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THERMAL CHARACTERIZATION OF TETRAMETHYLPHOSPHONIUM PERCHLORATE, -NITRATE AND -PICRATE

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ABSTRACT

Tetramethylphosphonium perchlorate, -nitrate and -picrate have been characterized thermally employing differential thermal analysis and thermogravimetric techniques. The thermal stability of these compounds is found to be in the order, perchlorate>nitrate>picrate. A similar trend in stability has been observed in the case of the corresponding ammonium compounds. These observations have been explained in terms of the dissociation of these salts prior to their decomposition. Explosion sensitiveness of these compounds has been determined by explosion delay measurements which also seem to indicate the same order of relative stability. The ammonium compounds appear to be more stable than their phosphonium counterparts.

INTRODUCTION

It is well known that certain phosphorous compounds burn in air either spontaneously or with the application of a small amount of friction[1] whereas some of the others are so stable that they have been used for flame-proofing. Elemental phosphorous has been employed as a self-igniting, hot-burning ingredient in the manufacture of incendiary bombs. The effect of heat on quaternary phosphonium salts with non-oxidising anions, e.g., halides[2], ethoxides[3] etc., has been studied to some extent. However, thermal decomposition studies of phosphonium compounds with oxidising anions have not been reported so far. It is interesting to note that PH_4ClO_4, the immediate analogue of NH_4ClO_4, which has been used extensively as oxidizer in solid rocket propellants, is highly unstable and explodes violently in the dry state[4]. Substituted phosphonium perchlorates are relatively stable at ordinary conditions[5–7]. Tetramethylphosphonium perchlorate exploded slightly above 370°C and the corresponding picrate exploded with a flame on rapid heating in a sealed tube[6]. No systematic thermal decomposition study of these compounds has, however, been reported in the literature so far.

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In this paper we report our investigations on the thermal decomposition of tetramethylphosphonium perchlorate, -nitrate and -picrate using differential thermal analysis (DTA), thermogravimetry (TG) and explosion delay measurements. The results have been compared with the corresponding ammonium compounds and interpreted postulating dissociation of the compounds preceding the decomposition.

EXPERIMENTAL

Materials

Trimethylphosphine was prepared as reported in the literature[8] by the reaction between PCl_3 and CH_3MgI. Tetramethylphosphonium iodide was prepared by reacting trimethylphosphine with methyl iodide in ether which was then converted into the perchlorate or the nitrate by treating it with the corresponding acid. Tetramethylphosphonium picrate was prepared from the corresponding iodide by metathesis with sodium picrate as reported in the literature[9]. These compounds were recrystallised from aqueous alcohol and dried under vacuum. The chemical analysis for phosphorous and the anion contents agreed well with those expected for these compounds. The proton magnetic resonance spectrum showed only the expected signals, i.e., a doublet at τ 8.1 with J_{PCH} about 15 cps in each case.

Methods

The DTA, TG and explosion delay measurements were carried out with the equipment already mentioned in a previous paper[10]. 20 mg of sample were employed in each of the DTA and TG runs. Explosion delay measurements were carried out with 40 mg of the substance in each case.

RESULTS AND DISCUSSION

The DTA and TG results of the phosphonium compounds along with those of the corresponding ammonium compounds obtained in the present investigation are summarized in Table 1. Tetramethylphosphonium perchlorate shows two endotherms, one at 300 °C and the other at 360 °C. The endotherm at 300 °C appears as exotherm when the system is allowed to cool after having been heated up to 320 °C. This endotherm cannot be due to melting since the compound appears to melt only at ~360 °C in a capillary just before decomposition. It is possible, therefore, that the observed endotherm at 300 °C may be due to a phase transition as observed in the case of tetramethylammonium perchlorate[11] whereas the one at 360 °C is due to melting. The DTA traces of tetramethylphosphonium nitrate and -picrate do not show any endotherm which can be ascribed to phase transitions, but the latter showed an endotherm at 320 °C which may be due to melting since the compound is known to melt[6] at 328–330 °C. Here again, decomposition proceeds just after melting. The DTA trace of tetramethylammonium nitrate shows a small endotherm at 325 °C. This may be due to a crystal transformation since it does not appear to melt below 335 °C.

TABLE 1

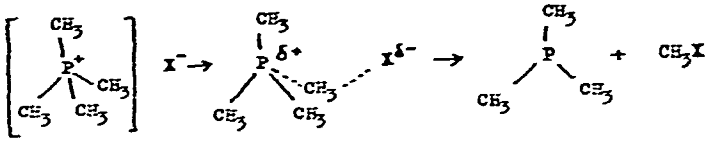
THERMAL DECOMPOSITION DATA

Compound	*DTA peak temp.* (°C)[a]	*TG*		*Activation energy* (*kcal mol*$^{-1}$)
		Decomposition temp. (°C)	*% weight loss*	
$(CH_3)_4PClO_4$	300(−), 360(−), 392(+)	347	98.9	44 (α0.1→0.5)
$(CH_3)_4PNO_3$	332(+)[b]	342	98.8	40(DTA)
$(CH_3)_4PC_6H_2N_3O_7$	320(−), 331(+)	331	97.3	29 (α0.1→0.5) 32.5(DTA)
$(CH_3)_4NClO_4$[c]	402(+)	422	98.5	50.4 (α0.25→0.75)
$(CH_3)_4NNO_3$	325(−), 373(+)	363	98.2	—
$(CH_3)_4NC_6H_2N_3O_7$	319(−), 337(+)	354	92.3	—

[a] (+) and (−) after temperatures represent exotherm and endotherm, respectively. [b] The compound was diluted with alumina. [c] Data reported in ref. 10.

Tetramethylammonium picrate gives an endotherm at 319 °C which may be due to melting, since in a capillary it was observed to melt at 322 °C with decomposition.

The decomposition temperatures of tetramethylphosphonium perchlorate, -nitrate and -picrate are in the decreasing order, perchlorate>nitrate>picrate. The decomposition temperature from TG and activation energy for decomposition also point to the same trend, indicating thereby that the picrate is the least stable. A similar trend is observed in the case of the corresponding ammonium compounds also. All these results could be explained to a certain extent if it is assumed that these decomposition reactions are controlled by a dissociation process which can be represented as follows:



X^- = perchlorate, nitrate or picrate

Such a process can be expected to be influenced by the nucleophilicity of the anion, the cation being the same. The order of decreasing $R_4N^+X^-$ stability with respect to R_3N+RX is roughly that of increasing X^- nucleophilicity[12]. Among the cases in which the attachment to a particular atom (e.g., oxygen) is compared, there is a correlation between basicity and nucleophilicity[13]. Since the basicity order of these anions is known[12] to be perchlorate<nitrate<picrate, the observed trend in thermal stability of these compounds can be accounted for based on a corresponding nucleophilicity order and a corresponding relative ease of dissociation.

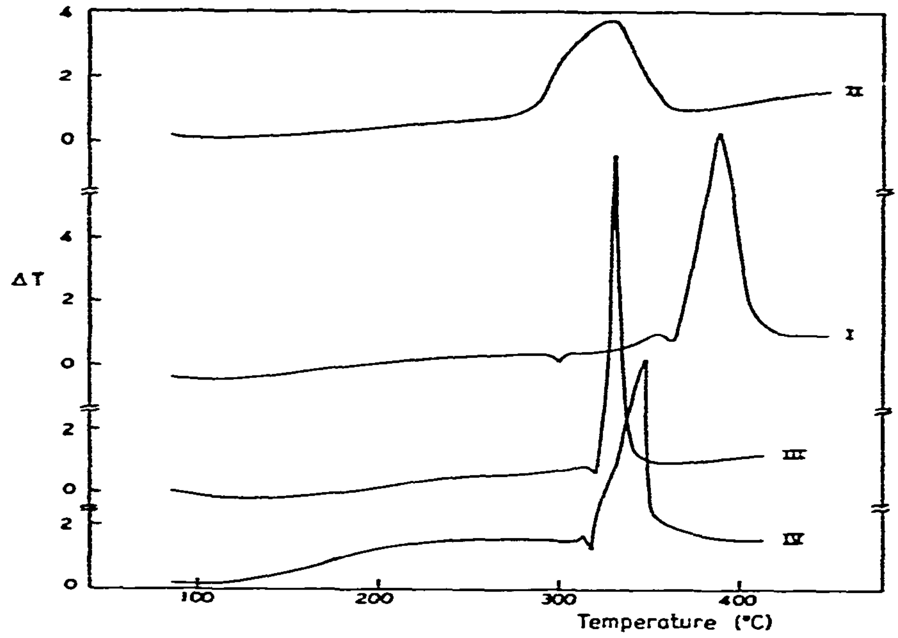


Fig. 1. DTA traces of tetramethylphosphonium perchlorate(I), -nitrate(II) and -picrate(III) at atmospheric pressure and of tetramethylphosphonium picrate at ~1 mm Hg(IV).

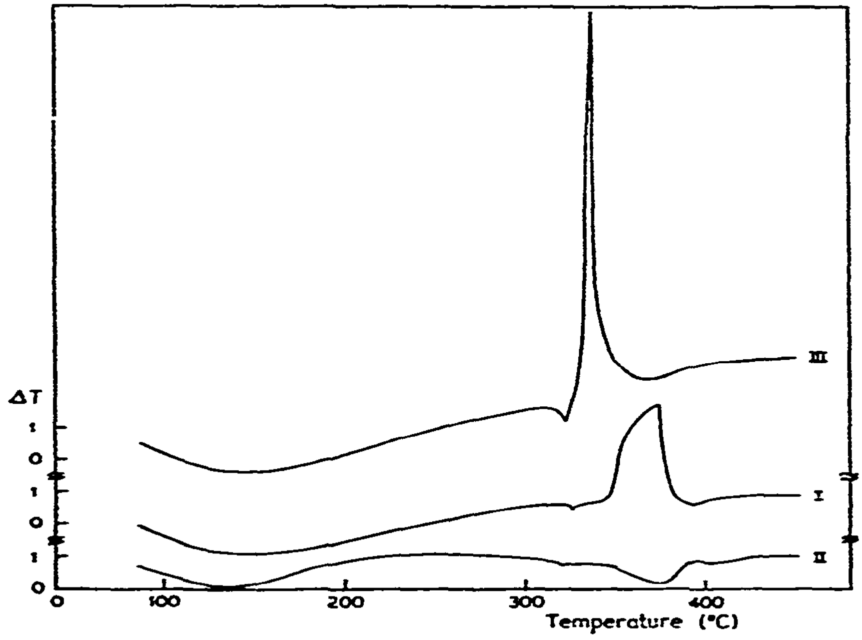


Fig. 2. DTA traces of tetramethylammonium nitrate at atmospheric pressure(I) and at ~1 mm Hg(II), and of tetramethylammonium picrate at atmospheric pressure(III).

It is now fairly well established that the thermal decomposition of ammonium perchlorate[14], methyl-substituted ammonium perchlorates[15] and ammonium nitrate[16] proceeds via a dissociation process. Such a step is not established in the case of phosphonium compounds with oxidising anions although the phosphonium halides appear to dissociate first on heating[2]. It is to be noted that the DTA exotherm due to decomposition of these compounds which decompose via dissociation is invariably observed as an endotherm or exotherm with reduced intensity when the DTA is carried out at low pressure[7,17–19], sublimation being predominant at low pressures.

In order to ascertain the dissociation step in the present case, the DTA of the compounds was carried out at low pressure (~1 mm Hg) (Figs. 1 and 2). In the case of tetramethylammonium compounds at low pressure, the nitrate showed a clear endotherm while the perchlorate showed an exotherm with reduced intensity[10]. Only a small reduction in intensity was noticeable in the case of the picrate. These compounds gave a sublimate when the DTA was carried out under reduced pressure. In the case of tetramethylphosphonium perchlorate and -picrate at low pressure, the DTA trace of the latter showed a reduction in intensity of the exotherm, whereas that of the former showed virtually no reduction in intensity. Both these compounds, however, yielded sublimate in minute quantities when they were decomposed carefully in a sublimation apparatus.

It is tempting, therefore, to conclude that the decomposition of all these compounds may proceed via a dissociation process. Non-reduction in the intensity of the exotherm in the case of tetramethylphosphonium perchlorate may, to some extent, be explained to be due to the extreme reactivity of trimethylphosphine towards oxidising species. Most of the methylperchlorate formed as a dissociation product may decompose and oxidise trimethylphosphine in situ, resulting in the observed exothermic reaction. It is also possible that an endotherm or a reduced exotherm may result at a much lower pressure in this case.

The kinetics of the solid-state decomposition of tetramethylphosphonium perchlorate and -picrate have been studied using isothermal TG technique. Typical α–t plots are shown in Fig. 3. The activation energy (Table 1) for thermal decomposition was calculated by the Jacob Kureishy method[20] (Fig. 4). Activation energy for the thermal decomposition of tetramethylphosphonium nitrate was found from DTA trace[21]. As can be seen, the activation energy values for thermal decomposition of these compounds decrease in the same order as their decomposition temperatures. It is possible that the activation energy in the present case corresponds to the dissociation process, the relative ease of which is thus shown to increase in the order perchlorate < nitrate < picrate.

Explosion sensitiveness of tetramethylphosphonium perchlorate and -picrate has been determined. The results of explosion delay measurements of these compounds, along with the values obtained for tetramethylammonium perchlorate[10], -nitrate and -picrate are presented in Table 2. It is interesting to note that the explosion delay data also show a trend similar to the thermal decomposition results, thus confirming the relative thermal stability of these compounds to be in the same

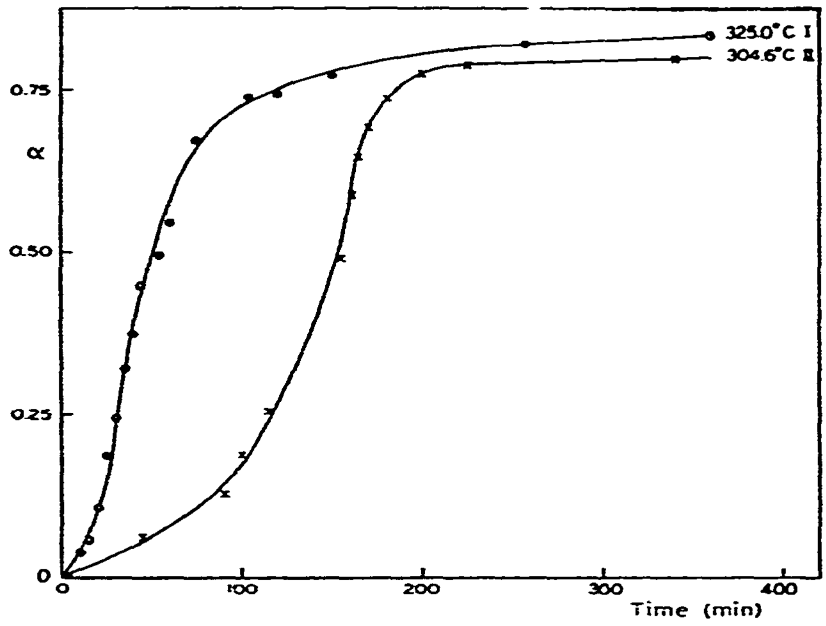


Fig. 3. Typical α–t plots of tetramethylphosphonium perchlorate (I) and of tetramethylphosphonium picrate(II).

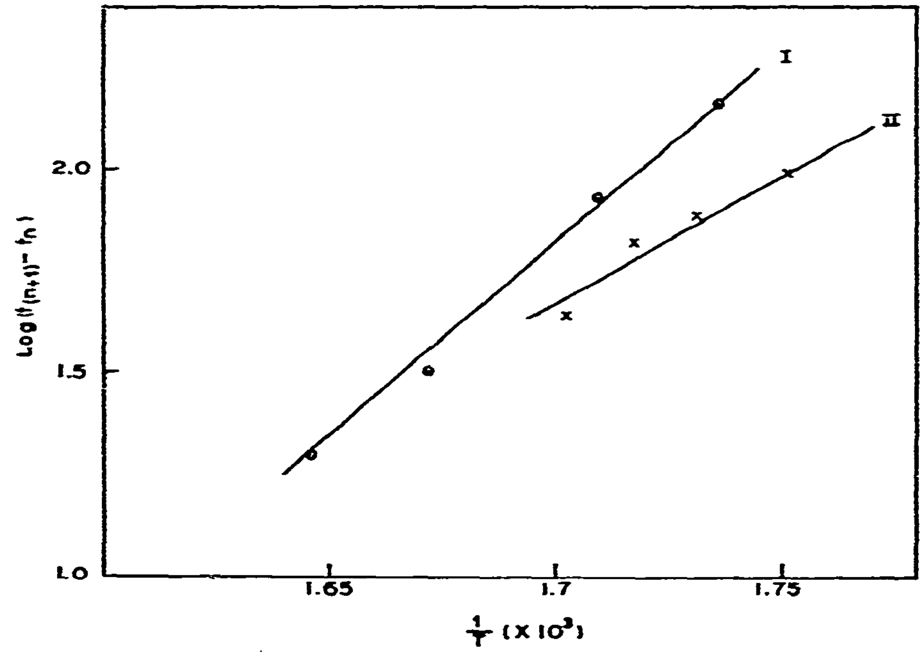


Fig. 4. Log ($t_{n+1} - t_n$) vs. $1/T$ plots for tetramethylphosphonium perchlorate (I) and for tetramethylphosphonium picrate (II).

TABLE 2

EXPLOSION DELAY DATA

Compound	*Time (sec.) for explosion at*						*Activation energy (kcal mol^{-1})*
	360°C	*380°C*	*390°C*	*400°C*	*410°C*	*420°C*	
$(CH_3)_4PClO_4$	61.1	38.5	—	31.5	—	24.3	13.5
$(CH_3)_4PC_6H_2N_3O_7$	45.6	30.5	—	28.8	—	20.8	11.4
$(CH_3)_4NClO_4$	—	—	—	81.0	59.0	47.1	25.3
$(CH_3)_4NNO_3$	—	48.0	35.5	29.8	—	—	21.0
$(CH_3)_4NC_6H_2N_3O_7$	—	38.2	29.8	23.9	—	—	20.7

order as discussed before. The explosion delay measurements of tetramethylphosphonium nitrate, however, could not be carried out because of its extreme hygroscopicity. It may further be noted that there appears to be a direct correlation between thermal decomposition and explosion delay[10] results.

The thermal characteristics of tetramethylphosphonium perchlorate, -nitrate and -picrate could, at this stage, be compared with those of the corresponding ammonium compounds. The values of the decomposition temperature, time for explosion at a particular temperature and activation energy for the physicochemical process controlling explosion delay are all lower for the phosphonium compounds than for their ammonium counterparts (Tables 1 and 2). This order of relative stability of the phosphonium and ammonium compounds could also be explained in terms of dissociation of these salts. Anions being the same, the relative ease of the dissociation process may depend upon the basicity of the amine or the phosphine. Trimethylphosphine is known[22] to be a weaker base than trimethylamine and therefore tetramethylphosphonium compounds may dissociate relatively more easily than the corresponding ammonium compounds. A similar observation has been made with regard to the relative stability of the phosphonium and ammonium halides[23].

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