[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

The Simultaneous Reduction of Vanadic Acid and Oxygen by Iodide. Induced Catalysis of Oxygen Reactions

BY WILLIAM C. BRAY AND J. B. RAMSEY

The unexpected excess of iodine formed during the reduction of vanadic acid by iodide in solutions of less than 4 normal acid concentration was first shown by Edgar[1] to be due to the enhanced rate of reduction of oxygen present, and not to partial reduction of the pentavalent vanadium below the tetravalent state as supposed by earlier investigators. The equations of the two reactions occurring simultaneously may be written

$$2HVO_3 + 3KI + 3H_2SO_4 = 2VOSO_4 + KI_3 + K_2SO_4 + 4H_2O \qquad (1)$$
$$O_2 + 6KI + 2H_2SO_4 = 2KI_3 + 2K_2SO_4 + 2H_2O \qquad (2)$$

In some preliminary experiments carried out during a study of the iodimetric determination of vanadium[2] it was found possible to vary this excess of iodine from one to three hundred per cent.

The nomenclature adopted in the study of such "coupled" or "induced" reactions has been fully discussed by Luther and Schilow.[3] The "induction factor" for the vanadic acid–oxygen reduction is defined by the relation

$$\text{Induction factor} = \frac{O_2\text{ reduced, equivalents/liter}}{HVO_3\text{ reduced, equivalents/liter}}$$

All such "coupled" reactions have been shown by these authors[3] to be grouped in two general classes which may be distinguished experimentally by the way in which the induction factor changes with a variation in the initial concentrations of the reactants, and particularly by its magnitude when the experimental conditions are made more and more favorable for the induced reaction. In the present example, as the initial concentration of oxygen relative to that of vanadic acid, $(O_2)/(HVO_3)$, is increased, the induction factor will either increase without limit, Class 1, or will approach as a limit a definite small value such as 1 or 2 or $\frac{1}{2}$, Class 2. Luther and Schilow designated these classes as (1) "catalysis with destruction of the catalyst" and (2) "coupling due to a single intermediate compound." We have adopted the shorter and more empirical terms, (1) "induced catalysis" and (2) "simple coupling."

At present there is no basis for predicting the class to which a given pair of coupled reactions belongs. It has been the purpose of this investigation to determine whether the simultaneous reduction of vanadic acid and oxygen by iodide is a case of induced catalysis or of simple coupling.

Experimental Procedure

The solutions of $NaVO_3$ and $Na_2S_2O_3$ were made up approximately 0.1 *N* and

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(1) Edgar, THIS JOURNAL, **38**, 2369 (1916).

(2) Ramsey, (a) *ibid.*, **49**, 1138 (1927); (b) Thesis, University of California, September, 1923.

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

standardized as described elsewhere.[2,a] The sulfuric acid solutions were standardized in the usual manner with sodium carbonate. All chemicals used were of C. P. grade.

In each experiment 350 cc. of a solution containing a known quantity of vanadate and sulfuric acid was prepared in one-liter, round-bottomed short-necked flasks, provided with a mercury-sealed stirrer, an outlet and inlet tube for air or oxygen, and an opening for removing portions for analysis. This solution and 0.4 N potassium iodide, to be added later, were well stirred in contact with air or oxygen for at least one-half hour before mixing. In order that the time required for adding the 50 cc. of potassium iodide solution might be as short as possible relative to the time required for complete reduction of the vanadic acid, it was added from a pipet calibrated for delivering in less than six seconds. The solutions were kept in a thermostat maintained at 25 ± 0.01° during saturation with air or oxygen and during the reaction.

After addition of the potassium iodide solution, 50-cc. portions were pipetted from each solution, at intervals extending over a period of two to six hours, and added to sufficient water to prevent further reaction during the time necessary to determine the free iodine by titration with standard thiosulfate. Approximately 0.01 N sodium thiosulfate was used, always freshly prepared from the 0.1 N stock solution. The titration results, expressed in milliequivalents of iodine per liter of solution, were plotted against the time in minutes after the addition of the potassium iodide solution. The rate of oxidation of iodide by oxygen in the absence of vanadic acid was determined simultaneously in the same way at the same concentrations of sulfuric acid and iodide.

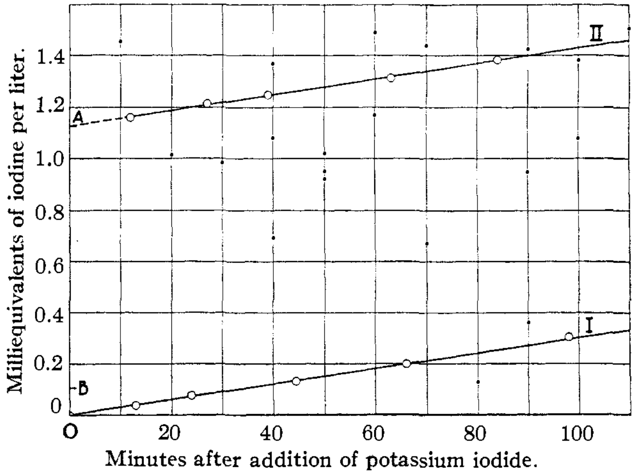


Fig. 1.—Curve II, (H_2SO_4), 3.00 N; (KI), 0.050 N; (HVO_3), 0.1034 millimole/liter. Expt. 3d, Table I. Curve I, same as for Curve II except without HVO_3.

The results of a typical experiment are shown in Fig. 1 to illustrate the method of determining the induction factor. Under all conditions used in this investigation the rate of the oxygen–iodide reaction, in the dark, in the presence of tetravalent vanadium and triiodide formed during reduction of vanadic acid (Curve II) is the same as that in the absence of vanadium (Curve I). In a few cases, at the lowest sulfuric acid concentration, the first two or three 50-cc. portions were removed and analyzed before the vanadic acid was completely reduced. The curve obtained rose steeply from the origin and soon became coincident with the straight line. In order therefore to determine the number of milliequivalents of iodine per liter formed due to the presence of vanadic acid, Curve II is extrapolated to intersect the Y-axis. Correction is thus made for the relatively slow liberation of iodine in the given solution which occurs during and after the reduction of the vanadic acid. The intercept, OA, represents the total quantity of iodine formed per liter during reduction of the vanadic acid, and OB the amount equivalent to the vanadic acid used. The difference, AB, is a measure of the induced reaction, and the ratio, AB/OB, is the induction factor. Its value for the experiment represented is 9.9 ± 0.1.

Results

Representative results are given in Table I. The induction factors (given in the last column) were shown to be reproducible within the estimated limits, with a single set of stock solutions, by repeating several of the experiments. The results were also not changed appreciably by increasing the rate of stirring to five times the normal rate, nor by adding the vanadic acid last instead of the potassium iodide (in a duplicate of Expt. 2d). The solutions were saturated with air in experiments 1a–6a, and with oxygen at atmospheric pressure in the three other groups of experiments, b, c and d. The actual concentrations of oxygen were calculated by assuming that the value with air is one-fifth the solubility of oxygen, and that the latter value depends only on the concentration of

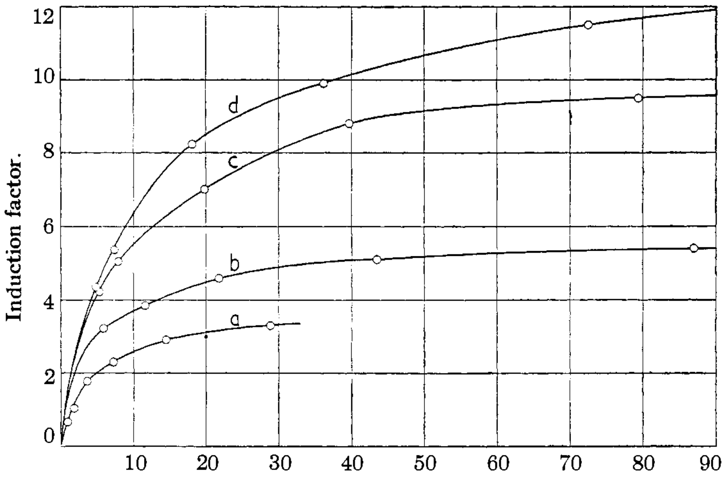
TABLE I

EXPERIMENTAL DATA

Expt.	H_2SO_4, eq./l.	Iodide moles/l.	HVO_3 milli-moles/l.	$\frac{(O_2)}{(HVO_3)_0}$	Iodine formed millieq./l.	Oxygen reduced millieq./l.	Induction factor
1a	3.00	0.050	0.0259	28.9	0.112	0.086	3.3 ± 0.5
2a	3.00	.050	.0517	14.5	.200	.149	2.9 ± .2
3a	3.00	.050	.1034	7.2	.346	.243	2.3 ± .1
4a	3.00	.050	.2068	3.6	.573	.366	1.77 ± .05
5a	3.00	.050	.4120	1.8	.837	.425	1.03 ± .02
6a	3.00	.050	.8250	0.9	1.373	.548	0.66 ± .01
1b	1.00	.050	.0259	174.0	0.178	.152	5.9 ± .4
2b	1.00	.050	.0517	87.0	.333	.281	5.4 ± .2
3b	1.00	.050	.1034	43.5	.634	.531	5.1 ± .1
4b	1.00	.050	.2068	21.8	1.155	.948	4.60 ± .05
5b	1.00	.050	.3877	11.6	1.883	1.495	3.85 ± .03
6b	1.00	.050	.7755	5.8	3.266	2.490	3.21 ± .01
1c	2.00	.050	.0259	158.8	0.288	0.262	10.1 ± .4
2c	2.00	.050	.0517	79.4	.545	.493	9.5 ± .2
3c	2.00	.050	.1034	39.7	1.011	.908	8.8 ± .1
4c	2.00	.050	.2068	19.9	1.645	1.447	7.00 ± .05
5c	2.00	.050	.5170	7.9	3.118	2.601	5.03 ± .02
6c	2.00	.050	.7755	5.3	4.059	3.283	4.23 ± .01
1d	3.00	.050	.0259	144.9	0.339	0.313	12.1 ± .4
2d	3.00	.050	.0517	72.5	.646	.594	11.5 ± .2
3d	3.00	.050	.1034	36.2	1.127	1.024	9.9 ± .1
4d	3.00	.050	.2068	18.1	1.909	1.702	8.22 ± .05
5d	3.00	.050	.5170	7.3	3.299	2.782	5.38 ± .02
6d	3.00	.050	.7755	4.8	4.160	3.384	4.36 ± .01

the sulfuric acid.[4] The results given in the fifth column of Table I are the values of the ratio of the concentration of oxygen to the initial concentration of vanadic acid, $(O_2)/(HVO_3)$, each expressed in equivalents per liter.

Each curve in Fig. 2 shows the variation in the induction factor with the concentration-ratio, $(O_2)/(HVO_3)_0$, at constant concentrations of oxygen, sulfuric acid and initial potassium iodide. For a given value of this concentration-ratio, the induction factor increases more than two-fold with a five-fold increase in the concentration of oxygen (Curves a and d), and increases also as the concentration of sulfuric acid is raised from 1 to 3 *N* (Curves b, c and d). The latter increase was found not to continue when the acid concentration was raised to 4.8 *N*. The presence of +4 vanadium salts was shown to have little or no effect by pairs of experiments in which the initial concentrations were, respectively, zero and equal to that of the vanadic acid; these experiments were similar to 2b, 3b, 4b and 1d. In other experiments the concentration of iodide, the reducing agent, was varied within the range 0.01 to 0.10 *M:* a five-fold increase had but little effect in 3 *N* acid, but caused a more than two-fold increase in the induction factor in 1 *N* acid solutions.



Ratio milliequivalents of O_2 per liter/milliequivalents of HVO_3 per liter, $(O_2)/(HVO_3)_0$.

Fig. 2.—Curves a, b, c, and d, correspond to Expts. a, b, c, and d, in Table I.

It is evident from these results that the simultaneous reduction of vanadic acid and oxygen by iodide in acid solutions is a case of "induced catalysis" and not a case of "simple coupling," since the induction factor increases without limit as the concentration ratio, $(O_2)/(HVO_3)_0$, is in-

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(4) The results of Geffcken, *Z. physik. Chem.*, **49**, 257 (1904), show that at 25° and 1 atm. pressure the solubility of oxygen ranges from 4.499 milliequivalents per liter in 1 *N* sulfuric acid to 3.746 in 3 *N* sulfuric acid.

creased. In the course of our experiments the induction factor has been raised from 0.01 to approximately 12, and it is certain that still higher values could be obtained.

Induced Catalysis of Oxygen Reactions[5]

Some time after the conclusion stated above was reached in our first experiments,[2b] we discovered that Lenssen and Löwenthal,[6] in 1862, in a paper entitled "Zur Katalyse des Sauerstoffs," had demonstrated the catalytic character of several induced oxygen reactions. The term "induced reaction," it may be noted, did not come into general use until a year later, when Kessler[7] published his well-known paper on induced reactions. One of Kessler's classes of examples involved one reducing agent and two oxidizing agents. In his list of this class the only induced reaction is the reduction of oxygen, and all but one of the examples cited had been studied by Lenssen and Löwenthal. Kessler, of course, had no intention of denying that some or all of these oxygen reactions might be catalytic.[8]

The investigation of Lenssen and Löwenthal[6] had its origin in a study of the error observed in the volumetric determination of tin based on the oxidation of stannous salts.[9,10] They continued the experiments of Löwenthal[10] on the amount of the oxygen error obtained under different experimental conditions during the oxidation of stannous chloride by dichromate. They stressed the fact that, while a small quantity of dichromate is being rapidly reduced by stannous chloride or sulfurous acid in an acid solution which contains dissolved air, the amount of the reducing agent oxidized by oxygen is several times that oxidized by dichromate. They did not list the value of this ratio, which we now call the "induction factor," but it may be calculated from their data.

Their results with stannous chloride and potassium dichromate prove that the induction factor increases rather rapidly as the initial concentration of the reducing agent is increased or that of the oxidizing agent ($K_2Cr_2O_7$) is diminished. A three-fold change in the concentration of hydrochloric acid had but little effect, and a decrease of the induction factor with decreasing concentration of oxygen was indicated. The analogy with the iodide-vanadic acid results in Table I is evident, and is illustrated by four experiments described on page 202. In each of these, about 1 liter

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(5) Much of the material presented in this section was discussed in a paper read at Pasadena, June, 1931. *Cf.* the report of the symposium on Reaction Mechanism, *Science*, **74**, 113 (1931).

(6) Lenssen and Löwenthal, *J. prakt. Chem.*, **86**, 193–215 (1862).

(7) Kessler, *Pogg. Ann.*, **195**, 218–247 (1863).

(8) *Cf.* Skrabal, *Sammlung Chemischer Vorträge*, **13**, 321 (1908).

(9) Kessler, *Pogg. Ann.*, **172**, 332–339 (1855), proved that the oxygen dissolved in the water used is responsible for the error observed when stannous chloride is oxidized by potassium dichromate in the presence of hydrochloric acid.

(10) Löwenthal, *J. prakt. Chem.*, **76**, 484–497 (1858), showed that the oxygen error is zero or very small when ferric chloride in excess is added to the stannous chloride solution before titration with potassium dichromate or potassium permanganate.

of a very dilute potassium dichromate solution in 0.06 *M* hydrochloric acid saturated with air was titrated with stannous chloride with an outside indicator: the values of the induction factor (which we have calculated) were 6, 9, 19 and 23 when the quantities of potassium dichromate were 3.3, 1.7, 0.67 and 0.33 × 10^{-5} mole, respectively. The already high value of the induction factor in the last expression, 23, was increased to 57 when 106 × 10^{-5} mole of stannous chloride was added rapidly, and the excess stannous salt determined by analysis of the resulting solution.

Lenssen and Löwenthal extended their investigation to include other combinations of reducing and oxidizing agents, and obtained the results summarized in Table II. Two of the stannous chloride–potassium dichromate experiments described above are also listed. In each experiment in IIA the reducing agent, R, and the oxidizing agent, O_α, were allowed to react in a large volume of solution which contained hydrochloric acid and dissolved air. R was the last reagent added in the first, second and eighth experiments, O_α in the remaining five. We have calculated the number of moles of R and O_α initially present, and the induction factor, (R oxidized by O_2)/(R oxidized by O_α).

TABLE II

EXPERIMENTAL RESULTS OF LENSSEN AND LÖWENTHAL

A. The reaction O_2 + R is induced by O_α + R

R, moles × 10^{-5}		O_α, moles × 10^{-5}		Final vol., cc.	HCl mole/l.	Induction factor
$SnCl_2$	24	$K_2Cr_2O_7$	0.33	1015	0.06	23
	106	$K_2Cr_2O_7$	.33	1032	.07	57
	91	$KMnO_4$	6.2	1055	.12	4.5
	50	O_3	1.5	1035	.15	27
	91	H_2O_2	27	1050	.12	0.7
	450	ClO_2	64	1705	.09	1.3
H_2SO_3	28	$K_2Cr_2O_7$	0.67	1075	.14	10
	41(?)	$KMnO_4$	5	1050	.12	1(?)

B. Negative results in dilute hydrochloric acid solutions

R	O_α
$SnCl_2$	$FeCl_3$ (*cf.* Ref. 10), Cl_2, Br_2, I_2 at low concn. of KI, CuCl
H_2SO_3	H_2O_2, O_3, ClO_2, Cl_2, Br_2, I_2
H_2S	$KMnO_4$, ClO_2, Cl_2
$FeCl_2$	$KMnO_4$, $K_2Cr_2O_7$. *Cf.* Refs. 9 and 10

We may accept the conclusion of these investigators that the six additional examples are analogous to the stannous chloride–potassium dichromate case. It is nearly certain, even though it has not been proved experimentally, that values of the induction factor still higher than those shown in IIA could be obtained by altering the concentrations of R, O_α and O_2 in the manner outlined above.

One other factor must be considered when the reaction between R and O_α is very rapid, namely, variation in the method of mixing the reagents.

When under the conditions of the experiments the reduction of O_α by R is so slow that but little reaction occurs during the time consumed in mixing the reagents, then it will make no difference whether R or O_α is added last, since the concentrations during reaction will be the same in both experiments. This case was realized in our work with the iodide–vanadic acid system (Table I). On the other hand, if much of the reaction between R and O_α takes place during the mixing, then we may expect to obtain higher induction factors by adding the O_α solution last, by adding this solution slowly, and by stirring the mixture vigorously during this addition, for these conditions ensure higher values of the O_2/O_α ratio during the reaction. Also a high initial concentration of R (or a high local concentration if R is added last) may be expected to increase the induction factor.

These predictions have recently been verified by numerous stannous chloride–potassium dichromate experiments, which were initiated to check the work of Lenssen and Löwenthal, and which included experiments with oxygen gas, as well as control tests of the stannous chloride–oxygen reaction in the absence of dichromate. When allowance is made for the large mixing effect our results are in satisfactory agreement with those of Lenssen and Löwenthal.

Another illustration of a mixing effect which may be correlated with a high rate of the reaction between R and O_α is furnished by the observation of Bray and Miller[11] that, in the reaction between I^- and $Cr_2O_7^=$ in 0.6 *M* hydrochloric acid containing dissolved air, the oxygen error is increased from less than 0.1% to over 0.4% when the dichromate solution is added last instead of the iodide. The explanation suggested at the time is incorrect, and may now be replaced by the statement that the induced catalysis of the I^-–O_2 reaction in 0.6 *M* hydrochloric acid is not negligible when the concentration of $Cr_2O_7^=$ is very small. Still another illustration of a mixing effect is mentioned in Footnote 13.

Two remarkable examples of induced oxygen reactions are described in detail in one[12] of Bäckström's papers on chain reactions of oxygen: R is $SO_3^=$ and O_α is $S_2O_8^=$ or H_2O_2. Bäckström determined in each experiment the increase in the amount of oxygen absorbed due to the presence of peroxysulfate or hydrogen peroxide. The ratio of this quantity of oxygen (in moles) to the number of moles of O_α used, which is listed on page 30, is half the induction factor, ($SO_3^=$ oxidized by O_2)/($SO_3^=$ oxidized by O_α).

TABLE III

EXPERIMENTAL RESULTS OF BÄCKSTRÖM

O_α	$K_2S_2O_8$				H_2O_2			
Moles × 10^{-5}/l.	100	5	1	0.2	1120	50	10	5
Induction factor	65	430	990	1400	1.3	19	44	48

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(11) Bray and Miller, THIS JOURNAL, **46**, 2209 (1924).

(12) Bäckström, *Medd. Vetenskapsakad. Nobelinst.*, **6**, No. 16 (1927).

The range of the results and the high values of the induction factor at low initial concentration of O_α are shown in Table III.

When the induction factor is plotted against the concentration ratio, O_2/O_α, the curves obtained are similar in shape to those shown in Fig. 2. It is evident that these results differ only in degree and not in kind from our own and those of Lenssen and Löwenthal. In comparing the data in Tables II and III, it should be noted that the experimental conditions chosen by Bäckström were especially favorable for the induced reaction: high concentration of $SO_3^=$ (0.59 *M* sodium sulfite, 0.01 *M* sodium bisulfite and 0.01 *M* mannite), low concentration of O_α, the use of oxygen instead of air, vigorous shaking and the method of mixing the solutions.

It seems safe to conclude, even though the data are rather meager, that many other examples of this type of induced catalysis will be found; that under more favorable conditions positive results may be obtained in some of the examples listed in Table IIB, such as sulfurous acid with hydrogen peroxide or ozone; that the oxidizing agents, $S_2O_8^=$, $Cr_2O_7^=$, HVO_3, MnO_4^-, O_3, H_2O_2 and ClO_2, during reaction with certain reducing agents in acid solution, have the power of inducing the reduction of oxygen; and that the amount of this induced catalysis obtained with various reducing agents usually decreases in the order[13] $SO_3^=$, $SnCl_2$, H_2SO_3 and I^-. It is of interest that the results in acid solution have been negative when the oxidizing agent is Cl_2, Br_2 or $FeCl_3$ and also when the reducing agent is Fe^{++}. The reactions are highly specific with respect to O_α and R. They may also vary greatly with the concentration of hydrogen ion.

The empirical term "induced catalysis" merely states that under favorable conditions several molecules of R react with oxygen while one is reacting with O_α; and leaves it an open question whether the reaction $R + O_2$ (1) is catalyzed by O_α or its derivatives; or (2) is "self-catalytic" when once it is started, *i. e.*, is a chain reaction. Recent evidence[14] that many oxygen reactions are chain reactions is so conclusive that we need not question this explanation. On the other hand, when we attempt to apply the first theory, that O_α is a true catalyst, serious difficulties are encountered in several instances: thus we have been unable to formulate satisfactory mechanisms to provide for the regeneration of ozone in the stannous chloride–ozone example. Also Bäckström's evidence[12] that the $SO_3^= + O_2$ reaction is a chain reaction is unassailable. Accordingly, if the results for this group of analogous reactions are to be explained by a single theory, it seems necessary to assume that the reaction $R + O_2$

[13] This order for $SO_3^=$ and H_2SO_3 is confirmed by the results obtained by Lenssen and Löwenthal (Ref. 6, p. 209) in titrating sulfurous acid with *iodine;* the oxygen error was zero in acid solution and over 11% in the presence of bicarbonate. This oxygen error may also be eliminated by adding the sulfite slowly to a solution which contains I_3^- in excess (a change in the order of mixing), or by the presence of a negative catalyst; *cf.* Kolthoff and Furman, "Volumetric Analysis," Vol. II, p. 399 (1929); Kurtenacker and Wollak, *Z. anorg. Chem.*, **161**, 201 (1927).

[14] Milas, *Chem. Rev.*, **10**, 295–364 (1932).

is a chain reaction, and that chains are started during the reaction between R and O_α.

The conclusion of Lenssen and Löwenthal, on page 194, that these oxygen reactions are comparable only with the "combustion of an explosive mixture," is not without resemblance to the one that we have drawn. It is also remarkable that these investigators discovered and studied an example of negative catalysis, namely, the retarding effect of hydriodic acid on the reaction between oxygen and stannous chloride in the presence of potassium dichromate. They stated that this "mysterious" effect could not be due to the destruction of the oxidizing agent by the hydriodic acid, "for this effect is greatest when so little chromic acid is present that interaction with hydriodic acid is almost impossible" (p. 201). We have confirmed their result.

Induced oxygen reactions of the other class listed by Kessler,[7] in which oxygen reacts with two reducing agents, have attracted the attention of many investigators.[15] In this type the reaction between oxygen and **R** is induced during the reaction between oxygen and R_α. As a result of early investigations, it seems to have been assumed for many years that the induction factor would never exceed unity. This "simple coupling" was interpreted as evidence for the formation of an intermediate peroxy compound, and its reduction, under favorable conditions, by R instead of by R_α. However, two examples of induced catalysis have been discovered in Wieland's laboratory.[16] The oxidation of hypophosphorous acid is induced during the reaction between O_2 and Fe^{++}; and the induction factor rises to over 11.5 when the concentration-ratio, $(H_3PO_2)/(Fe^{++})$, is very large. (Even higher values are stated to have been obtained when tartaric acid is used instead of H_3PO_2.) Recently Richter[16b] has found that the induction factor is lowered by the presence of typical negative catalysts, and has concluded that the reaction between O_2 and H_3PO_2 is a chain reaction. The specific character of these reactions may be again illustrated by citing the proof of Manchot and Schmid[17] that, when arsenious acid is substituted for hypophosphorous acid, the limiting value of the induction factor is unity.

Conclusion and Summary

When certain oxidation-reduction reactions take place in aqueous solution, a reaction is induced between dissolved oxygen and the reducing agent. The results are highly specific with respect to the reducing and oxidizing agents, R and O_α. Whenever an induced oxygen reaction of this type has been studied in detail, the induction factor, (R oxidized by O_2)/(R oxidized by O_α), has been found to increase without limit as the

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(15) (a) *Cf.* Ref. 14, p. 323; (b) Engler and Weissberg, "Autoxydation," Braunschweig, 1904.

(16) (a) Wieland and Franke, *Ann.*, **464**, 101–226 (1918); (b) Richter, *Ber.*, **64B**, 1240–1243 (1931).

(17) Manchot and Schmid, *ibid.*, **65B**, 98 (1932).

experimental conditions are made more and more favorable for the induced reaction. These have accordingly been classed as examples of "induced catalysis," rather than as examples of "simple coupling." The results support the theory that oxygen reactions in general are chain reactions.

In a systematic investigation of the amount of the reaction between oxygen and iodide ion (R) which is induced during the reduction of vanadic acid (O_α) in acid solution, the induction factor has been raised from 0.01 to 12. Evidence that this is a case of induced catalysis is presented in Table I and Fig. 2.

Bäckström in 1927 studied the induced reaction between oxygen and sulfite ion under favorable conditions. His results show that induction factors as high as 48 and 1400 were attained when the oxidizing agents were hydrogen peroxide and peroxysulfate ion, respectively (Table III).

Credit for the discovery of induced catalysis belongs to Lenssen and Löwenthal, who in 1862 studied in detail the induced reaction between oxygen and stannous chloride in acid solution when the oxidizing agent was dichromate ion. They extended their investigation to include many other combinations of reducing and oxidizing agents (Table II).

In cases in which the reaction between oxygen and a reducing agent is induced while oxygen is reacting with a second more reactive reducing agent, examples of both simple coupling and induced catalysis are known.

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Influence of Temperature on Certain Properties of Zirconium Oxide Sols

BY FRANCIS J. ROBINSON AND GILBERT H. AYRES

According to the method of preparation, zirconium oxide or hydroxide hydrosols have been found to show large variations in their properties as evidenced by the variety of sols, including so-called "ortho" and "meta" forms, described in the literature.[1] In this investigation the flocculation values, relative viscosities, *P*H values and intensities of scattered light of zirconium oxide sols which had been heated to temperatures ranging from 100 to 273° were determined.

Ayres and Sorum[2] have shown that the viscosities of pure ferric oxide sols which had been heated to temperatures above 100° decreased with

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(1) Gmelin and Kraut, "Handbuch der anorganischen Chemie," Vol. VI (1), p. 698; Mellor, "A Comprehensive Treatise on Inorganic Chemistry," Longmans, Green and Co., New York, 1927, pp. 129–134; Weiser, "The Hydrous Oxides," McGraw-Hill Book Co., Inc., New York, 1926, pp. 241–244.

(2) Ayres and Sorum, *J. Phys. Chem.*, **34**, 875, 2629, 2826 (1930).