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SOME INVESTIGATIONS

ON THE

IODATES OF GROUP IV A.

Thesis presented for the MSc. degree examination

by

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SOME INVESTIGATIONS ON THE IODATES OF GROUP IV A.

During work on certain iodates it was found very difficult to obtain some of them pure.

In the case of thallic iodate this was found impossible, when water was the solvent, even after considerable work; and other solvents could not be found for the materials.

Mixtures of basic salts were apparently formed and in the case of ceric iodate the normal salt was only obtained pure after several trials.

Investigations of this substance lead to an attempt to discover whether any definite basic compound could be isolated, and when this was found to be the case, the investigation was extended to thorium and zirconium iodates, since the hydroxides of these metals did not differ very much in strength from that of ceric hydroxide.

An examination of the literature showed that nothing conclusive in connection with the basic iodates of these elements had been established.

The following is a resumé of what was found concerning their iodates.

Zirconium iodate was described by Davis (American Chemist Journ: 11. 26. 1899) as a difficultly soluble salt formed on

precipitating a soluble zirconium salt with potassium iodate.

Venable and Smithey (Journ: Am: Chem: Soc.41, 1722, 1919) describe a series of basic zirconium iodates, which they prepared by the action of iodic acid on zirconyl chloride. The product varied very much according to the conditions of preparation and the thoroughness of washing.

They describe the following compounds:-

- (1) $ZrO(OH)_2 \cdot 2 ZrO(I.O_3)_2$ precipitated in concentrated solution and analysed without washing.
- (2) $5 ZrO(OH)_2 \cdot 8 ZrO(I.O_3)_2$ precipitated in more dilute solution, also analysed without washing.
- (3) $3 ZrO(OH)_2 \cdot 4 ZrO(I.O_3)_2$, analysed after washing with cold water.
- (4) $2 ZrO \cdot ZrO(I.O_3)_2$ analysed after washing for some time with hot water.

The hydrolysis was thus progressive.

They expressed the intention of attempting the preparation of the normal iodate; but no work seems to have been published on this point.

Apparently Venable and Smithey were not dealing with Chemical individuals.

The amount of washing changed the composition of their substances in so marked a manner that their products probably did not represent definite basic compounds; but only mixtures

of such compounds.

Ceric iodate was described by Barbieri (Atti: R. Accad: Lincei (5) 16.1.644, 1907) (ABS. Chem. Soc. 1907. 11. 467) as having been prepared by the action of iodic acid on cerous nitrate, in the presence of concentrated nitric acid. He stated that the salt was sparingly soluble in the latter acid, and somewhat hydrolysed by water. It was yellow in colour.

Barbieri pointed out that though ceric iodate decomposes hydrogen peroxide; this does not necessarily prove that the cerium was present in the ceric conditions, as iodic acid and the iodates do this also.

Brinton and James (J. Am. Chem: Soc: 41,1080,1919) used this salt as a means of separating cerium from the other rare earths, because it is sparingly soluble in nitric acid. Cerous iodate is unique among the iodates of the rare earths in being oxidised by potassium bromate and nitric acid, as it is the only rare earth which forms quadrivalent compounds.

They tested this method of separating cerium rigorously, and gave details of the method of precipitation.

The yellow ceric iodate was filtered off from the nitric acid solution, treated with concentrated oxalic acid solution, and the cerium weighed as dioxide.

It must be noted that they were not necessarily concerned with the purity of the ceric iodate, but only with the removal in this form of all the cerium present in the mixture and there is nothing to indicate that they were dealing with the pure substance.

Thorium iodate was prepared by Cleve (Bull. Soc. Chem: 1874⁽²⁾ 21. 116) by precipitating soluble thorium salts with alkali iodates, as an amorphous white powder.

Meyer and Speter (Zeitsch. Anorg. Chem: 11, 65, 1911) noted the fact that thorium and cerous iodates differ from the iodates of the rare earths in being sparingly soluble in nitric acid. This gave them a method of separating Thorium and Cerium from the rare earths, and was found satisfactory in detecting minute quantities of these elements.

Meyer (A. 1911. 11 825) also described a method of determining thorium by precipitation as the oxalate in the presence of a little hydrochloric acid. This method was adopted here, and will be described later.

We have now to consider the conditions under which a sparingly soluble basic salt separates from an aqueous solution.

That such a ^{precipitate} salt is a uniform basic compound is by no means certain.

It may be more often a mixture of a basic salt and a normal salt, or of two basic salts.

A definite test of the individuality of basic salts may be applied by using the principles of the phase rule.

In this case $Ce(I.O_3)_4$, and H_2O can be taken as a three component system, the components being: $Ce.O_2$, I_2O_5 , and H_2O .

When equilibrium has been attained after shaking, we have the four phases, normal iodate, basic iodate, solution and vapour.

$$\therefore \text{As } F+4 = 3+2 \quad \therefore F = 1$$

That is, the system is univariant. But as we have fixed the temperature the system is invariant, and the concentration of the solution should be constant as long as there are two solid phases.

When the normal salt has been entirely converted into a basic salt we have lost a phase, and, the system being now univariant the concentration of the solution should now vary as long as this basic salt alone persists. When hydrolysis of the solid begins again the concentration of the solution should again become constant.

The following are examples of the application of the rule.

Lash Miller and Kendrick (Proc. Roy. Soc. Canada 1901 (11) J. 252.) (Journ. Phys. Chem: 7, 1903, 259) described such a method as applied to basic salts generally, referring to their work

on basic chlorides of lead, and to that of their associates on basic salts of antimony, bismuth and copper.

(*Zeitsch. Anorg. Chem.* 1904, 40, 146)
A.J.Cox in a dissertation at Breslau (1904) applied their method to the isolation of various basic mercurous and mercuric salts, and Spencer (*J. Chem. Soc.*:1913, 107, 1265) used a similar method in isolating basic ceric sulphates.

This method was also used in examining ceric and thorium iodates in the work to be described.

Ceric iodate being known to be somewhat hydrolysed by water was first prepared pure, and then treated with water under known conditions, so that existence of possible basic salts might be detected.

Thorium iodate was also examined in the same way, but in the case of zirconium no normal iodate could be prepared.

Finally it was found satisfactory to wash with nitric acid (1:5) on a hardened filter paper.

In this way the excess of H.I.O₃ was removed and only a small loss of ceric iodate resulted.

The washed ceric iodate was dried in a desiccator over lime in a steam oven till of constant weight.

The product was analysed for Ce as directed by Bratton.

THE PREPARATION OF PURE CERIC IODATE.

Brinton & James' method, with modifications, was found in the end to yield the pure salt.

That of Barbieri was found unsatisfactory, as by no means all the cerium was precipitated as ceric iodate.

A quantity of cerous chloride solution containing 1 gm. of cerium was evaporated to dryness and dissolved in the smallest quantity of dilute nitric acid.

A solution of 66 grms. of $K.I.O_3$ in 660 cc water and 230 cc $H.N.O_3$ was added, but no precipitation occurred even on warming until a pinch of $KBrO_3$ was added.

A copious precipitate of bright yellow ceric iodate then appeared. So far the method of preparation was that given by Brinton & James: but to obtain the iodate pure was a matter of some difficulty.

Finally it was found satisfactory to wash with nitric acid (1:5) on a hardened filter paper.

In this way the excess of $K.I.O_3$ was removed and only a small loss of ceric iodate resulted.

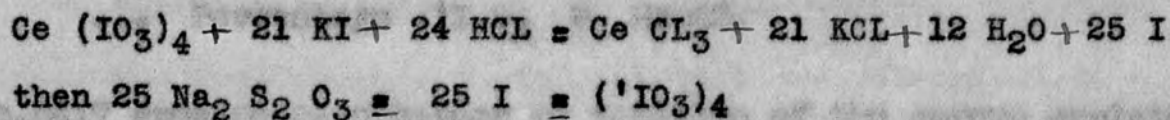
The washed ceric iodate was dried in a dessicator over lime in a steam oven till of constant weight.

The product was analysed for Ce as directed by Brinton

& James by treating a known weight of it with excess of a concentrated solution of oxalic acid. Iodine was copiously evolved and cerous oxalate was precipitated, washed, dried and ignited.

The 'I O₃ group was determined by adding to the solution a few crystals of potassium iodide, and about 5 cc of dilute H.Cl. The whole was diluted to 250 cc and the iodine titrated with approximately 0.1N. sodium thio-sulphate solution.

Presuming the reaction to be the following:



From which, if z grms of ceric iodate require x ces of 0.1N. Na₂ S₂ O₃.

Then the percentage of 'IO₃ in the iodate = $\frac{1}{25} \times \frac{x}{z}$

RESULTS OF ANALYSIS.

1. 61.9 c.c. 0.1N. sodium thio sulphate solution required for
0.2070 grms salt

∴ Percentage $I_2O_5 = 83.73$

0.0416 grms Ce_2O_3 obtained by ignition of the cerous oxalate
obtained from the above.

∴ Percentage $Ce = 16.36$

2. 90.6 c.c. 0.1N. sodium thio sulphate solution required for
0.3040 grms salt.

∴ Percentage $I_2O_5 = 83.43$

0.0617 grms Ce_2O_3 obtained by ignition of the cerous oxalate
obtained from the above

∴ Percentage $Ce = 16.52$

i.e. average percentage of Ce found = 16.44

" " " I_2O_5 " = 83.53

and $Ce(I_2O_5)_4$ requires $Ce = 16.6$ per cent.

$I_2O_5 = 83.4$ " "

HYDROLYSIS OF CERIC IODATE.

A known weight of the iodate, containing therefore a known weight of $Ce.O_2$ and I_2O_5 , was weighed into a glass bottle securely stoppered.

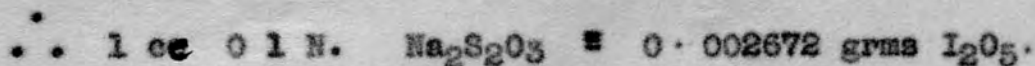
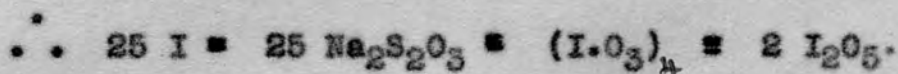
A known volume of water was added and the bottle was shaken in a thermostat at $25^{\circ} C$ for about three days.

After allowing the solid to settle completely, a known volume of the solutions was removed and analysed, and a known volume of water was added to the bottle. The bottle was again shaken.

Calibrated withdrawal and delivery pipettes were used.

The I_2O_5 present in the solution was determined as previously described, by adding potassium iodide, a few drops of $H.Cl$ and titrating the iodine with standardised sodium thio sulphate solution. A decinormal solution was found to be of suitable strength.

From the equation given previously,



The cerium was also estimated in each sample by precipitating it with excess of warm saturated oxalic acid solution, and

weighed as $Ce \cdot O_2$. It was always very small in amount.

This method of estimating Ce was first tested and found to be satisfactory as it was obviously necessary to determine I_2O_5 and $Ce \cdot O_2$ in the same solution.

After each determination the composition of the solid and the total contents of the bottle were calculated as in the following example.

Weight of $Ce(I_2O_5)_4 = 6.0400$ grams

Containing: 1.2370 grams $Ce \cdot O_2$
and 4.8030 " I_2O_5

$$\therefore \text{Ratio } I_2O_5 : Ce \cdot O_2 = \frac{172}{334} \times \frac{4.8030}{1.2370} \\ = 2.1$$

Volume of water at first = 200 c.c.

25 c.c. solution withdrawn and found to contain

0.00171 grams $Ce \cdot O_2$ and 0.02807 grams I_2O_5

$\therefore 0.01197$ grams $Ce \cdot O_2$ }
and 0.19649 " I_2O_5 }

remained in the solution (i.e. in 175 c.c.).

The solid therefore contained:

$1.2370 - 0.01368 = 1.22332$ grams $Ce \cdot O_2$

and $4.8030 - 0.22456 = 4.57844$ " I_2O_5

\therefore Ratio $I_2O_5 : Ce \cdot O_2 = 1.92 : 1.$

The bottle still contained (in solid and solution)

1.23529 grms $Ce.O_2$ and 4.7749 " I_2O_5 .

Table I appended gives the result of the experiment.

Column 1 gives the total volume of the solution; columns 2 and 3 the volumes of solution withdrawn, and of water added at each determination. In 5 and 6 is the volume and strength of the thiosulphate solution used; and in 7 the strength of I_2O_5 in grms mls: ($\times 10^{-2}$) found in the solution withdrawn. Then the weight of $Ce.O_2$ and I_2O_5 , found in the solution withdrawn, is given in columns 8 and 9; while the number of grams of each present in the solid is calculated in columns 10 and 11. Finally the ratio $Ce.O_2 : I_2O_5$ is calculated in column 12.

As there seemed no likelihood of further basic salt being formed, and the hydrolysis was exceedingly slow the experiment was stopped at the stage shown.

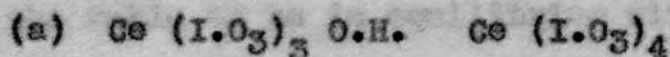
It will be seen on examining the table (column 12) that halts occur when the ratio $I_2O_5 : Ce.O_2$ is (a) $1.75 \approx 1$ (Expts: No. 6 - 11) and (b) $1 : 1$ (Expts No: 23 - 42).

When the composition of the solid is gradually changing the composition of the solution remains approximately constant; and when that of the solid remains constant there are irregular changes in the composition of the solution.

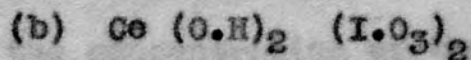
It appears likely then, that two basic ceric iodates may exist having compositions as given above.

(a) should be stable in the presence of I_2O_5 of a concentration of 0.48×10^{-2} - 0.58×10^{-2} gm $\frac{mols}{litre}$ I_2O_5 per litre.

(b) should be stable in the presence of I_2O_5 of a concentration of 0.194×10^{-2} - 0.155×10^{-2} gm $\frac{mols}{litre}$ I_2O_5 per litre, and the compounds should have the composition:



and



ISOLATION OF THE BASIC SALTS.

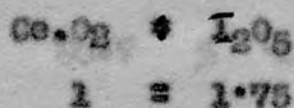
To test the validity of the conclusions drawn from the hydrolysis and to isolate the basic compounds, a known weight of normal ceric iodate was taken and the weight of I_2O_5 that it must lose to form a salt of the composition expected was calculated. A volume of water was then added so as to give a solution of the mean molecular concentration of I_2O_5 found from the table to be in equilibrium with such a salt.

The salt and water were then shaken for a week, by which time the concentration of the I_2O_5 was found to approximate to that calculated.

The solid was allowed to settle, filtered quickly, and drained and pressed rapidly on a porous plate.

After being air dried, it was analysed; the same methods of analysis as before being adopted.

PREPARATIONS AND ANALYSIS OF BASIC SALT I.



Suggested composition $\text{Ce}(\text{I.O}_3) \text{O.H. Ce}(\text{I.O}_3)_4$

∴ 1680 grms of $\text{Ce}(\text{I.O}_3)_4$ lose 167 grms I_2O_5
∴ 1 " " " would " 1 " "

A concentration of I_2O_5 which ought to be in equilibrium
= .49 -.58 $\times 10^{-2}$ gm mols per litre
= 1.76 grms per litre.

∴ 57 c.c. of water must be added to 1 gm of iodate to give
a solution of this concentration.

After shaking, analysis gave 1.89 grms I_2O_5 per litre as
the concentration of the solution.

- 1) 0.1268 grms solid required 35.90 c.c. $\text{N}/10$ thio:
∴ % I.O_3 = 89.55
0.0236 grms Ce.O_2 were obtained by ignition of oxalate
∴ % = Ce 18.8
- 2) 0.1022 grms solid required 29.60 c.c. $\text{N}/10$ thio:
∴ % I.O_3 = 81.1
0.0234 grms Ce.O_2 were obtained.
∴ % Ce. = 18.23

Composition calculated from above formula

= 18.33 % Co.

and

80.7 % $1.0g$

The product was a greenish yellow compound looking like pepper and differing decidedly ^{in appearance} from the normal iodate.

(The product was a greenish yellow compound looking like pepper and differing decidedly from the normal iodate.)

analysis of solution gave a concentration of 0.0112 gram I_2 per litre.

GENERAL EXPERIMENT

1) 0.001 gram salt required 10.0 cc. H_2O solution
of 0.1 N I_2
0.0010 gram Co_2O_3 were obtained
at 10.0 cc.

2) 0.002 gram salt required 20.0 cc. H_2O solution
of 0.1 N I_2
0.0020 gram Co_2O_3 were obtained
at 20.0 cc.

composition calculated from the formula $Co_2O_3 \cdot (H_2O)_2$

PREPARATION AND ANALYSIS OF BASIC SALT 2.

The methods of preparation and analysis adopted were the same as those just described.

0.5 gm of normal iodate was shaken with 300 c.c. of water to give a ^{conc.} ~~conc.~~ of I_2O_5 of 0.16×10^{-2} grams (or 0.5242 grms per litre.)

Analysis of solution gave a concentration of 0.4912 grms I_2O_5 per litre.

ANALYSIS OF SOLID.

1) 0.0841 grms salt required 20.20 c.c. $N/10$ thio:

≡ 67.3 % $I.O_3$

0.0274 grms $Ce.O_2$ were obtained

≡ 26.5 % $Ce.$

2) 0.6392 grms salt required 16.3 c.c. $N/10$ thio:

≡ 66.11 % $I.O_3$

0.0175 grms $Ce.O_2$ were obtained

≡ 20.6 % $Ce.$

Composition calculated from the formula $Ce(O.H)_2 (I.O_3)_2$

= 26.72 % Ce.

66.8 % I.O_3

The appearance of this substance was somewhat similar to that of the first salt, but it was decidedly yellower in appearance.

Only small quantities of it could be prepared owing to the large volume of water required in its preparation.

It can be said therefore that the evidence for the existence of at least two basic ceric iodates of the formulae $\text{Ce}(\text{I.O}_3)_3 \text{OH}$, $\text{Ce}(\text{I.O}_3)_4$ and $\text{Ce}(\text{OH})_2 (\text{I.O}_3)_2$, is two fold.

1st. The application of the phase rule to the hydrolysis of the normal salt indicates their existence.

2nd. Preparation of the substances in accordance with data given by the experiments gives products of the expected composition.

Several other points were investigated concerning ceric iodate.

The Action of Heat.

1. The salt was stated by Brinton and James to be converted into Ce.O_2 in ignition, though the residue was always found by them to contain iodide.

Some of the salt was heated in a platinum crucible in an air oven in order to discover if possible whether the decomposition took place in stages.

The salt began to turn violet, indicating evolution of

iodine at 120°C , and at 180°C began to lose weight in a marked manner.

2. Attempt to prepare a double salt with sodium iodate.

Equimolecular quantities of ceric and sodium iodates were warmed in acetone under a reflux condenser for some time. They dissolved, but no double salt appeared to be found on examining the evaporated solution under a microscope.

3. Attempt to prepare a double salt with aniline and pyridine hydrochlorides.

Koppel (Zeitsch. Inorg. Chem. 1898. 18. 305) describes stable compounds of Ce.Cl_4 with pyridine and aniline hydrochlorides though Ce.Cl_4 itself is not stable.

Grant and James (J. Amer. Chem. Soc. 1915. 37. 2652) also describe such salts, but state that their composition varies very much with the amounts of the re-acting salts. An attempt was therefore made to find whether ceric iodate would combine with such bases.

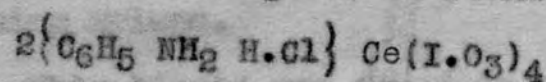
Molecular quantities ($2 \text{C}_6\text{H}_5 \text{NH}_2$ and $1 \text{Ce}(\text{I.O}_3)_4$) were placed in a small flask in which the $\text{Ce}(\text{I.O}_3)_4$ was suspended in methyl alcohol. Dry hydrochloric acid gas was passed in, and the ceric iodate gradually disappeared. The aniline became very dark in colour, indicating oxidation, and a greyish

white crystalline mass was formed.

This substance was certainly not aniline hydrochloride and on ignition gave a small residue of $Ce.O_2$.

The percentage of Cl found = 12.2 %

and



requires 12.7 % Ce. It did not, however, appear to be a ceric derivat^{ive} because of its colour.

Owing to lack of time the matter was not further investigated at the moment.

THE DENSITY OF CERIC IODATE.

This was found by using a specific gravity bottle containing xylene.

This liquid was found to have no action in the salt, and was not volatile.

Results (at 15°).

1. Density of xylene = 0.8539
Wt: iodate = 1.0516 grms
Wt: bottle filled with xylene = 32.7354 grms
Wt: bottle filled with xylene with iodate inside it = 33.8726 grms
• • Wt: xylene displaced by 1.0516 grms iodate = 0.2144 grms.
• • Density of iodate = 4.193.

2. 1.7792 grms iodate displaced 0.3620 grms xylene.
• • Density of iodate = 4.193

The very small weight of xylene displaced made a source of error.

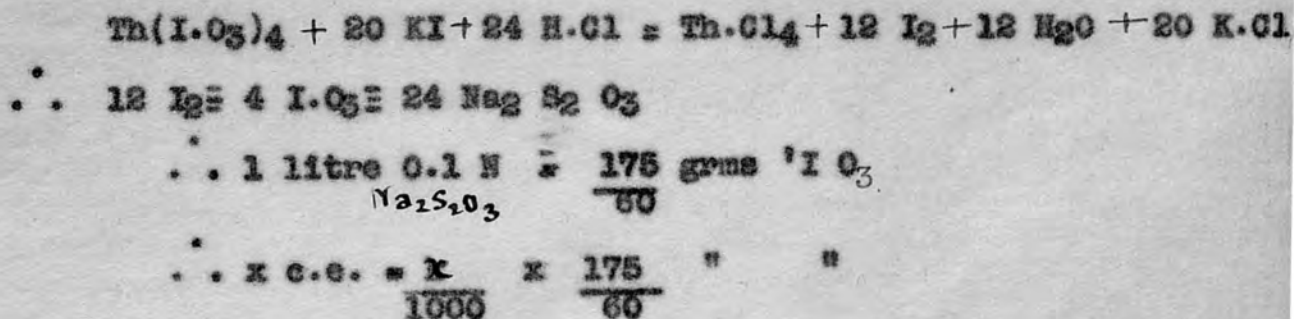
Mean density = 4.193.

PREPARATION OF THORIUM IODATE.

No special difficulty was experienced in obtaining this salt pure by precipitating it from a solution of thorium nitrate by adding a slight excess of a solution of potassium iodate.

It was washed with nitric acid, dried and analysed as described for ceric iodate. It was a white amorphous powder.

In the estimation of 'I.O₃ the following was the equation presumed to represent the reaction, no oxidation taking place as with ceric salts.



and if $\frac{y}{x}$ grms of salt are ^{found} taken = x c.c. thio., the percentage of 'I O₃ = $\frac{7x}{24y}$
or
1 c.c. 0.01 N thio = 0.0002783 grms I₂O₅

The thorium was precipitated as oxalate by adding cold, saturated oxalic acid solution, stirring vigorously and allowing the solution to stand in a warm place for some time. The precipitate was washed with water containing a little H Cl and ignited to ThO₂ and weighed. This method was given by Meyer.

RESULTS OF ANALYSIS.

1. 1.0190 grms salt gave 0.2802 grms Th O₂

Percentage Th = 24.2

0.2780 grms salt = 64.5 c.c. sodium thio sulphate solution

0.111 N.

Percentage I O₃ = 74.9

2. 0.4472 grms salt gave 0.1270 grms Th O₂

Percentage Th = 24.9

and 0.1300 grms salt = 29.6 c.c. sodium thio sulphate solution

0.111 N.

Percentage I O₃ = 75.27

Th(I O₃)₄ requires 24.8 per cent Th

75 " " I O₃

ATTEMPTED HYDROLYSIS OF THORIUM IODATE

This was carried out in exactly the same manner as for ceric iodate and the results were calculated in a similar manner.

It was soon apparent that the hydrolysis was very slight even in the presence of large quantities of water.

The results are appended in Table II and indicate that basic thorium iodates are not formed ^{easily} under these conditions.

Thorium iodate, as might be expected, was a much more stable substance than the corresponding ceric salt.

Though attempts to prepare a double salt with sodium iodate ~~and~~ and aniline hydrochloride were made none of them had any success.

The action of heat on thorium iodate.

This was investigated by heating the salt gradually in a platinum crucible. As with ceric iodate a marked violet colouration appeared at 140° and then rapid decrease in weight occurred till the weight remained constant at 300° C even after prolonged heating.

i 1.4672 grms lost 0.3911 grms or 26.65 per cent.

ii 0.7753 grms lost 0.2330 grms or 30.0 per cent.

It was noted that a salt having the approximate

composition $4 \text{ThO}_2 \cdot 5 \cdot \text{I}_2\text{O}_5$ would occasion a loss of 26.8%

On heating more strongly copious loss of iodine and oxygen occurred and ThO_2 quite free from iodide resulted.

The mean density of thorium iodate was found to 4.308 the method used being the same as for ceric iodate.

As used in the process.

The iodide salt does not dissolve appreciably in nitric acid, or in aqueous solutions, as when the substance is heated it with readily precipitates cerium hydroxide in the presence of these solutions.

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ATTEMPTS TO PREPARE ZIRCONIUM IODATE.

As will be seen from the papers quoted above, normal zirconium iodate has not been prepared.

If such a compound could be made it would be expected to hydrolyse very readily, and water could not therefore be used in the process.

As iodic acid does not dissolve appreciably in nitric acid, or in organic solvents, no action was detected on heating it with freshly precipitated zirconium hydroxide in the presence of these solvents.

Nor did any re-action occur when the two substances were heated together; though the melting point of iodic acid is low.

Decomposition of the iodic acid was all that could be noticed.

To summarise the results of the work just described, it may be said that the properties of the iodates considered are those that would be expected.

The usual increase in basicity of hydroxides with increase of atomic weight is evident.

Zirconium iodate cannot be prepared; ceric iodate hydrolyses with comparative ease, apparently forming two basic iodates, and thorium iodate is a compound stable towards water.

SUMMARY.

1. Ceric iodate has been prepared pure, and the products of its hydrolysis examined. The existence of the compounds $\text{Ce}(\text{I O}_3)_3 \cdot \text{OH}$, $\text{Ce}(\text{I O}_3)_4$ and $\text{Ce}(\text{OH})_2 (\text{I O}_3)_2$ has been established.

Thorium ^{iodate} has been found to hydrolyse with extreme slowness.

2. The density of ceric iodate has been found to be 4.193, and that of thorium iodate to be 4.308.
3. Ceric iodate has been found to react with aniline hydrochloride.
4. Ceric iodate has been found to begin to decompose at 120° and to do so rapidly at 180° ; while thorium iodate begins to decompose at 140° and appears to form the compound $4 \text{ Th O}_2 \cdot 5 \text{ I}_2\text{O}_5$ stable at 300° .

The subject of this work was suggested by Dr. T. F. Spencer to whom I am indebted for assistance & advice.

Bedford College for Women,

University of London,

May, 1923.

T A B L E I. HYDROLYSIS OF CERIC IODATE:

| 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. | 11. | 12. |
|-----|------------|----------------------|------------------------------|------------------|-------------------|---|---|--------------------------------|--|-------------------------------|--|
| No. | Vol. Soln. | Vol. soln. withdrawn | Vol. H ₂ O added. | Vol. thio: used. | Factor of Thio.N. | Grm. ^{MoIe} I ₂ O ₅ in 1 litre soln. x 10 ² . | Wt. I ₂ O ₅ withdrawn | Wt. CeO ₂ withdrawn | Wt. I ₂ O ₅ in solid | Wt. CeO ₂ in solid | Ratio CeO ₂ : I ₂ O ₅ in solid. |
| 1. | 200 | - | - | - | - | - | 0.03807 | 0.0044 | 4.8030 gm. | 1.2370 gm. | 1 : 2 |
| 2. | " | 25 ce | 25 ce | 11.6 | 0.112 H. | 0.456 | 0.0344 | 0.0035 | 4.5784 " | 1.2233 " | 1 : 1.92 |
| 3. | " | " | " | 11.5 | " | 0.412 | 0.0383 | 0.0022 | 4.4996 " | 1.2072 " | 1 : 1.82 |
| 4. | " | " | " | 12.8 | " | 0.498 | 0.0337 | 0.0001 | 4.4340 " | 1.2141 " | 1 : 1.88 |
| 5. | " | " | " | 11.2 | 0.1135 | .404 | 0.0486 | 0.00051 | 4.3224 " | 1.2297 " | 1 : 1.86 |
| 6. | " | " | " | 11.7 | 0.1396 | .582 | 0.0473 | 0.00041 | 4.2794 " | 1.2254 " | 1 : 1.79 |
| 7. | " | " | " | 11.4 | " | .577 | 0.0417 | 0.0004 | 4.2411 " | 1.2265 " | 1 : 1.78 |
| 8. | " | " | " | 10.08 | " | .499 | 0.0417 | 0.0004 | 4.2384 " | 1.2286 " | 1 : 1.77 |
| 9. | " | " | " | 10.05 | " | .499 | 0.0386 | 0.0007 | 4.1987 " | 1.2244 " | 1 : 1.76 |
| 10. | " | " | " | 9.3 | " | .462 | 0.0386 | 0.0007 | 4.1798 " | 1.2216 " | 1 : 1.76 |
| 11. | " | " | " | 9.7 | " | .483 | 0.0440 | 0.0008 | 4.1279 " | 1.2201 " | 1 : 1.74 |
| 12. | " | " | 50 | 10.6 | " | .515 | 0.0440 | 0.00051 | 4.0138 " | 1.2212 " | 1 : 1.69 |
| 13. | 225 | 100 | 100 | 10.4 | " | .1315 | 0.0432 | 0.0003 | 3.9771 " | 1.2235 " | 1 : 1.67 |
| 14. | " | 25 | 25 | 9.0 | 0.1010 | .291 | 0.0243 | 0.0011 | 3.9744 " | 1.2152 " | 1 : 1.68 |
| 15. | " | 150 | 150 | 64.6 | " | .349 | 0.1745 | 0.00231 | 3.9071 " | 1.2205 " | 1 : 1.65 |
| 16. | " | 200 | 225 | 58.2 | 1.03 | .240 | 0.1604 | 0.00211 | 3.8138 " | 1.2191 " | 1 : 1.61 |
| 17. | 250 | 225 | " | 65.5 | " | .2356 | 0.1770 | 0.00221 | 3.6372 " | 1.2171 " | 1 : 1.54 |
| 18. | " | " | " | 62.3 | " | .2235 | 0.1680 | 0.0004 | 3.3701 " | 1.2168 " | 1 : 1.43 |
| 19. | " | 50 | 50 | 15.5 | 0.1010 | .251 | 0.0419 | 0.0001 | 3.1793 " | 1.2164 " | 1 : 1.35 |
| 20. | " | 100 | 100 | 31 | " | .251 | 0.0858 | 0.0011 | 3.1374 " | 1.2150 " | 1 : 1.33 |
| 21. | " | 150 | 150 | 44.3 | " | .301 | 0.1507 | 0.0025 | 3.0120 " | 1.2125 " | 1 : 1.28 |
| 22. | " | 140 | 100 | 39.4 | 0.1104 | .249 | 0.1164 | 0.0053 | 2.9046 " | 1.2046 " | 1 : 1.24 |
| 23. | 210 | 100 | " | 26.8 | " | .232 | 0.0793 | 0.0025 | 2.8295 " | 1.2036 " | 1 : 1.21 |
| 24. | " | 175 | " | 18.4 | " | .274 | 0.0686 | 0.0056 | 2.7243 " | 1.1907 " | 1 : 1.18 |
| 25. | 235 | 125 | 125 | 29.7 | " | .210 | 0.0879 | 0.0195 | 2.6829 " | 1.1641 " | 1 : 1.19 |
| 26. | " | " | " | 27 | 0.1115 | .191 | 0.0795 | 0.0105 | 2.6108 " | 1.1618 " | 1 : 1.16 |
| 27. | " | " | 100 | 28.4 | " | .202 | 0.0841 | 0.0111 | 2.5127 " | 1.1496 " | 1 : 1.13 |
| 28. | 210 | 50 | 40 | 10.8 | " | .194 | 0.0323 | 0.0085 | 2.4509 " | 1.1239 " | 1 : 1.11 |
| 29. | 200 | 50 | 50 | 11.0 | " | .197 | 0.0329 | 0.0039 | 2.4327 " | 1.1255 " | 1 : 1.11 |
| 30. | " | " | 50 | 11.75 | 0.097 | .183 | 0.0305 | 0.0076 | 2.4091 " | 1.1068 " | 1 : 1.12 |
| 31. | " | 100 | 100 | 23.6 | " | .184 | 0.0614 | 0.0222 | 2.3781 " | 1.0870 " | 1 : 1.13 |
| 32. | " | 100 | 100 | 20.6 ce | 0.097 N | .161 | 0.05357 | 0.0126 | 2.3229 " | 1.0831 " | 1 : 1.13 |
| 33. | " | " | " | 20.8 | " | .162 | 0.0541 | 0.0117 | 2.3224 " | 1.0723 " | 1 : 1.08 |
| 34. | " | 25 | 25 | 5.2 | 0.097 | .166 | 0.01384 | 0.0039 | 2.2117 " | 1.0528 " | 1 : 1.08 |
| 35. | " | 75 | 75 | 16.3 | " | .169 | 0.0424 | 0.0107 | 2.2132 " | 1.0561 " | 1 : 1.13 |
| 36. | " | 100 | 100 | 23.0 | " | .179 | 0.0598 | 0.0054 | 2.1466 " | 1.0586 " | 1 : 1.04 |
| 37. | " | " | " | 21.4 | " | .167 | 0.05555 | 0.0132 | 2.0951 " | 1.0575 " | 1 : 1.04 |
| 38. | " | " | " | 19.85 | " | .155 | 0.05163 | 0.0109 | 2.0475 " | 1.0290 " | 1 : 1.025 |
| 39. | " | " | " | 20.00 | " | .156 | 0.0521 | 0.0124 | 1.9949 " | 1.0161 " | 1 : 1.01 |
| 40. | " | " | " | 17.5 | " | .136 | 0.0455 | 0.0196 | 1.9550 " | 0.9883 " | 1 : 1.02 |
| 41. | 200 | " | " | 19.9 | " | .155 | 0.05176 | 0.0130 | 1.8980 " | 0.9779 " | 1 : 1 |
| 42. | " | " | " | 21.4 | 0.10 | .173 | 0.05782 | 0.0160 | 1.8341 " | 0.9608 " | 1 : 0.98 |
| 43. | " | " | " | 27.05 | " | .244 | 0.07475 | 0.02133 | 1.7424 " | 0.9341 " | 1 : 0.96 |
| 44. | 200 | 50 | 50 | 9.7 | " | .157 | 0.02622 | 0.01093 | 1.7123 " | 0.9117 " | 1 : 0.97 |
| 45. | " | 25 | 25 | 5.15 | " | .167 | 0.01392 | 0.00353 | 1.6796 " | 0.9155 " | 1 : 0.94 |
| 46. | " | 50 | 50 | 10.4 | " | .169 | 0.0281 | 0.00593 | 1.66465 " | 0.9172 " | 1 : 0.93 |
| 47. | " | 100 | 100 | 20.85 | " | .169 | 0.05335 | 0.01293 | 1.63625 " | 0.9091 " | 1 : 0.93 |
| 48. | " | " | " | 19.9 | 0.102 | .161 | 0.05377 | 0.01563 | 1.5851 " | 0.8908 " | 1 : 0.92 |
| 49. | " | " | " | 18.0 | " | .147 | 0.04911 | 0.00170 | 1.5405 " | 0.9030 " | 1 : 0.88 |
| 50. | " | 150 | 150 | 28.7 | " | .156 | 0.07830 | 0.01793 | 1.4853 " | 0.8808 " | 1 : 0.87 |
| 51. | " | 50 | 50 | 9.0 | " | .147 | 0.02455 | 0.00673 | 1.4132 " | 0.8599 " | 1 : 0.85 |

TABLE II
HYDROLYSIS OF THORIUM IODATE: 1st. Expt.

| No: | Vol. soln. | Vol. soln. withdrawn | Vol. H ₂ O added | Vol. Thio: used | Factor of Thio: | Wt. I ₂ O ₅ withdrawn | Wt. ThO ₂ withdrawn | Wt. I ₂ O ₅ in solid | Wt. ThO ₂ in solid | Ratio ThO ₂ :I ₂ O ₅ in solid. |
|-----------|------------|----------------------|-----------------------------|-----------------|-----------------|---|--------------------------------|--|-------------------------------|---|
| 1 | 150 cc | - | - | - | - | - | - | 3.8807 grms | 1.8220 grms | 1:2 |
| 2 | 150 cc | 50cc | 50 cc | 27.15 cc | 0.01044 N | 0.01615 | 0.00211 grms | 3.8023 " | 1.8105 " | 1:1.99 |
| 3 | 150 " | 25 " | 25 " | 26.75 " | 0.0096 " | 0.007206 | 0.00131 " | 3.7910 " | 1.8102 " | 1:1.984 |
| 4 | 150 " | 25 " | 25 " | 19.70 " | 0.0095 " | 0.008172 | 0. - | 3.7963 " | 1.8068 " | 1:1.98 |
| 5 | " | " | " | 16.15 " | 0.0093 " | 0.0048 | 0.00151 " | 3.7969 " | 1.8078 " | 1:1.99 |
| 6 | " | " | " | 14.6 " | 0.0091 " | 0.00375 | 0.00171 " | 3.7955 " | 1.8051 " | 1:1.99 |
| 7 | " | " | " | 13.6 " | 0.0091 " | " | 0.00141 " | 3.7917 " | 1.8051 " | 1:1.99 |
| 8 | " | " | " | 11.45 " | 0.0112 " | 0.00377 | 0.00011 " | 3.7807 " | 1.8115 " | 1:1.98 |
| 9 | " | " | " | 11.50 " | 0.0116 " | 0.00309 | 0.00061 " | 3.7846 " | 1.8084 " | 1:1.98 |
| 10 | " | 55 " | 55 " | 27.4 " | 0.0116 " | 0.0087 | 0.000291 " | 3.7291 " | 1.8025 " | 1:1.97 |
| 2nd. Expt | | | | | | | | | | |
| 1 | 150 " | - | - | - | - | - | - | 3.3066 " | 1.3070 " | 1:2 |
| 2 | " | 25 " | 25 " | 23.95 " | " | 0.00942 | 0.00051 " | 3.2493 " | 1.3039 " | 1:1.97 |
| 3 | " | " | " | 24.6 " | 0.0116 N | 0.0077 | 0.00091 " | 3.2497 " | 1.3010 " | 1:1.97 |
| 4 | " | " | " | 18.6 " | 0.0111 " | 0.0051 | 0.00031 " | 3.2446 " | 1.3056 " | 1:1.97 |
| 5 | " | " | " | 17.45 " | " | 0.0056 | " | 3.2310 " | 1.3053 " | 1:1.97 |
| 6 | " | " | " | 17.6 " | " | " | " | " | " | " |

Supplementary Paper,

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Room
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THE DIRECT INTERACTION OF MAGNESIUM AND
ALKYL HALIDES.

BY

JAMES FREDERICK SPENCER

AND

MARY S. CREWDSON.

From the Transactions of the Chemical Society, 1908. Vol 93.

CLXXX.—*The Direct Interaction of Magnesium and Alkyl Halides.*

By JAMES FREDERICK SPENCER and MARY S. CREWDSON.

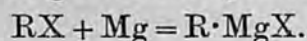
IN a previous paper (Spencer and Stokes, *Trans.*, 1908, **93**, 68), it has been shown that aryl bromides and iodides react directly with magnesium when heated; it had not, however, been observed at the time that aryl chlorides or alkyl halides react with magnesium under the conditions employed in the experiments in question. Löhr

(*Annalen*, 1891, 261, 72) has shown that methyl iodide reacts with magnesium when the two substances are heated together in the presence of a small quantity of ethyl acetate in a sealed tube. Ethyl and propyl iodide also react with magnesium when heated in sealed tubes, giving mixtures of saturated and unsaturated hydrocarbons, together with small quantities of organo-magnesium compounds. The present communication shows that both aryl chlorides and alkyl halides will react directly with magnesium when they are heated together under suitable conditions.

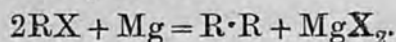
Aryl chlorides, and all the lower alkyl halides up to the butyl derivatives, only react with magnesium when heated to about 270° in a sealed tube for several hours.

Alkyl halides higher in the series than the butyl derivatives react with magnesium when they are heated with it at their boiling point for a few minutes. The reaction is regarded by the authors as taking place along the two lines indicated.

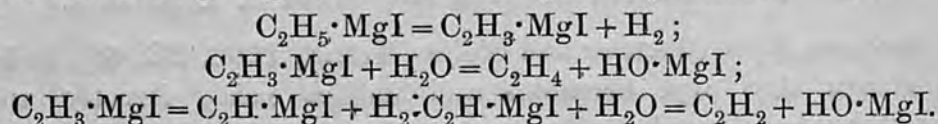
1. The formation of a magnesium alkyl halide, thus :



2. The formation of a hydrocarbon containing twice as many carbon atoms as the original halide, thus :



In addition to these compounds, however, unsaturated hydrocarbons are also found in the gaseous portion of the reaction products obtained from all interactions effected in sealed tubes. These unsaturated hydrocarbons, consisting as they do of both acetylenes and olefines, are due in all probability to the action of heat on the original halide, or on the initial products of the reaction, for Miss Kahan (*Trans.*, 1908, 93, 133) has shown that methyl and ethyl iodides are decomposed by heat with the formation of unsaturated hydrocarbons. Saturated hydrocarbons are not the only products when water is added to the solid product obtained by the action of an alkyl halide on magnesium in a sealed tube. In addition to the saturated hydrocarbon expected, unsaturated hydrocarbons, consisting of both acetylenes and olefines, are also formed. The presence of these compounds in the product can be explained if we assume that the magnesium alkyl halide first formed has been decomposed by the action of heat with the formation of an unsaturated organo-magnesium halide and free hydrogen, as indicated by the equations :



The invariable occurrence of large quantities of hydrogen in the gaseous products can be regarded as confirmation of this assumption.

In all reactions where it was unnecessary to use a sealed tube, unsaturated hydrocarbons were not found among the products.

The magnesium alkyl halides are all white, crystalline compounds, and are produced in larger quantities the higher in the series the corresponding hydrocarbon stands; thus *sec.*-octyl iodide furnishes a magnesium compound, which, on treatment with water, gives 85 per cent. of the theoretical yield of octane, whilst *isoamyl* iodide gives 60 per cent. of the theoretical quantity of pentane. Halogen substituted compounds, other than the hydrocarbon derivative, also react directly with magnesium; for example, methyl bromoacetate reacts very readily with magnesium on heating to its boiling point. We should like to point out here that, while this work was proceeding, and after the reaction with methyl bromoacetate had been completed, we received a copy of a paper from J. B. Tingle and E. E. Gorsline (*J. Amer. Chem. Soc.*, 1907, 37, 483), acquainting us with their work on the Grignard reaction; this paper contained an account of the influence of solvents on the ease with which the reactions take place. These investigators draw our attention especially to a reaction between magnesium and ethyl chloroacetate in ether and other solvents, and mention in their letter that they have also induced this reaction to take place without solvents, presumably, since it is stated neither in their letter nor the paper cited, with the formation of ethyl acetate. In our experiments, methyl acetate was one of the products, but dimethyl succinate was also formed, and to a much larger extent.

EXPERIMENTAL.

In all experiments where sealed tubes were not used, the method of carrying out the reaction was exactly the same as that adopted in the paper already quoted.

In those reactions which only proceeded in sealed tubes, the theoretically proportionate quantities of the halide and magnesium were sealed up, and heated at about 250° for from five to eight hours. When the tubes were cold, they were immersed in liquid air and opened; generally there was no pressure on opening when the tubes were treated in this manner, a fact which would indicate the absence of any large quantity of hydrogen. The tube was then removed from the liquid air, and connected with a gas holder, in which the evolved gas collected as the tube became warmer. This gas invariably contained large quantities of hydrogen, a fact which suggests that magnesium possesses the property of absorbing hydrogen at low temperatures. We are at present investigating this point. The gas was analysed in the usual way. After the tube had attained the atmospheric tempera-

ture, and no more gas was evolved, the solid residue was treated with water, and the gas or liquid evolved was collected and analysed.

Interaction of Magnesium and Methyl Iodide.

Ten grams of methyl iodide and 1.75 grams of dry powdered magnesium were heated in a sealed tube for seven hours at 280°. An inflammable gas was obtained, which consisted of 56 per cent. of hydrogen, 42 per cent. of ethane, 1 per cent. of acetylene, and 0.5 per cent. of ethylene. On treating the solid in the tube with water, a gas was obtained which was inflammable, burning with a smoky flame, and consisting of 72.6 per cent. of hydrogen, 9.2 per cent. of methane, 13.6 per cent. of acetylenes, and 3.3 per cent. of olefines.

Interaction of Magnesium and isoAmyl Iodide.

Ten grams of isoamyl iodide were heated in a hard glass flask with 1.5 grams of magnesium for about half a minute, when a violent reaction set in; this completed itself without further heating, and a white, microcrystalline substance was formed, which, on the addition of water, yielded 62 per cent. of the theoretical quantity of isopentane.

Interaction of Magnesium and sec.-Octyl Iodide.

Ten grams of sec.-octyl iodide were heated in a hard glass flask with one gram of magnesium for a few seconds, when a violent reaction commenced and proceeded to completion without further heating. The product of this interaction was a white, crystalline compound, which reacted violently with water, producing an oil. The oil was separated and fractionated, and constituted a yield of 84 per cent. of octane. The intermediate compound obtained in this experiment was purified and analysed in the following manner: it was washed twice with cold ether to remove any unchanged octyl iodide, then with warm ether to separate the compound from unchanged magnesium, the ethereal solution evaporated to dryness, and the product heated to 100° to decompose any double compound with ether. In this way, a white, crystalline substance was obtained in long, rhombic needles, which were quickly weighed, treated with water and dilute nitric acid, and evaporated to dryness; the magnesium was estimated as pyrophosphate:

0.1037 gave 0.0420 $\text{Mg}_2\text{P}_2\text{O}_7$. Mg = 8.78.

$\text{C}_8\text{H}_{17}\text{IMg}$ requires Mg = 9.08 per cent.

This compound dissolves in ether with extreme readiness.

Interaction of Magnesium and Ethyl Chloride.

Ten grams of ethyl chloride and 4 grams of magnesium were heated together for six hours in a sealed tube at 260°. The gaseous products were found to consist of 45 per cent. of butane, 20 per cent. of olefines, and 22 per cent. of hydrogen. The yield of these gases was large, about 350 c.c. of the mixture being collected. On adding water to the white solid remaining in the tube, an inflammable gas was evolved, which consisted of 86 per cent. of hydrogen and 13 per cent. of ethane; there were no unsaturated hydrocarbons formed in this experiment.

Interaction of Magnesium and isoButyl Chloride.

Ten grams of *isobutyl* chloride were heated with 2.4 grams of magnesium in a sealed tube at 260° for seven hours. On opening the tube, only a small quantity of gas was evolved, and this, on analysis, proved to be practically all hydrogen; there was, however, in the tube a considerable quantity of a liquid; this was removed from the solid product by draining, and was found to consist of unchanged *isobutyl* chloride and *diisobutyl*, boiling at 108°; 2.5 grams of the latter were obtained, which constituted a yield of 40 per cent. The solid residue in the tube was then treated with water, and the gas evolved, collected, and analysed; it consisted of 58 per cent. of hydrogen, 18 per cent. of butane, 11.3 per cent. of acetylenes, and 11.6 per cent. of olefines.

Interaction of Magnesium and Ethyl Bromide.

Twelve grams of ethyl bromide were heated together with 2 grams of magnesium in a sealed tube for eight hours at 260°. The gaseous products consisted of 56 per cent. of hydrogen, 12 per cent. of olefines, 7 per cent. of acetylenes, and 24 per cent. of butane. The white compound left in the tube, on treatment with water, gave an inflammable gas, consisting of 90 per cent. of hydrogen, 6 per cent. of ethane, 2.5 per cent. of acetylenes, and 1 per cent. of olefines.

Interaction of Magnesium and isoAmyl Bromide.

Ten grams of *isoamyl* bromide and 1.6 grams of magnesium were heated together in a small, hard glass flask until the reaction commenced, that is, for about three minutes. The reaction was not very violent, but nevertheless it completed itself without further heating. The product was a light, bulky, white powder, together with an oil; the whole was treated with water, when the usual violent reaction

set in. The mixture was distilled in a current of steam, and the oil dried and fractionated. It was found to consist of a small quantity of *isopentane*, and a 67 per cent. yield of *diisoamyl*, boiling at 150°.

Interaction of Magnesium and Methyl Bromoacetate.

Twenty-one grams of methyl bromoacetate were heated with 3 grams of magnesium in a hard glass flask for about a minute, when an extremely violent reaction took place. After the products had cooled, water was added, and, again, a violent reaction took place. The whole was now distilled in a current of steam, and the distillate was separated, dried, and fractionated. Forty-one per cent. of the bromoacetate was regained unchanged, and two other fractions were also obtained. The first, boiling at 57—63°, was methyl acetate, and constituted a 34 per cent. yield on the bromoacetate which had reacted, and the second, boiling at 190—200°, was dimethyl succinate, the yield being 48 per cent. This compound, which on redistillation boiled at 197°, was hydrolysed by boiling with potassium hydroxide, and the potassium salt was converted into the barium salt by treatment with barium hydroxide solution. The barium salt was analysed by converting it into barium sulphate :

0.2084 gave 0.1943 BaSO₄. Ba = 54.86.

C₄H₄O₄Ba requires Ba = 54.2 per cent.

Interaction of Magnesium and Chlorobenzene.

Ten grams of chlorobenzene were heated in a sealed tube with 2.5 grams of magnesium for six hours at 270°. On opening the tube, there was no evolution of gas, but, mixed with a somewhat charred mass having a strong odour of benzene, were white crystals. The whole, on treatment with water, became very hot, and benzene was liberated in fairly large quantities, the average yield being 60 per cent. We are proposing to pursue this reaction further.

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