

γ -o-Chloro-	$C_9H_{12}ONCl$	straw-col. oil	151.5 (3.5 mm.)	1.200	n_D^{20} 1.574	0.6038	28.73 cc. of 0.1115 $N H_2SO_4$	7.6	7.5
γ -p-Chloro-	$C_9H_{12}ONCl$	straw-col. oil	.167 (3.5 mm.)	1.205	n_D^{19} 1.580	0.5849	27.14 cc. of 0.1115 $N H_2SO_4$	7.6	7.8
γ -p-Ethoxy-	$C_{10}H_{13}O_2N$	straw-col. oil and wh. plates from ether and lig.	M. p., 42- 42.5 B. p., 177 (3.5 mm.)	0.4964	23.24 cc. of 0.1115 $N H_2SO_4$	7.2	7.4
γ -p-Carboxy-	$C_{11}H_{13}O_3N$	wh. needles from hot water	M. p., 151-152	0.4825	22.73 cc. of 0.1115 $N H_2SO_4$	7.2	7.4
γ , α -Naphthyl- amino-pro- panol	$C_{13}H_{15}ON$	yellowish oil	B. p., 201.5 (3.5 mm.)	1.137	...	0.4978	19.70 cc. of 0.1115 $N H_2SO_4$	7.0	6.2

In the case of the γ -p-carboxyanilino-propanol, the product remains dissolved in the excess alkali and is obtained by careful acidification with hydrochloric acid.

Summary

1. γ -Chloropropyl aryl carbamates were formed from aromatic amines and γ -chloropropyl chloroformate.
2. γ -Chloropropyl aryl carbamates and potassium hydroxide in alcohol solution are converted into tetrahydro-1,3,2-oxazones when 1 mol. of alkali is used, into γ -arylamino propanols when 4 mol. of alkali are used.

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THE PREPARATION OF OXALIC ACID FROM ACETYLENE

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Received November 17, 1922

In 1919, it was found by the authors that oxalic acid could be prepared on a practical scale, in almost pure condition, from acetylene and nitric acid, with mercuric nitrate as a catalyst. It was desired to discover, if possible, the course of the reaction which afforded the oxalic acid, and the role played by the mercuric nitrate in the reaction. Not much work has been published on the reactions of acetylene with nitric acid or with mercuric nitrate.

Baschieri¹ used fuming nitric acid with acetylene, and obtained nitroform and carbon dioxide, together with a mixture of acids, crystallizing in part from benzene in pale yellow needles, and two neutral substances: (1) a small quantity of a yellow oil, and (2) a solid, $C_6H_4O_2N_4$, separating from ether, alcohol, light petroleum or water in yellowish-white needles. When strongly heated, this latter substance gave hydrocyanic acid.

Giuseppe Testoni and L. Mascarelli² repeated Baschieri's experiment with some modifications, and found in addition to Baschieri's nitroform and neutral substances: (1) a straw-yellow "explosive substance," which when crystallized from benzene or

¹ Baschieri, *Atti. acad. Lincei*, **9**, 391 (1900).

² Testoni and Mascarelli, *ibid.*, **10**, 442 (1901).

petroleum ether gave a neutral substance, $C_4H_2O_3N_4$, and nitrous fumes; and (2) a monobasic acid, $C_4H_3O_3N$, separating from toluene in large, faintly yellow crystals.

Luigi Mascarelli³ found that the "explosive substance" had the formula $C_4H_2O_7N_6$, that it decomposed when heated with light petroleum, giving the compound $C_4H_2O_3N_4$ (the neutral substance which Testoni and Mascarelli had found) and N_2O_4 . He also found that a small quantity of an oily liquid was formed during the nitration.

Orton and McKie⁴ found that acetylene is readily absorbed by conc. nitric acid, or a mixture of nitric and sulfuric acids. An increase in temperature and the addition of mercury salts accelerate the absorption. The products of this reaction were: (1) substances which on treatment with sulfuric acid yield tetranitromethane, and (2) "other substances." The only substance identified in (1) was nitroform; and in (2) oxalic acid.

Hofmann⁵ passed acetylene through a solution of mercuric nitrate, acidified with nitric acid, and obtained a fine colorless crystalline precipitate, having the composition, $C_2HHg_2NO_4$. On passing the acetylene through the solution for several hours, a black precipitate was formed which was insoluble in water and dil. nitric acid; with warm, dil. hydrochloric acid it gave acetaldehyde and mercuric chloride. Erdmann and Kothner⁶ obtained small, white crystals on saturating a hot solution of mercuric nitrate with acetylene. These crystals yielded acetaldehyde on treatment with dil. acids.

Preparation of Oxalic Acid

Apparently, oxalic acid was not obtained in quantity from any of the above-mentioned reactions. When we passed acetylene into nitric acid containing mercuric nitrate, crystals of oxalic acid separated in large quantity. Carbon dioxide and nitrogen oxides were formed in the reaction. A study was made by varying the amount of the catalyst and the concentration of the nitric acid, for the purpose of determining the proportions which would give the best yield of oxalic acid. The results showed that the amount of the catalyst made very little difference in the yield, but varying the concentrations of the nitric acid gave widely different results. The best yield was obtained from the proportion of 3 parts of nitric acid (sp. gr., 1.42) to 1 part by volume of water. The yield of oxalic acid was greatly increased by passing air or oxygen into the mixture at the same time as the acetylene, so that the nitric oxide formed in the reaction would be oxidized to the dioxide and retained in the mixture for further combination with the acetylene or the acetylene derivatives. The formation and loss of nitrogen and nitrous oxide in the reaction prevents the commercial use of the process.

The following statement of the experimental work will make clear the process of making oxalic acid.

Three flasks were connected in series to an acetylene gasometer. In each flask was placed a mixture of 900 cc. of conc. nitric acid (d. 1.42) 300 cc. of water and 25 g. of mercuric nitrate. Acetylene and air were passed into the first flask and allowed

³ Mascarelli, *Gazz. chim. ital.*, **33**, 319 (1903).

⁴ Orton and McKie, *J. Chem. Soc.*, **117**, 283 (1920).

⁵ Hofmann, *Ber.*, **31**, 2212 (1898).

⁶ Erdmann and Kothner, *Z. anorg. Chem.*, **18**, 48 (1898).

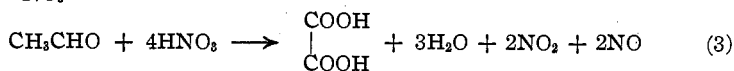
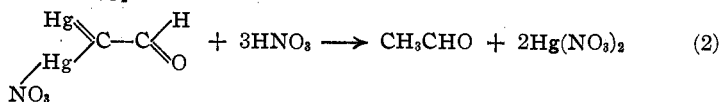
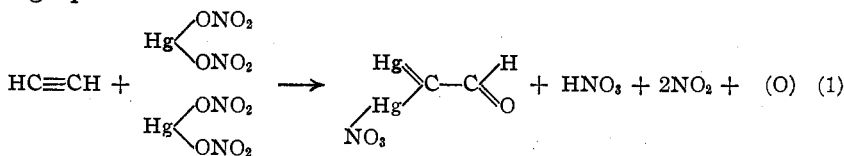
to pass through the other 2 flasks, the first flask being continuously agitated. When the reaction in the first flask had moderated, the first and second flasks were transposed, and the process was repeated until the 3 flasks had thus been exchanged. The 3 mixtures were then combined, and acetylene passed through until all evidence of reaction had ceased. The oxalic acid which had separated in crystalline form was washed with distilled water and dried. The yield was approximately 1000 g.; no attempt was made to concentrate the mother liquor for further production, though it was found afterward that more could be obtained thus. The purpose of connecting the flasks in series was to save the nitrogen oxide fumes generated in the first flask by passing them through the other 2 flasks. When the acid in the flasks was spent and no further reaction was evident, the addition of nitric acid to the spent liquor, in the proportion of 3 parts of the acid to one of the liquor, renewed the reaction, and increased the yield.

Reactions

An attempt was made to determine whether the reaction for the preparation of oxalic acid from acetylene, nitric acid and mercuric nitrate could be shown to take place in steps.

Acetylene was passed into a solution of mercuric nitrate, slightly acidified with nitric acid. A precipitate was formed. The reaction mixture was filtered, the precipitate washed and treated with hot, dil. nitric acid. The precipitate dissolved, forming aldehyde. More nitric acid was added and heat applied to the solution. Brown fumes were evolved. When the reaction had ceased, sodium hydroxide was added to precipitate the inorganic mercury. This mixture was filtered and the filtrate tested for oxalic acid, which was found to be present.

This led to the conclusion that the oxalic acid resulted from the change of the mercuric nitrate to the acetylene-mercury compound which yielded aldehyde with the nitric acid, and that the aldehyde thus formed was oxidized to oxalic acid. The reaction was probably according to the following equations.



All of the reactions with acetylene, nitric acid and mercuric nitrate were in aqueous solutions. For the purpose of further determining the role played by the mercuric nitrate in the reaction giving oxalic acid, the effect of acetylene on the dry mercuric nitrate was examined.

Acetylene was passed into a flask containing mercuric nitrate in fine powder. Brown fumes soon appeared. The powder changed to a semi-solid, colorless mass. The mass assumed a somewhat yellow color, then became a white solid, probably the

mercury compound of Hofmann, and Erdmann and Kothner. Some of the white solid was removed from the flask and treated with nitric acid which dissolved it. Sodium hydroxide was added to this solution to remove any inorganic mercury which might be present. The mixture was filtered and the filtrate tested for oxalic acid which was found to be present. This confirms the conclusion that the oxalic acid resulted from the change of the mercuric nitrate to the acetylene-mercury compound yielding aldehyde when treated with mineral acids; the aldehyde was, in turn, oxidized to oxalic acid.

Acetylene was further passed into the reaction flask. The white solid became gray; metallic mercury was noticed in the flask, and a white substance deposited on the reaction flask above the nitrate. The gases evolved from the reaction flask were passed through 3 wash-bottles; the first contained water, for the purpose of preventing the mercury compounds from passing into the second bottle, which contained nitric acid; the third bottle contained a solution of calcium hydroxide. Pure oxalic acid was formed in the nitric acid bottle. Oxidation was indicated by the formation of brown fumes during the process. A white precipitate in the calcium hydroxide showed that carbon dioxide was evolved during the reaction. The odor of acetaldehyde was strong in the reaction flask, and in the wash-water in the first bottle. Positive confirmatory tests for aldehyde were obtained. The wash-water solution was partially distilled into dil. nitric acid (3 parts of acid to 1 part of water). Much heat and brown fumes were evolved and oxalic acid was formed. During the crystallization of the oxalic acid from the solution the odor of acetic acid was noticed, and the test for its presence was obtained.

To determine whether aldehyde could be the source of the oxalic acid, aldehyde vapor was passed into nitric acid of the same concentration, with exactly the same results, the evolution of brown fumes, much heat, the formation of acetic acid and of oxalic acid crystals. This confirms the conclusion that one source of the oxalic acid in the reaction is the aldehyde. A further confirmation of this conclusion was found when acetylene was passed directly into nitric acid of the same concentration as that into which the aldehyde was distilled. There was very little evidence of a reaction, and a mixture similar to the compounds of Baschieri and others resulted. Another source of the aldehyde in the reaction flask, besides the decomposition of the mercury compound, might be the hydration of the acetylene by the water formed in the oxidation of the acetylene to carbon dioxide. In the reaction flask, into which the acetylene had been passed over the dry mercuric nitrate, were found metallic mercury, a yellow substance crystallizing from water, and oxalic acid. The yellow substance was thought to be the compound found by Baschieri.

The presence of the oxalic acid in the reaction flask containing the dry mercuric nitrate seemed to indicate an oxidation reaction by the nitrogen oxides which were evolved when the acetylene was passed into it. To verify this assumption, nitrogen oxides (made by the action of conc. nitric acid on copper) were passed into a reaction flask into which acetylene was passed at the same time. Crystals of oxalic acid were formed in the flask. The gases evolving from the flask were passed through nitric acid. Pure

oxalic acid was produced in the nitric acid. Carbon dioxide was formed in the reaction.

It was thought that the odor of cyanogen was detected several times during these operations, but because of the small quantity formed and the presence of other gases the presence of cyanogen was not definitely proved. It was shown that cyanogen would yield oxalic acid with nitric acid under the same conditions as did the aldehyde.

To determine whether nitrogen oxides would oxidize acetaldehyde to oxalic acid, the oxides of nitrogen and aldehyde vapor were passed into a reaction flask at the same time. A liquid formed in the flask. When the operation had been continued for some time, a white solid formed in the flask. After the process had been stopped for a short time, and the oxide fumes had disappeared from the flask, the odor of acetic acid was noticed, and a test for acetic acid obtained. The solid gave a test for oxalic acid, and later the oxalic acid crystallized.

To determine whether metallic mercury with nitrogen oxides would react with acetylene in the same manner as the mercuric nitrate, metallic mercury was subjected to the action of the oxides of nitrogen. When the mercury had changed to a salt, acetylene was passed into the flask. After a short time the mercury compound began to turn gray, without the evolution of brown fumes. Aldehyde was formed, and the remainder of the reaction was the same as that with the mercuric nitrate. The mercury salts may be regenerated after reduction by means of the nitrogen oxides.

In the above-mentioned reactions with the dry salts of mercury, the aldehyde may be obtained by condensing the vapors.

Summary

1. Oxalic acid can be prepared on a practical scale by passing acetylene into a mixture of 3 parts by volume of nitric acid and 1 part by volume of water, with mercuric nitrate as a catalyst.

2. The course of the reaction for the formation of the oxalic acid in the above-mentioned mixture was shown to be the formation of an acetylene-mercury compound which yielded aldehyde with part of the nitric acid. The aldehyde was oxidized to oxalic acid by part of the nitric acid.

3. Oxalic acid can also be formed by the action of (1) nitrogen oxides on acetylene (2) nitrogen oxides on acetaldehyde (3) aldehyde vapor on nitric acid.

4. Aldehyde can be obtained by passing (1) acetylene over dry mercuric nitrate (2) nitrogen oxides over metallic mercury, and then passing acetylene over the resulting salt. The aldehyde can be condensed.

5. By means of nitrogen oxides the mercury salts can be regenerated after reduction.