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THE THERMAL DECOMPOSITION OF LEAD NITRATE*

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Abstract—The thermal decomposition of lead nitrate has been investigated in the temperature range from 250 to 435°C. Information obtained from the infra-red analysis of the decomposition products indicate that the reaction proceeds via a basic nitrate or metallic nitrite structure, while gasometric analysis indicates that the decomposition proceeds essentially via the loss of nitrogen oxide and oxygen, without significant oxidation of the lead ion.

THE thermal decomposition of lead nitrate has been investigated as part of a programme to investigate the interaction of nitrogen dioxide and metallic oxides. It has been found in preceding investigations,(1,2) that nitrogen dioxide is the prime decomposition product in the decomposition of nitrates. Further, the effect of the decomposition is such that oxidation of the metallic ion can be initiated. In particular, in the decomposition of cerium [III] nitrate(2) the decomposition leads directly to cerium dioxide under all conditions, with an apparent progression in oxidation states as the decomposition proceeds. In the case of the decomposition of praseodymium nitrate the picture is considerably complicated by a whole progression of oxidation states from an effective oxidation state of Pr(III) to Pr(IV). The picture is further complicated by the appearance of intermediate nitrate–nitrite products.

The present investigation has been conducted as an extension of the above work with consideration given to the variable oxidation state of lead as well as the greater instability of the higher oxides of lead.(3) As in the preceding work gasometric and infra-red analysis of the decomposition products was used as a means of following the reaction path.

RESULTS

The material used in this study was a single batch of high purity Baker lead nitrate. This material was desiccated under vacuum over magnesium perchlorate and weighed in desiccated containers. The samples were then placed in the decomposition chamber,(1) which consisted of an oil manometer and associated traps. The sample was then raised to the desired temperature within a period of 1–3 min. The reaction was followed by means of the oil manometer as previously described. The pressure–time curve was found to assume a sigmoidal shape as indicated in Fig. 1.

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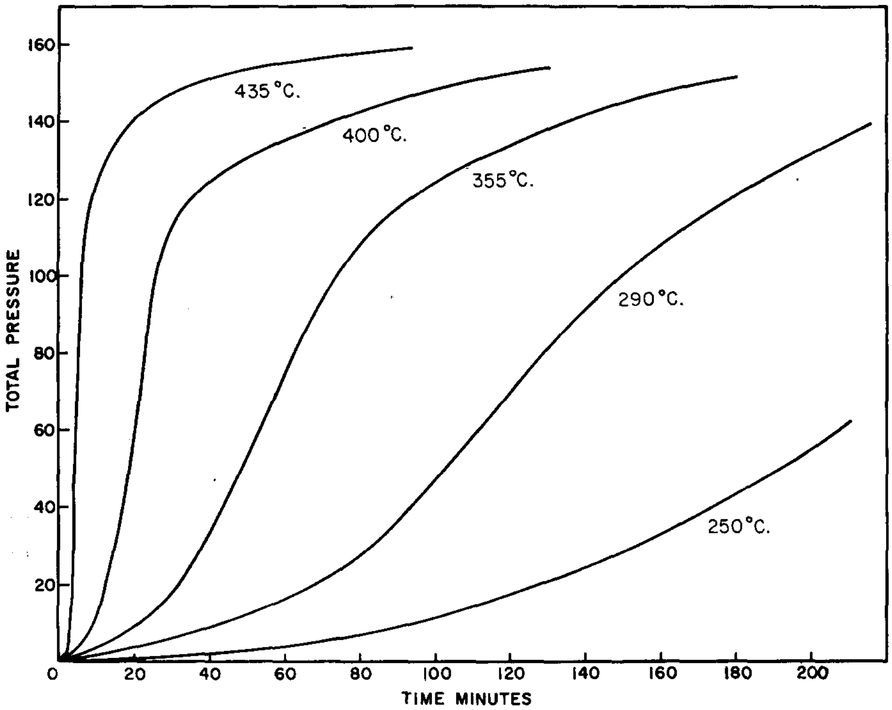

FIG. 1.—Kinetics of the thermal decomposition of lead nitrate; total pressure in mm vs. time in min.

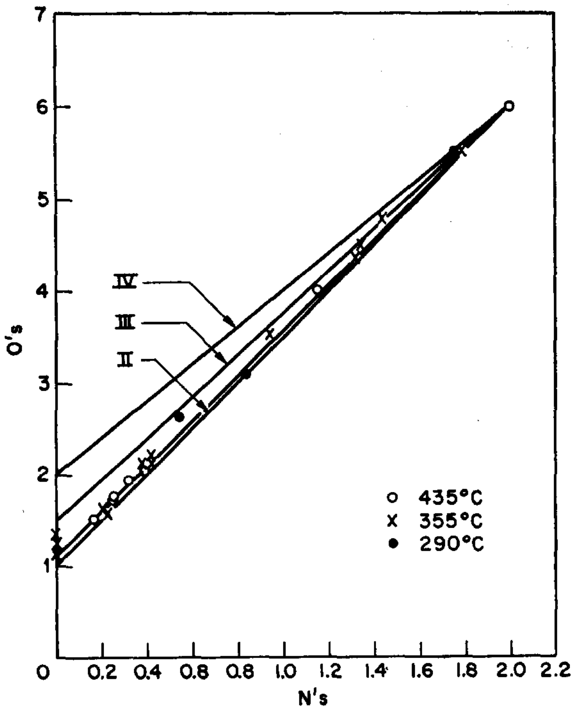

FIG. 2.—Composition correlation in the thermal decomposition of lead nitrate; oxygen stoichiometry vs. nitrogen stoichiometry; II, III, IV indicates the theoretical oxidation axis for the lead ion.

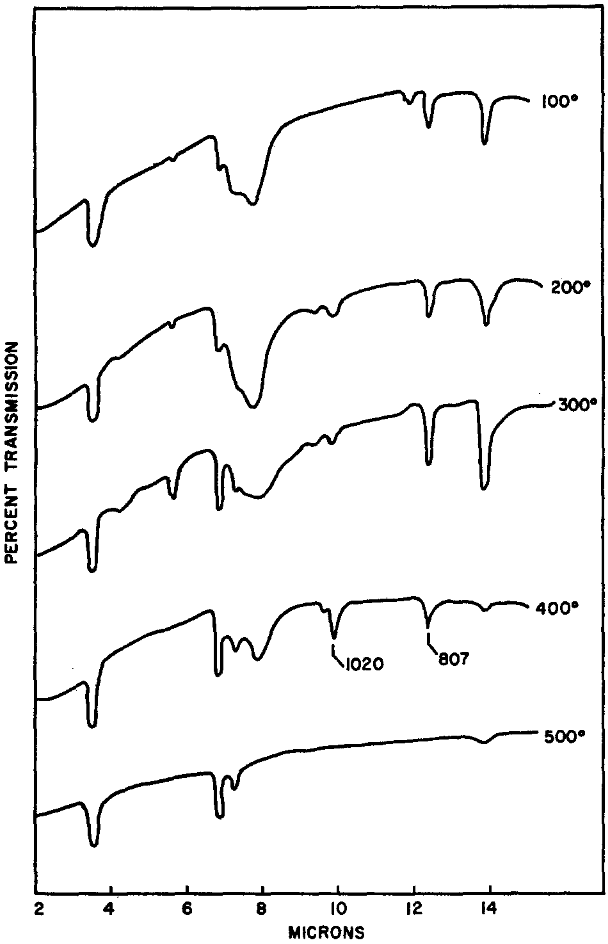

FIG. 3—Infra-red spectra of the decomposition products of lead nitrate obtained at various temperatures; spectra obtained in Nujol with rock salt optics.

It may be seen in this figure that at the lowest temperature (250°C) the decomposition is approximately 30 per cent complete in 200 min while at 400°C the reaction is essentially complete in 50 min.

Gas analysis was performed by condensation of the nitrogen dioxide at liquid nitrogen temperatures to obtain the partial pressure of oxygen. Upon removal of the oxygen the partial pressure of NO_2–N_2O_4 was obtained. The absence of the lower oxides of nitrogen was established by the absence of a discoloration of the condensate and by the infra-red analysis of the gas. Details of the analysis are given in Reference (1).

It was found from the above analysis that the oxygen–nitrogen content of the decomposition products executed a straight line through the composition $Pb(NO_3)_2$ and PbO as seen in Fig. 2. Thus, one may presume that the oxidation state of the lead ion remained essentially divalent (II) as indicated by the correlation with the theoretical divalent axis. The fact that some oxidation has occurred is borne out by the scatter of points between the (II) and (III) oxidation co-ordinates.

On conclusion of the decomposition run, the sample was subjected to infra-red analysis. The spectrum was obtained in the 2 to 15 μ region in a Nujol null. A representative progression is shown in Fig. 3 for products obtained at increasing decomposition temperatures. Nujol lines are evident at ~3·5, 6·8 and 7·3 μ. The bands at ~7·4, 7·6–7·8, 12·4 and 13·9 μ are due to the presence of metallic nitrate.(4) It may be seen that as the decomposition temperature is increased the intensity of these bands decrease. Further in evidence are two bands at ~9·3 and 9·8 μ. These bands are due to the presence of metallic nitrite(5) and as such occur at intermediate stages of the decomposition.

DISCUSSION

In contrast to the decomposition of cerium (III) nitrate the present study indicates that the lower oxidation state is preferred under the conditions of the decomposition. The scatter of points above the (II) oxidation axis and below the (III) axis is strongly in accord with the work of ANDERSON and STERNS(3) who found that the monoxide of lead can be oxidized under modest conditions to the nonstoichiometric intermediate of PbO_x where $1{\cdot}0 \leqslant x \leqslant 1{\cdot}5$. In general this transition was found to be strongly time dependent requiring as much as 20 hr at 310°C and 600 mm P_{O_2} to reach $PbO_{1{\cdot}5}$. It is therefore not surprising that the presence of a partial pressure of 60 to 100 mm of oxygen and/or nitrogen oxide has no greater effect than that noted in Fig. 2. It is suggestive in this regard that the egress of nitrogen oxide and oxygen from lead nitrate leave the lead as Pb(II) and only on extended exposure does the transition-up in oxidation state occur. A further point in evidence of the direct egress of NO_2 is indicated by the nitrite structure which occurs in the intermediate decomposition regions and can conceivably act as a decomposition intermediate to nitrogen dioxide. The next logical step in this study is an investigation of the interaction of lead monoxide and nitrogen dioxide.(6)

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