.10 MHz.

Spectra.—The spectrum of PF_2CN was initially calculated by assuming a pyramidal structure and a plane of symmetry. The assignment of the normal species was based on the characteristic Stark effect of the three *a*-type $J = 1 \rightarrow 2$ transitions. Spectra for the isotopic species were assigned in the same fashion. The frequencies of the observed transitions in the ground vibrational state of the three isotopic species are listed in Table I, and the corresponding rotational parameters are given in Table II. Transitions belonging to excited states of the lowest frequency vibrational mode of the three isotopic species were also observed and fit and are given in Table III; the corresponding rotational parameters are in Table IV. At Dry Ice temperature the ratio of the intensity of a transition in the first excited state to that of a corresponding transition in the ground state is approximately

TABLE I

FREQUENCIES[a] OF GROUND STATE ROTATIONAL TRANSITIONS FOR ISOTOPIC SPECIES OF PF_2CN

Transition	PF_2CN	$PF_2{}^{13}CN$	$PF_2C^{15}N$
$1_{01} \rightarrow 2_{02}$	11,613.94 (0.14)[b]	11,506.42 (−0.35)	11,239.05 (−0.18)
$1_{11} \rightarrow 2_{12}$	11,024.66 (0.24)	10,926.68 (0.16)	10,682.31 (0.07)
$1_{10} \rightarrow 2_{11}$	12,349.86 (0.37)	12,227.12 (−0.01)	11,921.86 (0.15)
$2_{02} \rightarrow 3_{03}$	17,243.59 (0.04)	17,090.54 (0.27)	16,706.15 (0.03)
$2_{12} \rightarrow 3_{13}$	16,493.14 (−0.04)	16,348.22 (0.09)	15,985.41 (−0.54)
$2_{21} \rightarrow 3_{22}$	17,530.81 (0.38)	17,365.71 (0.49)	16,953.06 (0.10)
$2_{11} \rightarrow 3_{12}$	18,475.52 (−0.19)	18,294.43 (0.14)	17,841.27 (0.11)
$2_{20} \rightarrow 3_{21}$	17,817.57 (0.25)	17,640.21 (0.01)	17,200.09 (0.29)
$3_{03} \rightarrow 4_{04}$	22,690.52 (0.11)	22,497.01 (−0.16)	22,011.64 (−0.08)
$3_{13} \rightarrow 4_{14}$	21,916.52 (−0.04)	21,726.45 (0.37)	21,250.61 (0.52)
$3_{31} \rightarrow 4_{32}$	23,506.02 (−0.17)	23,279.85 (−0.76)	22,717.95 (−0.39)
$3_{12} \rightarrow 4_{13}$	24,536.53 (0.09)	24,299.32 (0.31)	23,704.95 (−0.28)
$4_{04} \rightarrow 5_{05}$	27,963.57 (−0.25)	27,733.79 (−0.27)	27,156.52 (−0.02)
$4_{22} \rightarrow 5_{23}$	30,305.97 (−0.27)	29,992.32 (−0.10)	29,212.32 (−0.02)
$4_{14} \rightarrow 5_{15}$	27,289.35 (−0.26)	27,055.18 (−0.16)	
$4_{13} \rightarrow 5_{14}$	30,498.12 (−0.02)	30,209.53 (0.05)	29,486.35 (0.22)
$0_{00} \rightarrow 1_{10}$	10,656.72 (0.08)		
$1_{01} \rightarrow 2_{11}$	17,162.57 (−0.08)		

[a] Uncertainty in observed frequencies is ±0.10 MHz. [b] Numbers in parentheses are differences between observed and calculated values of the frequencies. Rotational parameters are in Table II.

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[1] (a) Supported in part by grants from the National Science Foundation. (b) Presented at the 161st National Meeting of the American Chemical Society, Los Angles, Calif., March 1971.

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