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THERMAL PROPERTIES OF POLY(TERTIARY PHOSPHINE OXIDES)

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ABSTRACT

DTA and TGA (in air and in nitrogen) are presented for the poly(tertiary phosphine oxides), $C_6H_5[(C_6H_5)P(O)CH_2CH_2]_nP(O)(C_6H_5)_2$, where $n = 1$, 2, or 3.

INTRODUCTION

Tertiary phosphine oxides are considered to be the most stable organophosphorus compounds[1]. Trimethyl- and triphenylphosphine oxides are reported to be thermally stable[2] up to almost 700°C. In this paper the thermal stability of a series of poly(tertiary phosphine oxides) is investigated.

EXPERIMENTAL

Measurements

The DTA data were obtained on a DuPont 900 DTA calorimeter cell in air as well as in nitrogen, with the heating rate at 20°C min^{-1}. The samples were contained in small platinum cups.

The TG measurements were made on a Perkin-Elmer TGS-1 in air as well as in nitrogen, with the heating rate at 20°C min^{-1}. The temperature was calibrated using the Curie point magnetic standards supplied by the manufacturer.

Materials

The poly(tertiary phosphine oxides), $C_6H_5[(C_6H_5)P(O)CH_2CH_2]_nP(O)(C_6H_5)_2$ ($n = 1, 2, 3$), were prepared by oxidizing the corresponding phosphines with 30% aqueous H_2O_2 in glacial acetic acid at 60–80°C. The precursor phosphines ("Diphos", "Triphos", and "Tetraphos I") were purchased from Strem Chemicals, Inc., Danvers, Mass. The phosphine oxide for $n = 1$ was recrystallized from benzene/diethylether, the compounds for $n = 2$ and $n = 3$ were isolated by pouring the above acetic acid solutions of the phosphine oxides into a large excess of distilled water. The resulting white precipitate, upon standing over night, was filtered, washed with water, and dried at 120° in vacuo. Analyses and physical data are summarized in Table 1.

TABLE 1

ANALYTICAL AND PHYSICAL DATA

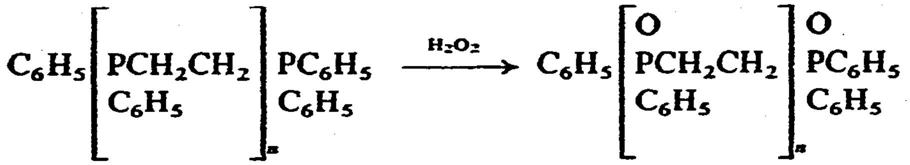
$\overset{O}{} \quad \overset{O}{}$ $C_6H_5[PCH_2CH_2]_nP(C_6H_5)_2$ C_6H_5	M.p. (°C)	Yield (%)	Analyses[a]	
			C (%)	H (%)
$n=1$	268[b]	88	—	—
$n=2$	298	85	70.08 (70.10)	5.70 (5.71)
$n=3$	344[c]	91	68.43 (68.66)	5.64 (5.76)

[a] Calculated values in parentheses. [b] Lit.[3]: 269–270 °C. [c] Lit.[4]: "does not melt below 400 °C".

RESULTS AND DISCUSSION

In view of the remarkable thermal stability of some tertiary phosphine oxides, it was of interest to explore the thermal stability of a series of poly(tertiary phosphine oxides) having 2, 3, and 4 phosphorus atoms in the molecule.

The poly(tertiary phosphine oxides) of this study were prepared by H_2O_2 oxidation of the corresponding phosphines which are commercially available ($n = 2$, 3, or 4).



$$C_6H_5\left[\begin{array}{l}PCH_2CH_2\\C_6H_5\end{array}\right]_n\begin{array}{l}PC_6H_5\\C_6H_5\end{array}\xrightarrow{H_2O_2}C_6H_5\left[\begin{array}{l}O\\PCH_2CH_2\\C_6H_5\end{array}\right]_n\begin{array}{l}O\\PC_6H_5\\C_6H_5\end{array}\qquad(1)$$

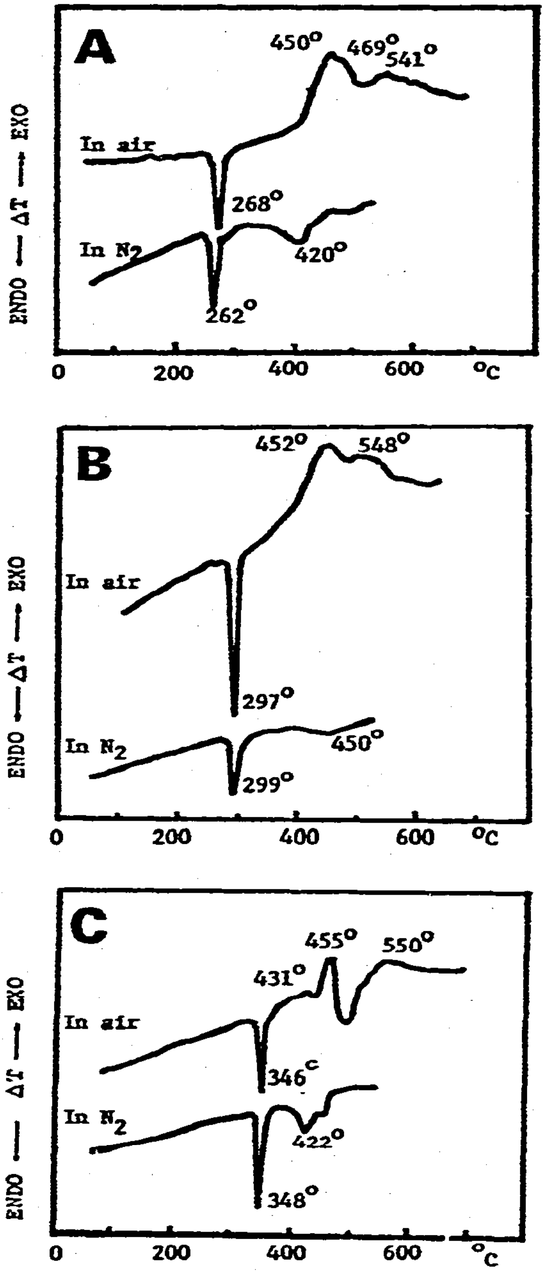
The reaction of eqn (1) proceeds rapidly and quantitatively resulting in the products described in Table 1.

Differential thermal analysis data of the three phosphine oxides are displayed in Fig. 1. It is seen that for all three compounds [$n = 1$, 2, and 3 in eqn (1)], sharp endotherms are seen at the temperatures corresponding to the melting of the compounds. The temperatures at which these endotherms occur agree quite well with the melting points of the corresponding compounds listed in Table 1.

Above about 400 °C, in nitrogen atmosphere, in all three cases, endotherms are seen which may be interpreted as thermal degradation and/or sublimation. In air, in this temperature range, exotherms are observed indicating that oxidative degradation of the phosphine oxides is the predominant reaction.

Sublimation of unoxidized phosphine oxide as well as of P_2O_5 oxidation product[5] may occur also to some extent in this temperature range.

Thermogravimetric data of the three phosphine oxides are shown in Fig. 2. These data, in agreement with the corresponding DTA data, show that rapid and substantially quantitative weight loss occurs at or above 400 °C depending on n in eqn (1). Only slight differences are seen for the weight-loss curves in air or nitrogen.



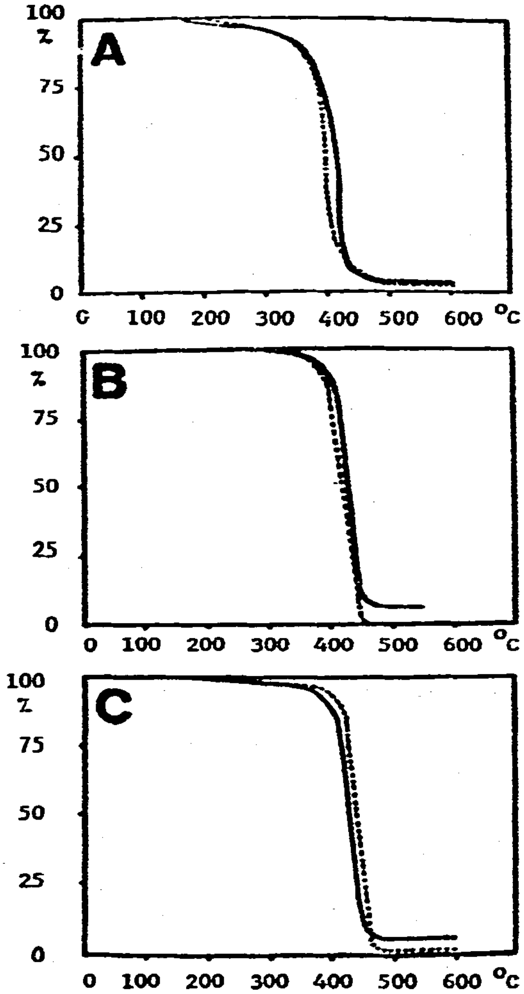


Fig. 1. DTA curves of poly(tertiary phosphine oxides), $C_6H_5[(C_6H_5)P(O)CH_2CH_2]_nP(O)(C_6H_5)_2$, in air and nitrogen. (A) $n = 1$; (B) $n = 2$; (C) $n = 3$.

Fig. 2. TG curves of poly(tertiary phosphine oxides), $C_6H_5[(C_6H_5)P(O)CH_2CH_2]_nP(O)(C_6H_5)_2$. In air (solid lines) and in nitrogen (dashed lines). (A) $n = 1$; (B) $n = 2$; (C) $n = 3$.

These data confirm the conclusions drawn from the DTA data and indicate that the poly(tertiary phosphine oxides) of this paper indeed are remarkably temperature-stable organophosphorus compounds.

ACKNOWLEDGMENT

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