The Action of Hydrochloric Acid on Manganese Dioxide

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THE ACTION OF HYDROCHLORIC ACID
ON MANGANESE DIOXIDE

BY

VERNE RALPH ROSS

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THESIS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Verne R. Ross.

ENTITLED The Action of Hydrochloric Acid on Manganese Dioxide.

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Master of Arts.

Willis B. Holmes.
In Charge of Major Work
Head of Department

Recommendation concurred in:

Committee on Final Examination
When manganese dioxide is treated with aqueous hydrochloric acid, chlorine is evolved, and a deep brown solution is obtained. This solution in the cold becomes lighter in color and slowly evolves more chlorine. When heated the evolution of chlorine is much more rapid. In either case a clear, light green liquid is obtained. This liquid contains manganous chloride. The equation ordinarily used to express the reaction is:

\[ \text{MnO}_2 + 4\text{HCl} = \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2 \]

It is quite evident that higher chlorides of manganese are formed as intermediate products. Many chemists have devoted considerable time to the study of these compounds, and have demonstrated beyond doubt that they do exist but they have not as yet been isolated as simple salts.

In 1821 Forchammer stated that when either manganese dioxide, sesquioxide, or trimanganese tetroxide is dissolved in hydrochloric acid, a brown solution results. On adding water to such a solution a mixture of oxides of manganese is precipitated.

Dumas\(^1\) in 1828 predicted that a class of perchlorides corresponding to the peroxides such as hydrogen peroxide or manganese dioxide should exist. He reasoned that if two atoms of oxygen unite with one of manganese, four atoms of chlorine ought to unite with manganese forming the compound manganese tetra-chloride.

All attempts to establish the existence of such a com-

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pound proved unsuccessful until 1865 when Nicklés published results of experiments with manganese dioxide and hydrochloric acid. He suspended manganese dioxide in anhydrous ether and passed hydrogen chloride into the solution. A green solution resulted. When water was added to this solution, he claimed that only manganese dioxide was precipitated. The green solution contained a compound in which ether and water were always present as constituents. He assigned to this the formula,

\[ \text{MnCl}_4 \cdot 12(C_2H_5)_2O \cdot 2H_2O \]

His determination of manganese was based upon the assumption that only manganese dioxide was precipitated by adding water to the green etherial solution. By dissolving trimanganese tetroxide in an etherial solution of hydrochloric acid he claimed to have obtained the compound,

\[ \text{Mn}_2\text{Cl}_3 \cdot 6(C_2H_5)_2O \cdot 3\text{HCl} \cdot 3\text{H}_2\text{O} \]

None of these compounds were definite, as it was impossible to get two analyses to agree.

Fisher studied the action of aqueous hydrochloric acid on manganese dioxide, and concluded that the only intermediate product of the reaction was manganese tetrachloride.

He determined the ratio of total manganese to chlorine above that required for manganese dichloride, basing his determinations upon the assumption that only the dioxide was precipitated by water. He determined the amount of available chlorine by the amount of iodine it liberated from potassium iodide.

He supposed the original action to be represented by the equation,
\[ \text{MnO}_2 + 4\text{HCl} = \text{MnCl}_4 + 2\text{H}_2\text{O}. \]
When water is added to this solution it decomposes, according to the equation,
\[ \text{MnCl}_4 + 2\text{H}_2\text{O} = \text{MnO}_2 + 4\text{HCl}. \]
The action with potassium iodide is,
\[ \text{MnCl}_4 + 2\text{KI} = \text{MnCl}_2 + 2\text{KCl} + \text{I}_2. \]
Thus for every atom of manganese precipitated there are two of iodine liberated. The ratio was found to be one to two. He studied the action of hydrochloric acid on manganese sesquioxide and trimanganese tetroxide, and concluded that only MnCl₄ was formed in each case.

Pickering¹ repeated Fisher's work, obtained the same results, but severely criticised Fisher's conclusions. He contended that the trichloride would give the same results with water and potassium iodide. The reactions would take place thus:
\[ \text{Mn}_2\text{Cl}_6 + 2\text{H}_2\text{O} = \text{MnO}_2 + \text{MnCl}_2 + 4\text{HCl} \]
\[ \text{Mn}_2\text{Cl}_6 + 2\text{KI} = 2\text{MnCl}_2 + 2\text{KCl} + \text{I}_2. \]
For every atom of manganese precipitated as dioxide there are two of iodine liberated, but all of the manganese is not precipitated as Fisher claimed. He showed that the compound precipitated by water is not the dioxide, but is a mixture of manganous oxide and the dioxide. Taking this fact into consideration he determined the ratio of total manganese to available chlorine to be about 1:1.64. He found the sesquioxide to form a compound which gave the same results. He supposed the

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reactions to take place thus:

\[ \text{MnO}_2 + 8\text{HCl} = \text{Mn}_2\text{Cl}_6 + \text{Cl}_2 + \text{H}_2\text{O} \]

\[ \text{Mn}_2\text{O}_3 + 6\text{HCl} = \text{Mn}_2\text{Cl}_6 + 3\text{H}_2\text{O}. \]

Christensen\(^1\) agreed with Pickering that \(\text{Mn}_2\text{Cl}_6\) and not \(\text{MnCl}_4\) was formed. He undertook to show that Nickles green ethereal solution did not contain \(\text{MnCl}_4\) but \(\text{Mn}_2\text{Cl}_3\). He determined idometrically the ratio between total manganese and available chlorine and found it to be about 1 : 1.

In a later work\(^1\) he repeated Nickles work obtaining the same green ethereal solution, but using a different method of analysis. He mixed concentrated hydrochloric acid and ether, and found that the mixture on standing separated into two layers, the upper containing a solution of hydrochloric acid in ether, and the lower a solution of ether in hydrochloric acid. When these two layers were separated and manganese dioxide added to each, the solution of ether in hydrochloric acid gives a green color, and the other a violet color.

The solution of ether in hydrochloric acid contains water while the solution of hydrochloric acid in ether does not. Christensen attributed the green color of the compound to the presence of water. The violet and green colors were due to the same compound. The mean ratio of manganese to available chlorine in a number of analyses was found to be 1 : 1.06. This indicates the trichloride. When the green solution was made at minus temperatures as low as ten degrees the ratio of manganese to

2. Ibid. 35 : 57.
available chlorine, was found to be about 1 to 1.5, indicating that at low temperatures the tetrachloride is possible.

Franke repeated Christensen's work on the etherial solutions, but came to entirely different conclusions. He stated that an etherial solution of hydrochloric acid contains more hydrochloric acid than a solution of ether in hydrochloric acid. When manganese dioxide is added to each solution the former is green and the latter violet. Franke concluded that the green color was due to a compound chloromanganic acid.

The reaction took place thus:

$$\text{MnO}_2 + 6\text{HCl} = \text{H}_2\text{MnCl}_6 + 2\text{H}_2\text{O}.$$ 

The violet solution contained MnCl₄.

These solutions on analysis gave a ratio from 1 : 1.68 to 1 : 2.35 of manganese to available chlorine. Manganese chloride was always present as a decomposition product and this reacted with the chloromanganic acid.

$$\text{MnCl}_2 + \text{H}_2\text{MnCl}_6 = \text{Mn} . \text{MnCl}_6 + 2\text{HCl}.$$ 

The green solution on dilution with ether turned violet. Apparently the ether caused the Mn . MnCl₆ to decompose forming the tetrachloride. On passing more gaseous hydrochloric acid into this solution the green color returned.

Vernon² by means of a Victor Meyer apparatus determined the volumes of chlorine evolved from the solution of manganese dioxide in hydrochloric acid, in definite length of time. He used these data for plotting a curve - time as abscissae, and

volume as ordinates, and found that the resulting curve was perfectly regular. This would not be the case if MnCl₃ were first formed. He concluded that only MnCl₄ was formed according to the equation,

\[ \text{MnO}_2 + 2\text{HCl} = \text{MnCl}_4 + 2\text{H}_2\text{O}. \]

All attempts prior to 1890 to isolate the higher chlorides of manganese failed. About this time there was considerable interest manifest in double salts of these compounds.

Neumann¹ saturated concentrated hydrochloric acid with chlorine and hydrogen chloride, and added hydrated manganese dioxide to it. Then the solution was filtered more chlorine and hydrogen chloride passed in, and a solution of ammonium chloride added. A dark violet crystalline mass separated which proved to be the double salt \( 2(\text{NH}_4)\text{Cl} \cdot \text{MnCl}_3 \). In a similar manner he obtained the potassium double salt, \( \text{MnCl}_3 \cdot 2\text{KCl} \).

Reitzenstein² treated pyrolusite with pyridine hydrochloride and obtained the compound \( \text{MnCl}_4 \cdot 2\text{C}_5\text{H}_5\text{N} \).

Rice³ repeated Neumann's work and obtained the same double salts with a molecule of water of crystallization.

Meyer and Best⁴ by treating manganese dioxide with an alcoholic solution of hydrochloric acid and adding the organic bases quinoline and pyridine obtained the compounds, \( \text{MnCl}_3 \cdot 2\text{C}_9\text{H}_7\text{N} \cdot \text{HCl}, \) and \( \text{MnCl}_3 \cdot 2\text{C}_5\text{H}_5\text{NCl} \).

By using acetic acid as a solvent for hydrogen chloride they obtained from permanganates and alkali chlorides the following double salts:

\[
\text{MnCl}_3 \cdot 2\text{KCl}, \text{MnCl}_3 \cdot 2\text{CsCl}, \text{MnCl}_4 \cdot 2\text{KCl}.
\]

They also prepared \( \text{MnCl}_4 \cdot \text{MnCl}_3 \cdot 5\text{KCl} \).

Weinland and Dinkelacker\(^1\) by the action of concentrated aqueous hydrochloric acid on permanganates and an alkali chloride obtained the following double salts:

\[
\begin{align*}
\text{MnCl}_4 & \cdot 2\text{RbCl}, \quad \text{MnCl}_4 \cdot 2\text{NH}_4\text{Cl} \\
\text{MnCl}_3 & \cdot 2\text{RbCl}, \quad \text{MnCl}_3 \cdot 2\text{CsCl}, \\
\text{MnCl}_3 & \cdot 2\text{KCl}, \quad \text{and} \quad \text{MnCl}_3 \cdot 2\text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}.
\end{align*}
\]

There have been so many conflicting opinions regarding the composition of the compounds formed when hydrogen chloride acts on manganese dioxide, that this work was undertaken to determine if possible, whether the tri-or tetra-valent compound is formed, and whether or not they can be isolated as definite compounds, or only as double salts.

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Experimental Part.

Various qualitative methods of preparation of the higher chlorides were undertaken. Manganese dioxide was placed with sulphuryl chloride in a flask, and chlorine passed through the liquid. There was no apparent action. Dry hydrogen chloride was then passed through the same mixture. Some of the resulting solution was placed in ether and a violet color was noticed. This indicated the presence of the trichloride. No attempt was made to determine the exact constitution, as the compound was contaminated with other products of the reaction, and it decomposed before it could be separated.

Manganous chloride was substituted for the manganese dioxide and the above treatment repeated. There was no evidence of the formation of the higher chlorides. Sulphur monochloride was substituted for the sulphuryl chloride and treated with chlorine and hydrogen chloride. There was no evidence of the higher chlorides. Manganous oxide was substituted for the dioxide and the process repeated with both sulphuryl chloride and sulphur monochloride used as solvents. There was no evidence of any of the higher chlorides. Silver permanganate was mixed with sulphur monochloride and treated with chlorine and hydrogen chloride. The resulting solution was filtered and ether poured through. The ether was colored violet indicating the presence of the trichloride. Silver permanganate treated with sulphuryl chloride in an analogous way gave the violet color to the ether.
A quantitative study of the action of hydrogen chloride, in different solvents, on manganese dioxide prepared by different methods was made. The solvents were glacial acetic acid, anhydrous ethyl and propyl alcohol, and anhydrous ether. The dioxides were the precipitated, electrolytic, and ignited. Kahlbaum's precipitated dioxide was treated for several days with dilute nitric acid, to dissolve any impurities, thoroughly washed and dried. On analysis it showed the following composition.

\[
\begin{array}{ccc}
\text{MnO}_2 & \text{MnO} & \text{H}_2\text{O} \\
90.28\% & 5.62\% & 4.10\% \text{ (by difference)} \\
90.17 & 5.54 & 4.29
\end{array}
\]

The electrolytic dioxide was prepared by the electrolysis of manganous sulphate. It was treated several days with dilute nitric acid, thoroughly washed and dried. It gave the following results on analysis.

\[
\begin{array}{ccc}
\text{MnO}_2 & \text{MnO} & \text{H}_2\text{O} \\
90.08\% & 2.84\% & 7.08\% \text{ (by difference)} \\
89.99 & 2.74 & 7.27
\end{array}
\]

The ignited dioxide was prepared by igniting manganous nitrate, and then treating with dilute nitric acid, washing and drying. Its composition was as follows;

\[
\begin{array}{ccc}
\text{MnO}_2 & \text{MnO} & \text{H}_2\text{O} \\
97.39\% & 1.50\% & 1.11\% \text{ (by difference)} \\
97.12 & 1.66 & 1.22
\end{array}
\]

The general method of procedure in each case was as follows. One hundred cubic centimeters of the solvent was placed in a flask and immersed in a mixture of ice and salt. Dry hydrogen chloride was passed into the solvent until it was
saturated. Two grams of dioxide were then added, the solution
being kept cold. When the dioxide had apparently dissolved the
solution was quickly filtered by suction through a Büchner fun-
nel into a cooled flask. This was done to remove any dioxide
that may not have been acted upon by the acid. Then two grams
of potassium acetate dissolved in glacial acetic acid were added
to the solution. The precipitate formed was filtered by suction
onto a Büchner funnel, and washed with carbon tetrachloride.
This precipitate was then ready for analysis. It was reddish
brown in color and was a double salt of manganese and potassium
chlorides.

Throughout the entire work the greatest possible pre-
cautions were taken to avoid the presence of moisture. All the
flasks and vessels used were thoroughly dried, and protected by
calcium chloride tubes where possible. The compounds formed
both before and after the addition of the potassium acetate evol-
ed considerable chlorine, and it was necessary to carry on the pro-
cess after the addition of the dioxide with rapidity, to avoid
as much as possible, the decomposition of the compound. In
spite of these precautions some of the chlorine was lost and the
results are all lower than theory requires.

When the dioxide was placed in the hydrogen chloride
solution, it dissolved evolving some chlorine, and imparting to
the solution a beautiful deep green color. On the addition of
the potassium acetate solution a deep reddish brown precipitate
was thrown down. When this was filtered out, and left in a
dessicator, it slowly became lighter in color and evolved chlor-
and

ine. It finally took on a very pale rose colored tint consisted of a mixture of potassium and manganous chlorides.

The compound when precipitated was as quickly as possible filtered, washed free from chlorine with carbon tetrachloride and thrown into an acid solution of potassium iodide. The compound was decomposed liberating all the chlorine, over that required by manganous chloride, which replaced iodine in the potassium iodide. The free iodine was then titrated with tenth normal sodium thiosulphite. From this weight of available chlorine was determined.

The Gooch\(^1\) method was used to determine the total manganese. To an aliquot part of the manganese solution, after titration of free iodine, enough ammonium chloride was added to make a ten per cent solution. Five cubic centimeters of a saturated solution of microcosmic salt, and ammonia in slight excess were added. A gelatinous precipitate was thrown down, which was filtered onto a perforated platinum crucible, washed, ignited and weighed as pyrophosphate.

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1. Amer. Jo. of Science, 156 - 233.
I. Alcoholic Solutions.

Trial 1 - Materials: 100 cc. saturated solution of HCl; 2 gms. precipitated MnO₂; 2 gms. C₃H₅COOK in glacial acetic acid. The reddish brown precipitate gave the following results on analysis.

<table>
<thead>
<tr>
<th>Total Mn</th>
<th>Available Cl</th>
<th>Ratio Cl/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>.2312 gm.</td>
<td>.2896 gm.</td>
<td>1.252</td>
</tr>
<tr>
<td>.2318 &quot;</td>
<td>.2896 &quot;</td>
<td>1.249</td>
</tr>
</tbody>
</table>

The trichloride contains one atom, and the tetrachloride two atoms of available chlorine for every atom of manganese. The respective ratios are \( \frac{Cl}{Mn} = \frac{35.5}{55} = .645 \) and \( \frac{Cl^2}{Mn} = \frac{71}{35} = 1.29. \) The ratio found in this case indicates the formation of the tetrachloride.

Trial 2 - Material: 100 cc. saturated alcoholic solution of HCl; 2 gms. ignited MnO₂; 2 gms. CH₃COOK in glacial acetic acid. The precipitate gave the following results.

<table>
<thead>
<tr>
<th>Total Mn</th>
<th>Available Cl</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0492 gm.</td>
<td>.0574 gm.</td>
<td>1.167</td>
</tr>
<tr>
<td>.0497 &quot;</td>
<td>.0574 &quot;</td>
<td>1.154</td>
</tr>
</tbody>
</table>

If four molecules of the tetrachloride were formed to one of the trichloride the ratio of total manganese to available chlorine would be 1.169. The ratio found in this case indicates that both compounds have been formed.

Trial 3 - Material: 100 cc. saturated alcoholic solution of HCl; 2 gms. electrolytic MnO₂; 2 gms. CH₃COOK in glacial acetic acid.
Trial 4 - Material: Same as in trial 3.

<table>
<thead>
<tr>
<th>Total Mn</th>
<th>Available Cl</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3079 gm.</td>
<td>0.2871 gm.</td>
<td>0.932</td>
</tr>
<tr>
<td>0.3061 &quot;</td>
<td>0.2871 &quot;</td>
<td>0.938</td>
</tr>
</tbody>
</table>

If the trichloride and tetrachloride were both formed in equal amounts, the ratio of available chlorine to total manganese would be 0.968. The electrolytic dioxide seems to yield the two chlorides in equal amounts.

Trial 5 - Material: 100 cc. saturated solution of HCl in propyl alcohol; 2 gms. precipitated MnO₂; 2 gms. CH₃COOK in glacial acetic acid.

<table>
<thead>
<tr>
<th>Total Mn</th>
<th>Available Cl</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0501 gm.</td>
<td>0.0493 gm.</td>
<td>0.983</td>
</tr>
<tr>
<td>0.0509 &quot;</td>
<td>0.0493 &quot;</td>
<td>0.968</td>
</tr>
</tbody>
</table>

Five molecules of the tetrachloride to one of the trichloride give the ratio 1.182 between available chlorine and total manganese. Apparently both compounds were formed, the tetrachloride being much in excess.

II Etherial Solutions.

Trial 1 - Materials: 100 cc. saturated etherial solution of HCl; 2 gms. precipitated MnO₂; 2 gms CH₃COOK in glacial acetic acid.

<table>
<thead>
<tr>
<th>Total Mn</th>
<th>Available Cl</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0677 gm.</td>
<td>0.0564 gm.</td>
<td>0.632</td>
</tr>
<tr>
<td>0.0679 &quot;</td>
<td>0.0564 &quot;</td>
<td>0.830</td>
</tr>
</tbody>
</table>
Trial 2 - Materials: Same as in trial 1.

Total Mn Available Cl Ratio
.4159 gm. .3076 gm. .740
.4179 " .3076 " .736

The ratio in trial 1 corresponds to nine parts of the trichloride to two of the tetrachloride. Eleven parts of the trichloride to two of the tetrachloride give a ratio of .762 to which that found in trial 2 corresponds.

III Glacial Acetic Acid Solutions.

The method of procedure with glacial acetic acid was varied slightly. After the dioxide had been added to the hydrogen chloride solution hydrogen chloride was again passed in for fifteen or twenty minutes. The procedure from this point was identical with the general method previously described.

Trial 1 - Materials: 90 cc. glacial acetic acid and 10 cc. ethyl alcohol saturated with HCl; 2 gms. precipitated MnO₂; 2 gms. CH₃COOK in glacial acetic acid.

Total Mn Available Cl Ratio
.1256 gm. .1268 gm. 1.009
.1254 " .1268 " 1.011

This ratio corresponds very closely to 1.032 which is that of the available chlorine to the total manganese of two molecules of the trichloride to three of the tetrachloride.

Trial 2 - Materials: 95 cc. glacial acetic acid and 5 cc. ethyl alcohol; 2 gms. precipitated MnO₂; 2 gms. CH₃COOK in glacial acetic acid.
The ratio between available chlorine and total manganese for three molecules of the tetrachloride to one of the trichloride is 1.129.

Trial 3 - Materials: 95 cc. glacial acetic acid and 5 cc. ethyl ether saturated with HCl; 2 gms. precipitated MnO₂; 2 gms. CH₃COOK in glacial acetic acid.

This ratio indicates the formation of the tri and tetra-chlorides in equal amounts.
Conclusion.

1. All attempts to isolate the tri- and tetrachlorides proved unavailing.

2. Hydrogen chloride in ethyl alcohol acting on manganese dioxide, at a temperature a few degrees below zero, forms manganese tetrachloride. Owing to its instability it has been impossible to isolate this compound. But it can be isolated as a double salt with potassium chloride.

3. Hydrogen chloride, dissolved in alcohol, acting on either the ignited or precipitated dioxides produces both the tri- and tetrachlorides which may be isolated as double salts with potassium chloride. The tetrachloride is much in excess.

4. Propyl alcohol used as a solvent for the hydrogen chloride gives with the precipitated dioxide a mixture of the two chlorides the tetravalent compound being in excess.

5. Hydrogen chloride dissolved in glacial acetic acid, which contains small amounts of ether or alcohol, acting on the precipitated dioxide yields both chlorides the tetravalent predominating.

6. When ether is used as the solvent for the hydrogen chloride both compounds are formed, the trichloride being much in excess.

7. It is impossible to predict just what chloride will be formed when hydrogen chloride acts on manganese dioxide. It seems to depend largely upon the solvent used and to a less extent upon the kind of dioxide used. Neither chloride has been isolated as a simple salt, but both can be obtained as double salts.