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TGA-MS study of the decomposition of phosphorus-containing ionic liquids trihexyl(tetradecyl)phosphonium decanoate and trihexyltetradecylphosphonium bis[(trifluoromethyl)sulfonyl] amide

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Abstract The phosphorus-containing ionic liquids (IL) decompose where ion pairs fall apart. Trihexyl(tetradecyl)phosphonium decanoate, sold as Cyphos IL 103, and Trihexyltetradecylphosphonium bis[(trifluoromethyl)sulfonyl] amide, sold as Cyphos IL 109, decompose in 200–475 °C range in air and the fragments containing organophosphorus are found here among other major fragments of hydrocarbon arms. Black residues are found after heating in air to 740 °C in TG in 5.0 and 0.6 mass/% for Cyphos IL 103 and 109, respectively. They were presumably containing P_2O_5 after oxidation. Not all the phosphorus can be counted for at 740 °C and falls short of calculated values of 10.9 and 9.3 mass/%, if residues contain nothing else but P_2O_5. Among the fragments the authors found in MS the organophosphorus fragments from decomposition of the cationic C_{32} H_{68} P + including P with 3–4 hydrocarbon attached as well as the major fragments of linear hydrocarbon arms. Water evolves early at lower temperature and continues to 740 °C. CO_2 comes from oxidation of carbon at high temperatures. The SO, SO_2, CF_3, CF_2CF_2 evolve in sulfur and fluorine containing anion in Cyphos IL 109. H_3PO_4 is detected, which is most likely from the reaction product of P_2O_5 and water. No P_2O_5 was found. Ash content examined by inductively coupled plasma spectroscopy (ICP) found that the phosphorus P in the ashes after burning in air to 700 °C and found 3200 ppm (or 0.62 mass/%) and 30 ppm (0.003 mass/%) in Cyphos IL 103 and 109, respectively.

Keywords Phosphorus-containing · Ionic Liquids · TG-MS · ICP

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Introduction

Ionic liquids are the class of materials of ionic pairs that has many utilities, best known its solvating ability for a range of polar and non-polar compounds. They frequently exhibit low-vapor-pressure and are moderate to poor conductors of electricity, highly viscous, stable at high temperatures, and are able to act as solvents for a wide variety of compounds and gases [1] due to the weakly coordinating pair of anions and cations, which are able to stabilize polar transition states. The miscibility of ionic liquids with water or organic solvents varies with side chain lengths on the cation moiety and with choice of anion.

Ionic liquids show great potential for use as a heat transfer and storage medium in solar thermal energy. Utilizing the energy of the sun by focusing it onto a receiver which can generate temperatures of around 600 °C. Ionic liquids such as [C_4mim] [BF_4], 1-Butyl-3-methylimidazolium tetrafluoroborate, have been identified with more favorable liquid-phase temperature ranges (−75 to 459 °C) in 2001 and could therefore be excellent liquid thermal storage media and heat transfer fluids in solar thermal power plants [2]. Recently, the phosphorus containing ionic liquid was described by Wu et al. [3] as photoconductor in substrate and good lateral charge migration resistance and cyclic stability properties. The phosphorus containing ionic liquids also show significant improvement for use as an additive in dispersion and coating of films and the quality of thermally transferred films for application in color filter for displays. Because of many potential usage of phosphorus containing ionic liquids and are readily available commercially, the authors studied in this study the potential impact of the ionic liquids could have when they subject to thermal degradation upon heating and environmental issues.

Materials

Trihexyl(tetradecyl)phosphonium decanoate, min. 95% Cyphos® IL 103 (CAS number 465527-65-5) and Trihexyl(tetradecyl)phosphonium bis[(trifluoromethyl)sulfonyl]amide, min 97% Cyphos® IL 109 (CAS number 460092003-9) were purchased from Strem Chemicals, Inc. 7 Mulliken Way, Newburyport, MA.

Experimental

The 16–17 mg of ionic liquid was heated in an alumina pan in air purged TG in skimmer coupling to QMS. The instrument is commercially available from Netzsch Instruments in two step pressure reductions by three pumps from 10^3 to 10^{-1} to 10^{-5} mbar through orifice coupling. The MS ion currents were detected in trigger mode at the start of TG scan. The N_2 ($1.1–1.2 \times 10^{-6}$/A) and O_2 ($2.3–2.6 \times 10^{-7}$/A) from air as well other components were checked prior to start. An empty alumina pan was subject to the same experiment separately, thus the subtracted fragment intensities can be realized as non-noise. Please note that coupled MS is not heated, thus the ion current intensities are observed versus cycle or time in linear heating.

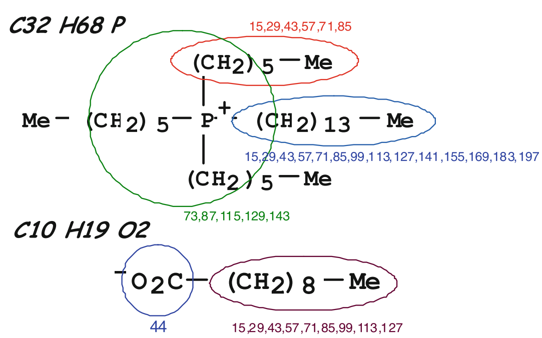


Fig. 1 The anticipated decomposition fragments masses of Cyphos® 103 of $C_{32}H_{68}P + C_{10}H_{19}O_2-$

TG-MS: Netzsch STA 409/QMS 403, skimmer coupling
MS: cathode 70 eV, SEM 1600 V, MS 10-400 amu at 50 ms cycle speed
TG: 20 °C to 750 °C in 10 °C/min in air with total purging rate of 100 mL/min.

The phosphorus content in the ash after burning 10 g of specimen from ambient temperature to 700 °C was determined in inductively coupled plasma spectroscopy (ICP).

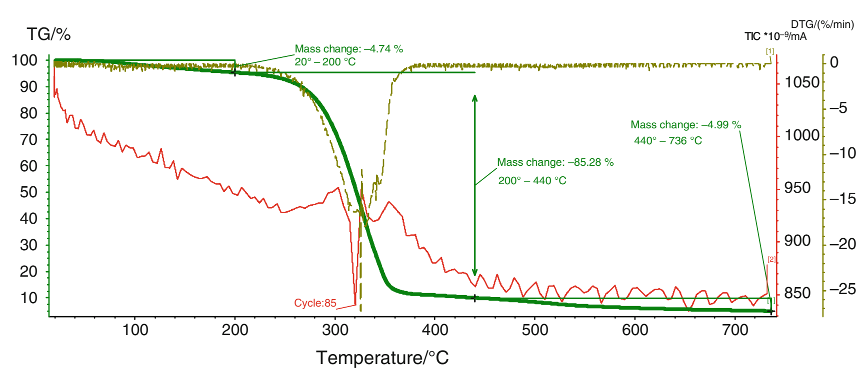
Results and discussion

Ionic liquid Cyphos® IL 103, Trihexyl(tetradecyl)phosphonium decanoate

This IL has the formula mass of 655 and its structure with anticipated fragments is shown in Fig. 1. The phosphorus-containing ionic liquids decompose where ion pairs fall apart at 200–440 °C. Black residue is found after heating in air to 740 °C at 5.0 mass/%. Had all phosphorus been counted for at 740 °C in air, the residue would have been calculated at least 10.9 mass/% in the form of P_2O_5, but it is much less. The authors look for the organophosphorus fragments as well as other major fragments from hydrocarbon arms at decomposition temperature range among the off-gas. The TG weight of this ionic liquid shows one-step decomposition and total ion current peaks cycle 85, 321 °C and also a lower temperature absorbed water loss 4.7 mass/% up to 200 °C centering at cycle 42, 127 °C (shown in Figs. 2, 3). Water comes off as OH, H_2O (mass 17, 18) ions in 1 to 4 ratio. The additional water evolution is the oxidation of hydrocarbon.

Arms in Cyphos® IL 103. In Fig. 3 (and other ion current versus time/cycle hereafter), the intensities of mass 17, 18 have been subtracted from that of the background of empty alumina pan. The CO_2 and hydrocarbon arms are the principal fragments when ionic liquid pair falls apart between 200 and 440 °C as shown in the bar graph of cycle 85, 321 °C (not shown). The linear hydrocarbon fragments of different lengths are seen in clusters of mass 14. There is

Fig. 2 TG mass loss, derivative DTG (%/min), and the total ion current (TIC $\times 10^{-9}$/A) of heating Cyphos® IL 103 in air-absorbed water evolution, decomposition/oxidation, and residue at 5 mass/%



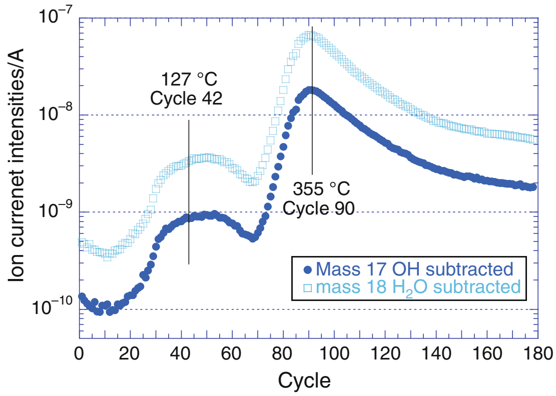


Fig. 3 The intensities of ion current intensities/A of water evolution as OH, H2O (mass 17, 18)—the absorbed and oxidation products—of heating Cyphos® IL 103 in air

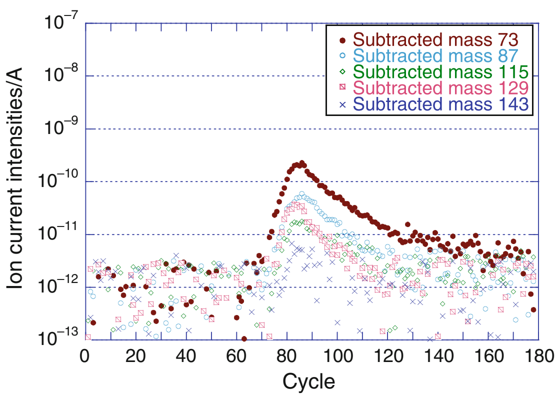


Fig. 4 The fragment mass intensities/A of mass 73 (*filled circle*), 87 (*open circle*), 115 (*diamond*), 129 (*enclosed times*), 143 (*times*) from organophosphorus of heating Cyphos® IL 103 in air

no CO_2 evolution before 258 °C; it comes from decomposition of Cyphos® IL 103 and oxidation of hydrocarbons.

The organophosphorus compounds are counted for the intact of P–C bonds in the ions of different number and length of the hydrocarbon arms, i.e., $P(CH_2)_3$, $P(CH_2)_4$, $CH_2{=}P(CH_2CH_2)_2$, $CH_2{=}P(CH_2CH_2)_3$, $P(CH_2CH_2)_4$ (mass 73, 87, 115, 129, 143). In Fig. 4, the ion current intensities/A of these organophosphorus fragments are plotted as a function of cycle/time. In addition, the oxidation of phosphorus to H_2PO_4 is also found as a major fragment (mass 98). The linear hydrocarbon fragments of CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13} (mass 15, 29, 43, 57, 71, 85) are found abundant and are shown in Fig. 5. The intensities are the subtracted signals from that of the backgrounds. Please note that the backgrounds of the small fragment CH_3, C_2H_5 (mass 15, 29) are high- thus it is important to see that the subtracted fragment intensities can be realized as non-noise. The authors analyzed the ash content of phosphorus and others by ICP, tabulated in Table 1. The phosphorus is

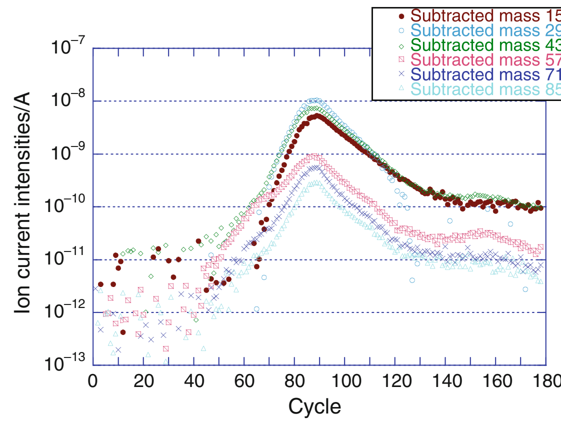


Fig. 5 The fragment mass intensities/A of mass 15 (*filled circle*), 29 (*open circle*), 43 (*diamond*), 57 (*enclosed times*), 71 (*times*), 85 (*triangle*) from linear hydrocarbon of heating Cyphos® IL 103 in air

Table 1 Phosphorus content in ash in ppm

P and other elements in the ash (ppm)		
	Trihexyl(tetradecyl) phosphonium decanoate Cyphos IL 103	Trihexyltetradecylphosphonium bis[(trifluoromethyl)sulfonyl] amide Cyphos IL 109
% Ash	1.91%	0.05%
Al	1	3
B	<1	1
Ba	<1	
Ca	4	7
Cr	<1	2
Cu	<1	<1
Fe	3	23
K	2	
Mg	1	<1
Mn	<1	<1
Na	3000	<1
P	6200	30
S	1	7
Si	4	1
Sr	<1	<1
Ri	<1	<1
Zn	<1	<1
Zr	<1	

6200 ppm of total ash of 1.91% (or 0.62%), which can not be counted for all the phosphorus being oxidized as P_2O_5.

Ionic liquid Cyphos® IL 109,
trihexyltetradecylphosphonium
bis[(trifluoromethyl)sulfonyl] amide

This IL has a formula mass of 763 and the structure with its anticipated fragments is shown in Fig. 6. The phosphorus-

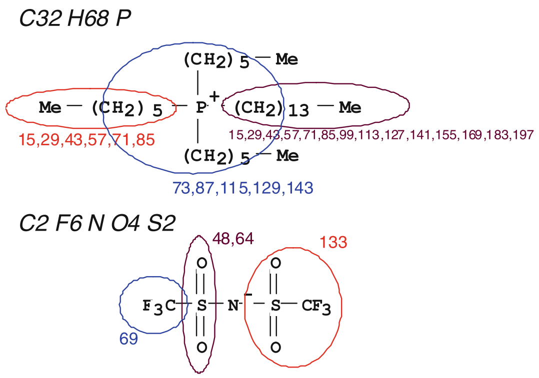


Fig. 6 The anticipated decomposition fragment masses of Cyphos® IL 109 of $C_{32}H_{68}P + C_2F_6NO_4S_2-$

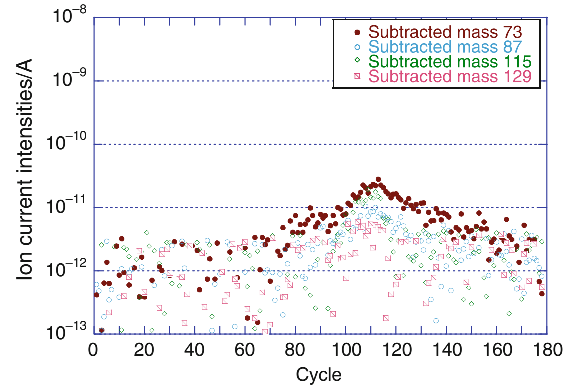


Fig. 8 The organophosphorus fragment intensities/A of mass 73 (*filled circle*), 87 (*open circle*), 115 (*diamond*), 129 (*enclosed times*) of heating in air Cyphos® IL 109 versus MS cycle

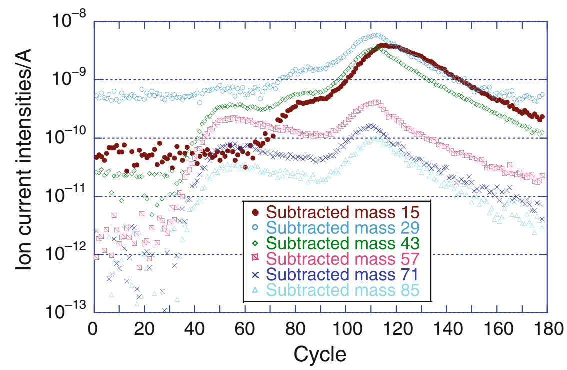
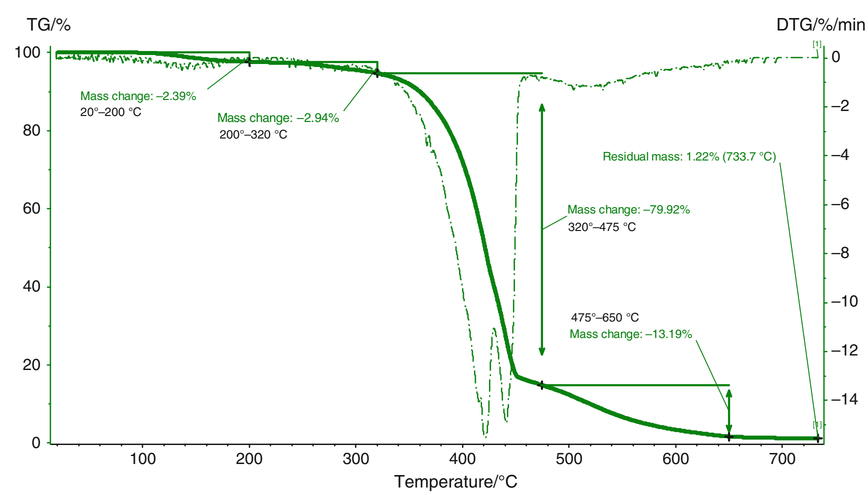


Fig. 9 The fragments of hydrocarbon arms of mass 15 (*filled circle*), 29 (*open circle*), 43 (*diamond*), 57 (*enclosed times*), 71 (*times*), 85 (*triangle*) of heating in air Cyphos® IL 109 versus MS cycle

fluorine-sulfonyl-containing ionic liquids decompose where ion pairs fall apart at 320–475 °C. Black residue is found after heating in air to 740 °C at 0.6 mass/%. Had all phosphorus been counted for at 740 °C in air, the residue would have been calculated at least 9.3 mass% in the form of P_2O_5, but it is much less. The TG mass loss and derivative DTG are indicated below in Fig. 7 in two-step decomposition/oxidation centering at ~440 and 550 °C. The water evolution comes at lower temperature from the absorbed and continues to 740 °C as the ionic liquid hydrocarbon arms being oxidized. The CO_2 evolution from oxidation of hydrocarbon arms in cation $C_{32}H_{68}P+$ occurs at higher temperatures. The organophosphorus compounds are counted for the intact of P–C bonds in the ions of different number and length of the hydrocarbon arms, i.e., $P(CH_2)_3$ (mass 73), $P(CH_2)_4$ (mass 87), $P(CH_2CH_2)_3$ (mass 115), $CH_2{=}P(CH_2CH_2)_3$ (mass 129), shown in Fig. 8. In addition, H_3PO_4 (mass 98) are found as an oxidized off-gas in both two decomposition steps. Linear hydrocarbon fragments from cationic arms $C_{32}H_{68}P+$, CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15} (mass 15, 29, 43, 57, 71, 85, 99) and SO, SO_2, and $O_2S–CF_3$ (mass 48, 64, 133) are found anionic moiety $C_2F_6NO_4S_2$- in this phosphorus-fluorine-sulfur containing ionic liquid (Figs. 9, 10). So are the HF, CF_3, CF_2CF_2 (mass 20, 69, 50).

Fig. 7 TG mass loss and derivative DTG (%/min) of heating Cyphos® IL 109 in air



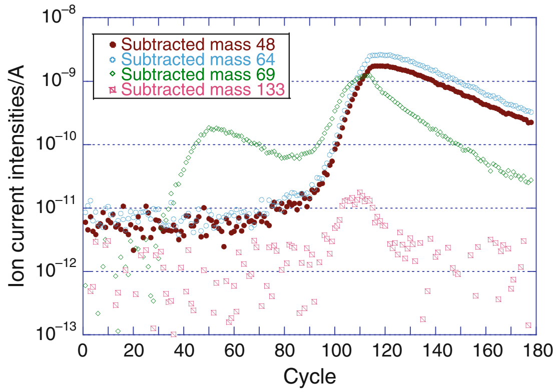


Fig. 10 The fragments from phosphorus–fluorine–sulfur containing anionic moiety—SO, SO_2, CF_3, $O_2S–CF_3$, mass 48 (*filled circle*), 64 (*open circle*), 69 (*diamond*), 133 (*enclosed times*) versus MS cycle

Among the off-gases, the H_3PO_4 is detected (mass 98), which is most likely from the oxidation product of P_2O_5 and water. ICP examines the P content in the ashes after burning in air to 700 °C and found 30 ppm (0.003 mass/%) in Cyphos IL 109 (shown in Table 1).

Conclusions

The two selected phosphorus-containing ionic liquids Cyphos IL 103 and 109 were studied using TG-MS. The phosphorus-carbon (P–C) bonds were found intact among the off-gases as various length and number of hydrocarbon arms attached to phosphorus. The fragments of $P(CH_2)_3$ (mass 73), $P(CH_2)_4$ (mass 87), $P(CH_2CH_2)_3$ (mass 115), $CH_2{=}P(CH_2CH_2)_3$ (mass 129) are seen in both ionic liquids. The phosphorus-fluorine-sulfur containing Cyphos IL 109 is seen the fragments of SO, SO_2, and $O_2S–CF_3$ (mass 48, 64, 133) as well as HF, CF_3, CF_2CF_2 (mass 20, 69, 50). The ICP ashes after oxidation show oxides with 0.62 and 0.003 mass% of element Phosphorus in Cyphos IL 103 and 109, respectively. The authors would like to conclude that Cyphos IL 103 is better and safer to environment issues because Cyphos IL 109 decomposes releasing HF.

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References

1. Petra C, Nandor N, Katalin B-B. J Membr Sci. 2010; 349(1–2):6–11.
2. Wu B, Reddy RG, Rogers RD. Novel ionic liquid thermal storage for solar thermal electric power systems. Washington DC: International Solar Energy Conference;2001. p. 445–451.
3. Wu J, Grabowski EF, Evans KJ, Levy DV, Lin L-B. (Xerox Corporation, USA). US Pat. Appl. Publ., 19 pp US 2009092914 A1 20090409. Application: US 2007-869246 20071009.