[Contribution from the Department for Inorganic and Analytical Chemistry of the Hebrew University]

Catalysts for Peroxide Decomposition. II. The Catalytic Decomposition of Hydrogen Peroxide by Chromic Acid and Dichromate

By M. Bobtelsky, A. Glasner and L. Bobtelsky-Chaikin

1. Introduction.—The object of this work was the study of the catalytic decomposition of hydrogen peroxide by chromic acid and dichromate in various solvents. The rate of decomposition depends very much on the solvent as well as on the presence of concentrated neutral salts, cations of varying valencies and the *p*H of the solution. There are two intermediate compounds, the one *blue* and the other *violet*, which can be identified and studied during catalytic decomposition of hydrogen peroxide. These colored compounds are in equilibrium with each other, their proportions changing mainly with the *p*H and with the specific character of the solution. The relation between them is most probably that of an undissociated acid and its ion. A number of formulas were proposed by various investigators for the intermediates formed. Riesenfeld, *et al.*,[1] isolated three compounds ($PyHCrO_6$, MH_2CrO_7 and M_3CrO_8). Spitalsky[2] studied the rate of the catalytic decomposition of hydrogen peroxide. He concluded that at least three intermediates exist, one of which is rather stable ($KH_5Cr_4O_{18}^{=}$) and therefore does not participate in the main catalytic decomposition. It should be emphasized that Spitalsky's calculations leave ample room for other compositions of the intermediates, not considered by him. Spitalsky himself suggests that his calculations could not bring a complete solution and regrets the lack of more suitable experimental methods. The premises of his calculations were the variations in the hydrogen ion concentration of the solutions, obtained from conductivity measurements. It is clear that this method is subject to errors, inaccurate and not applicable in the range of neutral solutions.

Kobozev[3] continued Spitalsky's work on the same lines, and proposed for the intermediates the formulas $Cr_2O_9^{=}$ and $HCr_2O_9^{-}$. It should be mentioned that these formulas are not in agreement with those given by Riesenfeld[1] or Schwarz and Giese[3a] for the perchromates they have isolated. Neither Spitalsky nor others dealt with the catalytic decomposition in any other solvent but pure water solutions. As the exact formulas of the intermediates are controversial, we preferred, for the time being, the use of the expressions *blue* and *violet* compounds to describe them. From the experimental results obtained by us the composition of the blue and the violet intermediates could be calculated, but in order not to enlarge the present paper unduly, we thought it more reasonable to devote to this problem a separate report, the more so, as the catalytic process could be studied without involving the problem of the composition of the existing colored intermediates.

The maximum catalytic effect of hydrogen peroxide decomposition will be achieved when the velocities of formation and decomposition of the intermediate compounds are large. Again the best condition for a study of the intermediate compounds is given when the velocity of formation is large compared to the velocity of decomposition. Both these conditions can be realized by changing the solvent, the supplementary salts and the temperature of the reacting mixture.

Even the study of the above-mentioned catalytic reaction in pure water solution is very complicated. There are a few side reactions involved, which cause many difficulties. In the following work we endeavored to study the various reactions under conditions where the side reactions were eliminated as far as possible.

For the study of the catalytic decomposition of hydrogen peroxide we employed mainly gasometric measurements. For the study of the intermediate compounds photometric measurements served. Parallel *p*H measurements were also made.

2. Experimental

All reagents used in this paper were analytically pure. The stock solution of hydrogen peroxide was Merck "perhydrol." The given temperatures were kept constant within ±0.1°.

Gasometric measurements were made with a special apparatus built in our laboratory, which has been described already in a previous article.[4] Concerning the order in which the solutions were mixed, it was ascertained that it made no difference which of the reagents (CrO_3, $Na_2Cr_2O_7$ or H_2O_2) was added the last to the reacting solution.

The photometric measurements were made with a Hellige Panphotometer to which a small thermostat, built by us around the glass tube, was attached. The temperature was kept constant by a regular current of water driven through the thermostat from a water-bath by an electrically driven water-pump. The same water-bath contained also the reaction flasks. In each experiment, after adding the last reagent, the solution was stirred well by a mechanical glass stirrer. At definite intervals, small amounts of the solution were pipetted out into the tube of the photometer, which was first rinsed by the same solution. The time taken from the removal of the solution from the reaction flask, till the end of a measurement, was about forty-five seconds. The times recorded in the tables and diagrams are the mean of the actual measurements, these taking about twenty seconds. The liquid layer taken for a measurement was always the same: we

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[1] E. Riesenfeld, *et al.*, *Ber.*, **38**, 3578 (1905); **41**, 2826 (1909).

[2] E. Spitalsky, *Z. anorg. Chem.*, **53**, 184 (1907); **56**, 72 (1907); **69**, 179 (1910); E. Spitalsky and N. Koboseff, *Z. physik. Chem.*, **127**, 129 (1927).

[3] N. I. Kobozev and E. E. Gal'braikh, *C. A.*, **36**, 5414 (1942).

[3a] S. Schwarz and H. Giese, *Ber.*, **65**, 871 (1932); **66**, 310 (1933).

[4] M. Bobtelsky and A. E. Simchen, This Journal, **64**, 2492 (1942).

have used a 10-mm. glass tube for the chromic acid solutions, and a 5-mm. tube for the dichromate solutions.

It has been found that the maximum difference in extinction between a pure chromic acid solution and the same solution containing also hydrogen peroxide is obtained with the 530, 550 and 570 filters, E_{550} ($E_{Bl.} - E_{CrO_3}$) being 5% greater than E_{530} and 3% smaller than E_{570} (if only the blue intermediate is present). In case of the dichromate solutions, the violet compound gives a maximum difference of extinction with filters 530 and 550, E_{530} being 1% higher than E_{550}. In the following "extinction" (E) is written shortly for the measured extinction less the extinction of a pure chromic acid or dichromate solution of the same concentration.

The *p*H measurements were made with a Beckmann "shielded" glass-electrode and a saturated calomel reference electrode. The measuring apparatus was a Sargent *p*H meter. The electrode was daily calibrated with buffer solutions of known *p*H. Measurements made on different days gave reproducible values within ±0.1 *p*H.

For making a series of measurements the desired solutions, without the hydrogen peroxide, were mixed in a cylindrical reaction vessel immersed in a thermostat. After the elapse of about fifteen minutes, the *p*H of the solution was ascertained and then the hydrogen peroxide was added, starting a stop-clock at the same time. The solution was now well stirred for fifteen seconds and the *p*H measurements made at frequent intervals with the glass electrode dipping in the solution during the whole course of a reaction.

3. The Catalytic Decomposition of Hydrogen Peroxide by Chromic Acid

Reaction in Pure Water Solutions.—When hydrogen peroxide is added to a chromic acid solution in water, a blue compound is formed which decomposes very quickly at room temperature. In dichromate solutions the hydrogen peroxide decomposition goes through a violet compound. A *chromate* solution, again, does not act catalytically on hydrogen peroxide and yields no visible intermediate compound.

The course of the catalytic decomposition of hydrogen peroxide in chromic acid–water solution is very complicated as several simultaneous reactions are involved. Figure 1 shows the course of the evolution of oxygen from solutions containing various amounts of chromic acid as well as experiments with a constant concentration of chromic acid and varying amounts of hydrogen peroxide. The general composition of the solutions was: x cc. 0.0667 M CrO_3 + y cc. 1.67 M H_2O_2 + $(20 - x - y)$ cc. H_2O; $T = 15°$. The concentration of the chromic acid and hydrogen peroxide is indicated on the respective curves. It can be seen that the dependence of the velocity of decomposition of hydrogen peroxide on the chromic acid is very considerable. Again, the hydrogen peroxide is in a great excess and further addition of this reagent even retards slightly the decomposition. In the following the solution containing 1 cc. of 0.0667 M CrO_3 and 1 cc. of 1.67 M H_2O_2 served as the fundamental experiment to which all the others were compared. The curve obtained in Fig. 1 for this solution is of the S type; in the first part of the reaction the evolution of oxygen is quick, then it slows down and at the end it accelerates again. Similar experiments were made at 5°. Table I gives the respective times of half reactions. It is readily seen that the influence of temperature rises with rising chromic acid concentration. The temperature coefficient is not constant. This indicates that there are several reactions taking place simultaneously.

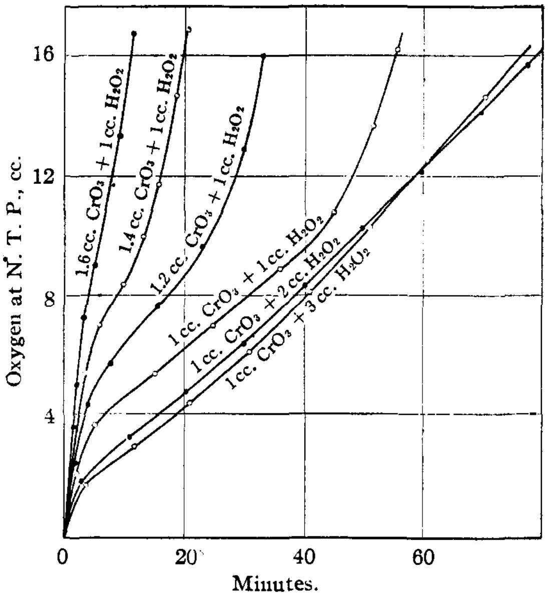

Fig. 1.—Decomposition of hydrogen peroxide in pure water solution at 15°: y cc. of 1.67 M H_2O_2 + x cc. of 0.0667 M CrO_3 + $(20 - x - y)$ cc. of water.

TABLE I

TEMPERATURE COEFFICIENTS IN PURE WATER SOLUTION

x cc. 0.0667 M CrO_3 + 1.0 cc. 1.67 M H_2O_2 + $(19 - x)$ cc. H_2O

CrO_3, cc.	$t_{R/2}$ in minutes at 15°	at 5°	t_5/t_{15}
1.0	32.5	139	4.27
1.2	17.5	92	5.26
1.4	9.0	54	6.00
1.6	4.5	31	6.89

Reaction in Neutral Salt Solutions.—Previous work carried out in this Laboratory showed that the concentrated neutral salt solutions used in the following have no measurable catalytic effect by themselves on the decomposition of hydrogen peroxide. Figure 2 shows the course of oxygen evolution of some experiments in various salt solutions. The general composition of these experiments was: 1 cc. 1.67 M H_2O_2 + 1 cc. 0.0667 M CrO_3 + 18 cc. salt solution; $T = 15°$. The final concentration of the additional salts is indicated on the curves. The course of the reaction (excepting ammonium sulfate) is linear and side reactions apparently are eliminated. Potassium fluoride in the given concentration stops the reaction entirely, and no formation of a colored intermediate compound is observed. Ammonium chloride accelerates the reaction more than any of the other salts. In solutions contain-

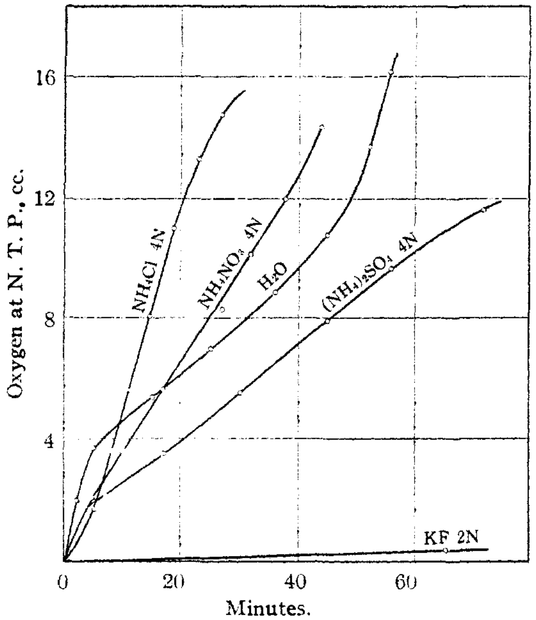

Fig. 2.—Decomposition of hydrogen peroxide in concd. neutral salt solutions at 15°: 1 cc. of 1.67 M H_2O_2 + 1 cc. of 0.0667 M CrO_3 + 18 cc. of concd. salt solution.

ing two to four normal ammonium chloride pure catalytic constants ($k_0 = x/t$) are obtained almost to the complete decomposition of the hydrogen peroxide present. At lower concentration of ammonium chloride x/t is no more constant and the course of the reaction approaches that of pure water solutions. The influence of ammonium nitrate is very much like that of ammonium chloride. In order to ascertain that the effects of the ammonium salts are not due to the NH_4^+ ion, we have made some experiments with solutions containing sodium chloride (2 and 4 N). The results were almost identical with those of the corresponding ammonium chloride solutions giving slightly higher k_0 values.

Table II brings the velocity of decomposition in various ammonium chloride solutions. Compared with the pure water solution, the velocity of decomposition in concentrated ammonium chloride solution is doubled.

TABLE II

DECOMPOSITION IN AMMONIUM CHLORIDE SOLUTIONS

1.0 cc. 0.0667 M CrO_3 + 1.0 cc. 1.67 M H_2O_2 + x cc. 5 M NH_4Cl + (18 − x) cc. H_2O, T = 15°

NH_4Cl, cc.	$t_{R/2}$, min.	$k_0 = x$ cc. $O_2/t_{\text{min.}}$
H_2O	32.5	..
4	31.0	..
8	21.6	0.38
12	17.0	.505
16	15.5	.62

Table III shows the catalytic constants in 3.75 N ammonium chloride solution on increasing the chromic acid concentration. The constants are almost *proportional* to the concentration of chromic acid (contrary to the pure water solutions).

TABLE III

DECOMPOSITION IN AMMONIUM CHLORIDE SOLUTION

x cc. 0.0667 M CrO_3 + 1.0 cc. 1.67 M H_2O_2 + 15 cc. 5 M NH_4Cl + (4 − x) cc. H_2O, T = 15°

CrO_3, cc.	k_0	k_0/cc., CrO_3
0.75	0.43	0.57
1.00	.62	.62
1.20	.74	.62
1.50	1.06	.71

Table IV shows the dependence of the catalytic constants on the initial concentration of hydrogen peroxide. The influence of hydrogen peroxide is insignificant. The special regulating effect of the ammonium chloride on the course of the reaction is consequently limited to the chromic acid.

TABLE IV

DECOMPOSITION IN AMMONIUM CHLORIDE SOLUTION

0.6 cc. 0.0667 M CrO_3 + x cc. 1.67 M H_2O_2 + 15 cc. 5 M NH_4Cl + (4.4 − x) cc. H_2O, T = 15°

M, $H_2O_2 \times 10^2$	k_0
16.70	0.36
8.35	.32
5.56	.31
4.17	.30

TABLE V

DECOMPOSITION IN AMMONIUM SULFATE SOLUTION

x cc. 0.0667 M CrO_3 + 1.0 cc. 1.67 M H_2O_2 + 10 cc. 4 M $(NH_4)_2SO_4$ + (9 − x) cc. H_2O, T = 15°

CrO_3, cc.	$t_{R/2}$, minutes
1	47
2	14.4
3	3.5

As we can see the complications observed in the pure water solutions are absent in the ammonium chloride solutions and we obtain a pure catalytic reaction of zero order. The velocity of formation of the blue compound is in all cases very considerable compared with the velocity of decomposition, and therefore the last reaction is the one measured by the constants obtained.

It is very interesting to compare the results of varying the chromic acid concentration in concentrated ammonium sulfate or ammonium chloride solution (Tables V and III). In the case of the sulfate the time of half reaction changes considerably on varying the chromic acid concentration, although not as much as in the pure water solution. The most expressed regulating effect is thus observed in concentrated *chloride* solutions.

In ammonium sulfate solutions, too, the experiments have shown that the liberation of oxygen changes only slightly with a variation of the hydrogen peroxide.

Reaction in Ethyl Alcohol–Water Mixtures.—It is known to us from previous works that a dilute solution of chromic acid oxidizes ethyl alcohol at room temperature at a measurable velocity only in the presence of strong acids. In the absence of the last, this side reaction can be neglected.[5] The object of the following experiments was to change the solvent gradually, hop-

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[5] M. Bobtelsky and Ch. Radovensky-Cholatnikow, *Z. anorg. allgem. Chem.*, **199**, 241 (1931); M. Bobtelsky and R. Cohen, *ibid.*, **210**, 225 (1933).

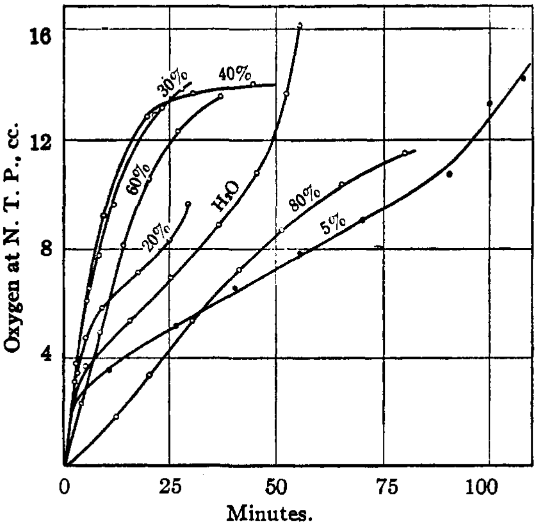

Fig. 3.—Decomposition of hydrogen peroxide in alcohol-water mixtures at 15°: 1 cc. of 1.67 *M* H_2O_2 + 1 cc. of 0.0667 *M* CrO_3 + *x* cc. of 96% EtOH + (18 − *x*) cc. of water.

ing that, by doing so, the catalytic decomposition will become more regular. Figure 3 brings some of a series of experiments, made at 15°, of the general composition: 1 cc. 0.0667 *M* CrO_3 + 1 cc. 1.67 *M* H_2O_2 + *x* cc. C_2H_5OH 96% + (18 − *x*) cc. H_2O. (The alcohol used in all the solutions was only 96% by volume, but for the sake of simplicity we took it as 100% in calculating the final volume per cent. of the alcohol throughout this work.) The percentage of alcohol in the solutions is indicated on the respective curves. The S curve observed in pure water solutions *vanishes* already in a 30% ethyl alcohol solution. With the elimination of the S curve the evolution of oxygen increases, till it reaches a maximum at about 30% alcohol. The growing alcoholic concentration from approximately 60% upward, *stabilizes* more and more the blue intermediate compound and the velocity of oxygen evolution decreases. In these solutions the course of the reaction is more regular—the first half being linear (catalytic) and then tends to become of the monomolecular form.

Figure 4 shows the variation in the time of half reaction for such a series of experiments made at 15 and at 5°. *Small* amounts of ethyl alcohol up to about 5% retard the velocity of the reaction. Besides this retardation effect, the half time reaction decreases linearly with increasing alcoholic concentration. This course continues up to 30% alcohol approximately. The effect of the alcohol concentration in this zone is so great that the velocity of decomposition of hydrogen peroxide increases almost ten-fold between 5 to 30% alcohol (at 5°). This effect is more pronounced at a lower temperature. Between 30 to 50% ethyl alcohol the velocity of the reaction shows a steady maximum and then falls off rapidly with rising alcohol concentration owing to the stability of the blue intermediate compound in these alcoholic solutions.

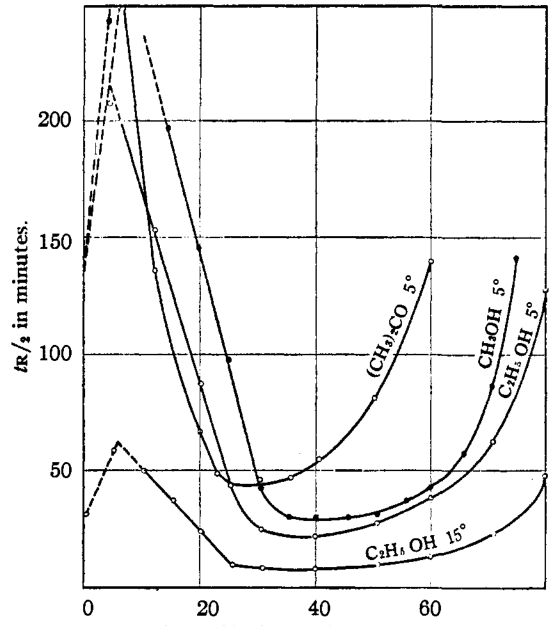

Fig. 4.—The rate of decomposition of hydrogen peroxide in organic solvents: 1 cc. of 1.67 *M* H_2O_2 + 1 cc. of 0.0667 *M* CrO_3 + *x* cc. of organic solvent + (18 − *x*) cc. of water.

Tables VI and VII show the dependence of the hydrogen peroxide decomposition in 70% alcoholic solutions on the concentration of the chromic acid or hydrogen peroxide. As we can see, the velocity of the decomposition *is nearly proportional* to the chromic acid concentration, contrary to the enormous effect of chromic acid concentration in pure water solution. As to the hydrogen peroxide (Table VII), the time necessary for the decomposition of a third of the hydrogen peroxide present is nearly proportional to the initial concentration of this reactant. The velocity of the reaction is consequently independent of the concentration of hydrogen peroxide. The reaction in alcoholic solutions is thus analogous in some aspects to concentrated chloride solutions.

TABLE VI

DECOMPOSITION IN 70% ALCOHOLIC SOLUTION

x cc. 0.0667 *M* CrO_3 + 1.0 cc. 1.67 *M* H_2O_2 + 14 cc. C_2H_5OH 96% + (5 − *x*) cc. H_2O, $T = 15°$

CrO_3, cc.	$t_{R/3}$, minutes
1	23
2	9.3
3	6.0

TABLE VII

DECOMPOSITION IN 70% ALCOHOLIC SOLUTION

1.0 cc. 0.0667 *M* CrO_3 + *x* cc. 1.67 *M* H_2O_2 + 14 cc. C_2H_5OH 96% + (5 − *x*) cc. H_2O, $T = 15°$

M $H_2O_2 \times 10^2$	$t_{R/3}$, minutes
8.35	15.0
16.70	24.5
25.05	38.0

Table VIII contains the calculated temperature coefficients in the various ethyl alcohol–water mixtures (compare Fig. 4). As we can see we have between 5 to 20% alcohol a constant temperature coefficient which is about 3.4. From 30 to 80% alcohol the temperature coefficient is again constant and equal to 2.7. This would indicate that in these two ranges the reactions measured are different.

Table VIII

Temperature Coefficients in Alcoholic Solution

1.0 cc. 0.0667 *M* CrO_3 + 1.0 cc. 1.67 *M* H_2O_2 + x cc. C_2H_5OH 96% + (18 − x) cc. H_2O

Vol. % C_2H_5OH	$t_{R/2}$ in minutes at 15°	$t_{R/2}$ in minutes at 5°	t_5/t_{15}	
5	60	208	3.47	3.45
12.5	47	154	3.28	
20.0	24.3	88	3.62	
30	9.0	25.2	2.80	2.7
40	8.5	22.0	2.59	
50	10.4	28.0	2.69	
60	14.5	39.4	2.72	
70	23.0	62	2.70	
80	47.5	127	2.67	

Reaction in Methyl Alcohol–Water and Acetone–Water Mixtures.—Experiments with methyl alcohol or acetone were made at 5 and at 15°. The general composition of the solutions was: 1 cc. 1.67 *M* H_2O_2 + 1 cc. 0.0667 *M* CrO_3 + x cc. CH_3OH or $(CH_3)_2CO$ + (18 − x) cc. H_2O. In order to save space we forego giving detailed results here. Fundamentally the same picture is obtained as from the experiments with ethyl alcohol–water mixtures, as can be seen from the respective curves in Fig. 4. The maximum velocity of oxygen evolution is obtained at approximately 30% methyl alcohol or acetone. Here, too, two distinct temperature coefficients are obtained and these are identical with the corresponding temperature coefficients in ethyl alcohol. Experiments with varying amounts of chromic acid or hydrogen peroxide were made in 60% acetone solutions. The results are shown in Table IX. The velocity of the hydrogen peroxide decomposition is nearly proportional to the chromic acid. The dependence on the hydrogen peroxide is at higher concentrations insignificant.

Table IX

Decomposition in 60% Acetone Solution

x cc. 0,0667 *M* CrO_3 + y cc. 1.67 *M* H_2O_2 + 12 cc. $(CH_3)_2CO$ + (8 − x − y) cc. H_2O, $T = 15°$

M $H_2O_2 \times 10^2$	*M* $CrO_3 \times 10^3$	$t_{R/2}$, minutes
8.35	3.33	44.0
8.35	6.67	18.7
8.35	10.00	12.0
16.70	3.33	29.5
25.05	3.33	27.0

4. The Catalytic Decomposition of Hydrogen Peroxide in the Presence of Dichromate

The catalytic decomposition of hydrogen peroxide in the presence of dichromate was studied by E. Spitalsky,[2] N. Kobozev,[3] A. C. Robertson[6] and M. Bobtelsky and L. Chaikin.[7] Spitalsky and Kobozev studied the kinetics of the reaction and the others the function of promoters.

On mixing dichromate and hydrogen peroxide in pure water solution a violet compound is formed which decomposes with evolution of oxygen. The velocity of decomposition of hydrogen peroxide is directly proportional to the concentration of dichromate as well as to the concentration of hydrogen peroxide.[1,7] In experiments with constant dichromate concentration containing a big excess of hydrogen peroxide the course of the oxygen evolution is of the first order. The influence of concentrated solutions of neutral ammonium salts is very small.[7]

In alcoholic solutions we found that the hydrogen peroxide decomposition is retarded with increasing amounts of ethyl alcohol. There are many cations which act as promoters for this reaction. *In absence of promoters*, the violet complex on decomposing evolves active oxygen which oxidizes the alcohol to acetaldehyde but the oxidation can be depressed by some promoters. This observation is at the moment under study in our laboratory and it will be the subject matter of another paper.

5. Photometric Measurements

The object of the photometric measurements was the study of the intermediate blue and violet compounds, their concentration and stability under various conditions. In solutions containing dichromate only, the violet compound exists. In solutions containing chromic acid the main colored intermediate compound is blue mixed with the violet compound, the concentration of which depends on the composition of the respective solution. As concentrated alcoholic solutions stabilize these intermediate compounds most of the experiments were made in such solutions. In the case of the blue compound which is formed rather quickly the experiments were made at 0°. At this temperature the oxidation of the concentrated alcohol by the intermediate compounds is practically zero.[8,9] As to the violet compound its formation at 0° is very slow and therefore experiments were made at 18° (±0.1).

Experiments with Chromic Acid.—Figure 5 brings a series of experiments with varying concentration of alcohol. The general composition of the solutions was: 3 cc. 0.02069 *M* CrO_3 + 6 cc. 0.069 *M* H_2O_2 + x cc. C_2H_5OH 96% + (41 − x) cc. H_2O, $T = 0°$. The volume per cent. of alcohol is marked on the respective curves. The measurements were made with a 550 filter. In all cases the curves show a maximum which is very quickly reached and then decreases slowly.

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(6) A. C. Robertson, This Journal, **49**, 1630 (1927).

(7) M. Bobtelsky and L. Bobtelsky-Chaikin, *Compt. rend.*, **203**, 1158 (1936).

(8) O. H. Wiede, *Ber.*, **31**, 520 (1898).

(9) E. M. Riesenfeld, *et al.*, *ibid.*, **38**, 1885 (1905).

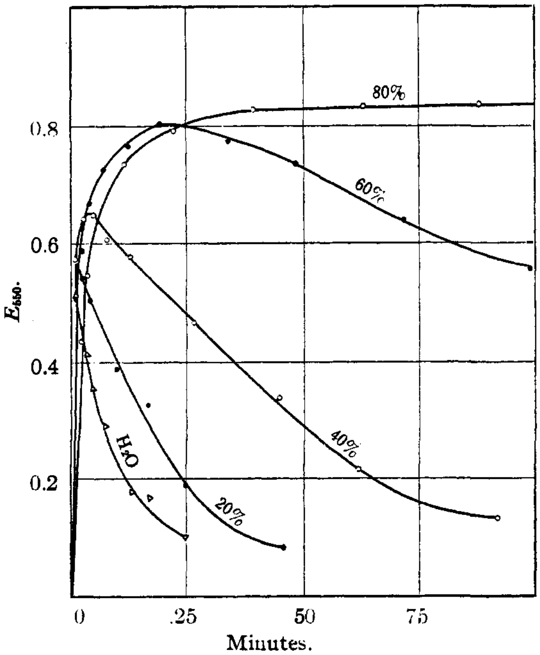

Fig. 5.—Extinctions in ethyl alcohol-water mixtures at 0°: 6 cc. of 0.069 M H_2O_2 + 3 cc. of 0.00269 M CrO_3 + x cc. of 96% EtOH + $(41 - x)$ cc. of water.

(The time necessary to reach these maxima corresponds to that of the pH maxima in Fig. 9, further on.) The height of the maxima seems to grow with growing concentration of alcohol, and at the same time the velocity of decomposition of the blue compound decreases. At about 80% alcohol the blue compound is quite stable.

Figure 6 brings a series of experiments made in 80% alcoholic solutions at 0°, with increasing hydrogen peroxide concentration. The general composition of the solutions was: 3 cc. 0.02256 M CrO_3 + x cc. H_2O_2 + 40 cc. C_2H_5OH 96% + $(7 - x)$ cc. H_2O. The concentration of hydrogen peroxide is marked on the curves. With increase of hydrogen peroxide there developed a more and more intensive blue color until about the proportion $H_2O_2/CrO_3 = 9$ was reached. On further increasing the hydrogen peroxide concentration the intensity of the colored solutions did not change any more but they acquired a violet tint (no change with filter 550 but a lower extinction through filter 570). From the horizontal part of the various curves we may conclude that in all cases there exists a steady state in which the velocities of formation and decomposition are balanced.

Table X shows the dependence of the maximum extinction ($E_{\text{max.}}$) on the initial concentration of chromic acid in 80% alcoholic solutions. The general composition of the solutions was: x cc. 0.02069 M CrO_3 + 5 cc. 0.0637 M H_2O_2 + 40 cc. C_2H_5OH 96% + $(5 - x)$ cc. H_2O, $T = 0°$. It is seen that the concentration of the blue compound is proportional to the initial concentration of the chromic acid.

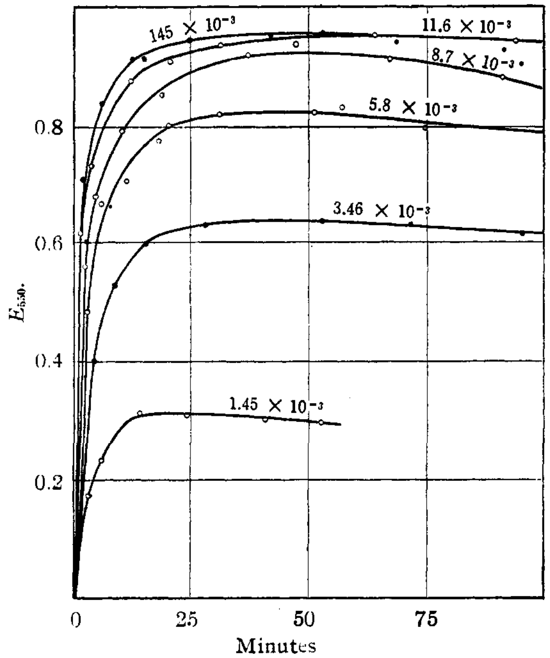

Fig. 6.—The influence of hydrogen peroxide concn. on the extinction of the blue compound in 80% alcoholic solution at 0°: x cc. of H_2O_2 + 3 cc. of 0.02256 M CrO_3 + 40 cc. of 96% EtOH + $(7 - x)$ cc. of water.

TABLE X

MAXIMUM EXTINCTIONS IN 80% ALCOHOLIC SOLUTION

x cc. 0.02069 M CrO_3 + 5 cc. 0.0637 M H_2O_2 + 40 cc. C_2H_5OH 96% + $(5 - x)$ cc. H_2O, $T = 0°$

CrO_3, cc.	$E_{\text{max.}} \times 10^3$	$E_{\text{max.}} \times 10^3/CrO_3$, cc.
1	260	260
2	506	253
3	768	256
4	980	245

Comparing the photometric with the gasometric measurements (Table VI), we see that the velocity of the catalytic decomposition depends on the blue compound and is proportional to the concentration of this compound. From Fig. 6 it can be deduced, also, that the course of the catalytic decomposition of hydrogen peroxide, through the blue compound, is regular and catalytic ($k_0 = x/t$), only if the hydrogen peroxide is in large excess compared with the chromic acid. When this ratio, during the decomposition of the hydrogen peroxide, becomes equal to that represented in Fig. 6, the velocity of the evolution of oxygen will fall with time as the concentration of the blue compound decreases.

Experiments with Sodium Dichromate.—A study of the violet compound in water solution, even at 0°, could not be undertaken because of the vigorous evolution of oxygen, which makes the photometric measurements impossible. In concentrated alcoholic solutions the violet compound on decomposing oxidizes the alcohol and no bubbles disturbed the measurements. Disregarding the oxidation of the alcohol, the photometric curves obtained are rather interesting. It is to be emphasized that in all these experiments the concentration of the alcohol all through the reaction remains *constant*.

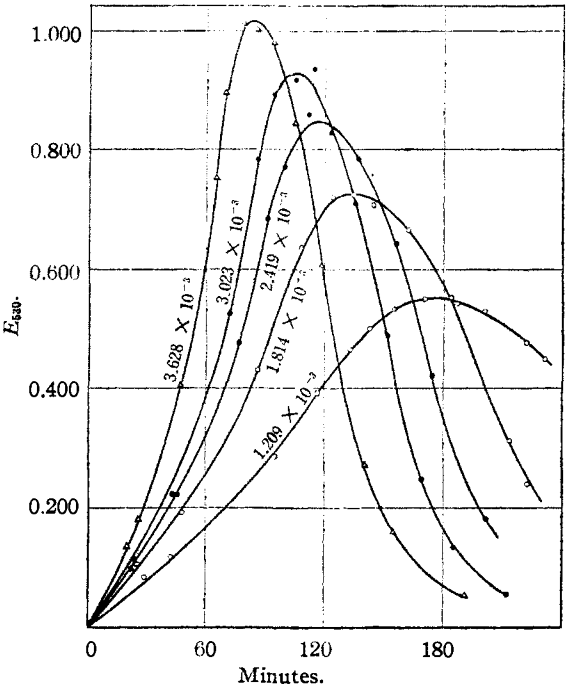

Fig. 7.—The influence of the concn. of sodium dichromate on the extinction of the violet compound in 80% alcoholic solution at 18°: 3 cc. of 0.698 M H_2O_2 + x cc. of 0.06047 M $Na_2Cr_2O_7$ + 40 cc. of 96% EtOH + (7 − x) cc. of water.

In Figs. 7 and 8 are shown the results of two series of experiments in 80% alcoholic solution at 18°. The general composition of the solutions was: 3 cc. 0.698 M H_2O_2 + x cc. $Na_2Cr_2O_7$ + 40 cc. C_2H_5OH 96% + (7 − x) cc. H_2O (Fig. 7) and 2 cc. 0.06047 M $Na_2Cr_2O_7$ + x cc. H_2O_2 + 40 cc. C_2H_5OH 96% + (8 − x) cc. H_2O (Fig. 8), respectively. In both figures the concentration of the reactant varied is marked on the curves. The measurements were made with a 530 filter. The figures show the changes with time in the concentration of the violet compound in the various solutions. Very striking is the symmetrical shape of the single curves so that there are two points on each curve corresponding to the same extinction; while the first point is passed when the concentration of the violet compound tends to increase, the second symmetrical point is passed when the concentration of the violet compound tends to fall. This shape of the curves is the result of two co-measurable reactions, namely, the formation and decomposition of the violet compound. At the point of maximum extinction ($E_{\max.}$), the velocity of formation and decomposition are equal. In both figures, and for all the curves, the time necessary for the complete decomposition of the violet compound increases with decreasing values of $E_{\max.}$.

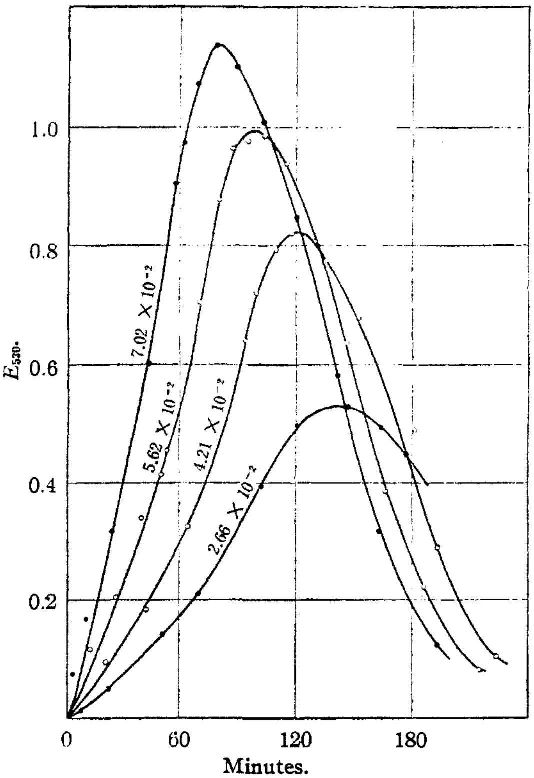

Fig. 8.—The influence of the concn. of hydrogen peroxide on the extinction of the violet compound in 80% alcoholic solution at 18°: x cc. of H_2O_2 + 2 cc. of 0.06047 M $Na_2Cr_2O_7$ + 40 cc. of 96% EtOH + (8 − x) cc. of water.

As to the connection between the maximum extinctions and the time intervals ($t_{\max.}$) in which they are obtained, simple calculations show that the formula $E_{\max.}t_{\max.} = K_m$ yields good constants. The interpretation of these curves will be the subject matter of another paper.

6. *p*H Measurements

We were convinced by the preceding experiments that in chromic acid solutions the *p*H of the solution undergoes certain changes during the catalytic decomposition of hydrogen peroxide. This is obvious from the fact that the concentration of the free chromic acid in the solution depends on the concentration of the hydrogen peroxide present, and varies with the milieu. A few chosen experiments containing chromic acid and hydrogen peroxide, which were previously studied by the gasometric method, were repeated now under similar conditions (without shaking the vessel) and studied potentiometrically with a glass electrode. In all cases the *p*H values were established almost instantaneously. Figure 9 shows the results of these measurements. For the sake of comparison an experiment with sodium dichromate is recorded also in the figure. The composition of the single experiments was as follows: curves 1 and 2, x cc. 0.167 M CrO_3 ($x = 1.0$ or 1.6) + 5 cc. 0.95 M H_2O_2 + (45 − x) cc. H_2O; curve 3, 1.0 cc. 0.167 M CrO_3 + 5 cc. 0.95 M H_2O_2 + 40 cc. 5 M NH_4Cl + 4 cc. H_2O; curves 4, 5 and 6, 1.0 cc. 0.167 M CrO_3 + 5 cc. 0.95 M H_2O_2 + x cc. 96% C_2H_5OH + (44 − x) cc. H_2O; and curve 7, 1.4 cc. 0.06214 M $Na_2Cr_2O_7$ + 5 cc. 0.95 M H_2O_2 + 43.6 cc. H_2O, $T = 15°$. The parallel gasometric measurements can be seen in Figs. 1, 2 and 3.

In all cases there is a steep rise in pH on the addition of hydrogen peroxide to the solution, reaching a maximum value after the elapse of a few minutes. This time corresponds to the time of formation of the blue compound. The reached maximum pH-value remained in some cases almost constant till the complete decomposition of hydrogen peroxide. In other cases, again, there is a break in the pH curves when the hydrogen peroxide is only partly decomposed, and the decrease is more abrupt.

It is very interesting to note that of all the chosen experiments with chromic acid, only in two cases the course of the gasometric curve is irregular, having an S shape. Just for these experiments, the maximum in the pH curves lies *above* a definite critical value (about pH 4), which lies very close to the pH value of pure dichromate water solutions. In all cases where the pH curves lie *below* this critical value, the catalytic decomposition of hydrogen peroxide is regular and is independent of the pH changes in the solution.

7. Discussion

The catalytic decomposition of hydrogen peroxide by chromic acid is of a rather complicated nature, due to the number of factors regulating simultaneously the decomposition velocity. The main factors to be mentioned are: the equilibrium between chromium trioxide, water and chromic acid (of the various compounds thus obtained the $CrO_4^=$ ion does not act catalytically); the relation of hydrogen peroxide to chromium trioxide and to the dichromate ion, on changing the milieu or the pH of the solution; the stability of the blue and violet intermediates, their relation to one another and the mechanism of their decomposition under various conditions.

From the photometric measurements of solutions containing chromic acid we may conclude that in all cases the maximum extinction is achieved (even at 0°) after the elapse of a few minutes only. Similarly the pH value of the solutions (Fig. 9) rises to its maximum after a corresponding short interval.

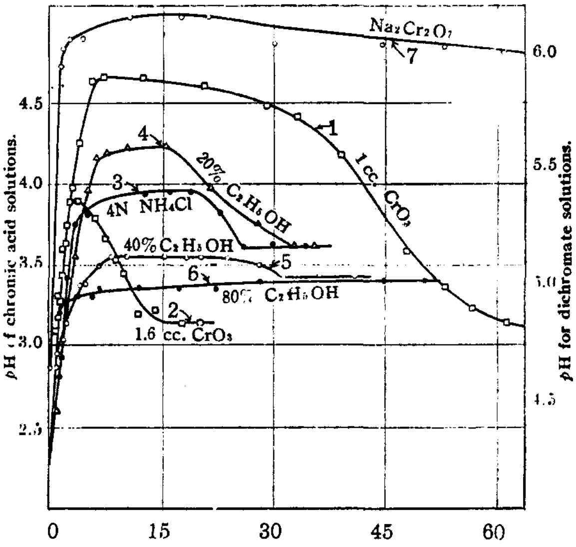

Fig. 9.—Changes in pH during the decomposition of hydrogen peroxide.

The great sensibility of the catalytic decomposition of hydrogen peroxide to the *initial* concentration of chromic acid in pure water solutions (Fig. 1), is closely connected with the S shape of the respective gasometric curves (such S curves appear only when the initial molecular ratio of hydrogen peroxide to chromic acid increases above a definite value). This irregular course of the catalytic hydrogen peroxide decomposition can be eliminated by using instead of pure water, concentrated solutions of neutral chlorides or nitrates, or by binding the water molecules by the addition of ethyl alcohol or acetone. (From previous works made in our laboratory[5] we know that in alcohol–water mixtures three zones are discernible: (1) the water zone from zero to about 30% alcohol, (2) the mixed zone of various alcohol–water associates from 30 to about 60% and (3) the alcoholic zone from 60% upward. A concentration of about 30% alcohol suffices to bind up all the water molecules.) Using these solvents the catalytic decomposition becomes strictly *proportional* to the initial concentration of the chromic acid, and the course of the hydrogen peroxide decomposition becomes linear. The parallel photometric measurements in highly concentrated ethyl alcohol (the only one which could be conveniently measured), show a direct proportionality between the initial concentration of chromic acid and the E_{max} values. This, together with the above-mentioned parallelism between $E_{max.}$ and $pH_{max.}$, is good evidence that in experiments (with chromic acid) showing a regular course of hydrogen peroxide decomposition, the *catalytic intermediate is the blue compound only*.

The above leads to the conclusion that in pure water solutions in the pH range of 4–4.5, the blue and the violet forms must exist side by side in equilibrium in considerable amounts. These two intermediates decompose with different velocities. Acting simultaneously the mixed catalysts cause the appearance of S curves, which can be resolved into three parts. In the first part of the gasometric S curve, the initial concentration of the chromic acid is the decisive factor, the undissociated blue compound is dominant and the hydrogen peroxide decomposition is swift. The middle part, in some gasometric curves, is the result of a *mixed* action of the blue and violet intermediates. In the last part, a considerable portion of the hydrogen peroxide has decomposed already and more and more *free* chromic acid appears in the solution. Correspondingly the *p*H decreases, the conditions become again favorable to the formation of the blue compound and the velocity of decomposition increases again.

It is noteworthy that the *p*H of dichromate solutions is about 4.5 and it is most probable that only when the *p*H of a chromic acid solution comes close to this value, there is a possibility of the formation of the violet compound. In agreement with this Fig. 9 shows that only in those cases the gasometric curve is of an S shape where a part of the corresponding *p*H curve is in the above mentioned critical zone. It is interesting to note that the different shapes of the *p*H curves *below* *p*H 4 do not involve irregularities in the catalytic decomposition of hydrogen peroxide. This means that the formation and decomposition of the blue compound is not sensitive to changes in *p*H (below the above-mentioned zone).

The catalytic decomposition of hydrogen peroxide below *p*H 4 goes through at least *three* successive reactions: the *formation* of the blue compound from hydrogen peroxide and hexavalent chromium (I), the *decomposition* of the blue intermediate to oxygen and chromium of a lower valence (II), and finally the *reoxidation* of the chromium by the free hydrogen peroxide in the solution (III).

As to the percentage of the reduced chromium found at the end of the catalysis, this was studied thoroughly by Spitalsky. It seems to us that this reduction resulting from a side reaction depends on the comparative velocities of reactions (II) and (III). At a lower *p*H, reaction (III) is slower and consequently at the end of the catalytic decomposition a higher percentage of the hexavalent chromium remains in the reduced form. This explains the fact that in strong acid solutions a complete reduction of chromic acid takes place.

In the *p*H zone above 4.5, the first step leads to the formation of the *violet* intermediate, while the second reaction is the *decomposition* of this compound into oxygen and dichromate. A third reaction is excluded in this case as no reduction of the dichromate solution is observed. Under similar conditions of temperature and milieu (besides the *p*H) the decomposition of the violet is slower than that of the blue compound. In both cases (as Fig. 9 shows) the formation of the colored intermediates is connected with a use-up of hydrogen ions. Also it may be assumed that in both cases the intermediates are formed from the same components (dichromate ion and hydrogen peroxide) but at higher *p*H the *violet anion* and at lower *p*H the *undissociated* blue acid are dominant.

In concentrated chloride or nitrate solutions the decomposition of hydrogen peroxide in presence of chromic acid goes through the *blue* intermediate only (below *p*H 4!) and it is of zero order ($x/t = k_0$). On comparing the half-times of the hydrogen peroxide decomposition in pure water and in concentrated chloride solutions (taking into consideration only the more concentrated chromic acid solutions), a retardation effect is observed in the last media. This is most probably to be attributed to an influence on the velocity of reaction (I), namely, the velocity of formation of the blue intermediate.

The influence of the organic solvents consists first, in the exclusion of a mixed action of two intermediates and, second, in their effect on the rate of decomposition of the blue compound.

The two distinct temperature coefficients obtained for chromic acid in various alcoholic solutions indicate, too, that in solutions up to 30% alcohol (where free water molecules are present) the hydrogen peroxide decomposition is of another character than in more concentrated alcoholic solutions.

If we assume that in alcoholic solutions there exists a coördinated compound between the alcohol and the blue intermediate this compound will be most stable in the highly concentrated alcoholic zone. Should there again exist an analogous compound between water and the blue intermediate, this would be most stable in *pure water* solution. Both coördinated compounds will be labile in the middle alcohol–water zone, where in reality the maximum velocity of hydrogen peroxide decomposition is observed.

Summary

1. The catalytic decomposition of hydrogen peroxide in chromic acid solutions goes chiefly through a blue intermediate. This is formed very quickly and at the same time the *p*H rises to a maximum.

2. The course of decomposition in water solutions is of an S type. This S shape is the result of a mixed catalytic action of two intermediates: a blue and a violet compound. The velocity of decomposition of the blue intermediate is greater than that of the violet. The catalysis is very sensitive to changes in the concentration of chromic acid.

3. A smooth catalytic decomposition curve of hydrogen peroxide is obtained in concentrated solutions of neutral salts, such as ammonium chloride, sodium chloride, or ammonium nitrate. The velocity of the reaction in these solutions is independent of the concentration of hydrogen peroxide almost to its complete decomposition.

4. The rate of decomposition is greatly retarded by an addition of small amounts of organic solvents (methyl alcohol, ethyl alcohol or

acetone) to the water solution, but increases very much on a further addition of these solvents. The maximum velocity is reached in solutions containing from 30 to 50% organic solvent. At higher concentrations the decomposition of the blue compound slows down more and more. It was assumed that the blue intermediate yields coördinated compounds with the organic solvents as well as with water molecules, which are most stable in the corresponding pure solvent and are unstable when deprived of the coördinating partner.

5. In highly concentrated alcoholic solutions of dichromate and hydrogen peroxide mixtures, the velocities of formation and decomposition of the violet compound are small and co-measurable. The photometric curves are composed of two symmetrical halves with the maximum extinction in the middle.

6. The relation between the violet and blue compound is that of an anion to its undissociated acid form, both being formed from the dichromate ion and hydrogen peroxide. The resulting compound depends on the *p*H: above *p*H 4.5 the violet anion exists chiefly; below *p*H 4 the undissociated blue form is dominant. The velocity of decomposition of the blue form below *p*H 4 does not vary with the *p*H of the solution.

7. The mechanism of the catalytic decomposition of hydrogen peroxide below *p*H 4 was explained by assuming the existence of three successive reactions: the formation of the blue perchromate, its decomposition, and the regeneration of hexavalent chromium. Above *p*H 4.5 the catalysis is simpler, consisting of two successive reactions only: the formation and the decomposition of the violet perchromate.

JERUSALEM, PALESTINE RECEIVED JULY 24, 1944

[CONTRIBUTION FROM THE ILLINOIS STATE GEOLOGICAL SURVEY]

Molecular Associations between Montmorillonite and Some Polyfunctional Organic Liquids[1]

BY W. F. BRADLEY

The considerable amounts of data which have been available on the nature of montmorillonite and its relationship with water,[1a,2,3] have suggested that some interest might attach to the more or less analogous instances of association between the clay mineral and organic liquids of the types illustrated below. Attention has previously been directed to the activity of organic bases in base exchange, and to the value of such reactions in estimations of van der Waals thicknesses.[4,5] More recently, MacEwan[6] has called attention to the value of polyhydric alcohols for the identification of montmorillonite.

The organic liquids employed in the present study are chiefly of these two related types: (1) the aliphatic di- and polyamines and (2) the glycols, polyglycols and polyglycol ethers. Members of the two groups tend to differentiate themselves both in the nature of the clay complexes which they form and in the fact that the amines are active in base exchange, but the glycols are not. A few incidental unrelated liquids were also included.

The better established details of the structure of the montmorillonite type mineral, to which Dr. S. B. Hendricks had contributed heavily, can probably be best enumerated with reference to Fig. 1. The salient feature of the structure is the four-high packing of oxygen and hydroxyl ions coördinated about three layers of cations as shown. A "triple layer" configuration of this sort can be electrostatically neutral, as illustrated by the common mineral pyrophyllite, or can carry a residual negative charge due to substitution of lesser valent cations into either of the two types of coördination positions. In mica this charge is regularly distributed and arises from the substitution of aluminum for one-fourth of the silicon ions in the tetrahedrally coördinated positions. It is balanced by the presence of one potassium ion in each of the positions of 12-fold coordination which occur between adjacent triple layers. The structure is stable and three dimensional, marked only by the familiar perfect basal cleavage, and those potassium ions not actually in a cleavage surface are fixed. In the montmorillonite minerals this residual charge is less regularly distributed, arises in the main from the substitution of magnesium for aluminum ions in octahedrally coördinated positions, and occurs considerably less frequently than do the comparable charges of mica. Interlayer ions, usually sodium or calcium, again balance the total electrostatic charge, but under these conditions of reduced interlayer attraction, water is observed to interleave between layers effectively making each triple layer surface equivalent to an exterior surface, and the balancing interlayer ions are exchangeable.

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