

XXXII.—ON THE ACTION OF HYPONITRIC ANHYDRIDE ON ORGANIC BODIES.

BY ALBERT R. LEEDS, PH.D.

I.—ACTION UPON BENZINE.

The author was led to an extended study of the action of hyponitric anhydride upon organic bodies, by certain theoretical considerations as to the nature of the derivatives which could possibly be obtained by the operation of this powerfully oxidizing anhydrous radical upon benzine. The results having exceeded in number and importance the most sanguine expectations entertained at the outset, the investigation has been extended to a large number of bodies in the aromatic group, and in the future will be made to include as many organic substances, as will be likely to undergo change when submitted to this reagent. So far as we have been able to discover, but few investigators have turned their attention in this direction. Guthrie found that when hyponitric anhydride is passed into a flask containing amylene and surrounded by a freezing mixture, the gas is instantly absorbed, and the amylene is gradually converted into a pasty mass of minute crystals, which may be purified by washing with cold alcohol, recrystallization from boiling ether, and drying in vacuo over sulphuric acid. Its analysis gave the formula $C_5H_{10}(NO_2)_2$, which would make it a direct combination of the monatomic radical nitrile with the radical amylene, a *nitrilide of amylene*.*

According to Semenoff,† when dry ethylene gas is passed through liquified hyponitric anhydride, or when the mixture of the two gases is heated to 60° or 70° , ethylene nitrite, $C_2H_4(NO_2)_2$, is formed, together with an oily body. It may be obtained in a pure condition and more abundantly, by passing ethylene into anhydrous ether, liquid hyponitric anhydride being added at the same time, drop by drop, and, after the liquid has cooled, drying the crystals, which separate, between filter paper and finally over sulphuric acid. It is insoluble in water, easily soluble in alcohol and ether, and crystallizes in four-sided tables, melting at 37.5° .

Finally it is stated,‡ that certain nitro-derivatives have been formed by the direct action of hyponitric anhydride upon organic bodies, *e. g.* mononitronaphthalene, $C_{10}H_7(NO_2)$. But more explicit

* Quar. Journ. Chem. Soc., 13. 45, 129.

† Zeitschr. Chem. Pharm., 1864, 129.

‡ Dictionary of Chemistry, Watts, 4, 77.

references to the reactions alluded to, we have not succeeded in finding.

In the first experiments, benzine was treated with nitric oxide, to determine whether this body would exert an action upon it, and when negative results were obtained, dry hyponitric anhydride was used. The absorption, both in the cold and in boiling benzine, is energetic, the liquid becoming of a deep red color, and the increase in volume, in the case of cold benzine, very striking. At the beginning, before many unsuccessful experiments had acquainted us with the method of obtaining more satisfactory results, the mistake was made of subjecting the benzine, thus hyponitrified in the cold, to distillation. Large volumes of hyponitric anhydride were given off, and a brownish-red viscid mass remained behind. In some of the earlier experiments this residue was found to contain nitrobenzine, in other trials, none. A portion, free from nitrobenzine, was treated with caustic potash, with which it readily combines, and precipitated again with hydrochloric acid. This operation was repeated several times, but without obtaining a body capable of crystallizing from any solvent. Finally, the original residues were dissolved in ether, and the concentrated ethereal solutions washed repeatedly with water. The viscid mass, left on evaporation of the ether, solidified into a translucent, dark red substance. This, on analysis, gave a formula corresponding to $C_6H_6(NO_2)_2(OH)_2$.

	FOUND.		THEORY.
	I.	II.	
Carbon	34.7 per cent.	34.2 per cent.	35.3 per cent.
Hydrogen	3.2 “	4.2 “	3.9 “
Nitrogen	...	14.0 “	13.7 “

The extreme improbability of having formed a substance with this constitution, and the failure to have obtained it in a crystalline condition, made it well-nigh certain that the body analyzed was a mixture. The method of preparation was therefore entirely changed. The benzine, contained in a series of wash-bottles surrounded by cold water, was treated with a slow stream of hyponitric anhydride for many days, until it ceased to increase in volume or weight. The product was set aside for several weeks, the bottles being loosely plugged with cotton-wool. The excess of uncombined gas passed off, and the liquid separated into two layers, both of a yellow color, but the lower of an oily character and consisting of nearly pure mononitrobenzine.

To determine what was the nature of the gases evolved during nitration, they were passed into a jar over alcohol, in order to dissolve

any escaping benzene, and after standing for some time, were examined for oxygen, nitric oxide, etc. It was found that they consisted mainly, if not entirely, of nitrous oxide, N_2O . No nitric oxide was detected, and this very interesting result makes strikingly evident the energy of hyponitric anhydride as an oxidizing agent for organic substances.

On distilling the liquids, the temperature finally rose to 209° , after the unaltered benzene had gone off, and the oil of bitter almonds distilled over. Surrounded by a freezing mixture, it solidified into a mass of long colorless, prismatic crystals, proving that the oil was pure mononitrobenzene, $C_6H_5(NO_2)$. Prior to distillation, the liquids deposited crystals, which were either white, or stained to a greater or less extent by adhering drops of a dark red oil. A great deal of time was wasted in endeavoring to purify these crystals by crystallizing them from various solvents, benzene, acetic acid, alcohol and ether, in the last-named of which they dissolve easily. But, unfortunately, the result proved that the same source of error was present here, as when the original product of hyponitrication was dissolved in ether—the crystals were never entirely free from a foreign body likewise soluble in ether. An analysis of the crystals obtained by recrystallization from this solvent, afforded: carbon, 22.03 per cent., hydrogen, 4.22; corresponding to the formula, $C_6H_{14}O_{15}$. The melting point of the crystals was 99° , beyond which point they were decomposed with evolution of water and deposition of fine needles.

The above, very improbable, formula led to the abandonment of the methods of purification heretofore employed, and the substitution of an entirely different one. The crystals were dissolved in water, in which they were readily soluble, and their lead and silver salts precipitated by plumbic acetate and argentic nitrate. Both salts were entirely insoluble in water, the lead salt, after repeated treatment with hot water, remaining of a fawn yellow color.

0.689 grm of the lead salt yielded 0.6806 grm $PbSO_4$, or 67.4 per cent. of lead to 32.6 per cent. of the organic radical. This would require that the equivalent obtained for the organic radical should be multiplied by three, in order to make it correspond with the equivalent of $C_6H_{14}O_{15}$.

1.0941 grm of the silver salt yielded 1.0065 grm $AgCl$, or 69.2 per cent. of silver to 30.8 per cent. of the organic radical. Hence, the number found for the latter had to be multiplied by six, in order to make it correspond with the equivalent of $C_6H_{14}O_{15}$.

Some of the crystals obtained from this acid body by sublimation, as detailed above, were dissolved in water, and an analysis made of the lead salt precipitated from this solution. 0.3568 grm of the salt yielded 0.3496 grm PbSO_4 , or 66.8 per cent. of lead to 33.2 per cent. of the organic radical. This salt was evidently identical with that obtained from the hydrated acid in the first instance, and the equivalent deduced from the analysis had to be multiplied by three, in order that it should correspond with the equivalent of $\text{C}_6\text{H}_{14}\text{O}_{15}$.

These results made it appear eminently probable that the body was $3(\text{C}_2\text{H}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$, or, in other words, that the empirical formula, $\text{C}_6\text{H}_{14}\text{O}_{15}$, corresponded to three molecules of oxalic anhydride plus two molecules of water, the excess in hydrogen being due to a slight admixture of a foreign body. That the acid substance produced by the oxidation of benzine with hyponitric anhydride was oxalic acid, had been long suspected, but the lack of exact correspondence in properties, as for instance, the obtaining of a slightly colored lead salt, the somewhat explosive nature of the silver salt, etc., had demanded a more satisfactory verification.

To this end, a number of apparently pure crystals were picked out of the deposit on the sides and bottom of the nitrobenzene mother liquor, and after careful drying between filter paper, and recrystallization from alcohol, were placed in a desiccator over sulphuric acid. In their original condition they were perfectly colorless, like glass, and melted at 99° with disengagement of water; after desiccation, the same crystals were entirely white, non-transparent, melted at 185° , yielded no water, but, before melting, partly sublimed in the form of prismatic needles.

0.316 grm of the desiccated crystals, yielded, on analysis, 28.22 per cent. of carbon, and 1.89 per cent. of hydrogen, corresponding to the formula $\text{C}_6\text{H}_4\text{O}_{11}$.

Another portion of the crystals, picked out and freed from all adherent foreign matter with exceeding care, was recrystallized from acetic acid, and a weighed portion of the product thus obtained was subjected to desiccation over sulphuric acid, and, after complete drying, to analysis—0.4518 grm of the acid, after desiccation, had diminished to 0.3213 grm, a loss of 28.88 per cent.

0.2894 grm of the anhydrous body, yielded 0.2840 grm carbonic anhydride and 0.068 grm water.

	FOUND.	THEORETICAL.
Carbon	26.76 per cent.	26.66 per cent
Hydrogen	2.61 " "	2.22 " "
Oxygen	71.11 " "

Or the anhydride had the composition, $C_2H_2O_4$, and the water percentage corresponded to two molecules H_2O , proving that the crystalline substance was no other than $C_2H_2O_4 \cdot 2H_2O$, oxalic acid.

The experience thus obtained made the separation of the other products of nitration comparatively easy. After all the excess of hyponitric anhydride had passed off, and the crystals of oxalic acid had separated out, the liquid portion was boiled with a large excess of water; this drove off the unaltered benzene and the mononitrobenzene. On filtering the intensely yellow colored solutions thus obtained, and concentrating the filtrates, a large mass of fern-shaped, yellow crystals separated out. On washing and drying, their melting point was found to be 118° , and instead of washing the entire mass with water alone, a mixture of hydrochloric acid and water was used, the crystals being less soluble in the acidulated liquid. Of the various solvents employed in recrystallizing the impure substance melting at 118° , such as alcohol, acetic acid and chloroform, the last was found to afford the best results. The final crystallization from chloroform was in brilliant prisms, one and one-half c.m. in length, apparently trimetric, doubly terminated by the faces of the unit octahedron, and exhibiting the vertical and macrodiagonal prisms. Though the melting point could not be raised by recrystallization higher than 122° , and the crystals were not entirely colorless, yet the attempt to deprive them entirely of their yellow tint, by repeated crystallization, was unsuccessful. The solution of these crystals in water was a golden yellow, staining the skin intensely, and permanently dyeing wool and silk. Its taste was extremely bitter. These properties, its crystalline form, the presence of nitrogen, and melting point, all rendered it highly probable that the substance was trinitrophenol or picric acid, $C_6H_3(NO_2)_3OH$; a supposition which was confirmed by the analysis:

	FOUND.	THEORETICAL.
Carbon	31.51 per cent.	31.44 per cent.
Hydrogen	1.76 " "	1.31 " "
Nitrogen " "	18.34 " "
Oxygen " "	48.91 " "

After the various extracts with water, ceased to deposit crystals, they were evaporated to dryness on the water-bath. The reddish-yellow crystalline mass thus obtained, was found to consist of oxalic acid, picric acid, a small amount of the non-identified reddish coloring matter, and a quantity, likewise small, of a substance exploding with violence when heated. This last body was too minute in amount to isolate, but was supposed to be a compound of picric acid with the mono- or one of the dinitro-derivatives of benzene.

It has previously been mentioned that the best results were obtained when a slow current of hyponitric anhydride was passed through a series of wash-bottles containing benzine, and surrounded with cold water. In this case, after standing for several weeks, large colorless crystals of oxalic acid separated out, which might be purified from foreign matters most effectually by crystallization from their solution in acetic acid. It has also been mentioned, that when these crystals were formed in benzine, which had been hyponitrified at higher temperatures, they were accompanied by a deep red oil, from which they were purified with extreme difficulty. Still more was this the case, when the hyponitric anhydride was passed over benzine, which was heated on a water-bath, and provided with an apparatus for condensing vapors.

In one instance, however, there was a *mass of yellow crystals found in the bottle containing the distillate*. This consisted of two entirely different bodies; the one, soluble in alcohol more especially when boiling, and from which it was finally obtained on the third recrystallization, as slender prismatic needles, not exceeding a few millimeters in length, and of a faint reddish-yellow color. On heating, it does not melt, but at 215° begins to sublime, and deposits light yellow, prismatic needles, which, though extremely fine, are, in the case of some crystals, as much as a centimeter in length.

The other substance is insoluble in alcohol, but soluble in benzine, from which it crystallizes in brilliant lemon yellow prisms. These prisms exhibit vertical prismatic faces, with lateral replacements, and are twinned in columnar aggregates. Unlike the crystals soluble in alcohol, which polarize magnificently, those obtained from benzine do not polarize, neither do they melt, but sublime at a point a few degrees higher than the other substance, or, as near as could be ascertained, at 220° .

0.3207 grm of the crystals soluble in alcohol, yielded 0.923 grm CO_2 and 0.1152 grm water, corresponding to the formula, $\text{C}_6\text{H}_4\text{O}$. Repeated trials showed the entire absence of nitrogen.

	FOUND.	THEORETICAL.
Carbon	78.49 per cent.	78.26 per cent.
Hydrogen	3.86 " "	4.35 " "
Oxygen	... " "	17.39 " "

Whilst the formation of quinone might not unreasonably be anticipated, yet it is evident that the new substance which we have obtained, differs strikingly not only in composition but in physical characters, from quinone. For while the latter crystallizes in golden

yellow prisms, it melts at 116° , and even at common temperatures sublimes in shining needles. Moreover, its odor is so pungent as to excite tears, while the new substance is entirely odorless. For the lack of a better name, I shall provisionally call this new oxygen derivative of benzene, monoxybenzine.

The other body, the one soluble in benzene, I did not obtain in quantity sufficient for analysis. Very many attempts were made, the details of the experiments being varied in every way which promised favorable results, but without success. It is hardly necessary to say that the failure to obtain a second time, so important a new substance as the monoxybenzine, and the accompanying body as well, was utterly inexplicable, and the inability to devise any new explanation of the failures, or any different method of work, must be my apology for making known at this stage in the investigation, what was actually accomplished in the first, and by accident apparently, the only successful experiment.

II. ACTION UPON NAPHTHALENE.

In the first experiment, 120 grms of naphthalene were treated in the cold with hyponitric anhydride, until the weight had increased to 199 grms. The naphthalene at first became liquid and of reddish color, and then began to deposit needle-shaped crystals. The resulting product was first distilled with water, in order to get rid of any naphthalene not acted upon, and the residue distilled off at a temperature of 303° . The distillate, which was a yellowish-white solid mixed with some oily matter, was recrystallized a number of times from alcohol, until it yielded nearly white, prismatic needles, having a melting point of 60° , and was thus shown to be nitronaphthalene, $C_{10}H_7(NO_2)$.

As there were evidently other substances formed, besides the nitronaphthalene, it was thought possible that by the action of reducing agents some of these might undergo reduction and others not, and in this way a method of separation be arrived at. After reduction by tin and hydrochloric acid, and separation of the dissolved tin, a clear reddish solution was obtained, from which, on the addition of ammonia, a greenish precipitate was thrown down. This dissolved in alcohol to a red liquid, which exhibited a beautiful blue fluorescence. A portion of the original nitrated mass did not appear to undergo reduction. It dissolved readily in alcohol, but did not crystallize from this or any other solvent. Its solution was of a red color, but not fluorescent. Later on, it was found that the fluorescent body was contained in the first portion of the greenish precipitate, with

ammonia. Moreover, it was found that it was less soluble in hydrochloric acid than the naphthylamine, with which it was associated. After treating the precipitate a number of times with hydrochloric acid, and reprecipitating with ammonia, a substance was obtained which fluoresced very strongly, but which failed to crystallize from any solvent employed. This mode of separation was therefore abandoned.

In the third trial, 150 grms of naphthalene increased in weight to 270 grms, and after first becoming liquid, on the continued passage of the gas, again solidified. After twice distilling with water, the residue was repeatedly treated with cold alcohol. The portion remaining was then dissolved in hot alcohol, from which it separated in colorless, prismatic needles, subliming without decomposition. By their containing nitrogen and by their melting point, these were proven to be α -dinitronaphthalene, $C_{10}H_6(NO_2)_2$.

Finding that ligroine did not dissolve the red coloring matters, while it did dissolve the nitro-derivatives, a portion of the nitrated mass was treated four times with this solvent raised to the boiling point. The residue was then repeatedly treated with cold alcohol, which dissolved out the coloring matter, and from the undissolved portion was obtained β -dinitronaphthalene.

An attempt was then made to isolate the bodies accompanying the nitro-derivatives, by treating the original mass with potash. On boiling, this effected a nearly complete solution, and after filtration the solution was treated with excess of hydrochloric acid. The filtrate was then exhausted with ether. This operation was repeated a number of times, until a considerable quantity of a red viscid mass was obtained on evaporating the ethereal extract. This was again subjected to the same process as before, until a dark red, and apparently, a homogeneous non-crystalline substance, was obtained. Further examination, however, proved that this was not the case, the dark red oil accompanying the nitro-derivatives, effecting a partial solution of these bodies when the mass was treated with potash, and causing them to pass to a certain extent into the final product. This process was therefore abandoned.

280 grms of the naphthalene, heated upon a water-bath, in a retort provided with a wide condensing apparatus, were now hyponitrified. The action was very energetic, streams of oil running down the sides of the retort, and the condensing chamber becoming covered with long white crystals of nitronaphthalene. The final product, which solidified on cooling, was distilled, the temperature rising as the mass

darkened, from 213° to 320°, and the distillate being collected in several portions. The first portions, after repeated crystallizations from alcohol, yielded nitronaphthalene, with a melting point of 59–60°. But neither benzine, ether, alcohol, chloroform, acetic acid or ligroine, were able to extract from the distillates or from the original product, any other substances than the mono- and dinitro-derivatives, the associated red coloring matter resisting all attempts to obtain it in a state of purity.

Another portion of naphthalene, nitrated while hot, was repeatedly boiled with water. On cooling, the solutions were filtered and evaporated, until a thick mud-like sediment had settled. It weighed on drying 33 grms; the naphthalene from which it was obtained weighed 300 grms, and had increased on nitrating to 450 grms. The dried aqueous extract was placed in a retort, and the temperature raised to 215°, at and somewhat below which point, white opaque needles were sublimed off, with a melting point of 127°. Afterwards a white crystalline mass came over. On resubliming the crystals first obtained, long flat, pearly needles were formed, with a melting point of 131°. These polarized finely, while the former did not, a result attributed to some impurity. Later on it was found, what at the time was not anticipated, that this sublimate consisted of two white crystalline substances.

Analyses of the sublimate (melting point, 131°):

	I.	II.	III.	IV
Carbon	65.44 per ct.	51.14 per ct.	66.40 per ct.	66.07 per ct.
Hydrogen	2.75 “	2.78 “	1.96 “	2.44 “
Oxygen (by diff.)	31.81 “	46.08 “	31.64 “	31.49 “

Corresponding to the formulae, (I) $C_{11}H_5O_4$, (II) $C_{10}H_5O_7$, (III) $C_{11}H_4O_4$, (IV) $C_{11}H_5O_4$.

These irrational formulae manifested the probable impurity of the substance, and search was made to find appropriate solvent. It was insoluble in water, slightly soluble in chloroform, easily soluble in acetic acid, ether, alcohol and benzine. *The entire sublimate* (see above) was therefore dissolved in hot benzine. On cooling, minute fern-like crystals separated out, and then, after a long interval, and considerable evaporation, another crop of crystals, entirely different in form and appearance from the preceding, was obtained. The latter, on slow recrystallization from benzine, formed large prisms, apparently monoclinic, perfectly colorless, and of a high vitreous lustre. Another crop of this substance formed twin crystals, some of them of great size, one weighing 0.3 grm and being 42 m.m. long,

7 m.m. wide and 1 m.m. thick. The melting point was 131° . The other substance, far less soluble in benzine, had a melting point of 225° . The analysis of the latter was as follows: 0.153 grm of the substance yielded 0.5301 grm CO_2 and 4.16 grm H_2O , corresponding to the formula, $\text{C}_{10}\text{H}_8\text{O}_4$.

	THEORETICAL.	FOUND.
Carbon	62.50 per cent.	62.40 per cent.
Hydrogen	4.16 "	4.16 "
Oxygen	33.34 "	33.44 "

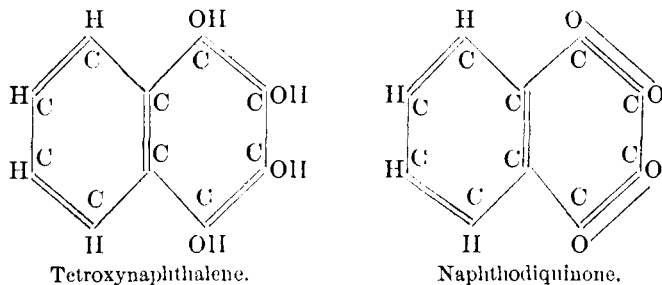
A number of analyses of the substance, with melting point, 131° , were made, with the following results :

- (1) 0.3812 grm yielded 0.8961 grm CO_2 and 0.1601 grm H_2O .
- (2) 0.2327 " " 0.5569 " " " 0.0602 " "
- (3) 0.2793 " " 0.6580 " " " 0.0736 " "
- (4) 0.2049 " " 0.4804 " " " 0.0540 " "

The formula deduced from the above is $\text{C}_{10}\text{H}_4\text{O}_4$.

	(1)	(2)	(3)	(4)	THEORETICAL.
Carbon	64.04	63.98	64.29	63.94	63.83
Hydrogen	2.91	2.87	2.89	2.43	2.13
Oxygen	31.05	33.15	32.82	33.63	34.04

The substance $\text{C}_{10}\text{H}_8\text{O}_4$ would therefore be tetroxynaphthalene, the substance $\text{C}_{10}\text{H}_4\text{O}_4$, naphthodiquinone, and the structural formulae of the two bodies might be represented by:



The discussion of the derivatives obtained from these extremely interesting new bodies, and of their theoretical relationships, will be left to a subsequent paper.

III. ACTION UPON CYMENE.

240 grms of cymene were treated in the cold, with hyponitric anhydride for a number of days. Unfortunately, the total increment in weight was lost, but eventually the cymene, after the operation

had been interrupted, and the excess of gas had been allowed to diffuse off, was found to have been converted into a very viscid dense liquid, of a light yellow color. This was repeatedly boiled with large quantities of water, until no more went into solution, the yellow liquid thus obtained depositing abundant crops of light yellow crystals on cooling. By repeated crystallization from boiling water, these crystals became perfectly white. They melted at 178° , afterwards subliming in thick needle-shaped crystals, and proved to be paratoluic acid, $C_8H_8O_2$.

In the first portions of the distillate, obtained when the raw product was being boiled with water, a small amount of a light yellow oil came over, which differed very slightly in specific gravity from the water condensed at the same time. It was purified by repeated washing with boiling water. Owing to the small quantity obtained, its specific gravity was determined with difficulty, the number found being 1.05. A qualitative analysis showed the presence of nitrogen, and the oil was therefore assumed to be α -nitrocymene, the specific gravity of which is stated to be 1.03.

The residue, after the extraction of the paratoluic acid and α -nitrocymene, was a viscid red mass, which resisted all attempts to crystallize or sublime, and was therefore set aside.

The yellow solutions from which the paratoluic acid had crystallized out, were evaporated to dryness, with the result of obtaining merely residual traces of paratoluic acid, and some of the red viscid body (probably containing a dinitro-derivative) above mentioned.

A large number of other substances, toluene, xylene, phenol, aniline, etc., are being treated with the hyponitric anhydride, and in a subsequent communication I hope to set forth the very interesting results which are being obtained.

In conclusion, I desire to acknowledge with great pleasure the aid rendered by my friend and assistant, Dr. Edgar Everhart, throughout this long and somewhat laborious research.