

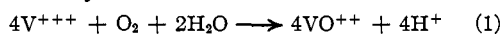
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Kinetics of the Trivalent Vanadium-Oxygen Reaction

BY J. B. RAMSEY, ROY SUGIMOTO AND HOWARD DEVORKIN

From a consideration of the kinetics of a number of oxidations of iodide by oxygen-containing oxidants, Bray¹ concluded that the initial rate-determining step in these oxidations involves the conversion of iodide to hypoiodite ion or hypoiodous acid. Since pentavalent vanadium exists in moderately acid solutions primarily as the vanadyl ion, $V(OH)_4^+$, or VO_2^+ ,² it seems probable that the vanadium is initially reduced by iodide to the trivalent state. Additional confirmation of this assumption is given by the results of preliminary kinetic experiments, which show that the pentavalent vanadium-iodide reaction in perchlorate-perchloric acid solutions is first order with respect to iodide and to vanadium over a considerable range of iodide and vanadium concentrations.³ If oxygen is present during this reaction, a portion of the trivalent vanadium may be reoxidized by oxygen to the pentavalent state. Such reoxidation would make the induced catalysis of the oxygen-iodide reaction by the pentavalent vanadium-iodide reaction⁴ a case of true catalysis, since the rate of the pentavalent vanadium-iodide reaction in a given acid solution is very much greater than that of the oxygen-iodide reaction.

This investigation of the kinetics of the trivalent vanadium-oxygen reaction has therefore been carried out for the value it may have in establishing the mechanism suggested for the induced catalysis. Since trivalent vanadium is oxidized very rapidly in acid solution by pentavalent vanadium to give tetravalent vanadium, the over-all reaction may be written



Preparation and Standardization of Solutions.—Sodium oxalate from the Bureau of Standards was the primary standard for the solutions of potassium permanganate, sodium thiosulfate, potassium iodate and perchloric acid. Accepted procedures previously used⁵ were followed in preparing and standardizing these solutions. The sodium perchlorate and ammonium vanadate (C. P. grade) were further purified by fractionally recrystallizing twice from

water. A very slight alkalinity persisting in the perchlorate thus obtained was just neutralized with perchloric acid. Sixty per cent. perchloric acid, reported by the manufacturer to be of very high purity, was used without further purification. This was justified by the results of the last runs in which the perchloric acid used was obtained by distilling the sixty per cent. solution.

The stock solutions of vanadic perchlorate, $V(ClO_4)_3$, containing perchloric acid and a relatively small quantity of vanadyl perchlorate, $VO(ClO_4)_2$, was prepared electrolytically and analyzed as previously described,⁵ except for the following modifications: oxygen-free nitrogen was used to provide the inert atmosphere for the stock solutions during preparation and while in use, instead of carbon dioxide. To obtain the concentration of the trivalent vanadium alone, iodate, in excess, was used instead of vanadate. The procedure with iodate is much simpler in that it is unnecessary to remove oxygen from the solution in order to determine iodometrically the excess oxidant remaining. To assure completion of the trivalent vanadium-iodate reaction within a minute or two, it was found necessary to have the acid concentration 0.3 *N* or above, and to use such an excess of iodate that its concentration remained appreciable throughout the oxidation. The excess iodate is determined by adding solid potassium iodide and titrating with standard thiosulfate. No measurable loss of iodine occurred during the short time required for the vanadium-iodate reaction. The results agreed precisely with those obtained with vanadate.

The water used in the preparation of all reagents entering the reaction mixture was obtained by redistilling the ordinary laboratory supply of distilled water from alkaline permanganate in an all-Pyrex still. Consistent and reproducible results could not be obtained with ordinary distilled water. These variable results were attributable to the catalytic effect of copper which was found present in sufficient quantity by the micro-method of Hurd and Chambers.⁶

Rate Measurements.—Perchlorate was the only negative constituent present in the reaction mixtures, except for a trace of chloride, formed by the very slow reaction between trivalent vanadium and perchlorate in the stock solutions, which were between 0.15 and 0.20 molar in vanadic perchlorate and between 0.1 and 0.2 molar in perchloric acid. The reaction took place in one-liter, three-necked, round-bottom flasks, which were fitted with mercury-sealed glass stirrers. All rubber stoppers that might contact the reaction mixture were thoroughly cleaned by boiling in 3 *N* sodium hydroxide and finally in redistilled water. The oxygen-containing gas was washed successively with acidified permanganate, dilute sodium hydroxide and water before entering the solution. Prior to the addition of the oxygen-free vanadium solution, the last reagent to be added, the main portion of the reaction mixture (never less than nine-tenths of the total volume),

(1) Bray, *Z. physik. Chem.*, **54**, 463 (1906).(2) (a) Yost and Coryell, *THIS JOURNAL*, **55**, 1909 (1933); (b) Carpenter, *ibid.*, **56**, 1847 (1934).

(3) L. C. Pack, M. A. Thesis, University of California, Los Angeles, 1940.

(4) Bray and Ramsey, *THIS JOURNAL*, **55**, 2279 (1933).(5) Ramsey and Heldman, *ibid.*, **58**, 1153 (1936).(6) Hurd and Chambers, *Ind. Eng. Chem., Anal. Ed.*, **4**, 236 (1923).

containing the desired quantities of other reagents involved, was saturated with the oxygen-containing gas. The passage of the gas through the well stirred solution was continued during the rate measurement. The reaction flasks were well submerged in a thermostat kept within 0.01° of the desired temperature, 25.00°, unless otherwise specified.

The reaction was followed by determining at suitable intervals the concentration of trivalent vanadium according to the iodate procedure described above. Ten milliliters of the reaction mixture was added to a measured volume of standard iodate (0.01 *N*) in excess, to which sufficient sulfuric acid had been added to maintain the acid concentration at approximately 0.3 *N*.

Neither the artificial light of the laboratory nor the tetravalent vanadium, present initially or formed during the reaction, had any detectable influence on the rate. That the rate measured was that of a homogeneous reaction was established by the fact that a considerable increase in stirring and in atomization of the gas produced no change in rate under conditions giving the maximum rate observed. In the absence of oxygen no measurable change in the trivalent vanadium content occurred in the maximum time taken to establish the rate curve and under conditions most favorable for oxidation by perchlorate, *viz.*, at the highest concentration of acid used, 0.5 *N*.

Order of the Reaction

Without Addition of Copper.—The initial rates obtained in a few experiments in which the concentrations of vanadic perchlorate, perchloric acid and oxygen were varied, indicated that the rate was proportional to the trivalent vanadium concentration and to the oxygen pressure, and inversely so with respect to the perchloric acid concentration. That the rate was not changed by a large variation in ionic strength was also apparent. The rate equation suggested by these results is

$$-\frac{d(V^{+3})}{dt} = k \frac{(O_2)(V^{+3})}{(H^+)} = K \frac{(V^{+3})}{(H^+)} \quad (2)$$

in which (V^{+3}) is the total, or volume formal, concentration of trivalent vanadium, and $K = k(O_2)$. Integration of this equation is possible if the concentration of the acid is expressible in terms of the concentration of the total trivalent vanadium. This can be done if it is assumed that the concentration quotient of the first step in the hydrolysis of trivalent vanadium, namely



is sufficiently small to make the concentration of the hydrolyzed vanadium, VOH^{++} , negligible compared to that of the acid, as well as to that of the total trivalent vanadium, in the solutions used. This assumption seems warranted, not only from the results obtained by its adoption,

but also from consideration of the probable value of the solubility product of $V(OH)_3$, approximately 10^{-30} , inferred from the solubility products of the closely related trihydroxides of scandium, chromium, ferric iron and cobaltic cobalt given by Latimer,⁷ along with the value of the equilibrium constant of the first step in the hydrolysis of ferric iron reported by Bray and Hershey,⁸ and by Lamb and Jacques.⁹ It follows from this assumption and the over-all reaction (1) that

$$(H^+)_t = (H^+)_0 + (V^{+3})_0 - (V^{+3})_t \quad (4)$$

Substitution of eq. (4) into eq. (2) and integrating from the beginning of the reaction to any time, t , gives the equation

$$-2.303[(H^+)_0 + (V^{+3})_0] \log_{10} \frac{(V^{+3})_t}{(V^{+3})_0} + (V^{+3})_t - (V^{+3})_0 = Kt \quad (5)$$

The value of the constant, K (moles liter⁻¹ hour⁻¹) for a given experiment is the average of those obtained from at least three well-distributed points on the best concentration-time curve. Typical results with one of the stock solutions of vanadium (designated A) are recorded in Table I. The ionic strength is determined solely by the concentrations of the reactants.

TABLE I
KINETIC RESULTS WITHOUT ADDITION OF COPPER; STOCK SOLUTION A

Initial Concentrations in Formula Weights per Liter				
$[V(ClO_4)_3]_0$	$(HClO_4)_0$	$P_{O_2}, \text{atm.}$	μ	$K \times 10^3$
0.0100	0.0161	1.0	0.0797	0.53
.0190	.0330	1.0	.159	.50
.0473	.0802	1.0	.400	.51
.0179	.0830	1.0	.208	.53
.0179	.0539	1.0	.175	.51
.0144	.0376	0.21	.141	.11
.0144	.0380	1.0	.141	.54

These results substantiate the rate law (eq. 2) over the concentration range of the reactants used (approximately five-fold for each).

That the rate is independent of the ionic strength over the range involved in these experiments is shown by the results of experiments with a different stock solution (B) of trivalent vanadium, given in Table II. Sodium perchlorate was used to obtain the desired ionic strength.

It is seen that the value of the constant obtained with stock solution B is approximately three times that with solution A. Even though each of the five different stock solutions used in this work gave

(7) Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, Appendix III, p. 309.

(8) Bray and Hershey, *THIS JOURNAL*, **56**, 1889 (1934).

(9) Lamb and Jacques, *ibid.*, **60**, 967, 1215 (1938).

TABLE II
EFFECT OF IONIC STRENGTH ON RATE WITHOUT ADDITION
OF COPPER; STOCK SOLUTION B

μ	$K \times 10^3$
0.129	1.5
.299	1.6
.458	1.7
.584	1.5
.623	1.5
1.034	1.3
1.493	1.3

a different K -value, nevertheless the same rate law was found to hold. This is exemplified by the results (Table III) with stock solution C which gave the highest value of K obtained.

TABLE III
KINETIC RESULTS WITH STOCK SOLUTION C

$[V(ClO_4)_3]_0$	$(HClO_4)_0$	P_{O_2}	μ	$K \times 10^3$
0.0158	0.0200	1.0	0.311	2.5
.0313	.0400	1.0	.311	2.3
.0156	.0320	1.0	.311	2.4
.0159	.0200	0.21	.311	0.47

This variation in the K -value is to be expected, even though much care was taken to assure the absence of impurities, on account of the well known sensitivity of oxygen reactions to catalysis, both positive and negative.

With Addition of Copper.—The presence of some common catalytic impurity in the ordinary laboratory supply of distilled water was suspected from the lack of reproducibility and consistency in the results obtained while using it. Ferric sulfate and ferrous sulfate were without effect except for the oxidation of vanadic by ferric ions. Copper sulfate had a pronounced catalytic effect. As previously noted copper was found present in the ordinary distilled water in sufficient quantity to account for the variable results obtained therewith.

Again, from consideration of the variation in the initial rates upon changing the initial concentrations of each of the reactants, it was apparent that the rate increased with increase in the vanadium and copper concentrations, and decreased with increase in acid concentration. However, in contrast to the results obtained without copper addition, the rate was independent of the oxygen pressure with the copper concentration ($1 \times 10^{-5} M$) used in the preliminary experiments. Also a definite positive salt effect was observed.

The values of K given in Table IV are again obtained by the use of eq. (5) and include in this case both the concentration of oxygen and of cop-

per, existing in a given experiment. Vanadium stock solution A (Table I) was used.

TABLE IV
KINETIC RESULTS WITH ADDITION OF COPPER

Expt.	$(CuSO_4) \times 10^5$	$[V(ClO_4)_3]_0$	$(HClO_4)_0$	P_{O_2} atm.	μ	$K \times 10^3$
1	1.00	0.0394	0.0906	1.0	0.400	23.3
2	1.00	.0777	.0182	1.0	.400	21.5
3	1.00	.0770	.0183	0.21	.400	20.0
4	1.00	.00799	.0183	1.0	.400	20.9
5	5.00	.00785	.0181	1.0	.153	69.4
6	5.00	.00818	.0343	1.0	.153	68.6
7	5.00	.0162	.0358	1.0	.153	72.6
8	1.00	.00858	.0173	1.0	.0764	12.5
9	2.00	.00847	.0175	1.0	.0764	27.0
10	5.00	.00788	.0181	1.0	.0764	60.0
11	10.00	.00751	.0185	1.0	.0764	108.4
12	0.01	.0147	.0373	1.0	.153	0.59
				0.21		0.15

The results of experiments 1 to 4, with copper sulfate concentration, $1.00 \times 10^{-5} M$, and at constant ionic strength, 0.400, show that the rate is directly proportional to the trivalent vanadium concentration, inversely so with respect to acid, and independent of the oxygen pressure over a five-fold concentration range of these reactants. Experiments 5 to 7, with copper at $5 \times 10^{-5} M$, show the same dependence on the vanadium and acid concentrations. The relation of the velocity constants to the copper concentration shown by the results of experiments 8 to 11 are in agreement with others not given, in demonstrating that the rate is proportional to the copper concentration over the range $1-5 \times 10^{-5}$, but deviates noticeably from proportionality at higher concentrations. The ratio of the K -value at 1×10^{-4} to that at 5×10^{-5} is 1.8 and agrees with that found with a different stock solution.

At a sufficiently low copper concentration, the rate should become dependent upon the oxygen pressure, as it does at $1 \times 10^{-7} M$ (experiment 12). This merely means that the copper catalyzed rate has become but a small fraction of the total rate at such low copper concentrations. In other experiments (results not given) the rate was found to be independent of the oxygen pressure (0.1 to 1 atm.) with copper at 2.0 and $5.0 \times 10^{-5} M$.

A small but definite positive salt effect is shown by the results given in Table V. The ionic strength is varied by use of sodium perchlorate. That the sodium perchlorate used contained no catalytic impurity was shown by the fact that the rate of the reaction without added copper was not changed by a large variation in its concentration (Table II).

TABLE V
EFFECT OF IONIC STRENGTH ON THE COPPER CATALYZED REACTION

$[\text{V}(\text{ClO}_4)_3]_0$	Ionic strength	$K \times 10^3$
0.00470	0.132	101.0
.00474	.300	123.0
.00501	.500	147.0
.00466	1.00	171.0

Temperature Coefficient.—The effect of temperature on the rates of the “uncatalyzed” and of the copper catalyzed reaction is shown by the results given in Table VI. K_u and K_c are the K -values for the uncatalyzed and copper-catalyzed reactions, respectively.

TABLE VI
EFFECT OF TEMPERATURE

Temp., °C.	“Uncatalyzed” $K_u \times 10^3$	$K_u/(\text{O}_2)$	(Cu^{++}) = 10^{-5} M, $\mu = 0.114$ Catalyzed $K_c \times 10^3$	$K_c = \left(\frac{K}{K_u}\right) \times 10^3$
25.00	2.09	1.68	18.6	16.5
29.70	3.27	2.96	30.5	27.1
35.10	4.80	4.58	48.5	43.7
40.10	8.50	8.58	75.0	66.5
45.09	12.5	14.19	114.0	101.5

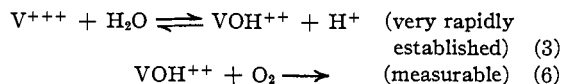
The concentration of oxygen required to evaluate $K_u/(\text{O}_2)$ at the ionic strength of the solution, namely, 0.1, was estimated from the variation in the solubility of oxygen in water and in 1.0 *N* sodium chloride with temperature obtained by Winkler.¹⁰

The best straight lines representing the values of $\log K$ vs. $1/T$ for each of these reactions are shown in Fig. 1. The critical increments ($= RT^2 d \ln K/dT$) obtained from the slopes of these lines are for the “uncatalyzed” reaction, 20,100 calories; and for the copper catalyzed, 17,200 calories. If the mechanisms proposed later are accepted, each of these critical increments include the heat of hydrolysis of trivalent vanadium (V^{+++} to VOH^{++}), and shows that the energy of activation of the Cu^{++} - VOH^{++} reaction is some 3000 calories less than that of the O_2 - VOH^{++} reaction. This is therefore an example of the most common effect of catalysis, *viz.*, the lowering of the energy of activation. The temperature quotients, K_{35}/K_{25} , are for the “uncatalyzed” reaction 2.7 and for the catalyzed 2.6.

Discussion

Reaction without Addition of Copper.—An apparent interpretation of the rate law established is shown by the following equations

(10) Winkler, *Z. angew. Chem.*, **24**, 341, 831 (1911).



To account for the different values of K obtained with different stock solutions (noted above), one might assume the oxygen involved in the rate step, eq. 6, to be solely that which is bonded molecularly to some foreign substance present in different amounts or in different states in the different stock solutions of trivalent vanadium. If we assume with Rice¹¹ that these foreign substances may be primarily dust particles, and that the bonding of oxygen is that of adsorption, it follows from the dependence of the rate on the oxygen concentration that only a small fraction of the surface of the particles is occupied by oxygen; also, that the rate of establishing this adsorption equilibrium is very rapid relative to the rate of reduction of the adsorbed oxygen. An appreciable induction period was observed with the second stock solution prepared, during which time no measurable oxidation of trivalent vanadium occurred. However, after this period was over in a given experiment, the rate law stated was found to hold. It may be of interest to note that this induction period diminished in length as the stock solution was used until, finally, it had completely disappeared. Also, the induction period was consistently shorter with oxygen at one atmosphere than with air. This phenomenon seems to be explained by the “dust particle” hypothesis if it is assumed that some other substance present in this stock solution displaced the oxygen

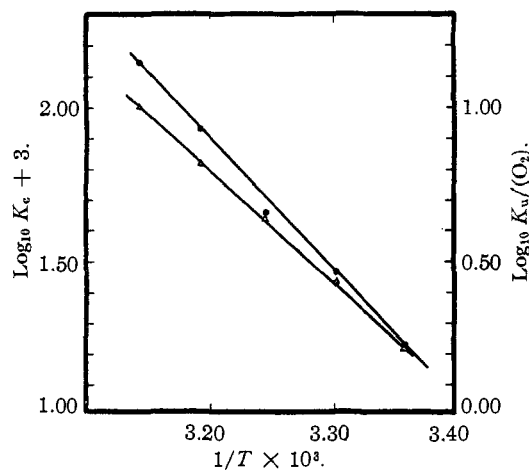


Fig. 1.—Variation of rate with temperature: ●, in absence of copper; Δ, with copper present at 10^{-5} M.

(11) (a) Rice, *THIS JOURNAL*, **43**, 2099 (1926); (b) Rice and Reiff, *J. Phys. Chem.*, **31**, 1352 (1927).

from the activating surface of the particles, and was oxidized to non-adsorbed products during the induction period. This same oxidation could have occurred slowly in the stock solution on standing.

The only restriction placed on the intermediates initially produced in reaction (6) is that they must be converted relatively rapidly to vanadyl vanadium and oxide oxygen. Two different sets of intermediates meet this requirement and seem possible: (a) pentavalent vanadium, $V(OH_4^+)$, and peroxide oxygen, and (b), tetravalent vanadium, VO^{++} , and superoxide oxygen (valence $-1/2$). An attempt was made to detect pentavalent vanadium by carrying out the oxidation under conditions most favorable to the formation and persistence of as large a steady state concentration of pentavalent vanadium as possible, *viz.*, by slow addition (dropwise) of the trivalent vanadium solution to a flowing solution, saturated with oxygen at one atmosphere and buffered at *pH* 5.0 with sodium acetate and acetic acid. At this *pH* the rate of oxidation by oxygen was found to be very rapid as expected (90% complete in approximately two minutes), and by pentavalent vanadium relatively slow. Approximately one minute was required for the solution to pass from the point of addition of the trivalent vanadium to the place where it was delivered into a solution of lead acetate. Tests had shown that a detectable precipitate of lead vanadate should have been obtained had the quantity of pentavalent vanadium present been equivalent to 0.2% of the total trivalent vanadium added. No precipitate was observed. This is by no means conclusive evidence that pentavalent vanadium is not formed since conditions locally may have been such as to permit its complete reduction to the tetravalent state. The absorption spectra of the reacting mixture under favorable conditions may permit the detection of pentavalent vanadium as the intermediate, and such a study is in progress.

In a critical study of the investigations of the kinetics of oxygen reactions, Bray¹² has pointed out that the presence of some peroxide during such reactions can be demonstrated in many cases. He listed a number of reactions in which a nearly quantitative isolation of a peroxide has been accomplished. Until recently this peroxide oxygen has been generally accepted as the initial

product of reduction of free oxygen in aqueous solution. The fact that no peroxide could be detected in certain cases was attributed to the relatively rapid reduction of the peroxide by the reducing agent. Bray¹³ has stressed the importance of considering the formation of superoxide oxygen, as the initial product of reduction of oxygen. The formation of HO_2 as the initial product in those cases where the presence of peroxide oxygen has been established is not excluded since it was shown by Harcourt¹⁴ that HO_2 is very unstable and decomposes very rapidly into oxygen and hydrogen peroxide in acid solution. Bäckstrom¹⁵ has assumed this valence state of oxygen in his interpretation of the sulfite-oxygen reaction. In the interpretation of the kinetics of the oxidation of ferrous bicarbonate by oxygen, Just¹⁶ seems to have been the first to consider superoxide oxygen the initial reduced state of oxygen.

On the basis of the experimental results so far obtained it is not possible to exclude with certainty either of the two possible intermediate valence states of oxygen (peroxide or superoxide) in its reaction with trivalent vanadium. In either case the peroxide formed would react instantaneously with the lower valence states of vanadium to give pentavalent vanadium which in turn is instantly reduced by trivalent vanadium.

That the rate was unchanged by varying the ionic strength from 0.1 to 1.5 (Table II) was unexpected in view of the fact that the iodine-trivalent reaction had a considerable negative salt effect.⁵ The rate determining step of the iodine reaction differs from the oxygen reaction solely in that iodine molecules are involved instead of oxygen molecules; the other molecular species being hydrolyzed vanadium ions, VOH^{++} , in both cases. The negative salt effect in the iodine oxidation was assumed to be due to a decrease in the degree of hydrolysis of trivalent vanadium with increasing salt concentration. This decrease seemed probable from a consideration of the effect which increasing ionic strength might have on the activity coefficients of the different ions involved in the hydrolysis equilibrium. Apparently this assumption is not valid if the mechanism proposed for each of the reactions is correct. From the interpretation given by Liebafsky¹⁷ for the

(13) Bray, private communication.

(14) Harcourt, *J. Chem. Soc.*, **14**, 267 (1862).

(15) Bäckstrom, *Z. physik. Chem.*, **25B**, 122 (1934).

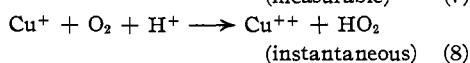
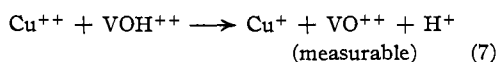
(16) Just, *Ber.*, **40**, 3695 (1907).

(17) Liebafsky, *Chem. Rev.*, **17**, 89 (1935).

(12) Bray, unpublished work, presented at the Pasadena meeting of the American Association for the Advancement of Science, June, 1931.

anomalous temperature coefficients of the equilibrium and rate constants of reactions involving the halogens, it seems probable that the negative salt effect observed for the iodine-vanadium reaction may be attributed to a specific influence of salt concentration on the reactivity of iodine. Further work is in progress with the iodine-vanadium reaction to test this hypothesis.

Reaction with Added Copper.—Since the rate is independent of the oxygen pressure over a wide range of copper concentration, from 1×10^{-5} to 1×10^{-4} *M* the rate determining step does not involve oxygen. Moreover, the dependence of the rate on the copper concentration (above 1×10^{-5} *M*), the vanadium concentration and the acid concentration warrants the assumption that the rate step involves cupric ions and hydrolyzed vanadium ions, VOH^{++} . These facts are adequately represented by the equations



Wieland and Franke¹⁸ have shown that cuprous copper is very rapidly oxidized by oxygen in acid solution and that hydrogen peroxide is formed. The very rapid reduction of hydrogen peroxide by the lower valence states of vanadium has been mentioned previously.

The fact that the rate with copper at 1×10^{-4} *M* is significantly less than double that with copper at 5×10^{-5} *M* (shown by the results in Table II and by others not given) may be attributed to a decrease in the concentration of the hydrolyzed vanadium ion below its equilibrium value. At copper concentrations below 5×10^{-5} *M*, the rate of establishing the hydrolysis equilibrium (eq. 3) is apparently sufficiently rapid in relation to the rate of oxidation to maintain the equilibrium concentration of VOH^{++} . That the hydrolysis equilibrium is not established instantaneously seems probable in view of the findings of Lamb and Jacques⁹ regarding the time required to establish the corresponding equilibrium of ferric iron.

The positive salt effect found for this reaction is in agreement with the postulate that the rate determining step is the one between the hydrolyzed vanadium ion, VOH^{++} , and cupric ions.

(18) Wieland and Franke, *Ann.*, **473**, 291 (1929).

Application of Brönsted's theory¹⁹ to this reaction results in the expression

$$-\frac{d(\text{V}^{+3})}{dt} = k_B(\text{VOH}^{++})(\text{Cu}^{++}) \frac{\gamma_{\text{VOH}^{++}} \gamma_{\text{Cu}^{++}}}{\gamma_{\text{VOH}^{++} \cdot \text{Cu}^{++}}} \quad (10)$$

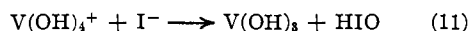
in which k_B is the Brönsted specific rate constant and the γ 's are activity coefficients. The activity coefficient of the critical complex, $\text{VOH}^{++} \cdot \text{Cu}^{++}$, a tetravalent ion, decreases much more rapidly with increasing ionic strength than does the product of the activity coefficients of VOH^{++} and Cu^{++} . Thus a positive salt effect would be expected. It is understood that specific influences of different ions, known to be present at the ionic strengths involved, have been neglected.

It may be of interest to note that with cupric copper and oxygen, as with iodine, each a non-oxide containing oxidant, the partially hydrolyzed ion is substantially the only species of trivalent vanadium that is oxidized at a measurable rate at ordinary temperatures. Qualitative results have shown that the rates of oxidation of trivalent vanadium by perchlorate, iodate and vanadate are increased by increasing the acid concentration. We may tentatively predict that all non-oxide containing oxidants will be found to react more rapidly with hydrolyzed vanadium ion than with unhydrolyzed, whereas this may or may not be so with oxide-containing oxidants. This is expected since the initial product of oxidation of trivalent vanadium contains vanadium intimately bonded to oxide oxygen, *viz.*, VO^{++} or $\text{V}(\text{OH})_4^+$.

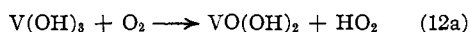
If the induced catalysis of the oxygen-iodide reaction by the pentavalent vanadium-iodide reaction (in acid solution)⁴ is a case of "true catalysis" involving trivalent vanadium, it is necessary, first, that the trivalent vanadium reasonably assumed to be formed as the initial reduction product of pentavalent vanadium, should be more rapidly oxidized by oxygen than is iodide; and, second, that the products of this oxidation include pentavalent vanadium, or be such that they are rapidly transformed to pentavalent vanadium. The highest induction factors were obtained with oxygen at the maximum pressure used, one atmosphere, and with the maximum acid concentration, 3.0 *N* sulfuric acid. Under these conditions of acid and oxygen concentrations, it is to be expected from the effect of acid on the rate of the oxygen-trivalent vanadium reaction shown, that the rate of this reaction would be very small, much less than the rate of the oxygen-iodide re-

(19) Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

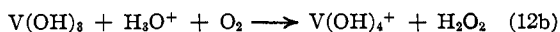
action under the same conditions and with iodide at concentrations used in obtaining the maximum induction factors. This would seem to exclude the possibility that trivalent vanadium is involved in the induced catalysis, and would do so if the trivalent vanadium initially formed in the pentavalent vanadium-iodide reaction were in the same state as that present in solutions of trivalent vanadium of equal acidity. It seems more probable that the trivalent vanadium initially formed is temporarily in a highly hydrolyzed state, since the pentavalent vanadium exists over a wide range of acid concentration principally as the vanadyl ion, $V(OH)_4^+$.² It seems probable from our results that in this highly hydrolyzed state the trivalent vanadium may be very rapidly oxidized by oxygen, and could therefore be involved in the induced catalysis. This possibility may be formulated as follows



followed either by



or by



If an appreciable fraction of the trivalent vanadium is oxidized in either of these ways, the induced catalysis becomes a case of "true catalysis." The hydrogen peroxide formed in either case is very rapidly reduced by iodide, in the presence of pentavalent vanadium, and also by tetravalent vanadium (eq. 12a). A decision regarding the most probable mechanism of this induced cataly-

sis cannot be made on the basis of the results available.

Summary and Conclusions

The rate laws of the trivalent vanadium-oxygen reaction have been established in absence of copper and when catalyzed by copper. Probable mechanisms have been proposed.

Variation in the "dust particle" content of the different stock solutions of trivalent vanadium is suggested as a possible reason for the different values of the rate constants obtained for the uncatalyzed reaction.

The critical increments have been determined and found to have the relative values expected for a catalyzed and an uncatalyzed reaction.

The rate of the uncatalyzed reaction is independent of the salt concentration, while that of the copper-catalyzed reaction has a positive salt effect over the range of ionic strength, 0.1 to 1.0. The latter has been interpreted in terms of the Brönsted theory.

On the basis of the results of this investigation a mechanism of the induced catalysis of the oxygen-iodide reaction has been suggested.

It is considered significant that the two "non-oxide" containing oxidants, oxygen and cupric copper, like iodine, react at a measurable rate solely with hydrolyzed trivalent vanadium, even though it constitutes but a very small fraction of the total trivalent vanadium present in the acid solutions used.

LOS ANGELES, CALIFORNIA

RECEIVED SEPTEMBER 26, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

Molecular Surface Energy of Sulfur Dioxide Addition Compounds. I¹

BY J. RUSSELL BRIGHT AND JOSEPH J. JASPER

Gaseous sulfur dioxide dissolves in dimethylaniline to form a red-colored oily liquid.² A recent investigation³ has shown the existence of a single 1:1 addition compound in the binary system sulfur dioxide-dimethylaniline. This compound

(1) Presented before the Division of Physical and Inorganic Chemistry at the Atlantic City meeting of the American Chemical Society, September, 1941.

(2) Hill and Fitzgerald, *THIS JOURNAL*, **67**, 250 (1935). These workers found no solid formation at temperatures as low as -10° .

(3) Unpublished results by Bright and Fernelius, presented before the Division of Physical and Inorganic Chemistry at the Detroit meeting of the American Chemical Society, September, 1940.

melts at 12° ,³ but it is very easily supercooled.² The density and surface tension of pure dimethylaniline at 20° , for example, are 0.9562 g./ml. and 36.56 dynes/cm., respectively⁴; the Eötvös constant is 2.4.⁴

The purpose of the present investigation was to measure certain important physical constants of this sulfur dioxide molecular addition compound over the temperature range 0 to 30° .

(4) "Int. Crit. Tables," Vol. IV, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p. 458.