*Thermochimica Acta*, 58 (1982) 379–382
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands


## Note

# THERMAL BEHAVIOUR OF DIPHENYLAMMONIUM PERCHLORATE

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(Received 13 April 1982)

The high oxygen content of perchlorates makes them useful in the domain of explosives, pyrotechnics and solid state rocket propellants [1]. The extent of exothermicity of the solid state decomposition of these salts depends on the presence of reducing moieties. As part of our investigation on the thermal stabilities of -onium type perchlorates [2–4], the preparation and characterization of diphenylammonium perchlorate are reported in this paper. The study was followed using XRD, IR, TG, DTA and MS techniques.

## EXPERIMENTAL

Diphenylammonium perchlorate, $[(C_6H_5)_2NH_2]\ ClO_4$ (DPP), was prepared by neutralizing an alcoholic solution of diphenylamine with 40% perchloric acid. The resultant very weakly acidic solution was concentrated over a water bath and cooled, thereby the separated colourless crystals were collected on a filter and dried. Analysis: C, 53.1; H, 4.2; N, 5.3%. Calculated for $C_{12}H_{12}NO_4Cl$: C, 53.4; H, 4.5; N, 5.2%.

The X-ray powder diffraction patterns were taken using $CuK_\alpha$ radiation on a Philips diffractometer. The IR spectra were recorded on a Perkin-Elmer 257 spectrometer using KBr pellet technique. TG and DTA studies were carried out in air and nitrogen atmosphere using a Du Pont thermal analyzer taking 5–7 mg samples. The mass spectra were recorded on a VG micromass 70-70FF double focussing mass spectrometer with a VG 2235 data system.

## RESULTS AND DISCUSSION

The crystals of DPP are non-hygroscopic and fairly stable in air. The interplanar spacings calculated from the X-ray powder patterns of the compound are (in Å): 8.44w, 7.69s, 6.51s, 5.61m, 4.87m, 4.55s, 4.42s, 4.27w, 4.21m, 3.88m, 3.78w, 3.46m, 3.30s, 3.18m, 3.13w, 3.03w, 2.93m, 2.84w, 2.61w. The IR spectrum exhibited characteristic bands due to $NH_2$, CH, CC

0040-6031/82/0000–0000/$02.75 

and $ClO_4$ groups [5]. Thus the frequencies appearing at 3380 and 1600 $cm^{-1}$ are due to $\nu_{NH_2}$ and $\delta_{NH_2}$. The bands around 3000, 1420 and 800 $cm^{-1}$ are assigned to $\nu_{CH}$, $\nu_{CC}$ and $\pi_{CH}$, respectively. The Cl–O stretching frequencies are found at 1090 and 620 $cm^{-1}$.

The thermal behaviour of DPP in an atmosphere of nitrogen is quite different from that in air. The thermal plots are reproduced in Fig. 1. The TG curve in air indicates that the decomposition takes place in two stages in the temperature ranges 140–375 and 430–600°C. No residue remained at 600°C, indicating complete oxidation to gaseous products. The weight loss observed at the end of the first stage is found to be 50%. In a separate experiment a known amount of DPP was heated to 400°C and the chemical analysis of the black residue obtained is found to be mainly carbon. The second stage of decomposition is thus attributed to the oxidation of this carbonaceous matter. The TG curve in an atmosphere of nitrogen suggests that the compound starts to decompose at 210°C and loses 36% of the initial weight by 400 °C. Above this temperature, the weight loss is very sluggish, registering about 6% of the initial weight up to 600°C. The end product at

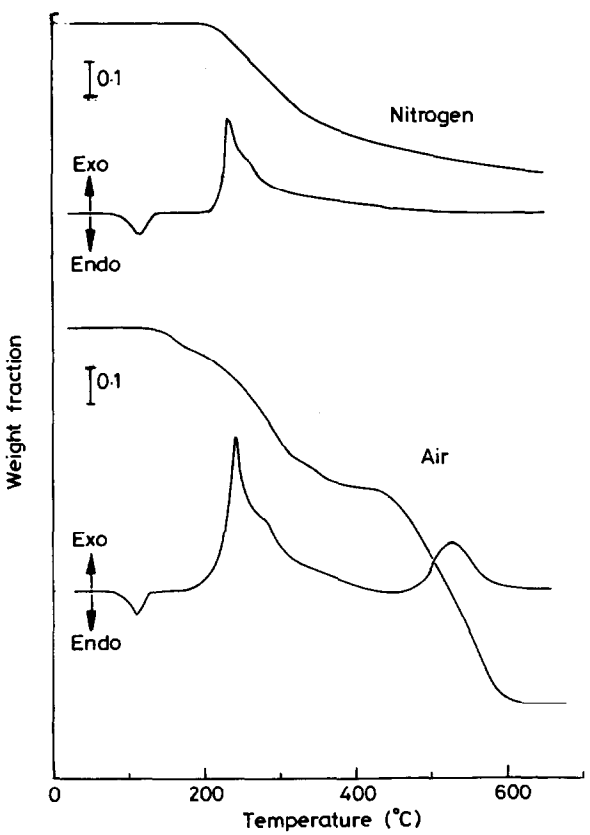


Fig. 1. TG and DTA plots of diphenylammonium perchlorate in air and nitrogen.

TABLE 1

Mass spectral results of diphenylammonium perchlorate

| *m/e* | Ion ($m^+$) |
|---|---|
| 28 | CO |
| 32 | $O_2$ |
| 35 | Cl |
| 36 | HCl |
| 51 | ClO |
| 52 | HClO |
| 66 | $C_5H_6$ |
| 67 | $ClO_2$ |
| 68 | $HClO_2$ |
| 77 | $C_6H_5$ |
| 84 | $HClO_3$ |
| 102 | $C_6H \cdot C_2H_2$ |
| 115 | $C_6H_4 \cdot C_2HN$ |
| 141 | $C_6H_5 \cdot C_5H_4$ |
| 142 | $C_6H_5 \cdot C_5H_5$ |
| 154 | $C_6H_5 \cdot C_6H_5$ |
| 167 | $C_6H_4 \cdot NHC_6H_4$ |
| 168 | $C_6H_5N \cdot C_6H_5$ |
| 169 | $C_6H_5 \cdot NHC_6H_5$ |
| 170 | $C_6H_5NH_2 \cdot C_6H_5$ |

600°C is confirmed to be carbonaceous matter by chemical analysis.

The DTA plots both in air and nitrogen exhibited an endothermic effect at 115°C which is attributed to the melting of the salt. The exothermic peaks observed at 242 and 520°C in air are assigned to the decomposition of DPP and the oxidation of carbonaceous residue, respectively. However, only one exotherm at 245°C is observed in nitrogen due to the decomposition of the perchlorate. Thus, it is inferred that during the decomposition process, the perchlorate oxidizes only a part of the organic moiety.

The significant mass spectral fragments are tabulated in Table 1 with the probable assignments. No molecular peak of DPP, *m/e* 269, appeared in the spectrum, suggesting the non-volatility of the salt. The spectral data suggest that the fragmentation products resulted from the decomposition of diphenylammonium cation, perchlorate anion and the oxidation of the organic group by the perchlorate. The spectral patterns of diphenylammonium cation are found to be similar to those of diphenylamine [6,7].

ACKNOWLEDGEMENT

The author wishes to express his thanks to Dr. M.A. Hitchman for providing the mass spectrum of the compound.

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