JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 18
1984

The Formation of NO_2ClO_4 as an Intermediate during the Low-temperature Decomposition of Ammonium Perchlorate

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Analytical evidence has been obtained that an oxidized nitrogenous species is formed during the low-temperature thermal decomposition (*ca.* 500 K) of NH_4ClO_4; the estimated rate of reaction of NO_2ClO_4 closely accounts for the observed rate of ammonium perchlorate breakdown and nitryl perchlorate is therefore identified as the reaction intermediate.

Many papers in the literature have accepted the proposal[1] that the initial step in the low-temperature thermal decomposition of ammonium perchlorate (AP) is proton transfer. An investigation of the electrical conductivity of AP did not support this mechanism, however, and it was concluded,[2] therefore, that the decomposition reaction proceeded through electron transfer. This model does not explain the relatively low temperature at which AP reacts, some 300 K below the temperature of breakdown of the alkali perchlorates.[3] Solymosi[4] has suggested that the stability of the ClO_4^- ion is reduced on covalent bond formation and this leads us to the conclusion that AP decomposition proceeds through the intermediate nitryl perchlorate. The decomposition of NO_2ClO_4 is rapid[5] at the temperature (*ca.* 500 K) of AP reaction.

Prompted by the earlier suggestion,[6] that ammonium nitrate (AN) may be a decomposition product of all ammonium salts of sufficiently oxygenated acids, we further[6] investigated the influence of this additive on the AP reaction. Although AN was sublimed rapidly at *ca.* 500 K *in vacuo,* it caused a marked reduction (×0.3) in the induction period to AP reaction and it slightly accelerated (×1.5) the subsequent decomposition rate. Examination in a scanning electron microscope of partially (10—20%) decomposed AP single crystals in the initial presence of AN showed that reaction had started more rapidly than usual on all AN covered surfaces. There was no evidence of liquid or melt formation and the structure of the residual product[6] was identical with that obtained from the reaction of the pure salt. It was also shown that AN promoted further breakdown of the low-temperature reaction residual product[7] and that other nitrates [$Mg(NO_3)_2 \cdot 6H_2O$ and KNO_3] were similarly capable of reducing the induction period to onset of AP decomposition.

Following the observation that nitrates were capable of initiating AP decomposition, we demonstrated analytically that a small amount of an oxidized nitrogenous species was also present in partially reacted (50%) *pure* AP. Samples of pure AP, after reaction to an appropriate extent, were dissolved in ammonia-free water and quantitatively analysed by the following two methods. In one, the solution was mixed with brucine sulphate under specified[8] acidic conditions and the absorption at 405 nm measured spectrophotometrically. In the other, the solution was boiled with alkali (NaOH) until it was ammonia-free, reduced when cool with Devarda's alloy, and Nessler's reagent added. Suitable blanks were prepared and absorptions were compared with standards containing known amounts of NO_3^- or NH_4^+ respectively.

The quantities of oxidized nitrogen detected were small ($0.08 \pm 0.04\%$ NO_2ClO_4) and were here believed[4] to be present as nitryl perchlorate under the strongly acidic[6] conditions obtaining within the nuclei. If this steady-state concentration is maintained during the median region of the sigmoid yield–time curve, it is estimated, from extrapolation of kinetic data for reaction[5] of NO_2ClO_4 and assuming zero-order behaviour, to result in completion of AP decomposition in 70 min at 503 K. This estimate is in very satisfactory agreement with the observed time of 85 min, also at 503 K, and this is strong evidence for the identification of NO_2ClO_4 as the essential intermediate in the AP reaction. Further support is given by the close agreement of apparent activation energy values (130 kJ mol^{-1}) for the decomposition of NO_2ClO_4 and of AP.

We suggest that the rate-limiting step in nitryl perchlorate breakdown proceeds as in reaction (1) (the rupture of covalent bonds occurs more readily than the reaction of ionic perchlorates[3]). The products regenerate NO_2^+ through ammonia oxidation (NH_4NO_3 is a product of NH_4ClO_3 decomposition[4]) thereby regenerating the intermediate. This mechanism also accounts for the intervention of $NOClO_4$ in NO_2ClO_4 breakdown.[5]

$$NO_2^+ClO_4^- \longrightarrow O_2NO\text{–}ClO_3 \longrightarrow O_2 + NO^+ + ClO_3^- \qquad (1)$$

On the assumption that the NO_2ClO_4 is present in the form of mobile small particles, or droplets of liquid,[9] this reaction model is capable of explaining the unusual structure of the residual product from AP decomposition. It is suggested that such particles advance by eroding reactant in their paths and leave a hollow tube behind. This extends a previous discussion[9] of the probable role of mobile participants, even liquids, in nucleation and growth reactions of solids.

M. A. M. thanks the Egyptian Government and the O.R.S. Award Schemes for Scholarships held during this research.

Received, 12th June 1984; Com. 822

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