CXX.—*Action of Alkalis on the Nitro-compounds of the Paraffin Series. Part II. Reactions and Constitution of Methazonic Acid and the Mode of Formation of Isoxazoles.*

By WYNDHAM R. DUNSTAN, F.R.S., and ERNEST GOULDING, B.Sc.

IN 1891 (Trans., 1891, 59, 410), one of us, in conjunction with Mr. T. S. Dymond, gave an account of the action of alkalis on the nitro-compounds of the paraffin series. We showed that, in the case of nitroethane and primary nitropropane, trimethyl- and triethyl-isoxazole respectively are formed. With nitromethane and secondary nitropropane no isoxazole is formed, and the reaction appears to follow a different course. The mechanism of the change by which the isoxazole is formed from the nitro-compound was at the time not clear, and the discussion was therefore postponed.

In the present paper an account is given of the mode of action of alkalis on nitromethane and on secondary nitropropane, whilst what we believe to be a satisfactory suggestion as to the probable course of the remarkable action of alkalis on the nitroparaffins generally is put forward.

Action of Alkalis on Nitromethane.

In the paper referred to above, it is pointed out that no isoxazole can be isolated from the product of the action of aqueous alkalis on nitromethane. A very vigorous change occurs, the mixture becoming warm, dark coloured, and finally almost black. A nitrite is

produced, together with much cyanide and a considerable quantity of resin, and also a compound having acid properties, of which we are now able to give a full description.

Action of Ammonia on Nitromethane.—The action of ammonia is the least vigorous and best adapted for the study of the products of the change. When nitromethane stands in contact with strong aqueous ammonia for several hours, the liquid becomes dark brown and deposits a crystalline substance. The small crystals thus obtained are coloured, and very difficult to purify. The following plan has been found to answer best.

Twenty c.c. of nitromethane contained in a small bottle are mixed with 8 c.c. of strong aqueous ammonia, and ammonia gas is then passed into the mixture until it is completely saturated. The bottle is now stoppered and kept at a temperature not exceeding 10° for about a day, the crystals which have separated are removed and reduced in the moist state to a fine powder. This powder is drained on a porous tile and dried by exposure to air. The residual liquid is again saturated with ammonia gas and allowed to stand, the crystals being then removed, powdered, and dried as before. This process is repeated until the whole of the nitromethane has disappeared. By this means 20 c.c. of nitromethane furnish about 12 grams of the crystalline substance.

By washing with aqueous ammonia the crystals may be obtained quite colourless, but this method of purification is very wasteful owing to the loss by solubility. The crystals are soluble in methyl alcohol, less soluble in ethyl alcohol and nearly insoluble in ether or chloroform. When heated, they decompose with production of hydrogen cyanide. When ferric chloride is added to an aqueous solution it produces a purplish-brown colour which is discharged by heating or by dilute acids. Ammonia is liberated by the action of cold aqueous potash. The crystals are therefore evidently the ammonium salt of an acid.

0.1442 gave 44 c.c. nitrogen at 24° and 764 mm. $N = 34.3$.

$C_2H_3O_3N_2 \cdot NH_4$ requires $N = 34.7$ per cent.

Silver nitrate produces an abundant pale yellow precipitate in an aqueous solution. The silver salt thus obtained is purified by washing with water and alcohol, after which it is dried by exposure to the air. If heated near 100° , it explodes. It is readily dissolved by dilute nitric acid or by ammonia. On analysis it furnished the following results:

0.2630 gave 0.1080 CO_2 and 0.0424 H_2O . $C = 11.2$; $H = 1.8$.

0.3722 „ 0.1575 CO_2 „ 0.0576 H_2O . $C = 11.5$; $H = 1.7$.

0.1280 „ 15 c.c. moist nitrogen at 19° and 760 mm. $N = 13.2$.

0.2266 „ 26 c.c. „ „ at 19° „ 766 mm. $N = 13.2$.

0.2041 „ 0.1373 $AgCl$. $Ag = 50.6$.

$C_2H_3O_3N_2Ag$ requires $C = 11.3$; $H = 1.4$; $N = 13.2$; $Ag = 51.1$ per cent.

Mercuric chloride produces in a solution of sodium methazonate a yellow precipitate which is chiefly composed of *basic mercuric methazonate*. This salt explodes when heated, and is converted by dilute hydrochloric acid into a soluble, crystalline *mercuric methazonate*. The *lead* salt is insoluble, and explodes on heating.

Methazonic Acid.

The acid is readily isolated from the ammonium salt by mixing a strong aqueous solution with the equivalent quantity of dilute sulphuric acid and extracting with ether. The ethereal solution is dried with calcium chloride and evaporated in a vacuum. By this means an acid crystallising in plates is isolated, which very readily changes into a red resin. It is best purified by recrystallisation from warm benzene or chloroform. The acid may be obtained from the silver salt by the same means. It is identical with the *methazonic acid* briefly described by Lecco (*Ber.*, 1876, 9, 705) as resulting from the action of alcoholic soda on nitromethane; little or nothing, however, was recorded as to its reactions or constitution.

Methazonic acid crystallises in colourless plates which are easily soluble in water, alcohol, ether, acetone, warm benzene, or chloroform. It is strongly acid to litmus and to methyl-orange, and effervesces in contact with alkali carbonates. When quite pure, the acid is colourless, but on standing it soon becomes dark red, and in a short time almost completely changes into a red resin. It melts between 60° and 70°, the precise melting point depending on the rate of heating. During the heating the substance suffers decomposition, becoming at first red; as the heating is continued, the colour darkens, and at about 100° gas is evolved and water is deposited on the cool parts of the tube. At about 110°, the substance suddenly decomposes explosively, evolving hydrogen cyanide and some nitrous fumes, a black residue remaining.

Action of Acids and Alkalis.—Numerous experiments have been conducted on the action of acids and alkalis on the acid and its salts. The results justify the conclusion that the substance is decomposed, by hydrolysis following internal oxidation, into carbon dioxide, hydroxylamine, and hydrocyanic acid, as shown by the following equation:

The silver salt was boiled with hydrochloric acid (20 per cent.) for three hours in a flask with an upright condenser attached to a bottle containing soda solution; in this solution, both carbonate and cyanide were found, whilst the residual acid liquid in the flask when

evaporated furnished hydroxylamine hydrochloride together with some red resin. The same products, together with a little formic acid, are obtained by heating the ammonium salt with sulphuric acid (50 per cent.).

0.2272 gram of pure methazonic acid was mixed with concentrated hydrochloric acid and boiled for about an hour. The hydroxylamine in the residue was estimated by decinormal iodine solution in the presence of magnesia. It was proved that 0.0693 gram of hydroxylamine had been produced, which is about 96 per cent. of that required by the equation given above.

When heated with aqueous alkalis, methazonic acid is decomposed furnishing hydroxylamine, carbonate, and cyanide. If the heating is continued, nitrate and ammonia are also produced from the decomposition of the hydroxylamine.

0.1549 gram of the pure acid dissolved in water (free from carbon dioxide) was mixed with baryta water and the mixture heated in a sealed tube for four hours at 100° ; the precipitate of barium carbonate was washed from the tube, converted into sulphate and weighed.

0.332 gram of barium sulphate was obtained, equivalent to 0.0627 gram of carbon dioxide, which is 95.7 per cent. of that required by the equation given above. It is therefore clear that alkalis and acids produce similar changes in the compound.

Oxidation and Reduction.—On oxidation with permanganate in either acid or alkaline solution, the same products were invariably obtained, namely carbon dioxide, hydrogen cyanide, and nitric acid. The same result ensues when chromic acid or hydrogen peroxide is used as the oxidising agent. Many experiments have been made on the slow reduction of methazonic acid in the hope of obtaining a definite nearly related reduction product. Sodium amalgam, sodium in moist ethereal solution, zinc-dust and water, zinc and tin with dilute hydrochloric acid, as well as other reducing agents have been tried. In every case the same products were obtained, namely, ammonia and formic acid together with more or less resin. No trace of either ethylenediamine or methylamine could be found. It therefore seems probable that hydrolysis preceded, or accompanied, reduction in all these cases.

Red Resin.—The red resin which is so readily formed from methazonic acid is apparently very closely related to it in constitution, since it furnishes the same products on hydrolysis, reduction, and oxidation. It is probably a condensation product formed by the elimination of water or possibly a polymeride.

Action of Alkyl Iodides on Silver Methazonate.—When ethyl or methyl iodide is added to silver methazonate suspended in ether, reaction slowly occurs with separation of silver iodide. On filtering

and evaporating the solution in a vacuum desiccator a reddish-brown resin is obtained in which long, needle-shaped crystals are imbedded. The crystals may be extracted by warm benzene and obtained from this solution almost colourless. The yield, however, is extremely small, and it appears that the alkyl salts, $C_2H_3(CH_3)O_3N_2$, $C_2H_3(C_2H_5)O_3N_2$, of methazonic acid are even more unstable than the acid itself, readily changing into resinous products.

Constitution of Methazonic Acid.—Lecco has suggested that methazonic acid is an anhydride, $\begin{array}{c} CH_2 \cdot NO \\ | \\ CH_2 \cdot NO \end{array} > O$, formed from two molecules of nitromethane. This formula is, however, clearly inadmissible.

The reactions of the acid described above lead to the conclusion that the constitution of methazonic acid is represented by the follow-

ing formula, $\begin{array}{c} H_2C \cdot NH \\ | \quad | \\ HO \cdot N \cdot C \cdot O \\ | \\ O \end{array}$, which satisfactorily explains the formation of the products obtained by hydrolysis, reduction, and oxidation.

Action of Alkalis on Secondary Nitropropane.

Secondary nitropropane is much less readily attacked by alkalis than the primary nitro-compound. On heating with excess of aqueous soda in a closed tube for two hours at 115° , the liquid still contained some unaltered nitropropane. The products of the action are *acetone*, *nitrous acid*, and *hydroxylamine*, together with a small quantity of *hydrogen cyanide*. If the liquid is acidified, *propylpseudonitrole* is obtained, owing, no doubt, to the action of nitrous acid on the unchanged nitro-compound. As stated in the paper already referred to, no isoxazole is formed by the action of alkalis on secondary nitro-compounds.

Mechanism of the Action of Alkalis on Nitroparaffins.

In the previous paper (*loc. cit.*) it was pointed out that the remarkable action of alkalis on nitroparaffins "cannot be satisfactorily explained if the usual formula for nitroethane be rigidly adhered to," but that an explanation could be found if the tautomeric formula, containing a hydroxyl group, were employed.

Since this was written, Nef (*Annalen*, 1894, 280, 263) has published an important paper on the constitution of the salts of nitroparaffins, in which he supposes that their reactions can only be explained by adopting the view that the metal takes the place of the hydrogen of the hydroxyl group attached to nitrogen in the tautomeric formula of the nitro-compound. Thus for sodium nitroethane the formula $CH_3 \cdot CH : NO \cdot ONa$ is suggested, and for the sodium salt of secondary nitropropane the formula $(CH_3)_2C : NO \cdot ONa$.

The experimental evidence which Nef has brought forward in support of the tautomeric formula for the salts of nitroparaffins appears to us to be very strong, and his view seems to be much more in accordance with the facts than the assumption of V. Meyer that the metal is joined to the carbon owing to the influence exercised by the negative nitro-group on the hydrogen which is united to the same carbon atom.

The evidence for Nef's formula may be summarised as follows :

(i) When the cold aqueous solution of the salt of a nitroparaffin is decomposed with cold dilute acids the nitroparaffin is regenerated to a very small extent, the greater part of it being decomposed into nitrous oxide and an aldehyde (from primary compounds) or a ketone (from the secondary compounds) in accordance with the following equations :

This mode of decomposition indicates that the salts have not the same constitution as the original nitro-compounds, for if this were the case, on the addition of acid they would be completely reconverted into them.

Nef found that the sodium salt of nitroethane is almost quantitatively decomposed by dilute sulphuric acid in accordance with the above equation. This renders it probable that the first product of the action of the dilute acid on sodium nitroethane is the tautomeride, $CH_3 \cdot CH : NO \cdot OH$, which then undergoes intramolecular oxidation thus $2CH_3 \cdot CH : NO \cdot OH = 2CH_3 \cdot CHO + \begin{smallmatrix} N \cdot OH \\ | \\ N \cdot OH \end{smallmatrix} (= N_2O + H_2O)$.

The sodium salts of nitromethane and secondary nitropropane behave in a precisely similar manner. Moreover, when the mercuric chloride derivative of nitroethane, $C_2H_4(HgCl)NO_2$, is mixed with hydrochloric acid, nitrous oxide and acetaldehyde are produced, but no nitroethane.

(ii) If aqueous mercuric chloride is added to an aqueous solution of sodium nitromethane, mercuric fulminate is formed.

Nef has suggested that mercuric nitromethane is first produced and by intramolecular oxidation loses water, passing into mercuricfulminate.

Nef has adduced additional facts in support of this constitution of the fulminate, in particular the production of monochloroformoxime by the action of dilute hydrochloric acid, whilst more recently Scholl (*Ber.*, 1899, 32, 3492) has confirmed this formula by showing that benzaldehyde is produced by the action of mercuric fulminate on benzene in the presence of aluminium chloride.

(iii) By the action of methyl iodide on the silver salt of dinitroethane,

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formaldehyde and ethylnitrolic acid are produced. This is most simply explained by supposing that the methyl ether of dinitroethane is first formed and then undergoes intramolecular oxidation.

By the same supposition, the action of ethyl iodide on silver dinitroethane forming acetaldehyde and ethylnitrolic acid may be explained.

Although Victor Meyer (*Ber.*, 1895, 28, 202) still maintained the correctness of his formula for the metallic derivatives of the nitroparaffins, it must be admitted that all the experimental evidence produced by Nef very strongly supports the alternative contention that these compounds should be regarded as derivatives of the tautomerides of the nitroparaffins.

We are therefore justified in assuming the correctness of this tautomeric formula in discussing the mechanism of the remarkable reactions of alkalis and nitroparaffins first described by one of us in 1891.

It has been shown that when nitroethane is warmed with aqueous alkali, trimethylisoxazole, acetonitrile, and nitrous acid are formed in the proportions given by the equation

Representing the sodium salt of nitroethane by the formula $\text{CH}_3 \cdot \text{CH} : \underset{\text{O}}{\underset{\text{O}}{\text{N}}} \cdot \text{ONa}$, the existence of oxygen doubly linked to nitrogen enables the compound to act as a powerful oxidising agent.

The sodium derivative of acetaldoxime is thus formed, together with sodium nitrite and a residue $(\text{CH}_3 \cdot \text{C})_2$. Sodium acetaldoxime dissociates in the presence of water and the oxime tends to change into its tautomeric form, $\text{CH}_3 \cdot \text{CH} \cdot \text{NH}$,

and this then joins itself on to the $\text{CH}_3 \cdot \text{C}$ residues, forming trimethylisoxazoline,

which, in the presence of unaltered sodium nitroethane, is immediately oxidised, forming trimethylisoxazole and acetaldoxime.

The dehydration of this acetaldoxime accounts for the production of the acetonitrile,

Thus, starting with the tautomeric formula of nitroethane, we can at any rate now understand how the remarkable reaction described in the former paper may take place. The phases of the action may be summarised thus :

1. $3\text{CH}_3 \cdot \text{CH} \cdot \underset{\text{O}}{\underset{||}{\text{N}}} \cdot \text{ONa} = \text{C}_6\text{H}_{11}\text{ON} + 2\text{NaNO}_2 + \text{NaOH}.$
2. $\text{CH}_3 \cdot \text{CH} \cdot \underset{\text{O}}{\underset{||}{\text{N}}} \cdot \text{ONa} + \text{C}_6\text{H}_{11}\text{ON} = \text{CH}_3 \cdot \text{CH} \cdot \text{N} \cdot \text{OH} + \text{C}_6\text{H}_9\text{ON} + \text{NaOH}.$
3. $\text{CH}_3 \cdot \text{CH} \cdot \text{N} \cdot \text{OH} = \text{CH}_3 \cdot \text{CN} + \text{H}_2\text{O},$

or in one equation,

which agrees precisely with that given in the previous paper as the result of experiment.

With nitromethane the result is very different, the action of alkalis producing no isoxazole, but instead methazonic acid. The formation of this compound can, however, be understood if the tautomeric formula is adopted. The sodium salt of nitromethane being $\text{H}_2\text{C} \cdot \text{NO} \cdot \text{ONa}$, in aqueous solution it would react by intermolecular oxidation according to the following scheme :

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The sodium salt of formaldoxime thus generated will be dissociated into the tautomeric form of the oxime, $\text{H}_2\text{C}\cdot\text{NH}$, which, condensing with the nitromethane residue, will form the sodium salt of methazonic acid,

The different behaviour of the sodium salt of secondary nitropropane furnishing acetone, nitrite, and hydroxylamine when acted on by alkalis may be explained by its greater stability owing to the absence of the CH or CH₂ group which makes it less susceptible of intermolecular oxidation.

It is probable that the decomposition takes place by hydrolysis,

the "oxy-hydroxylamine" undergoing immediate decomposition with the production of hydroxylamine and nitrous acid,

The Reduction of Nitroparaffins and their Salts.

In the foregoing discussion, the reduction of the metallic derivatives of nitro-compounds to those of oximes is assumed to be possible. It has been previously stated (Dunstan and Dymond, Proc., 1894, 10, 139) that by the reduction of the nitroparaffins under certain conditions, the corresponding aldoximes and ketoximes are apparently produced, and it was suggested that these may possibly be intermediate products between the nitro-compounds and the substituted hydroxylamines, the formation of which has been observed by V. Meyer, Bamberger, and others.

In order to further elucidate this question, we have carried out a number of experiments on the reduction of the oximes, but in no case has the formation of any substituted hydroxylamine been observed. It therefore appears probable that the substituted hydroxylamines obtained by the reduction of nitro-compounds are not derived from previously formed oximes, and, moreover, our results seem to indicate that the oximes and hydroxylamines are not produced together, but each separately and under different conditions. The nitro-compounds themselves (reduction in acid or neutral solution) yield the hydroxylamines, whilst their salts (reduction in alkaline solution) furnish the

oximes (or their reduction products). This may be readily demonstrated by warming a few drops of nitroethane with either zinc dust and dilute acid or with zinc dust and water. After a minute or two the solution when filtered is found to reduce Fehling's solution powerfully in the cold, owing to the action of β -ethylhydroxylamine. On the other hand, if nitroethane is dissolved in solution of caustic soda and reduced with zinc dust, the filtered liquid has no reducing property.

These results are in accordance with the view that the salts of the nitroparaffins possess a different configuration from that of the nitro-compounds themselves. The first stage of the reduction of the nitroparaffins and of their salts may therefore be expressed by the following equations:

Since the suggestion above mentioned was published, two cases have been recorded in which nitro-compounds have been directly reduced to the corresponding oximes. Hantzsch and Schultze (*Ber.*, 1896, 29, 2252) have shown that phenylnitromethane, when reduced in alkaline solution with zinc dust or sodium amalgam, yields *syn*-benzaloxime. Bamberger and Weiler (*J. pr. Chem.*, 1898, ii, 58, 333) obtained 2-amino-3:5-dimethylbenzaloxime by reducing 2-nitro-3:5-dimethylphenylnitromethane (ω -2-dinitromesitylene) by means of sodium amalgam. It is noteworthy that in each case the reduction is effected in an alkaline solution.

SCIENTIFIC DEPARTMENT,
IMPERIAL INSTITUTE, S.W.