XCIX.—*The Effect of Reducing Agents on Tetranitromethane, and a Rapid Method of Estimation.*

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PREVIOUS work by one of us (T., 1915, **107**, 87) indicated that tetranitromethane contained one labile nitro-group, and it appeared likely that this would be removed in reduction, so that guanidine seemed the most probable product of extreme reduction. Acid reduction experiments with tin and nickel-coated zinc carried out by Rakshit (*J. Amer. Chem. Soc.*, 1914, **36**, 1221) resulted in the production of guanidine. A study of alkaline and electrochemical reduction methods has been undertaken by us, and in this paper the effect of some alkaline reducing agents is recorded. It is hoped to communicate later the results of electrochemical methods.

The reductions now described have resulted in the removal of the labile "nitroite" group, with the production of salts of nitroform, which may be conveniently and safely prepared by the methods described. The procedure consisted in agitating the nitro-

compound with aqueous solutions of the reducing agents containing a requisite amount of potassium hydroxide, which neutralises the nitroform produced, precipitating it as the sparingly soluble potassium salt. The solutions are thereby prevented from becoming acid, and secondary action with the reducing agent is avoided. Aqueous potassium hydroxide itself attacks tetranitromethane, with the formation of the potassium salt of nitroform, together with nitrate, nitrite, and carbonate of potassium, the quantities of which vary with concentration. The decomposition in such case, however, is much slower than when a reducing agent is present, and in the latter case the tetranitromethane is generally all converted into nitroform without the loss entailed in the formation of potassium carbonate.

Results have been obtained, amongst others, with sodium sulphite, potassium sulphite, sodium potassium tartrate, and hydrazine. In all cases, the nitroform salt has been identified by estimation of the percentage of potassium contained in the salt recrystallised from water; this was decomposed by sulphuric acid and the potassium weighed as sulphate.

Other reducing agents have also been tried with success; potassium phosphite and potassium sulphide may be mentioned as instances. In the case of the sulphide, much sulphur is precipitated, from which the nitroform salt is removable only with some difficulty. Aqueous solutions of sulphur dioxide do not attack tetranitromethane even after long-continued shaking. Ammonium sulphide readily decomposes it, but in this case the reduction seems to be carried past the nitroform stage, and the products, as yet, have not been identified.

Sodium Sulphite.—On shaking an aqueous solution of sodium sulphite with tetranitromethane, the solution gradually becomes coloured, and the odour of tetranitromethane ultimately disappears. Nitrous fumes are evolved as the reaction proceeds, and the solution becomes acid. If sodium hydroxide is added to the solution at the beginning of the reaction, the decomposition is more satisfactory, and if the solution does not become acid, there is no evolution of nitrous fumes. When the reduction is complete, the solution contains the sodium salt of nitroform, and responds to tests for nitrites and sulphates. Sodium hydroxide is used up in the reaction, and if sufficient is not present the solution becomes acid. The reaction proceeds according to the equation

In an actual experiment, 40 grams of sodium sulphite were dissolved in 300 c.c. of water, sodium hydroxide solution being present. Eighteen grams of tetranitromethane were added, and

the mixture was shaken for half an hour. Sodium hydroxide was added at intervals as required. After about an hour, the odour of tetranitromethane had completely disappeared, and the solution was deep orange. No nitroform salt separated out, but, on acidifying with sulphuric acid and extracting with ether, nitroform was obtained. The yield may be ascertained by adding potassium alkylxide to an aliquot part of the ethereal solution to precipitate the characteristic potassium salt. The yield of potassium salt from the above quantities was 12 grams.

Potassium Sulphite.—The use of this is preferable to sodium sulphite, since the sparingly soluble potassium salt of nitroform is precipitated, and may be isolated by filtration. The solution is liable to become acid during the process, and small quantities of potassium hydroxide solution must be added at intervals. After the experiment, the solution responds to tests for sulphate, and it is therefore evident that the initial strength of the sulphite solution must be such that the less soluble sulphate will not finally be present in quantities sufficient to saturate the solution and crystallise out, contaminating the nitroform salt.

Arsenious Acid.—This proves a very good reducing agent, degrading tetranitromethane to the nitroform salt in a short time. In a typical experiment, 25 grams of arsenious oxide were dissolved in 200 c.c. of water, a sufficient quantity of potassium hydroxide being added. On the addition of 10 grams of tetranitromethane, the yellow nitroform salt separated out after a little vigorous shaking. After a short time, the tetranitromethane was completely decomposed, and 7.8 grams of dry nitroform salt were collected. The crystals so obtained are dull yellow, but, after recrystallisation from water, have the characteristic yellow appearance of the pure salt. The filtrate responds to the usual tests for nitrites and arseniates.

Hydrazine.—Preliminary experiments indicated that tetranitromethane was rapidly acted on by hydrazine, nitrogen being evolved. In an experiment on a larger scale, 20 grams of hydrazine sulphate and 40 grams of potassium hydroxide were added to 500 c.c. of water. Thirty grams of tetranitromethane were then added in small quantities, the mixture being gently shaken in an unstoppered bottle. The potassium salt of nitroform rapidly separated, and the reduction was complete in a quarter of an hour. Twenty-five grams of the dry nitroform salt were collected from this experiment. The reaction proceeds according to the equation

It appeared probable that a method for estimating tetranitromethane could be based on this reaction, and it is found that the

method gives results within the limit of experimental error. Half a gram of tetranitromethane is a convenient amount to use, as it liberates some 30 c.c. of nitrogen from hydrazine solutions. As the estimation is carried out in a Lunge nitrometer graduated to 0.2 c.c., the experimental error in reading the volume of gas evolved in the reaction may well be this amount. From the quantitative relation given above, 0.2 c.c. of nitrogen corresponds approximately with 0.0035 gram of tetranitromethane. Using half a gram of the nitro-compound, the error in reading the nitrometer should theoretically be within a margin of 1 per cent. The results obtained are well within this limit.

Phenylhydrazine has been substituted for hydrazine in some observations, but the volume of nitrogen liberated was some three times greater than the calculated quantity. The reduction with this reagent is evidently carried past the nitroform stage, and in actual experiments, phenylhydrazine was found to liberate more than the additional two volumes when it acted on the potassium salt of nitroform.

As hydrazine itself does not attack the nitroform salt, the method can be applied to estimate tetranitromethane in solutions which also contain nitroform, and since the reaction takes place in the presence of excess of potassium hydroxide, it may be used for estimation of solutions containing nitrous and nitric or other mineral acid in addition to the nitro-compound.

In the estimation, a Lunge nitrometer is filled with mercury, as in the Crum method of estimating nitrates. A 10 per cent. solution of tetranitromethane in alcohol is of a convenient strength for use. The nitro-compound was purified by repeated washings with water and by subsequently freezing and melting several times. It was colourless and melted at about 13.4° . The hydrazine solution is prepared by adding 10 grams of hydrazine sulphate and 20 grams of potassium hydroxide to about 80 c.c. of water, filtering, and diluting to 100 c.c. Five c.c. of the freshly prepared hydrazine solution contain an excess of the reagents required by 5 c.c. of the tetranitromethane solution. One c.c. of the hydrazine solution is introduced into the nitrometer, and the last traces are washed in with small quantities of water. This acts as a cushion, which prevents contact of the solution of the nitro-compound with the mercury. Five c.c. of the tetranitromethane solution are now carefully introduced and washed in with alcohol. This solution floats on the top of the hydrazine solution previously introduced, and little reaction takes place. Four more c.c. of the hydrazine solution are now added, and, on falling through the tetranitromethane solution, a reaction rapidly ensues. Nitrogen is quickly

evolved, and the potassium salt of nitroform is precipitated. On account of the rapidity with which the nitrogen is evolved, it is imperative to have the mercury poured out of the side-limb of the nitrometer before the introduction of the hydrazine solution. If this is not done, there is an inevitable loss of nitrogen, as the mercury is driven down quickly, and consequent pressure develops almost immediately. The main reaction is over in less than a minute, but further traces of nitrogen are evolved on shaking once to mix the solutions thoroughly. As the reaction is exothermic, the nitrometer must be allowed to remain for some time before a volume reading is taken.

Sodium hydroxide may be substituted for potassium hydroxide, but the latter is preferable. The following are typical results, obtained at various times by different observers. Five c.c. of a 10 per cent. solution of tetranitromethane in alcohol were taken in each case, and the weights of tetranitromethane in 100 c.c. of solution were found to be: (1) 9.938; (2) 9.904; (3) 9.994; (4) 9.926 grams.

It is therefore evident that the reduction of tetranitromethane by hydrazine is quantitative, and the reaction affords an easy and rapid method for estimating the nitro-compound. Conversely, standard solutions of tetranitromethane may be employed in the estimation of hydrazine in solutions of its salts.

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