36. *The Thermal Decomposition of Guanidine Perchlorate. Part I. Reaction Products and Mechanism.*

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The behaviour of guanidine perchlorate at 300—450° has been studied, and from the analysis of the gaseous and (intermediate) solid products a tentative mechanism for the decomposition is proposed.

ALTHOUGH guanidine perchlorate may be expected to have more favourable properties as an explosive than, *e.g.*, ammonium perchlorate (Lothrop and Handrick, *Chem. Reviews*, 1949, **44**, 419), its thermal decomposition does not appear to have been studied. Pyrolysis of ammonium perchlorate has been investigated by Dode (*Bull. Soc. chim.*, 1938, **5**, 170) and that of the guanidine chromates by Chuk-Ching Ma (*J. Amer. Chem. Soc.*, 1951, **73**, 1333).

The following observations were made of the behaviour of guanidine perchlorate (m. p. 240°) at high temperatures and atmospheric pressure: (*a*) When it is heated at or below 300° for several hours it suffers only a very slight loss of weight. (*b*) Above 400° ignition occurs, but always after a definite period of initiation, and with the formation of a yellow solid residue. (*c*) In the range 300—400°, decomposition proceeds at a measurable rate and the reaction goes to completion.

The intermediate and the gaseous final products obtained at 340—390° are now described, and a mechanism for the thermal decomposition in this range is proposed.

EXPERIMENTAL

Guanidine perchlorate, prepared from the chloride and sodium perchlorate, and twice recrystallised from water, had m. p. 240° (Found: N, 25·9. Calc. for $CH_5N_3,HClO_4$: N, 26·3%).

The volume of the gases evolved was determined in Pyrex apparatus similar to that used by Glasner and Weidenfeld (*J. Amer. Chem. Soc.*, 1952, **74**, 2464). Temperatures were measured with a calibrated chromel–alumel couple and kept constant by manual regulation of a powerstat. Samples of 0·1 g. were used for each experiment, as larger quantities might be explosive, and the gases were analysed in the conventional manner.

The vacuum-apparatus has been described by Glasner and Simchen (*Bull. Soc. chim.*, 1951, **18**, 233). The initial pressure measured by the McLeod gauge was 6 μ; it rose by the end of the experiment (after 1 hour) to 9 mm. From the pressure and the known volume of the apparatus, the volume of the gases evolved was calculated.

For the determination of chlorides, the gases evolved and the apparatus were washed with distilled water. Aliquot parts of the solution thus obtained were titrated with 0·01N-sodium hydroxide and 0·1N-silver nitrate (Volhard).

Gaseous Products.—Analyses of the gases formed indicates that the thermal decomposition can be described by the equations:

$$2CH_5N_3,HClO_4 \longrightarrow 2HCl + 5H_2O + CO + CO_2 + 3N_2 \quad (1)$$
$$2CH_5N_3,HClO_4 \longrightarrow 2HCl + 2NH_3 + O_2 + 2N_2 + 2CO_2 + 2H_2O \quad (2)$$

In addition, small quantities of chlorine, hydrogen, and (above 400°) nitrogen dioxide were formed. The amount of permanent gases collected was within 90—94% of that expected for both equations, *viz.*, 2·5 mols. The balance may be accounted for by a small residue of ammonium perchlorate.

From the amount of carbon monoxide or carbon dioxide, or from the ratio of free hydrogen chloride to ammonium chloride, the relative importance of the two reactions can be determined. The following data show that, generally, reaction (2) predominates, reaction (1) becoming more pronounced with increasing temperature.

Temp.	345°	370°	380°
HCl/NH_4Cl	24·4/75·6	38·6/61·4	39·5/60·5

The results for the relative weights of reactions (1) and (2), calculated from determinations of the carbon dioxide formed, accord well with those obtained from the chloride determinations;

e.g., the percentage of carbon dioxide in the gases obtained after complete decomposition at 370° was 32·3%, corresponding to a relative importance of 61·5% for reaction (2).

The total volume of gases obtained from the decomposition of the salt *in vacuo* at 350° was only 18% of that obtained at atmospheric pressure, and the greater part of the sample was converted into the above-mentioned yellow substance. This appears to be connected with the observation that, under these conditions, ammonium perchlorate is deposited on the cooler parts of the reaction vessel.

Solid Intermediates.—In the temperature range 320—390°, the molten salt gradually changed into a waxy solid before decomposing completely. When the reaction was stopped at this stage, the solid was found to consist partly of ammonium perchlorate; this dissolved in cold water, and the remainder of the solid was separated by boiling water into a soluble fraction (A) (Found: C, 18·8; H, 3·4; N, 39·8; Cl, 12·6; O, by diff., 25·4%) and an insoluble fraction (B) (Found: C, 19·8; H, 3·4; N, 41·3; Cl, 10·8; O, by diff., 24·7%) which, however, closely resembled A. The microanalyses are averages of a large number of runs. Neither of the products dissolved in any of the usual organic solvents or showed a definite m. p.; when heated, both turned into the " yellow solid " which decomposed above 500°. Their reactions with alkali, acid, and copper sulphate resembled those of melamine, ammeline, and melam (Bamberger, *Ber.*, 1883, **16**, 1074, 1703; Davis and Abrams, *Proc. Amer. Acad. Arts Sci.*, 1926, **61**, 437), so it can be assumed that the products represent mixtures of the perchlorates of these bases. The yellow product should therefore be mainly mellon.

It is in accord with these conclusions that similar products were obtained from guanidine chloride at about 350°, and that the products A and B as well as the yellow solid were oxidised completely to gaseous products when heated with potassium or ammonium perchlorate.

In the pyrolysis (at 355°) of guanidine perchlorate, a gradual increase in the nitrogen content of the insoluble residue is observed:

Time of reaction (min.)	20	33	75	150
N, %	33·55	35·53	44·7	46·65

Since ammonia is evolved with the gaseous products, this increase can best be explained by the assumption of an initial self-condensation of guanidine, followed by gradual conversion of the condensate into less basic substances of progressively smaller tendency to salt formation with perchloric acid.

DISCUSSION

Mechanism of Decomposition.—The results support the following mechanism for the decomposition of the salt. (*a*) Ammonia is evolved, cyanamide and perchloric acid being formed; (*b*) cyanamide undergoes self-condensation, *e.g.*, to melamine:

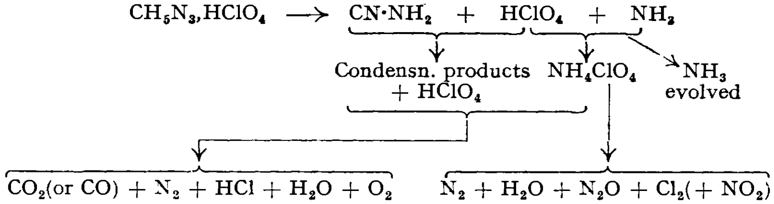
$$CH_5N_3,HClO_4 \longrightarrow CN{\cdot}NH_2 + HClO_4 + NH_3 \qquad (3)$$

$$3CN{\cdot}NH_2 \longrightarrow C_3H_6N_6 \text{ (Melamine)} \qquad (4)$$

(*c*) these condensation products are oxidised in stages, by perchloric acid or ammonium perchlorate, to the gaseous products found, amongst them hydrogen chloride, which may eventually combine with ammonia.

Under atmospheric pressure and at lower temperatures, ammonia will tend to evaporate preferentially and leave perchloric acid, which is available for the oxidation of the condensation products. At low temperatures, therefore, complete oxidation to carbon dioxide takes place, and a considerable amount of ammonium chloride is obtained (equation 2). As the temperature rises, or under reduced pressure, more perchloric acid enters the gas phase, thus reducing the oxygen available for oxidation of the solid, and increasing the proportion of carbon monoxide in the gaseous oxidation products (equation 1). Indeed, it has been shown that *in vacuo* almost complete evaporation of the ammonium perchlorate takes place, and the condensation to mellon proceeds undisturbed, as in the pyrolysis of guanidine chloride.

Above 390°, as observed by Dode (*loc. cit.*), the vaporised ammonium perchlorate explodes. The accompanying rise of temperature increases the rate of evaporation of the ammonium perchlorate and leads again to the formation of the yellow mellon. Under these conditions the gaseous products are not only rich in oxygen, but also contain appreciable amounts of chlorine and nitrogen dioxide.



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