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A DERIVATOGRAPHIC STUDY OF THE THERMAL DEGRADATION OF TETRABUTYL AMMONIUM PERCHLORATE

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ABSTRACT

This article presents the results of non-isothermal analysis, under static air and dynamic argon atmospheres, of tetrabutyl ammonium perchlorate (TBAP), alone and in the presence of MnO_2 as a thermal catalyst. Thermogastitrimetry and mass spectrometry were used to identify some of the gaseous products. The effects of the four butyl groups on the thermally excited ammonium nitrogen atom are discussed. The thermal stabilities of TBAP and the parent molecule, ammonium perchlorate, are compared. The effects of using different sample weights, atmospheres and crucible materials were tested.

INTRODUCTION

Organic and inorganic perchlorates are powerful oxidizing agents and are used extensively as oxidants in solid propellants, explosives and pyrotechnics, either alone or in mixtures with powdered metals, metallic oxides, organo-metallic compounds and other additives [1–3]. Jasim and co-workers have carried out thermoanalytical investigations of $Ba(ClO_4)_2$ and ten transition and non-transition metals [4,5]. In organic solvents such as toluene and alcohol, organic perchlorates are versatile reagents for oxidation. Tetraalkyl ammonium perchlorates, and in particular tetrabutyl ammonium perchlorate (TBAP) and tetraethyl ammonium perchlorate (TEAP), have been used as supporting electrolytes in organic voltametry and amperometry. There are no reports of thermoanalytical investigations of TBAP in the chemical literature, and the present work was intended to meet this need.

EXPERIMENTAL

Simultaneously recorded TG, DTG, DTA and T curves for TBAP and ammonium perchlorate, alone and in mixture with MnO_2, were obtained

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TABLE 1

Experimental conditions

Sample weights	200 and 500 mg
Sample and reference crucibles	Platinum and ceramic, large size, cylindrical
Reference	α-Al_2O_3
Heating rate	10 ° C min^{-1}
Heating program	Ambient to 900 ° C
Atmospheres	(1) Static air (2) Dynamic argon (flow rate of 50 cm^3 min^{-1})
Sensitivities: TG	200 and 500 mg
DTG	1/10
DTA	1/10

using an MOM–Photorecording derivatograph. The experimental conditions were as described in Table 1.

An MOM thermo-gas-titrator was used to measure some of the gaseous products, such as ammonia and CO_2. Mass spectra of the condensing pyrolysates of the decomposition of TBAP were recorded using a Nermag–Delsi automatic quadrapole gas analyser–mass spectrometer. All the chemicals used were of analytical grade puriss.

The samples were dried at 110 ° C for 1 h, cooled in a desiccator, and stored there when not in use.

RESULTS AND DISCUSSION

The compound loses moisture completely on heating to 110 ° C. The TG and DTG curves (Fig. 1) indicate that the colourless anhydrous compound, $(CH_3CH_2CH_2CH_2)_4NClO_4$, is thermally stable up to 290 ° C. Decomposition then begins, at a marked rate, and proceeds topochemically and quite violently through the formation of a mixture of gaseous products. This is accompanied by a substantial exothermic effect. The small sharp melting endotherm on the DTA curve indicates that this crystalline compound melts ($T_{max} \simeq 213$ ° C, literature value $\simeq 210$ ° C) before degradation. The sharp high exopeak ($T_{max} = 320$ ° C) has an explosive character. The condensed products (Table 2) are $HClO_4$, HCl, NH_3, H_2O, $HClO_3$, NH_4Cl and hydrocarbon fragments. These were identified on the basis of thermogastitrimetric curves (not shown, for brevity), and data obtained by injecting the condensed pyrolysates into the mass spectrometer and characterizing them by field ionization (rather than fragmentation).

Appreciable differences were observed between the thermal analysis curves recorded under static air and dynamic argon. The values of T_{max} for peaks recorded under argon were shifted slightly ($\simeq 18$ ° C) towards lower temper-

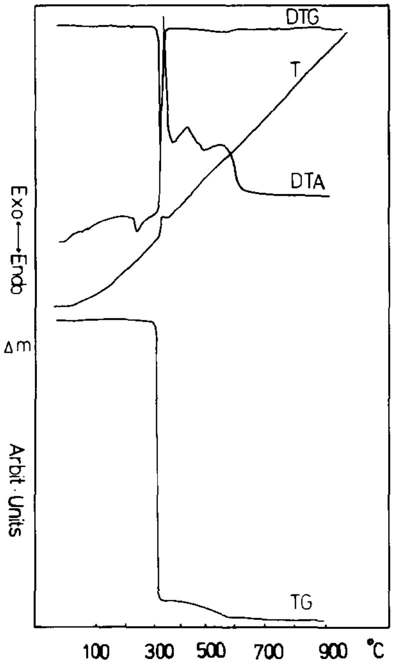

Fig. 1. Simultaneous T, TG, DTG and DTA curves for tetrabutyl ammonium perchlorate.

atures; and the two exotherms recorded at T_{max} = 400 ° C and 520 ° C under air were not present in the curves recorded under argon. Almost identical results were obtained for both sample weights (200 and 500 mg). A shift of 5 ° C towards lower values of $T_i - T_f$ was observed when ceramic crucibles were used. Also, the melting and burning endotherms obtained under both atmospheres were broader (as compared with runs performed using platinum crucibles); but their areas, as measured by planimeter units, were almost the same whether ceramic or platinum crucibles were used.

TABLE 2

Characterization of condensed pyrolysates of TBAP at 300 ° C using field ionization mass spectrometry (argon atmosphere)

m/z	Condensed pyrolysates	Intensity (%)
100	$HClO_4$	83
84	$HClO_3$	85
36	HCl	68
17	NH_3	30
18	H_2O	35
44	CH_2-CH_2-NH_2	11
57	CH_3-CH_2-CH_2-CH_2	16

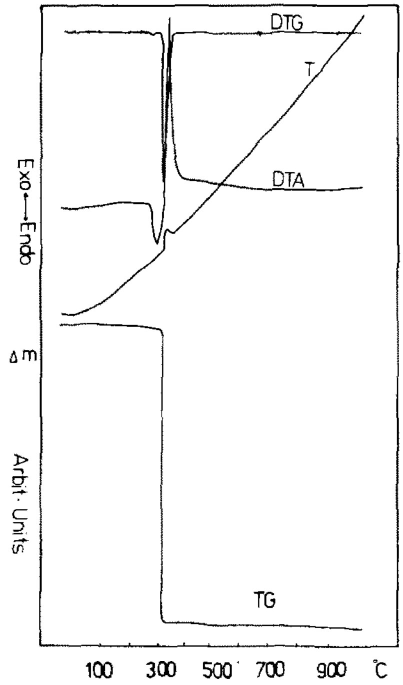

Fig. 2. Simultaneous T, TG, DTG and DTA curves for ammonium perchlorate.

For the sake of comparison of the heat stability of TBAP with that of the parent molecule, ammonium perchlorate (AP), derivatographic curves for the latter were recorded under identical experimental conditions (Table 1). From the results (Fig. 2), it can be concluded that TBAP is thermally less stable than AP, for which melting and degradation occur almost instantaneously (Fig. 2). A hypothetical explanation for this behaviour can be put forward as follows. The electronic outer level of thermally excited nitrogen atom is expanded owing to the presence of the four butyl groups. Its electronegativity is thereby increased and therefore also its capacity to abstract the thermally excited hydrogen atoms of neighbouring butyls. This transition state brings about some sort of unbalanced polarity of the TBAP molecule, and perhaps increases its entropy and the likelihood of its being easily melted and decomposed as compared with the parent (AP) molecule. Manually, it is difficult to perform sound calculations to determine parameters of the decomposition thermodynamics (enthalpy, free energy and entropy) or kinetics (n, E_a and z) of the transient decomposition peaks of TBAP and AP. Of course, this would be possible were one to use a microprocessor-controlled thermal analyser supplied with adequate software.

It was thought worthwhile to test the effects of varying amounts of MnO_2 on the thermal degradation of TBAP (as a model of an organic perchlorate) and AP (as a model inorganic perchlorate). Optimum exothermicity of the main decomposition stage for TBAP was obtained with a mixture containing 20 wt.% MnO_2. The melting point minimum of TBAP was catalytically lowered by 17 ° C. This reduction was not simply due to dilution because the degradation began at 260 ° C in the presence of the catalyst, as compared with 300 ° C when no catalyst was present, and proceeded quite vigorously, accompanied by a transient sharply increasing exotherm. This was immediately followed by a rather broad medium-sized exotherm (T_{max} = 430 ° C). The catalyst also had the effect of merging the second exopeak obtained in runs without MnO_2 (Fig. 1) with the first exopeak.

In the presence of 20 wt.% MnO_2, the exothermicity of AP was appreciably increased and the heat stability was lowered by about 10 ° C. Other thermal effects were not tangibly altered.

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