Summary

The systems phosphine–boron trifluoride, arsine–boron trifluoride and hydrogen bromide–boron trifluoride were investigated. Immiscibility of the liquid components was encountered in certain regions of the arsine–boron trifluoride and the hydrogen bromide–boron trifluoride systems. No evidence was found for compound formation between arsine and boron trifluoride, nor between hydrogen bromide and boron trifluoride. However, there is evidence that two coördination compounds exist between phosphine and boron trifluoride in the solid state, namely, $PH_3 \cdot BF_3$ and $PH_3 \cdot (BF_3)_2$.

It is postulated that the arsenic atom in arsine is too large to approach sufficiently close to the boron atom of boron trifluoride to coördinate, although the tendency for these atoms to coördinate is sufficiently great. It is calculated that less steric hindrance is encountered with boron trichloride than with boron trifluoride. This postulate explains the fact that arsine coördinates with boron tribromide and boron trichloride, but not with boron trifluoride.

It is believed that the ionic character of the hydrogen–halogen bond of the hydrogen halides is the controlling factor in the formation of coördination compounds between the hydrogen halides and boron trifluoride, accounting for the fact that the more ionic hydrogen fluoride forms three coördination compounds, whereas hydrogen chloride and hydrogen bromide form none.

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[Contribution from the Chemical Laboratory of Northwestern University]

Solid Oxides and Hydroxides of Manganese[1]

By T. E. Moore,[2] Marylinn Ellis and P. W. Selwood

This paper describes an experimental study on the preparation and properties of the solid oxides and hydroxides of manganese. Special attention has been paid to the *identity* and *characterization* of each substance. The work was performed under contract with the Squier Signal Laboratory, Army Service Forces, Fort Monmouth, New Jersey, as part of their program for the improvement of dry cells.

Analytical and Experimental Methods

Analyses performed were for total manganese and for "active" oxygen. Manganese was determined by reaction with standard ferrous sulfate after all of the manganese had been oxidized to permanganate.[3] Solution of the sample was effected by treatment with dilute sulfuric acid containing ferrous sulfate. Oxidation of the manganese from a valence of two to seven was accomplished by the use of sodium bismuthate in nitric acid. This procedure was found satisfactory for all the preparations.

"Active" oxygen was determined by making use of the quantitative reaction of manganese in valence states greater than two with ferrous ion. A known excess of standard ferrous ammonium sulfate was employed in the dissolution of the sample and the excess was then titrated with standard permanganate.[4] The active oxygen content of the sample was then computed by multiplying the number of equivalents of ferrous ion oxidized by the manganese by the factor 8.00.

It should be pointed out that while these analytical methods proved satisfactory for our present purposes, they would not suffice without modification for the analysis of natural substances containing appreciable amounts of oxidizable elements such as iron.

All X-ray data reported here were obtained with powdered samples on a North American Philips Recording X-Ray Spectrometer. A copper target was used.

Magnetic susceptibility data were obtained on a Gouy balance, as described elsewhere.[5]

Preparative procedures are described under the individual compounds.

Manganese (Mon)Oxide

Preparation.—This compound occurs as the mineral *manganosite.* Classical methods for its synthesis include (a) reduction of a higher oxide, and (b) thermal decomposition of the carbonate or oxalate. The first method has been used by Millar[6] and others[7] in preparations for thermochemical studies. The second method has been the subject of a careful study by LeBlanc and Wehner.[8] This method was adopted for the work reported here, with minor modifications, as follows: J. T. Baker "reagent grade" manganous nitrate was recrystallized from water. The carbonate was precipitated by ammonium carbonate and washed free of ammonium and nitrate ions while protected from the air by a layer of

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[3] Blair, This Journal, **26**, 793 (1904).

[4] Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1942, p. 551.

[5] Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, p. 2.

[6] Millar, This Journal, **50**, 1875 (1928).

[7] Southard and Shomate, *ibid.*, **64**, 1770 (1942).

[8] LeBlanc and Wehner, *Z. physik. Chem.*, **A168**, 59 (1933).

carbon dioxide (from a piece of "dry-ice" in the Buchner funnel containing the precipitate). The carbonate was dried (after washing with alcohol and ether) by evacuation in a desiccator containing phosphorus pentoxide, and was then decomposed by heating at 500° for forty-eight hours under vacuum.

Properties.—The product obtained in this manner was of a bright green color, and moderately stable in air, although it takes up oxygen, becoming brown, on standing exposed to air. The length of heating has a marked effect upon the stability, and those samples heated longest were found to be the most stable in air. Analysis of the product yielded the following.

	Mn, %	"Active" oxygen
Calculated for MnO	77.44	0.00
Found	77.2	.3
Southard and Shomate[7]	77.42, 77.45	..
LeBlanc and Wehner[8]	77.4	.00

The product was, therefore, somewhat less pure than has been obtained by other workers, yet it was sufficiently pure for the purposes of this work.

The crystal interplanar spacings and relative intensities of reflection were found as follows:

d, Å.		I/I_{max}	
reported[9]	found	reported[9]	found
2.56	2.57	0.66	0.70
2.22	2.22	1.00	1.00
1.57	1.58	0.66	0.50
1.34	1.34	.23	.17
1.28	1.28	.17	.15

The magnetic susceptibility of this compound at 25° was found to be 67.7×10^{-6}. This is in satisfactory agreement with the susceptibility of 69×10^{-6} reported by Bizette, Squire and Tsai.[10]

The identity of this compound seems to be well established. The crystal habit is face-centered cubic, $a = 4.436 \pm 0.002$ Å., and the unit cell contains Mn_4O_4.[11] There may, however, be a second modification below the specific heat anomaly (115.9° K.).[12]

Reaction with Oxygen.—Manganese (mon)-oxide tends to take up oxygen. Samples obtained by thermal decomposition of the carbonate or oxalate vary greatly in their activity, depending on the temperature of decomposition; the more active samples being pyrophoric. Very thorough studies of the adsorption of oxygen have been made by LeBlanc and Wehner,[9] by Baroni,[11] and by several others. Samples of MnO derived from the carbonate above 500° or from the oxalate at somewhat lower temperature, may be described as "dead-burnt" and are much less active in oxygen adsorption than those samples ignited at lower temperatures. Those samples ignited below about 350° generally contain traces of carbonate, although, according to Baroni, pure MnO may be obtained by very prolonged heating at somewhat lower temperatures.

When the MnO so prepared is exposed to air or to oxygen, it is said[8] to take up oxygen until the formula corresponds to $MnO_{1.58}$. There is some evidence that the spontaneous absorption of oxygen is promoted by traces of alkali. This percentage of oxygen is accompanied by a change to Mn_3O_4 or to Mn_2O_3. The compound MnO can take up oxygen to $MnO_{1.13}$ without any change of lattice or development of a new phase, but beyond that point a higher oxide begins to appear in the X-ray pattern. The absorption of oxygen up to $MnO_{1.13}$ apparently takes place by a process of solid solution, and there is no indication of reversibility. The oxygen so taken up is "active," yet it does not yield any indication of its presence in the X-ray diagram. Although wide deviations from stoichiometric proportions are thus often found among the oxides of manganese, and of other elements, yet it should be emphasized that there is no X-ray evidence for any compound of manganese and oxygen other than MnO, Mn_2O_3, Mn_3O_4, and MnO_2 between the stoichiometric limits MnO_{1-2}. There are, however, polymorphic states of several of these oxides. These conclusions are based on a careful series of experiments involving fairly high pressures of oxygen, and temperatures up to about 900°.[12]

Consideration of the above results suggested that the problem of "active" oxygen in such systems might lend itself to magneto-chemical study.

The work described in this section was a parallel study of oxygen uptake by manganous oxide, as a function of X-ray diffraction pattern, magnetic susceptibility, and active oxygen analysis. The experimental procedure was to take a sample of MnO as previously described, to heat it in oxygen, and from time to time to remove samples for analysis and study.

The sample of manganous oxide used had been prepared by thermal decomposition of manganese carbonate at 500° for forty-eight hours. It contained 75.3% Mn and 0.1% active oxygen. The characteristic X-ray pattern was well developed.

After long heating in oxygen the substance had 67.9% Mn, 11.0% active oxygen, and had a well-defined X-ray pattern for Mn_2O_3. Complete data are given in Table I.

During this period the X-ray pattern of MnO diminished in intensity until, when the active oxygen concentration reached 8.9%, the strongest X-ray lines were only 20% as strong as originally. No new X-ray lines appeared until the final stage indicated, namely, between the thirty-third and thirty-fourth days of heating. At this

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(9) American Society for Testing Materials, Card Index.

(10) Bizette, Squire and Tsai, *Compt. rend.*, **207**, 449 (1938).

(11) Baroni, *Gazz. chim. ital.*, **70**, 478 (1940).

(12) Holtermann, *Ann. chim.*, **14**, 121 (1940).

TABLE I

ADDITION OF OXYGEN TO MANGANESE (MON)OXIDE

Days heated	Temp., °C.	Wt., inc./g.	Cumulative wt. inc./g.	% active oxygen	$\chi \times 10^6$			
					25°	−87°	−125°	−171°
0	...	.....	.....	0.10	69	81	83	73
3	100	0.00101	0.00101	0.28	..	...	...	...
10	100	.00428	.00529	0.74	..	...	...	...
18	150	.00609	.01138	1.46	67	81	84	81
20	200	.00740	.01878	2.21	73	90	92	91
25	200	.00745	.02623	2.96	63	76	81	83
26	200	.00881	.03504	3.89	65	78	84	90
27	250	.00198	.04702	4.78	59	76	79	89
30	300	.00926	.05628	5.98	61	75	84	95
31	350	.02878	.08506	8.58	59	74	87	104
33	300	.00921	.09427	8.90	58	77	85	104
34	300	.01557	.11034	11.0	78	111	124	135

point the pattern for MnO disappeared completely and that for Mn_2O_3 appeared.

The magnetic data tend to be somewhat erratic, as is generally the case when progressive chemical changes in solids are being studied. One of the features is the rapid disappearance of the magnetic anomaly found in MnO at 115° K.

By plotting all data at each temperature it proved possible to compare magnetic moments and Weiss constants for the system as a function of oxygen uptake. The data are given below:

% Active oxygen	Magnetic moment	Weiss constant
5	4.6	280
6	4.5	260
7	4.3	230
8	4.2	215

These data are obviously based only on the high temperature part of the susceptibility curve, where temperature *versus* reciprocal susceptibility gives nearly a straight line.

These results are not quite so accurate as might be desired, but they give a picture of the mechanism of oxygen take-up. The oxidation state of the manganese is shown to change progressively with increasing oxygen. The moments are all somewhat low, but that does not invalidate the general conclusion, that so-called "active" oxygen is a misnomer. The oxidizing power of the system is simply a function of manganese concentration in the +3 oxidation state. The oxygen presumably goes into the lattice as oxide ions, and the progressive oxidation of the manganese gives more room in the lattice for more oxygen.

There remains to explain why the X-ray pattern of Mn_2O_3 does not appear as soon as appreciable oxygen has been taken up. The reason must be that the manganese +2 ions are oxidized at random and that their centers do not move appreciably. But this process attenuates the MnO structure until it finally has insufficient stability to maintain itself. The whole structure then quickly transforms to the more stable Mn_2O_3 structure.

This picture of active oxygen has obvious applications to the lead–oxygen system and to other similar systems.

An attempt to investigate the reverse process, namely, the progressive removal of oxygen from Mn_2O_3, will be described below.

Manganese Dihydroxide, $Mn(OH)_2$

Preparation.—This compound occurs as the mineral *pyrochroite*. The preparative procedure adopted was that of Simon and Frohlich,[13] with some modifications. It is essential that access of air into the system be prevented during the preparation.

Approximately 350 g. of potassium hydroxide dissolved in 600 cc. of water was allowed to react with 32 g. of manganese chloride in 20 cc. of water. Prior to addition of the chloride the entire apparatus was thoroughly swept free of air by a stream of hydrogen gas which had been passed first over hot asbestos impregnated with copper, and then through alkaline pyrogallol solution. The mixture of manganese hydroxide and water was rapidly distilled in a current of hydrogen until about half of the initial liquid remained. The precipitated hydroxide was observed to dissolve. The temperature at this point was about 190°, and the solution was a clear amber color. Upon cooling, a deposit of small colorless crystals formed, and by maintaining the temperature slightly above solidification temperature, almost all of the hydroxide could be crystallized. The supernatant liquid was carefully drawn off. Boiled water saturated with hydrogen was added to the crystals in the reaction flask, and this mixture was siphoned into a Buchner funnel where the crystalline hydroxide was collected on filter paper.

The product was purified by washing with about 2 liters of oxygen-free water to free it from alkali and chloride. Final washing was done with alcohol saturated with hydrogen and then with peroxide-free ether. The crystals were dried in a vacuum desiccator over phosphorus pentoxide. Analysis of the product yielded

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(13) Simon and Frohlich, *Z. anorg. allgem. Chem.*, **232**, 369 (1937).

	Mn, %	"Active" oxygen
Calculated for $Mn(OH)_2$	61.7	0.00
Found	61.6	.09

No direct comparison is possible with the Simon and Frohlich preparation because they analyzed merely by ignition of the sample to Mn_3O_4. Two samples reported by them gave

Sample, g. $Mn(OH)_2$	Calculated, g. Mn_3O_4	Found, g. Mn_3O_4
0.3019	0.2599	0.2592
.2608	.2236	.2240

The preparation reported in this paper appears to be as nearly pure $Mn(OH)_2$ as any heretofore described.

Properties.—The crystals were almost pure white, with a marked tendency to turn brown unless sealed in glass under high vacuum.

The crystal interplanar spacings and relative intensities of reflection were found as follows:

d, Å.		$I/I_{max.}$	
reported[9]	found	reported[9]	found[b]
4.62	4.72	0.8	1.00
2.85	2.87	0.7	0.14
2.44	2.45	1.0	.35
2.35	2.36	0.4	.07
1.81	1.82	1.0	.21
1.65	1.66	0.8	.12
1.56	1.57	.8	.10
1.43	1.44	.6	.04
1.38	[a]	.8	
1.37	1.38	.8	.06
1.23	1.23	1.0	.05
1.18	1.18	0.5	.06

[a] Not resolved. [b] The lack of agreement between the intensities found and those reported by Simon and Frohlich may possibly be due to preferred orientation of the crystals in the powder sample. The (001) face of these crystals is predominantly developed. The 4.72 Å. reflection is due to the (001) plane.

The magnetic susceptibility of this compound was found

Temp., °C.	25	−44	−58	−73	−89	−106	−146
$\chi \times 10^6$	149	200	212	229	236	256	316

Albrecht[14] found a susceptibility of 154×10^{-6} at 7°. The unusual degree of magnetic dilution in this substance is doubtless related to the fairly large (3.3 Å.) distance between nearest manganese neighbors. This circumstance makes it possible to calculate the magnetic moment for the Mn^{+2} ion, which is found to be 5.8 Bohr magnetons, in gratifying agreement with the expected value. The Weiss constant has the modest value of only 10°.

The identity of this compound may be regarded as well established. The habit is hexagonal. Studies by Aminoff as given in Dana's System of Mineralogy[15] show that *pyrochroite* has the unit cell dimensions, $a = 3.34$, $c = 4.68$ Å. This is in excellent agreement with the data obtained by Simon and Frohlich on synthetic $Mn(OH)_2$. The unit cell contains $Mn(OH)_2$ and the structure is a layer lattice.

There is some geochemical evidence for the possible existence of an orthorhombic modification of *pyrochroite.* This hypothetical substance has been called *backstromite.* There have been claims for the artificial production of an orthorhombic modification of $Mn(OH)_2$, and Gregoriev[16] claims to have prepared the compound.

Trimanganese Tetroxide, Mn_3O_4

Preparation.—This compound occurs as the mineral *hausmannite.* All oxides and hydroxides of manganese form Mn_3O_4 if heated in air to about 1000°. The best supported preparation appears to be that of Shomate[17] who heated specially prepared electrolytic manganese dioxide to 1050°. Preparations almost as pure have been reported by Millar,[18] and by Southard and Moore[19] by prolonged ignition of pure manganous sulfate in air at about 1000°. A further preparation of interest is that of Krull[20] who reduced precipitated manganese dioxide in hydrogen at 200°. The method used for the present work was the thermal decomposition of manganous sulfate. The final product appeared as a dark purplish red solid.

Analysis of the product yielded:

	Mn, %	"Active" oxygen	MnO/Mn_3O_4
Calculated for Mn_3O_4	72.03	7.0	93.01
Shomate	...	7.00 7.01	93.06 93.03
Millar	...	7.01 7.03	...
Found	72.06	7.0	...

This is obviously one of the easiest manganese oxides to prepare in a high degree of purity.

Properties.—The crystal interplanar spacings and relative intensities of reflection were found as follows.

d, Å.		$I/I_{max.}$	
reported[9]	found	reported	found
4.92	4.90	0.20	0.21
3.08	3.08	.31	.42
2.87	2.87	.08	.16
2.75	2.76	.63	.60
2.48	2.48	1.00	1.00
2.36	2.36	0.13	0.25
2.03	2.03	.15	.21
1.79	1.80	.18	.34
1.57	1.58	.50	.32
1.54	1.55	.50	.63
1.44	1.44	.18	.26
1.28	1.28	.13	.14
2.22	Absent	.31	Absent

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(14) Albrecht, *Z. anorg. allgem. Chem.*, **232**, 382 (1937).

(15) Dana, "System of Mineralogy," 7th edition by Palache, Berman and Frondel, Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 501.

(16) Gregoriev, *Mem. Soc. Rurse Mineral*, **63**, 67 (1934).

(17) Shomate, THIS JOURNAL, **65**, 785 (1943).

(18) Millar, *ibid.*, **50**, 1875 (1928).

(19) Southard and Moore, *ibid.*, **64**, 1769 (1942).

(20) Krull, *Chem. Erde*, **7**, 473 (1932).

The magnetic susceptibility of Mn_3O_4 was found to be

Temp., °C.	$\chi \times 10^6$
25	54.2
−80	66.6
−185	126

Honda and Sone[21] give $\chi = 55.8 \times 10^{-6}$ at 20°.

The structure of Mn_3O_4 is a distorted spinel. The crystals are probably body-centered tetragonal. Aminoff[22] gives the unit cell dimensions as $a = 5.75$, $c = 9.42$ Å., and as containing $Mn_4Mn_8O_{16}$. There is, however, some possibility that the substance is face-centered cubic. A further question involves the possible oxidation states of the manganese. The electrical conductivity of Mn_3O_4 is low in contrast to that of Fe_3O_4. Verwey and de Boer[23] interpret this as meaning that the manganese is in +2 and +4 oxidation states as $Mn^{+4}Mn_2^{+2}O_4$ rather than as $Mn^{+2}Mn_2^{+3}O_4$. The compound is believed to have the same arrangement of positive ions as Co_3O_4, except that the Mn_3O_4 cell is distorted tetragonally. The problem is one which would appear to lend itself to the Krishnan magnetic anisotropy technique.[24] Obviously, the name "Mn II III oxide" is a misnomer if the structure is $Mn^{+}Mn_2^{+2}O_4$.

We may conclude with respect to this compound that its identity is firmly established, but that some doubts remain concerning its structure. The scope of this study did not include the cubic form of Mn_3O_4 reported by McMurdie and Golovato[25] as being stable above 1170°.

α-Manganese Sesquioxide, α-Mn_2O_3

Preparation.—Manganese sesquioxide exists in two forms. These will be referred to as α-Mn_2O_3 and γ-Mn_2O_3, although various authors, including the discoverer of the *gamma* form use a different nomenclature. Our reason for adopting α-, γ-nomenclature is that the parallel naming is well established for the structurally similar dimorphs of ferric oxide. Almost pure α-Mn_2O_3 is said to occur occasionally as the mineral *bixbyite*. More often *bixbyite* contains $[Mn,Fe]_2O_3$.

α-Manganese sesquioxide may be prepared through oxidation of a lower state, or through reduction of a higher state. Thermal decomposition of a manganese oxy-salt or hydrate in air almost invariably yields α-Mn_2O_3, provided the decomposition temperature is not so high that Mn_3O_4 results. Thus the nitrate, carbonate, oxalate, or chloride hydrate of divalent manganese all yield α-Mn_2O_3 if heated in air between 600 and 800°. But manganese sulfate does not decompose below about 900°, at which temperature Mn_2O_3 is converted to Mn_3O_4.

Amongst these procedures probably the most convenient for the preparation of α-Mn_2O_3 is to heat the pure nitrate hydrate. This compound decomposes yielding a composition near MnO_2. If now the temperature is raised, α-Mn_2O_3 results. This method has been used by Krull[26] who decomposed the nitrate at 154° under 20 mm. pressure, and then raised the temperature in oxygen to 550°, to decompose the dioxide to α-Mn_2O_3. The temperature must not rise much above 600° if stoichiometrically accurate Mn_2O_3 is to result. A closely parallel preparation by Bhatnagar, *et al.*,[27] involves decomposing the nitrate at 150–160°, then igniting to constant weight at 600°. The Bhatnagar procedure was followed. Analysis of the α-Mn_2O_3 yielded

	Mn, %	"Active" oxygen
Calculated for Mn_2O_3	69.59	10.14
Krull	69.50	10.07
Bhatnagar	69.63	10.14
Found	69.6	10.3

Our preparation appears to be almost as pure as any heretofore made. The product was black.

Properties.—The crystal interplanar spacings and relative intensities of reflection were found as follows.

d, Å.		$I/I_{\max}$.	
reported[9]	found	reported	found
3.86	3.82	0.1	0.2
2.72	2.71	1.0	1.0
2.35	2.34	0.1	0.2
2.01	2.00	.2	.1
1.84	1.84	.3	.2
1.66	1.66	.9	.4
1.45	1.45	.2	.1
1.42	1.42	.6	.2
1.39	1.39	.2	.01

The magnetic susceptibility of α-Mn_2O_3 was found

Temp., °C.	$\chi \times 10^6$
25	89
− 80	112
−185	~163

Bhatnagar, *et al.*,[27] give $\chi = 89.32 \times 10^{-6}$ at 20°.

This compound has been found by Zachariasen,[28] Montoro[29] and by Pauling and Shappell[30] to crystallize in the body-centered cubic "*c*" sesquioxide form, with $a = 9.401$ Å. The unit cell contains $Mn_{32}O_{48}$. The identity and characterization of this compound appear to be firmly established.

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(21) Honda and Sone, *Sci. Repts. Tohoku Imp. Univ.*, **3**, 139 (1914).

(22) Aminoff, *Z. Krist.*, **64**, 475 (1936).

(23) Verwey and de Boer, *Rec. trav. chim.*, **55**, 531 (1936).

(24) Krishnan and Banerjee, *Trans. Faraday Soc.*, **35**, 385 (1939).

(25) McMurdie and Golovato, *J. Research Natl. Bur. Standards*, **41**, 589 (1948).

(26) Krull, *Z. anorg. allgem. Chem.*, **208**, 134 (1932).

(27) Bhatnagar, Cameron, Harbard, Kapur, King and Prakash, *J. Chem. Soc.*, 1433 (1939).

(28) Zachariasen, *Z. Krist.*, **67**, 455 (1928).

(29) Montoro, *Gazz. chim. ital.*, **70**, 145 (1940).

(30) Pauling and Shappell, *Z. Krist.*, **75**, 128 (1930).

Reduction of α-Mn_2O_3—An investigation of the reduction of Mn_2O_3 to MnO was made to compare the results with the stepwise oxidation of MnO to Mn_2O_3 reported above. Attempts were made to remove oxygen from Mn_2O_3 by heating in vacuum. The sample was heated under high vacuum from 300 to 500° at which temperature it changed to a reddish purple color. An X-ray of this product showed the pattern for Mn_3O_4. Apparently it is impossible to pump off oxygen without converting the oxide to Mn_3O_4.

Reduction of Mn_2O_3 was then attempted by heating in hydrogen. A sample weighing 0.7513 g. was heated in hydrogen for about an hour at 300° with no loss of weight, but after being heated for about six hours, the sample weighed 0.7485 g. An X-ray analysis of the sample showed the pattern for MnO.

The sample was exposed to the atmosphere for several days before being analyzed for active oxygen. Results of analysis showed 5.0% active oxygen as compared to 10.14% for Mn_2O_3. The X-ray was repeated to see if any changes occurred while exposed to air. The X-ray still gave the MnO pattern and, in addition, the strongest line of the Mn_2O_3 pattern appeared.

The results of this investigation indicate that the partial reduction product consists of a mixture of crystalline MnO + Mn_2O_3. This is in contrast to the oxidation of MnO, in which MnO crystal structure alone is maintained until the oxidation is almost complete.

γ-Manganese Sesquioxide, γ-Mn_2O_3

Preparation (1).—This substance has not been reported to occur in nature. Addition of ammonium hydroxide to manganous sulfate solution in the presence of hydrogen peroxide yields hydrated manganese sesquioxide. Careful dehydration in vacuum at 250° is stated by Dubois[31] and by Verwey and de Boer[23] to yield γ-Mn_2O_3.

Two different methods were used for the preparations described here. In one a dilute solution of manganese sulfate (22 g. of $MnSO_4 \cdot 4H_2O$ in 3.5 l. of water) was oxidized by hydrogen peroxide (12 cc. of 30%). The sulfate and peroxide were mixed, and 500 cc. of 0.5 *M* ammonium hydroxide was added with stirring. The temperature of the solution was about 50°. After addition of the base the mixture was boiled. A brown precipitate approximating MnOOH was filtered from the solution, and washed thoroughly with water to free it from electrolytes. Drying was carried out in vacuum at 250° for about seventy-two hours. The product was black.

Analysis of the γ-Mn_2O_3 yielded

	Mn, %	"Active" oxygen	Loss on ignition
Calculated for Mn_2O_3	69.59	10.14	3.38
Verwey and de Boer	...	9.94	4.0
Found	68.8	9.3	..

Properties.—From these data it may appear that our preparation was barely so pure as that of Verwey and de Boer. However, the X-ray data given below indicate little doubt that the compound was actually obtained. No numerical data on the crystal interplanar spacings of γ-Mn_2O_3 have been reported. Verwey and de Boer merely state that the pattern is very like that of Mn_3O_4. For comparison in our table we give the accepted spacings for Mn_3O_4.

d, Å.		$I/I_{max.}$	
reported[9,a]	found	reported[9]	found
4.92	4.93	0.2	0.4
3.08	3.08	.3	.6
2.75	2.74	.6	.7
2.48	2.48	1.0	1.0
2.35	2.39	0.1	0.4
2.03	2.03	.2	.2
Absent	1.83	Absent	.3
1.79	1.79	0.2	.2
1.54	1.55	.5	.6
1.57	1.59	.5	.3

[a] For Mn_3O_4.

The magnetic susceptibility of this sample was 66 × 10^{-6} at 25°. No previous determination has been found.

Preparation (2).—In view of the scanty earlier reports on this substance a second preparation was attempted. This is based on a procedure given by Dubois.[32] So-called γ-MnO_2 (preparation (4) under Manganese Dioxide, Disperse Forms, below) was prepared from manganese sulfate, potassium nitrate and potassium permanganate. This substance was heated in vacuum at 500° for about seventy-eight hours. The product differed from that described above in being brown rather than black.

Analysis of this preparation gave the following results: Mn, 65.4%; "Active" oxygen, 10.6. A formula based on these results would be $Mn_2O_3 \cdot 0.44\ H_2O$.

Properties.—The X-ray pattern was identical with that given above. The magnetic susceptibilities were

Temp., °C.	$\chi \times 10^6$
25	60
− 80	76
−185	114

Samples from both preparations of γ-Mn_2O_3 were heated in an oxygen atmosphere at 250° for one hundred hours. The X-ray diagrams indicated a change toward complete disorder and the disappearance of the γ-Mn_2O_3 structure. No new crystalline phase was observed.

It is interesting to note that the % increase in "active" oxygen content was 12.2 for the sample prepared by thermal decomposition of γ-MnO_2 compared to 28% for the sample prepared by oxidation of Mn^{+2} by hydrogen peroxide; how-

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(31) Dubois, *Ann. chim.*, [11] **5**, 401 (1936).

(32) Dubois, *Ann. chim.*, [11] **5**, 401 (1936).

ever, these figures represent no more than a relatively small tendency for γ-Mn_2O_3 to take up oxygen. This seems surprising in view of Dubois' statement regarding the readiness with which γ-Mn_2O_3 is oxidized at moderate temperatures.

An evacuated sample of γ-Mn_2O_3 was heated at 500° for forty-eight hours. The appearance of the characteristic X-ray pattern of the alpha-modification and the disappearance of the gamma-structure was observed, indicating the phase transition, $\gamma \rightarrow \alpha$. This transition was also found to occur spontaneously in a sample which had been standing at room temperature for one year.

Prolonged heating of γ-MnO_2 under a moderately high vacuum at 500° was found to give successively: γ-Mn_2O_3, Mn_3O_4, and MnO. This method of preparation of γ-Mn_2O_3 shows clearly the close relationship between γ-Mn_2O_3 and Mn_3O_4. Loss of oxygen is progressive from γ-Mn_2O_3 to Mn_3O_4 with little observable alteration in structural symmetry, although a change in lattice dimensions doubtless occurs.

The nearly identical X-ray pattern of γ-Mn_2O_3 and Mn_3O_4 calls for some comment. The compound γ-Mn_2O_3 must be considered a defect structure, bearing the same relation to α-Mn_2O_3 as γ-Fe_2O_3 does to α-Fe_2O_3. The γ-Mn_2O_3 may also be considered to bear somewhat the same relation to Mn_3O_4 as the partially oxidized products obtained from MnO do to pure MnO, as described earlier.

From the results given it may be concluded that γ-Mn_2O_3 has a real existence. But its preparation and properties have not been characterized as well as might be desired. Attempts to prepare *ramsdellite* through oxidation of γ-Mn_2O_3 are described below.

Manganese Oxyhydroxide, MnOOH

Preparation.—The literature contains a good many claims and counterclaims concerning the preparation of this substance. Reasonably well substantiated preparations involve at least three modifications of MnOOH and several closely related substances. The mineral *manganite* has, however, a well defined existence and its structure has been studied. The problem of MnOOH preparation is discussed by Wilborn.[33] A reasonably satisfactory method is described by Feitknecht and Marti.[34]

The oxidation products of divalent manganese in basic solution depend upon the concentration of base, the nature of the oxidizing agent, and the time. No doubt temperature and other conditions also affect the final product. A restricted concentration of sodium hydroxide and a fairly short oxidation period with air or oxygen as the oxidizing agent yield a mixture of which the principal constituent may be a hydrous form of Mn_3O_4. Longer oxidizing action, with slight excess sodium hydroxide, yields products which may be non-stoichiometrical variants of MnOOH or which may be hitherto unrecognized polymorphs. Prolonged heating of these products in the absence of air yields a substance with an X-ray pattern almost identical with that of natural *manganite.*

The preparation of MnOOH adopted was exactly as described for the preparation of γ-Mn_2O_3, except that the precipitate of MnOOH was dried at 60° under 20 mm. pressure for about seventy-two hours. The product was black.

Analysis yielded the results

	Mn, %	"Active" oxygen
Calculated for MnOOH	62.5	9.1
Found	61.5	9.0

A formula based on these results is $Mn_2O_{2.98}\cdot 1.0\ H_2O$. No comparable data have been found in literature. It is important that the Mn/O ratio should be in the neighborhood of $^2/_3$ during the oxidation step, or the final product may contain Mn_3O_4.

Properties.—The final product is identified as similar to natural *manganite* on the basis of its X-ray diffraction pattern. The results given below were obtained for crystal interplanar spacings and relative intensities.

d, Å. reported[9]	d, Å. found	$I/I_{max.}$ reported[9]	$I/I_{max.}$ found
3.39	3.40	1.0	1.0
2.62	2.63	0.8	0.6
2.52	2.53	.4	.4
2.41	2.41	.8	.7
2.26	2.26	.6	.4
1.77	1.77	.8	.5
1.66	1.68	.7	.7
1.49	1.50	.7	.4
1.43	1.44	.7	.4
1.70	1.71	.7	.4
1.63	1.64	.7	.2

Preliminary measurements on the magnetic susceptibility of this compound indicated an unusual degree of magnetic concentration. The susceptibilities were studied more thoroughly in the expectation that MnOOH might show a magnetic anomaly similar to that shown by MnO The results are given below.

Temp., °C.	25	−1	−26	−41	−56	−70
$\chi \times 10^6$	38	39	39	39	39	39
Temp., °C.	−88	−106	−125	−147	−185	
$\chi \times 10^6$	39	39	39	39	36	

This compound shows virtually no temperature coefficient of magnetic susceptibility, and in this respect it is a sharp contrast to *pyrochroite,* $Mn(OH)_2$, which is a magnetically dilute compound. It will be noted that each manganese atom in MnOOH has two manganese neighbors at only 2.7 Å. distance. No earlier magnetic

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[33] Wilborn, *Farben-Ztg.*, **31**, 338 (1925).

[34] Feitknecht and Marti, *Helv. chim. acta*, **28**, 129 (1945).

susceptibility measurements have been found, although Krishnan and Banerjee[24] have measured the magnetic anisotropy of natural crystals.

The MnOOH when heated in oxygen for thirty-six hours at 200° was changed to pyrolusite. This contrasts sharply with the behavior of γ-Mn_2O_3.

The mineral *manganite* has received careful study by Buerger.[35] The crystals are said to be monoclinic, $a = 8.86$, $b = 5.24$, $c = 5.70$ Å., $\beta = 90°$. The unit cell contains $Mn_8O_8(OH)_8$. However, it cannot be considered that the structure has been established beyond doubt. There is even some possibility that the substance is orthorhombic rather than monoclinic. Furthermore, the magnetic anisotropy studies by Krishnan and Banerjee throw doubt on the equivalent oxidation state of all manganese atoms. They suggest that the manganese is half bivalent and half quadrivalent rather than all trivalent. This observation is supported by the action of MnOOH with acids. Nitric or sulfuric acids on natural *manganite* yield, as is well known, a mixture of the manganous salt plus hydrated manganese dioxide. We do not, however, as a rule attach very much weight to the structures of inorganic solids such as this derived from reaction studies.

Our general conclusion must be that synthetic MnOOH has been prepared. The preparation is not very satisfactory, and the properties and structure are not well characterized.

In addition to the preparation outlined, Feitknecht and Marti[34] claim the preparation of MnOOH in two other forms. The preparation given above is called by them γ-MnOOH and corresponds to the natural substance. The other forms are designated α- and β-MnOOH. There is also a supposed manganese manganite. None of these has a definite stoichiometrical formula, and the degree of hydration apparently varies in different preparations. While not denying that such substances may exist, we shall say no more about them pending more complete characterization studies. There is no evidence in the literature for $Mn_2O_3 \cdot H_2O$, although this formula is often used, nor for $Mn(OH)_3$, which is almost as frequently found.

Manganese Dioxide, MnO_2 (tetragonal)

Preparation.—The characterization of manganese dioxide is confused. *Pyrolusite* is the only form which has been synthesized, and for which relatively unequivocal preparation, structure, and properties are known. Reference will be made later to supposed polymorphs and other modifications.

This compound occurs widely distributed in nature. Preparations in the *pyrolusite* structure have been made in fairly high degrees of purity by several groups of workers. Because of the importance of this problem reference will be made to three different attempts at preparing MnO_2 of high purity.

Krull[20,26] heated manganese nitrate at 154° (cyclohexanol bath) under 20 mm. pressure (water pump). The time is not indicated, but must certainly have been many hours, if not days. The product resembled natural *pyrolusite* in its optical and X-ray properties.

The second preparation is that of Bhatnagar, *et al.*[27] "Analytically pure" nitrate was twice recrystallized from water and then heated at 150–160° for fifty hours. The residue was washed free from nitrate ion (presumably with water) and then dried at 200°. This gave $MnO_{1.99}$. The product was repeatedly treated with boiling nitric acid in order to dissolve lower oxides. It was finally washed with water and dried at 200° in vacuum.

The third preparation is that of Kelley and Moore.[36] The starting materials were pure electrolytic manganese and reagent quality nitric acid. The manganese was dissolved, and the product slowly decomposed at 200° over a period of several days. The resulting substance was pulverized, then heated at 500° in a stream of pure oxygen until removal of water was complete. These authors state that the final product was analyzed by reduction to the monoxide with hydrogen, and also by reaction with excess sodium oxalate and back titration with potassium permanganate.

These several preparations indicate some difference of opinion as to the best method. "Good" purity seems to be obtainable over a wide range of conditions, but the problem could bear further work with respect to obtaining still better samples. A modified Bhatnagar procedure was used.

Recrystallized manganese nitrate was heated to 120–125° until the entire mass was about to solidify. Water was added to the mass, and it was stirred and filtered. The solid was dried at 110° for twenty-four hours in air. It was ground through a 150-mesh sieve and reheated at 150° in air for twenty-four hours. The crystals were next washed with 1:1 nitric acid and finally with water to remove the nitric acid. The acid and wash water should both be boiling for best results. Final drying was done at 160° in air for fifty-two hours. The product appeared a dark gray color.

Analysis of the MnO_2 yielded the results:

	Mn, %	"Active" oxygen	Claimed purity
Calculated for MnO_2	63.19	18.4	..
Krull	63.14	..	99.9
Bhatnagar	63.33	18.24, 18.26	..
Kelley and Moore	...	..	99.88, 100.21
Found	63.1	18.3	

Our product appears to be as pure as any heretofore obtained.

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(35) Buerger, *Z. Krist.*, **95**, 163 (1936).

(36) Kelley and Moore, THIS JOURNAL, **65**, 482 (1943).

Properties.—Crystal interplanar spacings and relative intensities were found to be

d, Å.		I/I_{max}	
reported[9]	found	reported[9]	found
3.11	3.10	1.0	1.0
2.40	2.41	0.5	0.6
2.21	2.20	.04	.2
2.12	2.11	.1	.2
1.98	1.98	.04	.1
1.62	1.62	.5	.9
1.56	1.56	.12	.2
1.44	1.44	.08	.1
1.39	1.39	.04	.2
1.30	1.30	.2	.4

The magnetic susceptibility of this material was

Temp., °C.	$\chi \times 10^6$
25	27
− 80	31
−185	44

Bhatnagar, *et al.*, give $\chi = 26.03 \times 10^{-6}$ at 27°.

The structure[37,38] is now well established as tetragonal (*rutile* group) with $a = 4.38$, $c = 2.86$ Å.[38a] The unit cell contains Mn_2O_4. For a long time it was thought that *pyrolusite* was an orthorhombic form of manganese dioxide. The tetragonal form was called *polianite*. Orthorhombic *pyrolusite* is apparently due to pseudomorphism, based on its formation from *manganite*.[39]

On the basis of these results the tetragonal form of MnO_2, and its properties seem well characterized.

Manganese Dioxide, MnO_2 (orthorhombic)

Attempted Preparation.—Orthorhombic manganese dioxide is said to occur in nature as the rare mineral *ramsdellite*.[40] This has not been prepared synthetically, and it would be of considerable interest to develop preparation methods. The unit cell dimensions given are $a = 4.5$, $b = 9.2$, and $c = 2.83$ Å.[41]

Ramsdellite is said to change to pyrolusite above about 250°. Any preparation method must therefore keep below this temperature. γ-Mn_2O_3 is said to take up oxygen at moderate temperature (although the results reported have cast some doubt on this).

An effort was made to synthesize *ramsdellite* as follows: γ-Mn_2O_3 was heated in dry air for thirty-six hours at 200°. The product had an X-ray pattern almost identical with the starting material. Heating at 250° for sixty hours gave a material showing no definite X-ray pattern. The attempted synthesis procedure was then modified so that moist rather than dry oxygen was used. A sample of γ-Mn_2O_3 having the formula $Mn_2O_{3.1}\cdot 0.44\ H_2O$ was placed in a small glass tube having a sintered glass disk. Oxygen was bubbled through water and then passed over the sample. The tube was placed in a furnace and the temperature increased from 200 to 400° during the course of the experiment, which continued over a period of three months.

The tube was removed from the furnace at frequent intervals and the increase in weight noted as the sample was heated. About twice a week an X-ray of the sample was taken. The pattern shifted slightly and showed an increased crystallinity over a period of time. When, after three weeks, the X-ray pattern did not approach that reported for *ramsdellite*, the temperature was raised to 300°, although ramsdellite is said to change to *pyrolusite* at this temperature.

At the end of the first month the sample was found to contain 13.2% active oxygen as compared with 10.6% in the original sample.

The sample was replaced in the tube and the temperature increased gradually to 400°. The sample continued to gain weight very slowly, and and the X-ray pattern became sharper. At the end of the three-month period the sample was again removed and analyzed. This final analysis showed the sample contained 14.6% active oxygen and 58.6% manganese. A formula based on these results in $MnO_{1.85}\cdot 0.91\ H_2O$.

The X-ray pattern of the final product showed it to be a mixture of alpha sesquioxide (*bixbyite*) and *pyrolusite*.

In view of the failure to synthesize *ramsdellite* it is necessary to reserve judgment on the identity and characterization of this substance.

Manganese Dioxide, Disperse Forms[41a]

Preparations and Properties.—The less unequivocally characterized oxides of manganese (IV) have recently been reviewed by Cole, Wadsley, and Walker,[42] and some of the preparations have been described in an article from this laboratory,[43] dealing with the magnetic dilution effect in disperse manganese dioxide. The remainder of the present article will be concerned chiefly with some newer data on these systems.

A supposed gamma manganese dioxide has been claimed by Glemser,[44] and supported by Alekseevski and Frid.[45] A supposed α-manganese dioxide has been claimed by Dubois,[31,32] and this

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(37) St. John, *Phys. Rev.*, **21**, 389 (1923).

(38) Ferrari, *Atti Accad. Lincei*, **3**, 224 (1926).

(38a) Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, N. Y., 1948; Chap. IV, table p. 15, gives $a = 4.44$, $c = 2.79$ Å.

(39) Strunz, *Naturwissenschaften*, **31**, 89 (1943).

(40) Ramsdell, *Am. Mineralogist*, **17**, 143 (1932).

(41) Fleischer, U. S. Geological Survey, private communication.

(41a) The term "disperse" is used in contrast to "massive," with reference to supported and self-supported oxides of the transition group elements. A major experimental difference between these two forms or states of matter is that the disperse forms are, as described below, magnetically dilute, while the massive forms are often magnetically concentrated.

(42) Cole, Wadsley, and Walker, Electrochem. Soc. preprint 92-2, Oct. 15–18 (1947), p. 11.

(43) Selwood, Eischens, Ellis, and Wethington, THIS JOURNAL, **71**, 3039 (1949).

(44) Glemser, *Ber.*, **72B**, 1879 (1929).

(45) Alekseevski and Frid, *J. Gen. Chem. (U. S. S. R.)*, **15**, 3 (1945).

TABLE II

PROGRESSIVE DEHYDRATION OF DISPERSE MANGANESE DIOXIDE

Dehydration conditions	Formula Mn/O	Formula H_2O	μ	Δ	X-Ray
5 days at 60°	$MnO_{1.96}$	$0.93H_2O$	3.6	75	Diffuse
Vac. des. over $Mg(ClO_4)_2$	$MnO_{1.93}$	$.55H_2O$	3.5	67	Diffuse
Vac. des. over P_2O_5	$MnO_{1.99}$	$.87H_2O^a$	3.8	85	Faint gel
200° in oxygen	$MnO_{1.98}$	$.68H_2O$	3.9	104	Faint gel
300° in oxygen	$MnO_{1.92}$	$.39H_2O$	3.9	200	Fair gel + pyrolusite
300° in oxygen	$MnO_{1.93}$	$.4H_2O$	4.1	270	Fair gel + pyrolusite
400°	$MnO_{1.84}$	$.4H_2O$	4.2	195	Gel + MnO_2 + Mn_2O_3
450°	$MnO_{1.74}$	$.4H_2O$	4.7	220	Mn_2O_3 + MnO_2

[a] In the early stages of dehydration it was not realized that the partially dehydrated gel would be strongly hygroscopic. After this apparent increase in water content, the sample was handled in a dry box.

is also supported by Alekseevski and Frid. It may be mentioned that these preparations are not unlike those of Whitesell and Frazer,[46] reported years earlier.

A comparison of the rather meager X-ray data given by various authors suggests that the Dubois *alpha* and the Glemser *gamma* are the same, or nearly the same, and that they may actually be poorly crystallized *pyrolusite,* or perhaps poorly crystallized mixtures of *pyrolusite* and *ramsdellite.*

In fairness it should be added that Feitknecht and Marti[34] believed they have prepared α-, β-, γ-MnO_2 and that these three forms have different X-ray patterns. They also believe they have obtained two different forms of the γ-modification.

In addition to the above we may mention a supposed naturally occurring γ-MnO_2 reported by Schossberger[47] and a δ-MnO_2 to which reference is made by McMurdie.[48] These are probably not related to the substances prepared by Dubois and by Glemser. They are apparently poorly crystallized samples of MnO_2 containing traces of active metals, and, in the case of the δ-MnO_2, more closely resembling *cryptomelane.* McMurdie,[25] on the basis of X-ray data and heating curves, has reached the conclusion that there are five different types of manganese dioxide.

Several attempts were made to prepare the substances described. These involve no new feature except the magnetic data: Preparation 1: Dubois, $HMnO_4$ + HNO_3, Formula, $MnO_{1.86}\cdot 0.6\ H_2O$; X-ray lines: d = 2.40, 2.15 Å.; susceptibility: $\chi \times 10^6 = 46$ (25°), 56 (−80°), 80 (−185°).

Preparation 2: Alekseevski and Frid, $HMnO_4$ + $MnSO_4$; formula, $MnO_{1.93}\cdot 0.7\ H_2O$; X-ray lines, d = 2.36 Å.; susceptibility, $\chi \times 10^6$ = 48 (25°), 63 (−80°), 88 (−185).

Preparation 3: Glemser, $MnSO_4$ + $(NH_4)_2S_2O_8$; formula, $MnO_{1.95}\cdot 0.25\ H_2O$; X-ray, d = 2.42, 1.62, 2.12, 1.40, 4.03, 2.06, 1.83 Å. (in order of decreasing intensity); susceptibility: $\chi \times 10^6$ = 44 (25°), 49 (−80°), 73 (−185°).

Preparation 4: Glemser, $MnSO_4$ + $KMnO_4$ + KNO_3; formula, $MnO_{1.93}\cdot 0.48\ H_2O$; X-ray, d = 2.42, 1.62, 2.12, 1.40, 4.03, 206 Å.; susceptibility: $\chi \times 10^6$ 44 (25°), 51 (−80°), 68 (−185°).

Preparation 5: prepn. 4 plus vacuum heating at 400° for eighteen hours; formula, $MnO_{1.89}\cdot 0.33\ H_2O$; X-ray, practically no change from prepn. 4; susceptibility, $\chi \times 10^6$ = 36 (25°), 45 (−80°), 70 (−185°).

The conclusions which may be drawn from these results are that preparations 1 and 2 do not give a product sufficiently characterizable to be considered a distinct form of manganese dioxide. Preparations 3 and 4 yield the same product, for which X-ray evidence tends to indicate a definite polymorphic form. Preparation 5 yields no new substance.

Dehydration Studies.—The surprising degree of magnetic dilution found in the substances observed above has been described earlier.[43] This phenomenon has been observed by Amiel[49,50,51] and co-workers who noted the increased susceptibility at room temperature in samples of manganese dioxide showed unusual catalytic activity. The interpretation of this effect given by the French workers is based on a supposed relaxation of covalent bonds between manganese and coördinated oxygen. X-Ray evidence tends to show that there may actually be an increased manganese–oxygen bond length in the active oxides as compared with that in massive (crystalline) *pyrolusite.*

An interpretation based on the work described here favors the idea of diminished numbers of paramagnetic ions surrounding each manganese, *i. e.*, a diminished "paramagnetic neighborhood," in the disperse systems as compared with the massive. The constancy of the magnetic moment at about 3.8 Bohr magnetons, corresponding to three unpaired "spin-only" electrons, tends to support this idea.

A magnetic study has been made of the effect of dehydration on disperse manganese dioxide gel obtained as described under preparation 3 above.

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[46] Whitsell and Frazer, THIS JOURNAL, **45**, 2841 (1923).

[47] Schossberger, *Physik. Ber.*, **22**, 1340 (1941).

[48] McMurdie, *Trans. Electrochem. Soc.*, **86**, 313 (1944).

[49] Amiel, *et al.*, Reports presented at the Conference on the Polarization of Matter, Paris, April 4-9 (1949).

[50] Amiel, Brenet and Rodier, *Compt. rend.*, **227**, 60 (1948).

[51] Brenet, *ibid.*, **227**, 1036 (1948).

The results are shown in Table II. The dehydration was cumulative.

The expected loss of oxygen occurred after long dehydration. The results show clearly that the magnetic dilution of manganese in this substance persists until the temperature is high enough to drive off oxygen. The removal of oxygen is, of course, attended with a reduction of the manganese. Dehydration may be carried a considerable distance without greatly changing the atomic environment of the manganese. It will be noted that at a certain stage of dehydration the product had both X-ray and magnetic properties not unlike that of natural African ore.

Acknowledgment.—It is a pleasure to acknowledge the assistance of Kathryn Wethington in this work.

Summary

Preparation and properties are given for accurately characterized samples of MnO, $Mn(OH)_2$, Mn_3O_4, α-Mn_2O_3, γ-Mn_2O_3, MnOOH, and MnO_2. Some less well characterized products are described.

EVANSTON, ILL. RECEIVED JUNE 22, 1948

[CONTRIBUTION FROM THE DEPARTAMENTO DE QUIMICA, FACULDADE DE FILOSOFIA, CIENCIAS E LETRAS, UNIVERSIDADE DE SÃO PAULO]

Selenenyl Selenocyanates

BY HEINRICH RHEINBOLDT AND ERNESTO GIESBRECHT

Members of the new class of aromatic selenenyl selenocyanates, ArSeSeCN, are obtained in a similar way as the correspondent sulfenyl selenocyanates, ArSSeCN,[1] by the reaction of selenenyl bromides with dry, powdered potassium selenocyanate suspended in an inert solvent such as benzene. In this manner the selenocyanates of 2-nitrobenzeneselenenyl, 2-nitro-4-chlorobenzeneselenenyl, 2-nitro-4-bromobenzeneselenenyl and 2-nitro-4-methylbenzeneselenenyl were prepared in a pure state, and 2,4-dinitrobenzeneselenenyl selenocyanate in a less pure state. Attempts to obtain benzeneselenenyl selenocyanate and 4-nitrobenzeneselenenyl selenocyanate were not successful, since these products were not stable under the conditions which were effective for the other selenenyl selenocyanates. Selenenyl selenocyanates, in opposition to the corresponding selenenyl thiocyanates,[2] cannot be obtained by mixing, at 0°, solutions of the selenenyl bromides and potassium selenocyanate in methanol or methanol–ethyl acetate mixtures; an immediate separation of diselenides and selenium is observed in these cases.

The properties of the selenenyl selenocyanates are, under various aspects, very different from those of the sulfenyl selenocyanates. The former compounds melt without decomposition, and at a higher temperature selenium is separated with formation of aryl selenocyanates; no formation of diselenides is observed. The melting points of selenenyl selenocyanates are in general higher than those of the corresponding bromides, with exception of the 2,4-dinitrobenzene compound. This behavior is analogous to that of the corresponding sulfenyl thiocyanate.[3] Another difference is the relative insensibility of the selenenyl selenocyanates against water and methanol, which act only slowly; in this case the selenenyl selenocyanates are similar to the sulfenyl thiocyanates.[4] Alcoholic ammonia or bromine in dry chloroform cause a rupture of the selenium–selenium bond, with practically quantitative formation of the diselenides; this behavior is analogous to that of the sulfenyl selenocyanates.[1] The selenenyl selenocyanates, contrary to the sulfenyl selenocyanates, do not condense with methanol, with dry ammonia in benzene solution, with acetone, acetophenone or N-dimethylaniline. In the three first cases diselenides are formed; in the reaction with acetophenone only a very little amount of diselenide was formed and with N-dimethylaniline no reaction is observed. By hydrolysis selenenyl selenocyanates give aryl selenocyanates. These reactions are described in detail, in the experimental part, in the case of the *o*-nitrobenzeneselenenyl selenocyanate.

Experimental

I. **2-Nitrobenzeneselenenyl Selenocyanate.**—A solution of 11.2 g. (0.04 mole) of *o*-nitrobenzeneselenenyl bromide (m. p. 65°, from petroleum ether; yield 75%)[5] in 50 cc. of dry pure benzene was mechanically shaken in an opaque closed flask for twenty-two hours at about 20° with 7.2 g. (0.05 mole) of dry finely powdered pure potassium selenocyanate. The benzene solution was then filtered off from the solid which was washed with dry benzene. After removing the solvent from the benzene solutions under reduced pressure at 35–40° a crystalline reddish-yellow solid remained which melted at 102–106°; yield 10.5 g. or 86%. After two recrystallizations from dry pure carbon tetrachloride, small canary-colored, odorless needles of melting point 109–110° (microscope hot stage) were obtained.

Anal. Calcd. for $C_7H_4O_2N_2Se_2$: Se, 51.60; N, 9.15. Found: Se, 51.76; N, 9.27.

The crystals are not very sensitive toward the humidity of the air; however, when exposed for a long time to the daylight and to the atmosphere, they become darker and

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[1] H. Rheinboldt and E. Giesbrecht, THIS JOURNAL, **71**, 1740 (1949).

[2] O. Foss, *ibid.*, **69**, 2236 (1947); Rheinboldt and Madeleine Perrier, unpublished work.

[3] N. Kharasch, H. L. Wehrmeister and H. Tigerman, *ibid.*, **69**, 1612 (1947).

[4] H. Lecher and K. Simon, *Ber.*, **54**, 637 (1921).

[5] O. Behaghel and H. Seibert, *ibid.*, **66**, 713 (1933).