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A Study of the Kinetics of the Oxidation of Oxotetraaquo vanadium(IV) with Hypochlorous Acid and Chlorine in Aqueous Solution

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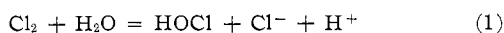
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The kinetics of the oxidation of vanadium(IV) with hypochlorous acid and chlorine have been studied independently in acidic aqueous solution at 1.0 *M* ionic strength at 25°. Both reactions were found to be first order in each reactant. The reaction rate for the vanadium(IV)-hypochlorous acid reaction was observed to depend upon the hydrogen ion concentration. The experimental rate law determined for this reaction is $^{-1/2}d[V(IV)]/dt = \{k_1/(1 + K[H^+])\}[V(IV)][HOCl]$. Best fit values for k_1 and K are $39.5 \pm 4.0 M^{-1} \text{sec}^{-1}$ and $6.02 \pm 0.87 M^{-1}$, respectively. The hydrogen ion dependence is attributed to the reversible formation of a complex between the reactants. The oxidation of vanadium(IV) by aqueous chlorine solutions occurs *via* two separate pathways. For one pathway, Cl_2 is the oxidant. The other path involves oxidation by HOCl which arises from chlorine hydrolysis. The Cl_2 pathway is inhibited by acid. A brief discussion of the mechanism for the vanadium(IV)-chlorine reaction is given.

Introduction

The oxidation of vanadium(IV) by chlorate ion produces chlorine(I) and chlorine as intermediate reactive species. There seems to be some controversy about the stoichiometry of this reaction at room temperature.¹⁻³ Preliminary indications³ suggested that the rate of reaction of vanadium(IV) with chlorine may be slow enough to result in complications in the vanadium(IV)-chlorate reaction.

Oxidation of vanadium(IV) with chlorine(I) can be studied without interference by chlorine if the samples are prepared in a medium free from chloride ion. However, a complicating factor in the oxidation of vanadium(IV) with aqueous chlorine arises from the hydrolysis of chlorine as shown in eq 1. Even though



the hydrolysis constant for chlorine is $6.4 \times 10^{-4} M^2$ at 1.0 *M* ionic strength⁴ and 25°, sufficient chlorine(I) is produced that it could contribute significantly to the reaction rate. In that the slow rate of reaction between vanadium(IV) and chlorine may be responsible for the variable stoichiometry in the vanadium(IV)-chlorate reaction, the rate of oxidation of vanadium(IV) with chlorine(I) and chlorine was determined in an attempt to provide data to aid in the resolution of the controversy.

Experimental Section

Solutions of chlorine(I) were prepared as described by Cady.⁵ Analysis of the solutions for chlorine(I) content was accomplished by standard iodometric methods. The chlorine(I) solutions were always prepared from the carbon tetrachloride solution of chlorine monoxide and were analyzed just prior to the kinetic experiments. The solutions were prepared in standard acid solutions which were free of chloride ion.

Chlorine solutions were prepared by bubbling chlorine gas through a sulfuric acid scrubbing column and by collecting the

purified chlorine in a solution of the appropriate hydrogen ion and chloride ion concentration. The ionic strengths of all reactant solutions were adjusted to $1.00 \pm 0.05 M$ by adding the appropriate amounts of either sodium perchlorate or sodium chloride.

Vanadium(IV) perchlorate solutions were prepared and analyzed as reported previously.⁶ Sodium perchlorate was prepared and purified by the method of Gordon and Tewari.⁷ Other reagents were used directly as obtained from the supplier.

The stoichiometry of the vanadium(IV) reactions with chlorine(I) and chlorine was studied under pseudo-first-order conditions. Several stoichiometric runs were made with each reactant in excess. The reaction mixture was analyzed for excess reactant after the reaction had gone to completion. In experiments in which either chlorine(I) or chlorine were in excess, the excess oxidant was determined iodometrically. If vanadium(IV) was in excess, the excess reagent was titrated with standard potassium permanganate.

The kinetics of the vanadium(IV)-chlorine(I) reaction were studied by using a Gibson-Durrum stopped-flow spectrophotometer and by monitoring the change in absorbance as a function of time at 760 nm and 25.0°. Constant temperature was maintained by circulating water from a constant-temperature bath through the reservoir containing the drive syringes. A calibrated Dymec quartz thermometer was employed to monitor the temperature. A Tectronix Model 564 storage-type oscilloscope and a Polaroid camera were used to monitor and record the output from the photomultiplier.

The concentrations of vanadium(IV) and chlorine(I) for the kinetic experiments were varied in the ranges $1.2 \times 10^{-3} M \leq [V(IV)] \leq 2.0 \times 10^{-2} M$ and $3.4 \times 10^{-2} M \leq [Cl(I)] \leq 5.2 \times 10^{-1} M$. Chlorine(I) was always present in large excess to ensure that pseudo-first-order conditions obtained. The effect of variation in the hydrogen ion concentration on the observed second-order rate constant was investigated in the hydrogen ion concentration range of 0.06–1.00 *M*.

The oxidation of vanadium(IV) with chlorine at 25° was slow enough such that the reaction could be followed on a Cary 14R recording spectrophotometer with an expanded-scale slide-wire at 760 nm. The sample compartment of the Cary was thermostated at 25.0° and the temperature was determined with the quartz thermometer. The chlorine solution was stored in a 50-ml ground-glass syringe⁸ which was enclosed in a water jacket. This solution was thermostated by circulating water from a constant-temperature bath through the water jacket for at least 30 min. Samples of vanadium(IV) were thermostated in the reservoir of the same constant-temperature bath. Mixing of the reactants was achieved manually and the sample cell was sealed and placed in the sample compartment of the Cary without delay. In all of the kinetic experiments, the chlorine concentration was in at least 13-fold excess to provide pseudo-first-order conditions.

Analysis of the kinetic data for the vanadium(IV)-chlorine(I)

(1) C. W. Fuller and J. M. Ottoway, *Analyst (London)*, **95**, 791 (1970).

(2) D. R. Rosseinsky and J. Zlotnick, *J. Chem. Soc. A*, 1200 (1970).

(3) W. Melvin and G. Gordon, Atomic Energy Commission Research Report AT(11-1)-1780, University of Iowa, 1970.

(4) A conductometric value of 3.94×10^{-4} is reported for the equilibrium constant extrapolated to zero ionic strength by R. E. Connick and Y. Chia, *J. Amer. Chem. Soc.*, **81**, 1280 (1959). R. A. Silverman and G. Gordon (University of Iowa, unpublished results, 1971) reported a spectrophotometric value of $(6.4 \pm 0.8) \times 10^{-4}$ for the constant at 1.00 *M* NaClO₄ at 25°. The apparent discrepancy between these two values is due to the manner in which the values are calculated in that R. E. Connick and Y. Chia have employed activities rather than concentrations.

(5) G. H. Cady, *Inorg. Syn.*, **5**, 156 (1957).

(6) H. Tomiyasu, K. Dreyer, and G. Gordon, *Inorg. Chem.*, in press.

(7) G. Gordon and P. H. Tewari, *J. Phys. Chem.*, **70**, 200 (1966).

(8) R. A. Silverman, private communication, 1970.

reaction was carried out by using a nonlinear least-squares computer program⁹ which calculated values of the second-order observed rate constants from the absorbance-time data. In order to minimize errors due to improper weighting in the least-squares program, data points were selected at constant-absorbance intervals and each point was given unit weights. The observed rate constants were dependent upon the hydrogen ion concentration of the sample. A subroutine of the nonlinear least-squares program was used to calculate the appropriate constants. The input data consisted of the hydrogen ion concentration and the observed second-order rate constant. Since each rate constant is known to the same precision,¹⁰ the data were weighted by $1/k_{\text{obsd}}^2$ in order to minimize the per cent error between the observed and fitted values of the dependent variable.

The kinetic data for the reaction between vanadium(IV) and chlorine were analyzed under pseudo-first-order conditions. Thus, it was possible to obtain apparent overall second-order rate constants¹¹ for initial portions of the reaction. The initial reactant concentrations determined the exact initial species concentrations of chlorine(I) and chlorine. By means of these concentrations and the measured rate constants for the HOCl-V(IV) reaction, it was possible to obtain estimates for the rate of the Cl₂-V(IV) reaction. These estimates were limited to the initial portions of the reaction under conditions such that the overall concentration of chloride ion remained invariant. In order to obtain better estimates of the rate constants over wider portions of the reaction, the appropriate simultaneous differential equations were solved by a numerical integration process.¹² By using this technique, it was possible to calculate a second-order rate constant for the Cl₂-V(IV) reaction by calculation and correction for the effect of chloride ion on that portion of the reaction which occurs *via* a chlorine(I) pathway.

Results

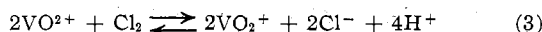
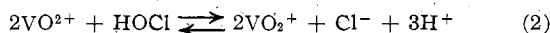
Stoichiometry.—The stoichiometry of the vanadium(IV)-chlorine(I) and vanadium(IV)-chlorine reactions is shown in Table I and can be represented by

TABLE I
STOICHIOMETRIC RATIOS FOR THE VANADIUM(IV)-HYPOCHLOROUS ACID AND -CHLORINE REACTIONS IN 1.0 M PERCHLORIC ACID AT 25°

—Total amt, mmol—		Excess reactant unreacted, mmol	V(IV) consumed/oxidant consumed
V(IV)	Oxidant		
6.201	1.564 ^a	3.028	2.03
6.201	1.564 ^a	3.079	1.99
1.236	3.915 ^a	3.292	1.97
0.706	0.105 ^b	0.942	2.02
0.706	1.165 ^b	0.814	2.06

^a HOCl; average stoichiometric ratio 2.0 ± 0.04 . ^b Cl₂; average stoichiometric ratio 2.0 ± 0.02 .

the expressions given in eq 2 and 3 regardless of which reactant is in excess.



Kinetics of the Vanadium(IV)-Chlorine(I) Reaction.—Pseudo-first-order graphs of $\log(A_t - A_0)$ as a function of time were linear to at least 85% reaction and visual inspection of the residuals from the com-

(9) A description of the algorithm of the computer program is given in Los Alamos Publication LA-2387 and addenda. A modified version of this program is presently available from G. Gordon at the University of Iowa.

(10) As will be seen from the data reported in Table II, the standard deviation in the fit for each rate constant is less than 0.8% of the rate constant itself.

(11) The rate law for the reaction can be written as $1/2 d[\text{V(IV)}]/dt = k^{\text{HOCl}}_{\text{obsd}}[\text{Cl(I)}][\text{V(IV)}] + k^{\text{Cl}_2}_{\text{obsd}}[\text{Cl}_2][\text{V(IV)}]$. If this expression is rewritten in terms of the fraction of total chlorine species present as chlorine(I) and chlorine, an apparent second-order rate constant (k_2) can be calculated in terms of total concentration of chlorine-containing oxidizing agents and vanadium(IV).

(12) J. M. McCormick and M. G. Salvador, "Numerical Methods in Fortran," Prentice-Hall, New York, N. Y., 1964, p 100.

puter fits showed no discernible trends. From this it was concluded that the reaction was first order in vanadium(IV). A log-log plot of these first-order rate constants as a function of chlorine(I) concentration was linear with a slope of 0.98 ± 0.03 which was used as an indication that the reaction was also first order in chlorine(I).

The dependence of the reaction rate on the hydrogen ion concentration was investigated and the results are tabulated in Table II. An analysis of this data reveals

TABLE II

VALUES OF THE OBSERVED AND CALCULATED RATE CONSTANTS FOR THE VANADIUM(IV)-HYPOCHLOROUS ACID REACTION AT 25°

[H ⁺], M	$k^{\text{HOCl}}_{\text{obsd}}, M^{-1} \text{sec}^{-1}$	Calcd	[H ⁺], M	$k^{\text{HOCl}}_{\text{obsd}}, M^{-1} \text{sec}^{-1}$	Calcd
1.00	5.47 ± 0.027	5.62	0.402	12.3 ± 0.071	11.5
0.902	6.00 ± 0.028	6.15	0.302	17.9 ± 0.119	14.1
0.851	6.41 ± 0.037	6.46	0.201	21.6 ± 0.156	17.9
0.801	6.78 ± 0.033	6.79	0.138	22.3 ± 0.142	21.6
0.751	6.85 ± 0.036	7.16	0.100	23.3 ± 0.159	24.7
0.650	7.53 ± 0.032	8.04	0.060	26.8 ± 0.189	29.0

^a The uncertainties correspond to one standard deviation in the rate constant as calculated directly by the nonlinear least-squares program.

that the rate law for the vanadium(IV)-chlorine(I) reactions has the form

$$-1/2 \frac{d[\text{V(IV)}]}{dt} = \frac{k_1}{1 + K[\text{H}^+]} [\text{V(IV)}][\text{Cl(I)}] \quad (4)$$

The best fit value for k_1 was evaluated as $39.5 \pm 4.0 M^{-1} \text{sec}^{-1}$. A value of $6.02 \pm 0.87 M^{-1}$ was computed for K . These error limits correspond to one standard deviation and are calculated directly by the nonlinear least-squares program.⁹

Kinetics of the Vanadium(IV)-Chlorine Reaction.—With solutions of aqueous chlorine in 1.0 M hydrochloric acid, it was shown that enough chlorine(I) is produced by chlorine hydrolysis such that approximately 35% of the overall reaction occurs *via* a chlorine(I) pathway. The interconversion of chlorine to chlorine(I) appropriate to eq 1 is rapid under the conditions of these experiments as can be seen from the data of Eigen and Kustin.¹³ This required that the rate data for the vanadium(IV)-chlorine reaction be corrected for the contribution of the chlorine(I) pathway. The rate constants for the vanadium(IV)-chlorine(I) reaction were those determined in the first part of this paper. This allowed for a direct estimation¹¹ of the second-order rate constant for the chlorine pathway. Table III is a presentation of the apparent second-order rate constant for the oxidation of vanadium(IV) in terms of the total concentration of oxidizing species¹¹ and the individual contributions of both the chlorine(I) and chlorine pathways in the reaction. Analysis of the $k^{\text{Cl}_2}_{\text{obsd}}$ values for the chlorine pathway clearly indicates that the reaction is inhibited by the square of the hydrogen ion concentration. Thus the apparent rate law for the chlorine pathway can be written as

$$-1/2 \frac{d[\text{V(IV)}]}{dt} = k^{\text{Cl}_2} \frac{[\text{V(IV)}][\text{Cl}_2]}{[\text{H}^+]^2} \quad (5)$$

The best fit value for k^{Cl_2} at 25° is $(0.7 \pm 0.1) \times 10^{-2} M^{-1} \text{sec}^{-1}$. The average deviation between the

TABLE III
OBSERVED AND CALCULATED RATE CONSTANTS FOR THE OXIDATION OF VANADIUM(IV) BY
CHLORINE^a AND HYPOCHLOROUS ACID AT 1.0 M IONIC STRENGTH AT 25°

[H ⁺], M	[Cl ⁻], M	10 ³ [HOCl], M	10 ² k ₂ , ^b M ⁻¹ sec ⁻¹	k ^{HOCl} _{obsd} , ^c M ⁻¹ sec ⁻¹	10 ² k ^{Cl} _{obsd} , ^d M ⁻¹ sec ⁻¹	Rel con- tribution of HOCl path
1.0	1.0	2.81	1.02	5.62	0.67	34.9
0.75	1.0	3.74	1.5	7.16	1.08	36.0
0.50	1.0	5.63	3.7	9.85	2.58	33.0
0.25	1.0	11.3 ^e	13.3	15.8	11.2	26.4
0.14	1.0	20.1 ^f	49.6	21.4	48.9 ^g	16.8
1.0	0.80	3.52	1.21	5.62	0.70	39.2
1.0	0.75	3.74	1.13	5.62	0.82	39.0
1.0	0.69	4.07	1.14	5.62	0.67	42.4
1.0	0.60	4.69	1.40	5.62	0.75	43.2
1.0	0.40	7.04	1.60	5.62	0.92	49.2
1.0	0.20	14.1	2.56	5.62	0.81	68.7
1.0	0.10	28.2	3.48	5.62	0.46	89.9
1.0	0.060	46.8	5.26	5.62	0.54	>99

^a The reaction mixtures contained $(3.9-4.7) \times 10^{-2}$ M total chlorine and $(1.7-2.1) \times 10^{-3}$ M vanadium(IV). ^b Apparent second-order rate constant¹¹ for the overall vanadium(IV)-chlorine reaction. ^c This is the observed rate constant for the HOCl-V(IV) reaction calculated directly from eq 4. ^d Second-order rate constant for the chlorine pathway. The standard deviation of the fit for each individual run was always less than 1%. However, the reproducibility for replicate runs was no better than $\pm 5\%$. These large error limits are in part due to the volatility of chlorine and the possible contamination by chloride ion. ^e 1.5×10^{-3} M vanadium(IV). ^f 6.2×10^{-4} M vanadium(IV). ^g The rate of the reaction at acid concentrations below 0.20 M is such that only the latter 50% of the reaction is observable with the technique employed. Since the rates at higher acid concentrations deviated from a first-order plot after approximately 60% reaction, the observed second-order rate constants at acidities less than 0.20 M should be considered only as rough approximations.

observed and fitted rate constants is about 14%. This large error is not too surprising in that the calculated rate constants for the vanadium(IV)-chlorine system reflect the use of the difference method and possible losses of chlorine due to volatility.

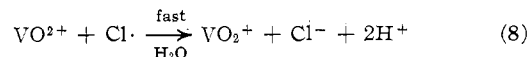
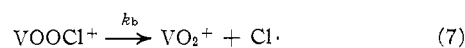
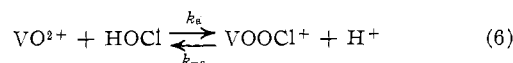
Discussion

The experimental rate law for the vanadium(IV)-chlorine(I) reaction, shown in eq 4, requires that a bimolecular interaction between the reactants must occur either as the rate-determining step or as a precursor to the rate-determining step. The form of the hydrogen ion dependence for the vanadium(IV)-chlorine(I) reaction suggests that an acid-dependent equilibrium process occurs during formation of the activated complex. The acid dissociation constant¹⁴ for HOCl at 25° is 2.90×10^{-8} M. At 25°, the hydrolysis constant¹⁵ for VO²⁺ is 10^{-6} M. Neither of these values compares favorably with the value of 6.02 M^{-1} calculated from the kinetic data. Thus, it can be inferred that neither dissociation of HOCl nor hydrolysis of VO²⁺ is important under the prevalent conditions.

It has been suggested^{16,17} that protonated forms of both VO²⁺ and HOCl are present in highly acidic aqueous solutions. The observed hydrogen ion dependence of the vanadium(IV)-chlorine(I) reaction could be accounted for if the protonated forms of the reactants were present in relatively large concentrations and if the protonated reactant is unreactive with respect to the oxidation-reduction reaction. In 1.0 M acid, the protonated form of one or the other of the reactants would have to comprise more than 85% of the analytical concentration of that reactant. Neither HOCl nor VO²⁺ shows any indication of protonating to such a large extent. Thus, we have concluded that

the protonation of the reactants could not be responsible for the observed hydrogen ion dependence.

Formation of a complex between vanadium(IV) and chlorine(I) with the concomitant loss of a proton is also consistent with the experimental data. The complex VOOC⁺ would be formed in a bimolecular process with the concurrent loss of a proton. This process would have to be reversible in order to give rise to the observed hydrogen ion dependence. If the steady-state assumption is applied to VOOC⁺, a rate law identical in form with the experimental rate law is obtained. On this basis, we propose the mechanism¹⁸

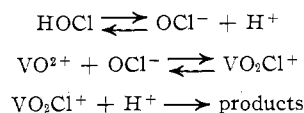


The rate law derived from this mechanism can be written as

$$-1/2 \frac{d[\text{VO}^{2+}]}{dt} = \frac{k_a}{1 + (k_{-a}/k_b)[\text{H}^+]} [\text{VO}^{2+}][\text{HOCl}] \quad (9)$$

which is identical with the experimental rate law. The best fit values of k_1 and K can be correlated directly

(18) It should be noted that the observed rate law is consistent with the Haim ambiguity (A. Haim, *Inorg. Chem.*, **5**, 2081 (1966)) which applies in this case. In other words, the rate law specifies only the composition of the activated complexes; the rate law does not indicate the order of formation of these activated complexes. For example, the alternate mechanism



cannot be ruled out mathematically. These two mechanisms differ fundamentally in that the mechanism proposed above suggests that the effect of acid is to decompose the intermediate VO₂Cl⁺ into products, whereas in eq 6-8, acid caused the intermediate to decompose into reactants. On the basis of general acid-base characteristics and the behavior of HOCl, we tend to prefer eq 6-8. Clearly, the data do not allow us to distinguish.

(14) J. C. Morris, *J. Phys. Chem.*, **70**, 3798 (1966).

(15) F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, **9**, 1177 (1955).

(16) A. I. Rivkind, *J. Struct. Chem. (USSR)*, **4**, 615 (1963).

(17) P. B. D. de la Mare, A. D. Ketley, and C. A. Vernon, *J. Chem. Soc.*, 1290 (1954).

with the mechanism. Thus, $k_1 = k_a = 39.5 \pm 4.0 M^{-1} \text{ sec}^{-1}$ and $K = k_{-a}/k_b = 6.02 \pm 0.087 M^{-1}$. This value of k_{-a}/k_b corresponds to the ratio of the decomposition of the VOOCl^+ intermediate to the production of product. It is unfortunate that the formation constant for VOOCl^+ cannot be determined directly from the available data.

Several studies have been published^{1,19} in which complexes between vanadium(IV) and oxyhalogens have been proposed as intermediates. Thus, it should not be too surprising that HOCl might also form a complex with vanadium(IV).

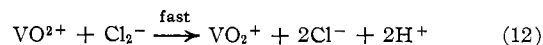
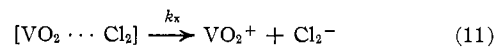
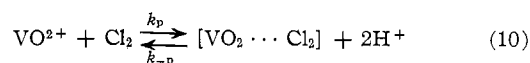
Previous studies^{20,21} have proposed that the product of a one-electron reduction of HOCl is a chlorine radical. The 2:1 stoichiometry of the vanadium(IV)-chlorine(I) reaction suggests that a reactive chlorine intermediate must be formed in the reaction following the rate-determining step. This intermediate is most probably the chlorine radical.

The inverse second-order hydrogen ion dependence for the vanadium(IV)-chlorine reaction may arise from one of at least three sources: (1) a double hydrolysis of vanadium(IV), (2) the hydrolysis of both vanadium(IV) and chlorine, and (3) the formation of a complex with concurrent loss of two protons.

Under the conditions used for this investigation, the concentration of the doubly hydrolyzed vanadium(IV) species would have to be less than $10^{-16} M$. This would require that the second-order rate constant for the reaction exceed $10^{12} M^{-1} \text{ sec}^{-1}$. This unreasonably large value of the predicted rate constant allows the double hydrolysis mechanism to be discarded.

It should be recalled that in the derivation of the observed rate constants for the vanadium(IV)-chlorine reaction, the total rate of the reaction was corrected for the rate of the vanadium(IV)-chlorine(I) reaction. Since chlorine(I) is the hydrolysis product of chlorine, it seems unlikely that additional chlorine hydrolysis could play an important part in the aqueous chlorine pathway. Thus, the second of the three proposed acid-dependent steps can be also ruled out.

Complex formation between vanadium(IV) and chlorine may conceivably give rise to an inverse second-order acid dependence if eq 10 describes this process. A proposed mechanism for the overall reaction is given in eq 10-12, where the water molecules are unspecified.



The rate law derived from this mechanism is identical with the experimental rate law described by eq 5 if the rate of the actual electron-transfer step is much smaller than the rate of decomposition of $[\text{VO}_2 \cdots \text{Cl}_2]$ into reactants, *i.e.*, $k_x < k_{-p}[\text{H}^+]^2$. This mechanism is not unlike the mechanism proposed by Gordon and Andrewes²² for the reaction between uranium(IV) and bromine. In the uranium(IV)-bromine reaction it was proposed that uranium(IV) hydrolyzed twice prior to the bimolecular rate-determining step in the reaction. The proposed mechanism for the vanadium(IV)-chlorine reaction includes a step in which a double hydrolysis is assisted by the formation of a complex between the reactants.

In conclusion, a comparison of the rates for the two reactions reported here with the rate for the vanadium(IV)-chlorate reaction can be made. The second-order rate constants for all three of these reactions at 25° are tabulated in Table IV.

TABLE IV
SECOND-ORDER RATE CONSTANTS FOR THE OXIDATION OF
VANADIUM(IV) IN 1.0 M ACID AT 25°

Oxidant	$k,$ M^{-1} sec^{-1}	Oxidant	$k,$ M^{-1} sec^{-1}	Oxidant	$k,$ M^{-1} sec^{-1}
ClO_3^-	0.013 ^a	HOCl	5.6	Cl_2	0.007

^a See ref 3 and W. Melvin and G. Gordon, *Inorg. Chem.*, submitted for publication.

It is readily apparent that the assumption made by Fuller and Ottoway¹ that the rate of oxidation of vanadium(IV) with chlorine(I) was much greater than the rate of reaction of vanadium(IV) with chlorate ion is indeed correct. However, the rates of oxidation of vanadium(IV) by chlorine and chlorate ion are quite comparable. This suggests that interpretation of the kinetic data for the vanadium(IV)-chlorine(V) reaction cannot completely neglect the contribution from the vanadium(IV)-chlorine reaction.

Acknowledgments.—The authors wish to acknowledge the Atomic Energy Commission for financial support and the NDEA for a fellowship.

(22) G. Gordon and A. Andrewes, *Inorg. Chem.*, **3**, 1733 (1964).

(19) C. W. Fuller and J. M. Ottoway, *Analyst (London)*, **94**, 32 (1969).

(20) M. G. Ondrus and G. Gordon, *Inorg. Chem.*, **10**, 474 (1971).

(21) T. J. Conocchioli, E. J. Hamilton, and N. Sutin, *J. Amer. Chem. Soc.*, **87**, 926 (1965).