

A Selected Oxidizing Reaction
of N_2O_4 and a
Comparison of the Decomposition
of Certain Organic Compounds

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the requirements for the degree of
Bachelor of Science with Special
Attainments in Chemistry at Washington
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Harry G. Ballance, Jr.

I. A.

A great deal of $Pb(NO_3)_2$ was finely ground in a mortar and pestle and dried overnight in the oven. This was removed and placed in a dessicator pending further use.

I. B.

Ten grams of $Pb(NO_3)_2$ were placed in a side arm distilling flask, connected to a condenser, decomposition products was collected in a dry ice bath.

Quite a bit of time was spent with this set up, trying to get a proper heating arrangement, and the best dry ice bath. In each trial, the N_2O_4 was collected and combined with that produced in previous attempts. Methods of heating tried were a hotplate, heavyduty hot plate with sand bath, a burner with a sand bath, a burner with an asbestos plate, and a burner with asbestos centered wire guaze. For the dry ice bath, suspensions of dry ice in acetone, trichlorethylene, and equal parts of chloroform and carbon tetrachloride were tried. The best results were obtained from heating the $Pb(NO_3)_2$ with a bunsen burner and wire guaze. The acetone and dry ice proved to be a rather volatile mixture in the presence of an open flame, so it was discarded in favor of the other two baths, both of which, being non-volatile, seemed to work equally well. Finally a blue solid was collected.

I. C.

The solid should have been white, indicative of pure N_2O_4

but it was a sky blue. This blue color is due to impurities, including NO_2 and N_2O_3 .

The blue solid was placed in an ice bath to liquify it, and it turned to a green color, resembling pistachio nut ice cream. Once, the N_2O_4 was in the liquid state, Oxygen was bubbled through it in order to convert everything to N_2O_4 . This was evident when the liquid turned a transparent brown, resembling a mixture of coffee and tea. Once frozen, the compound turned white, indicating pure N_2O_4 .

I. D.

About 20 ml of chloroform was placed in an eight inch test tube and frozen in a dry ice bath. Ten ml of N_2O_4 were distilled into it and frozen. The two were allowed to liquify, forming a solution of N_2O_4 in CHCl_3 .

1.5 grams of thio-bisphenol were added to this solution, and it was allowed to stand overnight in an ice bath. The next morning the solution had turned a bluish black, and after three days it was noticed that a yellow, curdy looking solid had precipitated out.

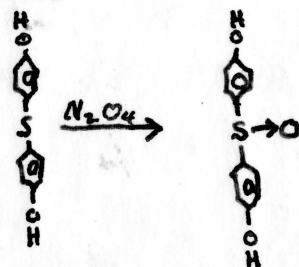
I. E.)

The crystals and the mother liquor were connected to a suction pump, and as much of the volatile mixture as possible was allowed to distill off. Finally, moist yellowish - orange, needle-like crystals were left, along with a slight amount of the mother liquor. The crystals were allowed to dry and were recrystallized from an ethanol-water pair. The

crude crystals weighed 2.4 grams, and 2.0 were recrystallized, with a final yield of .7 grams of pure crystals.

I. F.

Due to the fact that a small quantity of the unknown was available, no attempt was made to fully identify it. There were few possibilities for a final product and the identity of the product hinged upon whether or not Nitrogen entered the compound when it was oxidized with N_2O_4 . To this end^I ran a Sodium fusion test on the pure crystals. Even though the crystals were dry, they had a violent reaction with the Sodium at room temperature. The bottoms dropped out of three of the test tubes, finally necessitating that the fusion be run in a test tube resting in a crucible top. A qualitative test for Nitrogen was run according to Shriner and Fuson, and no Nitrogen was found to be present. On the basis of these observations the reaction proceeds as follows to produce Thio-bis-phenol-sulfoxide.



II. A. It was noted that $\text{C}_6\text{H}_5\text{C}(\text{OH})=\text{CH}-\text{N}-\text{NH}-\text{C}(\text{O})-\text{CH}_2-\text{C}(\text{O})-\text{OH}$, (III) when heated on a Wood's metal bath, would form $\text{C}_6\text{H}_5\text{C}(\text{OH})=\text{CH}-\text{N}-\text{NH}-\text{C}(\text{O})-\text{OH}$ (IV) by splitting out CO_2 and HOAc . It was desired to see if the splitting out of CO_2 was necessary for the reaction to proceed, so a similar reaction was run using $\text{C}_6\text{H}_5\text{C}(\text{OH})=\text{CH}-\text{N}-\text{NH}-\text{C}(\text{O})-\text{CH}_3$ (I).

II. B. 1.0 gm of (I) were heated on a Wood's metal bath in a 30 ml beaker. At $225^\circ - 250^\circ$ a white gas came off which smelled faintly like acetic acid, and the compound melted. The liquid was yellow at first. The gas proved to be acidic to litmus, but only faintly so towards Congo Red. The heating was continued for roughly 30 minutes, until the gas had stopped being evolved. At this point the solution had turned into a strawberry burgundy color, which had the consistency of a thick syrup. Whitish crystals were also deposited on the sides of the beaker. At no point was the temperature allowed to go below 220°C or above 255°C .

The crystals were scraped from the sides of the beaker, and, along with the syrup, were recrystallized from 95% EtOH . The yield from this procedure was on the order .3 gm. The product (II) was not sufficiently pure, but its quantity was not sufficient to warrant a second recrystallization. It's M P was taken on the block, and it melted at $215 - 216^\circ$.

II. C.

The same reaction was run again, but this time in a more quantitative manner. 50 gms of (I) were heated in a 10 ml sidearm flask immersed in a Wood's metal bath, to which was attached a condenser so that the vapor observed could be collected. The heat was applied very slowly so as to determine more closely the temperature range over which the gas was emitted. At 227° pot, some liquid began to appear around the bulb of the thermometer in the flask. The white gas began to distill at 109° head and 230° pot. The head temperature remained at around 137° for most of the experiment, but actually fluctuated quite a bit. The pot temperature was carried to 295°C.

The condensed liquid collected smelled like acetamide (says Shillington) and acetic acid. It was a colorless liquid, and some small crystals, similar to those of acetamide, formed on the sides of the condenser and the collection vehicle. This gives evidence of acetamide being codistilled ^{with} HOAc , or else some being carried over mechanically. The weight of the distillate was 0.6 gms.

The material left in the pot (II) consisted of short, dark, reddish, brown crystals with a needle-like structure. It weighed 3.7 gms. It was first rexed from 30 ml of EtOH . The yield from this recrystallization was 0.8 gms. I next tried to rex it from H_2O , but it was insoluble in it. In this respect it is not at all similar to (IV), because

(IV) is soluble in H_2O . Obviously the products of the two reactions aren't the same, and the elimination of CO_2 must be a necessary step. A knot's hair of the results of the first recrystallization was retained for comparison; the rest was recrystallized from 15 ml of 95% $Et.OH$. After the first recrystallization, it was a cream yellow solid with short needles. After the second recrystallization, it took on a more whitish hue. The yield from the second recrystallization was 0.5 gms. It's M P was $228 - 229^\circ$.

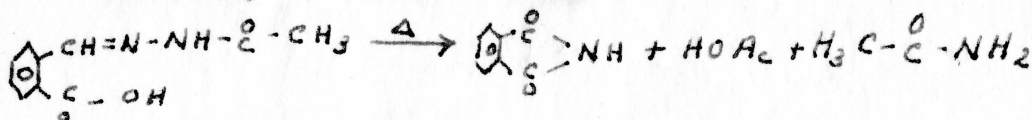
A Na fusion was run on the product (II) to see if it contained Nitrogen. It gave the characteristic Prussian blue color, confirming the presence of Nitrogen.

The solubility class of the compound was class M. It should be A_2 ; was A_2 finally.

The M P, Na fusion, and solubility tests aren't conclusive, or complete for a real identification, but it confirms that (II) is $\text{C}_6\text{H}_4(\text{CO})_2\text{NH}_2$, phthalimide, the most probable substance present. The literature M P of phthalimide is 238°C . This reaction doesn't follow the same mechanism as had been hoped for.

T.S.

Conclusion;

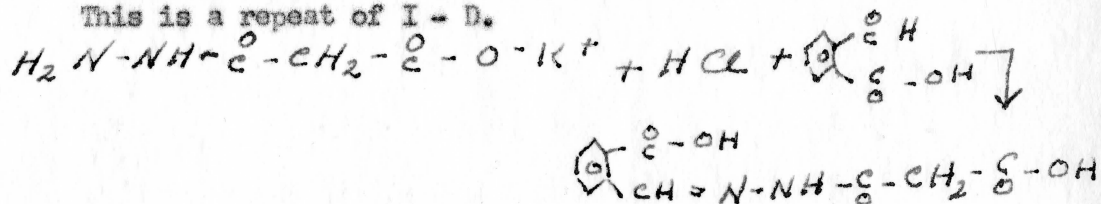


II. D.

It was decided to run Shillington's original reaction over, this time in a more quantitative manner.

II. F.

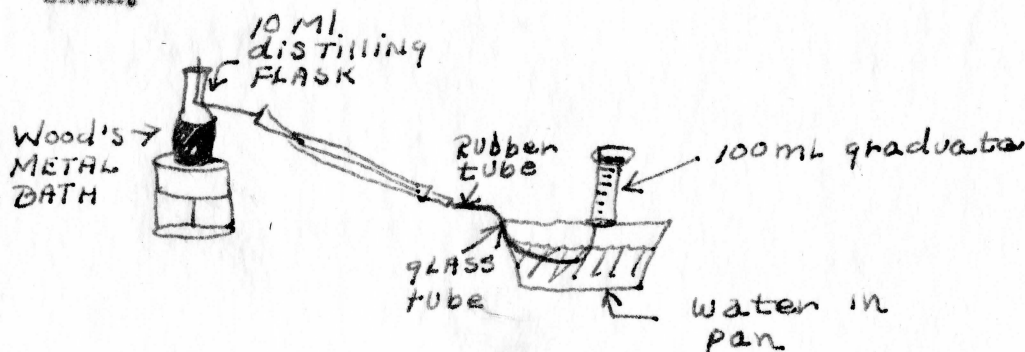
This is a repeat of I - D.



40.0 gm of reagent was dissolved in 200 ml of H_2O and added to a solution of 38.0 gm of o-phthalaldehydic acid in 110 ml of methyl alcohol. It was acidified with 6M HCl, and a whitish powdery substance precipitated out. It had crystals that resembled sugar outwardly. I had a rather large amount of crude product, but some was inadvertently thrown out. Fortunately 16.8 gms of crude product were rescued, and this was recrystallized twice from Et.OH- H_2O . Finally 6.7 gms of pure product were produced.

II. G.

This is essentially a repeat of I. E., Shillington's original reaction. The approximate amounts of all products, i.e., HOAc and $\begin{array}{c} \text{H} \\ \parallel \\ \text{C} - \text{N} \\ \diagup \\ \text{C} - \text{NH} \end{array}$, were known except for the quantity of CO_2 liberated. The reaction was run fairly quantitatively, and the amounts of everything produced but the CO_2 were ignored, in an attempt to collect the CO_2 . The CO_2 was collected over H_2O in an apparatus similar to the one shown.



1.0 gm of starting material was used, and the reaction was carried out as in I. E. 26 ml of gas, considerably less than expected, was observed to have been collected, after corrections for the air in the system had been made.