Journal of Thermal Analysis, Vol. 7 (1975) 587–592

THERMAL DECOMPOSITION OF METHYLAMMONIUM PERCHLORATE

P. R. NAMBIAR, V. R. PAI VERNEKER and S. R. JAIN*

Indian Institute of Science, Bangalore, 560 012, *India*

(Received December 7, 1973; in revised form May 7, 1974)

The thermal decomposition of methylammonium perchlorate (MAP) has been studied under isothermal and non-isothermal conditions. Differential thermal analysis of MAP showed, in addition to the exotherm due to decomposition, another exotherm at 408° which was observed for the first time. Chemical analysis and the infrared spectrum of the residue left behind after the decomposition proved it to contain NH_4ClO_4. The results have been explained on the basis of a methyl group transfer in addition to proton transfer in the decomposition process.

Unlike ammonium perchlorate (AP), methylammonium perchlorate (MAP) $CH_3NH_3ClO_4$ is an explosive material [1, 2] and has not been so thoroughly investigated. Its thermal properties have been studied only in recent years, various techniques being used [2–6]. Early literature reports, however, indicate its explosive nature; for example, Datta and Chatterjee [7] reported the explosion temperature of this compound to be 338°. Recent differential thermal analysis (DTA) data, reported by Stammler et al. [2], show that MAP undergoes crystallographic transitions at 48 and 178°, melts at 255° and decomposes at around 330°. Mack and Wilmot [3] and Guillory and King [4] using a matrix infrared (IR) technique and mass spectrometry, respectively, have concluded that the decomposition of MAP takes place via dissociation involving a proton transfer mechanism. However, no kinetic studies of the thermal decomposition of this compound have been reported.

While carrying out a detailed study on the thermal sensitivities of substituted ammonium perchlorates and related compounds, we noticed an additional exotherm in the DTA of MAP above its decomposition point. This, we believe, is a new observation and needs an explanation. In this paper we report some of the results of thermal decomposition of MAP, along with a possible explanation of the new observation.

---

* To whom all correspondence should be addressed at the Department of Aeronautics.

Experimental

a/ Material

Methylammonium perchlorate (MAP) was prepared by reacting an aqueous solution of methylamine with perchloric acid (70 per cent). The salt recrystallised from aqueous alcohol was vacuum-dried and was checked for purity by NMR and chemical analysis. The NMR spectrum showed the resonances due to $-CH_3$ protons and $-NH_3$ protons to be at τ7.46 (τ7.40 reported [8]) and τ2.60 (τ2.57 reported [9]), respectively. Chemical analysis of the perchlorate content agreed well with that calculated for MAP.

b/ Apparatus

The details of the differential thermal analysis (DTA) and thermogravimetric analysis (TGA) units are given in an earlier paper [10]. Heating rates employed were 10°/min and 5°/min for DTA and TG, respectively. The atmosphere in both cases was static air.

Results and discussion

The DTA trace of MAP at atmospheric pressure shows all the features reported by Stammler et al. [2] up to its decomposition point, and in addition an exotherm, at 408°. To help understand the process responsible for the second exotherm, residual analysis of the products was carried out just after decomposition. The sample was allowed to cool to room temperature by removing the furnace just after the first exotherm, i.e. at 355°. Chemical analysis of the residue showed the presence of AP, giving positive tests for NH_4^+ ion with Nessler's reagent (MAP does not give a positive test with this reagent), and for ClO_4^- ion with methylene blue. The IR spectrum of the residue also agreed well with that of an authenticated sample of AP and does not contain the absorptions characteristic of methyl groups. The presence of AP in the residue, and absence of MAP after the decomposition at 355°, indicates that the exotherm at 408° in the DTA trace of MAP might be due to the secondary decomposition of AP, which is reported to take place at ~400° [11].

When the DTA was carried out at reduced pressure (~1 mm Hg), instead of the two previous exotherms, an endotherm was observed at 309°, with a small exotherm at 414° (Fig. 1).

Dynamic TG of MAP shows an inflection point at 319°, the sample losing about 87 per cent of its weight at this point (Fig. 2). From 320 to 400°, the TG trace shows a gradual weight loss, and at 400° the total weight loss is 97.5 per cent. The gradual terminal weight loss seems to indicate the decomposition of AP formed as a result of the first decomposition. Since the TG curve does not clearly show two decomposition steps, it is possible to argue that from 320 to 400° the compound undergoes a gradual terminal weight loss only. However, TG results together with DTA data suggest that the decomposition beyond the inflection point may be that of AP.

The thermal decomposition of MAP under isothermal conditions in the temperature range 270 – 290° was followed by a thermogravimetric technique. An insignificant amount of sublimate was formed on the cooler parts of the TG set-up at atmospheric pressure, indicating dissociation [4] of the salt. The α vs. t plots are presented in Fig. 3. There appears to be a break in the curves at $\alpha = 0.5$ to 0.55.

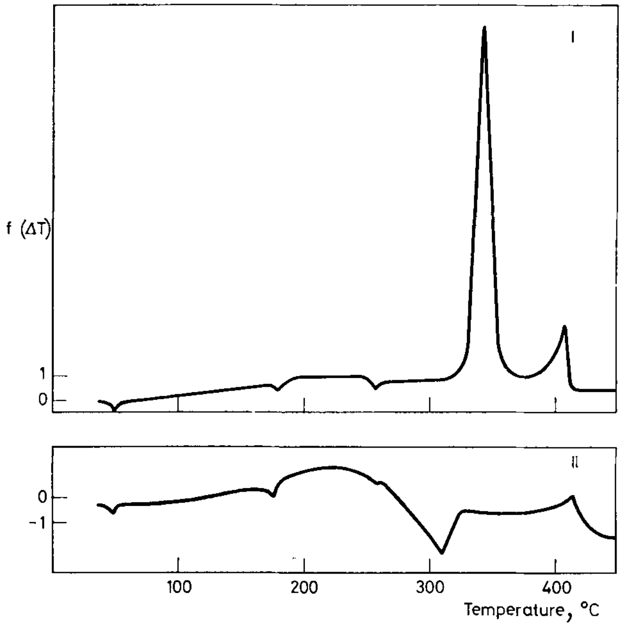

Fig. 1. DTA traces of MAP at atmospheric pressure (I) and at 1 mm Hg, (II)

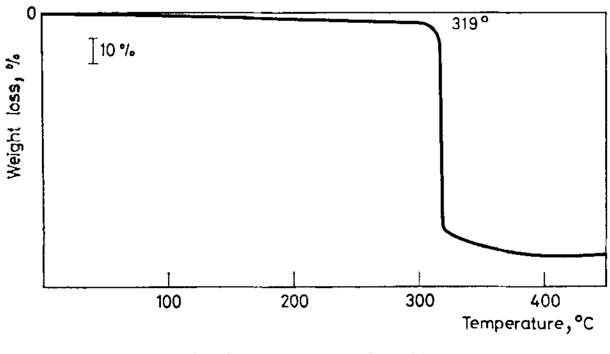

Fig. 2. TG trace of MAP

The activation energies for the two parts were calculated by the Jacobs – Kureishy method [12] and found to be 14.4 kcal/mole for $\alpha = 0.1$ to 0.5, and 18.4 kcal/mole for $\alpha = 0.55$ to 0.75. Here again chemical tests show the presence of AP in the residue left behind after 55 per cent weight loss. The IR spectrum of the residue showed no absorption characteristic of methyl groups, thus indicating the absence of MAP. The IR spectrum of this residue was identical to that of the residue obtained in the DTA experiment after the first exotherm. As a matter of fact, both spectra were superimposable on that of an authenticated sample of AP. It therefore follows that when the weight loss is 55 per cent, MAP is completely decomposed and converted to AP. The decomposition curves above $\alpha = 0.55$ can therefore only correspond to the decomposition of AP. Further, the second activation energy value of 18.4 kcal/mole is close to that reported [13, 14] for the thermal decomposition of AP in this temperature range. AP is also formed below $\alpha = 0.55$. However, it can decompose only very slightly in such a short time interval and the main process taking place at $\alpha = 0.1$ to 0.5 is the decomposition of MAP. We are therefore tempted to propose that the activation energy in the range $\alpha = 0.1 - 0.5$ is related to the process of thermal decomposition of MAP, whereas the activation energy in the range $\alpha = 0.55 - 0.75$ is that for AP.

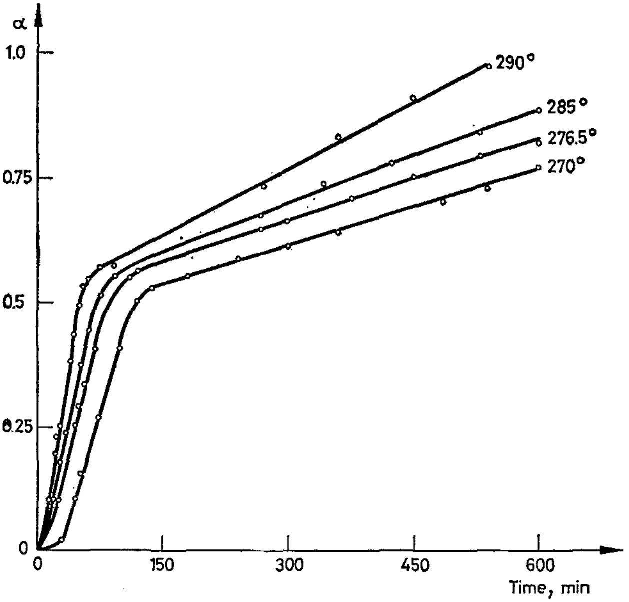

Fig. 3. α vs. t plots

The formation of AP as a decomposition product may be explained as follows. The decomposition of MAP is known [3 – 5] to take place via a proton transfer.

Whereas most of the reaction occurs via a proton transfer mechanism, it is possible to envisage that a small fraction of the decomposition may take place via a methyl group transfer. The dissociation processes can then be represented as follows:

$$\begin{array}{lll} & \nearrow CH_3NH_2 + HClO_4 & \quad\text{(i)} \\ CH_3NH_3ClO_4 & & \\ & \searrow NH_3 + CH_3ClO_4 & \quad\text{(ii)} \end{array}$$

Methyl perchlorate, being unstable in this temperature range, may decompose as soon as it is formed. However, the NH_3 formed may combine to a certain extent with perchloric acid to yield NH_4ClO_4.

A similar methyl group transfer to perchlorate anion has been proposed in the thermal decomposition of tetramethylammonium perchlorate [15], the DTA traces of which at atmospheric pressure and at 1 mm Hg showed that the intensity of the exotherm was very much reduced at low pressure compared to that at atmospheric pressure. In the case of MAP, the DTA trace at 1 mm Hg shows an endotherm instead of an exotherm. The effect of dissociation from steps (i) and (ii) and consequent sublimation is endothermic, which is enhanced at low pressures because the reaction products can diffuse away from the hot reaction zone. The exothermic effect results from the decomposition and/or the reaction of the dissociation products, which takes place preferentially at atmospheric pressure rather than at low pressure since the time of residence of the oxidizing and the oxidizable species in the reaction zone is longer at normal pressure. The observed exotherm at normal pressure is therefore the net effect of these two processes, which occur simultaneously. At low pressure the exothermic effect is more than compensated by the endothermic process. Similar results have been obtained on analogous compounds such as AP and ammonium nitrate, where dissociation and decomposition take place simultaneously [16–18]. In both these cases the exotherm at normal pressure appears as an endotherm at low pressures [19, 20]. In the present case, some evaporation of the molten material may also contribute to the endothermic effect. The small exotherm at 414° at 1 mm Hg may again be due to the combined effect of the decomposition/sublimation of AP.

It may further be argued that the thermal decomposition of other methyl-substituted ammonium perchlorates, e.g. $(CH_3)_2NH_2ClO_4$ and $(CH_3)_3NHClO_4$, may also occur via a competitive proton and methyl group transfer mechanism. A careful examination of DTA and TG results for these compounds, however, has not provided any evidence so far for the presence of decomposition products formed as a consequence of the reaction taking place partially via a methyl group transfer mechanism.

References

1. Encyclopedia of Explosives and Related Items, Vol. I, Picatinny Arsenal Dover, New Jersey, 1960, p. A 227.
2. M. Stammler, R. Bruenner, W. Schmidt and D. Orcutt, Advan. X-ray Anal., 9 (1966) 170.
3. J. L. Mack and G. B. Wilmot, J. Phys. Chem., 71 (1967) 2155.
4. W. A. Guillory and M. King, J. Phys. Chem., 73 (1969) 4367.
5. W. G. Schmidt, NASA Contract Report 1969, NASA-CR-66757, p. 54.
6. G. V. Ivanov, A. M. Viktorenko and A. G. Tereshchenko, Izv. Vyssh. Ucheb. Zaved. Khim. Khim. Technol., 15 (1972) 1628. CA 78: 113520 (1973).
7. R. L. Datta and N. R. Chatterjee, J. Chem. Soc., 115 (1919) 1006.
8. K. Tori, T. Iwata, K. Aono, M. Ohtsura and T. Nakagawa, Chem. Pharm. Bull. (Japan), 15 (1967) 329.
9. B. M. Fung, J. Phys. Chem., 72 (1968) 4708.
10. S. R. Jain and P. R. Nambiar, Indian J. Chem. 12 (1974) 1087.
11. R. C. Mackenzie, Differential Thermal Analysis, Vol. I, Academic Press, London and New York, 1970. p. 373.
12. P. W. M. Jacobs, and A. R. T. Kureishy, J. Chem. Soc. (1964) 4718.
13. J. N. Maycock and V. R. Pai Verneker, Proc. Roy. Soc., A 307 (1968) 303.
14. G. B. Manelis and Yu. I. Rubstov, Zh. Fiz. Khim., 40 (1966) 770; CA 65: 3058 (1966).
15. P. R. Nambiar, V. P. Pai Verneker and S. R. Jain, J. Thermal Anal. (Submitted).
16. S. P. Tang and J. B. Fenn, J. Phys. Chem., 77 (1973) 940.
17. G. Feick, J. Am. Chem. Soc., 76 (1954) 5858.
18. G. Feick and R. M. Hainer, J. Am. Chem. Soc., 76 (1954) 5860.
19. V. R. Pai Verneker, M. McCarthy, Jr. and J. N. Maycock, Thermochim. Acta, 3 (1971) 37.
20. P. Breisacher, H. H. Takimoto, G. C. Denault and W. A. Hicks, Combustion and Flame, 19 (1972) 144.

Résumé — On a étudié la décomposition thermique du perchlorate de méthylammonium (PMA) en conditions isothermes et anisothermes. L'analyse thermique différentielle des perchlorates de méthylammonium a montré, en plus du phénomène exothermique dû à la décomposition, un second pic exothermique à 408°C, observé pour la première fois. L'analyse chimique et le spectre infrarouge du résidu de décomposition ont établi la présence de NH_4ClO_4. Les résultats s'expliquent bien par le transfert d'un groupe méthyle accompagné d'un transfert de proton lors du processus de décomposition.

Zusammenfassung — Die thermische Zersetzung von Methylammonium-Perchlorat (MAP) wurde unter isothermen Bedingungen untersucht. Die DTA zeigte neben der exothermen Spitze für die Zersetzung noch eine weitere bei 408°, über die noch nie berichtet wurde. Die Analyse des Zersetzungsrückstandes ergab NH_4ClO_4. Diese Ergebnisse wurden durch einen zusätzlich zur Protonenübergabe ablaufenden Methylgruppentransfer erklärt.

Резюме — Было изучено термическое разложение перклората метиламмония (МАП) при изотермических и не изотермических условиях. Дифференциальный термический анализ этого соединения показал наряду с экзотермой, обусловленной разложением, наличие другой экзотермы при 408°, которая наблюдалась нами впервые. С помощью химического анализа и инфракрасных спектров было установлено, что остаток после разложения содержит NH_4ClO_4. Полученные результаты объяснены совместным переносом метильной группы и протона в процессе разложения.