

XLII.—*On some Metallic Derivatives of Coumarin.*

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Bleibtreu has remarked (*Ann. Chem. Pharm.*, lix, 177; Gm. xiii, 321) that coumarin dissolves in hot potassic hydrate, forming a yellow solution, from which acids precipitate the coumarin unchanged.

Mr. Perkin has stated (*Chem. Soc. J.*, xxii, 192) that this yellow liquid is not simply a solution of coumarin in potash, but is a chemical compound of coumarin with the alkali: and he has shown that by employing an excess of the former, and adding a solution of argentic nitrate to the product, a yellow precipitate is formed of the composition $C_9H_6O_2 \cdot \frac{Ag}{Ag} \} O$, which is analogous to a silver derivative obtained by Bleibtreu from nitro-coumarin, viz., $C_9H_5NO_2O_2 \cdot \frac{Ag}{Ag} \} O$ (*Ann. Chem. Pharm.*, lix, 177; Gm., xiii, 321; Perkin, *Chem. Soc. J.* [2], vi, 53, 472).

He also mentions that the homologues of coumarin dissolve in potassic hydrate, and in these instances, by boiling the solution until it is very concentrated the alkaline derivative separates out as an oily fluid, which, on cooling, forms a tenacious mass.

As this peculiar class of derivatives has not been examined at all in detail, it was thought desirable to investigate them more fully, and as it seemed probable that the alkaline derivatives might be useful for the preparation of other metallic compounds, it was considered expedient that they should be examined first.

Sodic Hydrate and Coumarin.

Pure sodic hydrate, prepared by dissolving sodium in water, was boiled for a few minutes with an excess of coumarin. The solution was then cooled and filtered, and the filtrate was freed from uncombined coumarin by treatment with hot benzol, which was well agitated with the solution and decanted. This operation usually had to be repeated five or six times, and after boiling off the adhering benzol, a solution of the pure sodic compound was obtained.

This solution has a pale-yellow colour, and when diluted it exhibits a very marked green fluorescence.

It is immediately decomposed by acids, the coumarin separating as a white flocculent precipitate.

It is gradually decomposed even by carbonic anhydride, so that it must not be much exposed to the air.

At first I thought that this precipitation of the coumarin might afford an easy method of separating it quantitatively from the sodium, by simply filtering and estimating the sodium in the liquors. Owing, however, to the partial solubility of coumarin in the filtrate and the difficulty of extracting it, complete separation by this method was impracticable.

I therefore evaporated the solution to dryness, and heated the residue to 120° till its weight became constant. Combustions and sodium determinations were then made, which gave the following numbers :—

Preparation 1.	{	·287 gram of substance yielded
		·184 „ of sodic sulphate.
		·316 „ of substance gave
		·548 „ of carbonic anhydride, and
		·104 „ of water.
Preparation 2.	{	·346 „ of substance gave
		·597 „ of carbonic acid.
		·552 „ of substance gave
		·3475 „ of sodic sulphate.
Preparation 3.	{	·454 „ of substance gave
		·284 „ of sodic sulphate.

These numbers give percentages agreeing with those for the formula $C_9H_6O_2 \cdot 2NaHO$, as the following comparisons will show :—

		Experiment.		
	Theory.	I.	II.	III.
C ₉	108 47·78	47·34	47·05	—
H ₆	8 3·54	3·64	—	—
O ₄	64 28·33	—	—	—
Na ₂	46 20·35	20·63	20·32	20·28
	226 100·00			

Having determined the relative proportions of sodium to coumarin in the compound, in all subsequent experiments two equivalents of sodic hydrate to one of coumarin were boiled together, thus avoiding excess of coumarin and obviating the troublesome treatment with benzol.

A solution prepared in this way was placed *in vacuo* over sulphuric acid. It evaporated to a thick, yellow, gummy product, which did not crystallise or dry up even after a fortnight. At 100° it became stiffer and lost water, and after a few hours the whole became a crystalline mass. The crystals were first formed on the sides of the vessel in flat circular discs, with radiations from a central nucleus. At about 150° they lose water and become anhydrous, but at the same time undergo some change in constitution, as their solution no longer gives coumarin on being acidulated. In my experiment the loss of water was slightly below the theoretical, but an analysis of the product gave numbers not far differing from theory.

·218 gram of substance gave

·144 „ of sodic sulphate.

This represents 21·39 per cent. of sodium.

Theory, $C_9H_6O_2.Na_2O$ requires 22·11 per cent. of sodium.

The composition of a di-sodic coumarate would be $C_9H_6Na_2O_3$, which is identical with that of the above formula, $C_9H_6O_2.Na_2O$. Di-sodic coumarate, though a possible compound, has not yet been obtained, but if this were that product, it would yield coumaric acid on treatment with an acid. This would have been of considerable interest, as there is no satisfactory method of obtaining coumaric acid in quantity.

It was disappointing therefore to find that on acidulating no appreciable amount of coumaric acid was formed, but instead there was a quantity of a brown, plastic, uncrystallisable substance, which was easily soluble in alcohol and caustic alkalis, but insoluble in water and ammonia. It fuses below 100° . I have not examined it further.

Potassic Hydrate and Coumarin.

The potassic derivative is obtained in exactly the same way as the sodic, by substituting potassic for sodic hydrate.

In the specimen analysed an excess of coumarin was employed, and subsequently removed, as above, with hot benzol.

The specimen analysed was dried at 120° . It was not crystalline, though no doubt it might have been obtained so. In all other respects it resembles the sodic derivative, and a determination of the potassium gave the following numbers:—

·260 gram of substance yielded

·168 „ of potassic sulphate,

corresponding to 29·00 per cent of potassium.

The formula $C_9H_6O_2.2KHO$ requires 30·21.

Some difficulty was experienced in obtaining good numbers in the sodic and potassic derivatives, as they are extremely deliquescent and readily decomposed by carbonic anhydride.

I have found it best to dry them in a current of pure air, which passes over the salt, contained in a small flask. After heating for some time at 100° — 120° the salt is to be transferred to a hot mortar and pounded. This operation is conducted inside a water oven. The powder is then returned to the flask and heated to 120° till the weight is constant.

Combustions were made with chromate of lead; and sodium determinations by partial ignition, then exhausting the residue with water, and weighing as sulphate.

Coumarin and Baric Hydrate.

A boiling solution of baric hydrate dissolves coumarin, forming a yellow liquid. This on evaporation leaves a sticky, gummy mass, which stiffens on heating further, forming a brittle and deliquescent substance. The specimen analysed continued to lose water up to 200° , but the weight then became constant and a determination of the barium was made.

·299 gram of substance gave

·222 „ of baric sulphate.

This corresponds to 43·64 per cent. of barium.

The formula $C_9H_6O_2 \cdot Ba \begin{smallmatrix} HO \\ HO \end{smallmatrix}$ requires 43·21.

The barium salt is similar in properties to the alkaline derivatives, and like them it is easily decomposed by acids and is excessively soluble in water. I have not obtained it crystalline.

By heating baric hydrate and coumarin in a sealed tube to 200° C. for a few hours a different barium compound is formed.

The liquid in the tube becomes darker coloured and decomposes, a bright yellow granular precipitate gradually depositing. This was separated from the mother-liquor and both were examined. The liquor was warmed and acidulated, when a reddish-brown, pasty precipitate appeared, but no coumaric acid crystallised out on cooling. This red precipitate was insoluble in water, but freely dissolved by hot potash and also by alcohol.

The bright yellow precipitate was found to be largely mixed with baric carbonate, and it was almost insoluble in water. On treatment with acids it yielded a red amorphous powder, soluble in hot alcohol.

Argentio Oxide and Coumarin.

When sodic hydrate is saturated with coumarin, as above, and a solution of argentic nitrate added, a beautiful canary-yellow precipitate is formed, which Mr. Perkin briefly described some time ago (*Chem. Soc. J.*, xxii, 192), and he assigned to it the formula $C_9H_6O_2.Ag_2O$.

The following analyses were undertaken to confirm this formula:—

Preparation 1.	{	·252 gram of substance gave
		·143 „ of silver.
		·5355 „ of substance gave
		·572 „ of carbonic anhydride, and
		·092 „ of water.
Preparation 2.	{	·338 „ of substance gave
		·190 „ of silver.
		·4535 „ of substance gave
		·476 „ of carbonic anhydride, and
		·073 „ of water.

These numbers give percentages agreeing with those calculated from the formula $C_9H_6O_2.Ag_2O$.

		Theory.	I.	II.
C_9	108	28·57	29·13	28·65
H_6	6	1·59	1·90	1·79
O_3	48	12·70	—	—
Ag_2	216	57·14	56·76	56·50
	378	100·00		

The silver was estimated as metal by ignition, the carbon and hydrogen by combustion with oxide of copper.

In order to obtain the pure silver derivative, some precautions are necessary. The precipitation must be made in the cold, and only a few drops of argentic nitrate at first added, to remove any traces of free caustic soda in the product. The slight precipitate is then to be filtered off and the precipitation completed in the filtrate. The resulting precipitate is to be well washed on a filter with cold water and subsequently with alcohol and ether, which removes any free coumarin.

It must be dried carefully, as it blackens above 100° , and sometimes below. On strongly heating it gives off coumarin, which is also liberated by treating it with nitric acid.

It is very definite and uniform in composition, and appears to be permanent if kept in the dark, but it gradually blackens on exposure to light.

Plumbic Oxide and Coumarin.

Plumbic nitrate or acetate precipitate a light yellow compound when added to a solution of the sodic derivative afore mentioned.

Accompanying this precipitate there is always a very large amount of free coumarin. For analysis I have found it best to precipitate in three fractions, working only with the second one, which must be washed with water, dried and pounded. The powder must then be digested several times with ether until all free coumarin has been removed.

Lead determinations were made by drying at 100°, decomposing with nitric acid, and precipitation as sulphate. This precipitate must be well washed with alcohol to remove coumarin.

- 1.—·324 gram of substance gave
 ·327 „ of plumbic sulphate.
- 2.—·319 „ of substance gave
 ·326 „ of plumbic sulphate.

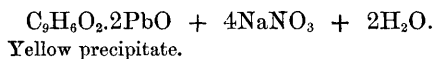
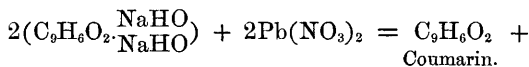
Calculated into percentages, these numbers represent—

- 1.—69·5 per cent of lead.
- 2.—69·82 „ „

The formula $C_9H_6O_2 \cdot 2PbO$ requires 69·93.

This lead salt does not, however, seem very definite in constitution, as two combustions both came out rather low in the carbon, and the different fractions seem to vary in composition.

A given weight of the sodic derivative yields on precipitation only about half the weight of lead precipitate that the coumarin in it might form, but as a large amount of free coumarin also separates, the reaction probably is as follows:—



The lead salt is insoluble in water, alcohol, and ether, but dissolves in an excess of plumbic nitrate, and falls again on stirring as a yellow granular precipitate.

Many other metallic derivatives may be formed by precipitation from a solution of the sodic salt.

Cupric sulphate gives a yellowish-green precipitate which is somewhat soluble in excess, and is decomposed on boiling into cupric hydrate and coumarin. It is very unstable, and I have not determined its composition.

Zinc sulphate forms a white gelatinous precipitate, insoluble in water.

A solution of alum also forms a white gelatinous precipitate insoluble in water, but easily soluble in excess of the precipitant.

With ferric chloride a chocolate-brown precipitate is produced, and with ferrous sulphate one of a brilliant grass-green colour.

Stannous chloride produces a bulky white precipitate.

The only other derivative requiring to be noticed is a product formed on heating the dry sodic salt with ethylic iodide to 150° in a sealed tube.

After heating for a few hours, the tube was emptied of the yellow liquid it contained, and this, on evaporation and heating to expel excess of ethylic iodide, consisted of sodic iodide and a stiff, brown oil, which becomes more fluid on warming. This substance appears to be remarkably stable, and is not apparently attacked even by boiling potash.

Acetic anhydride also forms a compound when heated to 100° with the sodic derivative. Sodic acetate is produced at the same time, but may be separated by mixing with ether and filtering. The new compound is dissolved in the filtrate, and may be obtained in a gummy state by expelling the ether and excess of acetic anhydride by heating in a dish.

These experiments have been conducted in the laboratory of Mr. Perkin, and I cannot conclude without expressing my warmest thanks to him, for his superintendence, and the assistance he has constantly rendered me during their prosecution.
