# *The Thermal Decomposition of Guanidine Perchlorate. Part III.* Catalysts and Time-lag before Ignition.*

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The kinetics of the thermal decomposition of guanidine perchlorate in the presence of catalysts were studied. The catalysts are divided according to their effects and known properties into three groups: (1) basic oxides, (2) redox catalysts, (3) catalysts for the synthesis (or decomposition) of ammonia. In the proposed reaction mechanism a definite role is assigned to the intermediary formation of perchloric acid.

Conditions under which guanidine perchlorate explodes or deflagrates are defined. The activation energies obtained from the rate of decomposition, and from the times of induction before the ignition of guanidine perchlorate and of ammonium perchlorate, average about 31·3 kcal./mole, indicating that the rates of these three processes are determined by the same fundamental reaction.

IN Part I (*J.*, 1953, 182) the behaviour of guanidine perchlorate on thermolysis and the mechanism of decomposition, and in Part II the kinetics of this decomposition have been described. The present paper reports measurements of the time lag (induction period) before ignition, and the influence of catalysts on the thermal decomposition of guanidine perchlorate at several temperatures.

## EXPERIMENTAL

Guanidine perchlorate (m. p. 240°) was prepared as described in Part I. Ammonium perchlorate and potassium perchlorate were of Baker's Analysed C.P. grade. Dicyandiamide, guanidine chloride, and the various oxides used as catalysts were all analytical reagents.

The apparatus for kinetic measurements consisted of a Pyrex reaction vessel and reaction tube connected to a gasometer which contained saturated salt solution for levelling (Glasner and Weidenfeld, *J. Amer. Chem. Soc.*, 1952, **74**, 2464) in a manually-controlled electric furnace fitted with calibrated chromel–alumel thermocouples.

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* Part II, *Bull. Res. Council, Israel*, 1953, 89.

For experiments with catalysts or other added materials, the ingredients were weighed separately and mixed in the reaction tube. Decompositions made in the same reaction tube gave closely reproducible curves, but on changing the reaction tubes different rates were obtained at the same temperature, even when the dimensions of the tubes were nearly the same. Therefore, series of runs to be compared with each other were always carried out in the same tube.

For the measurement of the time lag, the reaction vessel was replaced by a vertical Pyrex tube closed at the bottom into which a micro-test-tube was lowered on copper wire. When the system attained the desired constant temperature, the test tube was raised for a moment and a weighed sample of guanidine perchlorate ($\sim$70 mg.) dropped into it. The time lag was measured by a chronometer (to 0·01 min.) as the time from the moment the tube was returned to the furnace until a flash was seen, or a quick deflagration with a hissing noise was heard.

The same tube was used for a series of measurements, and it was thoroughly cleaned before each experiment. Values reported are the mean of at least three measurements, the maximum difference between two extreme readings at the same temperature being always less than 0·05 min.

## RESULTS

*Time Lag.*—The mean induction periods of ignition of guanidine perchlorate and ammonium perchlorate are recorded in the Table. The lags for ammonium perchlorate were larger than those of guanidine perchlorate at the same temperature but a mixture of 26·3% dicyandiamide and 73·7% ammonium perchlorate (having the overall composition of guanidine perchlorate) gave values similar to those for pure guanidine perchlorate.

*Time lag before ignition.*

| | | | | | | |
|---|---|---|---|---|---|---|
| Guanidine perchlorate : | Temp., °c ...... | 390 | 400 | 415 | 427 | 440 |
| | $10^2t$, min. ......... | 256 | 166 | 93·6 | 79 | 51·7 |
| Ammonium perchlorate : | Temp., °c ...... | 440 | 452 | 460 | 478 | |
| | $10^2t$, min. ......... | 130 | 94 | 63 | 42 | |

Small additions of the oxides of iron(III), copper(II), cobalt(II), vanadium(V), and chromium(III) to guanidine perchlorate, ammonium perchlorate, or ammonium perchlorate–dicyandiamide mixtures greatly reduced the minimum temperature of ignition, in some cases to just above 300°.

As a rule, all oxides that cause an explosive reaction with guanidine perchlorate do the same with ammonium perchlorate though at a somewhat higher temperature. For example, mixtures of CuO, $Ag_2O$, $Hg_2O$, and $MoO_3$ with guanidine perchlorate exploded at 300°, 320°, 345°, and 345°, respectively, whilst mixtures of the same oxides with ammonium perchlorate exploded at 345° (CuO) and at 400° ($MoO_3$).

When the log of the induction period (Fig. 1) is plotted against the reciprocal of the absolute temperature the apparent energies of activation for guanidine perchlorate and for ammonium perchlorate are found to be 30·5 and 31·0 kcal./mole.

*Kinetic Measurements.*—The rates of evolution of gaseous products from guanidine perchlorate at four different temperatures between 345° and 380° have been measured. A plot of the percentage of gas evolved against time $t$, shows a slow acceleration of the reaction up to about 15% after which a constant rate of gas evolution is reached. Above 70% decomposition, a new increase in the reaction rate occurs accompanied by a rise in temperature so that the pyrolysis may end in a final deflagration followed by a small decrease in volume when the gases have cooled again to the constant temperature of the furnace. If powdered Pyrex glass (10%) is added to the guanidine perchlorate, the pyrolysis is more regular and the plot of the volume of gas evolved against reaction time is a straight line.

The rate constant $k$ for the middle part of the thermal decomposition may be expressed by the equation $k = 2{\cdot}4 \times 10^{11}e^{-32400/RT}$ %/min. (see Fig. 2).

For comparison, equimolar mixtures of dicyandiamide (26·3 mg.) with ammonium perchlorate (73·7 mg.), and of guanidine chloride (59·7 mg.) with ammonium perchlorate (73·7 mg.), were decomposed at 355° and 365°. Points for both mixtures fall approximately on the same curve at corresponding temperatures (the times of slow reaction seem to be shortened somewhat in comparison with those for guanidine perchlorate, and there is also a slight increase in the slope of the main reaction curve). Mixtures of guanidine chloride (59·7 mg.) with potassium perchlorate (86·8 mg.) have a very slow rate of thermal decomposition.

The catalytic effect of some dry metal oxides was examined. They were mixed with the guanidine perchlorate in amounts approximately proportional to their formal weights (2—5% by wt). The reaction curves obtained at various temperatures are shown in Figs. 3(*a, b, c*).

FIG. 1. *Logarithm of the induction time,* t, *as a function of the reciprocal of absolute temperature.*

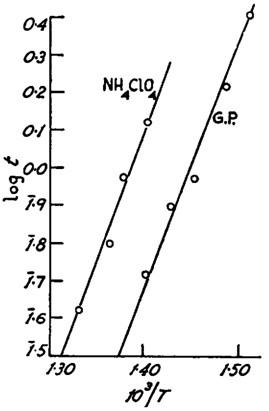

FIG. 2. *Logarithm of the rate constants* k *as a function of the reciprocal of absolute temperature.*

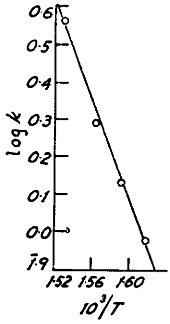

FIG. 3. *Decomposition* (%) *of guanidine perchlorate as a function of time in the presence of catalysts.*

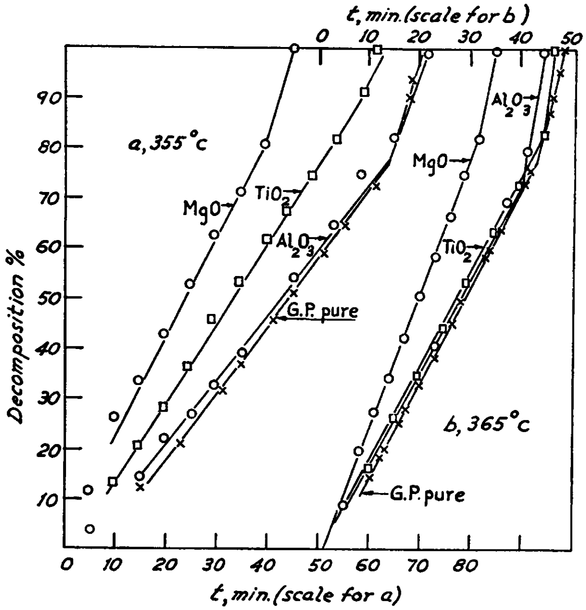

FIG. 3*a and* 3*b*.

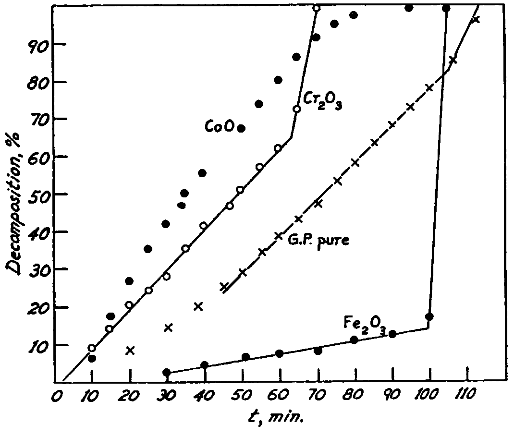

FIG. 3*c*.

CoO *and* $Fe_2O_3$ *at* 296°; *Guanidine perchlorate and* $Cr_2O_3$ *at* 345°.

The catalysts may be divided according to their effects into the following groups:

(1) Metal oxides with a constant valency, such as MgO and $Al_2O_3$, exert a small accelerating effect, but do not change the general character of the pyrolysis.

(2) Oxides of the transition metals, such as $TiO_2$, $Cr_2O_3$, and CoO, have a more pronounced catalytic effect and may cause an explosion or early deflagration at comparatively low temperatures.

(3) Some specific metal oxides (and metals), *e.g.*, $V_2O_5$, $Fe_2O_3$, (CuO), and platinum (in the form of a small foil), cause an explosion at any temperature above 300°. In this connection

the decomposition curves of guanidine perchlorate with $Fe_2O_3$ and with CoO at 296° (see Fig. 3*c*) are of a special interest.

## DISCUSSION

The reaction curves for the decomposition of guanidine perchlorate are composed of three nearly straight lines with increasing slopes. The main reaction covers from 15—20 to 75—85% of the decomposition and is of zero order and was shown to be catalysed by Pyrex glass, of which the reaction tubes consisted.

The following considerations give an insight into the nature of the reaction. The fact that pure guanidine perchlorate and its mixtures with equimolar amounts of ammonium perchlorate decompose at the same rate, indicates that ammonium perchlorate is produced from guanidine perchlorate in a primary reaction which, however, is not the determining step in the thermal decomposition of guanidine perchlorate. On the other hand, the very slow rate found for a guanidine chloride–potassium perchlorate mixture (which at the temperatures employed forms a homogeneous melt) excludes the possibility that the perchlorate ion is involved in this reaction. It is therefore suggested that free perchloric acid is the effective oxidising agent. The step determining the extent of the main reaction would then be the dissociation of ammonium perchlorate taking place on the walls of the reaction vessel: $NH_4ClO_4 \longrightarrow NH_3 + HClO_4$(3′) (following the numbering of the equations adopted in Part I). This is in agreement with the sequence of reactions proposed in Part I on the basis of the analysis of the products of the thermal decomposition of guanidine perchlorate:

$$CN_3H_5,HClO_4 \longrightarrow CN{\cdot}NH_2 + NH_3 + HClO_4 \quad . . . . . \quad (3)$$

$$3CN{\cdot}NH_2 \longrightarrow C_3H_6N_6 \quad . . . . . . . . . . . \quad (4)$$

$$C_3H_6N_6 \text{ and other condensates} + HClO_4 \longrightarrow \text{gaseous products} \quad . . . \quad (5)$$

The amendment suggested now implies that reaction (3) consists of two distinct steps, the second supplying the oxidising agent, perchloric acid. For the rate of oxidation, as measured by the volume ($v$) of permanent gases evolved, one can thus write in general terms:

$$dv/dt = k_5[\text{condensates}]^m[HClO_4]^n \quad . . . . . . . . . \quad (6)$$

If a stationary concentration of the perchloric acid is assumed to exist during the main reaction stage, the change of perchloric acid concentration with time will be given by the equation

$$d[HClO_4]/dt = k - k_5[\text{condensates}]^m[HClO_4]^n = 0 \quad . . . . . . . \quad (7)$$

where $k$ is the reaction constant of (3) or (3′).

By substitution of (7) into (6) $k$ is obtained. Thus the decomposition of guanidine perchlorate is seen to be a simple function of the rate of production of perchloric acid, which is a constant determined by the area of contact between the walls of the reaction vessel and the ammonium perchlorate present.

The comparatively slow reaction at the beginning of a run is explained by the initial absence of ammonium perchlorate. Indeed, in mixtures initially containing ammonium perchlorate there is no induction period. The final deflagration may be ascribed to the amount of organic matter decreasing below a certain limit, whilst perchloric acid continues to be produced at the same constant rate.

For example, it has been shown in Part I that at lower temperatures a relatively large proportion of ammonia escapes oxidation so that the concentration of free perchloric acid in the reaction mixtures will be greater at low than at high temperatures, and the percentage of guanidine perchlorate decomposed before deflagration sets in is gradually lowered with decreasing temperature.

The above observation may help to elucidate the specific step of the postulated sequence of reactions influenced by a catalyst: A substance that will catalyse only reaction (5) (oxidation) will deter deflagration, whilst one that catalyses reaction (3) (formation of free perchloric acid) will shorten the main thermal decomposition and cause an early deflagration. Many of the oxides used by us seem to catalyse both reactions (3) and (5) in varying measures, thus giving a variety of reaction curves.

1. *Basic oxides.* The perchlorates of these are known to hydrolyse at the temperature of the experiments into the oxides and free perchloric acid (Marvin and Woolaver, *Ind. Eng. Chem. Anal.*, 1945, **17**, 474); they may accelerate the evolution of ammonia because of their basicity, increasing thereby the rate of production of perchloric acid, and subsequently the rate of oxidation. A good example is magnesium oxide which accelerates the pyrolysis but does not change the general form of the curves. On the other hand, alumina, having a lower basicity, shows no appreciable effect on the decomposition.

2. *The oxides of transition metals.* These may act as basic oxides and also as agents for the transfer of oxygen. A comparison between the effects of chromium oxide and titanium oxide may illustrate this point. The former, combining the two properties mentioned, greatly accelerates the decomposition, and causes an early deflagration. On the other hand, titanium oxide accelerates only the rate of oxidation but does not enhance the formation of free perchloric acid so that deflagration occurs only at a later stage of decomposition.

3. *Catalysts of the type employed in the synthesis of ammonia.* These seem to form a special group with regard to their catalytic influence on the decomposition of guanidine perchlorate. This group is represented by $Fe_2O_3$, (CuO), $V_2O_5$, and platinum metal. They are all good catalysts for oxidation reactions, $Fe_2O_3$ and CuO having basic properties in addition. The catalytic effect of these substances is the most violent, being enhanced probably by the partial non-oxidative decomposition of ammonia caused by them.

Judged from its effectivity, cobalt oxide might be classified with the third group of catalysts; in fact it is but an extreme example of the catalysts of group 2, being more effective than chromium sesquioxide because of its higher basicity. This point is well brought out by comparing the decomposition curves of the mixtures of ferric oxide and cobalt oxide with guanidine perchlorate at 296°. At this low temperature cobalt oxide does not act any more as a hydrolytic agent, but its properties as an oxidation catalyst are very pronounced. Indeed, one of us (A. G., unpublished work) has shown that cobalt oxide catalyses the oxidation of organic salts (for example sodium formate) by potassium perchlorate at 200°.

Further evidence that the decomposition of ammonia is involved in the occurrence of explosions is obtained from the fact that all catalysts causing explosion of guanidine perchlorate show a similar effect in their mixtures with ammonium perchlorate, though at a somewhat higher temperature. Oxides which do not interfere with the decomposition of ammonia may cause a deflagration of guanidine perchlorate only after the elapse of a considerable period of induction. In the same way, the difference in the temperature of explosion of guanidine perchlorate and ammonium perchlorate observed with the pure substances (cf. the Table) may be due to the interaction between the organic substance and the perchloric acid. Some evidence to prove this suggestion has been obtained by the effective lowering of the explosion temperature of ammonium perchlorate to 390° by the addition of very small amounts of dicyandiamide or methyl methacrylate.

The activation energies obtained from the rate of decomposition of guanidine perchlorate, and the respective time lags before explosion for guanidine perchlorate and for ammonium perchlorate, are all close to about 31·3 kcal. This tends to confirm the view that the mechanism of the decomposition of these two substances is governed by the rate of the dissociation of ammonium perchlorate.

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