

JOURNAL

OF

THE CHEMICAL SOCIETY.

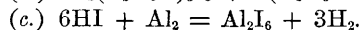
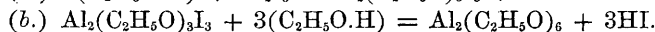
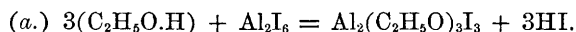
PAPERS READ BEFORE THE CHEMICAL SOCIETY.

I.—*Aluminium Alcohols. Part I. Their Preparation by Means of the Aluminium-Iodine Reaction.*

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IN a communication made to this Society in 1876, **29**, p. 158 of this Journal, we stated that aluminium or aluminium iodide singly is without action on absolute alcohol, but that together they decompose the liquid with facility. The resulting bodies are hydrogen and two new organic aluminic compounds, aluminic iodo-ethylate, $(C_2H_5O)_3I_3Al_2$, and aluminic ethylate, $Al_2(C_2H_5O)_6$. We showed too that the metallic iodide and the metal need not exist together in equivalent proportions, in order either to initiate or to continue this decomposition, and in fact that one molecule of the iodide suffices to bring about the combination of very many atoms of aluminium with the oxy-radical of the alcohol.* We also showed that the amount of hydrogen set free is equivalent to that of the metal which disappears, and is quite independent of the quantity of iodide present.

With regard to the part which this salt plays, two views were enunciated. The one for which we expressed a preference supposed that the reaction takes place through the intervention of intermediate bodies, thus :—



* We have since obtained the combination of as much as 54 atoms of aluminium by means of one molecule of the iodide.

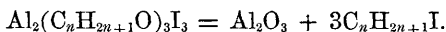
It will be understood that the complete conversion of the aluminic iodide into the iodo-ethylate, and this again into the ethylate, as by equations *a* and *b*, occurs only when the freed hydriodic acid is destroyed, as by equation *c*.

Whether, however, this be the true view, was not decided by our experiments. And it appears from both the suppositions referred to, that a relatively small quantity of the iodide should bring about the decomposition of an unlimited quantity of alcohol in presence of the metal. Such, it is evident, would be the case were it not for the mechanical interference of the solid products of the reaction.

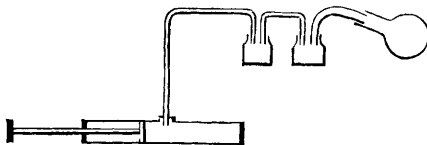
In the present communication, we establish more completely our knowledge of the composition and properties of the ethylate, and describe the results obtained on applying the *aluminium-iodine reaction* (*Proc. Roy. Soc.*, 1880, 546) to the preparation of analogous aluminium derivatives of other alcohols.

General Instructions.

Into a flask, fitted with an inverted condenser, place the alcohol, aluminium, and iodine in the proportions of 20* c.c. of the liquid, 2 grams of the metal, and 1 gram of iodine, and heat the substances by immersing the bulb of the vessel in boiling water. The elements quickly combine and produce the necessary aluminic iodide, and the decomposition of the alcohol begins before the whole of the free iodine passes into combination; and proceeds moderately rapidly until the metal disappears and the evolution of hydrogen stops. The contents of the flask are now heated to about 300° in an oil-bath, and continued at this temperature until distillation practically ends. The distillate consists of the excess of alcohol used, mixed generally with some of its iodide, which latter compound results from the decomposition in presence of alcohol of the intermediate iodo-body, very probably in accordance with the equation:



The flask is next attached to a receiver by means of a piece of short wide tubing, this receiver to another, and the second to a pump. The general arrangement is shown in the figure.



* With alcohols of high molecular weight, it is necessary to increase this volume to 30 or 40 c.c., and to heat to a higher temperature than 100° C.

The apparatus is now exhausted of air, the product in the flask melted and then heated till distillation is over, the pump being kept at work during the operation. Some of the distillate usually passes into the second receiver, but the greater part always collects in the first. Even when the vacuum is kept as perfect as possible some decomposition always occurs, the amount of which varies for the different compounds, as will be shown hereafter. Of the alcohols already isolated in this way, the ethylate distils with the greatest, and the amylate with the least facility.

The aluminium used was in the form of foil, cut into small pieces, and of such a thickness that 1 gram measured 110 square centimetres.

Aluminic Methylate.

We have stated in the paper to which reference has already been made, that methyl alcohol is not affected when boiled with aluminium and aluminium iodide. We find, however, that this liquid suffers some amount of decomposition when the iodide is formed in the boiling alcohol, but only while iodine remains in a free condition; further, that when the metal is conjoined with platinum deposited from the chloride, the decomposition of the alcohol continues long after the whole of the iodine has passed into combination.

In an experiment employing 2 grams of aluminium coated with platinum, 2 grams of iodine, and 20 c.c. of methyl alcohol, 800 c.c. of hydrogen were set free in three hours, on heating to the boiling point of the liquid. The atomic ratio of aluminium to iodine found in the residue was 1 to 0.62; and after 18 hours' heating, when the action was proceeding extremely slowly, 1 : 0.4. These numbers, and the knowledge of what takes place under practically analogous circumstances with other alcohols of the same series, enable the composition to be assigned to the solid product of this reaction with a considerable degree of probability. Calculating the iodine as iodo-compound, and the aluminium as methylate, and subtracting from this latter the methylate corresponding to the iodo-compound, 100 parts of the solid products when the experiment was stopped, would appear to consist of 55.6 parts of aluminic methylate, and 44.4 parts of aluminic iodo-methylate. Attempts made to separate these compounds were not successful, owing probably to the unstable character of the methylate.

Aluminic Ethylate.

We supplement the directions which have already been published for the preparation of this compound, by giving the details of an experiment, following the plan described under the heading "general instructions."

2 grams of iodine, 4 grams of aluminium, and 40 c.c. of alcohol were heated as directed. The first litre of hydrogen collected in 5 minutes, the second in 4, the third in 10, the fourth in 16 minutes. Evolution of gas continued for 10 more minutes. The total hydrogen collected measured 4,345 c.c. (corrected). The product in the flask was solid, and on heating at 300° , and then *in vacuo*, gave 12.5 grams of distillate quite free from iodide.

Several quantities of the substance collected as described were found on analysis to contain from 1—2 per cent. of aluminium in excess of that which ethylate would require. This discrepancy we thought might very probably arise from decomposition of the distillate while in the receivers. The first estimation of aluminium was made in a part of the last portion of distillate collected in the upper part of the tubule of an ordinary condenser, the analytical details of which we now subjoin, and also the results of the analysis of two other specimens, which were collected in small quantities in cooled receivers, the object of this being to induce rapid solidification, and to minimise the influence of the diminished pressure.

- I. 1.062 gram dissolved in dilute nitric acid, and aluminium precipitated by ammonia and ignited, gave 0.330 gram Al_2O_3 .
- II. 0.4465 gram of a different preparation, treated with water to decompose it, dried at 100° and ignited, gave 0.146 Al_2O_3 .
- III. 0.272 gram burnt with oxygen and oxide of copper gave 0.4395 gram CO_2 and 0.2385 gram H_2O .

			Found.		
		Calculated.	I.	II.	III.
Al_2	55	16.92	16.58	17.46	—
C_{12}	144	44.30	—	—	44.06
H_{30}	30	9.23	—	—	9.74
O_6	96	29.55	—	—	—
$\text{Al}_2(\text{C}_2\text{H}_5\text{O})_6$..	325	100.00			

Considering the difficulties attending the purification, these analytical numbers accord sufficiently well with those calculable on the supposition that the body examined has an atomic composition agreeing with the formula $\text{Al}(\text{C}_2\text{H}_5\text{O})_3$, and from analogy the molecular formula $\text{Al}_2(\text{C}_2\text{H}_5\text{O})_6$. Such a compound receives the name of aluminic ethylate, it being evidently an analogue of Williamson's potassium and sodium ethylates.

Aluminic Propylate.

Normal propyl alcohol boils, according to Chancel, at 96 — 97° ; to Rossi, at 96° ; and to Pierre and Puchot, at 98.5° . The alcohol used for the experiments about to be described boiled at 96° .

2 grams of aluminium, 1 gram of iodine, and 20 c.c. of the alcohol were heated to 100° . The first litre of gas collected in 18 minutes, and the second litre in 33 minutes. The action slowly continued for 15 more minutes. The total hydrogen evolved measured 2,145 c.c. (corr.). On heating the residue to 300° , considerable frothing was noticed, and a non-fusible substance was left in the flask. This was found to be free from iodine, and gave on treatment with water and ignition 61 per cent. of alumina. From this it would appear to consist in 100 parts, of 52.1 parts of aluminic propylate and 47.9 of alumina, showing that some 78 per cent. of the organic aluminium compound had suffered decomposition. In another experiment a similar residue was gradually heated to 145° , when the frothing became decided, and it was then analysed. 0.423 gram gave on solution in nitric acid and addition of silver nitrate 0.006 gram of silver iodide; and 0.576 gram gave on treatment with water and ignition 0.156 gram of alumina. These data, and considerations previously referred to, lead us to assign to the residue at this stage the percentage composition of—

1.23 aluminic iodo-propylate,
96.08 aluminic propylate,
2.69 alumina.

It was now heated *in vacuo*. A quantity of alcohol passed over, followed by 1.8 gram of a dense liquid, which solidified on cooling.

This small yield of what presumably was aluminic propylate led us to think that the large amount of decomposition which must have taken place was occasioned by the alcohol containing water. A portion of it was therefore digested with anhydrous potassic carbonate, then with caustic baryta, which treatment increased the boiling point about a degree. An experiment made with it similar to the last gave, however, but a slight increase in the quantity of the aluminium distillate, viz., 2 grams. But in another trial, where the whole distillation was done *in vacuo*, 4.6 grams of the aluminium compound passed into the first receiver, which shows that the decomposition is mainly due to temperature.

Aluminium was estimated in each of the distillates, with the following results, stated in 100 parts:—

I.	II.	III.	$\text{Al}_2(\text{C}_3\text{H}_7\text{O})_6$.
12.73	14.25	13.0	13.44

which numbers agree as well as could be expected, considering the nature and mode of preparation of the substance analysed, with those calculable on the supposition that the compound obtained as described is the third member of the series of aluminic alcohols, viz., aluminic propylate, $\text{Al}_2(\text{C}_3\text{H}_7\text{O})_6$.

Isopropyl Alcohol.

In our paper on the action of the couple upon the two propyl iodides (*Chem. Soc. J.*, 1873, **26**, 961), it was pointed out that the iso-iodide was the more readily decomposed; and, further, that zinc iso-propide, which we obtained in small quantity, splits up at a temperature of 132° into zinc and hydrocarbon gases, whilst the normal zinc compound distils without material change at 146° . We have just shown that the normal alcohol decomposes readily in presence of aluminium and its iodide, and the fact of the greater instability of the two derivatives of the iso-alcohol led us to expect that it would undergo decomposition still more rapidly in presence of aluminium and aluminic iodide. On heating the reagent, however, with a specimen of the alcohol that distilled between 82° and 85° , not a trace of decomposition was observable, which unexpected result induced doubts as to whether the substance employed was really isopropyl alcohol. To place this matter beyond dispute, a portion of the specimen was boiled with strong aqueous hydriodic acid, when an oily compound was produced, having the boiling point and specific gravity of isopropyl iodide. This iodide, when heated to 50° with the copper-zinc couple, underwent decomposition in a manner which left no doubt regarding its being the iodide of isopropyl alcohol.

Aluminic Isobutylate.

Isobutyl alcohol boils, according to Linnemann, at 108.4° , and according to Chapman and Smith at 109° . The alcohol we have employed boiled at $108-109^{\circ}$. In an experiment where 4 grams of aluminium, 2 grams of iodine, and 40 c.c. of the alcohol were heated to 100° , the first litre of hydrogen was evolved in 7 minutes, the second litre in 4 minutes, the third in $3\frac{1}{2}$, and the fourth in $7\frac{1}{2}$ minutes. The action slowly continued for 15 minutes longer. The total gas collected measured 4.044 c.c. (corr.). The residue, after heating to 300° , was distilled *in vacuo*, when 16 grams of an aluminium compound free from iodide passed into the receivers. Portions of different specimens of this substance were analysed.

- I. 0.478 gram dissolved in dilute nitric acid and aluminium precipitated by ammonia, gave 0.0982 Al_2O_3 .
- II. 0.689 gram, treated with water, dried at 100° , and ignited, gave 0.1473 Al_2O_3 .
- III. 0.2005 gram, treated as in II, gave 0.0425 Al_2O_3 .
- IV. 0.2457 gram, burnt with oxygen and oxide of copper, gave 0.5255 CO_2 and 0.226 H_2O .

These results, when set out as under—

			Found.			
		Calculated.	I.	II.	III.	IV.
Al ₂	55	11.15	10.97	11.41	11.31	—
C ₂₄	288	58.43	—	—	—	58.32
H ₅₄	54	10.95	—	—	—	10.22
O ₆	96	19.47	—	—	—	—
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Al ₂ (C ₄ H ₉ O) ₆ ..	493	100.00				

show that the body examined agrees in composition with the formula Al₂(C₄H₉O)₆, and, therefore, it being a derivative of the iso-alcohol, receives the name of aluminic isobutylate.

Aluminic Amylate.

The amylic alcohol of fermentation boils, according to various authorities, from 128—132°. That which we have employed boiled at 129—131°.

In illustration of the behaviour of aluminium and aluminic iodide with this alcohol, we subjoin the details of an experiment. 4 grams of the metal, 2 grams of iodine, and 40 c.c. of the alcohol were heated at 100°. The first litre of gas collected in four minutes, the second in two minutes, the third in two minutes, and the fourth in five minutes, showing that the action is decidedly more rapid with this than with the other alcohols. The total hydrogen obtained measured 3,985 c.c. (corr.). The residue heated to 300°, and *in vacuo*, gave 14 grams of an aluminium distillate, which, as well as another specimen prepared in like manner, were analysed.

I. 1.79 gram, dissolved, &c., gave 0.3056 Al₂O₃.

II. 0.6235 gram, treated with water, &c., gave 0.112 Al₂O₃.

III. 0.2815 gram, burnt with oxygen and copper oxide, gave 0.6455 CO₂ and 0.293 H₂O.

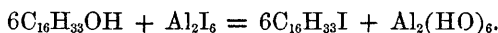
			Found.	
		Calculated.	I.	II.
Al ₂	55	9.53	9.12	9.59
C ₃₀	360	62.39	—	62.53
H ₆₆	66	11.44	—	11.56
O ₆	96	16.64	—	—
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Al ₂ (C ₅ H ₁₁ O) ₆ ..	577	100.00		

The analytical numbers, as shown by the above statement of results, agree with the formula Al₂(C₅H₁₁O)₆, which is that of the fifth member of the series of aluminic alcohols, viz., aluminic amylate.

Cetyl Alcohol.

Methyl alcohol, as has been shown, does not undergo decomposition when boiled with aluminic iodide and aluminium, but this may arise from the low boiling point of the liquid. The difference in the rate at which the other alcohols part with hydrogen under analogous conditions is not well marked. The study of the action of the reagent upon a much higher member of the series it was thought would show definitely whether the stability of these compounds, which may be presumed to be of the same constitution, increases or not with their molecular weight, and also whether the replacement of hydrogen might be expected to take place in the intermediate members not examined.

Cetyl alcohol, $C_{16}H_{33}OH$, being the first solid member of the series, and sufficiently removed from amylic, was selected. This compound, gradually heated with Al_2I_6 , underwent no visible change until between 200° and 250° , when action was indicated by the solidification of the melted contents of the flask. On treating this solid product with alcohol, aluminic hydrate was found in the residue, and cetyl alcohol and a solid organic iodide—presumably cetyl iodide—in solution. The action, therefore, appears to be one of double decomposition, and to accord with the equation—



The alcohol gradually heated with Al_2I_6 and aluminium gave a little hydrogen; but at about 200° the gas evolution ceased, 100 c.c. having been collected. The contents of the flask were solid, and resembled the product of the action of heat on the alcohol and Al_2I_6 alone. On heating with free iodine and aluminium, about 150 c.c. of hydrogen were evolved as the temperature rose to 150° , when the evolution of gas quickly ceased as before, the contents of the flask having solidified.

In each of the experiments, 18.5 grams of the alcohol (about 10 c.c. when melted) were employed. In the first also 2 grams of Al_2I_6 ; in the second, 2 grams of Al_2I_6 and 0.5 gram of aluminium; and in the third, 2 grams of iodine and 0.5 gram of aluminium.

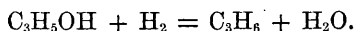
We conclude that cetyl alcohol is much more stable in presence of Al_2I_6 and aluminium than amylic alcohol, or the other members of the series which have yielded to these reagents, and that under their influence hydrogen is evolved and aluminic cetylate accordingly formed, but that the temperature at which this action takes place, being so close to that at which the double decomposition occurs previously referred to, prevents any quantity of this compound being produced.

Monohydric Alcohols of other Series.

Allyl alcohol.—After a preliminary trial or two, which showed that aluminic iodide could be boiled with this compound without either substance undergoing change, 2·2 grams of the iodide were dissolved in 20 c.c. of the alcohol, and heated with 1 gram of aluminium in the usual manner. Gas was slowly evolved for about an hour, when it almost ceased, 550 c.c. having been collected. The gas burned with a luminous smoky flame, and contained 37 per cent. by volume of an olefine, the remainder being hydrogen.

Another experiment was made by heating 20 c.c. of alcohol with 2 grams of iodine and 1 gram of aluminium. In 15 minutes 700 c.c. of gas were evolved, and in 10 more minutes action ceased. The whole of the aluminium was used up, and the gas collected measured 870 c.c., of which 270 c.c. were absorbed by bromine, the remainder being hydrogen. The compound produced by the union of a part of the gas with bromine, possessed the properties of propylene dibromide, showing that the hydrocarbon gas was propylene.

The explanation of these results is probably as follows:—The initial action is doubtless identical in character with that which takes place with the alcohols of the methyl series. In place, however, of the whole of the freed hydrogen escaping, as in the action with these compounds, about 30 per cent. of the gas, after decomposing the alcohol, enters into combination with both its negative and positive radicals, forming propylene and water, thus:—



Aluminic allylate, some of which must have been formed, could not be isolated by the distillation *in vacuo* of the non-gaseous products of this reaction. Little, however, of this compound may have existed at any moment, for as soon as any appreciable quantity of water had been formed by the hydrogenisation of the hydroxyl group of the alcohol, the reagents may have acted upon the water then present in preference to the alcohol.

Phenyl, Cresyl, and Thymol Alcohols.—Aluminium in presence of aluminium iodide, very rapidly decomposes these compounds at 100°, hydrogen being evolved equivalent to the metal employed, and aluminic phenylate, cresylate, or thymolate formed. The aluminium compounds cannot be obtained in a pure state by distillation *in vacuo*, but on heating the respective alcohols to about 200°, with the theoretical amount of aluminium, and enough iodine to start the action, and pouring off the semi-fluid product, they were obtained approximately pure. Thus a specimen of the phenylate prepared as described gave on analysis 9·49 per cent. of aluminium, the calculated being 8·97; a

specimen of cresylate 7.57, the calculated being 7.89; and a specimen of thymolate 5.96, the calculated being 5.79.

The phenylate hardens as it cools, whilst the cresylate and thymolate remain plastic for some considerable time.

Aluminium itself when boiled with phenyl and cresyl alcohols, very slowly decomposes them, phenyl alcohol being the more readily acted upon. Thymol does not appear to act at all on the metal, when boiled with it.

Benzyl Alcohol.—The hydrogen in this alcohol is also replaced by aluminium in presence of aluminium iodide. The action is very violent, the greater part of it being over in a few seconds. The aluminium compound undergoes complete decomposition on heating *in vacuo*.

Aluminium alone has no action on this compound, but aluminic iodide readily decomposes it on gently heating, an organic iodide having a violent action on the eyes and skin—probably benzylic iodide—being produced.

Naphthol.—At a temperature between its melting and boiling points, this alcohol is acted on by aluminium alone, hydrogen being evolved equivalent to the metal. The aluminic naphtholate, as in the case of the phenol compounds, does not distil *in vacuo*. The naphthol used was the β -naphthol, melting at 121–122° C.

Alcohols of other Atomicities.

Ethylene Alcohol.—When a solution of aluminic iodide in this alcohol was heated to a little above 100°, the mixture turned brown, and at about 160° a few bubbles of gas were produced containing an olefine. When heated to a higher temperature, a liquid having a lower boiling point than the alcohol was formed, which, from its action upon potassium and anhydrous copper sulphate, was concluded to be water. When heated with Al_2I_6 and aluminium or aluminium and free iodine, little or no difference was noticed in the action until the liquid referred to, collecting in the tubule of the condenser, fell into the flask, when after each drop a few bubbles of gas escaped, probably hydrogen, from its decomposition. We conclude, therefore, that the basic hydrogen of this alcohol is not replaced by the reagents employed.

Propenyl Alcohol (Glycerol).—Aluminic iodide dissolves somewhat slowly in this compound, but when the mixture is heated to about 140°, both substances undergo decomposition, aluminic hydrate, free iodine, and an oily body having the properties of allyl iodide being produced. The reaction doubtless accords with the equation:—



from which it would follow that were the substances heated in presence of metallic aluminium, the sole products of the chemical change would be aluminic hydrate and allyl iodide. The experiment, details of which follow, show that this is the case:—

4 grams of aluminium iodide, and 2 grams of aluminium foil were heated with 30 c.c. of dry glycerine* until the reaction was completed.

Hydrogen was not evolved nor any other gas. On further heating the product, 1.2 c.c. of the organic iodide distilled. The residue, being now almost solid, 30 c.c. of glycerol were added to it, and again heated, when 1.5 c.c. more of the iodide passed over, which together with the first portion, approximates very closely to the calculated amount.

Dr. Hodgkinson, working on the lines of our paper already referred to, has also obtained allyl iodide, and almost in amount corresponding to the iodide employed, by heating glycerol with aluminium and free iodine (*Chem. News*, 1877, p. 237).

General Properties.

The aluminic alcohols are non-crystalline, and solid at the ordinary temperature, and those obtained pure are yellowish-white in colour. They are all more or less decomposed on heating at the ordinary atmospheric pressure, but those of the methyl series distil at reduced pressures, affording the first examples of organic compounds containing both oxygen and a metal capable of distillation.† The solubility in alcohol, ether, and benzol, of those which have been obtained pure, are roughly indicated in the annexed table:—

Aluminic compound.	In alcohol.	In ether.	In benzol.
Ethylate.	Nearly insoluble.	Slightly.	Moderately.
Propylate.	Very slightly.	Slightly.	Moderately.
Butylate.	Moderately.	Very.	Very.
Amylete.	Moderately.	Moderately.	Very.

The aluminium-compounds of the methyl series possess in a marked degree the property of remaining fluid below their fusing points. Thus specimens of ethylate and butylate, which melted at 130° and 140° respectively, remained fluid at 70° for at least an hour; and a

* Obtained by bubbling hydrogen through the liquid heated to 160° for three days.

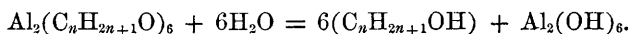
† In 1877 Conrad showed that another aluminic compound, $C_{18}H_{27}O_3Al$, and an analogous copper salt, are capable of distillation (*Liebig's Ann.*, 188, 272).

specimen of amylate which melted at 70° remained fluid for days at the ordinary temperature. The propylate decomposes somewhere near its melting point, which was found to be about 60° . Another peculiarity of these bodies is that they solidify first into a transparent, or semi-transparent mass, but after the lapse of some days, they become opaque. The numbers given as the melting points we regard only as approximations, for different specimens of some of these compounds, especially the amylate, have been found to differ in this respect.

The specific gravities of the compounds at 4°C. , were found to be, for the—

Ethylate,	1.147
Propylate,	1.026
Butylate,	0.9825
Amylate,	0.9804.

The action of water upon the ethylate was found to give aluminic hydrate and alcohol:—



The ease with which the positive radical of the water, in this latter (probably typical) action, combines with the negative radical of the aluminic alcohols, points to a great number of probable syntheses; and from the atomicity and other chemical qualities of aluminium, it is very probable that compounds of very considerable interest will result therefrom.

Theoretical Note.

We have offered two possible explanations of the part which the relatively small quantity of aluminic iodide plays in these aluminium substitutions. The one for which we expressed a preference, as already mentioned, was the one requiring the formation of hydriodic acid in the first step of the reaction. No direct evidence, however, of the production of this substance was found until our experiments with the phenyl group of alcohols, when, on gently warming each of these compounds with aluminic iodide, an appreciable quantity of hydriodic acid was evolved. This matter is more fully discussed in our paper on the aluminium-iodine reaction in the *Proceedings of the Royal Society*.