

# Action of Mineral Acids on

## Primary

## Nitroparaffins<sup>1</sup>

Convenient and economical procedures have been developed for the preparation of acetic, propionic, butyric, and isobutyric acids in good yields from the corresponding primary nitroparaffins by refluxing them with 85 per cent sulfuric acid. Hydroxylamine acid sulfate is a by-product of the reaction. Propionohydroxamic acid has been prepared from 1-nitropropane and concentrated sulfuric acid in fair yield.

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RECENT researches at Purdue University (5) have made available the nitro derivatives of methane, ethane, propane, butanes, pentanes, and other hydrocarbons. An interesting reaction common to the primary nitroparaffins is their conversion to fatty acids and hydroxylamine salts by the action of mineral acids and water. The action of a number of acids on primary nitroparaffins has been studied. Sulfuric, hydrochloric, and orthophosphoric acids were tried, and conversions to fatty acids obtained in each case. If the mineral acid is volatile, such as hydrochloric, the mixture must be heated under pressure. If the acid is a strong oxidizing or reducing agent, it causes the destruction of the hydroxylamine. Sulfuric acid was found to be the best of those studied. It gives rapid reaction rates and good yields of both the fatty acid and of hydroxylamine. It is convenient to use and is cheap. Only the experiments with sulfuric acid will be described, and the examples will be limited to those giving approximately optimum results.

Previous to this investigation the reaction of primary nitroparaffins with mineral acids had been studied by several

<sup>1</sup> This article is the eighth in a series on the subject of syntheses from natural gas hydrocarbons. The others appeared in INDUSTRIAL AND ENGINEERING CHEMISTRY, 23, 352 (1931); 27, 1190 (1935); 28, 333, 339, 1178 (1936); 29, 1335 (1937); 30, 67 (1938).

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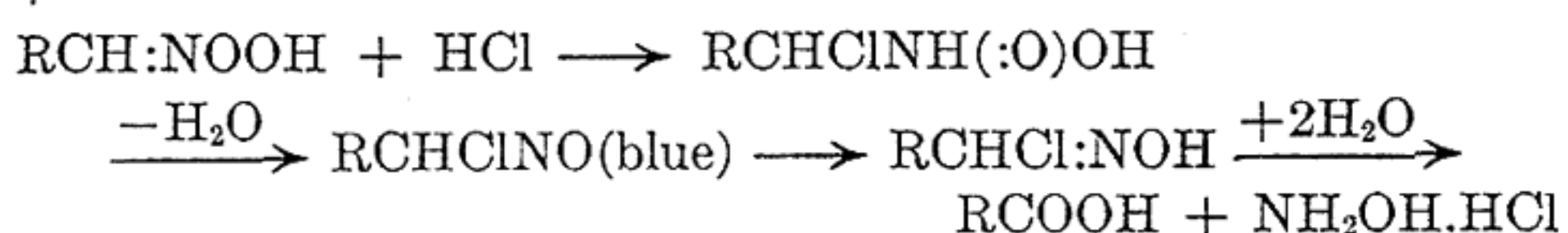
investigators. Meyer and associates (9, 10, 11) studied the action of sulfuric acid on nitroethane and obtained acetic acid and hydroxylamine sulfate. Preibisch (13) showed that sulfuric acid converts nitromethane to carbon monoxide and hydroxylamine sulfate. Donath (2) and Mel'nikov (8) also studied this reaction; the latter found that carbon dioxide and ammonium salts are formed simultaneously. Worstall (17) investigated the action of sulfuric acid on 1-nitroheptane, obtaining the expected heptanoic acid.

The action of hydrochloric acid upon primary nitro compounds was studied by Meyer and Locher (10), who prepared formic, acetic, and propionic acids; by Werner (15), who prepared acetic acid; by Zublin (18), who prepared butyric acid; by Henry (6), who prepared succinic acid from  $\omega$ -nitrobutyronitrile; by Gabriel and Koppe (3), who prepared benzoic acid from phenylnitromethane; and by Worstall (16), who prepared caproic, heptanoic, octanoic, and nonanoic acids from the corresponding primary nitroparaffins.

Geuther (4) reported that phosphorous acid converts nitroethane to acetic acid and ammonium phosphate.

Bamberger and Rust (1) showed that hydroxamic acids,  $RCH(OH):NOH$ , are formed as intermediate products in the conversion of primary nitroparaffins to fatty acids. They obtained yields of hydroxamic acid of only about 2 per cent.

Nenitzescu and Isacescu (12) proposed the following series of steps as representing the mechanism of the reaction:



Junell (7) found the rearrangement of nitroethane to aceto-hydroxamic acid in 1 *N* hydrochloric acid at 69.85° C. to be a first-order reaction with *k* equal to 0.0025 per minute.

Because of the time and expense involved in making aliphatic nitro compounds, these men worked with small quantities of material. Except in a few cases they did not give the yields obtained. Optimum conditions for carrying out the reaction are not to be found in the literature. In view of these facts, it was felt that a study should be made in which special attention would be paid to these points.

### Acids from Nitroparaffins<sup>3</sup>

**ACETIC ACID FROM NITROETHANE.** A mixture of one mole of nitroethane and one mole of 85 per cent sulfuric acid was charged into a 500-cc. three-necked flask equipped with a reflux condenser, mechanical stirrer, and thermometer. The thermometer was adjusted so that the bulb was in the reaction mixture. Agitation was started and the mixture boiled vigorously for a few minutes. As the boiling subsided, the mixture was heated again just enough to keep it boiling for 8 hours, during which time the temperature rose to 117° C. It was then analyzed:

Conversion to acetic acid, 88 per cent; yield, 90 per cent  
Conversion to hydroxylamine, 86 per cent; yield, 88 per cent  
Conversion to ammonia, 7 per cent

Conversions and yields are based on the amount of nitroparaffin introduced and the amount of nitroparaffin consumed, respectively.

More concentrated sulfuric acid may be used and similar conversions obtained in less time. However, because of the exothermic nature of the reaction, it is not advisable to mix the two reactants and heat them as described above. Rather the sulfuric acid should be dropped into the boiling nitroparaffin at such a rate that a vigorous reflux is maintained. Even when 85 per cent sulfuric acid is used, a pan of cold water is kept at hand so that if the reaction becomes too vigorous the mixture may be cooled by immersing the flask in cold water.

**PROPIONIC ACID FROM 1-NITROPROPANE.** Propionic acid was prepared from 1-nitropropane by the method described for acetic acid. The mixture of one mole of the nitroparaffin and one mole of 85 per cent sulfuric acid was heated, with stirring, to 120° C. and the source of heat was removed. The temperature rose to 128° C. and the mixture boiled vigorously for a few minutes. It was then heated sufficiently to maintain a gentle reflux for 8 hours, the temperature rising to 140° C. The reaction mixture was analyzed:

Conversion to propionic acid, 92 per cent; yield, 96 per cent  
Conversion to hydroxylamine, 88 per cent; yield, 91 per cent  
Conversion to ammonia, 6 per cent

**PROPIONOHYDROXAMIC ACID FROM 1-NITROPROPANE.** One mole of 1-nitropropane and one mole of 100 per cent sulfuric acid were mixed at room temperature and carefully heated to 60° C.; the temperature was watched, and the mixture cooled at any indication of rapid heating. When there was no tendency for the temperature to rise above 60° C., it was maintained at 50–60° C. for 16 hours, then heated to 100° C., and held at 95–100° C. for 5 hours. The mixture was cooled

<sup>3</sup> The processes described in this article are covered by U. S. Patent 2,113,812, assigned to the Purdue Research Foundation.

and poured over crushed ice, the sulfuric acid was neutralized with calcium carbonate, the calcium sulfate was filtered out, and the filtrate was concentrated at reduced pressure, such that the temperature of the boiling solution was about 60° C. When the volume had been reduced to about 500 cc., the mixture was filtered again and the filtrate allowed to evaporate at room temperature. The last of the solvent was removed *in vacuo*. The resulting sirup was seeded with crystals of propionohydroxamic acid. This caused the entire mass to solidify. The weight of the crude propionohydroxamic acid was 39 grams (44 per cent of the theoretical). This was recrystallized from ethyl acetate yielding 21.4 grams of product melting at 92.5° to 93.5° C., the reported melting point of propionohydroxamic acid.

**BUTYRIC ACID FROM 1-NITROBUTANE.** Equimolecular quantities of 1-nitrobutane and 85 per cent sulfuric acid were mixed and heated to 140° C. with stirring. The temperature rose to 145° C., and the mixture began to reflux. After a few minutes when spontaneous boiling had subsided, the mixture was heated to maintain a reflux for 2 hours. The temperature rose to 158° C. during this period. Analysis of the mixture gave the following results:

Conversion to butyric acid, 91 per cent; yield, 94 per cent  
Conversion to hydroxylamine, 85 per cent; yield, 88 per cent  
Conversion to ammonia, 7 per cent

**ISOBUTYRIC ACID FROM 1-NITROISOBUTANE.** Isobutyric acid was prepared from 1-nitroisobutane using the above method, the temperature rising from 137° to 154° C. during the 8 hours it was kept boiling:

Conversion to isobutyric acid, 90 per cent; yield, 90 per cent  
Conversion to hydroxylamine, 86 per cent; yield, 86 per cent

### Analytical Procedure

The following analytical procedure was adopted so that the yields obtained in a large number of experiments could be determined without actually isolating the products. At the end of a reaction period the mixture contained (a) the unreacted nitroparaffin, (b) the fatty acid, (c) hydroxylamine as a salt of the mineral acid, (d) a small amount of ammonia as the salt of the mineral acid, and (e) the mineral acid, free and in the form of salts. This mixture was steam-distilled. The first portion of the distillate contained the unreacted nitroparaffin and a portion of the fatty acid. Separate experiments showed that when the aqueous layer became as great as the oil layer, substantially all of the nitroparaffin had been distilled, and at this point receivers were changed and the distillation continued until the distillate was no longer acid to litmus. The amount of fatty acid in each portion of the distillate was determined by titrating with standard alkali. Neutral red was used as the indicator for this titration since the nitroparaffins, especially nitroethane and 1-nitropropane, are acid to phenolphthalein. The unreacted nitroparaffin in the first portion of the distillate was simply measured in a graduate if it was more than 5 cc. in volume. If less than 5 cc., it was determined by adding an excess of standard alkali and back-titrating with standard acid, using thymolphthalein as the indicator. The presence of the neutral red in the determination of the fatty acid in this portion did not interfere with the thymolphthalein end point.

The hydroxylamine in the residue from the steam distillation was determined by Raschig's method (14) which depends on the reduction of ferric ion to ferrous ion by the hydroxylamine and a subsequent determination of the ferrous ion by titration with a standard solution of potassium permanganate. The ammonia present was not always determined but, when it was, the hydroxylamine in an aliquot of the residue was destroyed by adding hydrogen peroxide and heat-

ing to 40–60° C. This oxidized the hydroxylamine to nitric acid, and the ammonia was determined by making the mixture basic, distilling into a measured quantity of standard acid, and back-titrating.

## Separation and Purification of Reaction Products

At the end of the refluxing period in the experiments described, the reaction mixtures consisted of two layers, an upper crude fatty acid layer and a lower crude hydroxylamine acid sulfate layer. Attempts to obtain normal hydroxylamine sulfate directly from the reaction of 0.5 mole of sulfuric acid with 1 mole of nitroparaffin always resulted in less than 50 per cent conversion of the nitroparaffin to fatty acid, leaving the salt in the form of hydroxylamine acid sulfate. Several methods were used for separating the products from one another. Separation of the layers by means of a separatory funnel was not satisfactory, since each layer was saturated with the other component. Seeding the mixture with a crystal of hydroxylamine acid sulfate and filtering, using a fritted glass funnel, gave somewhat better results. Still better separations were obtained by extracting with ligroin. By repeated extractions all of the fatty acid was removed from the mixture, but the method was not the most desirable because it contaminated the fatty acid with ligroin. The most satisfactory separation was made by vacuum distillation. The fatty acid was distilled from the mixture at a pressure of not more than 10 mm. of mercury, and the temperature of the residue was not taken above 140° C. This gave nearly complete separation.

After the separation by any of these methods each product was purified. The fatty acid was simply and easily purified by rectification. Since hydroxylamine acid sulfate is very hygroscopic, it was converted to the normal sulfate by one of the following methods: (a) The crude material was dissolved in water and the excess acid neutralized with calcium carbonate or calcium hydroxide. When the mixture reacted basic to methyl orange it was filtered, the precipitate was washed with water, and the filtrate and washings were evaporated. Successive crops of crystals were filtered off until the last of the filtrate had evaporated. (b) The acid

sulfate was treated with about five times its weight of 95 per cent ethanol. This threw out a white precipitate of the normal sulfate which, after filtering and washing with several portions of alcohol, was quite pure. A considerable amount of hydroxylamine sulfate remained in the alcohol. In either case the salt was recrystallized from hot water, giving pure hydroxylamine sulfate.

## Acknowledgment

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