slightly higher. Basing our calculations on the higher value which is presently given the greater emphasis, and correcting for absorption as indicated above, we obtain the following G values for the decomposition of methyl iodide induced by Co^{60} γ-radiation: (Fe oxid. = 20.4); $I_2 = 1.26$; $C_2 = 1.28$; $CH_4 = 0.57$; $H_2 = 0.08$. It is seen that the G for iodine production compares very favorably with the value ($G_{I_2} = 1.38$) obtained in electron bombardment studies where the energy input was measured directly in terms of the electron current and particle energy.[5]

The γ-radiation and fast electron yields are apparently very similar. One must, however, be careful in identifying these yields in this case, at least in principle, since effects of intensity may be present in the fast electron studies. Such effects are apparently minimized in this particular system. It is indeed surprising that for the large difference in the rates of energy absorption, 4×10^{18} ev./cc./min. in the fast electron experiments and 6×10^{14} ev./cc./min. in the γ-radiation experiments, the decomposition yields are found to be so similar.

Accurate yield calculations for the X-ray experiments are more difficult since in the region of 0.2–0.4 Å. the absorption of the water is due to both the photoelectric and Compton effects. Because of the inhomogeneity of the radiation the precise fractional absorption in the water is not known. The calculation is aided somewhat by the fact of complete absorption in methyl iodide. If an absorption of 5.5% of the incident energy is assumed for the water (corresponding to an effective wave length of 0.3 Å.) then the yield of iodine corresponds to G_{I_2} of 1.20. This latter value, which is somewhat in question because of the uncertainty in the absorption, indicates that there is no extreme dependency of the reaction yield upon energy or intensity. As mentioned previously, the constancy in the relative yields in going from the X-ray to the more energetic but less intense Co^{60} γ-radiation would indicate that the yields should be very similar in both of these cases.

Acknowledgment.—The authors wish to express their appreciation to Mr. Paul Forsyth for his aid with the monitoring measurements.

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

Kinetics of the Simultaneous Reduction of Oxygen and Pervanadyl Ion by Iodide Ion in Acid Solution

BY M. H. BOYER AND J. B. RAMSEY

RECEIVED FEBRUARY 6, 1953

The effect of the concentrations of each of the ions, hydrogen, pervanadyl and iodide, and of oxygen on the catalysis of the oxygen–iodide reaction, manifest during the simultaneous occurrence of the pervanadyl–iodide reaction, has been determined. The observed dependence of the induction factor on these concentrations has been shown to be satisfactorily accounted for by the assumption that diiodide ion, I_2^-, is the intermediate of the pervanadyl–iodide reaction which acts as the catalyst of the oxygen–iodide reaction. Contributory evidence, substantiating this assumption, has been presented.

Historically, interest in induced reactions arose from the fact that large errors were found when an attempt was made to determine a number of oxidizing agents by means of their reaction with known quantities of certain reducing agents (or *vice versa*) in the presence of air. It was subsequently shown that these errors were due to an accelerated rate of reduction of oxygen. According to the nomenclature adopted in the study of such phenomena,[1] in general, the reduction of oxygen was said to have been induced. The catalytic character of a number of these induced reductions of oxygen was demonstrated long ago by Lenssen and Löwenthal[2] in their paper, entitled "Zur Katalyse des Sauerstoffs." For example, they stressed the fact that, while a small quantity of dichromate is being reduced by stannous chloride in acid solution containing dissolved air, the quantity of stannous tin oxidized by oxygen is several times greater than that oxidized by the dichromate, and than that which would have been oxidized by the oxygen (of the air) in the absence of the dichromate–stannous reaction under otherwise the same conditions.

Although a considerable number of induced reductions of oxygen have been reported, none have been investigated in such a way as to permit the formulation of a probable mechanism of the induction. However, in their study of the induction of the oxygen–iodide reaction by the pervanadyl–iodide reaction in acid solutions, Bray and Ramsey[3,4] varied the initial concentrations of pervanadyl ion, $V(OH)_4^+$ [hereafter symbolized by $(V^{+5})_0$], keeping the concentrations of oxygen, iodide ion, and acid constant. Over the lower range of initial concentrations of pervanadyl ion, from 2.6×10^{-5} to 10.3×10^{-5} m, their results conform to the relation

$$\text{Induction factor} = \text{Constant}/(V^{+5})_0^{1/2}$$

In this case the induction factor (hereafter symbolized by I. F.) is defined, in conformity with its general use, by the relation

$$\text{I. F.} = \frac{O_2 \text{ reduced, equivalents per liter}}{V^{+5} \text{ reduced, equivalents per liter}}$$

They obtained values of the induction factor as

---

[1] Fully discussed by R. Luther and N. Schilow, *Z. physik. Chem.*, **46**, 777 (1903).

[2] E. Lenssen and J. Löwenthal, *J. prakt. Chem.*, **86**, 193 (1862).

[3] W. C. Bray and J. B. Ramsey, THIS JOURNAL, **55**, 2279 (1933); considerable historical background included.

[4] See also I. M. Kolthoff and N. H. Furman "Volumetric Analysis," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1942, Chapter VII, for history and importance of induced oxidations by oxygen in volumetric analysis.

large as 12 without an apparent upper limit being approached as conditions were made more favorable for the induced oxygen–iodide reaction [*e.g.*, as the ratio, $(O_2)/(V^{+5})_0$, was increased]. It was shown by these investigators that the vanadyl ion, VO^{++}, the product of the reduction of pervanadyl ion by iodide ion, does not catalyze the oxygen–iodide reaction. It follows from their results that this induction belongs to the general class of induced reactions designated by Luther and Schilow[2] as "catalysis with the destruction of the catalyst." The interpretation of the catalysis of the oxygen–iodide reaction during the pervanadyl–iodide reaction has remained an open question. It has been the purpose of this investigation to resolve this open question.

Prologue.—Since the induction, *i.e.*, the enhancement of the rate of reduction of oxygen by iodide, occurs only during the time that pervanadyl ion is being reduced by iodide, it follows that the oxygen–iodide reaction must be catalyzed either by the pervanadyl ion or by an unstable intermediate of the pervanadyl–iodide reaction. In their interpretation of the kinetics of the pervanadyl–iodide–hydrogen ion reaction, Ramsey, Colichman and Pack[5] suggested vanadic ion, V^{+++}, and hypoiodous acid, HIO, as possible unstable intermediates of this reaction. The formation of these intermediates was inferred from the kinetic results and not established independently, even though considerable effort was made to detect vanadic ion during the reaction in the absence of oxygen. Two other initial products of the pervanadyl–iodide reaction seem equally probable, namely, vanadyl ion, VO^{++}, and atomic iodine, I^0. The four species, therefore, which are or may be present during the pervanadyl–iodide reaction and which could possibly act as catalysts of the oxygen–iodide reaction, are pervanadyl ion, vanadic ion, hypoiodous acid, and atomic iodine.

Although a mechanism is conceivable and may be formulated, whereby pervanadyl ion might catalyze the oxygen–iodide reaction, the relation between the I. F. and the $(V^{+5})_0^{1/2}$, derived therefrom, is not that required by the results of Bray and Ramsey[4] (and confirmed in this investigation). The possibility that vanadic ion might catalyze the oxygen–iodide reaction is excluded primarily by the fact that unpublished results, obtained in this Laboratory, have shown that vanadic ion does not catalyze the oxygen–iodide reaction in acid solutions. Hypoiodous acid may be excluded as a possible catalyst for the oxygen–iodide reaction since there is no apparent mechanism whereby it could enter into a cycle of changes, involving, as the net result, the reduction of oxygen and the oxidation of iodide. Also, the steady state concentration of hypoiodous acid, if formed, would be infinitesimal on account of the practically instantaneous rate with which it reacts with iodide ion in acid solution. The possibility that the reaction of hypoiodus acid with iodide ion in acid solution may induce the oxygen–iodide reaction needs to be considered. That this induction is highly improbable is shown by the fact that if a solution of known iodine content in potassium iodide solution containing dissolved oxygen is made alkaline and shortly thereafter (that is, while the yellow color of hypoiodite ion still persists) is made distinctly acid, the iodine formed agrees precisely with that present initially in the potassium iodine solution.

It remains to consider the possibility that atomic iodine, or preferably diiodide ion, I_2^- (formed by union of I^0 and I^-), may act as a catalyst for the oxygen–iodide reaction. It is shown (below) that from a probable mechanism for this catalysis, the inverse proportionality between the induction factor and the square root of the initial concentration of pentavalent vanadium follows. In this derivation the concentrations of the oxygen, the iodide ion, and the hydrogen ion are to be considered to remain essentially constant during the reduction of the pentavalent vanadium (as is the case in most of the experiments to be described later).

The following basic processes of the atomic iodine mechanism are proposed

$$V(OH)_4^+ + I^- + 2H^+ \longrightarrow VO^{++} + I^0 + 3H_2O \quad (1)$$

$$I^0 + I^- \underset{3}{\overset{2}{\rightleftarrows}} I_2^- \quad (2) \text{ and } (3)$$

$$I_2^- + I_2^- \longrightarrow I_3^- + I^- \quad (4)$$

$$I_2^- + O_2 + H^+ \longrightarrow I_2 + HO_2 \quad (5)$$

$$H^+ + HO_2 + I^- \longrightarrow I^0 + H_2O_2 \quad (6)$$

$$H_2O_2 + 2I^- + 2H^+ \longrightarrow 2H_2O + I_2 \quad (7)$$

It may be noted that reaction (1) is the inducing reaction and that reactions (2), (5), (6) and (7) constitute the catalytic cycle (*viz.*, the induced reaction) whereby oxygen and iodide ion are converted, respectively, into water and iodine. Reaction (4) is assumed to be the only chain-breaking process.

The rate law of reaction (1) has been shown[5] to be

$$-d(V^{+5})/dt = k_1(V^{+5})(I^-)(H^+)^2 \quad (8)$$

It is considered probable that reaction (5) is the rate determining step for the catalytic cycle and that its rate is given by the expression

$$d(I_2)/dt = k_5(I_2^-)(O_2)(H^+) \quad (9)$$

[The justification for considering this rate to be first order with respect to the (H^+) will be given later.] Under the conditions, previously specified, equation (8) may be written

$$-\ d(V^{+5})/dt = k'_1(V^{+5}), \text{ or}$$
$$(V^{+5})_t = (V^{+5})_0e^{-k_1't} \quad (10)$$

By definition the induction factor is given by the relation

$$\text{I. F.} = (I_2)_i^\infty/(V^{+5})_0 \quad (11)$$

where $(I_2)_i^\infty$ represents the equivalents of iodine per liter produced by the induced reaction (*viz.*, the catalytic process) during the reduction of the pentavalent vanadium, and $(V^{+5})_0$, the initial concentration of pervanadyl ion in equivalents per liter. The value of $(I_2)_i^\infty$ is obtained in terms of the concentrations of the reactants in the following manner.

---

[5] J. B. Ramsey, E. L. Colichman and L. C. Pack, THIS JOURNAL, **68**, 1695 (1946).

It is seen that the resultant rate of formation of atomic iodine is given by the equation

$$\frac{d(I^0)}{dt} = k_1'(V^{+5}) + k_3(I_2^-) + k_6'(HO_2) - k_2'(I^0) \qquad (12)$$

At the steady state this resultant rate, $d(I^0)/dt$, is considered negligibly small with respect to any of the other four rate terms in this equation. It follows that

$$k_2'(I^0) = k_1'(V^{+5}) + k_3(I_2^-) + k_6'(HO_2)$$

$$(I^0) = \frac{k_1'(V^{+5}) + k_3(I_2^-) + k_6'(HO_2)}{k_2'} \qquad (13)$$

Similarly from the rate equation

$$d(HO_2)/dt = k_5'(I_2^-) - k_6'(HO_2)$$

it follows that

$$(HO_2) = \frac{k_5'}{k_6'}(I_2^-) \qquad (14)$$

On substitution of this value of (HO_2) into equation 13 one obtains

$$(I^0) = \frac{k_1'(V^{+5}) + k_3(I_2^-) + k_5'(I_2^-)}{k_2'} \qquad (15)$$

Also it is seen that

$$\frac{d(I_2^-)}{dt} = k_2(I^0) - k_3(I_2^-) - k_4(I_2^-)^2 - k_5'(I_2^-) \qquad (16)$$

Substituting for (I^0) the value given in equation 15 and making the obvious cancellations gives

$$d(I_2^-)/dt = k_1'(V^{+5}) - k_4(I_2^-)^2$$

and at the steady state

$$(I_2^-) = (k_1'/k_4)^{1/2}(V^{+5})^{1/2} \qquad (17)$$

Now the quantity of iodine formed by the induced oxygen–iodide reaction is that produced by the catalytic cycle. Since reaction (5) is assumed to be the rate-determining step of the cycle, the rate of formation of iodine by the induced reaction is given by

$$d(I_2)_i/dt = k_5'(I_2^-) \qquad (18)$$

where $(I_2)_i$ is the concentration of iodine at time t, produced catalytically, *i.e.*, by the induced reaction. On substituting for (I_2^-) its value given by equation 17 and for (V^{+5}), its value given by equation 10, one obtains

$$\frac{d(I_2)_i}{dt} = k_5'\left(\frac{k_1'}{k_4}\right)^{1/2}(V^{+5})^{1/2}e^{-k_1't/2} \qquad (19)$$

Integration of equation 19 between the limits of $t = 0$ and $t = \infty$ gives the total concentration of iodine produced by the induced reaction, namely

$$(I_2)_i^\infty = \frac{2k_5'(V^{+5})_0^{1/2}}{(k_4k')^{1/2}} \qquad (20)$$

The value of the induction factor obtained on substitution of this value of $(I_2)_i^\infty$ in equation 11 is

$$\text{I. F.} = \frac{2k_5'}{(k_4k_1')^{1/2}(V^{+5})_0^{1/2}} \qquad (21)$$

which is the relation between the I. F. and the $(V^{+5})_0$ given by the results previously obtained[4] and confirmed in this investigation.

By substitution of $k_5(H^+)(O_2)$ for k_5' and $k_1 \cdot (I^-)(H^+)^2$ for k_1', one obtains

$$\text{I. F.} = \frac{2k_5(H^+)(O_2)}{(k_4k_1)^{1/2}(I^-)^{1/2}(H^+)(V^{+5})_0^{1/2}}$$

$$= \frac{2k_5(O_2)}{(k_4k_1)^{1/2}(I^-)^{1/2}(V^{+5})_0^{1/2}} \qquad (22)$$

It may be recalled that the dependence of the value of the I. F. on the concentration of the reactants given by equation 22 is predicted (1) on the condition that the concentrations of the I^-, the H^+ and the O_2 remain essentially constant during the reduction of V^{+5} in each experiment, (2) on the assumption that reaction 5 is the rate determining step of the catalytic cycle, and (3) that reaction 4 is the only chain-breaking process.

Experimental Results

Purification of Materials and Preparation of Reagents.—A few experiments had shown that the presence of copper sulfate at a known concentration of 2×10^{-6} *M* produced a very pronounced decrease in the value of the I. F. under conditions to be used. Also it had been found in previous work[5] that ferric iron at a concentration as low as 7×10^{-6} *M* caused a marked increase in the rate of the pervanadyl–iodide–acid reaction. That very small concentrations of iron and copper salts catalyze many oxidations by oxygen in aqueous solution is well known. Adequate removal of these rather common impurities is therefore essential.

Test for Copper.—It was found that a concentration of cupric copper at a concentration as low as 1.5×10^{-7} *M* is detectable (gives noticeable yellow color) in solutions of $HClO_4$, NaI and $NaClO_4$, at the highest concentrations to be used in the reaction mixtures, by use of sodium diethyldithiocarbamate in 0.1% aqueous solution.[6] This test for cupric copper was not applicable to solutions of sodium metavanadate, due to formation of a precipitate; nor to acid pervanadyl solutions, due to interference by the greenish-yellow color of pervanadyl ion. However, the adequate removal of ferric iron from the vanadium stock solutions had been assumed by the sensitive test to be described and it may be assumed that copper had been so removed also.

Test for Ferric Iron.—The thiocyanate test for ferric iron in acid solutions, previously described,[5] is capable of detecting ferric iron at a concentration as low as 10^{-6} *M*, in solutions of $HClO_4$ (less than 2.5 *M*) and of $NaClO_4$. This test was not applicable to NaI solutions on account of the reduction of ferric iron by iodide. Oxidation of thiocyanate by pervanadyl ion was detrimental to its use with vanadium solutions. Yoe and Jones[7] have shown that disodium 1,2-dihydroxybenzene 3,5-disulfonate (0.1 g. in 100 ml. of water) is capable of detecting ferric iron in neutral or alkaline solutions at a concentration as low as 10^{-7} *M*. This reagent was used in testing the stock solutions of $NaVO_3$ prior to conversion to pervanadyl perchlorate. With solutions of NaI a yellow, instead of the expected pink, color was produced.

Fortunately a method of detecting and estimating the ferric iron concentration in solutions of NaI was discovered during this investigation which is far more sensitive than any colorimetric method so far reported. This method is based on the observation that, at sufficiently large concentration of acid, the oxygen–iodide–acid reaction is induced very markedly by the ferric–iodide reaction. For example, in a solution kept saturated with oxygen at 745 mm., which is 3.00 *M* in $HClO_4$, 5×10^{-7} *M* in ferric iron (added as the sulfate) and 0.05 *M* in NaI (the last reactant added), the value of the induction factor is 250. The method of determining the I. F. has been previously described[4] and is the one used throughout this investigation. On varying the initial concentration of ferric iron, $(Fe^{+++})_0$, from one experiment to another (at the concentrations of $HClO_4$ and NaI given above) the number of equivalents of iodine per liter produced by the catalytic process (*viz.*, by the induced reaction) was found to vary proportionally to the $(Fe^{+++})_0^{1/2}$. The straight line obtained on plotting $(I_2)_i^\infty$ *vs.* the $(Fe^{+++})_0^{1/2}$ passes through the origin. By use of this line the concentration of ferric iron, as impurity, in the stock solution of NaI may be estimated from the value of the $(I_2)_i^\infty$, obtained without addition of ferric iron. A concentration of Fe^{+++} as low as 10^{-8} *M* in the reaction mixture may be detected in this way.

---

[6] Prepared and used as described by F. J. Welcher, "Organic Analytical Reagents," Vol. IV, D. Van Nostrand Co., Inc., New York, N. Y., 1948, pp. 82–93.

[7] J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944).

Purification Methods.—For $HClO_4$, a 70% solution was obtained by slow fractional distillation (under reduced pressure of about 150 mm.) of the commercially available 60% acid. For $NaVO_3$, the stock solution is prepared from recrystallized ammonium metavanadate, NH_4VO_3, as described previously.[8] For $NaClO_4$, two recrystallizations of the available $NaClO_4$ were adequate. For NaI, the commercially available NaI, which contained easily detectable quantities of both iron and copper salts, was recrystallized three times from aqueous solutions which were about 0.1 *M* in HI stabilized by metaphosphorous acid, H_3PO_2. This was followed by two recrystallizations from water. The purity of the NaI, thus obtained, was such that the concentration of ferric iron, introduced into the reaction mixture with the NaI, was in every case less than 10^{-6} *M*.

The water used in the purifications and in the reaction mixture was obtained by redistillation of the laboratory supply of distilled water from alkaline permanganate in an all Pyrex still. There were no detectable quantities of iron or copper in this redistilled water nor in any of the stock solutions of the reactants, with the exception of the NaI solutions, noted above.

Determination of the Induction Factor.—All determinations were carried out at 25.00 ± 0.01° in a 200-ml. three-necked flask, fitted with a mercury-sealed stirrer. The reaction flask was shielded from direct light. The desired volumes of the stock solutions of perchloric acid, of acidified pervanadyl perchlorate, and of sodium perchlorate (when used for ionic strength purposes) were added along with such a volume that on addition of the NaI solution (the last reactant added) a total volume of 100 ml. was obtained. The NaI solution was introduced with a pipet calibrated to deliver in less than two seconds. Prior to addition of the NaI the acid pervanadyl solution (never less than 70 ml.) was saturated with well-washed oxygen (or air). The stock solution of NaI at 25° was kept saturated with the desired gas which contained water vapor at a partial pressure substantially equal to that of the NaI solution.

The iodine concentrations to be determined were so small that their accurate determinations with standard sodium thiosulfate required a concentration of thiosulfate not greater than 0.002 *N* (approximately 0.001 *N* was used). For such low concentrations the use of starch is not feasible. Fortunately, the indicator system described by Foulk and Bowden[9] proved entirely satisfactory. The end-point is attained on disappearance of the diffusion current (produced as long as iodine is present) between two platinum electrodes (area, one cm.$^{-2}$), to which is applied a potential difference of 15 millivolts. The vanadyl vanadium, VO^{++}, always present, did not interfere. Titrations accurate to within a fraction of a drop of 0.001 *N* $Na_2S_2O_3$ were attainable.

The value of the induction factor is given by the relation

$$\text{I. F.} = \frac{(I_2)_e - (V^{+5})_0}{(V^{+5})_0}$$

as described previously.[4] The symbol $(I_2)_e$ represents the concentration of iodine in equivalents per liter obtained by extrapolation to zero time.

Dependence of the Induction Factor on the Composition of the Reaction Mixture.—The results obtained at two concentrations of $HClO_4$ and at two partial pressures of oxygen are given in Table I. The value of the I. F. given for each set of conditions is in most cases the average of not less than three determinations. The mean deviation from the average value was seldom greater than two per cent. It is seen that over the tenfold range of $(V^{+5})_0$, namely, from 0.01 to 0.1000 *M*, the I. F. varies inversely with the $(V^{+5})_0{}^{1/2}$, as required by equation 22.

TABLE I

(NaI) = 0.0483 *M*

$(V^{+5})_0$, $M \times 10^3$	$1/(V^{+5})_0{}^{1/2}$	$(I_2)_e$, $N \times 10^3$	I. F.
(a) $(HClO_4) = 3.00\ M;\ p_{O_2} = 156$ mm.			
0.0100	315	0.147	13.7
.0200	223	.216	9.8
.0500	141	.352	6.0
.1000	100	.501	4.0
.3000	58	.847	1.8
2.500	20	3.35	0.34
(b) $(HClO_4) = 1.50\ M;\ p_{O_2} = 745$ mm.			
0.0100	315	1.54	153
.0200	223	2.23	110
.0500	141	3.37	66.5
.1000	100	4.71	46.1
.3000	58	6.34	20.2

The small negative deviations of the I. F. from this relation, obtained at the largest vanadium concentrations [$(V^{+5})_0 > 0.1$ *M*], can be reasonably explained without predjucing the proposed mechanism of this induced reaction. In the derivation of equation 22 it is assumed that the oxygen concentration remains constant during the reduction of V^{+5}, *i.e.*, during the catalysis. Approximate estimates of the fraction of the dissolved oxygen reduced in the short time (not over 3 min.), required for reduction of the vanadium (at these highest concentrations), make it unlikely that the rate of diffusion of oxygen into the solution, even with the vigorous stirring maintained, would be sufficient to prevent a small, yet appreciable, decrease in the (O_2) during this time. Such a decrease in the (O_2) would cause a decrease in the value of the I. F. below that expected had the (O_2) remained constant as assumed. Another possible and probable process which may occur to an appreciable extent at the highest vanadium concentrations is the reaction

$$V(OH)_4{}^+ + I_2{}^- + 2H^+ \longrightarrow VO^{++} + I_2 + 3H_2O$$

In the derivation of equation 22 it is assumed (1) that pervanadyl ion is reduced solely by iodine ion (equation 1), and (2) that the chain carrier, $I_2{}^-$, is removed solely by reaction with itself (equation 4). It is apparent that the occurrence of the above reaction to an appreciable extent would produce a decrease in the steady state concentration of the catalyst, $I_2{}^-$, below that expected, and consequently a decrease in the I. F. for two reasons: (1) the rate of formation of the catalyst would be decreased, and (2) the catalyst, present, would be destroyed by this process (in addition to the one assumed, equation 4). In view of these considerations small negative deviations from linearity between the I. F. and the $(V^{+5})_0{}^{1/2}$, at the highest initial vanadium concentrations, is to be expected.

Before the effect of changing the $(HClO_4)$ and the (NaI) on the I. F. could be definitely established it was necessary to determine the influence of the ionic strength, μ, on the value of the I. F. It had been shown previously[5] that the rate of the pervanadyl–iodide–acid reaction did not change significantly over the range of the μ from 0.2 to 1.3. However, on changing μ from 1.15 [$(HClO_4) = 1.10$ *M*; $(NaI) = 0.0483$ *M*; $(V^{+5})_0 = 0.109 \times 10^{-3}$ *M*, $p_{O_2} = 156$ mm.] to 3.35 with purified $NaClO_4$, $NaHSO_4$ and $LiClO_4$, respectively, the value of the I. F. was decreased appreciably (from 8.9 to 2.4, 3.3 and 1.9, respectively). Maintenance of constant ionic strength is therefore neces-

---

[8] J. B. Ramsay, THIS JOURNAL, **49**, 1138 (1927).

[9] C. W. Foulk and A. T. Bowden, *ibid.*, **48**, 2045 (1926).

sary. It might be conjectured that the decrease in the I. F. caused by increasing μ may be attributable to an increase in the rate of the chain-breaking process assumed (equation 4).

The effect of changing the ($HClO_4$) at constant ionic strength is shown by the results given in Table II. It follows that the value of the I. F. remains substantially constant on changing the ($HClO_4$) from 1.00 to 3.00 M if the ionic strength is kept constant at either 3.05 or 4.05. This fact in itself makes it necessary to assume that the rate-determining step of the catalytic process (equation 5) is proportional to the first power of the hydrogen ion concentration. Otherwise the expression derived for the value of the I. F. would not be independent of (H^+) (see equation 22).

TABLE II

(NaI) = 0.0483 M; $(V^{+5})_0 = 0.100 \times 10^{-3}$ M; p_{O_2} = 156 mm.

($HClO_4$), M	($NaClO_4$), M	$(I_2)_e$, $N \times 10^3$	I. F.
	At $\mu = 3.05$		
3.00	0.00	0.513	4.13
2.00	1.00	.483	3.83
1.00	2.00	.494	3.95
	At $\mu = 4.05$		
3.00	1.00	0.334	2.34
2.00	2.00	.344	2.44
1.00	3.00	.373	2.73

The influence of the (NaI) on the value of the I. F. is shown by the results given in Table III. A straight line, passing through the origin, is obtained on plotting the I. F. *vs.* $1/(I^-)^{1/2}$. It is noted that this inverse proportionality between the I. F. and $(I^-)^{1/2}$ likewise conforms with equation 22.

TABLE III

($HClO_4$) = 3.00 M; $(V^{+5})_0 = 0.110 \times 10^{-3}$; p_{O_2} = 156 mm., μ = 3.30

(NaI), M	$1/(I^-)^{1/2}$	$(I_2)_e$, $N \times 10^3$	I. F.
0.293	1.88	0.261	1.37
.155	2.54	.310	1.81
.0478	4.58	.505	3.59
.0190	7.25	.714	5.49
.0094	10.3	.952	7.65

The effect of the (O_2) on the value of the I. F. was determined by use of pure oxygen and air. The results obtained are summarized in Table IV.

TABLE IV

(NaI) = 0.0483 M

($HClO_4$), M	$(V^{+5})_0$, $M \times 10^3$	p_{O_2}, mm.	I. F.	Ratio
3.00	0.0100	745	75.4	5.4
3.00	.0100	156	13.7	
3.00	.0500	745	33.8	5.6
3.00	.0500	156	6.0	
3.00	.300	745	10.0	5.5
3.00	.300	156	1.8	
1.50	.0100	745	153	5.0
1.50	.0100	156	30.4	

The ratio of the partial pressures of oxygen, 745/156, is 4.8. It is seen that in 3 M $HClO_4$ the I. F. increases with the partial pressure of oxygen to a power slightly greater than unity, *viz.*, 1.08. Even though this small deviation from strict proportionality between the I. F. and the (O_2) could be considered an insignificant divergence from equation 22, it may be worthwhile to consider briefly a possible interpretation. A reaction (not previously considered) which may be expected to have a greater probability of occurring to a small, yet significant, extent at the higher concentrations of $HClO_4$ and of O_2 is the oxidation of vanadyl ion by hydrogen peroxide (a probable intermediate, see equation 6), according to the equation

$$2VO^{++} + H_2O_2 + 6H^+ \longrightarrow 2V(OH)_4^+$$

It can be shown that, if this reaction did occur to a significant extent, the value of the I. F. would increase with oxygen concentration to a power slightly greater than unity.

The effect of the concentrations of the reactants (over the ranges used) on the value of the I. F., shown by these results, is thus given by the relation

$$\text{I. F.} = \text{Constant} \times \frac{(O_2)}{(V^{+5})_0^{1/2}(I^-)^{1/2}}$$

This agrees with the relation (equation 22) which has been derived on the basis of the assumptions that diiodide ion, I_2^-, is the intermediate of the pervanadyl–iodide–acid reaction (equation 1), which catalyzes the oxygen–iodide–acid reaction, and that it is destroyed solely by reaction with itself to form triiodide and iodide ions (equation 4).

Basis for Selection of Diiodide Ion Rather Than Atomic Iodine as the Catalytic Species.—In the derivation of equation 22 diiodide ion has been assumed to be the intermediate of the pervanadyl–iodide reaction which catalyzes the oxygen–iodide reaction. Its direct reaction with oxygen (equation 5) is considered to be the rate-determining step of the catalytic cycle. The possibility that atomic iodine, rather than diiodide ion, may be the catalytic species is not excluded since it is conceivable that it may participate in an analogous way to that assumed for diiodide ion. Also, it can be shown that the same relation between the I. F. and the concentrations of the reactants (equation 22) is obtained with atomic iodine as the catalyst, as with diiodide ion.

No reactions have been reported which may be used to identify diiodide ions in acidified aqueous solutions. However there is ample evidence that atomic iodine catalyzes a number of *cis–trans* isomerizations in non-aqueous media.[10] The catalysis of the isomerization of maleic acid to fumaric acid by atomic bromine in aqueous solutions has been demonstrated by Wachholz.[11] It is therefore to be expected that atomic iodine will act in the same way in aqueous solution.

To determine whether such catalysis does occur the following experiments were carried out. Two saturated solutions of fumaric acid (oxygen-free) were prepared, each containing maleic acid and perchloric acid (from 1 to 2 M). In addition one of the solutions contained iodine (at about 5×10^{-3} M) and the other contained the same quantity of iodine per liter along with iodide ion (from NaI)

---

[10] (a) A. Berthond and C. Urech, *Helv. Chim. Acta*, **13**, 437 (1930); (b) R. G. Dickinson and H. Lotzkar, THIS JOURNAL, **59**, 472 (1937).

[11] F. Wachholz, *Z. Elektrochem.*, **33**, 545 (1927).

at a molality considerably greater than that of the iodine. Each of these solutions was irradiated with a 300-watt incandescent lamp with reflecting back, and was kept at room temperature by passing tap water through a surrounding jacket. Periods of irradiation varied from 24 to 48 hours. A portion of each solution was kept in the dark for comparison. It was observed that (1), in the solution containing no iodide ion precipitation of fumaric acid took place shortly after irradiation began; (2), in the solution containing excess iodide no precipitation of fumaric acid occurred; and (3), no precipitation of fumaric acid occurred in either of the solutions kept in the dark.

There is ample published evidence which warrants the conclusion that the absorption of light of wave length less than about 5000 Å. produces dissociation of the iodine molecule into one normal and one activated iodine atom[12] and of the triiodide ion into a diiodide ion and an iodine atom.[13] Also the equilibrium constant of the reaction, $I^- + I^0 \rightleftarrows I_2^-$, has been estimated by Griffith, McKeown and Winn[13] to be greater than 10^4 by several powers of ten. If these conclusions are accepted it seems reasonable to infer from the above observations that (1), the iodine atoms formed by irradiation of the solutions containing iodine, in the absence of iodide, do catalyze the isomerization; (2), the iodine atoms formed in the solutions containing iodine along with an excess of iodide ion must unite practically instantaneously and quite completely with iodide ion to form diiodide ion, which does not catalyze the isomerization.

From these considerations it seems probable that the steady state concentration of iodine atoms present during the pervanadyl–iodide reaction at the concentrations of iodide used in this investigation would be so extremely low as to make the catalysis of the oxygen–iodide reaction by atomic iodine very unlikely. Nevertheless, a number of experiments were carried out in an effort to detect atomic iodine during the pervanadyl–iodine reaction. In these experiments oxygen was thoroughly excluded both from the solutions used and the system; also, the concentrations of the reactants and the order and rate of their mixing were adjusted to give most favorable conditions for producing the largest possible steady state concentrations of atomic iodine. No catalysis of the isomerization of maleic acid was detectable in any of these experiments.

On the basis of these observations and considerations it seems very probable that diiodide ion, rather than atomic iodine, is the intermediate of the pervanadyl–iodide reaction which catalyzes the oxygen–iodide reaction.

Contributory Evidence for the Catalysis of the Oxygen–Iodide Reaction by Diiodide Ion.—During this investigation it was found (as previously stated) that the oxygen–iodide reaction is greatly catalyzed during the ferric–iodide reaction in 3 *M* $HClO_4$. Also, that the concentration of iodine produced by this induction, $(I_2)_i^\infty$, is proportional to the square root of the initial concentration of ferric iron, $(Fe^{+3})_0$. It is recalled that this same linear relation between $(I_2)_i^\infty$ and $(V^{+5})_0^{1/2}$ is found to hold for the vanadium system (see equation 20). By the same reasoning as that used above for the vanadium system, it can be shown readily that this relation between $(I_2)_i$ and $(Fe^{+3})^{1/2}$ follows logically from the assumption that I_2^- is the catalyst in this case also. That diiodide ion is an intermediate of the ferric–iodide reaction is well substantiated by the results and conclusions of those who have studied the kinetics of this reaction. Wagner[14] was the first to advocate the intermediate formation of diiodide ion to account for the kinetics of the ferric–iodide reaction. Strong supporting evidence for this opinion is given by the results of his detailed study of the analogous reaction between ferricyanide ion and iodide ion. More recently Hershey and Bray[15] have made a thorough study of the kinetics of the ferric–iodide reaction and conclude that their results provide definite supporting evidence for the intermediate formation of diiodide ion. That previous investigators have not detected the induction of the oxygen–iodide reaction during the ferric–iodide reaction is attributable primarily to the low concentration of acid in the solutions that have been used.

On the basis of the previous considerations it may be predicted that under suitable conditions, the oxygen–iodide reaction will be induced (catalyzed) during those oxidations of iodide which occur with intermediate formation of diiodide ion. This prediction is predicated on the assumption that the diiodide ion, so formed, is not destroyed except by reaction with itself (see equation 4). From consideration of the findings of Taube[16] it seemed therefore probable that the oxidation of iodide ion by peroxydisulfate ion, $S_2O_8^{--}$, should induce the oxygen–iodide reaction. He showed that the $S_2O_8^{--} + I^-$ reaction induces the oxidation of oxalate ion by iodine (or triiodide) and that this induction may be satisfactorily interpreted by assuming the intermediate formation of atomic iodine (to give I_2^-), which catalyzes the oxalate–iodine reaction.

Since the rate of the $S_2O_8^{--} + I^-$ reaction is known to be independent of the concentration of hydrogen ion (at constant ionic strength)[17] it follows (to be justified later) that the catalysis of the oxygen–iodide reaction (if such occurs) should in this case be greater the larger the concentration of acid. Preliminary results have been obtained in this Laboratory by Mary A. Rotheram[18] which show that the oxygen–iodide reaction is induced (catalyzed) during the $S_2O_8^{--} + I^-$ reaction. The maximum value of the induction factor so far obtained at 25° is 16. The concentrations of the reactants at which this value of the I. F. was obtained were: $(HClO_4) = 2.92$ *M;* $(NaI) = 0.166$ *M;* $(S_2O_8^{--}) = 2.55 \times 10^{-5}$ *M* and $p_{O_2} = 750$ mm. That the induction of the oxygen–iodide reaction by the $S_2O_8^{--} + I^-$ reaction did not occur

---

[12] See E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 547 (1936).

[13] R. O. Griffith, A. McKeown and A. G. Winn, *ibid.*, **29**, 394 (1933).

[14] C. Wagner, *Z. physik. Chem.*, **113**, 269 (1924).

[15] A. V. Hershey and W. C. Bray, THIS JOURNAL, **58**, 1760 (1936).

[16] Henry Taube, *ibid.*, **64**, 161 (1942).

[17] T. S. Price, *Z. physik. Chem.*, **27**, 474 (1898).

[18] Atomic Energy Project, University of California, Los Angeles, California.

to a detectable extent in the solutions used by Taube is attributable to the low concentrations of hydrogen ion present (in no case greater than 10^{-5} *M*).

Additional evidence warranting the assumption that I_2^- catalyzes the $O_2 + I^-$ reaction is given by the results obtained by Berthoud and Nicolet[19] in their study of the kinetics of the photochemical oxidation of iodide ion by oxygen in aqueous acid solutions containing iodine (therefore I_3^-). To account for their results they assume atomic iodine formed by the photochemical dissociation of iodine molecules to be the catalyst for the $O_2 + I^-$ reaction and propose a mechanism for the catalytic cycle involving this catalyst. However, in view of the previous conclusion stated regarding the extent and rate of the reaction, $I^- + I^0 \rightarrow I_2^-$, it seems more probable that I_2^- is the catalyst. The results of Berthoud and Nicolet can be accounted for equally well by this assumption and by the catalytic cycle proposed for the vanadium system. Also Griffith, McKeown and Winn[13] have shown that the assumption that the reaction, $I_3^- + h\nu \rightarrow I_2^- + I^0$ occurs on absorption of light of wave length near 5000 Å. is necessary to account for the results obtained in their study of the photochemical oxidation of oxalate by iodine in solutions containing iodide ion. It seems therefore reasonable to conclude that the photochemical oxidation of iodide ion by oxygen in acid solutions containing iodine is primarily attributable to the catalytic effect of diiodide ion.

Further Comments on the Mechanism of the Catalytic Cycle.—It may be recalled that, in order to derive the established relation (equation 22) between the I. F. and the concentrations of the reactants, it is necessary to assume that the rate determining step of the catalytic cycle (see equation 5) is first order with respect to the H^+). This is a consequence of the facts that the rate of the pervanadyl–iodide reaction is second order with respect to the $(H^+)^5$, and that the value of I. F. is independent of the (H^+) [see results in Table II]. This assumption regarding the dependence of the rate determining step of the catalytic cycle on the (H^+) is consistent with the preliminary results obtained during this investigation with the Fe^{+++}–I^-–O_2 and the $S_2O_8^{--}$–I^-–O_2 systems. These results show that with these two systems the value of the I. F. increases with increase in the (H^+). This dependence of the I. F. on the (H^+) in these two systems follows logically from the assumption that the rate determining step of the catalytic cycle (assumed to be the same for these systems as for the vanadium system) is first order with respect to the H^+ and from the facts[14,15,17] that the rates of the inducing reactions in these two systems, namely, the $Fe^{+++} + I^-$ and the $S_2O_8^{--} + I^-$ reactions, are independent of the (H^+) at constant ionic strength.

The low steady state concentration of diiodide ion, I_2^-, makes it seem very unlikely that the rate determining step of the catalytic cycle is a trimolecular process involving this species, hydrogen ion and the oxygen molecule. This unlikelihood suggests an interesting possibility, namely, that O_2 may be sufficiently protophyllic to form the conjugate acid, HO_2^+, to an appreciable extent which reacts with I_2^- in the rate-determining step. The process involved in the catalytic cycle may then be characterized as

$$H_3O^+ + O_2 \rightleftharpoons H_2O + HO_2^+ \quad \text{(very rapidly established)}$$

$$HO_2^+ + I_2^- \longrightarrow HO_2 + I_2 \quad \text{(rate determining)}$$

$$HO_2 + I^- \longrightarrow HO_2^- + I^0 \quad \text{(very rapid)}$$

$$I^0 + I^- \rightleftharpoons I_2^- \quad \text{(very rapidly established)}$$

It is apparent that with HO_2^+ as the oxidant of I_2^- in the rate determining step, the formation of hydrogen superoxide, HO_2, as a direct product of this bimolecular (one electron exchange) process follows quite naturally. That the HO_2, so formed, would react very rapidly with I^- in a bimolecular (one electron exchange) process seems quite probable.

It may be concluded from the results of this investigation that if the O_2–I^-–H^+ reaction is induced (catalyzed) during the oxidation of I^- by another oxidant, atomic iodine (or I_2^-) is very probably formed in at least one path whereby the latter reaction occurs.

LOS ANGELES, CALIF.

---

[19] A. Berthoud and G. Nicolet, *Helv. Chim. Acta*, **10**, 475 (1927).