

among the widely varying results of different authors. It has been shown that treatment of the reaction as a Nernst chain, starting on the walls by a dissociation of chlorine molecules and ending by a reversal of that process will explain most of the experimental data.

The chain length in the thermal reaction at

200° has been calculated to be about 10^4 as contrasted with 10^6 in the photochemical reaction at room temperature. This explains the comparatively slight inhibition of the thermal reaction by oxygen as compared with the retardation in the photochemical reaction.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Nature of Aluminum Oxyiodide Hydrosols as Revealed by their Action on Hydrogen Peroxide

BY ARTHUR W. THOMAS AND BENJAMIN COHEN

In a previous paper¹ evidence was submitted showing that iodide which is bound to basic aluminum micelles in "aluminum oxide" hydrosols is several times more reactive in catalyzing the decomposition of hydrogen peroxide than free iodide ion. Thus there is available a technique which can be used to investigate qualitatively the iodo group \rightleftharpoons iodide ion equilibrium of these colloidal systems. Utilizing the technique and hydrosols previously described¹ some information has been obtained concerning this equilibrium and thus of the nature of the micelles under certain conditions.

Effect of Dilution of Sols upon Decomposition of Hydrogen Peroxide.—Since addition of water should shift the reaction iodo group \rightleftharpoons iodide ion to the right, one would expect a diminution of the velocity constant (calculated to original concentration) upon dilution of the hydrosol.

Sols were diluted with water and were permitted to stand in a thermostat at 25° overnight. In Table I are given the results obtained with two sols.² K (calcd.) was obtained by multiplying the velocity constant of the original sol by the concentration of sol used for the particular experiment. It is seen that as the sol is diluted the

difference between K (calcd.) and K (obsd.) becomes greater. Correction for the effect of water on the decomposition of hydrogen peroxide would tend to make this difference still larger.

Effect of Addition of Potassium Iodide to Sols.—Five cc. of the appropriate potassium iodide solution was added to 95 cc. of sol 3, and the mixture was kept in the thermostat overnight; 5 cc. of hydrogen peroxide was added to start the reaction. The results are recorded in Table II. K (calcd.) was obtained by assuming the catalytic effect of the added potassium iodide was purely additive.

TABLE II
EFFECT OF ADDED POTASSIUM IODIDE ON THE CATALYTIC ACTIVITY OF SOL 3

Final normality of KI $\times 10^4$	K (obsd.) $\times 10^4$	K (calcd.) $\times 10^4$
0	8.11	...
0.95	9.54	9.43
2.85	12.8	12.1
4.75	15.7	14.7

A similar result was obtained with Sol 8 where the velocity constant ($\times 10^3$) in the presence of 0.009 *N* potassium iodide was 4.81 as compared to the additively calculated value of 4.65.

These results indicate that for the concentration of potassium iodide used, a relatively small part of the added iodide becomes bound to the micelles. This small difference between K (obsd.) and K (calcd.) suggested the following experiment. Sol 5 was made at room temperature by permitting a dilute solution of hydriodic acid to react with an excess of hydrous alumina for a week, at the end of which time the resulting sol was centrifuged and dialyzed. Its velocity constant was found to be $5.7 \times 10^{-5} \text{ min.}^{-1}$ as compared to 5.6×10^{-5}

TABLE I

EFFECT OF DILUTION UPON VELOCITY CONSTANTS OF SOLS

Concn. of sol	Sol 1		Sol 2	
	K (obsd.) $\times 10^4$	K (calcd.) $\times 10^4$	K (obsd.) $\times 10^4$	K (calcd.) $\times 10^4$
1.0	7.84	...	4.29	...
0.75	5.79	5.88	2.93	3.22
.50	3.86	3.92	1.78	2.15
.33	2.18	2.61
.25	0.73	1.07

(1) A. W. Thomas and B. Cohen, *THIS JOURNAL*, **59**, 268 (1937).

(2) The sols are described in Table I of ref. 1.

min.⁻¹, calculated on the basis that the total iodide was unbound.³ Thus it would appear that the micelles of this sol prepared by the action of dilute hydriodic acid at room temperature contained very few iodo groups.

Effect of Aging of the Sols.—The data in Table III show a small but still a definite decrease in the velocity constants upon aging of the hydrosols at room temperature. This is interpreted to show that part of the iodo groups are converted to iodide ions upon aging.

TABLE III
EFFECT OF AGING OF SOL ON VELOCITY CONSTANT

Sol	Fresh sol velocity constant $\times 10^4$	Aged sol	
		Days of aging at room temp.	Velocity constant $\times 10^4$
2	4.29	2	4.12
3	8.40	3	8.11
4	77.4	4	73.2
8	35.9	7	35.3

The effect of aging can be intensified by heating, which was done in the case of Sol 6. This sol was heated at 95° for twenty-two days when the measurements recorded in Table IV were made. The iodide ion activities were determined by means of the silver-silver iodide electrode.⁴

Table IV shows (1) that the a_{H^+} and a_{I^-} are increased appreciably upon heating and (2) that the a_{H^+} and a_{I^-} of the heated sol diminish upon subsequent aging at room temperature. The information regarding the changes in pH resulting upon aging has been submitted previously from this Laboratory; this is the first instance, however, for it to be recorded for the "contra-ion."

TABLE IV
CHANGE OF pH AND IODIDE ION ACTIVITY^a OF A PREVIOUSLY HEATED SOL^b

Age in days at room temp.	pH	$a_{I^-} \times 10^3$
0	4.02	1.37
3	4.09	1.26
14	4.21	1.04

^a a_{I^-} was determined by use of the silver-silver iodide electrode. ^b Immediately before the heat treatment, the pH and a_{I^-} of the original sol were 5.69 and 0.79×10^{-3} , respectively.

Discussion

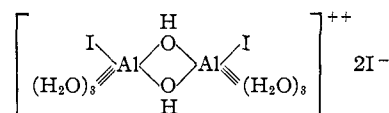
Iodide that is bound to a colloidal particle has been pictured to form an adsorbed layer of ions about the particle with an occasional halide ion embedded in the particle. Another picture is

(3) The value of 1.53 min.^{-1} was used for K^0 , the specific constant.

(4) Owing to the relatively low pH value of this heat-treated sol, catalytic experiments were avoided (because of the appreciable oxidation of I^- to I_2 by the H_2O_2).¹

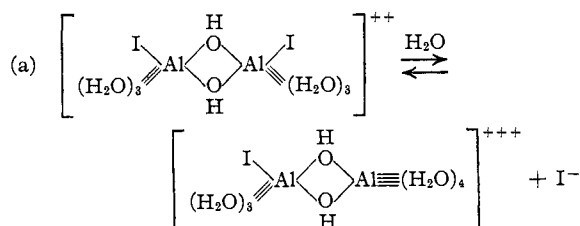
that given by an extension of the Werner-Pfeiffer theory of olation and Stiasny's postulate of oxolation to colloidal metallic oxides. In this latter picture the chemical nature of the bound iodide is altered; it is held coordinately to the metallic ion as iodo groups.

This postulation, that colloidal oxides are polynuclear complexes having properties similar to those for corresponding crystalloidal complexes has been used successfully in this Laboratory in explaining the behavior of several metallic oxy salt hydrosols. This theory accounts for the fact that the order of effectiveness of salts in increasing the pH values of highly basic metallic oxy salt sols is identical with that for the crystalloidal complexes of low degree of basicity. This order is essentially the same for the complex forming ability of those added salts. A dinuclear aluminum complex containing iodo groups may be schematically represented as

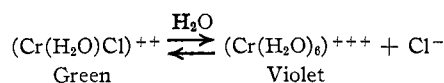


Some hydroxo groups also may be presented in a similar polynuclear complex. If one accepts the view that bound iodide exists in the form of iodo groups as pictured above, then the addition of anions should effect displacement of iodo groups to iodide ions and thus lower the catalytic activity of the hydrosol. Furthermore, one would expect the better the complex forming ability of the added anion, the more iodo groups should be displaced (if the coordination number of the aluminum is to remain constant). This should give the following order for the effectiveness in decreasing the catalytic activity of a sol, tartrate > sulfate > acetate > nitrate > water. This has been found to be the case and it is the order also for effectiveness in increasing the pH value of aluminum oxy salt hydrosols.

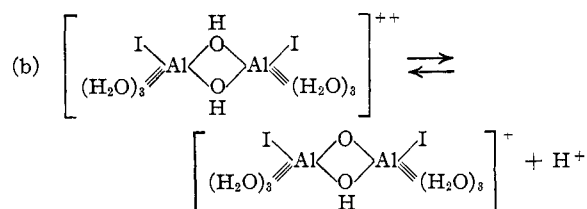
The decrease of catalytic effect of aged sols can be ascribed to the conversion of iodo groups to iodide ions according to the reaction type



which is similar to the reaction



Inasmuch as heating these sols greatly favors oxolation the following type of reaction must be considered



Allowing the heated sol to stand at room temperature should cause a reversal in (b) which was actually observed (Table IV) and has been reported before from this Laboratory. It is seen also that heating caused reaction (a) to go to the right, with reversal on subsequent aging at room temperature.

When the results recorded in this paper are reviewed in the light of the nature of the sols described in the previous paper,¹ it seems that increased concentration and elevation of temperature of preparation of aluminum oxyiodide sol favors the formation of bound iodide.⁵ Excessive

(5) In this connection one may cite the case⁶ of $\text{Cr}(\text{H}_2\text{O})_2\text{Cl}_3$ or $\text{Cr}(\text{H}_2\text{O})_5(\text{SO}_4)_2$ where boiling causes the anions to enter the complex. High concentration also favors this reaction.

(6) Stiasny, "Gerbereichemie (Chromgerbung)," Verlag Theodor Steinkopff, Dresden, Germany, 1931.

heating, however, tends to make the hydrous alumina less reactive toward the peptizing agent, hydriodic acid, thus causing less iodide to be bound.

Thus one can account for the fact that Sol 5 made at room temperature had the smallest promotion factor while Sol 4 made at 90° had the largest promotion factor. The cases of Sols 1 and 2 are of interest in this respect. Sol 1 had a smaller catalytic effect than Sol 3 although the latter sol had less iodide in the system. Sol 1 was prepared by boiling for twelve hours whereas Sol 4 was boiled for seven hours.

Summary

It has been shown by means of the catalytic decomposition of hydrogen peroxide by aluminum oxyiodide sol that: 1, water molecules can displace bound iodide; 2, addition of potassium iodide to a sol or the preparation of a sol in the cold causes relatively small amounts of iodide to become bound; 3, aging of a sol at room temperature causes part of the bound iodide to become unbound. This last effect can be made very noticeable upon heating the sol and using silver-silver iodide electrodes to measure the iodide ion activity.

An explanation of these results has been given based on the assumption that the micelles are polyolated and polyoxolated structures.

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The Energy of Activation of Enzyme Reactions, and their Velocity below 0°

BY HANS LINEWEAVER

Chemical changes suffered by biological material in cold storage are due chiefly to the intervention of microorganisms, and to the reactions catalyzed by inherent tissue enzymes. The former effects may be minimized, perhaps eliminated, by proper handling or treatment; the latter cannot be avoided without considerable injury to the tissues. This paper outlines certain conclusions reached by a study of the effects of low temperatures on these changes which are due to the ever-present enzymic factor.

Comparison of Enzymic and Non-Enzymic Catalysis.—The empirical Arrhenius equation,¹ $\ln k = -\mu/RT + C$, relating temperature, T , and reaction velocity, k , is suitable for the calculation and comparison of the changes in the velocities of many enzymic and non-enzymic reactions as the temperature is lowered. Consideration of the justifications and limitations of this pro-

(1) Stearn [*Ergeb. Enzymforsch.*, **7**, 1 (1938)] has used a different equation in connection with mechanism considerations, but extrapolations with either equation over the short temperature ranges to be used in this paper would lead to practically the same results.