

XLV.—*On a New Method of preparing Dinitroethylic Acid.*

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THE method first described by one of us (*Phil. Trans.*, **147**, 59) of preparing dinitroethylic acid ('N₂'EtOHo) by the action of zinc ethyl upon nitric oxide was difficult and inconvenient. Owing to the slowness with which zinc ethyl absorbs nitric oxide at ordinary pressures, it was necessary to work with the gas at a pressure of 20 atmospheres. The zinc-ethyl was contained in a copper digester, into which the nitric oxide was forced by means of a condensing syringe. Probably the difficulty of preparing it has prevented any further investigation of this singular compound, since its first discovery a quarter of a century ago. The method we are about to describe is based on the superior reactivity of sodic ethide, which effects a rapid absorption of nitric oxide at ordinary pressures, and renders possible the preparation of considerable quantities of dinitroethylic acid in a short time.

In our first experiments, thoroughly dried nitric oxide was passed into a flask containing the double compound of sodic ethide and zinc ethyl. This method was found not to work well; the double compound soon solidified, and was acted on only superficially by the nitric oxide. By employing less sodium than was required for the complete conversion of the zinc ethyl into the double compound, the fluidity of the mass was to some extent preserved; but even then the contents of the flask became pasty towards the close of the reaction, and the process was both tedious and wasteful. In addition to this, two explosions, one of them very violent, convinced us that it had the further disadvantage of being dangerous.

It seemed to us that all these disadvantages might be removed if a suitable solvent for the double compound could be found. Benzene was tried and was found to answer admirably, as it dissolved the substance readily, and was neither so volatile as to be carried away in any quantity by the indifferent gases, which had to be let off from time to time, nor of so high a boiling point as to present difficulties in the way

of getting rid of it when necessary. The benzene solution of zinc-sodic ethide lends itself to all the reactions of the undissolved substance, absorbing carbonic anhydride and carbonic oxide, the latter however, but slowly. It will probably be a convenient form in which to employ this otherwise rather unmanageable reagent.

The method which we have finally adopted for the preparation of dinitroethyllic acid is as follows:—

100 grams of pure zinc ethyl are introduced into a tubulated distilling flask and a quantity of sodium sufficient for the conversion of the whole of the zinc ethyl into the compound ZnNaEt_3 is added in thin slices. The flask must be immersed in water whenever the temperature shows a tendency to rise too high. A neglect of this precaution when working on this large scale may lead to loss, the heat evolved by the exchange of sodium for zinc being sufficient to boil off the zinc ethyl and totally destroy the product. When the action is complete, the contents of the flask will, if allowed to stand, solidify to a crystalline mass of zinc-sodic ethide. 100 c.c. of benzene are now added. The flask is fitted with a cork, through which passes a wide glass tube, reaching to within about an inch of the surface of the liquid, and serving for the introduction of the nitric oxide. The tube must be straight, so that in case of stoppage, it may be instantly cleared by passing a wire through it. To the tubulure of the flask is attached a short piece of black caoutchouc tubing closed by a clip, this opening being intended for the escape of unabsorbed gases. During the operation, the flask is wrapped in cloths and immersed in water. Pure nitric oxide, generated from nitre, ferrous sulphate, and dilute sulphuric acid, and collected in a glass gasholder, is thoroughly dried by passing through concentrated sulphuric acid, and is led through the wide glass tube into the flask containing the benzene solution of zinc-sodic ethide. Absorption takes place rapidly, and is further aided by shaking the flask. When it ceases owing to the accumulation of neutral gases (principally ethylic hydride, the formation of which is due to the presence of a trace of moisture in the nitric oxide), the clip is opened, and a rapid current of nitric oxide is sent through the apparatus. A sheet of white paper, placed behind the end of the exit tube, shows the escape of the nitric oxide by the formation of red fumes, upon which the tube is closed by the clip, and the absorption, aided by shaking, goes on as before. In this way about four liters of gas can be passed into the apparatus in the course of an hour. Towards the close, however, the absorption is more sluggish. If the mass becomes too pasty, more benzene may be added. As soon as the absorption has practically ceased, the flask is disconnected and ordinary commercial ether added to the contents, the flask being kept cool. This liquid contains sufficient alcohol and water to decompose

the excess of zinc ethyl in the mixture. The action of water, or even of alcohol, alone is too violent, and is apt to destroy a portion of the product. After a considerable quantity of ether has been employed and the action has begun to slacken, a little alcohol is gradually added. Finally, the decomposition is completed by means of an excess of water. Carbonic anhydride is then passed into the solution containing the precipitate of zincic hydrate. By this means both the free caustic alkali and the zincic hydrate are converted into carbonates, the former being thus prevented from exercising any destructive influence on the dinitroethylic acid during the subsequent evaporation, whilst the latter can be more readily filtered off. The liquid is now filtered roughly through calico, and the precipitate of zincic carbonate is carefully washed. The filtrate is evaporated to dryness and the mixed salts extracted with absolute alcohol, which dissolves only the sodic dinitroethylate. On evaporating the alcoholic solution, the latter salt remains as a crystalline deliquescent mass. The sodium salt is then converted into the copper salt, which, from its admirable crystalline properties, can readily be obtained in a state of perfect purity. For this purpose the sodium salt is dissolved in a small quantity of water, and an excess of concentrated solution of cupric sulphate is added. The mixed solution is evaporated nearly to dryness, the operation being best performed *in vacuo* in order to avoid decomposing the copper salt. On extracting with alcohol, a solution of almost pure cupric dinitroethylate is obtained, which, on evaporation, yields the characteristic large dark blue flat needles of this salt.

In some carefully conducted experiments, a yield of 50 per cent. of the theoretical quantity of the pure copper salt, calculating from the weight of sodium employed, was obtained.

We intend to study the reactions of dinitroethylic acid with a view to throw light upon its constitution.
