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A THERMOGRAVIMETRIC STUDY OF PHOSPHONIUM HALIDES *

ROSALIE G. FERRILLO and ALBRECHT GRANZOW

American Cyanamid Company, Chemical Research Division, Bound Brook, NJ 08805 (U.S.A.)

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ABSTRACT

The TG/DTG thermal curves for a series of phosphonium halides are presented. The stability of phosphonium salts increases in the order chloride < bromide ≈ iodide. While phosphonium salts with only nonpolar groups in the cation volatilize completely, increasing substitution by polar cyanoethyl groups results in residue formation. The kinetics of the thermal decomposition can be obtained using isothermal thermogravimetry.

INTRODUCTION

In this report, we discuss the effects of structure on the thermal stability of a series of phosphonium salts as studied by thermogravimetry. Many phosphonium salts are of interest as flame retardants for a variety of thermoplastic polymers [1]. However, in spite of their practical importance, comparatively little is known about the thermal stability of phosphonium compounds. The thermal decomposition of tetramethylphosphonium chloride was studied as early as 1886 and reported to result in the formation of trimethylphosphine, ethene, and hydrochloric acid [2]. However, later authors claimed that the thermal decomposition of this compound leads to the formation of methyl chloride and trimethylphosphine instead [3]. This example shows that the decomposition processes of even a simple phosphonium salt are complex, with the nature of the products apparently dependent on the pyrolysis conditions employed.

EXPERIMENTAL

Materials

All phosphonium salts were either commercial products or research samples by American Cyanamid Company.

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Procedures

The TGS-2, thermogravimetric instrumentation manufactured by Perkin-Elmer Corporation, was used in this study. The instrument's temperature scale was calibrated with Curie point standards, according to the manufacturer's specifications. Sample sizes were of the order of 5 mg. A dynamic gas atmosphere was maintained by a 25 cc min^{-1} stream of either dry air or dry nitrogen. With all simultaneous dynamic thermogravimetry/derivative thermogravimetry (TG/DTG) runs, the heating rate was 10° C min^{-1}.

In the isothermal experiments, the furnace was preheated to a given temperature and then placed in contact with the previously weighed sample. The recorder drive was started simultaneously.

RESULTS AND DISCUSSION

Effect of substitution at the phosphonium cation on thermal decomposition

The majority of phosphonium halides discussed in this study are chlorides and bromides with polar cyanoethyl substituents on the phosphonium cation. Phosphonium halides with no polar substituent groups volatilize without leaving a solid residue. As an example, the thermal curve of FR 3,

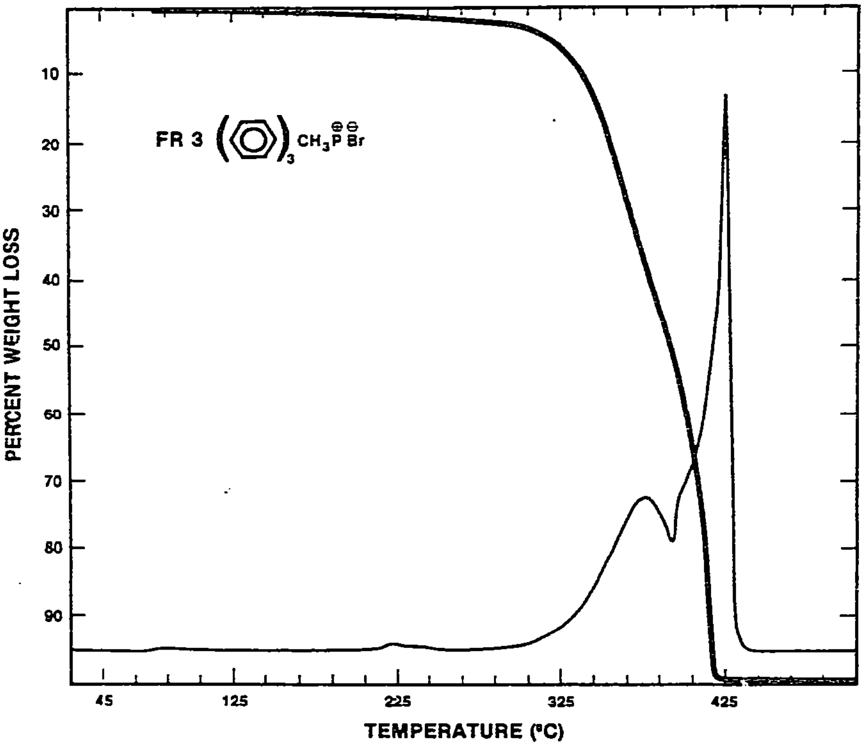

Fig. 1. Thermal curve of a phosphonium salt with no polar substituent in the cation: FR 3, methyltriphenylphosphonium bromide.

methyltriphenylphosphonium bromide, is shown in Fig. 1. Two volatilization processes, with an onset temperature of ca. 277°C for the lower temperature process, are apparent. The low temperature process corresponds to a weight loss of about 43%. This is indicative of a decomposition into phenylbromide and methyldiphenylphosphine, with the volatilization of the former decomposition product occurring at the lower temperature. Decomposition with formation of methylbromide does not appear to be taking place, since in this case a low temperature weight loss of only 26% is expected. Under isothermal conditions, the decomposition of FR 3 follows a zero-order time dependence which is satisfied by the rate equation $\log k = 14.01 - (37\,300/2.303RT)$, if k is given in % weight loss/min. The isothermal decomposition curves are shown in Fig. 2.

The effect on the thermal curve of introducing polar cyanoethyl groups into the phosphonium cation is shown in Fig. 3. As an example, the decomposition of FR 2, benzyltriphenylphosphonium chloride, and FR 7, benzyltris(2-cyanoethyl)phosphonium chloride, is considered. In the case of FR 2, which contains only non polar substituents, the decomposition occurs in two different steps and results in complete volatilization of the phosphonium salt. The weight loss of the low temperature process amounts to 9%, which is in accordance with the elimination of hydrochloric acid. The high temperature process occurs above 310°C and leads to complete volatilization of the remainder of the molecule. In the case of FR 7, the molecule is stable to approximately 245°C. Above this temperature, about 65% of the salt is volatilized, with a nonvolatile residue of 35%. The thermal curve is clearly sigmoidal, indicating complex volatilization kinetics.

Increasing substitution of cyanoethyl groups leads to an increase in the amount of nonvolatile residue, as shown in Fig. 4. The phosphonium bromide FR 13, bis(2-cyanoethyl)dimethylphosphonium bromide, contains two cyanoethyl groups and yields a residue of 20%; FR 11, tris(2-cyanoethyl)methylphosphonium bromide, has three cyanoethyl groups and

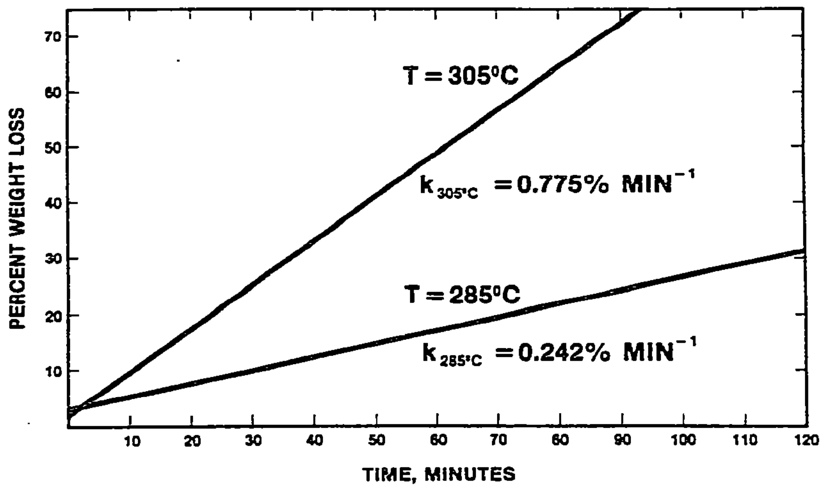

Fig. 2. Isothermal decomposition curves of FR 3, methyltriphenylphosphonium bromide, at 285 and 305°C.

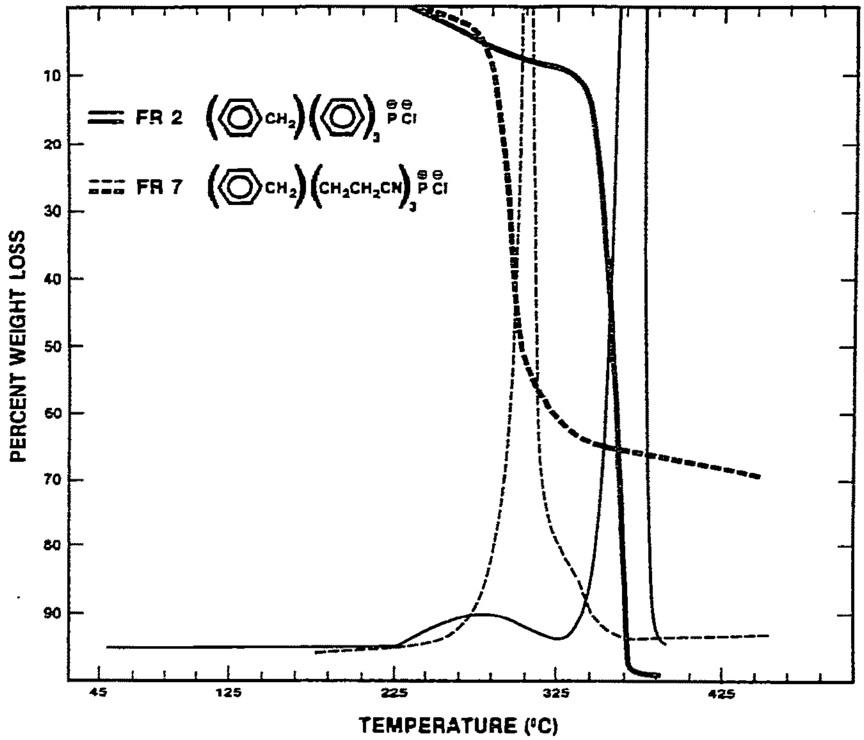

Fig. 3 . Thermal curves of a polar substituted and a non polar substituted phosphonium salt: FR 2, benzyltriphenylphosphonium chloride; FR 7, benzyltris(2-cyanoethyl)-phosphonium chloride.

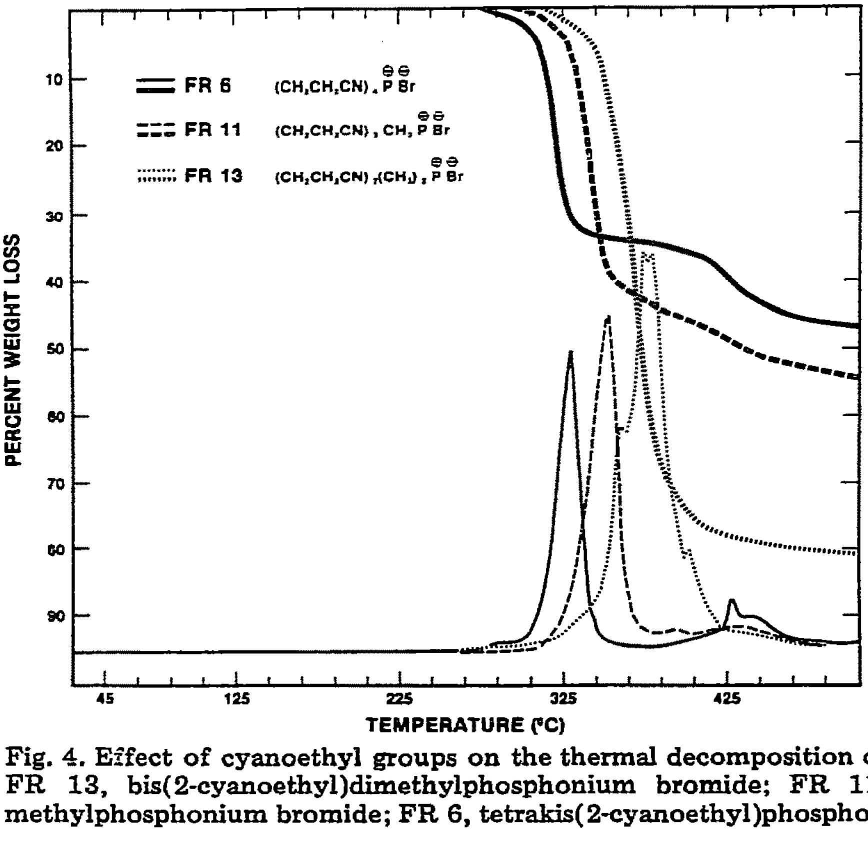

Fig. 4. Effect of cyanoethyl groups on the thermal decomposition of phosphonium salts: FR 13, bis(2-cyanoethyl)dimethylphosphonium bromide; FR 11, tris(2-cyanoethyl)methylphosphonium bromide; FR 6, tetrakis(2-cyanoethyl)phosphonium bromide.

gives a residue of 58% after the main decomposition step, while FR 6, tetrakis(2-cyanoethyl)phosphonium bromide, with four cyanoethyl groups shows a residue of 65%. The thermal stability, as expressed by the onset temperature of decomposition, decreases with increasing cyanoethylation. FR 13 has two cyanoethyl groups and a decomposition temperature of 319° C; FR 11 has three cyanoethyl groups and a decomposition temperature of 309° C; FR 6 has four cyanoethyl groups with a decomposition temperature of 268° C. One could explain this trend on statistical grounds with the assumption that the initial step in the decomposition involves the cyanoethyl group. An increase in the number of cyanoethyl groups should then increase the likelihood of decomposition. However, comparing the thermal curves of FR 11, tris(2-cyanoethyl)methylphosphonium bromide, and FR 12, tris (2-cyanoethyl)ethylphosphonium bromide, which both contain the same number of cyanoethyl groups but a methyl and an ethyl group, respectively, shows that replacement of the methyl by the ethyl group lowers the decomposition temperature from 309° C to 279° C. Therefore, the stability is also affected by other factors than the number of cyanoethyl groups. The thermal curves of the two compounds are depicted in Fig. 5.

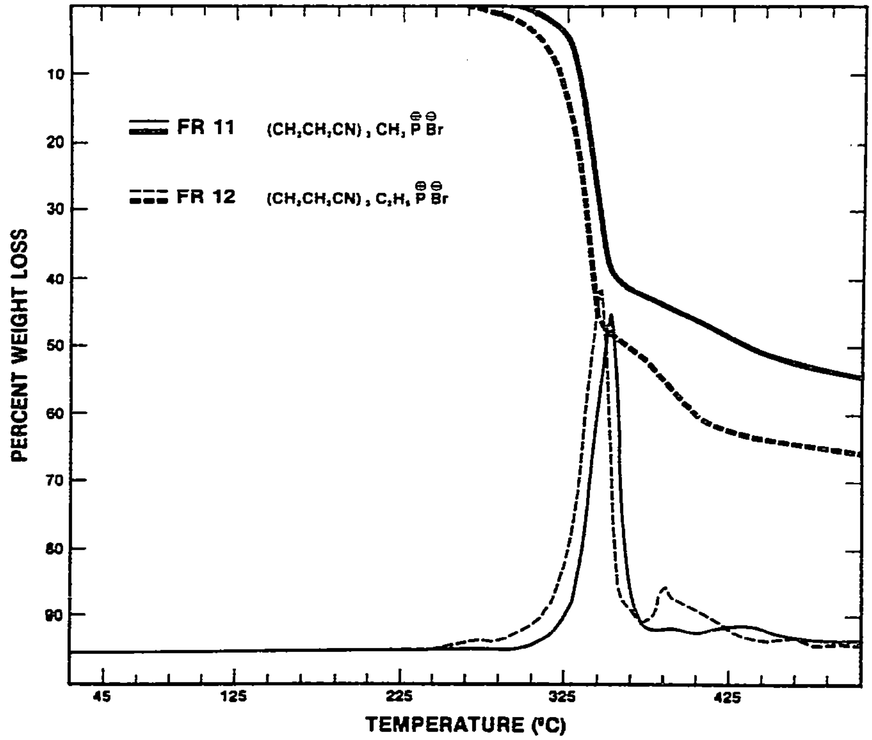

Fig. 5. Thermal curves of a methyl substituted and an ethyl substituted phosphonium salt: FR 11, tris(2-cyanoethyl)methylphosphonium bromide; FR 12, tris(2-cyanoethyl)-ethylphosphonium bromide.

Effect of the anion on thermal decomposition

The thermal curves of FR 6, tetrakis(2-cyanoethyl)phosphonium bromide, and FR 9, tetrakis(2-cyanoethyl)phosphonium chloride, are shown in Fig. 6. The chloride exhibits a weight loss of 6% below 100°C which is attributed to the loss of 1 mole of water. At higher temperatures, both the chloride and the bromide decompose in two major steps. The onset of the first process is observed at 292°C in the case of the chloride and at 325°C in the case of the bromide, and corresponds to a weight loss of about 35% for both compounds. The second process is observed around 315°C for the chloride and at 425°C for the bromide. One sees that the bromide is considerably more stable than the chloride, while the general decomposition pathways of the two salts are similar. Therefore, a change from chloride to bromide does not change the thermal decomposition pattern but only decreases the rate of this decomposition.

The thermal curves of a phosphonium bromide and a phosphonium iodide are compared in Fig. 7. Both salts, FR 11, tris(2-cyanoethyl)methylphosphonium bromide, and FR 4, tris(2-cyanoethyl)methylphosphonium iodide, show comparable thermal stabilities, with onset temperatures of 308°C and 309°C, respectively. Interestingly, the weight loss for the first volatilization step is greater for the bromide than for the iodide, although the formation of

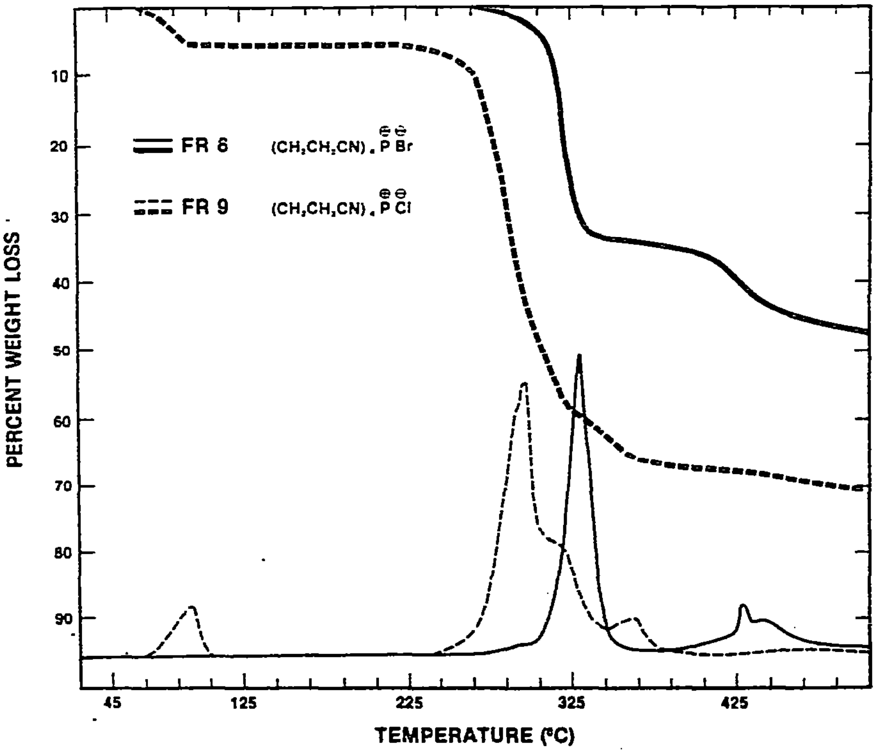

Fig. 6. Comparison of thermal curves of a phosphonium chloride and a phosphonium bromide: FR 9, tetrakis(2-cyanoethyl)phosphonium chloride; FR 6, tetrakis(2-cyanoethyl)phosphonium bromide.

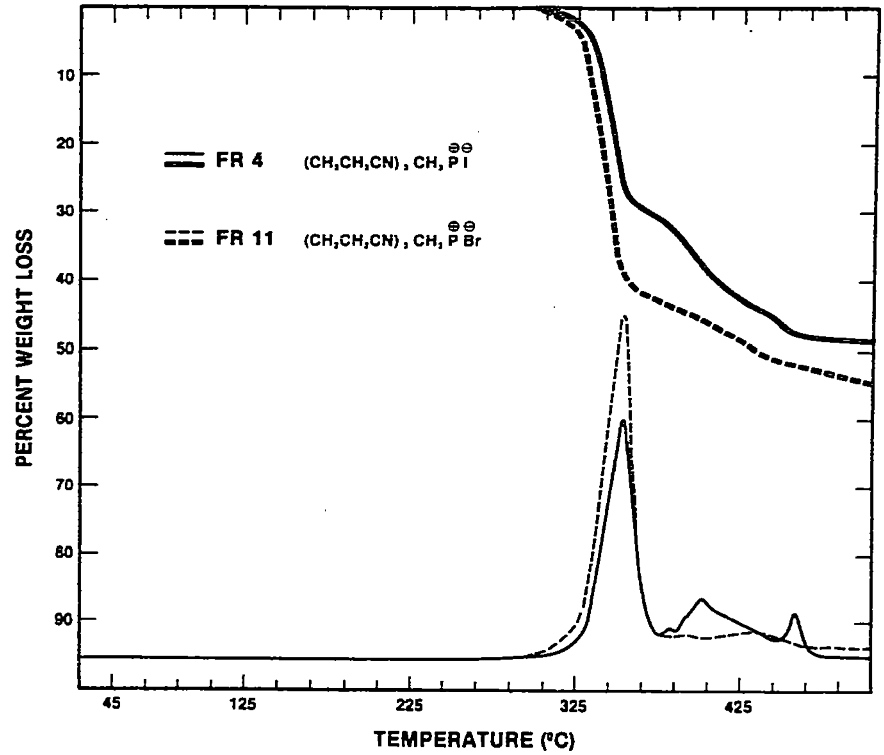

Fig. 7. Comparison of thermal curves of a phosphonium bromide and a phosphonium iodide: FR 11, tris(2-cyanoethyl)methylphosphonium bromide; FR 4, tris(2-cyanoethyl)-methylphosphonium iodide.

CH_3X or HX as the volatile fragments should result in a greater weight loss for the iodide. Therefore, one has to assume a different, probably very complex, pattern of thermal decomposition for each of the two compounds.

Thermal decomposition of bisphosphonium halides

A pronounced difference in thermal stabilities between phosphonium bromides and phosphonium chlorides is also observed in the class of bisphosphonium halides. As shown in Fig. 8, the bromide is again considerably more stable than the chloride. For FR 1, ethylenebis[tris(2-cyanoethyl)]-phosphonium bromide decomposes only at temperatures above 275°C. Decomposition occurs in two well-resolved steps, each of which amounts to a weight loss of 13.5%. These two processes can be accounted for by the consecutive loss of 2 moles of hydrogen bromide [4]. On the other hand, FR 8, ethylenebis[tris(2-cyanoethyl)]phosphonium chloride, loses 1 mole of water below 100°C and the onset of the main decomposition occurs at around 225°C. Again, the decomposition takes place in two separate steps, each amounting to a weight loss of about 23%. These two processes cannot be reconciled with the loss of 2 moles of hydrogen chloride, which would require volatilization of less than 8% for each step. One sees that, in this case, the decomposition mechanism is thoroughly altered by a change from

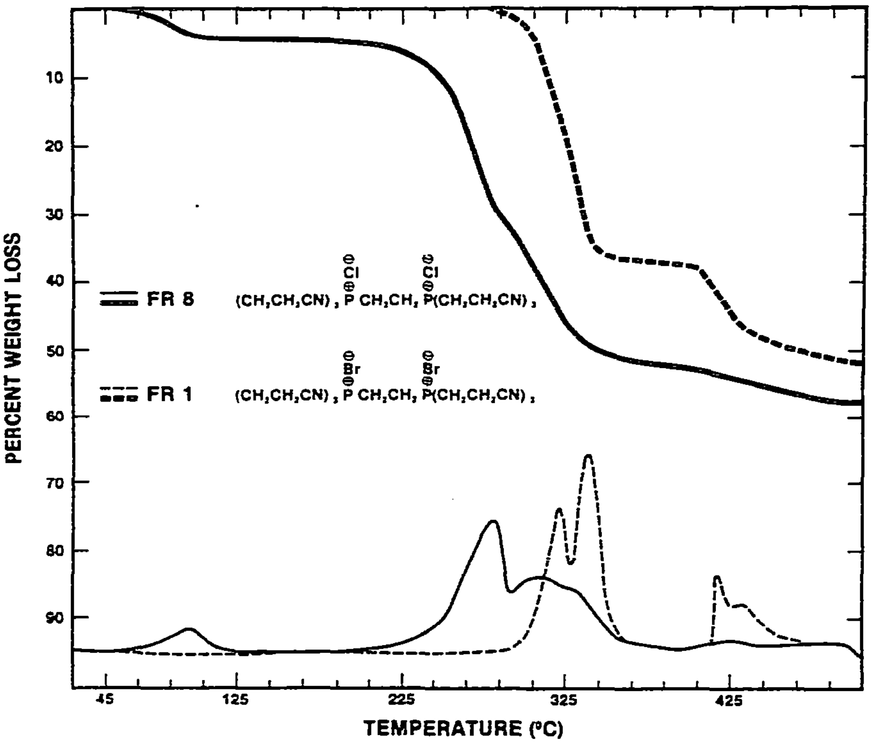

Fig. 8 . Thermal curves of bisphosphonium salts: FR 1, ethylenebis[tris(2-cyanoethyl)]-phosphonium bromide; FR 8, ethylenebis[tris(2-cyanoethyl)]phosphonium chloride.

bromide to chloride anion. However, it is noteworthy that both the bromide and the chloride decompose in two well-defined processes. For the bisphosphonium bromide, FR 1, each of the two consecutive steps amounts to a weight loss of 13.5%, while for the corresponding chloride, FR 8, each of the two steps results in a weight loss of 23%. This can only mean that the bisphosphonium structure is much less stable thermally than the phosphonium structure. This is supported by a comparison of the onset temperatures of decomposition for a phosphonium bromide and the analogous bisphosphonium bromide: FR 11 starts to decompose only above 309° C, while the decomposition of the bisphosphonium bromide, FR 1, occurs at 275° C.

The difference in thermal decomposition behavior of the bromide, FR 1, and the chloride, FR 8, becomes even more pronounced if the isothermal decomposition curves of the two salts are compared. The bisphosphonium bromide, FR 1, decomposes by way of a complex solid-state reaction, the kinetics of which can be satisfied by a Prout—Tompkins mechanism [5]. This kinetic model implies an autocatalyzed nucleation of a freely migrating nucleus with an already reacted site. As shown in Fig. 9A, this reaction model requires that the maximum rate of decomposition occurs at $\alpha = 0.5$, if α is the volatile weight fraction. The decomposition curve can be linearized by a plot in the coordinates of Fig. 9B, which yields a rate constant of 6.6×10^{-2} min^{-1} at 285° C. As in the nonisothermal case, a total weight loss of

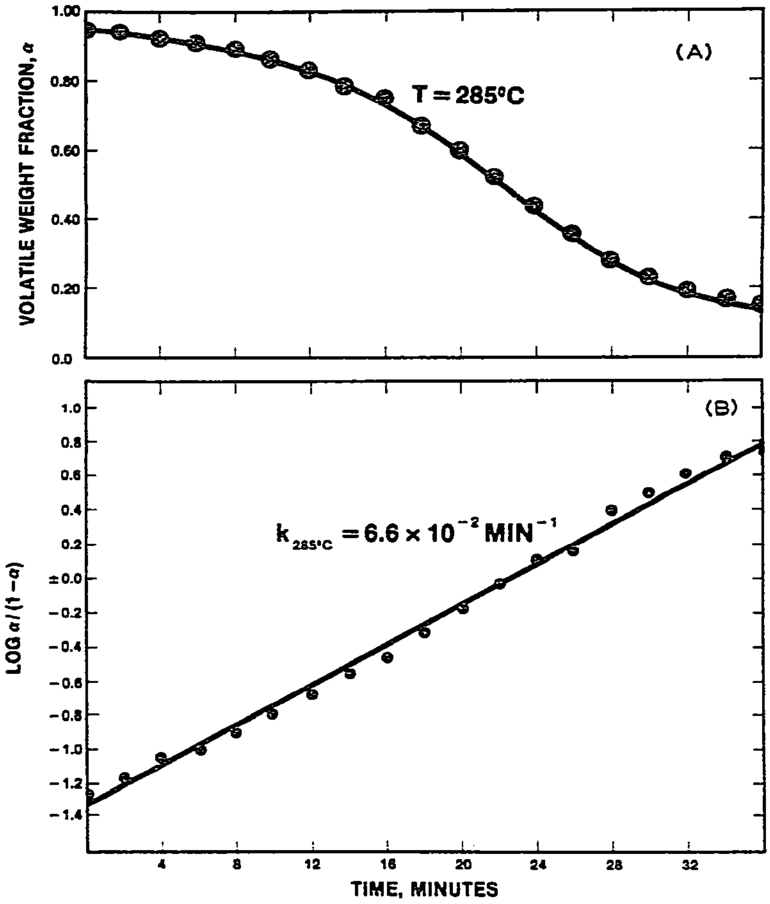

Fig. 9. Isothermal decomposition of FR 1 at 285°C. (A), Plot of volatile weight fraction, α, vs. time. (B), Prout—Tompkins plot.

27% is obtained, consistent with the loss of 2 moles of hydrogen bromide per mole of FR 1.

The isothermal decomposition kinetics of the bisphosphonium chloride, FR 8, are entirely different. As shown in Fig. 10A, the decomposition exhibits no initial induction period but follows first-order volatilization kinetics. According to Fig. 10B, rate constants of $k = 2.4 \times 10^{-2}$ min^{-1} at 225°C and $k = 3.6 \times 10^{-2}$ min^{-1} at 245°C are obtained.

A similar difference in thermal stability is observed in the case of FR 10, bis[tris-(2-cyanoethyl)]-*p*-xylyphosphonium bromide, and FR 14, bis[tris-(2-cyanoethyl)]-*p*-xylylphosphonium chloride, as seen in Fig. 11. The bromide is stable to about 280°C and the main decomposition occurs in two separate steps, amounting to weight losses of 25% and 18%. These steps cannot be accounted for by successive dehydrobromination, as in the case of the analogous ethylene-bridged FR 1. The chloride, FR 14, decomposes in at least four consecutive steps, the first two amounting to weight losses of 6% each and occurring at around 100°C and 240°C, respectively. Each step can be accommodated by the loss of 1 molecule of hydrochloric acid. Therefore,

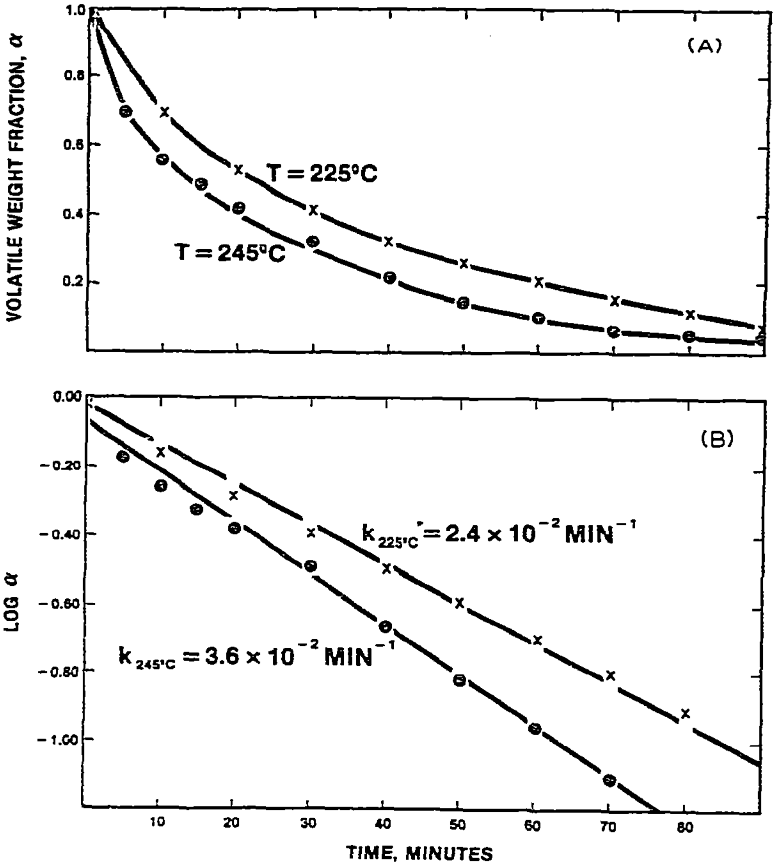

Fig. 10. Isothermal decomposition of FR 8 at 225 and 245°C. (A), Plots of volatile weight fraction, α, vs. time. (B), First-order plots.

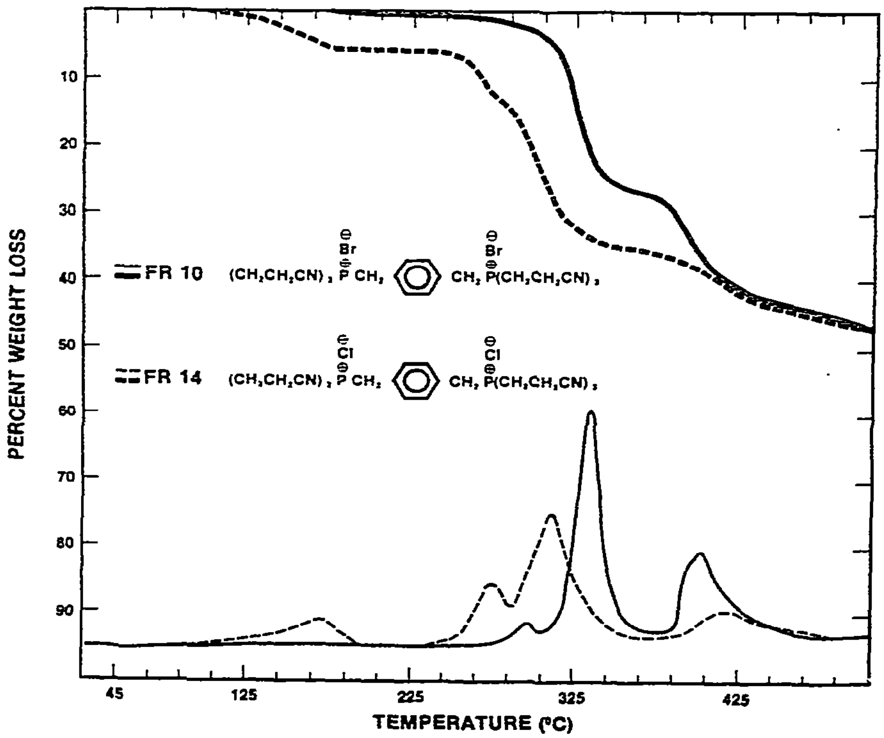

Fig. 11. Thermal curves of bisphosphonium salts: FR 10, bis[tris(2-cyanoethyl)]-*p*-xylylphosphonium bromide; FR 14, bis[tris(2-cyanoethyl)]-*p*-xylylphosphonium chloride.

the xylene-bridged bisphosphonium chloride, FR 14, and the ethylene-bridged bisphosphonium bromide, FR 1, decompose in a similar manner.

CONCLUSIONS

Phosphonium halides with no polar substituents volatilize without leaving a solid residue. As shown by isothermal TG, this volatilization process has a zero-order time dependence.

Increasing substitution by cyanoethyl groups leads to an increase in the amount of nonvolatile residue while the decomposition temperature decreases.

Replacement of the chloride anion by the bromide anion does not change the thermal decomposition pattern but only decreases the rate of decomposition. However, replacement of the bromide anion by the iodide anion affects the pattern of decomposition but does not seem to change the overall thermal stability.

The bisphosphonium structure is thermally less stable than the phosphonium structure. However, the bisphosphonium chlorides are less stable than the bisphosphonium bromides.

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