LVIII.—*The Decomposition of Nitric Esters by Lime.*

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Earlier Work on the Decomposition of Nitric Esters.

THE decomposition of nitric esters by water, acids, and alkalis has been investigated by many workers.

(a) Van Kerckhoff and Reuter (*J. pr. Chem.*, 1847, **40**, 262) studied the decomposition of "pyroxylin" or nitrocellulose by steam at 100°, and obtained as a principal product a "typhoxylin" or "cellulose dinitrate" containing 6.66 per cent. of nitrogen; they also record the separation of a lead salt, which was almost certainly identical with the lead hydroxypyruvate prepared by a similar method and described in detail by Will forty-four years later (*Ber.*, 1891, **24**, 401); by heating pyroxylin with potassium hydroxide at 60°, potassium nitrate, potassium nitrite, and a sugar were formed.

(b) The production of potassium acetate and potassium formate, together with potassium nitrate and potassium nitrite in the ratio $\text{KNO}_3 : 2\text{KNO}_2$, was recorded by Hay (*Mon. Sci.*, 1873, [iii], **15**, 424), who accounted for the fact that five molecules of potassium

hydroxide were required for the decomposition of one molecule of nitroglycerin by putting forward the equation

(c) Berthelot (*Compt. rend.*, 1900, **131**, 519) described the production of polymerisation-products of aldehyde by the action of solid potassium hydroxide on ethyl nitrate, and put forward (only to reject it in favour of an alternative view) the suggestion that the formation of nitrites in the action of potassium hydroxide on nitroglycerin might be due to a decomposition of the nitric ester into glyceraldehyde, as shown in the equation

(d) Silberrad and Farmer (*T.*, 1906, **89**, 1182, 1759) also detected acetic and formic acids, with nitric and nitrous acids, amongst the products of decomposition of 100 kilograms of nitrocellulose which had been stored at 54° during a period of twenty-three weeks; in addition, they proved the presence of ethyl nitrate, ethyl nitrite, and alcohol (perhaps derived from the alcohol-ether mixture used as a solvent in gelatinising the nitrocellulose), of butyric, dihydroxybutyric, oxalic, tartaric, and *isosaccharic* acids, and of a fermentable sugar, but they did not find either glycerol or cellulose amongst the products of decomposition of cordite by water or in presence of alkalis.

(e) Berl and Delpy (*Ber.*, 1910, **43**, 1421), by the action of alcoholic potassium hydroxide on nitroglycerin, obtained a glyceryl $\alpha\alpha'$ -dinitrate, but were unable to detect either the mononitrate or glycerol itself.

(f) Klason and Carlson (*Ber.*, 1906, **39**, 2752), by the action of alcoholic sodium hydroxide on nitroglycerin in the presence of phenyl mercaptan, were able to recover glycerol, the mercaptan being oxidised to phenyl disulphide; by the same method they obtained from nitrocellulose a sample of cellulose of correct composition and free from nitrogen, whilst under similar conditions, ethyl nitrate gave the nitrate and nitrite of the alkali, but no trace of polymerised aldehyde. These observations are in line with the well-known fact that glycerol can be recovered from nitroglycerin by the action of sodium sulphide. A similar action to that of phenyl mercaptan is observed when hydrogen peroxide is added to the mixture (Carlson, *Ber.*, 1907, **40**, 4191); the hydrogen peroxide acts here as a reducing agent, just as it does towards potassium permanganate, and gaseous oxygen is liberated as a by-product.

Products of Decomposition of Cordite by Lime.

During the early months of 1919, the authors of this paper had an opportunity of examining the products obtained by the decomposition of cordite by means of lime in the presence of pyridine. The use of pyridine as a catalyst in this action was discovered by Prof. Hodgkinson, and no other substance is known which is equally effective in promoting the controlled decomposition of cordite. The product is a brown sludge, which can be dried in thin layers on a hot plate to a hard, brittle, porous mass resembling ginger-biscuits. Drying on a large scale is more difficult, but when the sludge is evaporated at a low temperature until it contains only about 17 per cent. of water, it solidifies on cooling, probably owing to the crystallisation of calcium nitrate in the form of the tetrahydrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, or the basic compound,

(Bassett and Taylor, T., 1914, **105**, 1926); after casting, the solid product will dry spontaneously in a warm atmosphere, and can then be powdered without difficulty.

In addition to ammonia and the oxides of nitrogen, which escape during the decomposition, the following products have been detected in the sludge:

(a) "*Cellulose Trinitrate*."—When a half-decomposed cordite sludge is extracted with water and acid, and the dried residue is warmed with 95 per cent. alcohol and filtered, the addition of water to the alcoholic solution causes the precipitation of a yellowish-white, viscid precipitate, which contains $\text{N}=9.6$ per cent. and is highly inflammable. A similar substance has been described by Angeli (*Atti R. Accad. Lincei*, 1919, [v], **28**, i, 20), who obtained it by the addition of water to a solution of gun-cotton in pyridine (compare also Berl and Fodor, *Zeitsch. ges. Schiess.-u. Sprengstoffw.*, 1910, **5**, 254, 269). The formula $\text{C}_{12}\text{H}_{17}\text{O}_7(\text{NO}_3)_3$ requires $\text{N}=9.15$ per cent.

(b) "*Cellulose Dinitrate*."—Analysis by the Schultze-Tiemann method of black charred rods remaining undecomposed after thirty-three hours' treatment with an insufficient supply of lime showed the presence of 6.7 per cent. of nitrogen as compared with 12.2 per cent. in the original nitrocellulose. The composition of this residue agrees in a remarkable way with the figure obtained by van Kerckhoff and Reuter (*loc. cit.*). The percentage of nitrogen required for the formula $\text{C}_{12}\text{H}_{18}\text{O}_8(\text{NO}_3)_2$ or $\text{C}_6\text{H}_9\text{O}_4 \cdot \text{NO}_3$ is 6.76.

From these observations, it appears probable that the nitro-cellulose, which contains originally four or five NO_3 -groups for every twelve carbon atoms, is hydrolysed in successive stages to

compounds containing three and two nitro-groups, but that after this point has been reached, the molecule decomposes completely.

(c) *Glycerol*.—Prof. Hodgkinson had already shown that glycerol could not be extracted as a by-product from the residues obtained from the decomposition of cordite by lime and pyridine. Careful tests for the presence of glycerol were, however, carried out, in order to ascertain whether the toxicity to plants, which Dr. Russell reported in some of the earlier products, might not be due to the presence of glycerol in quantities insufficient for commercial recovery. A highly toxic solution obtained after forty-eight hours' treatment was found to contain no glycerol, and its toxicity was traced to the hydroxypyruvic acid which it contained (see below). A similar negative result was obtained on examining a sludge which had been heated during a period of only ten hours, at which stage practically all the nitroglycerin had disappeared, whilst most of the nitrocellulose was left unattacked in the form of brittle, porous rods.

In order to determine whether glycerol could be detected amongst the earliest products of decomposition, a special batch of sludge was prepared by heating, for one hour only at 95° to 100°, 450 grams of cordite clippings with the usual proportion of quicklime (225 grams), but using a very large excess of pyridine, namely, 4 litres of a 5 per cent. solution, that is, 44 per cent. of pyridine on the weight of cordite used instead of the usual proportion of 0.5 per cent. The decomposition was extremely rapid and complete; no traces of cordite could be seen at the end of one hour, and it was estimated that the action had proceeded at least as far as in twenty-four hours of treatment under ordinary conditions. The filtrate from this sludge was tested for glycerol, and traces of this compound were detected by the following tests:

(i) A drop of phenolphthalein was added to a 5 per cent. solution of borax; on adding the suspected liquid, the red colour was discharged, and, on boiling, it partly returned.

(ii) On heating the dry residue with potassium hydrogen sulphate, the choking odour of acrolein was noticed.

(iii) On heating with alkaline potassium permanganate, a partial reduction occurred.

(d) *Calcium Nitrate and Nitrite*.—A sample of sludge prepared by a similar method from 900 grams of cordite (with 22 per cent. of its weight of pyridine), after one hour's heating, gave for the first time an excellent yield of colourless, crystalline calcium nitrate. It is therefore possible that the action of pyridine on cordite differs from that of alkalis and of lime in giving an appreci-

able quantity of the products of direct hydrolysis, namely, glycerol and nitrates, and a much smaller proportion both of nitrites and of oxidised organic compounds; in other words, the decomposition by pyridine may perhaps be compared with that effected by alkali sulphides rather than by alkali hydroxides or by lime. The presence of nitrites is shown by the invariable liberation of oxides of nitrogen on acidifying the sludge.

(e) *Oxalic Acid*.—The fraction of the calcium salts which was soluble in hot dilute nitric acid, but insoluble in acetic acid, gave, after prolonged purification, a crystalline specimen of oxalic acid. A quantitative test by oxidation with potassium permanganate indicated that the calcium salts insoluble in acetic acid contained 62 per cent. of calcium oxalate.

(f) *Formic and Acetic Acids*.—Qualitative tests for these two acids gave in each case a positive result in only one of the tests applied, the other tests giving negative results. It is therefore clear that they can only have been present in very minute proportions, and that Hay's equations represent only a very minor part of the particular decomposition which we have studied.

(g) *Hydroxypyruvic Acid*, $\text{HO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$.—After calcium oxalate and calcium nitrate and nitrite, the calcium salt of this acid appears to be the most important product of decomposition. Will prepared it by the decomposition of nitrocellulose, and it does not appear to have been described as a separate product of decomposition from nitroglycerin; on the other hand, the fact that it appears at a very early stage in the decomposition of cordite by lime and pyridine, and tends to disappear during the latter part of the decomposition, suggests that in this action it may be derived, at least in part, from nitroglycerin, to which it can be related by very simple equations.

Hydroxypyruvic acid was found to be present in every case in which the products of decomposition of cordite were reported as having a toxic action on plants, and a specimen of the calcium salt sent to Rothamsted for trial was reported as being extremely toxic. The presence of the acid was confirmed by preparing the osazone.

(h) $\beta\gamma$ -*Dihydroxybutyric Acid*.—The residue from the preparation of the osazone, after removing the excess of phenylhydrazine by extraction with ether, can be re-precipitated as a lead salt and then converted into a calcium salt. This has the properties of the calcium salt of dihydroxybutyric acid (Silberrad and Farmer, *loc. cit.*), that is, the calcium salt is soluble, but gives an insoluble lead salt and does not yield an osazone; unlike the

hydroxypyruvate, this calcium salt was proved not to be toxic to plants.

The two calcium salts described under (g) and (h), instead of appearing as mere traces, like the formate and acetate, are often formed in considerable quantities, and in one experiment alone a test-tube full of the mixed lead salts was separated.

Decomposition of Nitric Esters not a Simple Hydrolysis.

The object of bringing forward these observations and comparing them with earlier work on the same subject is to direct attention to the wide divergence between the experimental facts and the traditional theory in which the decomposition of nitric esters by alkalis is described as if it were a normal case of the hydrolysis of an ester complicated only by secondary processes of oxidation and reduction of the primary products.

The absence of glycerol as a product of decomposition of cordite is specifically referred to by Silberrad and Farmer, who made experiments under a variety of conditions, and also by Berl and Delpy in their study of the action of alcoholic potassium hydroxide on nitroglycerin. Prof. Hodgkinson also noticed at a very early period of his experiments that glycerol cannot be recovered as a product of the decomposition of cordite by lime in the presence of a small proportion of pyridine. Our own experiments fully confirm this conclusion, and a recent French patent, in which it was claimed that glycerol as well as sodium nitrate could be recovered from the products of the action of sodium hydroxide on mixtures of nitrocellulose and nitroglycerin "by the ordinary methods of the soap-manufacturer," was based on experiments with nitrocellulose powders only, and must be regarded as evidence rather of the optimism of the inventor than of the actual behaviour of nitroglycerin towards sodium hydroxide. The general experience seems to be that, in the absence of a reducing agent, glycerol is not regenerated.

This anomalous behaviour of nitroglycerin is repeated in nitrocellulose, which does not give any cellulose when decomposed by water or by alkalis (Silberrad and Farmer), as well as in simpler compounds, such as ethyl nitrate.

In order to account for this anomaly, whilst maintaining the view that the fundamental action is a hydrolysis or saponification of the normal type, a number of hypothetical reactions have been postulated. Thus, Silberrad and Farmer found it "somewhat surprising that no unchanged cellulose or glycerol should be

regenerated on hydrolysis, for if nitric acid is brought into contact with cellulose or glycerol in the concentrations which come into consideration in the hydrolysis, no oxidation occurs." They were therefore driven to the conclusion "that the nitric acid which has just been set free from the nitric ester is in a more active condition than nitric acid in its ordinary form."

In a similar way, Hay explained the production of potassium nitrate, nitrite, acetate, and formate by the action of potassium hydroxide on nitroglycerin as due to three consecutive actions, the second of which (a decomposition of glycerol by potassium hydroxide) is purely hypothetical, thus:

(i) A primary hydrolysis producing glycerol and potassium nitrate according to the equation

(ii) A hypothetical action, whereby the glycerol was converted by the action of the alkali hydroxide into potassium acetate and formate, together with water and "nascent hydrogen,"

using up two additional equivalents of potassium hydroxide (above those required for hydrolysis), as observed in his experiments.

(iii) A reduction by the nascent hydrogen of two-thirds of the potassium nitrate already produced,

Alternative Explanations of the Decomposition of Nitric Esters.

(a) As an alternative to the hypothetical "hydrolysis" represented by the equation

Vignon and Maquenne (*Ann. Chim. Phys.*, 1891, [vi], **24**, 522) have assumed the intermediate formation and decomposition of an isomeric nitrite, $\text{R}\cdot\text{CH}(\text{OH})\cdot\text{O}\cdot\text{NO}$, which, by direct hydrolysis, would give rise to nitrous acid and a dihydroxy- (or carbonyl) compound, so that, for instance, the conversion of nitrotartaric acid into dihydroxytartaric acid may be represented by the following scheme:

This hypothesis has the disadvantage that no evidence has been produced of the concrete existence of the isomeric nitrite, and on many grounds we prefer the alternative views set out under (b) and (c) below. The paper is, however, important on account of the clear recognition by the authors of the fact that the decomposition of a nitric ester by an alkali may yield a ketone and a nitrite, instead of giving an alcohol and a nitrate as the primary products of decomposition.

(b) This alternative hypothesis was put forward in its simplest possible form in 1900 by Berthelot, who suggested that the decomposition of a nitric ester may proceed according to the equation

in place of the traditional equation

Our own experiments, confirming as they do the observations of earlier workers, indicate that Berthelot's equation actually represents the main course of the decomposition; indications of a real hydrolysis are apparently confined to the production, as by-products, of partly hydrolysed compounds, such as Berl and Delpy's dinitrate and the lower cellulose nitrates described in the early part of the present paper.

(c) An elaboration of Berthelot's view was put forward a few years later by Klason and Carlson (*loc. cit.*), who suggested that the primary products are not the alcohol and a nitrate, thus:

but an alcohol-peroxide and a nitrite,

In the ordinary course of events, the peroxide will decompose into an aldehyde and water,

but when a reducing agent, such as phenyl mercaptan, is present, the peroxide is reduced to the alcohol and the mercaptan is oxidised to phenyl disulphide,

In the same way, when hydrogen peroxide is present, the peroxide may be reduced to the alcohol, as shown in the equation

(d) If it be assumed that the primary decomposition of a nitric ester yields either a peroxide or an aldehyde, together with a nitrite, instead of an alcohol and a nitrate, it is easy to account for many of the products which have actually been obtained by the decomposition. Thus, in the case of nitroglycerin, complete

560 THE DECOMPOSITION OF NITRIC ESTERS BY LIME.

decomposition on these lines would give rise to a compound containing three carbonyl groups:

From this intermediate compound, mesoxalic acid, reported by Berl and Delpy as a product of "hydrolysis" of nitroglycerin by alcoholic potassium hydroxide, could be produced by the normal oxidation of an aldehyde to an acid,

the further oxidation of mesoxalic acid would yield oxalic acid, a principal product of decomposition in the case which we have studied. Hydroxypyruvic acid (the formation of which has, however, been recorded only in the case of nitrocellulose and of cordite, and not from pure nitroglycerin) could be produced by a mere addition of the elements of water to the intermediate product formulated above:

(e) In our experiments, the decomposition of nitroglycerin into acetic and formic acids takes place only to a very minute extent. The formation of traces of formic acid from the oxidised compounds set out above can be explained readily, but the production of acetic acid is a far more startling type of decomposition, since the formation of the methyl group in acetic acid necessarily involves a process of reduction in a medium in which the conditions appear to favour the oxidation rather than reduction of the organic constituents. It is conceivable that acetic acid and formic acid may be produced by the decomposition of pyruvic acid, formed by reduction from hydroxypyruvic acid,

There is, however, more evidence for the decomposition of this acid into acetaldehyde and carbon dioxide,

a change which has been postulated as an essential stage in alcoholic fermentation. In any case, the simultaneous oxidation and reduction which leads to the conversion of dextrose into carbon dioxide and alcohol finds strong analogies in the production, not only in the case of acetic acid, but also of butyric and dihydroxybutyric acids as products of the decomposition of nitrocellulose, since both of these acids agree with acetic acid in containing a fully-reduced methyl or methylene group.

Summary.

(1) Hydrolysis or saponification of the normal type is not the predominant action when cordite is decomposed by lime in the presence of pyridine.

(2) Traces of glycerol were detected only when a very large excess of pyridine was used; these conditions were also the only ones in which a clean, crystalline calcium nitrate was obtained. The calcium salt of hydroxypyruvic acid is, however, an important product of the action.

(3) Two partly denitrated celluloses, corresponding approximately with the formulæ $C_{12}H_{18}O_8(NO_3)_2$ and $C_{12}H_{17}O_7(NO_3)_3$, were obtained as by-products of incomplete decomposition, but no cellulose was obtained when the decomposition was carried to completion.

(4) It is therefore suggested that the main action is a decomposition of the nitric ester into a ketone or aldehyde and a nitrite, instead of a hydrolysis to an alcohol and nitric acid.

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