106. *Thermal Ignition in the System Ammonium Perchlorate–Cuprous Oxide.*

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The thermal decomposition of compressed pellets of ammonium perchlorate containing up to 60 moles % of cuprous oxide has been investigated. The principal result of this additive is to lower the explosion temperature of the perchlorate by some 200°. Direct measurements of self-heating have confirmed that the explosion has a thermal origin and that it can proceed by either of two mechanisms. One of these is the decomposition of ammonium perchlorate which is accelerated by the heat evolved from the oxidation of cuprous oxide. The second is the thermal decomposition of ammonium perchlorate catalyzed by cupric oxide.

THE catalytic effect of oxides of several transition metals on the thermal decomposition of ammonium perchlorate was first demonstrated by Bircumshaw and Newman.[1] Since that time, the effects of MnO_2,[2] NiO_2, Cr_2O_3, Co_2O_3, and Co_3O_4,[3] ZnO,[4] and Cu_2O [5] have been investigated. In this paper we present the results of further work on the decomposition of mixtures of ammonium perchlorate and cuprous oxide. In particular, the self-heating which occurs during chemical reaction has now been measured and the results confirm the mechanism suggested for the thermal explosion of mixtures of ammonium perchlorate and cuprous oxide.

EXPERIMENTAL AND RESULTS

Procedure.—The ammonium perchlorate used was of B.D.H. reagent grade, ground in an agate mortar and sieved to obtain salt of particle size $<66\ \mu$ (passing 240 mesh B.S.S.). The cuprous oxide was a Hopkin and Williams general-purpose reagent (minimum Cu_2O, 88%). Weighed amounts of the two salts were mixed by shaking them together in a sample tube for 10—20 min. until the mixture appeared to be uniform. Pellets were made by compression in either of two stainless-steel presses, in a hand-vice. One of the presses had two fine holes in the plunger, to accommodate the 40 S.W.G. wires of the Chromel–Alumel thermocouple embedded in the mixture. The thermocouple in the pellet was connected in opposition with a similar one in the Woods-metal bath in which the reaction vessel was immersed and the out-of-balance voltage was fed to a sensitive galvanometer. The measuring system was calibrated by means of a potentiometer so that the temperature difference between the two thermocouples could be calculated from readings of the galvanometer deflection. The bath temperature (T_0) was measured with a third calibrated thermocouple.

The reaction was normally studied under a pressure of 250 mm. of nitrogen, to suppress sublimation [6] of the ammonium perchlorate. The pressure evolved by the reaction could be measured by using a glass spiral gauge of sensitivity: 1 cm. deflection $\equiv$ 2·24 mm. Hg. Induction periods before thermal ignition were noted. The time taken (τ_0) for the pellet of reactants to reach T_0 could be measured accurately in those runs in which a pellet containing a thermocouple was decomposed.

Mixtures containing 45·4 *Moles per cent of Cuprous Oxide.*—In Fig. 1, a typical plot of pressure against time is shown. Its main features are an initial deceleratory process, an induction period, an instantaneous rise in pressure associated with the explosion of the pellet and, finally, a decrease in pressure associated with secondary reactions between products. The induction period τ is well defined and easily measured by watching the deflection of the light spot reflected

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[1] Bircumshaw and Newman, *Proc. Roy. Soc.*, 1954, *A*, **227**, 115; 1955, *A*, **227**, 228.

[2] Galwey and Jacobs, *Trans. Faraday Soc.*, 1959, **55**, 1165.

[3] Hermoni and Salmon, Eighth Symposium (International) on Combustion, Williams and Wilkins Co., Baltimore, in the press.

[4] Solymosi, personal communication.

[5] Jacobs and Kureishy, Eighth Symposium (International) on Combustion, Williams and Wilkins Co., Baltimore, in the press.

[6] Galwey and Jacobs, *J.*, 1959, 837.

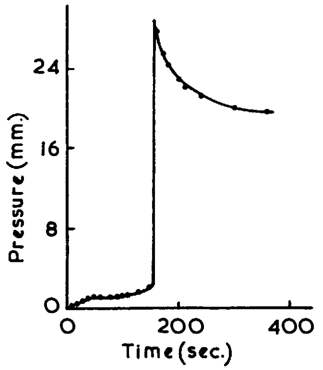

FIG. 1. The variation of pressure with time during the thermal decomposition of an ammonium perchlorate pellet containing 45·4 moles % of Cu_2O.

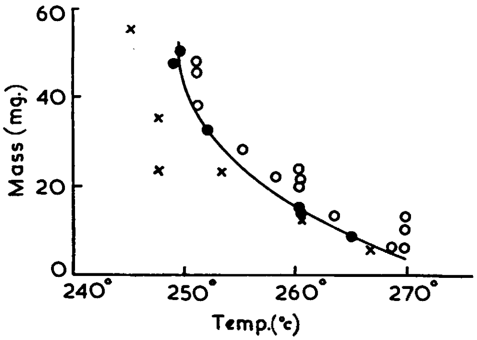

FIG. 2. Explosion limits, $m^*(T_0)$ for $NH_4ClO_4 + Cu_2O$ mixtures containing 45·4 moles % of Cu_2O. ○ indicates explosion, × no explosion, and ● rapid acceleration of the reaction without explosion.

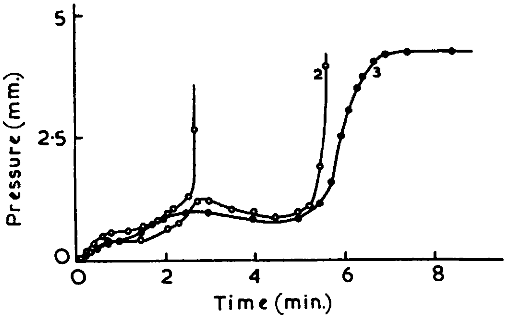

FIG. 3. Pressure–time curves for the decomposition of three pellets of ammonium perchlorate containing 23·9 moles % of Cu_2O. 1, $m = 30{\cdot}6$ mg., $T_0 = 269{\cdot}2°$; 2, $m = 18{\cdot}2$ mg., $T_0 = 268{\cdot}5°$; 3, $m = 16{\cdot}4$ mg., $T_0 = 267{\cdot}5°$.

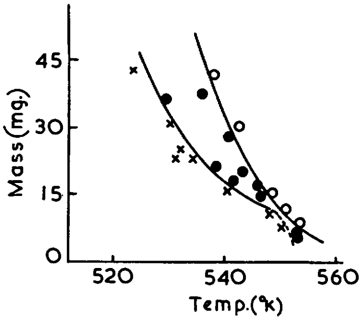

FIG. 4. Explosion limits, $m^*(T_0)$, for $NH_4ClO_4 + Cu_2O$ mixtures containing 23·9 moles % of Cu_2O. × no explosion, ● explosion by second mechanism, ○ explosion by first mechanism.

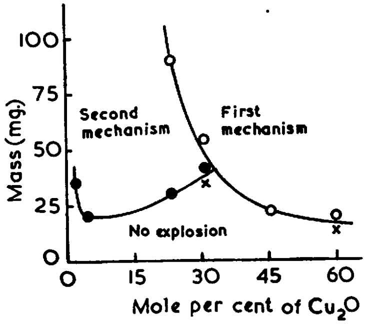

FIG. 5. Explosion limits, m^* (concentration), for the $NH_4ClO_4 + Cu_2O$ system at $T_0 = 257°$. Points on the lines were obtained by interpolation of experimental $m^*(T_0)$ curves (*e.g.*, Figs. 2 and 4) for the appropriate composition, at the desired temperature. Other symbols as in Fig. 4.

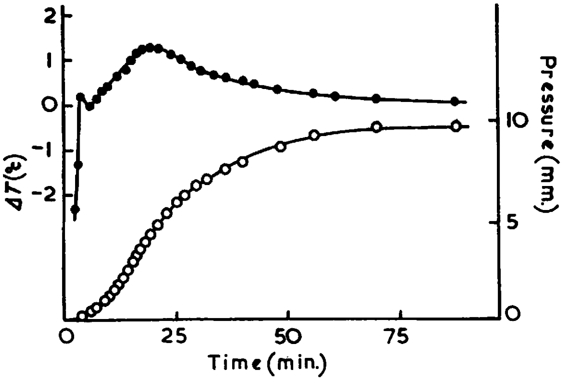

FIG. 6. The excess temperature, ΔT, and the pressure, p, as functions of time during the thermal decomposition of pure ammonium perchlorate, $T_0 = 255°$, $m = 45$ mg.

from the mirror of spiral gauge. The induction period τ was reproducible to within $\pm 10\%$ and no differences between the behaviour of small pellets (45 ± 5 mg.) and fragments of similar mass broken from a single large pellet were noticed. At constant T_0, the increase in τ with mass was of the order of 1 sec. per mg. As so little gas is evolved before the explosion the kinetics of the pre-ignition reaction could not be analysed.

Explosion limits were found by gradually decreasing the mass of the sample at a particular T_0 until it failed to explode. The boundary dividing the regions of explosion and non-explosion in the m-T_0 plane was found by repeating the procedure at various temperatures. The critical mass m^* necessary for this mixture to explode is shown as a function of T_0 in Fig. 2, where filled circles denote those pellets which, while failing to explode, showed a marked acceleration in the variation of pressure with time. The mass of these pellets must have been very close to the critical mass, m^*.

Mixtures containing 23·9 *Moles per cent of Cuprous Oxide.*—In Fig. 3 are shown the pressure–time curves for three runs with pellets of this mixture. A 30·6 mg. pellet at 269·2° behaves like the more concentrated mixtures and explodes after 156 sec. An 18·2 mg. pellet at 268·5° shows an acceleratory reaction after about 2 min.; this fails to lead to ignition and the pressure decreases slightly until a rapidly accelerating process sets in after about 4½ min. The second process leads to ignition after 333 sec. For a slightly smaller mass at a slightly lower temperature (16·4 mg. at 267·5°) both acceleratory processes are evident, but neither results in explosion. It seems that, at this concentration of cuprous oxide, explosion can occur by either of two mechanisms. The explosion limits are shown in Fig. 4. For example, as T_0 is increased at a constant mass of 30 mg., explosion by the second mechanism occurs at 531°K. With further increase in temperature, explosion by the first mechanism occurs at 541°K.

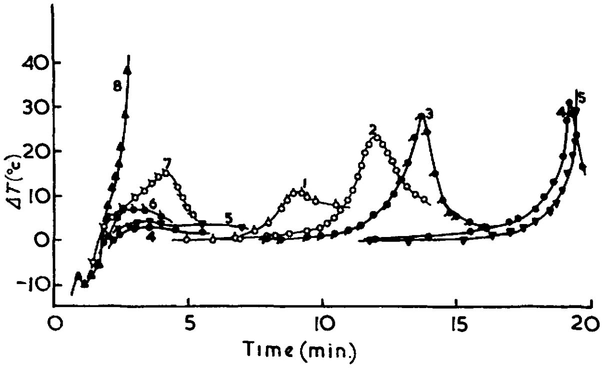

FIG. 7. Self-heating during the thermal decomposition of NH_4ClO_4 + Cu_2O mixtures. The molar % of Cu_2O is: 1, 0·5%; 2, 2·0%; 3, 4·6%; 4, 8·4%; 5, 17·8%; 6, 20·4%; 7, 29%; 8, 45·4%.

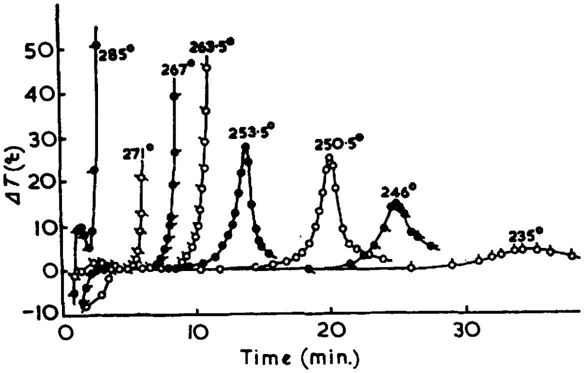

FIG. 8. The dependence of self-heating on bath-temperature for ammonium perchlorate containing 4·6 moles % of Cu_2O. The values of T_0 are shown on the curves.

Dependence of Explosion Limits on Concentration.—The critical mass m^* at which explosion occurs at a constant bath temperature T_0 of 257° is plotted against the molar concentration of cuprous oxide in Fig. 5. The complicated features of this reaction may be illustrated by considering what happens, for example, as the concentration is increased at a constant total mass of 30 mg. At concentrations of less than 2% of oxide, ignition fails to occur, and between

2% and 24% of the oxide explosion occurs by the second mechanism. At higher concentrations up to 39% cuprous oxide, mixtures do not ignite at this temperature but, above 39% (and up to a least 60%) oxide, explosion occurs by the first mechanism.

Self-heating Measurements.—The explosion limits exhibited in Figs. 2, 4, and 5 indicate that this reaction can culminate in a thermal explosion by either of two mechanisms. To confirm this hypothesis, we attempted to measure the actual temperature of the decomposing pellets. The results of these measurements on pellets containing a constant mass of ammonium perchlorate of 45 ± 5 mg. and various concentrations of cuprous oxide from 0·5 to 45·4 mole % at constant T_0 (255° ± 2°) are shown in Fig. 7. Plots of ΔT against t and of p against t on the same diagram (Fig. 6) reveal that, for pure perchlorate, self-heating is negligible. This small peak of about 1° is useful, however, since it enables us to assess whether any substantial time delay occurs between the evolution of heat by the chemical reaction and its being recorded by the thermocouple. Clearly, the peak in $\Delta T(t)$ coincides fairly well with the maximum rate of chemical reaction. In contrast, considerable self-heating occurs at all concentrations of cuprous oxide. The sensitivity of the method is sufficient to show up the endothermic phase transformation which occurs in ammonium perchlorate at 240° (Figs. 6, 7). Because of the high initial rate of heating of about 200° per minute, the inflection due to the phase transformation does not occur quite at the equilibrium temperature. The heat-up time can be accurately determined and is about 105 sec. in this apparatus. Low concentrations of cuprous oxide show a single self-heating peak; the induction period and $\Delta T_{\text{max.}}$ both increase with increasing concentration of oxide until, at a concentration of 17·8% of Cu_2O, ignition by the second mechanism occurs. As the concentration is further increased, the self-heating peak due to reaction by the first mechanism increases until this too leads to ignition with 45·4 moles % of the oxide.

The dependence of the amount of self-heating on T_0 is shown in Fig. 8 for a constant concentration of cuprous oxide of 4·6%. The mass of the pellets was approximately constant at $m = 57 \pm 5$ mg. With increasing temperature, the induction period decreases and the amount of self-heating increases, explosions occurring for $T_0 \geqslant 263{\cdot}5°$. There is practically no self-heating due to the first mechanism until $T_0 = 271°$ at which temperature a small maximum of 1° due to this process is just evident. At 285° considerable self-heating (10°) occurs because of the first reaction, but explosion still results because of self-heating from the second process. The induction period τ and the heat-up time τ_0 can both be found from Fig. 8 and a plot of log $(\tau - \tau_0)$ against $10^3/T$(°K) yields a good straight line, the slope of which corresponds to an energy of activation of 31 kcal./mole.

DISCUSSION

The pressure–time curves of Fig. 3 and the self-heating curves of Fig. 7 both illustrate the complexity of the chemical processes occurring when mixtures of ammonium perchlorate and cuprous oxide are decomposed. Fig. 1 shows that there is an initial decomposition of ammonium perchlorate which is catalysed by the cuprous oxide. The pure salt would show an induction period of about five minutes before decomposing at this temperature. This catalysed reaction shows similar features to that which occurs in mixtures of $NH_4ClO_4 + MnO_2$,[2] namely, that its rate decreases with increasing time, presumably because of loss of contact between the perchlorate and the catalyst in the rigid pellet. The mechanism of the low-temperature decomposition of ammonium perchlorate has been suggested to be an electron transfer from ClO_4^- to NH_4^+ followed by decomposition of the ammonium perchlorate " molecule " formed.[7] The activation energy associated with this process is about 32 kcal./mole. The advent of any chemical species which can function as an electron-acceptor then facilitates the reaction by trapping the electron and thus, by stabilizing the perchlorate radical, increasing the probability of its decomposition. Transition-metal ions should thus be particularly effective catalysts. The reaction is not sustained, however, because of loss of contact between the oxide and the perchlorate and the reaction quickly subsides (Figs. 1, 3).

[7] Galwey and Jacobs, *Proc. Roy. Soc.*, 1960, *A*, **254**, 455.

At low temperatures (*i.e.*, $<350°$) the decomposition of ammonium perchlorate can be expressed by the equation $4NH_4ClO_4 = 2Cl_2 + 3O_2 + 8H_2O + 2N_2O$. The oxygen produced by this preliminary reaction then proceeds to oxidise the cuprous oxide, a process which is highly exothermic. For high and intermediate concentrations of cuprous oxide, at sufficiently high temperatures (Figs. 2, 4), the heat evolved by the oxidation to cupric oxide is sufficient to raise the temperature of the sample (Fig. 7) and so set off the rapidly accelerating decomposition of ammonium perchlorate. For suitable combinations of the parameters m, T_0, and concentration, this reaction culminates in a thermal explosion. This reaction accelerates so rapidly (Fig. 1) that it was not possible to analyse the pre-ignition kinetics. It is doubtful, however, whether any activation energy deduced from such an analysis would have been meaningful, in view of the complicated chemical process envisaged, namely:

$$\begin{tikzcd}
2Cu_2O + O_2 \arrow[r] & 4CuO + \text{Heat} \arrow[d] \\
O_2 \arrow[u] & NH_4ClO_4 + \text{Heat} \arrow[l]
\end{tikzcd}$$

As the amount of cuprous oxide in the sample is decreased, the probability of explosion by the first mechanism outlined above, decreases, although substantial self-heating (Fig. 7) and decomposition (Fig. 3) can occur. Should ignition fail to occur by mechanism I, there exists the possibility of further reaction which we ascribe to the catalysed decomposition of ammonium perchlorate by cupric oxide. To verify this hypothesis, it is necessary to show (i) that cupric oxide can function as a catalyst, and (ii) that the induction period for the second reaction increases with increasing amount of catalyst (because of the longer time required for its oxidation). Evidence that (ii) is indeed valid is contained in Fig. 7. The ability of cupric oxide to act as a catalyst was demonstrated by the following experiment. Four pellets were made containing, respectively, the same molar concentration of cuprous oxide, lightly oxidised cuprous oxide, highly oxidised cuprous oxide, and cupric oxide. The colours of these pellets were pink, pink, violet, and black. Self-heating curves for the four pellets are shown in Fig. 9. Oxidation of cuprous oxide before the pellet is made decreases the induction period, in agreement with the proposed mechanism. As expected, only surface oxidation of the cuprous oxide particles is necessary in order to reduce τ. The magnitude of the self-heating peak is correspondingly reduced as the CuO : Cu_2O ratio is increased. This could be due to an increase in either the heat capacity or the amount of heat lost by radiation from the pellet. It is of interest, therefore, that explosions are more easily initiated by cuprous oxide which has undergone some surface oxidation, than by using cupric oxide as the catalyst. Presumably Cu^{2+} ions participate in the second reaction just as Cu^+ ions did in the initial process. This would require a renewal of contact between the oxide particles and the perchlorate, but some sintering or rearrangement of the oxide phase during oxidation could achieve this.

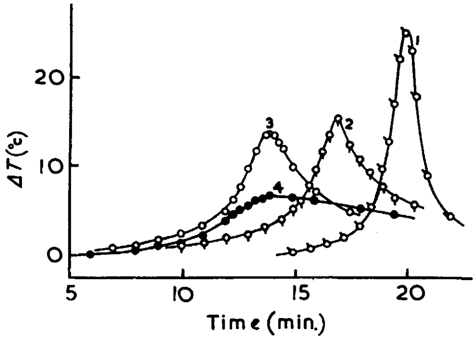

FIG. 9. Effect on the self-heating curves of the gradual oxidation of Cu_2O to CuO before pelleting. 1, Cu_2O; 2, lightly oxidised Cu_2O; 3, highly oxidised Cu_2O; 4, CuO.

Since the second explosion is caused essentially by self-heating, resulting from the catalysed decomposition of ammonium perchlorate, the activation energy deduced from the temperature-dependence of the induction periods should be the same as that for the electron-transfer reaction. The figure of **31** kcal./mole found supports this contention.

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