[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Kinetics of the Pentavalent Vanadium–Iodide Reaction; Correlation with the Induced Catalysis of the Oxygen–Iodide Reaction

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It is known[1a] that the rate of oxygen–iodide reaction in acid solution is greatly increased during the reduction of pentavalent vanadium by iodide in the same solution and that this induced reaction[2] belongs to that class of induced reactions designated by Luther and Schilow[3] as "catalysis with destruction of the catalyst," for which the shorter name, "induced catalysis," has been adopted more recently. As pointed out by Bray[4] definite conclusions regarding the mechanism of such induced reactions are unlikely until intensive investigations of a few cases are made. This investigation of the kinetics of the pentavalent vanadium–iodide reaction in the absence of oxygen constitutes a part of such an investigation of this particular induced reaction.

A very limited study of the kinetics of this reaction in hydrochloric acid solutions was reported by Luther and Rutter.[5] From the results of four rate experiments, in which two concentrations (differing by three-fold) of each reactant was involved, they concluded that the rate law was approximated by the equation $d(\Sigma I_2)/dt = k(I^-)(V^{+5})(H^+)^{1.5}$. The possibility of complications due to the presence of chloride complexes of pentavalent vanadium and the improbable order with respect to hydrogen ion make further study of the kinetics of this reaction desirable. In addition no mention was made of the exclusion of oxygen of the air from the reaction mixtures. Its presence would make any conclusions regarding the desired rate law unreliable.

It has been shown by Carpenter[6] that the principal ionic species of pentavalent vanadium in solutions having a wide range of acid concentrations, 0.02 to 0.9 N, is the pervanadyl ion, now generally formulated as $V(OH)_4^+$, in preference to VO_2^+, formerly accepted. The ionic equation of the over-all reaction may therefore be written

$$2V(OH)_4^+ + 3I^- + 4H_3O^+ \longrightarrow 2VO^{++} + I_3^- + 10H_2O$$

Experimental

Preparation and Standardization of Solutions.—All reagents were of the best C. P. grade. Sodium iodide was the only reactant not submitted to further purification. The sixty per cent. perchloric acid, commercially available, was distilled *in vacuo* in all-Pyrex still. The sodium vanadate solution was prepared by metathesis of ammonium vanadate (purified by one recrystallization from water) with an equivalent quantity of sodium hydroxide, followed by removal of the ammonia formed. Both the sodium perchlorate, which had been recrystallized from a dioxane-water solution, and the purified perchloric acid were tested and found free from quantities of possible impurities detectable by the procedures recommended by Murray.[7]

Since experiments had shown the reaction to be appreciably catalyzed by iron (ferrous or ferric) at very small concentrations (as low as 10^{-5} M), a sensitive test for iron was required. The test developed by David Appleman[8] was used. Ten to 25 ml. of the solution tested is treated with a drop or two of bromine water to oxidize all iron to ferric state and acidified with a small volume of iron-free concentrated sulfuric acid. To this is added such a quantity of ethyl acetate, which had been equilibrated with a saturated solution of potassium thiocyanate (in contact with excess solid potassium thiocyanate), that a small volume of an ethyl acetate rich layer remained after the mixture had been vigorously shaken for two or three minutes. A pink or red color in the acetate layer indicates presence of iron. This test is sensitive to somewhat less than 1 part of iron in ten million of solution (approximately 1×10^{-6} M). The only substance not so tested was the sodium iodide. All others, after purification, were tested at the highest concentrations to be used in the reaction mixtures and gave negative results.

Distilled water from the general laboratory supply was redistilled from alkaline permanganate in an all-Pyrex still in order to obtain the water used throughout. The solutions of the reactants and those of the reagents, required in the analytical procedures, were standardized by accepted methods previously used.[9]

Rate Measurements.—Accurately measured volumes of the known solutions of sodium metavanadate, perchloric acid and sodium perchlorate (when used for ionic strength purposes) were added to the reaction flask (750-ml. Erlenmeyer), along with such a volume of water that upon subsequent addition of the sodium iodide solution the desired concentration of each reactant would exist in a final volume of 300 ml. The oxygen-free sodium iodide solution was kept in the same thermostat blanketed with nitrogen. Prior to addition of the sodium iodide, oxygen was removed from the prepared mixture in the reaction flask by flushing out with a dispersed stream of nitrogen for at least one-half hour. Oxygen-free pure nitrogen was assured by a thorough washing of the tank nitrogen, commercially available, with an acidified chromous chloride solution, followed by sodium hydroxide solution and finally pure water.

The reaction was followed by determining, with standard sodium thiosulfate, the iodine present in 25.00-ml portions, removed from the reaction

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[1a] Bray and Ramsey, THIS JOURNAL, **55**, 2279 (1933).

[2] Kessler, *Pogg. Ann.*, **195**, 218–247 (1863).

[3] Luther and Schilow, *Z. physik. Chem.*, **46**, 777 (1903).

[4] Bray, in paper read at Pasadena, June, 1931; *cf.* the report of *symposium* on "Reaction Mechanism," *Science*, **74**, 113 (1931).

[5] Luther and Rutter, *Z. anorg. Chem.*, **54**, 6 (1907).

[6] Carpenter, THIS JOURNAL, **56**, 1847 (1934).

[7] Murray, "Standards and Tests for Reagents and C. P. Chemicals," D. Van Nostrand Co., N. Y., 1927.

[8] Appleman, Department of Agriculture, University of California, Los Angeles (personal communication).

[9] Ramsey and Heldman, THIS JOURNAL, **58**, 1153 (1936).

TABLE I

KINETIC RESULTS AT 25.00 ± 0.01°

Initial concentrations in gram formula weights per liter.

$(NaVO_3)$	$(HClO_4)$[a]	(NaI)	$-S$	$-S/(I^-)(H^+)$	$-S/(I^+)^2(H^+)$	$-S/(I^-)^2(H^+)^2$	$-S/(I^-)(H^+)^2$
0.004042	0.1995	0.08714	0.01600	0.920	10.6	53.2	4.61
.004042	.1995	.0384	.00614	.800	20.8	104.0	4.02
.004047	.1995	.02067	.00300	.725	35.0	175.0	3.65
.004024	.1998	.0102	.00160	.793	77.7	390.0	3.96
.004042	.3033	.0384	.01090	.937	24.4	80.5	3.09
.004047	.3033	.02067	.00573	.915	44.2	146.0	3.01
.004042	.5103	.0384	.03000	1.53	39.8	77.9	3.00
.008084	.5028	.0384	.03150	1.63	42.5	84.5	3.25
.004047	.5110	.02067	.01435	1.36	65.7	129.0	2.66
.004350	.4950	.0753	.0640	1.72	22.8	46.1	3.47
.004350	.2444	.0753	.0180	0.980	13.0	53.2	4.00
.004350	.4950	.0376	.0260	1.40	37.3	75.3	2.82
.004350	.4950	.0188	.0121	1.30	69.2	140.0	2.63
.004350	.4950	.0094	.0060	1.29	137.0	277.0	2.61
.004350	.2444	.0376	.0079	.863	23.0	93.8	3.52
.004350	.2444	.0188	.0038	.828	44.0	180.0	3.38
.004350	.2444	.0094	.0020	.872	92.8	380.0	3.56
.004350	.750	.0188	.039	2.76	147.0	196.0	3.69
.004350	1.010	.0188	.058	3.06	163.0	161.0	3.02
.004350	1.250	.0188	.116	4.94	264.0	211.0	3.95

[a] The concentrations of $HClO_4$ are obtained by subtracting from the quantity of acid added per liter that quantity used up in the conversion of metavanadate ion, VO_3^-, into pervanadyl ion, $V(OH)_4^-$, namely, two equivalents of acid per mole of VO_3^-. The assumption that further reaction of the pervanadyl ion with hydrogen is not appreciable at the acid concentrations used is justifiable on the basis of the results of electromotive force measurements of Carpenter (ref. 6) and of Coryell and Yost, THIS JOURNAL, 55, 1909 (1933).

mixture at suitable intervals. To prevent introduction of oxygen during removal of these portions the 25-ml. pipet was fitted tightly (with a rubber stopper) into a glass tube reaching through the stopper of the reaction flask to within a short distance from the bottom of the reaction mixture, the nitrogen outlet closed and the solution forced into the pipet by the nitrogen pressure developed. To assure adequate quenching the 25-ml. portions were delivered into 100 ml. of an ice-water mixture or of an iced sodium acetate solution in those experiments in which the acid and iodide concentrations were highest. The quenching was found to be entirely adequate. Tests with known triiodide solutions under same conditions showed the absence of any reducing material in the ice and sodium acetate used.

That oxygen had been adequately removed and excluded during an experiment was shown by the close duplication of the results of two rate runs at same initial concentrations of reactants and also by the fact that in every case the straight line plot of log (Σ V^{+5}) against time gave an intercept on the log (Σ V^{+5}) axis at zero time agreeing precisely with that calculated from the known initial concentration of pentavalent vanadium.

All rate measurements were made at 25.00 ± 0.01°.

Order of the Reaction.—A few preliminary experiments were sufficient to show that the rate increased on increasing the concentration of each of the reactants. In all experiments the concentrations of iodide and of acid were made so large relative to that of pentavalent vanadium that the pentavalent vanadium concentration alone changed appreciably during the time necessary to establish the rate curve. It follows that, if under these conditions the reaction is first order with respect to vanadium, the curve obtained on plotting ln (Σ V^{+5}) against the time should be a straight line. This linear relation was obtained in every experiment during the time required for reduction of a large fraction of the pentavalent vandium.

If it is assumed that the reaction occurs substantially completely *via* a single path, the kinetic equation may be written

$$-\text{d} \ln (\Sigma V^{+5})/\text{d}t = k(I^-)^m(H_3O^+)^n = \text{slope}$$

The orders with respect to iodide and acid, m and n, respectively, may be determined by finding the pair of probable values of m and n which give a constant value of the quotient, slope/$(I^-)(H_3O^+)$. The results obtained by trying four different pairs of such values are given in the following table in which S designates the slope of the straight line obtained on plotting log (Σ V^{+5}) *vs.* time in minutes.

The ionic strength of the reaction mixtures (between 0.2 and 1.3) are not given since results of separate experiments in which sodium perchlorate was used to vary the ionic strength had shown the rate to be independent of the ionic strength over this range.

It is seen that over a 6-fold range of acid concentration (0.2 to 1.25 N) and a 9-fold range of iodide concentration (0.01 to 0.09 *M*) the results given in the last column ($m = 1, n = 2$) are satisfactorily constant whereas they are not so for other probable values of m and n. It follows that under the conditions used the reaction proceeds substantially *via* a single path, the rate of which is first order with respect to each of the reactants, pentavalent vanadium and iodide, and second order with respect to hydrogen ion.

The results of a few rate determinations at acid concentrations below 0.2 *N* (between 0.02 and 0.12 *N*) indicate that at these lower acidities an appreciable fraction of the reaction occurs *via* at least one other path which is probably first order with respect to hydrogen ion. That other paths may become important at these low acid concentrations is not unexpected since it is known that molecular species containing pentavalent vanadium, other than pervanadyl ion, are present in such solutions. These were detectable spectrophotometrically in solutions 0.12 *N* in acid and became more pronounced with decreasing acid concentration.

Mechanism of the Reaction.—From a consideration of the kinetics of a number of oxidations of halide ion, X^-, by oxygen-containing oxidizing agents Bray[10] concluded that when the element reduced is bonded to less oxide oxygen in the reduced state than it was in the oxidized state, the primary oxidation product of the halide ion is the weak hypohalous acid, HXO, or the hypohalite ion, XO^-. Since pervanadyl ion, $V(OH)_4^+$, undergoes such a loss of oxide oxygen on reduction to either vanadyl ion, VO^{++}, or to vanadic ion, V^{+++}, and since its reduction by iodide is first order with respect to each of these reactants, it is reasonable, in view of Bray's conclusion, to assume that the rate determining step involves the initial formation of trivalent vanadium. That no detectable trivalent vanadium would be present during a rate determination is attributable to the fact that pentavalent and trivalent vanadium react practically instantaneously (to give tetravalent vanadium) at the acid concentrations used.

The second order dependence of the reaction rate on the acid concentration leads to the conclusion that the pervanadyl ion, as such, is not involved in the rate determining step if the possibility of a tetramolecular process is excluded. It seems probable therefore that an ionic species of pentavalent vanadium formed by the reaction of pervanadyl ion with hydrogen ion is involved. That pervanadyl ion is weakly basic (protophyllic) has been adequately shown by the results of Lanford and Kiehl[11] in a study of the system, vanadium pentoxide-sulfur trioxide-water at 30°. The following stable solids were obtained: (1) $V_2O_5 \cdot 2SO_3 \cdot 8H_2O$, in equilibrium with concentrations of sulfuric acid around 6 *M*; (2) $V_2O_5 \cdot 2SO_3 \cdot 3H_2O$, in the neighborhood of 12 *M* sulfuric acid and (3) $V_2O_5 \cdot 4SO_3 \cdot 4H_2O$, around 18 *M* sulfuric acid. Since the ratio of sulfur trioxide to vanadium pentoxide in each of these solids is greater than it would be in a simple pervanadyl sulfate, $(V(OH)_4)_2SO_4$, *viz.*, 1 to 2, it is reasonable to assume the cations of these salts to be products of the addition of one or more protons to the pervanadyl ion and to formulate them as follows (in order given above): (1) $V(OH)_3SO_4 \cdot 2.5H_2O$; (2) $V(OH)_3SO_4$; (3) $(V(OH)_2)_2(SO_4)_3 \cdot (H_3O)(HSO_4)$. The vanadium cation of each of the first two salts is thus conceived as the product of the addition of one proton to the pervanadyl ion, and the cation of the last, to the addition of two protons. It may be noted that such an ion as $V(OH)_3^{++}$ would not have been considered if pervanadyl ion were assigned the formula VO_2^+.

On the basis of these considerations it seems reasonable to conclude that in the acid solutions used in this investigation a small portion of the pentavalent vanadium exists as trihydroxypervanadyl ion, $V(OH)_3(H_2O)^{++}$, which is in instantaneous equilibrium with pervanadyl ion according to the equation

$$V(OH)_4^+ + H_3O^+ = V(OH)_3(H_2O)^{++} + H_2O \quad (1)$$

The reaction of this trihydroxy-ion with iodide ion and hydrogen ion

$$V(OH)_3(H_2O)^{++} + I^- + H_3O^+ = V(OH)(H_2O)_3^{++} + HIO \quad (2)$$

is assumed to be the rate-determining step. The trivalent vanadium initially formed reacts immeasurably rapidly with pentavalent vanadium, as previously stated, as does hypoiodous acid with hydriodic acid. The rate equation would thus be

$$-d(\Sigma V^{+5})/dt = k((V(OH)_3(H_2O)^{++})(I^-)(H_3O^+) \quad (3)$$

From the equilibrium expression of the pervanadyl ion–hydrogen ion reaction (Eq. 1), it follows that

$$(V(OH)_3(H_2O)^{++}) = K(H_3O^+)(\Sigma V^{+5})/(1 - K(H_3O^+) \quad (4)$$

if the concentration of the trihydroxy-ion is very small relative to that of the pervanadyl ion and if the concentrations of other pentavalent vanadium cations are negligibly small. Since the value of the equilibrium constant, *K* (of reaction 1), is very small ($< < 1$), equation 4 becomes

$$(V(OH)_3(H_2O)^{++}) = K(H_3O^+)(\Sigma V^{+5}) \quad (5)$$

Substitution of this value of the concentration of the trihydroxy-ion into equation (3) yields the rate law found, namely

$$-d(\Sigma V^{+5})/dt = kK(\Sigma V^{+5})(I^-)(H_3O^+)^2 \quad (6)$$

If the reasonable assumption is made that the reaction between an hydroxypervanadyl ion and iodide ion consists simply in the transfer of a positively charged hydroxyl, OH^+, from the former to the latter, the mechanism proposed may seem less arbitrary. It follows from this assumption that the greater the positive charge on the hydroxypervanadyl ion the more easily it would re-

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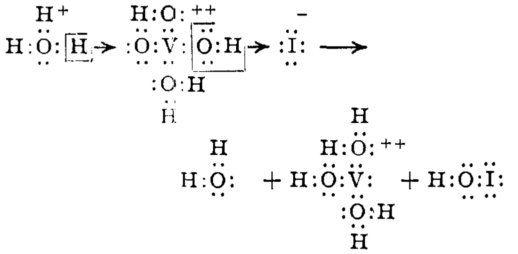
(10) Bray, *Z. physik. Chem.*, **54**, 463 (1906); *Chem. Rev.*, **10**, 166 (1932).

(11) Lanford and Kiehl, THIS JOURNAL, **62**, 1660 (1940).

lease positive hydroxyl, that is, the more rapidly it would react with iodide ion. This justifies the assumption that iodide ion reacts at a measurable rate with trihydroxypervanadyl ion, with the concerted action of the hydrogen (oxonium) ion, but not with the pervanadyl ion, even though the fraction of the pentavalent vanadium present as the trihydroxy-ion is very small. The rate determining reaction may be shown structurally by the equation



$$\mathrm{H{:}\ddot{O}{:}\overset{H^+}{\boxed{H}}} \rightarrow \mathrm{{:}\ddot{O}{:}\overset{H{:}\ddot{O}{:}^{++}}{\ddot{V}}{:}\boxed{\ddot{O}{:}H}} \rightarrow \mathrm{{:}\ddot{I}{:}^-} \longrightarrow$$

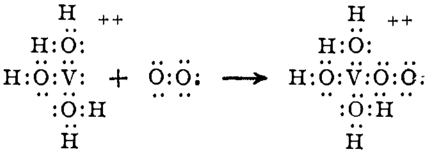
$$\begin{array}{c}\mathrm{H}\\ \mathrm{H{:}\ddot{O}{:}}\end{array} + \begin{array}{c}\mathrm{H}\\ \mathrm{H{:}\ddot{O}{:}^{++}}\\ \mathrm{H{:}\ddot{O}{:}\ddot{V}{:}}\\ \mathrm{{:}\ddot{O}{:}H}\\ \mathrm{H}\end{array} + \mathrm{H{:}\ddot{O}{:}\ddot{I}{:}} \qquad (7)$$

The transfer of a proton from the oxonium ion to the trihydroxy pervanadyl ion is considered to occur simultaneously with the transfer of a positive hydroxyl to the iodide ion. Also that neither transfer occurs to a detectable extent without the other is assumed.

It is recognized that if dihydroxypervanadyl ion, $V(OH)_2(H_2O)_2^{+++}$, could be considered present in the acid solutions used at an effective, though infinitesimally small, concentration, the bimolecular process involving this ion alone and iodide ion would account for the rate law found. However this seems very improbable in view of the very weak protophyllic nature of the pervanadyl ion as indicated by the evidence given above.

It may be worth noting that the oxidation–reduction process formulated in equation 7 does not involve the transfer of electrons. It seems fair to say that the electron-transfer interpretation of oxidation–reduction processes is inadequate and probably misleading in all but the simplest reactions. This has been stressed recently by Yost and Russell.[12]

Induced Catalysis of the Oxygen–Iodide Reaction.—An interpretation of the greatly enhanced rate of the oxygen–iodide reaction in acid solutions during the pentavalent vanadium–iodide reaction is indicated by the mechanism proposed above which seems more probable than that previously suggested.[13] It is known[14] that pentavalent vanadium catalyzes the oxidation of iodide by hydrogen peroxide in acid solution. This catalysis is most simply explained by assuming the recurrent formation and reduction of peroxypervanadyl ion to be much more rapid than the uncatalyzed reaction. Recently Jahr[15] has given evidence for the formation of pentavalent vanadium cations containing respectively one or two peroxide, O_2^- or HO_2^-, radicals, depending on the relative concentration of H_2O_2 to that of $V(OH)_4^+$. The monohydroxyvanadic ion, $V(OH^{++})$, formulated in equation 7, is seen to be neucleophyllic and, as has been shown,[12] is the only ionic species of trivalent vanadium that reacts at a measurable rate with oxygen in acid solutions even though only a small fraction of trivalent vanadium is present in the form of this ion. The structurally formulated equation of the reaction would then be



$$\begin{array}{c}\mathrm{H}^{\;++}\\ \mathrm{H{:}\ddot{O}{:}}\\ \mathrm{H{:}\ddot{O}{:}\ddot{V}{:}}\\ \mathrm{{:}\ddot{O}{:}H}\\ \mathrm{H}\end{array} + \mathrm{\ddot{O}{:}\ddot{O}{:}} \longrightarrow \begin{array}{c}\mathrm{H}^{\;++}\\ \mathrm{H{:}\ddot{O}{:}}\\ \mathrm{H{:}\ddot{O}{:}\ddot{V}{:}\ddot{O}{:}\ddot{O}{:}}\\ \mathrm{{:}\ddot{O}{:}H}\\ \mathrm{H}\end{array} \qquad (8)$$

Since the peroxymonohydroxypervanadyl ion formed reacts very rapidly with iodide and since the monohydroxyvanadic ion when initially formed is probably in an energy state above normal, and hence activated for reaction with oxygen, it follows that if oxygen is present during the reduction of pentavalent vanadium by iodide its reduction would be greatly enhanced. It may be noted that if this interpretation is valid the rate of reduction of pentavalent vanadium by iodide should be lower when oxygen is present than it is in its absence since pentavalent vanadium would be reproduced. Experiments are in progress to determine whether such is the case.

It may be of interest to note that the peroxymonohydroxypervanadyl ion, formulated in equation 8, would lose protons as the acid concentration is lowered and by loss of two protons become H_3VO_5 or HVO_4, the accepted formula of peroxyvanadic acid.

Summary

The rate law of the pentavalent vanadium–iodide reaction in acid solutions has been established over a wide range of acid and iodide concentrations.

A mechanism involving the transfer of positive hydroxyl from trihydroxypervanadyl ion to iodide ion with the initial formation of monohydroxyvanadic ion is proposed.

An interpretation of the induced catalysis of the oxygen–iodide reaction by this reaction is suggested which involves the rapid formation and reduction of the peroxymonohydroxypervanadyl ion.

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[12] Yost and Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, p. 262.

[13] Ramsey, Sugimoto and DeVorkin, THIS JOURNAL, **63**, 3480 (1941).

[14] Brode, *Z. physik. Chem.*, **37**, 260 (1901).

[15] Jahr, *Z. Elektrochem.*, **47**, 810 (1941).