724. *The Thermal Decomposition of Ammonium Permanganate.*

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The induction period of the thermal explosion in air, and the kinetics of the decomposition *in vacuo* and under oil, of ammonium permanganate have been studied. The possibility of self-heating of the salt and of interaction of some of the products of decomposition is discussed.

A NUMBER of solid decompositions of the type $A_{\text{sol.}} \longrightarrow B_{\text{sol.}} + C_{\text{gas}}$ have been investigated where B arises from the cation; *e.g.*, those of silver oxalate (MacDonald, *J.*, 1936, 832, 389), mercurous oxalate (Prout and Tompkins, *Trans. Faraday Soc.*, 1947, **43**, 148), lead azide (Garner and Gomm, *J.*, 1931, 2123), lead oxalate (Bircumshaw and Harris, *J.*, 1948, 1898), magnesium hydroxide (Gregg and Razouk, *J.*, 1949, S 36), mercury fulminate (Vaughan and Phillips, *J.*, 1949, 2741), and nickel formate (Bircumshaw and Edwards, *J.*, 1950, 1800). Only a very few cases, however, have been studied where the residual solid has its origin in the anion. Ammonium permanganate appeared to be an interesting example of such a type, and the present communication describes the results obtained in a study of its thermal decomposition (*a*) in air, (*b*) *in vacuo*, and (*c*) under oil, between 70° and 117°. With this substance there is an obvious possibility of the oxidation of the cation by the anion, and this complicating factor was found to occur.

EXPERIMENTAL.

Preparation of Ammonium Permanganate.—Since this salt is decomposed in hot solution, the best conditions for its preparation had to be sought. The method chosen is a modification of that of Christensen (*Z. anorg. Chem.*, 1900, **24**, 203); potassium permanganate (40 g.) was dissolved in boiling water (400 c.c.), and ammonium chloride (110 g.) added; the solution was filtered hot through a sintered-glass funnel, to remove manganese oxides, and cooled immediately in ice. The crystals were twice recrystallized from pure water, in the same manner.

The crystals were bright red-purple needles, up to several cm. long; they became steel-grey when kept for 1—2 weeks, presumably owing to surface reactions. Although, when freshly prepared, they were pure, within volumetric accuracy, they must have been covered with a superficial layer of manganese oxides which could influence the decomposition. The manganese oxides filtered off from the hot solution were apparently pseudomorphous with the original crystals, though steel-grey in colour. On storage, slow decomposition occurred, although after 3 months a sample was 96% pure with respect to permanganate. After 6 months, a sample was still mainly ammonium permanganate but it had the colour of iodine crystals and smelled strongly of nitrogen oxides.

Thermal Explosion in Air.—The induction period of the thermal explosion was studied over the temperature range 96—117°. The apparatus used was a vapour bath made from standard " Quickfit " parts, the reaction chamber being a B19 air-leak, with the lower end sealed. The other parts were a 1-litre flask, a two-way distillation head, and a water-cooled reflux condenser. The liquids used in the vapour bath were: *n*-propyl alcohol (b. p. 96°), water (100°), *iso*butyl alcohol (106°), toluene (110·7°), pyridine (115°), and *n*-butyl alcohol (117°). The temperatures were checked immediately before each experiment. Roughly 0·02 g. of ammonium permanganate was used for each experiment, this being enough to give a barely audible explosion.

During the induction period, the sample changed from a red-purple to a graphite grey in colour and then on explosion gave quantities of a finely divided mixture of manganese dioxide and manganic oxide. No ammonium nitrate could be detected in the residue. No quantitative analysis of these oxides was undertaken owing to difficuties in their collection.

Three series of experiments were conducted, on large single crystals freshly recrystallized, on groups of freshly recrystallized crystals, and on groups of small crystals which had been stored for 3 weeks. The induction periods were longest for single crystals and shortest for " old " crystals. The induction periods are given in the following table, each result being the average of at least three determinations.

Time for explosion (seconds).

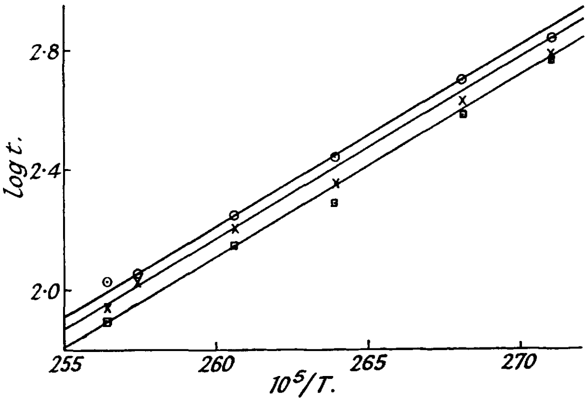
Temp.	96°	100°	106°	110·7°	115°	117°
Single crystals	697	502	272	175	114	109
Groups (new)	600	430	228	159	108	84
Groups (old)	602	385	195	140	90	79

A plot of log t (induction period) against the reciprocal of the absolute temperature is given in Fig. 1. From the three parallel straight lines an energy of activation of 27·9 kcals./g.-mol. was found, together with values for the temperature-independent factor, A in the equation $t = Ae^{-E/RT}$, of 8·13, 9·84, and $10{\cdot}05 \times 10^{-13}$ sec. for the three types of crystals, respectively.

This modified Arrhenius relationship holds for the induction periods of the thermal explosions of many explosives such as " nitroglycerine," trotyl, mercury fulminate, and cordite (see Brian and McDowell, *Trans. Faraday Soc.*, 1949, **45**, 213). Above 100°, the explosions were sharper and with a short yellow flash, perhaps due to the oxidation of the ammonium ion, and the solid products were more finely divided and a lighter brown than the dark products from the flashless explosions below 100°. Single crystals produced black oxides at all temperatures.

Interruption of heating does not lengthen the actual total time of heating before explosion. The explosion of one crystal was sufficient to explode the remainder, this being found by adding several crystals to one which had been heated for most of its induction period. The weight of ammonium permanganate present did not affect the induction period.

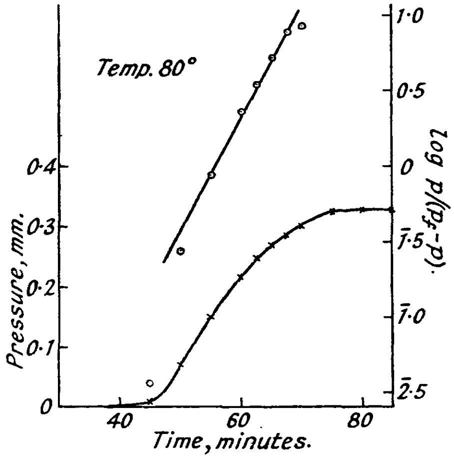
FIG. 1.



⊙ *Single new crystal.* ▢ *Groups of old crystals.* × *Groups of new crystals.*

Kinetics of the " Slow " Decomposition Experiments.—The high-vacuum apparatus used in the kinetic experiments was similar to that used by Bircumshaw and Edwards (*loc. cit.*), except that a liquid bath, essentially the same as that used by Prout and Tompkins (*Trans. Faraday Soc.*, 1944, **40**, 489), was incorporated. The liquid used in the bath was either benzene or toluene. The samples of ammonium permanganate (100 mg.) were placed in a small glass bucket which could be lowered into the inner tube of the liquid bath by means of a winch sealed on to a standard ground-glass joint. In the majority of the experiments the kinetics were followed by measuring the rise of pressure of the permanent gases ($O_2 + N_2$) produced after the pumps had been cut off and the bucket lowered into the reaction chamber.

FIG. 2.

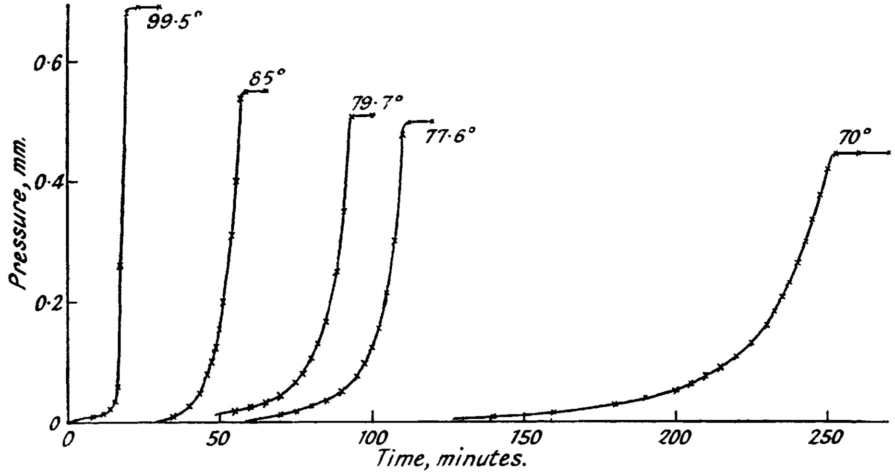


Results. The results proved indecisive owing to the uncertain course of the reaction. The induction period was followed by a brief acceleratory period during which the crystals moved about violently. During this period, especially if the crystals were confined by plugging the top of the bucket with glass wool, some or all of them might explode. This period was then followed by a long deceleratory period. A typical pressure–time curve is shown in Fig. 2. The lengths of the induction period, in the temperature range examined (70—80°), were such that they fit the same log t–$1/T$ graph as the explosive induction periods, giving a revised value for the energy of activation of 26 kcals./g.-mol.

The slow decomposition may be expressed by the Prout-Tompkins relationship $\log p/(p_f - p) = kt +$ const. (*loc. cit.*), which gives one straight line. Little significance is attached to this because of the briefness of the acceleratory period and the lack of reproducibility of the results.

The slow decomposition produces a steel-grey solid, pseudomorphous with the original crystals, consisting of a mixture of manganese dioxide, manganic oxide, and ammonium nitrate; the amount of the last varied enormously from experiment to experiment owing to various factors, including the age of the sample. The other products were nitrogen, oxygen, nitrous oxide, nitrogen dioxide, and water.

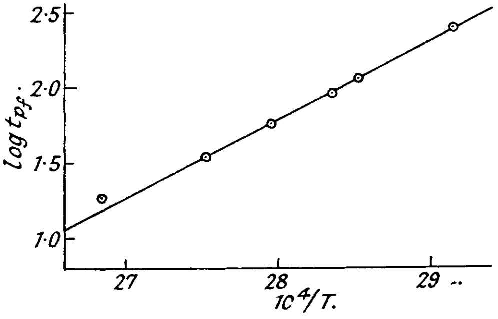
FIG. 3.



Decomposition under Oil.—More conclusive were experiments carried out with the crystals immersed in an inert oil. The kinetics were considerably altered, as was found by MacDonald (*loc. cit.*) in similar experiments on the decomposition of silver oxalate under oil. The experiments were conducted over the range 70—111°, and providing that not more than 200 mg. of ammonium permanganate were used, explosion did not occur. The effect of the oil was, of course, to prevent contact between individual crystals and damp down self-heating effects. It was independent of the nature of the oil used provided the latter was inert. Apiezon oil B was used because the attack by ammonium permanganate on this oil is negligible.

100-Mg. samples of ammonium permanganate were taken as before, covered with about 200 mg. of oil, a rather deeper bucket being used. Care was taken during evacuation, since air trapped around the crystals or dissolved in the oil caused frothing which, if not controlled, could carry the crystals out of the bucket.

FIG. 4.



The pressure–time curves show a long induction period, during which no reaction could be detected followed by a gradual acceleratory period, the rate building up to a maximum just before the reaction stops; *i.e.*, the rate of decomposition is greatest near total decomposition. Examples are given in Fig. 3. The best defined point on the graph is therefore the time taken to reach the final pressure tp_f. A plot of log tp_f against $1/T$ gives a straight line (Fig. 4) from which an energy of activation of 26 kcals./g.-mol. is found.

The final pressure increases with temperature but by no means regularly. As the temperature increases, the proportion of ammonium nitrate in the residue decreases.

A plot of $\log_{10} P$ against t gives two straight lines, showing that the equation $\log_{10}P = k_t +$ const., derived by Garner from Semenoff's degenerate chain branching theory, holds throughout the reaction. An example of this most unusual feature is shown in Fig. 5. No other known equation appears to fit these results.

The Catalytic Decomposition of Ammonium Nitrate.—Ammonium nitrate was shown to be formed in the decomposition and there was an obvious possibility of a reaction between this substance and the oxides of manganese also produced. A few experiments were made to investigate this point.

The reagents used were prepared as follows: Ammonium nitrate, "AnalaR," dried in a vacuum desiccator; manganese residues, the oxides from the permanganate decomposition at 40°; manganese dioxide, laboratory reagent boiled with dilute nitric acid to remove lower oxides; manganic oxide, manganese dioxide heated to a red heat in air for 4 hours.

The apparatus previously described for the kinetics experiment was used. An accumulative-pressure run was made at 110° on a mixture of manganese residues and the nitrate (83% NH_4NO_3). The rate–time graph obtained by differentiating this is shown in Fig. 6. Considerable decomposition occurred, producing approximately a 1 : 1 mixture of permanent gas and nitrous oxide. On Fig. 6 are also given the rate–time curve for a mixture of ammonium nitrate and manganic oxide (70 moles % NH_4NO_3) and the curve for a mixture of the salt with manganese dioxide (56 moles % NH_4NO_3). These graphs are all for 0·2-g. samples of the mixtures. The gaseous products from the manganic oxide-catalysed decomposition were entirely nitrous oxide. The manganese residues are known to contain manganese dioxide, as it is obvious, from these experiments, that the permanent gases (O_2, N_2) in the product are produced by the action of the manganese dioxide.

FIG. 5.

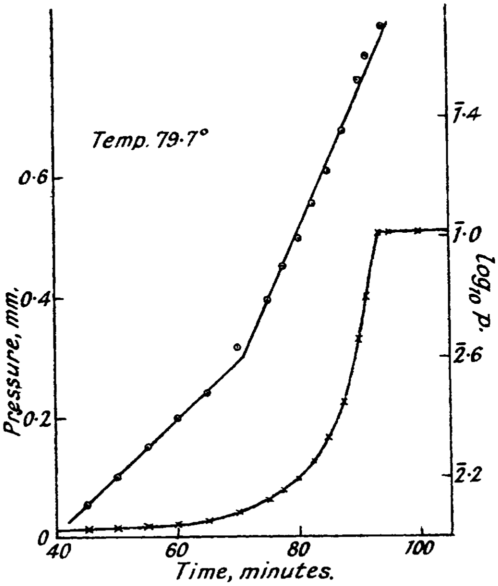
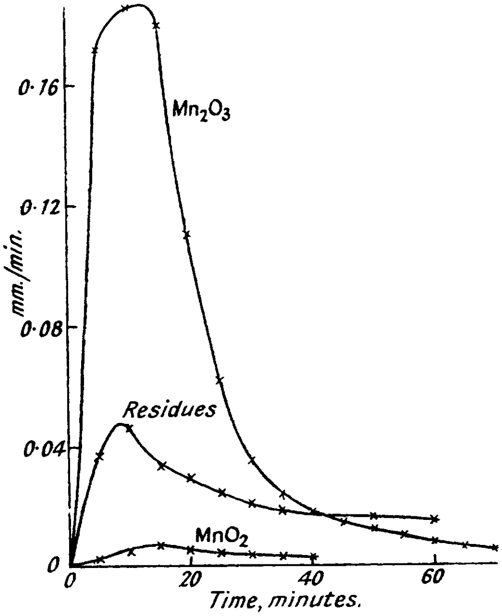


FIG. 6.



The manganese residues, manganic oxide, or manganese dioxide had no effect on the explosive induction periods in air of the ammonium permanganate. The experiment under oil cannot be made for obvious reasons.

DISCUSSION.

There is abundant evidence that the thermal decomposition of solids commences at nuclei, often on the surface, and then spreads throughout the mass, and there is no reason why this reaction should prove an exception. We have seen that during the initial stages of the reaction the crystals become the colour of the solid products, also the kinetics of the reaction correspond to the first type dealt with in Mampel's theory (*Z. physikal. Chem.*, 1940, *A*, **187**, 43, 235); so it would seem that nuclei completely cover the surface before they penetrate to any depth. Fischbeck and Spingler (*Z. anorg. Chem.*, 1939, **241**, 209), in similar work on ammonium chromates, observed this effect of surface decomposition to give oxides which then gave autocatalytic effects. As the colour of the crystal changes to that of the products, on storage, it would seem impossible to obtain two samples with the same degree of nucleation, and so the reaction would not be expected to give very reproducible results in the kinetics experiments.

It would seem that there are two major factors influencing the course of the reaction. They are the self-heating effect, important because of the high heat of reaction and rather low energy of activation, and the interaction of the solid products. The very different reaction under oil, where self-heating effects are damped, shows that the normal reaction is greatly accelerated by self-heating effects. The experiments ***in vacuo*** were probably under conditions where self-heating might be just enough to cause explosion. The fact that a large sample of ammonium permanganate (0·5 g.) will explode under oil at 110° shows that the effect of the oil is mainly one of damping the self-heating effects, and ensuring that the reaction course is more nearly isothermal.

The self-heating effects are discussed at length by Vaughan and Phillips (*loc. cit.*). Garner (*Trans. Faraday Soc.*, 1938, **34**, 986) has postulated that localised self-heating, extended over a few molecules only, is a precursor of thermal explosion. This is the basis of the theories of Garner and Gomm (*J.*, 1931, 2123) and of Muraour (*Compt. rend.*, 1932, **194**, 280), where the self-heating of a small group of molecules is said to be followed by the explosive propagation of chains. Vaughan and Phillips point out that the delay of explosions of mercury fulminate in atmospheres of hydrogen or helium (the effect being in the ratio of the thermal conductivities) found by Garner and Hailes (*Proc. Roy. Soc.*, 1933, *A*, **139**, 576) is most likely due to cooling effects and the damping of self-heating. They suggest that self-heating takes place on a much larger scale, and give experimental results to prove this point. In the present work it seems that general self-heating precedes explosion, for otherwise the oil could not prevent explosion by damping the self-heating.

The fact that if the crystals are confined explosion is more likely to occur shows that explosion only follows when the heat from the reaction can no longer be rapidly dissipated. Self-heating effects, possibly combined with an autocatalytic effect, will therefore, explain the brief and rapid acceleratory period in the normal decomposition *in vacuo*. The kinetics are further complicated by the interaction between the manganese oxides and the ammonium nitrate produced.

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