XV.—*The Simultaneous Action of Iodine and Aluminium upon Ether and Compound Ethers.*

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IT is well known that aluminium has no action upon either water or alcohol; but in previous communications to this Society we have shown that in presence of aluminic bromide or iodide, an action immediately takes place, with production of alumina and hydrogen in the case of water, and of aluminic ethylate and hydrogen in the case of alcohol. This led us to expect that if ether were exposed to the action of the same agents, it might give us either ethyl and aluminic

* Quoted in Watts's "*Dictionary of Chemistry*," vol. i, p. 715.

oxide, or ethyl and aluminic ethylate; and perhaps throw some light on the nature of the chemical change.

Upon trying the experiment, we found that ether remained unaffected, even when boiled with aluminium and aluminic iodide, but that an oily body formed when it was exposed to the simultaneous action of iodine and aluminium.

This reaction was investigated, and the following experiment illustrates the general course pursued and the results obtained:—

27 grams of iodine with 2 grams of finely cut aluminium foil, that is, rather more than an equivalent quantity of aluminium, were mixed in a flask, and 20 c.c. of pure ether were added. A sensible rise of temperature took place at once, and in a minute or so the ether boiled violently, and was prevented from escaping only by an inverted condenser to which the flask was attached. This continued for about five minutes, when the action gradually ceased. The flask was now connected with an ordinary condenser and heated by immersion in boiling water, when a slightly brown ethereal liquid distilled, from which, by agitation with water, 3·5 c.c. of a body containing iodine and heavier than water separated. A brown semi-solid residue was left in the flask, and this was now slowly heated to 150° C. by immersion in a paraffin-bath, when again an oily body containing iodine distilled, which, after shaking with water, measured 6·5 c.c. On heating to a still higher temperature (200°), the residue frothed somewhat, and ·5 c.c. more of the oily body was obtained, making a total of 10·5 c.c.

The different portions of the oily body were added together, washed, dried, and subsequently distilled. It began to boil at 55°, and quickly rose to 70°, between which and 72° the greater part passed over. This portion resembled ethyl iodide in odour, had the same boiling point, and a specific gravity of 1·884 at 17° C., which agrees fairly with the known specific gravity of that body. When 5 c.c. (9·4 grams) were added to a copper-zinc couple wet with water, 1191 c.c. of gas burning with a luminous flame were obtained at the ordinary temperature in 28 hours. Assuming the body to be pure ethyl iodide, it should have yielded, under the circumstances, and according to our previous work, 1249 c.c. of ethyl hydride.

The residue left in the flask, after heating for some time at 200°, was light brown in colour, and weighed 14·59 grams. It dissolved almost completely in alcohol and water. On heating the entire residue from another experiment, over a lamp, 200 c.c. of gas were obtained, of which 68·2 were absorbable by bromine, the remainder burning with a slightly luminous flame, and a residue was left in the flask which consisted of alumina with some iodine.

The formation of the ethyl iodide might be accounted for on the supposition—1. That the products are ethyl iodide and aluminic oxide.

2. That the products are ethyl iodide and aluminic oxyiodide or its elements. 3. That they are ethyl iodide and aluminic iodoethylate, or its elements. If the first of these were true, the residue, after distilling off the ethyl iodide would consist of alumina and be insoluble in water and alcohol, but as it is soluble in these menstrua, this supposition is negatived. If the second were true, the residue, consisting of oxyiodide, could certainly not have yielded hydrocarbons by heat. The inference is therefore, that the third supposition is in the main correct, but, as a somewhat greater quantity of ethyl iodide is produced than even this requires, the probability is that the iodoethylate slowly splits up into alumina and ethyl iodide under the influence of heat—a conclusion confirmed by the amounts of iodine and alumina in the 14·59 grams of residue mentioned above. The quantities of these substances found were—

Iodine	8·769
Alumina	3·866

If the iodine be calculated as aluminic iodoethylate, 13·135 grams of the residue are accounted for, which would be equivalent to 2·365 grams of alumina, leaving, therefore, 1·501 which, added to 13·135 equals 14·636. The close agreement of this number with the weight of the residue confirms the belief that it consists of aluminic iodoethylate with alumina, and leaves but little doubt as to the truth of the third supposition.

Aluminic Iodo-ethylate.

As we know nothing more about the properties of this body than what has been gathered from the study of the fixed product of the aluminium iodine and ether reaction, we sought for a process by which it could be prepared in a state of purity. As we had already suspected its presence in the reaction with alcohol (previously described by us), and as the proportions expressed in the equation—

$$6(C_2H_5O.H) + Al_2I_6 + Al_2 = 2Al_2\left\{\begin{matrix}(C_2H_5O)_3 \\ I_3\end{matrix}\right. + H_6,$$

appeared likely to give the iodo-ethylate, the following experiment was made:—

29 c.c. of alcohol containing 8·294 grams of aluminic iodide in solution were added to 0·556 gram of finely-cut aluminium foil, the inorganic constituents being in the proportions required by the above equation. The flask containing the materials was heated by immersion in boiling water, when hydrogen was at once evolved, and this continued for 15 minutes, 688 c.c. of gas being collected, that is, 7 c.c. above the calculated amount.

The product of the action left in the flask, which can consist of none other than aluminic iodo-ethylate or its elements mixed with or in combination with alcohol, was a liquid of a brown colour and perfectly miscible with water, and on evaporation *in vacuo* it dried up to a non-crystalline semi-solid mass.

The whole of the non-gaseous product of an experiment similar to the above was heated in a distilling apparatus by immersion in boiling water. It gave off alcohol and a little ethyl iodide, leaving a non-crystallised brown mass. When this was heated between 100° and 200°, a little more alcohol passed over accompanied by a greater quantity (3 c.c.) of ethyl iodide, leaving alumina with a small quantity of iodine in the flask, which clearly indicates that the iodo-compound splits up, in presence of alcohol, into alumina and ethyl iodide at a high temperature.

The fact of this splitting up of the iodo-ethylate on distilling and heating with alcohol led us to expect that the residue from the iodine ether reaction, after heating to 200°, would also yield ethyl iodide on heating with alcohol. Such was found to be the case. It at the same time led us to expect that the whole of the iodine employed could, by the assistance of alcohol, be converted into ethyl iodide, which is practically shown to obtain by the following experiment:—

The product from 27 grams iodine, 2 grams aluminium, and 20 c.c. ether gave, on distilling at 100° C., 3·75 c.c. of ethyl iodide. 20 c.c. of absolute alcohol were now added, which occasioned a considerable evolution of heat, sufficient to drive over 1·75 c.c. of ethyl iodide. On heating first to 100° and then to 200°, in addition to alcohol, 9·5 c.c. of ethyl iodide passed over, making a total of 15 c.c., the theoretical quantity being 17·3 c.c. The residue left in the flask was almost white alumina, containing 1·4 gram of iodine.

Taking the whole of the facts above detailed into consideration, the simultaneous action of iodine and aluminium upon ether may be thus represented:—

$$3\left\{\begin{matrix} C_2H_5O \\ C_2H_5 \end{matrix}\right. + Al_2 + I_6 = Al_2\left\{\begin{matrix} (C_2H_5O)_3 \\ I_3 \end{matrix}\right. + 3C_2H_5I.$$

This action of heat upon the aluminic iodo-ethylate when associated with alcohol, may be represented thus:—

$$Al_2\left\{\begin{matrix} (C_2H_5O)_3 \\ I_3 \end{matrix}\right. = Al_2O_3 + 3C_2H_5I,$$

but it is probably the product of two actions, thus:—

$$(1)\ Al_2\left\{\begin{matrix} 3C_2H_5O \\ I_3 \end{matrix}\right. + 3\left\{\begin{matrix} C_2H_5O \\ H \end{matrix}\right. = 3C_2H_5I + Al_2\left\{\begin{matrix} 3C_2H_5O \\ (HO)_3 \end{matrix}\right.$$

$$(2)\ Al_2\left\{\begin{matrix} (C_2H_5O)_3 \\ (HO)_3 \end{matrix}\right. = Al_2O_3 + 3\left\{\begin{matrix} C_2H_5O \\ H \end{matrix}\right. .$$

It might be anticipated that iodine and aluminium, if allowed to act simultaneously upon other ethers than the ethylic, would yield their corresponding iodides. Such the following experiment shows to be the case with amylic ether.

20 c.c. of this compound were added to a flask containing 2 grams of finely-cut aluminium foil, and 27 grams of iodine. There was no action apparent in 30 minutes, but soon afterwards the temperature was found to have risen sensibly, this quickly increased, and the action finished in 15 minutes.

The brown liquid left in the flask was heated by immersion in a paraffin-bath, slowly from the melting point of that substance, to 200° C. The distillate obtained after washing with water gave 15 c.c. of an oily body containing iodine.

It also appeared of interest to ascertain whether the reaction described is a general one with bodies containing C_nH_{2n+1} radicals, or is applicable only to simple ethers. Experiments were accordingly made with the acetates of ethyl and amyl.

In one experiment with amyl acetate, 16·5 c.c. of this body were placed together with 13·9 grams of iodine and 1 gram of aluminium. The contents of the flask quickly rose in temperature, and the action became very energetic; it was over in 30 minutes. The flask was now slowly heated by a paraffin-bath to 200°, when an oily body containing iodine distilled, commencing at about 140°, and after agitation with water it measured 12 c.c. On drying with calcium chloride the greater part passed over between 137°—142°, and it had a sp. gr. of 1·44 at 11° C. As the boiling point of amyl iodide is said to be 146° and its sp. gr. 1·511, this product probably contained a little undecomposed acetate.

In an experiment with the ethyl compound, 9·3 c.c. of it were mixed with the same quantities of iodine and aluminium as in the previous experiment. The action was extremely violent, being nearly over in five minutes, and necessitating constant agitation of the flask in cold water. The flask was afterwards heated to 100° for thirty minutes to destroy the last traces of aluminium, and the temperature was then slowly raised to 200° C. An oily iodide distilled which, after washing with water, measured 7 c.c. On drying with calcium chloride and distilling, the whole boiled between 70°—72°, had a sp. gr. 1·98 at 9° C., and possessed the odour of ethyl iodide, with which it accords perfectly in boiling point and specific gravity. The theoretical quantity of ethyl iodide obtainable is 7·2 c.c.

The residues of both experiments consisted of aluminic acetate with a little iodide.

It is therefore evident that the metal in these reactions combines with the $C_2H_3O_2$ of the acetate, just as it does with the $C_nH_{2n+1}.O$ of the ethers, while the C_nH_{2n+1} immediately enters into union with iodine forming the iodide, thus :—

$$6\left\{\begin{matrix} C_nH_{2n+1} \\ C_2H_3O_2 \end{matrix}\right. + Al_2 + I_6 = 6\left\{\begin{matrix} C_nH_{2n+1} \\ I \end{matrix}\right. + Al_2(C_2H_3O_2)_6.$$

This last research has placed us in a position to form a more definite opinion as to the manner in which the peculiar chemical change recently described by us, is brought about. Water, alcohols, and ethers are well known to be analogous bodies, and each may be considered as binary compounds in which the radical H or C_nH_{2n+1}. is united to the oxygen compounds of a similar radical, thus:—

Water	$H.HO$
Alcohols	$H.C_nH_{2n+1}.O$
Ethers	$C_nH_{2n+1}.C_nH_{2n+1}O$.

Now aluminium shows a great tendency to combine with hydroxyl. We know, for instance, that an aqueous solution of acetate of aluminium will form the hydrate $Al_2(HO)_6$, and give acetic acid by boiling or diffusion; and the iodide, bromide, or chloride of aluminium exposed to damp air gives off free acid. Similarly, we believe, the aluminium is ready to combine with $C_nH_{2n+1}O$, if a halogen be present to remove the H or C_nH_{2n+1}.

Our present belief is that the chemical change takes place through the intervention of intermediate bodies, thus:—

$$(a.)\ Al_2I_6 + 3H_2O = Al_2{}^{(HO)_3}_{I_3} + 3HI.$$

$$(b.)\ Al_2{}^{HO_3}_{I_3} + 3H_2O = Al_2(HO)_6 + 3HI.$$

$$(c.)\ 6HI + Al_2 = Al_2I_6 + 3H_2.$$

It will be understood that the complete hydration of the aluminium iodide, as by equation *b*, occurs only when the excess of hydriodic acid is destroyed, as by equation *c*, and thus the evolution of hydrogen will be continuous as long as aluminium and water are present, which accords with our experiments.

We find, moreover, that an aluminic iodo-hydrate corresponding with $Al_2{}^{(HO)_3}_{I_3}$ in composition readily dissolves in water, and when heated with aluminium gives an equivalent amount of hydrogen. We find also that an alcoholic solution of its carbo-hydrogen analogue also yields equivalent quantities of hydrogen when heated with aluminium. This tends to confirm the explanation above given, and also elucidates the decomposition of alcohol by the joint action of aluminium and its iodide, which may be represented in a similar way to the above, substituting the radical C_2H_5O for HO.

The reaction with ether is analogous to what occurs with water or alcohol according to equation (*a*), the elements being free, thus:—

$$Al_2 + I_6 + 3(C_2H_5.C_2H_5O) = Al_2\left\{\begin{matrix} (C_2H_5O)_3 \\ I_3 \end{matrix}\right. + 3C_2H_5I.$$