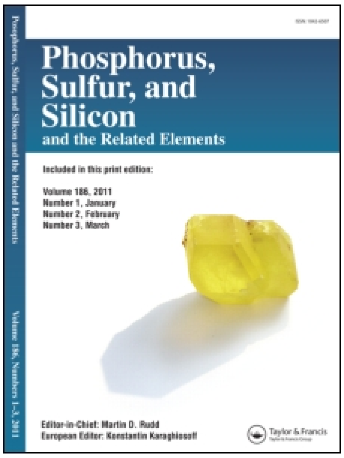

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UNEXPECTED FORMATION OF 1,4,2-OXAZAPHOSPHORINANE VIA THERMAL DECOMPOSITION OF POLY(URETHANE PHOSPHONATE)

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Communication

UNEXPECTED FORMATIOM OF 1,4,2-OXAZAPHOSPHORINANE VIA THERMAL DECOMPOSITION OF POLY(URETHANE PHOSPHONATE)

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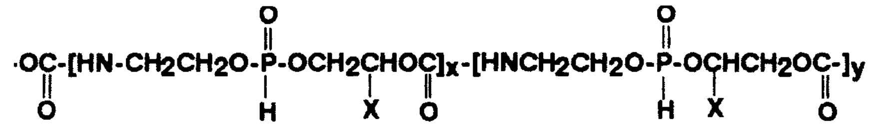
I report in this communication my finding on the formation of ammonium salt of 3-ethyl-2-oxo-1,4,2-oxazaphosphorinane via the thermolysis of poly(urethane phosphonate).

Keywords: poly(urethane phosphonate); thermolysis; 1,4,2-oxazaphosphorinane

Hydroxyalkyl carbamates ($R^1R^2NC(O)OCH_2CH_2OH$) are known to be thermally unstable[1] and when decomposed depending on their type a number of different compounds can be obtained.

Herein I report the initial results related to the formation of ammonium salt of 3-ethyl-2-oxo-1,4,2-oxazaphosphorinane via thermal decomposition of poly(urethane phosphonate)[2] obtained via transesterification of phosphonic acid diesters with hydroxyalkyl carbamate[3] based on propylene carbonate and 2-aminoethanol. I and co-authors recently have shown that *via* transesterification of phosphonic acid diesters with hydroxyalkylcarbamate poly(urethane phosphonate)s (**3**) with the following repiting units could be prepared.[2] It was established that the poly(urethane phosphonate) (**3**) obtained *via* transesterification of phosphonic acid diesters (**1**) with hydroxyalkylcarbamate (**2**) based on the propylene carbonate and 2-aminoethanol ($X = CH_3$) at temperatures higher than 160°C undergoes a thermal decomposition resulting in the formation of the ammonium salt of 3-ethyl-2-oxo-1,4,2-oxazaphosphorinane (**4**) (Scheme I). The urethane group of poly(urethane phosphonate) undergoes thermal decompositon

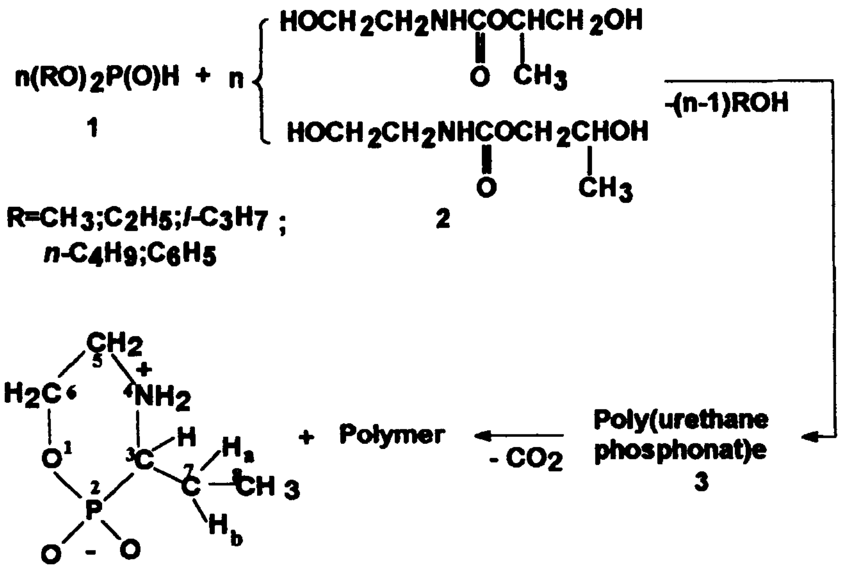


$$\text{-O}\underset{O}{\overset{}{C}}\text{-[HN-CH}_2\text{CH}_2\text{O-}\overset{O}{\underset{H}{P}}\text{-OCH}_2\underset{X}{C}\text{HO}\underset{O}{C}]_x\text{-[HNCH}_2\text{CH}_2\text{O-}\overset{O}{\underset{H}{P}}\text{-O}\underset{X}{C}\text{HCH}_2\text{O}\underset{O}{C}\text{-]}_y$$

3

X = H; CH_3

accompanied by the evolution of CO_2. The formation of ammonium salt of 3-ethyl-2-oxo-1,4,2-oxazaphosphorinane does not depend on the type of phosphonic acid diesters. It was established that ammonium salt of 3-ethyl-2-oxo-1,4,2-oxazaphosphorinane was formed at the transesterification of dimethyl, or diethyl, or dibutyl, or diisopropyl, or diphenyl phosphonates with hydroxyalkylcarbamate based on the propylene carbonate and 2-aminoethanol. On the other hand when carry out the transesterification of those diesters with hydroxyalkylcarbamate obtained from the ethylene carbonate and 2-aminoethanol no formation of ammonium salt of 3-ethyl-2-oxo-1,4,2-oxazaphosphorinane is observed. When carry out the transesterification of alkyl dialkyl esters of phosphonic acids $[(RO)_2P(O)R]$ with hydroxyalkylcarbamate obtained from



4

the propylene carbonate and 2-aminoethanol no formation of ammonium salt of 3-ethyl-2-oxo-1,4,2-oxazaphosphorinane is observed. This suggested that: (i) ammonium salt of 3-ethyl-2-oxo-1,4,2-oxazaphosphorinane is formed as a result of the thermal decomposition of a unit of the poly(urethane phosphonate) with the determined structure which is obtained during of transesterification reaction; (ii) in the formation of ammonium salt of 3-ethyl-2-oxo-1,4,2-oxazaphosphorinane P-H group takes part.

The ammonium salt of 3-ethyl-2-oxo-1,4,2-oxazaphosphorinane can be easily isolated in high purity in 18–20% yield. The structure of the ammonium salt of of 3-ethyl-2-oxo-1,4,2-oxazaphosphorinane was confirmed by ^{1}H, ^{13}C, ^{31}P NMR spectroscopy and IR spectroscopy, elemental analysis and FAB masspectroscopy. The salt is soluble only in water and decompose at 303°C when heated.

It should be noted that the thermal decomposition of poly(urethane phosphonate) provides a convinient single step preparative method for ammonium salt of 3-ethyl-2-oxo-1,4,2-oxazaphosphorinane. There are no literature data about the synthesis of ammonium salt of 3-ethyl-2-oxo-1,4,2-oxazaphosphorinane.

EXPERIMENTAL

^{1}H, ^{13}C, ^{31}P NMR sperctra were recorded on a GE NMR Omega, 400 MHz in D_2O as a solvent.

General Procedure

A mixture of phosphonic acid diesters and hydroxyalkyl carbamate, based on propylene carbonate and 2-aminoethanol, in molar ratio 1:1 was heated at 150°C for 3h and after that at 165°C for 4h. The ammonium salt of 3-ethyl-2-oxo-1,4,2- oxazaphosphorinane was separated with absolutly methanol and dried under the vacuum.

FOOTNOTES

^{1}H NMR (D_2O) of ammonium salt of 3-ethyl-2-oxo-1,4,2-oxazaphosphorinane, δ in ppm: 1.02–1.05, t, 3H,2J(H,H) = 7.3 Hz, CH_3 (H_8); 1.64–1.80, m, H; 1.83–1.97, m, H, CH_2 (H_{7a}, H_{7b}); 3.16–3.37, m, 3H, CH_2 (H_5) and CH (H_3); 4.18–4.36, m, 2H, P-OCH_2 (H_6); ^{13}C{H}DEPT 135 NMR (D_2O), δ in ppm:

10.11, CH_3 (C_8); 21.4, CH_2 (C_7); 44.7, CH_2 (C_5); 54.56–57.28, d, 1J(P,C) = 136.7 Hz, CH (C_3); 64.42, CH_2 (C_6); ^{13}C NMR (D_2O), δ in ppm: 8.15–11.90, q, 1J(C,H) = 125.8 Hz, CH_3, (C_8); 20.14–22.71, t, 1J(C,H) = 133.2 Hz, CH_2, (C_7); 43.16–44.03, t, 1J(C,H) = 148.0 Hz, CH_2, (C_5); 54.56–57.28, t, 1J(C,H) = 140.6 Hz, CH, (C_3); 61.48–64.24, t, 1J(C,H) = 148.0 Hz, CH_2, (C_6). $^{31}P\{H\}$ NMR (D_2O), δ in ppm: 10.21.

IR spectral (KBr) data for 4: ν/cm^{-1} 3420 ($+NH_2$), 2992 (CH_3CH_2), 1616 ($^+NH_2$), 1215 (P=O), 1082 ($POCH_2$), 1049 (N-C), 771 (P-C).

Elemental analysis for $C_5H_{12}NO_3P$: Calcul. %: C = 36.36; H = 7.27; N = 8.48; P = 18.78. Found, %: C = 36.35; H = 7.39; N = 8.48; P = 18.64. MS (FAB) MH^+ 166.1.

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