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XI.—*On Cadmium-ethyl.*

By J. A. Wanklyn,

ASSISTANT IN THE LABORATORY OF OWEN'S COLLEGE, MANCHESTER.

The close analogy subsisting between zinc and cadmium led me to expect that the latter would form a compound with ethyl corresponding to zinc-ethyl. In consequence of this expectation I instituted a preliminary experiment, which satisfied me that such is really the case. I then referred to the journals,* and saw that already, in 1853, Schüler had made an investigation with a similar object in view, but that he had altogether failed in the attempt. In the account which he has published of his experiment one or two little omissions struck me, which omissions, I believe, caused him to arrive at no positive result.

These considerations at once determined me to pursue the subject, and accordingly I made a number of preliminary experiments on the action of cadmium on iodide of ethyl mixed with ether. Several times in the course of these experiments I obtained undoubted proof of the existence of a body containing cadmium in combination with organic matter, and volatile below 200° C. In order to procure a sufficient quantity of the new substance for an examination of its properties, I resolved on performing an experiment on a large scale, which experiment I now describe at length.

* Ann. Ch. Pharm., lxxxvii., 56, 57.

About 2,000 grains of cadmium was beaten out into a thin lamina, which was then cut up by means of scissors into very narrow strips. Thus prepared, the metal was introduced into the copper digester used in the manufacture of zinc-ethyl. Perfectly dried iodide of ethyl and ether, 1,000 grains of the former and about an equal bulk of the latter, were next poured in. Then the digester was closed air-tight, and heated up to 130° C. for about an hour. The temperature was next lowered to 100° C. and not suffered to rise above that point during the remainder of the digestion. The whole time occupied by the digestion was about 50 hours, but this process was not continued uninterruptedly throughout that period, as the operation was arrested at night. Having completed this part of the process, the digester was allowed to cool, and afterwards opened by removing the screw-plug. Immediately a considerable quantity of gas escaped. A bent tube was then adapted, and the distillation made in an atmosphere of dry carbonic acid, just as recommended by Frankland in his memoir on zinc-ethyl. The disposition of the apparatus, and the general mode of performing this experiment, were such as Frankland has detailed in his memoir on zinc-ethyl, and to that paper I refer.*

During this distillation, a large quantity of ether and iodide of ethyl came over, but no fumes were evolved at temperatures below 170° C. When the temperature had reached 160° C. the receiver was changed, and between 180° C. and 220° C. a colourless fuming liquid distilled. This liquid, when exposed to the air, evolved first white fumes, and then brown fumes, owing to the formation of oxide of cadmium, and finally burst into flame, depositing brown spots on neighbouring objects. It effervesced with water, forming at the same time a white precipitate. In this respect it resembles zinc-ethyl, as also by the formation of a white solid on the slow absorption of oxygen. Its smell was peculiar, and not disagreeable, rather like that of zinc-ethyl. An estimation of cadmium was made by treatment with water. The precipitate so obtained was dissolved in dilute nitric acid, and the resulting solution evaporated to dryness, and finally ignited, when it left a residue of the deep brown colour characteristic of oxide of cadmium.

Treated in this way, 0·2085 grammes of the liquid gave 0·0877 grammes of oxide of cadmium. As a test of the purity

* Transactions of the Royal Society, 1855, p. 259.

of the oxide of cadmium, it was converted into chloride of cadmium, and weighed in that form, with these results:

Calculated.	Found.
0·0877 CdO	0·0877 CdO
0·1250 CdCl	0·1255 CdCl

The foregoing analysis proves that the distillate contained 36·78 per cent. of cadmium, which indicates that the substance was impure. This circumstance was by no means unexpected, as the total amount of distillate which came over above 160° C. did not much exceed one gramme and a half, and so small a quantity would be rendered very impure by the residual vapour of ether in the digester. If we take the formula of the new substance to be Cd C_4 H_5, the distillate would contain 55·92 per cent. of this substance. The remainder of the percentage would be ether, iodide of ethyl, and perhaps hydrocarbons—the result of the decomposition of this cadmium-ethyl whilst it was in the digester.

In order to obtain the new substance pure, the obvious course was to redistil the crude product, and endeavour to obtain a constant boiling point. For that purpose, more crude cadmium-ethyl was requisite. As the action in the digester had been very far from complete, the ether and iodide of ethyl which had come over first were poured back, along with a further quantity of these ingredients, into the digester, which was closed and heated to 125° C. for two or three days.

On submitting the product to distillation, the ether which came over below 170° C. was collected apart, and the receiver changed after the white fumes had been observed for some time. This second part of the distillate, which fumed as in the former operation, was redistilled in the oil-bath, but no constant boiling point could be obtained. The liquid boiled or evolved gas rapidly up to 165° C., indicated by a thermometer placed in the vapour, and deposited metallic cadmium on the sides of the flask, although the temperature of the surrounding oil-bath was never higher than 210° C. What came over between 95° C. and 165° C. was collected apart, and was found to be greatly altered in properties and composition. On exposure to the air, it fumed a little, but would not inflame spontaneously. Subjected to analysis it gave the following results: 0·093 grms. on treatment with nitric acid and subsequent ignition, yielded 0·0118 grms. of residue. In a second experiment 0·3228 grms. of substance gave, when similarly treated, 0·0387 grms. of residue. These residues, unlike that pre-

viously mentioned, contained, in addition to the oxide of cadmium, a quantity of oxide of zinc, and, instead of being brown, were white.* A combustion with oxide of copper was also made, wherein 0·1852 grms. of substance gave 0·4218 grms. of carbonic acid, and 0·1962 grms. of water.

Here are the collected per centage results of these analyses:

	I.	II.	III.
CdO and ZnO	12·69	11·99	
C			62·11
H			11·77

These numbers show that distillation decomposes in great part the ethyl-compound of cadmium.

The changes which ensue during the action of the materials in the digester present some points of interest, and were made the subject of study. Perfectly dry cadmium, ether, and iodide of ethyl, were sealed up in a glass tube, which was then placed in the water-bath, and frequently agitated during the digestion. For the first five hours there was no visible action. During the next ten hours some crystalline powder was deposited, afterwards the action seemed very rapid; the cadmium underwent great diminution in volume, and a large quantity of shining powder occupied the tube. This powder appeared more soluble in the liquid within the tube whilst hot than when cold. On breaking the tube and bringing out the contents into the air, they did not fume at all; very unlike the behaviour of the resulting oily body which exists in the digester previously to the distillation of zinc-ethyl. Yet this powdery substance, which did not fume, became hot on exposure to the air, and effervesced violently with water, giving a precipitate soluble in acids. In the distillation of cadmium-ethyl, as I have many times noticed, no fumes are given off until a temperature of about 170° C. has been attained; whilst with zinc-ethyl, hardly any of the ether distils before the fuming on exposure to air commences. These facts go to prove that, as first formed, and previously to distillation at 170° C., the cadmium-ethyl exists in stable combination with iodide of cadmium. In the case of zinc, there is a feeble compound of iodide of zinc with zinc-ethyl, as was pointed out by Frankland.† But a tempera-

* The appearance of zinc in this situation rather surprised me, as the cadmium employed in the experiments was almost absolutely free from zinc. Furthermore, I made an experiment some time ago on the behaviour of brass filings on iodide of ethyl at 150° C. I found that there was no action.

† Transactions of the Royal Society, 1855, p. 263.

ture which almost utterly breaks up the zinc compound into zinc-ethyl and iodide of zinc, fails to resolve the corresponding cadmium body into its proximate constituents. Some attempts were made to obtain this double compound of cadmium-ethyl with iodide of cadmium in a state of purity, but without success, as no means of separating the free iodide of cadmium from the double compound presented themselves. Ether dissolves iodide of cadmium slightly, especially under pressure, and ether appears to behave similarly with the double compound.

The contents of the digester, after the cadmium-ethyl had been distilled off in the experiment on the large scale, were examined. They consisted of cadmium unchanged and a grey powder. This residue was treated with hot water, and filtered. The filtrate was evaporated to dryness, and the solid product powdered and dried at a temperature considerably above 100° C. It proved to be pure iodide of cadmium, and gave the following results on analysis:

	Calculated.		Found.
I . .	126·88	69·48	69·42
Cd . .	55·74	30·52	30·29
	182·62	100·00	99·71

The residue on the filter from which the iodide of cadmium had been washed out contained some oxyiodide of cadmium, which, in all probability, was an after product, due to the reaction of finely-divided metallic cadmium on iodide of cadmium when exposed to air and moisture. This insoluble grey powder, which has obviously its origin in the decomposition of cadmium-ethyl previously formed, was very considerable in quantity; a fact which proves that a considerable amount of cadmium-ethyl had been in existence at some period of the operation.

In the experiments on the large scale, about 100 grammes of iodide of ethyl had been employed in the two operations, yet the entire amount of cadmium-ethyl which distilled over in these operations could not exceed 3 grammes. It follows, therefore, that a large proportion of cadmium-ethyl had been decomposed.

Seeing that the contents of a tube—in which cadmium has been digested with iodide of ethyl and ether in the water bath—are a white shining powder previously to distillation, and seeing that products examined subsequently to distillation consist of a

grey powder, I am entitled to conclude that this decomposition of the cadmium-ethyl goes on to a great extent during distillation.

I have arrived at the conclusion that the temperature required to decompose the double compound of iodide of cadmium and cadmium-ethyl breaks up nearly all of the cadmium-ethyl, a small proportion only of that substance being carried over unchanged by the hydrocarbons generated in that decomposition.

As cadmium-ethyl will not distil at ordinary pressures without undergoing decomposition, it was suggested to me by Professor Frankland that cadmium-methyl would be a more favourable body for investigation than the subject of this memoir; and as the presence of iodide of cadmium is a troublesome complication, it was likewise suggested that an alloy of sodium and cadmium should replace cadmium in the proposed experiments.

It has occurred to me also that the employment of an alloy of cadmium and zinc cannot fail to yield interesting results, which may throw great light upon the mode of formation and composition of this class of bodies. This last-mentioned train of research is already in progress, and that named immediately before will be begun as soon as practicable.

No one who reads this paper will doubt that the discovery of zinc-ethyl was an indispensable preliminary to that of cadmium-ethyl. To Professor Frankland for that, and assistance of a more personal nature, I return thanks.