and with the average, 1.76 ± 0.03 Å., observed for a number of compounds.[18]

As mentioned in the Introduction it has been suggested[6] that an unusually large amount of double bond character in the B–Cl bonds of B-trichloroborazole is accompanied by a smaller degree of double bond character in the B–N bonds than is characteristic of borazole. Far from supporting this suggestion, our data on bond lengths and on the molecular configuration would seem to exclude this possibility from further consideration.

The packing arrangement of the molecules is clear from a consideration of Figs. 1, 2 and 4. Mirror planes are shown as solid lines at $y = {}^1/_4$, $y = {}^3/_4$, diagonal glide planes with the glide $\frac{b}{2} + \frac{c}{2}$ are shown as alternately dotted and dashed lines at $x = {}^1/_4$, $x = {}^3/_4$, and axial glide planes with the glide $\frac{a}{2}$ are shown as dashed lines at $z = {}^1/_4$, $z = {}^3/_4$. The planes of the molecules are indicated in Fig. 4 by dotted lines.

Pairs of molecules (Fig. 1) straddle the mirror planes at $y = {}^1/_4, {}^3/_4$, occupy parallel planes which have a perpendicular separation of only 0.36 Å., and point in opposing directions along *a*. Successive molecules along *a* are tipped alternately +27.4° and −27.4° with respect to (001). The arrangement is such that every N–H bond is directed toward a chlorine atom of an adjacent molecule.

Along *c* the distance between the molecules is determined by contacts between equivalent chlorine atoms of neighboring cells. The corresponding Cl–Cl separation is c = 3.95 Å., or 0.35 Å. greater than the van der Waals separation expected from Pauling's tabulation.[19]

Perpendicular to *c*, the packing is determined by contacts between N–H groups and chlorine atoms. The closest approach along *a*, between N_4 and Cl_4, is 3.49 Å., along *b*, between N_8 and Cl_8, 3.56 Å. The electrostatic interactions N–H . . . . Cl implied by these distances are perhaps too weak to be called hydrogen bonding.

In terms of the loose packing of the molecules an averaged thermal parameter, $\bar{B}$ = 6.1 Å.^{2}, does not seem unduly large. The packing is especially free along the normal to the molecular plane and is tightest in the direction of the secondary molecular axis passing through fourfold atoms in the symmetry plane of the unit cell. These molecular axes are rotated about *b* by 27.4° from the positions of the *c* and *a* crystal axes, respectively.

All contours of eightfold chlorine peaks (Fig. 3) show a pronounced elongation normal to the molecular plane. The outer contours of fourfold chlorine peaks (Fig. 4) show a similarly oriented but much less pronounced elongation. This last seems to be true also for fourfold nitrogen peaks. It would appear that a libratory motion of the molecule about the secondary molecular axis lying in the mirror plane of the cell is superimposed upon and coupled with somewhat anisotropic lattice vibrations.

We are indebted to Mr. R. E. Hughes for computations of the differential syntheses leading to the accurate evaluation of parameters for eightfold nitrogen and boron atoms. We wish to thank Professor J. Monteath Robertson for encouraging and helpful discussions pertaining to accuracy and the nature of the reliability coefficient.

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[18] A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones and L. E. Sutton, *Trans. Faraday Soc.*, **33**, 852 (1937).

[19] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

ITHACA, N. Y. RECEIVED JULY 12, 1951

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Catalytic Activity of Supported Manganese Oxides for the Hydrogen Peroxide Decomposition[1]

BY JOHN MOOI AND P. W. SELWOOD[2]

The catalytic decomposition of hydrogen peroxide in dilute water solution on various supported manganese oxides has been studied. The activity of these catalysts as a function of the concentration of manganese on the support shows an increase with decreasing manganese concentration, followed by a sudden decrease for very low manganese concentrations. The influence of oxidation state, *p*H, support phase modification and temperature has also been studied. The data have been interpreted on the basis of a mechanism involving simultaneous oxidation and reduction of the catalyst by the hydrogen peroxide in which trivalent and tetravalent manganese take part. Low activities for samples of low manganese concentrations show the influence of the support in stabilizing one of these forms of the catalyst.

Information about the structure of supported oxides of manganese as obtained by the susceptibility isotherm method has been presented in two previous papers from this Laboratory.[1,3] The samples studied were several series of supported oxides and a few catalysts on various modifications of the support. The method of preparation of the samples was by impregnation with manganous nitrate solution followed by ignition to decompose the nitrate. By varying the concentration of the solution, series of samples of differing manganese content were prepared on high area so-called "γ"-alumina, on alumina containing sodium oxide, and on rutile. Ignition was generally at 200° with the exception of one series on "γ"-alumina, called the high-ignition series, for which the ignition

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[1] This is the eleventh paper from this Laboratory on the susceptibility isotherm. The tenth by Selwood and Lyon appeared in THIS JOURNAL, **74**, 1051 (1952). A Communication to the Editor in connection with the present paper appeared in THIS JOURNAL, **73**, 4333 (1950).

[2] Inquiries concerning this paper should be addressed to P. W. Selwood.

[3] P. W. Selwood, T. E. Moore, M. Ellis and K. Wethington, THIS JOURNAL, **71**, 693 (1949).

temperature was 600°. The studies showed that the manganese oxide appears on the surface of the support in patches which leave much of the support surface bare. These patches become smaller as less manganese is present in the sample. The oxidation states of the manganese were found to be +3 for the high-ignition series, +4 for the series on rutile, about 3.5 for the series on alumina containing sodium oxide, and to change from +4 to +3 with increasing dispersion in the case of the low-ignition (200°) series on "γ"-alumina. Catalysts prepared on various forms of alumina were found to be similar to those of the series on "γ"-alumina (low ignition). This paper is concerned with the relation between this structural information and the activity of these materials as catalysts for the hydrogen peroxide decomposition.

Experimental

The apparatus used to determine the activity of the supported manganese oxides consisted of a short large-diameter test-tube which served as the reaction vessel. This was fitted with a rubber stopper through which ran the tip of a buret, a stirrer and a connection to a flow meter. The reaction mixture was kept at constant temperature by immersion in a water-bath controlled manually.

The procedure followed was to introduce a weighed amount of the catalyst sample into the test-tube. This was washed in with 20 cc. of water. The test-tube was then fitted to the rest of the apparatus, the water-bath was brought into position, and stirring was begun. After thermal equilibrium was reached, as shown by a zero reading on the flow meter, 2.00 cc. of hydrogen peroxide solution was dropped on to the catalyst from the buret. Zero time was taken when the last of the 2.00 cc. of the solution reached the catalyst suspension. Time and flow meter readings were then taken at intervals of one-half to two minutes. A plot of rate of oxygen evolution *versus* time generally, with the exception of a short induction period, gave straight lines as shown in Fig. 1. The high ignition series gave no induction period. These plots were extrapolated to zero time for determination of the rate used as a measure of activity for the sample.

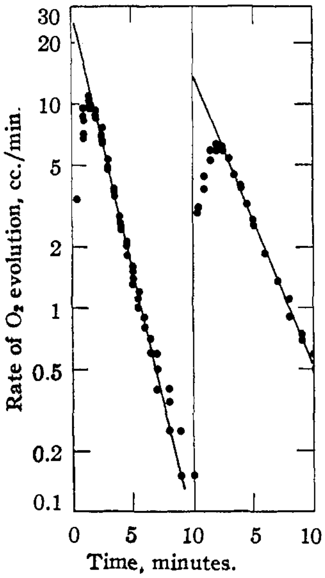

Fig. 1.—Semi-log plot of oxygen evolution, for extrapolation to zero time. The plot on the left is for 4.6% Mn on alumina at *p*H 4.5. The plot on the right is the same at *p*H 7.0

It was desirable to obtain the activity per unit weight of manganese so that the activity of the manganese oxide in the samples could be compared. The weight of each sample, then, was chosen so as to give a constant weight of manganese for each test.

The hydrogen peroxide solutions were made up freshly by diluting Superoxol (hydrogen peroxide 30% Merck and Co., Inc.) with water. These solutions were standardized to 1.14 ± 0.01 *M* H_2O_2 by titration in dilute sulfuric acid solution with standard potassium permanganate. The temperature was held at 25.5° except where otherwise noted.

In certain cases the *p*H of the suspension was altered by the addition of 0.1% NaOH or 1:50 HCl. In this work the *p*H was determined with a Beckman meter, Model G, before addition of the hydrogen peroxide and, in a number of cases, after decomposition was complete.

Results

In Fig. 2 are shown plots of activity *versus* manganese concentration for the low ignition series manganese oxide on "γ"-alumina. These data were obtained on samples of such size that they contained 4.60 mg. of manganese. The suspensions of the catalysts in water gave *p*H values close to 4.5. Data are given for the decomposition run on the suspensions without *p*H adjustment, and also on suspensions of which the *p*H had been adjusted to 7.0 by addition of 0.1% NaOH.

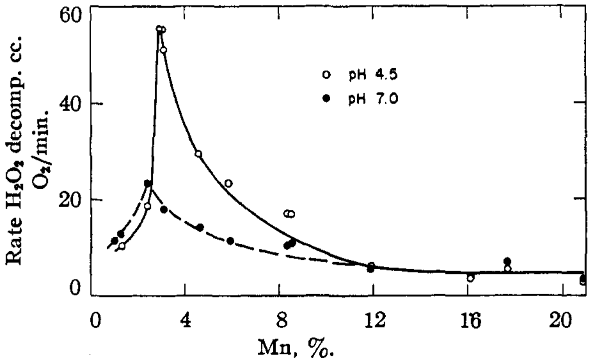

Fig. 2.—Catalytic activity of low-ignition manganese oxides on alumina as a function of manganese concentration.

Figure 3 shows the activity of the samples of the high-ignition series on "γ"-alumina and the series on rutile. The samples of the high-ignition series contained 4.60 mg. of manganese; those of the series on rutile contained 1.53 mg. of manganese. These samples gave *p*H values very near 7.0 when suspended in water, so that no *p*H adjustment was required.

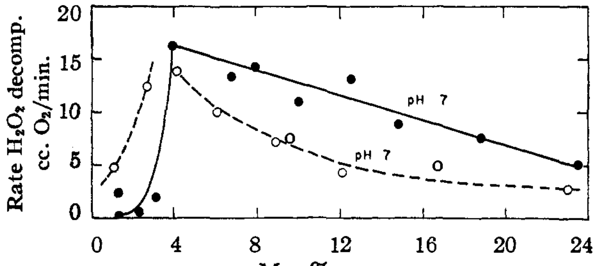

Fig. 3.—Catalytic activity of supported manganese oxides on rutile (●) and on alumina (high-ignition) (○).

Data obtained for the decomposition rates over manganese oxides supported on χ-, κ-, γ-, δ- and η-aluminas, on a number of samples on alumina containing sodium oxide, and on samples of manganese oxide supported on "sodium-free" alumina, are given in Fig. 4. Data on the sodium oxide–alumina and "sodium-free" aluminas were obtained on samples containing 2.30 mg. of manganese. The other data were obtained on samples containing 4.60 mg. of manganese. These are the identical samples for which magnetic data were presented in an earlier paper. The *p*H values of the sodium oxide–alumina and the sodium-free alumina samples were near neutral and no adjustment was made. The other samples were adjusted to *p*H 4.5 for comparison with the *p*H 4.5 curve of the series on "γ"-alumina, which curve is included in the figure for comparison.

The dependence of the decomposition rate on the amount of catalyst was determined by using portions of a low ignition sample on "γ"-alumina containing 3.1% manganese. The results showed that a 100% change of catalyst weight produced a linear change of activity within 2% limits.

The specific surface areas for three samples of the low ignition series manganese oxides on "γ"-alumina were determined by low temperature adsorption of nitrogen and the BET equation. The results showed that the tenfold change

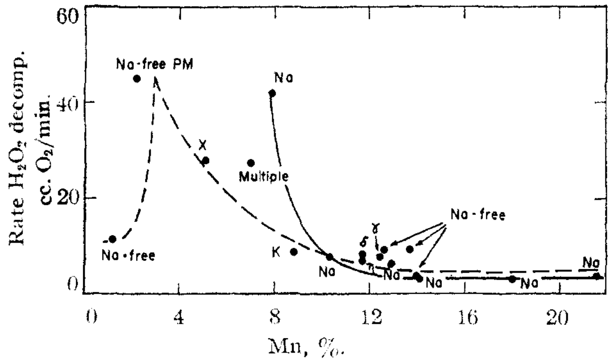

Fig. 4.—Catalytic activity of supported manganese oxides on a variety of modified alumina supports. Thus, "Na" refers to a sample prepared on alumina containing some alkali. "Multiple" refers to a sample prepared by repeated impregnation and ignition.

of catalytic activity which is found for this series is accompanied by only a 35% change in specific surface. Percentage concentrations of manganese and specific surface areas in m.^{2}g.$^{-1}$ were: 0.0 (pure support), 200; 1.3, 173; 8.3, 161; and 20.9, 129.

The oxidation state of the manganese in the samples used in the studies described in the previous paragraphs varied from plus three to plus four. It seemed advisable, therefore, to study the effect of changing the oxidation state. A sample of supported manganese oxide was prepared and analyzed by the procedures described in a previous paper[3] for samples of the low ignition series on "γ"-alumina. The manganese concentration in the sample was found to be 17.8%, all, as far as could be detected, in the plus four state. This material was reduced in hydrogen for two weeks at 150°. During this time samples were removed periodically and analyzed for total and active manganese. The samples were also tested for activity toward the hydrogen peroxide decomposition. The decomposition was first order for all samples. The results plotted as rate of H_2O_2 decomposition *versus* oxidation state of manganese are shown in Fig. 5.

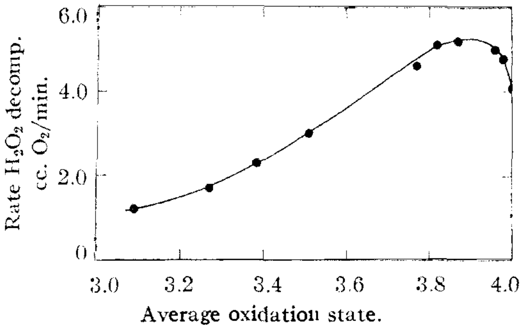

Fig. 5.—Catalytic activity *versus* oxidation state for a sample of supported manganese oxide subjected to slow reduction.

A series of studies was made on the effect of changing *p*H on the catalytic activity of the supported manganese oxide systems. For this experiment three samples from the low ignition series on "γ"-alumina were used. These were samples containing 8.5, 2.85 and 1.3% Mn. The average oxidation states of the manganese in these samples was, respectively: 3.96, 3.6 and 3.1. Also used was a sample from the high ignition series manganese oxide on "γ"-alumina. This sample contained 9.6% manganese. The data obtained are shown in Fig. 6. The data given are for the *p*H of the suspension before addition of hydrogen peroxide solution. In a number of cases the *p*H was also measured after the run. In each of these cases the final *p*H showed the solution had become more nearly neutral.

To determine whether the sudden drop in activity of the catalysts as the concentration of manganese falls below 2 or 3% was due to a loss in the amount of active catalyst or to a change in the activation energy of the reaction, the decomposition was run over a range of temperature. The temperature range used was from 0 to 30. Three samples were chosen from the low ignition series manganese oxide on alumina. One contained 2.85% Mn, and showed a high catalytic activity; another contained 1.3% Mn, and was below the peak of activity on the low concentration side; the third contained 16.1% manganese, and was below the peak of activity on the high concentration side. Also used was a sample of manganese oxide on rutile containing 14.8% Mn. Samples containing 4.60 mg. of manganese were used. The data are plotted according to the Arrhenius equation in Fig. 7. Table I gives the apparent activation energies and frequency factors for these samples.

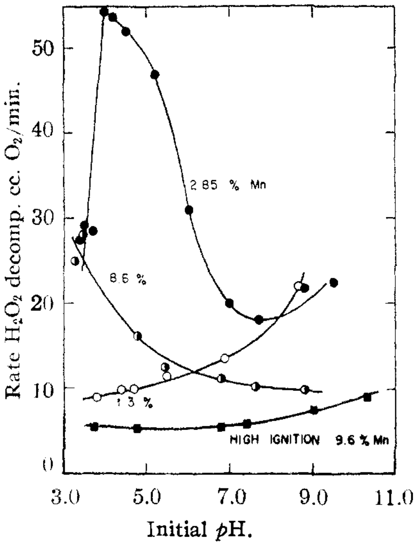

Fig. 6.—Effect of *p*H on catalytic activity of several supported manganese oxides.

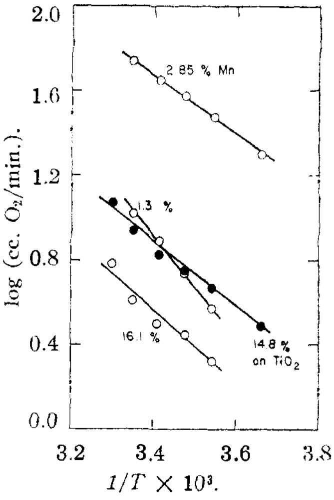

Fig. 7.—Arrhenius equation plot for several supported manganese oxide samples.

A series of measurements was made on miscellaneous supported oxides. Catalytic activity was negligibly small for the following: nickel oxide on alumina, nickel oxide on rutile, vanadia on alumina, vanadia on rutile, chromia on alumina, and cobalt oxide on alumina. A catalyst sample obtained through the courtesy of the Sinclair Refining Company gave activity results comparable with those found with supported manganese oxides. This sample consisted of cobalt and magnesium oxides, in the proportion Co:2Mg, supported on celite.

TABLE I

ACTIVATION ENERGIES AND FREQUENCY FACTORS OF THE H_2O_2 DECOMPOSITION ON SOME MANGANESE OXIDE CATALYSTS

Manganese, %	$E_{act.}$ kcal.	log A
1.3 (on alumina)	10.7	7.72
2.85 (on alumina)	6.52	5.45
16.1 (on alumina)	7.30	5.88
14.8 (on rutile)	7.05	6.12

Discussion

All curves relating hydrogen peroxide decomposition activity to manganese concentration have the same general shape for the several catalyst series. As the manganese concentration is decreased the activity first rises and then suddenly drops. The initial rise in the curve is to be expected on the basis of the magnetic measurements which showed the manganese to be more dispersed as the concentration was decreased. More manganese oxide is on the surface and less in positions inaccessible to the hydrogen peroxide. This first part of the hydrogen peroxide curve is similar to the curve for the activity of supported chromia for the dehydrocyclization of *n*-heptane.[4]

Changes in the support seem to have little effect on the rate of the hydrogen peroxide decomposition. The results in Fig. 4 show that the activities of the manganese oxides on χ-, κ-, γ-, δ- and η-aluminas are, within experimental error, the same as the activities of the samples of the low ignition series on the so-called "γ"-alumina. The presence of alkali in the support has apparently moved the activity curve over to higher percentages, so that the peak in activity seems to be at 8%. Unfortunately, it is characteristic of the alumina containing alkali that no uniform supported sample can be prepared on it of composition below 8%. It is, therefore, impossible to determine where exactly the peak in activity would come, or, for that matter, whether it would be present in this series.

The decrease in activity at low percentages does not seem to be caused by a decrease in the amount of manganese oxide surface. It is conceivable that through solid solution formation manganese oxide is lost from the surface. The values of the frequency factors of the three samples of the low ignition series indicate that this is not the case. The long extrapolation to $1/T = 0$ necessary to find the frequency factor introduces considerable error into the results, but the very appreciably larger value for the 1.3% sample indicates that this sample, although it shows a low catalytic activity, has more manganese oxide taking part in the reaction.

Proton relaxation times obtained on these samples by methods previously described[5,6] verify these conclusions. The relaxation times show no minimum, but show the expected decrease with decreasing manganese concentration.

Broughton and Wentworth[7] have presented a quantitative discussion of the manganese oxide catalyzed hydrogen peroxide decomposition. They studied the conditions under which the catalytic decomposition begins and showed them to be such that the solubility product of manganous hydroxide was just exceeded. They concluded that this was consistent with a mechanism in which manganese dioxide is reduced by hydrogen peroxide to manganous ion, and manganous ion is oxidized to manganese dioxide only when present as the hydroxide.

There is some evidence that makes the presence of manganous hydroxide under the conditions of the Broughton and Wentworth experiments seem improbable. First the approximate free energy of −20,600 calories given by Latimer[8] for the reaction $Mn(OH)_2 + MnO_2 + H_2O \rightarrow 2Mn(OH)_3$ suggests that the experimental conditions are favorable for stabilization of the manganic ion as the hydroxide or as some form of hydrous oxide. The work of Dubois[9] on the composition of manganese oxide colloids formed under conditions similar to those of the Broughton and Wentworth experiments show the colloids had compositions corresponding to $MnO_{1.5}$ to $MnO_{1.6}$ and gave X-ray diagrams showing certain lines of sesquioxide hydrate.

A more reasonable mechanism involves manganese in the plus three and plus four oxidation states, both in the solid phase. Written in terms of oxides, equations for the mechanism are

$$Mn_2O_3 + H_2O_2 \longrightarrow 2MnO_2 + H_2O$$

$$2MnO_2 + H_2O_2 \longrightarrow O_2 + Mn_2O_3 + H_2O$$

These reactions, which occur in one electron step, would also be in better accord with the radical mechanism of the hydrogen peroxide decomposition which has been shown to be operative with other catalysts.

If the above equations properly represent the reaction, the drop in activity at low concentrations can readily be explained. The peak in activity comes at 2.5 to 4% manganese. It is at these concentrations that the effect of valence inductivity begins to be strongly felt. It is possible that the support by stabilizing one of the forms of the catalyst slows down the entire reaction. This view is in agreement with the increased apparent activation energy for the 1.3% low ignition sample. The alumina support in this case is stabilizing the sesquioxide. The drop in activity of the high ignition series can be ascribed to the same cause, while the drop in activity of the series on rutile is probably due to the stabilization of MnO_2 on that support.

If the support shows an effect on the valence of the ions of supported material it is equally probable that the oxidation state of an ion on the surface of a crystal will be stabilized to correspond to those in the crystal body. This means that reduction of a manganese dioxide crystal is facilitated if there is a crystal of the low oxide nearby into which the reduced ions can fit. By this reasoning, the place where the catalytic decomposition of hydrogen peroxide will proceed with the greatest ease will be on an interface between crystals of the plus three and plus four oxides. A concomitant and obvious conclusion is that certain minimum crystal aggregates are necessary for activity. An atomic dispersion would be completely inactive for this reaction. The reduction experiment (Fig. 5) supports these conclusions by showing that the activity increases when plus three–plus four interfaces are created by partial reduction with hydrogen. The fact that the increase in activity comes near an average oxidation state of 3.9 instead of 3.5, as

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(4) R. L. Eischens and P. W. Selwood, THIS JOURNAL, **70**, 2271 (1948).

(5) P. W. Selwood and F. K. Schroyer, *Discussions Faraday Soc.*, No. 8, 337 (1950).

(6) R. B. Spooner and P. W. Selwood, THIS JOURNAL, **71**, 2184 (1949).

(7) D. B. Broughton and R. L. Wentworth, *ibid.*, **69**, 741, 744 (1947).

(8) W. M. Latimer, "The Oxidation States of the Elements," Prentice-Hall, Inc., New York, N. Y., 1938, p. 221.

(9) P. Dubois, *Compt. rend.*, **196**, 1401 (1933); **199**, 1310 (1934).

might have been expected on the basis of the above argument, is not surprising because the reduction undoubtedly starts on the surface with the result that the surface may have an average oxidation state of 3.5 while the manganese oxide in the body of the material is still largely unreduced.

Since no hydrogen ion is used in the reactions of the mechanism, the activity changes caused by hydrogen ion must be due to some other effect. The hydrogen ion concentration decreases during the reaction, and manganous ion can be detected in the clear solution after the catalyst has been allowed to settle. The manganous ion concentration at the end of a run can be calculated roughly from the change in hydrogen ion concentration determined by *p*H measurement. This calculation shows that even with the lowest initial *p*H, 3.5, the amount of manganese that dissolved would be only 6% of that present (considering a sample containing 4.60 mg. of manganese). The dissolving of this manganese and the oxygen evolved during its reduction does not change the kinetics of the reaction from first order, and, therefore, would not affect the validity of the results as a measure of catalytic activity.

Broughton and Wentworth found no catalysis with manganous solutions until manganese dioxide formed. The oxidation of a manganous ion in *solution* by hydrogen peroxide is not a very probable reaction since it involves either the formation of the unstable manganic ion or a nucleus of solid manganese dioxide. Manganous ion adsorbed on the surface of manganese dioxide, however, may be more active in catalysis since on oxidation it can join the already formed manganese dioxide lattice. The adsorbed manganous ion could either take part in the reactions itself or form a site for the formation of a crystal of manganese sesquioxide. This latter reaction seems the more likely since the samples of catalyst which contained all the manganese in the plus three state showed no increased activity with decreasing *p*H. These samples showed, however, an increase in activity with an increase in *p*H. This can be explained in a manner similar to the above in which an ion such as manganate or permanganate acts to form MnO_2 sites on an Mn_2O_3 surface.

Acknowledgment.—It is a pleasure to acknowledge receipt of the Sinclair Refining Company Fellowship, which was held by the junior author. Part of the work was done under contract with the Signal Corps Engineering Laboratories.

EVANSTON, ILLINOIS RECEIVED SEPTEMBER 20, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Some Metathetical Reactions of the Gaseous Fluorides of Group IV[1]

BY WALTER C. SCHUMB AND DONALD W. BRECK[2]

The extent of conversion of the tetrafluorides of carbon, silicon and germanium to the corresponding chlorides, or to mixed chlorofluorides, by reaction with anhydrous metal chlorides under known conditions of temperature and pressure, was measured. The metal chlorides selected were either (a) non-volatile, convertible to a non-volatile fluoride (chlorides of magnesium, calcium or barium) or (b) easily volatile, convertible to a non-volatile fluoride (aluminum or ferric chlorides). Reactions were carried out both at atmospheric and under increased pressures (in a steel autoclave). The order of increasing reactivity of the respective fluorides toward metal chlorides was found to be: $CF_4 < SiF_4 < GeF_4$; and the order of increasing thermal stability of the chlorofluorides of these elments, MCl_nF_{4-n}, was found to progress in the reverse direction: Ge < Si < C.

Introduction

In view of the existence of a complete series of chlorofluorides of carbon,[3] silicon[4] and germanium,[5] it seemed of interest to establish the conditions under which conversion of carbon, silicon and germanium tetrafluorides into the corresponding tetrachlorides, or into intermediate chlorofluorides, might be attained. The simplest and most direct method appeared to be the use of suitable anhydrous metal chlorides in a metathetical process.

Boron trifluoride may be converted to the trichloride or tribromide by the action of anhydrous aluminum chloride or bromide.[6]

Boron fluorochlorides or fluorobromides were not isolated and heating sodium fluorosilicate with aluminum chloride gave only silicon tetrachloride. By reaction with aluminum chloride, tris-(*n*-propyl)-fluorosilane is converted into the corresponding chloro-compound.[7] Henne and Newman[8] found that aluminum chloride converts benzotrifluoride into benzotrichloride in the presence of acetyl chloride, and 1,1,2-trichlorotrifluoroethane undergoes halogen exchange with aluminum chloride to form 1,1-difluorotetrachloroethane and hexachloroethane.[9]

Two types of chlorinating agents were considered. The first type was a non-volatile chloride possessing a non-volatile fluoride, and the second type a metal chloride which is easily volatilized and which possesses a relatively non-volatile fluoride. Anhydrous magnesium, calcium and barium chlorides were used as examples of the first type, and for the second type anhydrous aluminum and ferric chlorides were utilized. In addition, an-

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[1] Presented in part at the Cleveland Meeting of the American Chemical Society, April 11, 1951. Based upon a thesis presented by D. W. Breck to the Department of Chemistry in partial fulfillment of the requirements for the Ph.D. degree.

[2] U. S. Rubber Fellow, 1950–1951.

[3] O. Ruff and R. Keim, *Z. anorg. Chem.*, **192**, 249 (1930).

[4] W. C. Schumb and E. L. Gamble, THIS JOURNAL, **54**, 3943 (1932); H. S. Booth and C. F. Swinehart, *ibid.*, **57**, 1333 (1935); H. H. Anderson, *ibid.*, **72**, 2091 (1950); R. V. Lindsey, Jr., *ibid.*, **73**, 371 (1951).

[5] H. S. Booth and W. C. Morris, *ibid.*, **58**, 90 (1936).

[6] E. L. Gamble, P. Gilmont and J. F. Stiff, *ibid.*, **62**, 1257 (1940).

[7] C. Eaborn, *J. Chem. Soc.*, 2755 (1949).

[8] A. L. Henne and M. S. Newman, THIS JOURNAL, **60**, 1697 (1938).

[9] W. T. Miller, *ibid.*, **62**, 993 (1940).