

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

## The Autoxidation of Manganous Hydroxide

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The composition of the products obtained in the autoxidation of manganous hydroxide has received the attention of numerous investigators. The contributions of Meyer and Nerlich<sup>1</sup> and of Herman and Lievin<sup>2</sup> are of especial interest in this connection.

Meyer and Nerlich made a very complete study of the reaction in connection with the theories of the nature of trivalent manganese. They found that when manganous chloride, ammonium chloride and ammonium hydroxide were mixed and shaken in air, the product was manganic oxide, as evidenced by both the analysis of the product and the volume of oxygen absorbed. When potassium hydroxide, calcium hydroxide, or barium hydroxide was used, the product was stated to be manganese dioxide, although the volume of oxygen absorbed varied between 81 and 94% of the amount corresponding to the formation of manganese dioxide. According to Meyer and Nerlich, the autoxidation in the ammoniacal solution takes place through a manganous-ammonia complex which is oxidized to a manganic complex. The latter is subsequently hydrolyzed with the formation of manganic hydroxide or manganic oxide. For the autoxidation of manganous hydroxide precipitated by fixed alkali, these authors accept the mechanism proposed earlier by Meyer.<sup>3</sup> Meyer postulated that the first step is the formation of a moloxide,  $H_2MnO_4$ , or  $H_2MnO_2(O_2)$ , which is not identical with manganic acid. The moloxide easily gives up oxygen to an acceptor such as manganous hydroxide. These authors find that other acceptors such as sodium sulfite and sodium arsenite have no effect. They did not attempt to investigate the rate of the reaction.

Herman and Lievin carried out experiments in which a bulb of manganous sulfate solution was broken within a flask containing potassium hydroxide solution, the flask being connected with a gas buret filled with oxygen. The volume of oxygen absorbed was plotted against time. With an excess of potassium hydroxide the curves ob-

tained appeared to consist of two rectilinear portions connected by a curved portion. The ratio between the velocities indicated by the two sections varied with the amount of excess potassium hydroxide. These authors were unable to observe an absorption of more than 82% of the theoretical volume of oxygen necessary for the formation of manganese dioxide. With an excess of manganous sulfate, they found that there was a rapid absorption lasting about one minute, followed by a slow reaction at constant velocity, ending at a limit corresponding to the formation of manganic oxide. The greater the excess of manganous sulfate, the slower was the reaction, but in each case all of the manganese precipitated was in the form of manganic oxide.

The work described in this paper was undertaken to extend the knowledge of the factors affecting the rate of autoxidation of manganous hydroxide.

**Apparatus and Procedure.**—The apparatus was essentially that described by Filson and Walton.<sup>4</sup> An indented reaction flask containing a bulb of ammonium hydroxide or sodium hydroxide and the desired amount of manganous chloride solution was placed in a thermostated shaking device and connected with a gas buret. The system was evacuated and filled with oxygen. The reaction flask was rotated rapidly back and forth about a vertical axis which resulted in breaking the bulb and keeping the resulting reaction mixture saturated with oxygen. The volume of solution used was 60 cc. in each case. The reaction was followed by recording the buret readings at the end of definite time intervals. The temperature of the gas buret and the reaction flask was always 25° except as otherwise stated.

**Autoxidation in Solutions Containing Manganous Chloride, Ammonium Chloride, and Ammonium Hydroxide.**—Since ammonium chloride prevents the precipitation of manganous hydroxide by ammonium hydroxide, the effect of varying the ammonium chloride concentration was first studied. Because the reaction does not follow any ordinary rate law the results have been recorded (Table I) as volumes of oxygen absorbed in definite time intervals. A comparison of these volumes shows the effect of the concentration of ammonium chloride upon the reaction. The total volumes absorbed indicate definite limits. Each trial was continued until the buret level had remained constant for a period of from one-half to one hour.

The final volume of oxygen absorbed varied between 67 and 83% of the volume theoretically required for the formation of manganese dioxide (54.0 cc.). Curves represent-

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(1) J. W. Meyer and R. Nerlich, *Z. anorg. allgem. Chem.*, **116**, 117 (1921).

(2) J. Herman and O. Lievin, *Compt. rend.*, **200**, 1474 (1935); also J. Herman, *ibid.*, **202**, 419 (1936).

(3) J. Meyer, *J. prakt. Chem.*, **72**, 278 (1905).

(4) G. W. Filson and J. H. Walton, *J. Phys. Chem.*, **36**, 740 (1932).

TABLE I  
EFFECT OF AMMONIUM CHLORIDE CONCENTRATION  
MnCl<sub>2</sub>, 0.0692; NH<sub>4</sub>OH, 0.477 mole per liter

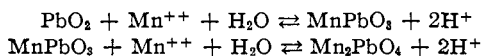
NH <sub>4</sub> Cl mole/liter	pH	Volume of oxygen, cc., absorbed in				Total volume ab- sorbed
		5 min.	10 min.	15 min.	20 min.	
0.0	9.59	34.4	35.9	36.6	37.2	41.55
.167		31.5	37.5	38.55	39.1	44.65
.250		21.7	35.7	37.6	38.3	41.75
.333		19.3	26.6	36.1	38.6	42.7
.417	9.12	17.6	21.7	27.9	35.1	41.7
.500		15.4	19.6	23.5	29.45	41.15
.583		13.1	17.9	21.8	26.9	39.7
.750		9.1	14.05	17.65	23.6	36.15
1.35	8.93	2.3	4.95	7.95	11.1	39.7
2.70	8.60	1.7	2.05	2.4	2.9	38.8
4.05	8.36	0.45	0.6	0.7	0.8	37.3

ing duplicate runs varied by not more than 2%. The pH values listed were obtained by preparing reaction mixtures identical with those autoxidized and measuring the pH immediately by means of the glass electrode. A precipitate of manganous hydroxide was formed immediately in samples of pH above 9.3. Samples of pH 9.0 precipitated after standing a moment or two, while those of pH below 8.8 precipitated only very slowly. In each case the precipitate was white when first formed.

The rate of oxygen uptake decreased at first after the reaction had proceeded for a period, and then increased appreciably before finally decreasing as the reaction approached completion. The possibility of an autocatalytic effect, suggested by this observation, was investigated by adding to the reaction mixture a small amount of the solid oxidation product from previous trials. This resulted in a much more rapid reaction, and the rate was found to decrease continuously. Since the oxidation product was presumably largely manganese dioxide, a pure sample of this substance was tried. It also catalyzed the reaction. The effect of the manganese dioxide was found to depend upon its state of subdivision. Four reaction mixtures of the following composition were prepared: manganous chloride, 0.0692 mole per liter, ammonium hydroxide, 0.477 mole per liter, ammonium chloride, 2.25 moles per liter. The results, expressed in terms of the time required for the absorption of 20 cc. of oxygen when 0.5 g. of manganese dioxide of the indicated fineness was added to the reaction mixture, were: 60-80 mesh, 28 minutes; 120-140 mesh, 15 minutes; 200 mesh, 9 minutes. A similar sample to which no solid material had been added required 82 minutes.

Commercial manganese dioxide, ferric oxide, diatomaceous earth, and ground glass gave effects similar to that of the prepared manganese dioxide. Thus the effect appears to depend upon the surface of the particles rather than upon their chemical composition.

In connection with the study of these solid accelerators, powdered lead dioxide was tried. In this case the autoxidation was found to be completely inhibited. The manganese precipitated from this slightly alkaline solution is in a form which is not affected by oxygen. The reaction may take place through the steps:



From these equations, the addition of neutral lead dioxide to manganous chloride solutions should result in a noticeable decrease in pH. That such a decrease actually occurs is shown by the following test: 1 g. of lead dioxide was added to 60 cc. of distilled water of pH 6.30. The pH of the supernatant liquid was 6.18. In a similar experiment with 60 cc. of 0.568 molar manganous chloride solution of pH 5.85, the pH was reduced to 3.20 by the addition of 1 g. of lead dioxide. The X-ray diffraction pattern of the product gave no lines other than those characteristic of lead dioxide, indicating that if a new product is formed, it is either amorphous or present in comparatively small amount. Powdered stannic oxide and red lead oxide had no effect upon the volume of oxygen absorbed; they showed, however, the accelerating effect of the other inert solids.

Since autoxidation reactions are frequently accelerated or retarded by phenols, nitrogen compounds, iodine compounds, etc., the effects of certain examples of these classes of compounds upon the autoxidation of manganous hydroxide were determined. The results may be summarized as follows:

Potassium iodide, urea, thiourea, aniline,  $\beta$ -naphthol, acetamide, ethylene glycol, ammonium thiocyanate, nickel chloride, calcium chloride, sodium chloride, and potassium chloride had no appreciable effect. Ammonium picrate and *m*-nitroaniline accelerated the reaction slightly. Dextrin, glycerol, and iodine retarded the reaction very markedly, but had no effect upon the total volume of oxygen absorbed. These substances perhaps act by being adsorbed at the surface of the oxidation product, thus reducing its catalytic effect. In some cases complex formation may also be a possibility.

Copper chloride, cobalt chloride, and ferric chloride accelerate the reaction, as shown by trials in which reaction mixtures of the following composition were used; manganous chloride, 0.0722 mole per liter, ammonium hydroxide, 0.477 mole per liter, ammonium chloride, 1.35 moles per liter. In each case the concentration of the catalyst used was 0.0018 mole per liter. The times required for the absorption of 20 cc. of oxygen were: cupric chloride, thirty-one minutes; cobaltous chloride, eleven minutes; ferric chloride, eight minutes. A similar sample to which nothing was added required 35.5 minutes. The effect of the ferric chloride is probably due to the large surface of the ferric hydroxide and is similar to that produced by other insoluble substances. The effects of copper and cobalt are probably due to their well-known property of acting as oxygen carriers. In the data recorded above, the concentration of the added salt was one-fortieth of the manganous chloride concentration. In other trials, the salt concentration was reduced to one-two-hundredth, but the accelerating effect was still noticeable.

In connection with the possibility of the formation of an intermediate peroxide in these solutions, it was of interest to determine whether or not the autoxidation of manganous hydroxide was capable of inducing the oxidation of certain acceptors. Dhar<sup>5</sup> and his co-workers have reported that the

(5) N. R. Dhar, *J. Proc. Asiatic Soc. Bengal Proc. 8th India Sci. Cong.*, **17**, CXXX (1921); through *Chem. Abs.*, **17**, 2220 (1923).

oxidation of sodium formate, sodium oxalate, sodium arsenite, sodium nitrite, and ferrous ammonium sulfate are induced by this reaction. In the present work these results were not confirmed. Sodium formate, sodium oxalate, sodium arsenite, sodium nitrite, and allyl alcohol were used as acceptors but in no case was any excess of oxygen absorbed over that required for the manganese alone. In view of these results the formation of a peroxide seems improbable.

When air was used in place of pure oxygen, the absorption was much slower and the total volume of oxygen taken up was much less. The volume absorbed with pure oxygen was about 32 cc., while with air it was about 18 cc. When air was used and the ammonium chloride concentration was varied, the volume of oxygen absorbed remained the same, while the effect of ammonium chloride upon the rate was the same as that observed when oxygen was used. In these trials all of the manganese was precipitated, although the volume of oxygen absorbed was only about 40% of that theoretically required for the formation of manganese dioxide. This surprising result may be explained if it is assumed that a secondary reaction takes place by which manganese is removed from solution without being oxidized. If this secondary reaction does not involve oxygen, it would be expected to continue at an undiminished rate when air is substituted for oxygen. Since the autoxidation reaction is slower in air, a larger proportion of the manganese would be removed by the secondary reaction, and the total volume of oxygen absorbed would be correspondingly reduced. The nature of the secondary reaction will be further discussed in connection with the effect of change in temperature.

**Autoxidation of Manganous Hydroxide Precipitated by Sodium Hydroxide.**—In the work described, ammonium hydroxide was used in the presence of such amounts of ammonium chloride as would give a conveniently measurable reaction velocity at 25°. It was of interest to determine the effect of temperature, but since the use of ammonium hydroxide did not lend itself satisfactorily to such measurements, a number of experiments were carried out in which sodium hydroxide was used. In all of these experiments the absorption of oxygen was very rapid, but the theoretical volume of oxygen required for the formation of manganese dioxide was never absorbed. However, temperature and the proportions of man-

ganous chloride and sodium hydroxide were found to have a very great effect upon the extent of the reaction as shown by Tables II and III.

TABLE II

EFFECT OF CONCENTRATION OF SODIUM HYDROXIDE AT 45°  
MnCl<sub>2</sub>, 0.0568 mole per liter

NaOH mole/liter	Ratio NaOH/2- MnCl <sub>2</sub>	Volume of oxygen, cc. absorbed in			Final vol. O <sub>2</sub> abs./theo. vol. for MnO <sub>2</sub>
		5 min.	10 min.	15 min.	
0.100	0.88	13.6	13.6	13.6	0.306 <sup>a</sup>
.114	1.00	16.0	16.0	16.0	.360 <sup>a</sup>
.128	1.13	22.4	22.5	22.5	.515
.171	1.51	31.0	31.8	32.1	.763
.186	1.63	32.0	32.7	33.2	.798
.200	1.76	34.2	35.0	35.4	.874

<sup>a</sup> See note *a* in Table III.

TABLE III

EFFECT OF CONCENTRATION OF SODIUM HYDROXIDE AT 0°  
MnCl<sub>2</sub>, 0.0568 mole per liter

NaOH mole/liter	Ratio NaOH/2- MnCl <sub>2</sub>	Volume of oxygen, cc., absorbed in			Final vol. O <sub>2</sub> abs./theo. vol. for MnO <sub>2</sub>
		5 min.	10 min.	15 min.	
0.100	0.88	18.5	20.8	21.8	0.537 <sup>a</sup>
.114	1.00	25.0	26.4	26.9	.664 <sup>a</sup>
.128	1.13	28.3	29.3	29.8	.722 <sup>a</sup>
.143	1.26	35.4	36.3	36.8	.902
.157	1.38	37.3	38.1	38.6	.935
.171	1.51	37.7	38.6	39.1	.948
.186	1.63	38.2	38.9	39.4	.957
.200	1.76	38.4	39.1	39.5	.957

<sup>a</sup> Analysis of solutions remaining after oxygen absorption had ceased indicated that in these trials not all of the manganese had been precipitated.

At the end of each run the samples were removed and filtered. The clear filtrate was tested for manganous ion by treatment with an excess of sodium hydroxide. A solution at 0° which had contained 1.13 times the amount of sodium hydroxide theoretically required to precipitate all of the manganese was found to contain an appreciable amount of manganese in solution; while in the corresponding trial at 45°, all of the manganese had been precipitated. Analysis of the solid oxidation products gave results in agreement with the volumes of oxygen absorbed.

Certain peculiarities in the results of these experiments are worthy of further consideration.

(1) In those trials at 45° in which all of the manganese was not precipitated, the composition of the precipitate was approximately Mn<sub>2</sub>O<sub>3</sub>, while in similar trials at 0°, the product had a composition intermediate between Mn<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub>.

(2) With excess of sodium hydroxide, the degree of oxidation at 45° was never as high as that in corresponding trials at 0°.

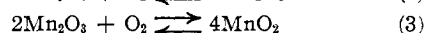
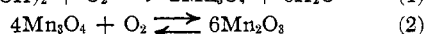
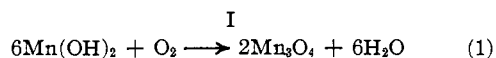
(3) Under no circumstances, regardless of tem-

perature or excess of alkali, was the product 100%  $\text{MnO}_2$ .

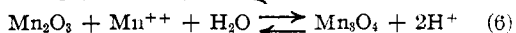
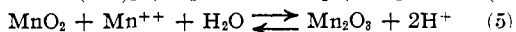
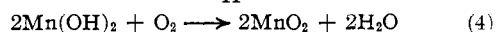
(4) At  $45^\circ$  the less sodium hydroxide present, the more abruptly the reaction stopped, while at  $0^\circ$  the reverse was true.

(5) The equivalent amount of sodium hydroxide does not cause complete precipitation of the manganese as manganous hydroxide.

The fact that the composition of the product varies between that corresponding to  $\text{MnO}_2$  and a product of lower degree of oxidation than  $\text{Mn}_2\text{O}_3$  can be explained by either of two mechanisms, represented by the following series of reactions



II



Series I would account for the results if steps (2) and (3) are equilibria which shift to the left at higher temperatures and to the right at higher sodium hydroxide concentrations. However, experiments showed that steps (2) and (3) do not take place in either direction under conditions comparable with those under which autoxidation was carried out.

Series II would explain the results provided steps (5) and (6) are rapid at high temperatures but almost negligibly slow at  $0^\circ$ . This mechanism also includes the secondary reactions needed to account for the results observed when air is used in place of oxygen. The fact that steps (5) and (6) do actually take place is indicated by the results of other investigators. Tillmans,<sup>6</sup> Hirsch, and Höffner in a very complete study of the reaction between manganese dioxide and manganous ions found that the reaction is favored by high temperature and by increasing  $p\text{H}$  in the range in which manganous hydroxide is not precipitated. They also found free acid is formed as indicated by step (5). The effect of excess alkali in repressing steps (5) and (6) would be expected since it would reduce the manganous ion concentration.

It will be noted that steps (5) and (6) correspond closely to the reactions previously proposed to account for the effect of lead dioxide.

As a further check on the nature of the oxida-

tion product the X-ray diffraction patterns of samples prepared under different conditions were determined and compared with the published patterns of the known manganese oxides. A sample prepared at  $90$ – $100^\circ$  in the presence of excess manganous chloride gave a pattern identical with that of hausmannite,  $\text{Mn}_3\text{O}_4$ . No patterns corresponding to  $\text{Mn}_2\text{O}_3$  or  $\text{MnO}_2$  were obtained from any of the samples prepared. Apparently if such products are formed they are amorphous. The product which approached the composition of  $\text{MnO}_2$  most closely showed faint suggestions of a pattern but not enough to permit its definite identification.

**Autoxidation in Solutions Containing Triethanolamine.**—In order to permit the study of the effect of  $p\text{H}$  without the complicating effect of ammonium ions, triethanolamine was used as the precipitating agent. The oxidation was much slower than under any previously studied conditions, but no induction period was observed, although the  $p\text{H}$  was in the same range as that of the ammonium hydroxide–ammonium chloride solutions previously described. However, when ammonium chloride was added to the triethanolamine solution, the resulting curve did show an induction period. The extreme slowness of the reaction is shown by the following data which give volumes of oxygen absorbed for various time intervals at  $25^\circ$ . The reaction mixture had the following composition:  $\text{MnCl}_2$ , 0.0568; triethanolamine, 0.317 mole per liter.

Minutes	5	15	60	220	366
Gas abs., cc.	12.0	15.2	18.6	24.2	26.7
Minutes	477	605	1320	1440	
Gas abs., cc.	28.0	28.95	47.2	48.2	

**The Nature of the Autoxidation Process in Ammoniacal Solution.**—In considering the autoxidation of manganous hydroxide in the solutions containing ammonium chloride and ammonium hydroxide, the question arises as to the substances present in the solution and which of these is actually undergoing autoxidation. In addition to the presence of manganous ions, undissociated dissolved manganous hydroxide, and in some cases a precipitate of manganous hydroxide in these solutions, there is a definite possibility that a complex ion of the type  $\text{Mn}(\text{NH}_3)_x^{++}$  is also present. The work of Brezena,<sup>7</sup> who made polarographic and cryoscopic studies of these solutions, has shown that manganous ions and

(6) J. Tillmans, P. Hirsch and J. Höffner, *Gas- u. Wasserfach.*, **70**, 26 (1927).

(7) J. Brezena, *Rec. trav. chim.*, **44**, 520 (1925).

ammonia molecules are both removed from solution with the formation of a complex when ammonium hydroxide is added to a manganous chloride solution containing ammonium chloride. The evidence of the present work seems to favor the existence of a mangano-complex in these solutions. The specific effect of ammonium chloride in producing a different shaped velocity curve from that obtained in triethanolamine solutions of the same  $pH$ , and the fact that changes in ammonium chloride concentration have no effect upon the composition of the final product may both be explained by the assumption of the existence of such a complex. However, since Brezena's work indicates that the amount of complex increases with increasing ammonium chloride concentration, while the present work has shown that the rate of autoxidation decreases with increasing ammonium chloride concentration, it is unlikely that the complex itself is the substance autoxidized. Undoubtedly precipitated manganous hydroxide is autoxidized, and it is probable that the dissolved undissociated manganous hydroxide behaves similarly. Since neutral solutions show no autoxidation, it is evident that manganous ions are not affected.

### Summary

1. The rate of autoxidation of manganous hydroxide in ammoniacal solution has been found to decrease with increasing ammonium chloride

concentration. An induction period exists when the ammonium chloride concentration is high.

2. Powdered manganese dioxide, stannic oxide, ferric oxide, red lead oxide, ground glass, and diatomaceous earth accelerate the reaction and eliminate the induction period.

3. In the presence of lead dioxide no autoxidation of divalent manganese occurs.

4. Cobalt chloride and copper chloride accelerate the reaction, while glycerol, dextrin, and iodine retard it. A large number of other substances were found to have no effect.

5. The autoxidation of manganous hydroxide does not induce the oxidation of sodium oxalate, sodium formate, sodium arsenite, sodium nitrite, or allyl alcohol.

6. The autoxidation by air is much slower and less complete than that by pure oxygen.

7. The autoxidation of manganous hydroxide precipitated by fixed alkali is very rapid. The product depends upon the temperature and the proportions of manganous ion and alkali. The X-ray diffraction patterns of the products were studied.

8. The autoxidation of manganous hydroxide precipitated by triethanolamine was found to be very slow. It did not display the induction period observed in ammoniacal solution.

9. A mechanism to account for the above results has been proposed.

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## The Dielectric Investigation of Polypeptides. II. The Dispersion of Simple Amino Acid Polypeptides

BY W. P. CONNER<sup>1</sup> AND C. P. SMYTH

Although important conclusions concerning the nature of polypeptide molecules have been drawn from consideration of their dielectric increments per mole of solute, it is recognized that a more complete picture may be obtained from measurement of the anomalous dispersion of the dielectric constants of their water solutions. The linear increase of increment values of the polypeptides with the number of glycine residues, as suggested by Wyman,<sup>2</sup> lends support to the view that there

is almost complete freedom of rotation about the valence bonds which make up the backbone of the peptide chains. Statistical calculations by Kuhn<sup>3</sup> of the polarization of a straight-chain molecule in which there is free rotation about the valence bonds and electrostatic attraction between the oppositely charged ends of the chain show that the polarization as measured by the static dielectric constant would be the same whether the chains underwent orientation polarization or dilation-contraction polarization. Because of the apparent lack of restriction in position of the electrically

(1) Research Assistant on Special Funds from the Rockefeller Foundation.

(2) (a) Wyman, *Chem. Rev.*, **19**, 213 (1936); (b) Wyman, *J. Phys. Chem.*, **43**, 143 (1939).

(3) Kuhn, *Z. physik. Chem.*, **175A**, 1 (1935).