

XXXII.—*On Aqua Regia and the Nitrosyl Chlorides.*

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THE experiments described in the present paper were undertaken originally in the hope of adding to the very limited number of nitroso-organic compounds at present known. My intention was to attempt the replacement of hydrogen by the radicle NO, through the agency of the chloride NOCl.

This idea has already been suggested by Professor Odling; but in those experiments of which an account has been published, he seems to have employed the mixture of gases which is evolved from *Aqua regia*, and which contains, not only the nitrosyl chloride or chlorides, but hydrochloric acid, and what is more important, a very large proportion of free chlorine. It occurred to me, therefore, that the effect must have been very much complicated by the presence of these bodies, and that by employing the nitrosyl monochloride in a pure state, or mixed only with hydrochloric acid, the oxidising action, which was the sole result observed by Odling, might perhaps be avoided, and the reaction simplified.

Although several reactions have been observed in which the body NOCl makes its appearance, I was not acquainted with any that would afford a ready method for the production of considerable quantities of the reagent. I therefore adopted the following process:—

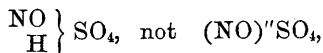
The gases which were evolved by gently heating a mixture of nitric acid (sp. gr. 1.42), with about four times its volume of hydrochloric acid (1.16) were dried by chloride of calcium, and were then passed into concentrated sulphuric acid as long as the yellow chloronitrous gas appeared to be absorbed. Chlorine and hydrochloric acid gases escape during the operation. These experiments were conducted in the winter, when the temperature of the laboratory during the night was frequently down to zero, or thereabouts. Under these circumstances the sulphuric acid thus charged with the nitrous gas deposits radiating masses of long thin prismatic crystals, which, after draining as completely as possible from the mother-liquor, present the composition and characters of the ordinary sulphuric acid chamber crystals.

Samples made at different times gave the following numbers. They were dried by pressure between porous tiles.

| | Experiment. | | | | Calculated for the formula. |
|------------------------------------|--------------------|--------|--------|-------|-----------------------------|
| | I. | II. | III. | IV. | |
| Substance taken | ·5300 | ·6044 | ·8260 | ·3320 | NOHSO ₄ |
| BaSO ₄ obtained | ·9824 | 1·1150 | 1·5405 | ·6064 | |
| | corresponding with | | | | |
| SO ₃ per cent. | 63·64 | 63·33 | 64·03 | 62·71 | 62·99 |

The experiment has been made a great many times, but in no case has any compound been obtained differing in appearance or composition from the foregoing. Moreover, when the liquid which has been drained from the crystals is exposed to the further action of the aqua regia gases, or is cooled by a freezing mixture, it furnishes only a fresh crop of crystals of the same compound. The crystals themselves undergo no change when subjected for a long time to contact with the chloronitrous gas from aqua regia. A sample which had been so exposed gave on analysis 62·88 per cent. of SO₃.

It appears, then, that only one nitrosyl sulphate is formed under the circumstances indicated. In order to make sure that the compound thus produced really contains hydrogen, and is represented by the formula



a quantity of it was heated with an excess of perfectly dry sodium chloride. It was found that, after the expulsion of the nitrosyl monochloride which is at first evolved, the application of a stronger heat caused the evolution of torrents of hydrochloric acid. It may also be observed that if a body having the composition represented by the second formula were produced, its action upon common salt would give rise either to free chlorine, or to a dichloride,



It will be shown presently that neither of these bodies is generated.

Some attempts to obtain the neutral, or dinitrosyl sulphate were unsuccessful. Thus, the acid sulphate was submitted to distillation, as it was thought possible that the distillate might yield this compound :



The crystals of acid nitrosyl sulphate were found to melt at 85°—87° C., and immediately afterwards vigorous decomposition commenced, with evolution of a yellow vapour. When about half the liquid had passed over, a distillate was obtained which refused to

crystallise, and contained 71 per cent. of SO_3 . Nitrous anhydride is therefore lost in the process. Another attempt was made to obtain dinitrosyl sulphate by passing dry nitrogen peroxide into sulphuric acid, as described by Gay-Lussac. Crystals were deposited, but analysis proved them to be merely the acid sulphate.

| | Exp. | I. | II. |
|------------------------------------|------|-------|-------|
| Substance taken | | ·4915 | ·5404 |
| BaSO_4 obtained | | ·8800 | ·9768 |

These numbers correspond with the following percentages of SO_3 —

| | I. | II. |
|-------------------------------------|-------|---|
| | 61·46 | 62·04 |
| Theory for NOHSO_4 | 62·9 | $(\text{NO})_2\text{SO}_4$ 51·2 |

The acid sulphate of nitrosyl may be obtained in the manner described from aqua regia without trouble, and in large quantity. This compound, when treated with a small quantity of water, forms a very convenient source of nitrous anhydride.

When mixed with perfectly dry sodium chloride, the crystals evolve nitrosyl monochloride, and if only a gentle heat is applied, the compound is obtained quite free from hydrochloric acid, and in a state of purity—



This was the process by which I at first prepared the compound I had been seeking, but it was afterwards found much more convenient, and quite as satisfactory, to employ sulphuric acid thoroughly saturated with the aqua regia gases, without taking the trouble to crystallise the sulphate.

Nitrosyl monochloride is an orange-yellow gas, the colour of which is quite different from that of chlorine. It liquefies readily when passed through a tube surrounded by ice and salt, and the deep orange limpid liquid thus obtained boils without decomposition at about -8°C . Several analyses of the vapour were made, and its specific gravity estimated with concordant results.

1. Vapour without previous liquefaction.

Weight of bulb and vapour at 10° and under 773 mm., 62·7030.

Weight of bulb and air at 10° and 773 mm., 62·5577.

Capacity of bulb, 85·6 cub. centims.

Hence sp. gr. ($\text{H} = 1$) 33·5 or ($\text{Air} = 1$) 2·33.

The vapour absorbed by water required an amount of standard solution of silver nitrate, indicating ·1334 of chlorine, or 52·5 per cent.

2. Vapour liquefied in the flask itself, then allowed to boil away, as in Dumas' method.

Weight of flask and air at 9° and under 755 mm. = 60·6698.

Weight of flask and vapour at 9·5°, and under 755 mm. = 61·0836.

Capacity of flask, 257·6 c.c.

Hence sp. gr. (H = 1) 33·0 or (Air = 1) 2·29.

Chlorine = 0·3939, or 53·6 per cent.

| | Experiment I. | Experiment II. | Calculated for NOCl. |
|---------------------|------------------|-------------------|----------------------|
| Chlorine | 52·5 | 53·6 | 54·1 |
| Specific gravity .. | 33·5 | 33·0 | 32·7 |

These results show that the compound thus obtained is free from hydrochloric acid, admixture of which, to a very small extent, would have raised the percentage of chlorine considerably.

At this stage of the investigation it seemed desirable to endeavour to get some further information as to the nature of the remarkable dichloride NOCl_2 , or $\text{N}_2\text{O}_2\text{Cl}_4$, which, according to Gay-Lussac (*Ann. Chim. Phys.* [3], xxiii, 203), occurs among the products of the decomposition of nitric by hydrochloric acid. From theoretical considerations, its existence seemed at least doubtful, no compound having any analogy with it being known, except the solid vanadyl dichloride, VOCl_2 , which has been described by Roscoe, and of which there is no means of determining the molecular weight. The nitrosyl dibromide of Landolt will be referred to hereafter.

The most probable assumption appeared to be, that the supposed dichloride, which Gay-Lussac never succeeded in getting in a definite state, is only a solution of chlorine in the liquefied monochloride. Gay-Lussac himself hints at such a possibility, which is not at variance with his own analytical results. Thus, in his analysis of the liquid obtained by condensation from the gases of aqua regia, he found 69·4 per cent. of chlorine.

Another specimen gave the following results:—100 volumes of the vapour furnished by the more volatile portions of the liquid contained 50 and 51·4 volumes of nitric oxide. The less volatile portions contained 65·7 and 71·7 volumes per cent. of NO. In a second series of experiments with another specimen of the liquid, 41·0, 60·2, and 75·0 per cent. of nitric oxide were the volumes obtained.

Specific gravity of the vapour, 31·8.

A mixture of nitrosyl monochloride with half its volume of chlorine would contain 70·3 per cent. of chlorine, 66·6 vols. per cent. of NO, and would have a specific gravity of 33·6.

The hypothesis remains, that the supposed dichloride may be a mixture of the monochloride with a trichloride, NOCl_3 (4 vols.). A body having the composition of such a trichloride would yield half its volume of nitric oxide, and some of the analyses of the more volatile

portions of the liquid made by Gay-Lussac gave results approaching this. But it must be remembered that this liquid is deposited from a mixture of gases containing a very large excess of free chlorine, and we should therefore expect that if a trichloride is capable of existing at all, it would not be accompanied by a lower chloride.

In order to get evidence as to the existence or non-existence of a trichloride, I made the following experiment:—

Nitrosyl monochloride, mixed with an excess of chlorine, was passed into a tube surrounded by a freezing mixture, and when a considerable quantity of liquid had been condensed, the neck of the tube was placed in communication with a series of vessels in which the vapour was, with due precautions, collected. Three separate analyses were made of the last portions of vapour evolved.

I. Last portion (129 c.c.) of vapour contained 53·9 per cent. of chlorine.

II. Last but one (85 c.c.); 54·1 per cent. of Cl.

III. Last but two (258 c.c.); 57·6 per cent. of Cl.

NOCl contains 54·1 per cent. of chlorine.

This shows that although chlorine had been absorbed by the liquefied nitrosyl monochloride, no definite chemical compound had been formed, the chlorine evaporating away with the first portions of vapour, leaving the latter portions of monochloride in a pure state.

Lastly, the compound obtained direct from aqua regia itself was examined. The gas was first liquefied by cold, and then the vapour from the liquid was collected in a series of three bulb-tubes, the third containing gold-leaf, and surrounded by ice and salt. When about three-fourths of the liquid had boiled away, the vapour was sealed up, and the chlorine determined.

I. gave 60·07 per cent. of chlorine.

II. gave 63·06 per cent. of chlorine.

III. The gold had entirely disappeared, having been converted into a yellow crystalline powder.

Platinum foil, under similar circumstances, is not instantly attacked, but in a few hours it also yields a yellow crystalline powder, which is probably identical with the compound described many years ago by Boyé and Rogers (*Phil. Mag.*, xvii, 397), and more recently by Weber (*Pogg. Ann.*, cxxxi, 441). If this should be the case, the formulæ given by these chemists must be erroneous, since no water can be present in the compound in any form. Both the platinum and gold salts effervesce when treated with water, nitric oxide escapes, and after boiling for a few minutes, a solution of the pure chloride is obtained. I intend to examine both these substances as soon as possible. Contrary to statements hitherto received, both platinum and gold are also attacked by the monochloride, but very slowly, platinum foil immersed

in the liquid showing no signs of change till after the lapse of twenty-four hours or more.

The vapour from another specimen of liquefied chloronitrous gas from aqua regia was passed into strong sulphuric acid. A considerable quantity of chlorine was left unabsorbed. On the other hand, the vapour of pure nitrosyl monochloride is completely decolorised; hydrochloric acid, entirely free from chlorine and from nitric oxide remains.

All the foregoing considerations, taken together, lead to the conclusion that the monochloride, NOCl, is the only true chemical compound of nitric oxide and chlorine, generated when hydrochloric and nitric acids are brought into contact with each other.

The vapour which is evolved upon the application of heat to such a mixture must be represented, therefore, as consisting solely of chlorine and nitrosyl monochloride—



When this vapour is exposed to a low temperature, the nitrosyl chloride, which condenses, dissolves some chlorine, the amount of which, however, is variable.

Landolt has described (*Ann. Chem. Pharm.*, cxvi, 177) three nitrosyl bromides, which he obtained by passing nitric oxide gas into bromine kept at a low temperature. The product, when submitted to distillation, evolved nitric oxide, the residue becoming progressively richer in bromine. It appears to me that it is not fair to assume that a particular fraction of this product is entitled to rank as a definite chemical compound, solely on the ground of its containing an amount of bromine nearly agreeing with the formula NOBr₂. The body to which Landolt assigns this formula evolves nitric oxide spontaneously and rapidly on the slightest elevation of temperature, and exhibits no definite characters. I have found that, on distilling a mixture of nitrosyl sulphate and dry potassium bromide, great quantities of nitric oxide are evolved before any liquid begins to distil over. The distillate obtained was a black heavy liquid, resembling bromine, but it could not be heated without evolution of nitric oxide. I have not further examined the compound.

To return to the starting-point of this research, I must content myself at present with mentioning that my anticipations as to the production of nitroso-compounds by the aid of nitrosyl chloride have been only partially fulfilled. Its action upon alcohol seems to give rise to

the same products that Professor Odling observed when employing the aqua regia gases.

I must reserve for a future communication an account of certain of its reactions, which I have already partly studied.

CLIFTON COLLEGE, *April*, 1874.
