Journal of Thermal Analysis, Vol. 18 (1980) 21—28

THERMAL DECOMPOSITION OF ETHYL AND ISOPROPYL AMINE PERCHLORATES

T. J. THOMAS* and U. S. NANDI

Department of Inorganic and Physical Chemistry
Indian Institute of Science
Bangalore — 560012, India

(Received September 2, 1978; in revised form May 31, 1979)

Thermal decomposition of ethyl and isopropyl amine perchlorates has been studied by methods such as DTA, TG, isothermal weight loss measurements and the decomposition products have been analyzed in a mass spectrometer. Activation energy values for thermal decomposition have been calculated from $\alpha - t$ plots. The proton transfer dissociation mechanism proposed for the thermal decomposition of ammonium perchlorate (AP) has been extended to explain the decomposition products of these two substituted amine perchlorates.

Substituted amine perchlorates have generated considerable interest in recent years since they can be used as auxiliary oxidizers and burning rate additives in composite solid propellants [1—7]. However, these substituted perchlorates are quite sensitive to explosive stimuli such as impact and friction, thus restricting their use in practical propellant systems. Stammler *et al.* [8] have studied mono-, di-, tri- and tetramethyl amine perchlorates by DTA and also determined their impact sensitivity. They have shown that monomethyl amine perchlorate is the most sensitive to impact and the relative thermal stability increases with substitution. The inductive effect of the methyl group is supposed to play a role in the thermal stabilisation by increasing the electron density on the nitrogen and thus making the proton transfer process more difficult. Nambiar *et al.* [4, 5] have studied the thermal decomposition of methyl amine perchlorate by DTA, TG, isothermal weight loss measurements, explosion delay and by mass spectrometricanalysis of the decomposition products. They have calculated the activation energy for thermal decomposition of various methyl substituted amine perchlorates by the Jacobs—Kureishy and the Prout—Tompkins equations. Activation energies increase with substitution upto trimethyl amine perchlorate. Tetramethyl amine perchlorate shows a different trend. This has been explained on the basis of the proton transfer dissociation mechanism which cannot take place in the case with four methyl substituents on nitrogen. The overall mechanism can be represented thus:

$$(CH_3)_n\,NH_{4-n}ClO_4 \rightarrow (CH_3)_nNH_{3-n} + HClO_4 \rightarrow \text{Products.}$$

---

* Present address: Propellant Engineering Division, Vikram Sarabhai Space Centre, Trivandrum — 695 022, India.

Mass spectrometric analysis shows that the final decomposition products are CO, CO_2, H_2O, Cl_2, etc. Recently Fogel'zang *et al.* [9] have reported the combustion of organic perchlorates and presented data on the burning rate (r)- pressure (p) dependence of these salts. Methyl amine perchlorates are found to show discontinuities in their $r-p$ curves as in the case of AP. The present work is an extension of these studies on ethylamine perchlorate and isopropyl amine perchlorate. Incidentally, these compounds are the model systems for polyethylenimine perchlorate and polypropylenimine perchlorate and the data generated in this study have been compared with those of the corresponding polymers. [10].

Experimental

Materials

Aqueous solutions (40 per cent, w/v) of ethyl amine and isopropyl amine have been neutralized with 70 per cent perchloric acid until there is a slight excess of perchloric acid. The solution is then evaporated on a water bath to a concentration which permits separation of the salts on cooling. The solutions are then cooled to about 5° when the corresponding amine perchlorate separates. The white crystals are filtered off using a sintered glass crucible and washed with small quantities of ice-cold water. Recrystallisation of the salts have been carried out from distilled water. The recrystallised samples are dried in a vacuum desiccator over phosphorous pentoxide.

Ethyl amine perchlorate and isopropyl amine perchlorate exist as white crystals which are highly hygroscopic. They are soluble in water, alcohol, dimethyl sulfoxide, etc. Both salts have been characterized by chemical analysis and IR spectra. Chemical analysis has been carried out by the method developed by Kurz *et al.* [11]. The compounds are more than 99 per cent pure and contained less than 0.2 per cent of water.

The IR spectra of these salts have been recorded both by the mulling technique using nujol and as a pellet with KBr. The infrared absorptions of these compounds are in good agreement with the values reported in literature [12, 13].

Apparatus and methodology

DTA, TG and isothermal weight loss experiments have been carried out with a custom made instrumental set up, the details for which have already been described by Jain and Nambiar [14]. An associated Electrical Industries MS 10 mass spectrometer is employed to analyse the decomposition products of the two salts. The sample is taken in a 90° bent long glass tube and connected to the mass spectrometer. The system is then evacuated to a pressure of about 10^{-8} torr and the background relative intensities are noted. The sample tube is then surrounded by a tubular furnace heated to the decomposition temperature of the salts. The decomposition products are led into the "ion source cage" until an optimum pressure builds up. The furnace is then removed and the sample tube is cut off from the mass spectrometer by means of a stop-cock. The relative ion intensities are then recorded against various *m/e* values. The difference between these values and the corresponding background values gives the ion intensities corresponding to the respective decomposition products/fragments.

Results and discussion

DTA, TG and isothermal weight loss measurements

Figures 1 and 2 show the DTA and TG traces for ethyl amine perchlorate and isopropyl amine perchlorate, respectively. The DTA traces of both salts show one exotherm each in the temperature regions of 290 and 300°. A melting point endotherm is also observed in the case of isopropyl amine perchlorate just before the exotherm. TG traces show only one weight loss region in the temperature range of 40 – 400°. Figures 3 and 4 shows the α-t curves from isothermal weight loss experiments for both salts conducted at different temperatures varying from 240 to 280°. Activation energies for both systems have been calculated by the method

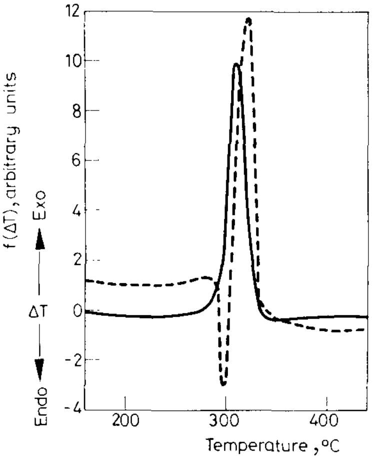

Fig. 1. DTA traces of ethyl (———) and isopropyl (— — — —) amine perchlorates. Sample weight: 25 mg. Atmosphere: air

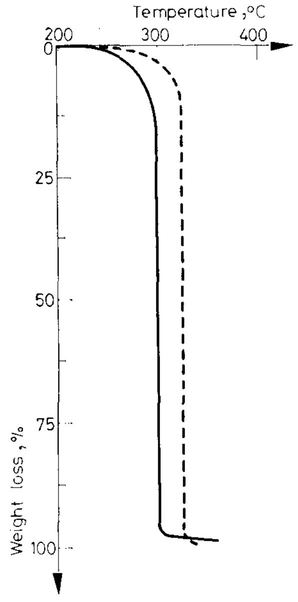

Fig. 2. TG traces of ethyl (———) and isopropyl (— — — —) amine perchlorates. Sample weight: 15 m. Atmosphere: air

of Jacobs and Kureishy [15]. The advantage of this approach is that the applicability of the equation depends on a single kinetic equation which need not even be known over a finite range of decomposition. Activation energies thus calculated are presented in Table 1. Values for mono-, di-, and tri-methyl amine perchlorates

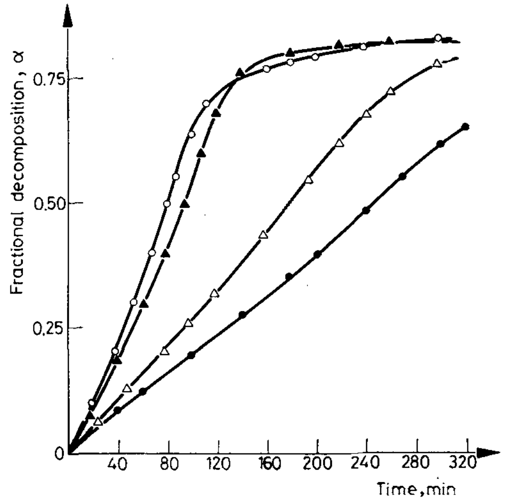

Fig. 3. Isothermal weight loss curves for ethyl amine perchlorate: 240° (•); 245° (△); 252° (▲); and 259° (○)

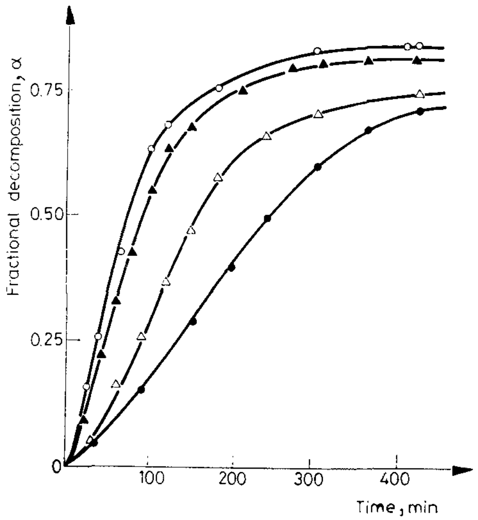

Fig. 4. Isothermal weight loss curves for isopropyl amine perchlorate: 260° (•); 270° (△); 275° (▲) and 280° (○)

Table 1

Activation energy for thermal decomposition of substituted amine perchlorates

Compound	Temperature region, °C	Range of α	E_a, kcal/mole
$CH_3NH_3ClO_4^a$	270–290	0.1 –0.5	40
$CH_3CH_2NH_3ClO_4$	260–285	0.1 –0.5	42
$(CH_3)_2\,CH\,NH_3ClO_4$	240–260	0.1 –0.50	34
$(CH_3)_2\,NH_2ClO_4^a$	260–285	0.1 –0.5	51
$(-CH_2NH_3ClO_4)_2^b$	265–295	0.1 –0.5	54
$(CH_3)_3\,NHClO_4^a$	269–287	0.25–0.75	80

[a] Values from reference 4.
[b] Reference 22.

as well as that for ethylene diamine diperchlorate have also been included for comparison.

From the DTA and TG curves, it can be seen that ethyl amine perchlorate decomposes at a lower temperature than isopropyl amine perchlorate. However, the activation energy value is comparatively less in the case of isopropyl amine perchlorate.

Mass spectrometric analysis of decomposition products

Table 2 presents the mass spectra of ethyl and isopropyl amine perchlorates. Eventhough considerable work has been carried out on the mass spectrometric analysis of the decomposition products of AP [15], very few such studies have been reported in the case of amine perchlorates. Since these compounds have the same elemental composition as that of a composite propellant, analysis of their decomposition products will be highly rewarding and can throw much light on the complex physico-chemical processes taking place during the combustion of propellants [16].

In the mass spectrometric experiments, 25 mg samples have been taken for the decomposition and the relative ion intensities of the products recorded after 30 minutes heating in each case. From Table 2 it is evident that the relative amount of various products are larger in the case of isopropyl amine perchlorate. This is partly due to the low activation energy for this salt compared to ethyl amine perchlorate. However, the concentration of CO_2 in the decomposition products shows a different trend and this can be explained on the basis of the stoichiometry of both salts.

Some of the species identified in the decomposition products of ethyl and isopropyl amine perchlorates are CO, CO_2, N_2, H_2O, HCl, HCN and O_2. Traces of oxides of nitrogen, N_2O and NO_2 are also found. Earlier to this work, Guillory

Table 2

Mass spectra of the thermal decomposition products of ethyl and isopropyl amine perchlorates

m/e	Probable assignment of fragment	Relative ion intensities	
		Ethyl amine perchlorate	Isopropyl amine perchlorate
12	C^+	9.3	10.2
14	CH_2^+, N^+	2.7	4.8
15	CH_3^+	6.0	18.4
16	CH_4^+, O^+	15.4	25.7
17	OH^+, NH_3^+	1.0	1.5
18	H_2O^+	4.0	5.0
22	CO_2^{++}	2.2	1.5
26	CN^+, $CH{\equiv}CH^+$	11.0	8.2
27	HCN^+	22.0	21.0
28	CO^+, N_2^+, $C_2H_4^+$	71.0	92.4
30	NO^+, CH_2O^+	1.2	0.8
32	O_2^+	2.7	0.3
35	$^{35}Cl^+$	0.1	–
36	$H^{35}Cl^+$	0.2	0.8
38	$H^{37}Cl^+$	0.06	0.3
44	CO_2^+, N_2O^+	77.0	60.7

and King [2] have studied the dissociation products of methyl amine perchlorates and Nambiar et al [4] have analysed the decomposition products from these compounds. Nambiar got definitive proof for the existence of CO_2 and CO in the decomposition products whereas Guillory and King failed to report these species. We have assigned the decomposition products following the same arguments adopted by Nam et al [4].

Based on the identity of the decomposition products and the kinetic data, a mechanism can be proposed for the thermal decomposition of substituted amine perchlorates. As in the case of AP [17, 18], proton transfer dissociation is the initial step in the thermal decomposition of amine perchlorates:

$$CH_3CH_2NH_3ClO_4 \rightarrow CH_3CH_2NH_2 + HClO_4 .$$

$$(CH_3)_2CH\ NH_3\ ClO_4 \rightarrow (CH_3)_2\ CHNH_2 + HClO_4 .$$

The free amine and perchloric acid thus produced will be held together in the form of a weak molecular complex as in the case of AP [19]. As the temperature increases, the two species separate and get adsorbed on the surface of the crystal. From the adsorbed state, the amine and $HClO_4$ can get either desorbed into the gas phase or the $HClO_4$ can decompose heterogeneously on the surface of the crystal. The heterogeneous decomposition assumption is supported by Levy's work [20] on the thermal decomposition of $HClO_4$. He has shown that the decomposition of $HClO_4$ is heterogeneously catalyzed below 325°, whereas it takes place in the gas phase above this temperature. Since the decomposition of ethyl and isopropyl amine perchlorates occurs at temperatures below 325°, it can reasonably be assumed to proceed by surface decomposition of $HClO_4$.

The heterogeneous decomposition of perchloric acid is found to have an activation energy of about 10 kcal/mole. More recently, heterogeneous decomposition of perchloric acid has been studied [21] between 150 and 260°. The following mechanism has been proposed:

$$2\,HClO_4 \xrightarrow{k_2} Cl_2 + 7/2\,O_2 + H_2O.$$

$$HClO_4 + H_2O \longrightarrow HClO_4 \cdot H_2O.$$

$$HClO_4 \quad H_2O \xrightarrow{k_1} 1/2\,Cl_2 + 3/2\,H_2O + 7/4\,O_2.$$

Activation energies have been calculated to be 8.9 and 21.3 kcal/mole for the second and first order steps, respectively. The existence of oxides of chlorine, especially chlorine monoxide, has been proved in the decomposition products of $HClO_4$. The following equilibrium may exist:

$$Cl_2 + O_2 \rightarrow 2\,ClO.$$

It is the reaction between these oxidizing species (formed from perchloric acid decomposition) and the amine perchlorate/free amine which results in the mass spectrometrically observed decomposition species from substituted amine perchlorates. In the case of a balanced system such as ethylene diamine diperchlorate [22], such an oxidation can lead into a stoichiometric reaction:

$$(-CH_2\,NH_3\,ClO_4)_2 \rightarrow 2\,CO_2 + 4\,H_2O + 2\,HCl + N_2.$$

The proton transfer dissociation mechanism finds further proof from Pittman's experiments [7] on the burning rate enhancement of propellants with ethyl and isopropyl amine perchlorates.

*

References

1. J. L. Mack and G. B. Wilmot, J. Phys. Chem., 71 (1967) 2155.
2. W. A. Guillory and M. King, J. Phys. Chem., 73 (1969) 4367.
3. G. V. Ivanov, A. M. Viktorenko and A. G. Tereshchenko, Izv. Vysshykh Uchebn Zavedenii, Khim i. Khim. Tekhnol., 15 (1972) 1628.
4. P. R. Nambiar, V. R. Pai Verneker and S. R. Jain, J. Thermal Anal., 8 (1975) 15.
5. P. R. Nambiar, V. R. Pai Verneker and S. R. Jain, J. Thermal Anal., 7 (1975) 587.
6. W. G. Schmidt, NASA Contract Report 1969, NASA — CR — 66 757.
7. C. U. Pittman Jr., AIAA J., 7 (1969) 328.
8. M. Stammler, R. Bruenner, W. Schmidt and D. Orcutt, Advan. X-ray Anal., 9 (1966) 170.

9. A. E. FOGEL'ZANG, B. S. SVETLOV, V. S. OPRYSHKO and V. YA. ADZHEMYAN, Fiz. Goreniya Vzryva, 8 (1972) 357.
10. T. J. THOMAS and U. S. NANDI, Ind. Eng. Chem.: Product R & D., 16 (1977) 186.
11. E. KURZ, G. Klober and M. Berl, Anal. Chem., 30 (1958) 1983.
12. G. WERNER and K. KELLER, Chem. Ber., 93 (1960) 1982.
13. R. M. SILVERSTEIN and G. C. BASSLER, Spectrometric Identification of Organic Compounds, John Wiley and Sons Inc., New York, 1967, p. 96.
14. S. R. JAIN and P. R. NAMBIAR, Indian J. Chem., 12 (1974) 1087.
15. P. W. M. JACOBS and A. R. T. KUREISHY, J. Chem. Soc., (1964) 4718.
16. T. J. THOMAS and U. S. NANDI, Proc. 3rd National Symp. I C Engines and Combustion, University of Roorkee, India, 1976, p. 451.
17. P. W. M. JACOBS and H. M. WHITEHEAD, Chem. Rev., 69 (1969) 551.
18. A. R. HALL and G. S. PEARSON, Oxidation and Combust. Rev., 3 (1968) 129.
19. P. W. M. JACOBS and A. RUSSEL, Jones, AIAA J., 5 (1967) 829.
20. J. B. LEVY, J. Phys. Chem., 66 (1962) 1092.
21. G. S. PEARSON, Advances in Inorganic and Radiochemistry (H. J. Emeleus and A. J. Sharpe, Eds.), Vol. 8, Academic Press, New York, 1966, p. 178.
22. T. J. THOMAS and U. S. NANDI, Combust. Flame (in press).

RÉSUMÉ — On a étudié, par des méthodes comme l'ATD, la TG et les mesures de pertes de poids isothermes, la décomposition thermique des perchlorates d'amines éthylique et isopropylique et on a analysé les produits de décomposition dans un spectromètre de masse. On a calculé les valeurs de l'énergie d'activation de la décomposition thermique à partir des fonctions α-t. On a étendu le mécanisme de dissociation du transfert de protons, proposé pour la décomposition thermique du perchlorate d'ammonium (AP), afin d'expliquer la formation des produits de décomposition de ces deux perchlorates d'amines substitués.

ZUSAMMENFASSUNG — Die thermische Zersetzung von Äthyl- und Isopropylaminperchloraten wurde durch die Methoden der DTA, TGA sowie durch isotherme Gewichtsverlustmessungen untersucht und die Zersetzungsprodukte in einem Massenspektrometer analysiert. Die Werte der Aktivierungsenergien der thermischen Zersetzung wurden aus α-t Funktionen berechnet. Der für die thermische Zersetzung von Ammoniumperchlorat (AP) vorgeschlagene Proton-Übergangs-Dissoziationsmechanismus wurde erweitert um die Zersetzungsprodukte dieser zwei substituierten Aminperchlorate zu erklären.

Резюме — Изучено термическое разложение перхлоратов этил- и изопропиламинов методами ДТА, ДТГ и измерениями изотермической потери веса. Продукты разложения анализировались масс-спектрометром. Значения энергий активации для термического разложения были вычислены из графиков α-t. Диссоциационный механизм переноса протона, предложенный для термического разложения перхлората аммония, был использован для объяснения продуктов разложения этих двух веществ.