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Catalytic Decomposition of Hydrogen Peroxide by Basic Beryllium Iodide Hydrosols

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In a previous paper¹ it was shown that iodide ions in the presence of colloidal hydrous alumina had a catalytic effect several times greater than that for iodide ions in crystalloidal solutions. Upon the addition of certain potassium salts to the colloidal solution a velocity constant was obtained which indicated that the total iodide of the system was in simple ionic form, having the same specific velocity constant as found by other investigators.² The purpose of the present research was to investigate the catalytic activity of iodide ions when bound to beryllium oxide micelles under various conditions. This oxide was chosen because like colloidal alumina the metallic oxide itself has a negligible catalytic effect upon hydrogen peroxide, moreover, the pH of the original hydrosols was never less than 5.5, nor did the pH of these systems go above 8 upon the addition of salt solutions. The significance of these properties has been discussed previously.¹

Preparation of Hydrosols.—Basic beryllium iodide hydrosols were prepared by a method similar to that given by Thomas and Miller.³ Beryllium hydroxide⁴ was precipitated from beryllium nitrate by ammonium hydroxide and the precipitate was washed by centrifuging. The hydroxide was then peptized with tenth normal hydriodic acid for eighteen hours, during which time the system was stirred continuously. The resulting hydrosols were dialyzed for several days in nitrocellulose bags against distilled water and then centrifuged for one hour at 1200 r. p. m. (42 cm. rotating diameter) to remove coarse particles.

Measurement of the Velocity of Decomposition of Hydrogen Peroxide.—The velocity of decomposition of hydrogen peroxide was determined as described by Thomas and Cohen.¹ In the present work, however, 50 cc. of hydrosol was used, to which 10 cc. of water or salt solution was added and the mixture kept at 25° overnight to ensure equilibrium. To start the reaction 2 cc. of hydrogen peroxide was then pipetted into the mixture. At various time intervals 10 cc. of reaction mixture was withdrawn and permitted to flow into an Erlenmeyer flask containing 100 cc. of sulfuric acid solution. Titration with potassium permanganate followed immediately.

The initial concentration of hydrogen peroxide was adjusted to 0.2 normal.

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

(2) Walton, *Z. physik. Chem.*, **47**, 185 (1904); Liebhaftsky, *THIS JOURNAL*, **54**, 1792 (1932).

(3) A. W. Thomas and H. S. Miller, *ibid.*, **58**, 2526 (1936).

(4) A suspension of the washed hydroxide had about the same catalytic effect (1×10^{-3} min.⁻¹) upon hydrogen peroxide as the distilled water used in this work.

The reaction was first order, as can be seen from some representative runs.

t, min.	SOL A	
	a - x, cc. of KMnO ₄	K × 10 ³
In absence of salts		
0	18.83	
32.4	17.78	(1.80)
107.4	15.66	1.72
341.5	10.48	1.72
390.7	9.59	1.74
1104.0	2.83	1.72
		Av. 1.73
In presence of 1.80×10^{-3} N potassium acetate		
0	18.93	
103.1	16.19	1.52
208.8	13.66	1.57
320.4	12.10	1.56
		Av. 1.55

Experimental Results

(a) **Effect of Potassium Salts.**—Results for the effect of the added salts on the velocity constants of sols A and B are given in Tables I and II. It can be seen from these results that the catalytic effect of the salt-free colloidal system on the decomposition of hydrogen peroxide is greater than can be accounted for on the basis that the total iodide content of the system is in simple ionic form. Thus the fraction of the iodide constituent that is bound by the beryllium oxide micelles has a catalytic activity greater than the fraction that is free; and a decrease in the velocity constant of the hydrosol on the addition of neutral salts indicates the displacement of bound iodide from the micelles to form free iodide ions. Tables I and II also show that sulfate and tartrate ions in sufficient concentration can displace practically all the bound iodide. The order of effectiveness for the displacement of bound iodide is generally tartrate = sulfate > nitrate ≥ acetate.

(b) **Effect of Dilution.**—The data listed in Table III show the effect of dilution upon these sols. *K* (calcd.) is the product of the velocity constant of the original sol and the concentration of the sol used for the particular experiment, and *K* (obsd.) is the observed velocity constant. It will be seen that the observed velocity constant is less than that calculated by assuming that the effect of dilution is purely additive. These re-

TABLE I

EFFECT OF POTASSIUM SALTS ON VELOCITY^a CONSTANT OF SOL A (Be = 84 meq./l.; I = 0.98 meq./l.)

The velocity constant for this system with all the iodide unbound should be 1.10×10^{-3} min.⁻¹. This value is obtained by using a specific constant of 1.39 for the iodide ion.

Final salt concn., equiv./liter $\times 10^4$	Nitrate	Acetate	Sulfate	Tartrate
0	1.73	1.73	1.73	1.73
2.70	1.69	1.70	1.50	1.55
6.30	1.62	1.61	1.32	1.41
9.60	1.53	1.59	1.17*	1.23*
18.00	1.50	1.55	1.15↓	1.16↓

^a Numbers represent $10^3 K$ min.⁻¹. * Signifies added salt produced a marked turbidity, and ↓ signifies that sol precipitated.

TABLE II

EFFECT OF POTASSIUM SALTS ON VELOCITY^a CONSTANT OF SOL B (Be = 79 meq./l.; I = 0.25 meq./l.)

The velocity constant for the system with all the iodide unbound should be 2.83×10^{-4} min.⁻¹.

Final salt concn., equiv./liter $\times 10^4$	Nitrate	Acetate	Sulfate	Tartrate
0	4.08	4.08	4.08	4.08
2.70	3.88	3.94	3.24	3.41
6.30	3.71	3.75	2.88↓	2.77↓
9.60	3.48	3.60
18.00	3.41	3.50	2.84↓	2.75↓

^a Numbers represent $10^4 K$ min.⁻¹.

TABLE III

EFFECT OF DILUTION ON SOLS A AND B

Concn. of sol	Sol A		Sol B	
	K (obsd.) $\times 10^3$	K (calcd.) $\times 10^3$	K (obsd.) $\times 10^4$	K (calcd.) $\times 10^4$
1	1.73	..	4.08	..
0.60	0.94	1.04	2.30	2.45
0.40	0.58	0.69	1.49	1.63

sults may be explained on the basis that the sorbed iodide ions are being displaced by water molecules, a phenomenon which is similar to the displacement of iodo groups by water molecules in the case of Werner⁵ complex compounds.

(c) **Effect of Aging.**—Upon aging at room temperature there was an appreciable decrease in the catalytic activity of the sols. For example, the velocity constant of sol A changed from 1.73×10^{-3} to 1.55×10^{-3} after aging for five weeks; sol B decreased from 4.08×10^{-4} to 3.71×10^{-4} after three weeks. This would indicate that the concentration of bound iodide decreases with aging.

Discussion

The catalytic behavior of beryllium oxyiodide hydrosols is strikingly similar to that of alumi-

num oxyiodide hydrosols in several respects. Thus both types of sols show a promotion effect. Also, tartrate ions are about equally as effective as sulfate ions in displacing iodo groups from the micelles to form iodide ions until practically all of the bound iodide is displaced. Aging or the addition of water to these sol systems will cause the displacement of iodo groups.⁶

Previous work from this Laboratory³ has shown that the effect of aging on beryllium hydrosols as indicated by the increase of the hydrogen ion activity of the system is quite marked whereas aluminum hydrosols are relatively stable.^{6,7} The same behavior has been observed regarding the iodide ion concentration of these systems on aging. This effect may be observed by the decrease in the velocity constant of these hydrosols. Sol A (of this paper) which contains 0.98 milliequivalent of iodide per liter affords a means of direct comparison with the (aluminum) sol (8) which had a total iodide concentration of 1.03 milliequivalents per liter.¹ At the end of one week the velocity constant of sol (8) decreased 1.7% whereas the beryllium hydrosol (A) decreased 4.3% during the same time interval.

It is interesting to note that the order of effectiveness of the displacement of hydroxyl groups³ from beryllium micelles is tartrate > acetate > sulfate > nitrate, whereas the order for the displacement of bound iodide from these micelles is generally tartrate = sulfate > nitrate ≥ acetate. Thus it appears that the relative capacity for anions to displace coördinately bound groups varies with the nature of the group to be displaced and the concentration of the added anion. Thomas and Miller³ found that the order of effectiveness for anions to displace (coördinately bound) aquo groups was also different from that obtained for the displacement of hydroxyl groups.

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Summary

In the decomposition of hydrogen peroxide it has been shown that the catalytic effect of the iodide ion sorbed by colloidal beryllium oxide is greater than that of the free iodide ion.

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(5) Werner, "New Ideas on Inorganic Chemistry," Longmans, Green and Co., New York, N. Y., 1911.

(6) A. W. Thomas and B. Cohen, *THIS JOURNAL*, **61**, 401 (1939).

(7) A. W. Thomas and A. P. Tai, *ibid.*, **54**, 841 (1932).