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Study of the Reactions of Dimethyl Hydrogen Phosphonate with Urethane and Acetanilide

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ABSTRACT: *In this article, a new reactivity of dimethyl hydrogen phosphonate is described. It was established that the reaction between dimethyl hydrogen phosphonate and urethane encompasses two simultaneous processes: an exchange reaction between the methoxy groups of the phosphonate and urethane groups and alkylation of the urethane. The reaction of dimethyl hydrogen phosphonate with acetanilide represents an alkylation of the amido group. The structure of the resulting products was studied by means of* ^{1}H, ^{31}P, *and* ^{13}C *NMR spectroscopy.* © 2000 John Wiley & Sons, Inc. Heteroatom Chem 11:205–208, 2000

INTRODUCTION

The present article represents a continuation of our investigation on the reactivity of phosphonic acid diesters [1–6]. It is known [7] that, when two symmetrical phosphonic acid dialkyl esters are heated, the resulting product is an unsymmetrical phosphonic acid dialkyl ester; that is, exchange of the alkoxy groups has taken place.

This article reports the occurrence of an exchange reaction between methoxy groups of dimethyl hydrogen phosphonate and urethane groups, as well as alkylation of urethane and amido groups during the reaction of dimethyl hydrogen phosphonate with urethane and acetanilide.

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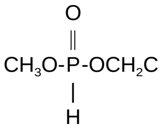
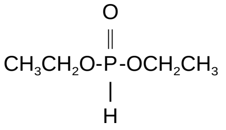
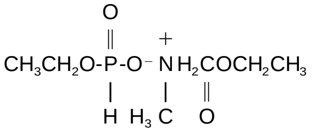
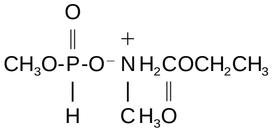
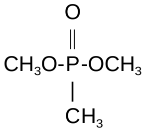
RESULTS AND DISCUSSION

Reaction between Dimethyl Hydrogen Phosphonate and Urethane

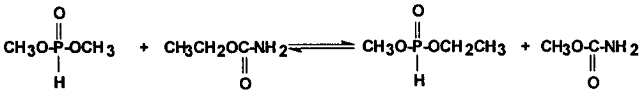
The $^{31}P\{H\}$ NMR spectrum of the reaction mixture obtained after heating dimethyl hydrogen phosphonate and urethane at 160°C revealed signals at $\delta = 3.26$, 5.10, 7.04, 8.30, 9.80, 11.57, and 34.22. The ^{31}P NMR spectrum showed that the signal at 9.80 ppm represents a doublet of sextets with ^{3}J(POCH) = 11.8 and 9.1 Hz and ^{1}J (P,H) = 695.8 Hz (Table 1) and can be assigned to the phosphorus atom of the ethyl methyl hydrogen phosphonate **3.** The signal at 8.3 ppm represents a doublet of quintets with ^{3}J(POCH) = 9.5 Hz and ^{1}J(P,H) = 693.6 Hz (Table 1) and can be assigned to the phosphorus atom in the diethyl hydrogen phosphonate **5.** The signal at 5.1 ppm, which represents a doublet of triplets with ^{3}J(POCH) = 8.9 and 9.1 Hz and ^{1}J (P,H) = 644.5 Hz (Table 1) can be assigned to the phosphorus atom of the product **6.** The signal at 7.04 ppm, which represents a doublet of quartets with ^{3}J(POCH) = 11.8 and ^{1}J (P,H) = 640.9 Hz (Table 1) can be assigned to the phosphorus atom of the product **7.** The formation of products **6** and **7** is confirmed by the value of the ^{1}J(P,H) constant. The presence of the negative charge on the oxygen atom, bonded to the phosphorus, determines a decrease of the ^{1}J(P,H) constant from 693.6 Hz for diethyl hydrogen phosphonate to 644.5 Hz for product **6** and from 691.8 Hz for dimethyl hydrogen phosphonate to 640.9 Hz for product **7.** The signal at 33.9–34.6 ppm, which represents a multiplet (Table 1) can be assigned to the phos-

TABLE 1 NMR Data of the Phosphorus-Containing Products of the Dimethyl Phosphonate and Urethane Reaction

N	*Structure*	^{31}*P NMR* (δ, *ppm; J, Hz*)	^{1}*H NMR* (δ, *ppm; J, Hz*)	^{13}*C NMR* (δ, *ppm; J, Hz*)
3	 $CH_3O\text{-}\underset{\underset{H}{\vert}}{\overset{\overset{O}{\Vert}}{P}}\text{-}OCH_2CH_3$	9.80, dsex. ^3J(P, H) = 9.1; 11.8 ^1J(P, H) = 695.8	1.16, t, ^3J(H, H) = 6.8, $C\underline{H}_3CH_2$; 3.68, d, ^3J(P, H) = 11.8 $P\text{-}OC\underline{H}_3$; 4.04–4.16, m, $P\text{-}OC\underline{H}_2CH_3$; 6.71, d, ^1J(P, H) = 695.8, P-$\underline{H}$.	16.4, d, ^3J(P, C) = 5.2, $POCH_2\underline{C}H_3$; 52.2, d, ^2J(P, C) = 5.8, $PO\underline{C}H_3$, 62.1, d, ^2J(P, C) = 5.8, $PO\underline{C}H_2CH_3$;
5	 $CH_3CH_2O\text{-}\underset{\underset{H}{\vert}}{\overset{\overset{O}{\Vert}}{P}}\text{-}OCH_2CH_3$	8.30, *d* quintets ^3J(P, H) = 9.5 ^1J(P, H) = 693.6	1.16, t, ^3J(P, H) = 6.8 $C\underline{H}_3CH_2$; 4.04–4.16, m, $POC\underline{H}_2CH_3$; 6.67, d, ^1J(P, H) = 693.6	16.4, d, ^3J(P, C) = 5.2, $POCH_2\underline{C}H_3$; 62.1, d, ^2J(P, C) = 5.8, $PO\underline{C}H_2CH_3$;
6	 $CH_3CH_2O\text{-}\underset{\underset{H}{\vert}}{\overset{\overset{O}{\Vert}}{P}}\text{-}O^-\,\underset{\underset{H_3C}{\vert}}{\overset{+}{N}}H_2\underset{\underset{O}{\Vert}}{C}OCH_2CH_3$	5.10, dt ^3J(P, H) = 8.9 ^1J(P, H) = 644.5	1.12, t, ^3J(H, H) = 6.8, $C\underline{H}_3CH_2$; 1.29, t, ^3J(H, H) = 7.3, $C\underline{H}_3CH_2OC(O)$; 3.27, s, $NC\underline{H}_3$; 4.01, q, ^3J(H, H) = 7.3, $CH_3C\underline{H}_2OC(O)$; 4.04–4.16, m, $POC\underline{H}_2CH_3$; 5.2, (br), $^+NH_2$; 6.69, d, ^1J(P, H) = 644.2, P-$\underline{H}$.	14.7, $\underline{C}H_3CH_2OC(O)$; 16.4, d$^3J$(P, C) = 5.2, $POCH_2\underline{C}H_3$; 55.5, $^+N\underline{C}H_3$ 60.5, $CH_3\underline{C}H_2OC(O)$; 62.1, d, ^2J(P, C) = 5.8, $PO\underline{C}H_2CH_3$; 158.0, C=O
7	 $CH_3O\text{-}\underset{\underset{H}{\vert}}{\overset{\overset{O}{\Vert}}{P}}\text{-}O^-\,\underset{\underset{CH_3}{\vert}}{\overset{+}{N}}H_2\underset{\underset{O}{\Vert}}{C}OCH_2CH_3$	7.0, dq ^3J(P, H) = 11.8 ^1J(P, H) = 640.9	1.29, t, ^3J(H, H) = 7.3, $C\underline{H}_3CH_2OC(O)$; 3.27, s, $^+NC\underline{H}_3$; 3.69, d, ^3J(P, H) = 12.5, $POC\underline{H}_3$; 4.01, q, ^3J(H, H) = 7.3, $CH_3C\underline{H}_2OC(O)$; 5.2, (br), $^+NH_2$; 6.65, d, ^1J(P, H) = 642.0, P-$\underline{H}$.	14.7, $\underline{C}H_3CH_2OC(O)$; 52.1, d, ^2J(P, C) = 2.4, $PO\underline{C}H_3$; 55.5, $N\underline{C}H_3$; 60.5, $CH_3\underline{C}H_2OC(O)$; 158.0, C=O
8	 $CH_3O\text{-}\underset{\underset{CH_3}{\vert}}{\overset{\overset{O}{\Vert}}{P}}\text{-}OCH_3$	33.9–34.6, m	1.40, d, ^2J(P, H) = 17.8, $PC\underline{H}_3$; 3.67, d, ^3J(P, H) = 12.1, $POC\underline{H}_3$.	10.2, d, ^1J(P, C) = 145.0, $P\underline{C}H_3$; 52.6, d, ^2J(P, C) = 2.5, $PO\underline{C}H_3$.

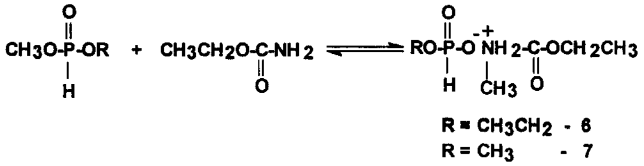
phorus atom in the dimethyl methylphosphonate **8.** The signal at 11.57 ppm which represents a doublet of septets with ^3J(POCH) = 12.1 Hz and ^1J(P,H) = 700.2 Hz can be assigned to the phosphorus atom in the dimethyl hydrogen phosphonate **1.** Data from ^{1}H NMR spectroscopy confirm the structure of the aforementioned compounds (Table 1). The signal at 4.04–4.16, which represents a multiplet is characteristic of $P\text{-}OC\underline{H}_2CH_3$ protons. The signal at 1.16 ppm which represents a triplet with ^3JH,H) = 6.8 Hz is characteristic of $POCH_2C\underline{H}_3$ protons. The singlet at 3.27 ppm can be assigned to the $N\text{-}CH_3$ protons. In the ^{13}C NMR spectrum there are new signals at 62.1 ppm with ^2J(P,C) = 5.8 Hz, which is characteristic of the $PO\underline{C}H_2CH_3$ carbon atom, and at 16.4 ppm with ^3J(P,G) = 5.2 Hz, which is characteristic of the $POCH_2\underline{C}H_3$ carbon atom. The signal at 3.3 ppm, which represents an octet with ^3J(POCH) = 11.1 Hz, can be assigned to the phosphorus atom in the phosphate structure. Because the content of this compound is too low at the present time, it is impossible to prove its structure in an adequate manner.

Ethyl methyl hydrogen phosphonate **3** is formed as the result of an exchange reaction between the alkoxy groups of the phosphonate and urethane (Equation 1).



(1)

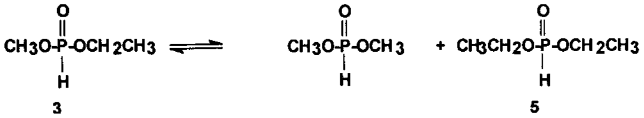
The products **6** and **7** are formed via alkylation of the urethane by ethyl methyl hydrogen phosphonate and dimethyl hydrogen phosphonate, respectively (Equation 2).



(2)

There are no readily apparent published data for the exchange reaction between alkoxy groups of phosphonic acid dialkyl esters and those of urethane groups or for the alkylation of a urethane by phosphonic acid dialkyl esters. The observation of an exchange reaction between the alkoxy groups of a phosphonic acid dialkyl ester and a urethane represents an important scientific result for polymer chemistry. The results obtained make the concept of an exchange reaction as an alternative to simple degradation of polyurethane waste products plausible. The alkylation of the urethane group is unexpected, keeping in mind the low basicity of the nitrogen atom of the urethane group.

Diethyl hydrogen phosphonate **5** is formed via disproportionation of ethyl methyl hydrogen phosphonate **3** (Equation 3).



$$\underset{\mathbf{3}}{CH_3O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}\text{-}OCH_2CH_3} \rightleftharpoons CH_3O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}\text{-}OCH_3 + \underset{\mathbf{5}}{CH_3CH_2O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}\text{-}OCH_2CH_3} \qquad (3)$$

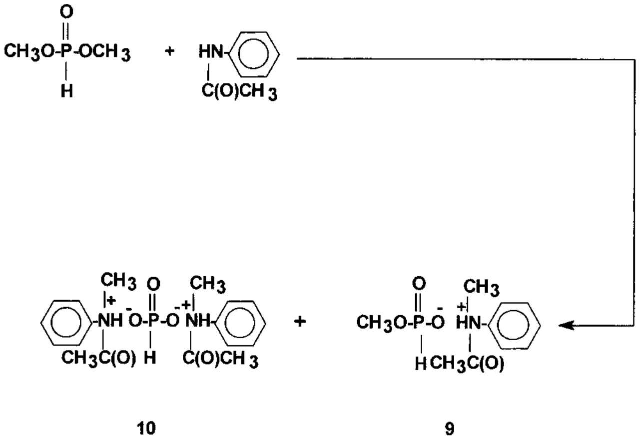
The thermal degradation [8] of dimethyl hydrogen phosphonate leads to the formation of dimethyl methylphosphonate **8.**

The results obtained show that the reaction between dimethyl hydrogen phosphonate and urethane at 160°C includes two simultaneous reactions: exchange reaction between the alkoxy groups of dimethyl hydrogen phosphonate and those of urethane groups, and alkylation of urethane by dimethyl hydrogen phosphonate.

Reaction between Dimethyl Hydrogen Phosphonate and Acetanilide

The $^{31}P\{H\}$NMR spectrum of the reaction mixture obtained after heating dimethyl hydrogen phosphonate with acetanilide at 150°C showed signals at $\delta = 4.45, 7.37, 11.57$, and 34.25 ppm. The ^{31}P NMR spectrum revealed that the signal at 7.37 ppm, which represents a doublet of quartets with $^3J(POCH) = 12.3$ Hz and $^1J(P,H) = 662.4$ Hz and can be assigned to the phosphorus atom in the product **9** (Table 2), and at 4.45 ppm, which represents a doublet with $^1J(P,H) = 664.2$ Hz, can be assigned to the phosphorus atom of the product **10** (Table 2). The measured value of the $^1J(P,H)$ constant confirms the ionic structure of compounds **9** and **10.** The signal of the phosphorus atom of compound **10** is strongly shifted down field due to the presence of two ionic bonds in this structure. $^1J(P,H)$ constants of **6** and **7** are smaller than the $^1J(P,H)$ of dimethyl hydrogen phosphonate. Signals at 11.57 ppm and 34.25 ppm are very weak. As seen from the $^{31}P\{H\}$ NMR spectrum, their concentration is lower than 0.5%. These signals can be assigned to the phosphorus atom in dimethyl hydrogen phosphonate and to dimethyl methylphosphonate, respectively.

The experimental results revealed that the reaction of dimethyl hydrogen phosphonate with acetanilide represents an alkylation of the amido group by dimethyl hydrogen phosphonate (Equation 4).



(4)

The amido group did not participate in an exchange reaction with the methoxy group of dimethyl hydrogen phosphonate.

EXPERIMENTAL

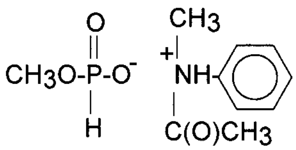
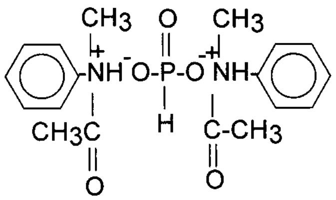
Materials

Dimethyl hydrogen phosphonate, urethane (ethyl carbamate), and acetanilide are all Aldrich products.

Reaction between Dimethyl Hydrogen Phosphonate and Urethane

Into a two-necked flask equipped with a stirrer, thermometer, and reflux condenser, 3.21 g (0.036 mol) of urethane and 7.93 g (0.072 mol) of dimethyl hydrogen phosphonate were placed. The reaction mixture was allowed to stand at 160°C for 6 hours. Dimethyl hydrogen phosphonate, ethyl methyl hydrogen phosphonate, diethyl hydrogen phosphonate, and dimethyl methylphosphonate were removed from the reaction mixture by vacuum distillation. Products **4, 6,** and **7** were not distilled but were identified by ^{31}P, ^1H, and ^{13}C NMR spectroscopy. We tried but we failed to isolate these products.

TABLE 2 NMR Data of the Phosphorus-Containing Products from the Dimethyl Phosphonate and Acetanilide Reaction

N	*Structure*	^{31}*P NMR* (*δ, ppm; J, Hz*)	^{1}*H NMR* (*δ, ppm; J, Hz*)	^{13}*C NMR* (*δ, ppm; J, Hz*)
9	9 	7.25, dq ^3J(P, H) = 12.7; ^1J(P, H) = 662.4	2.11, s, $C\underline{H}_3C(O)$; 3.56, s, NCH_3; 3.71, d, ^3J(P, H) = 12.3, $POC\underline{H}_3$; 6.64, d, ^1J(P, H) = 662.9, P-$\underline{H}$; 6.85 − 7.68, aromatic protons; 9.38, (br), $\overset{+}{N}H_2$.	24.8, $\underline{C}H_3C(O)$; 52.7, d, ^2J(P, C) = 2.6, $PO\underline{C}H_3$; 58.0, $\overset{+}{N}CH_3$; 120.5, 124.4, 129.1, 139.5, aromatic carbon atoms; 170.0, C=O
10	10 	4.45, d ^1J(P, H) = 664.0	1.93, s, $C\underline{H}_3C(O)$; 3.52, s, $\overset{+}{N}C\underline{H}_3$; 6.62, d, ^1J(P, H) = 662.3, P-$\underline{H}$; another signals overlapped with the signals of the product 9	overlapping with signals ofthe product 9

Reaction between Dimethyl Hydrogen Phosphonate and Acetanilide

Into a two-necked flask equipped with a stirrer, thermometer, and reflux condenser, 4.64 g (0.034 mol) of acetanilide and 7.55 g (0.069 mol) of dimethyl hydrogen phosphonate were placed. The reaction mixture was allowed to stand at 150°C for 1 hour. Dimethyl hydrogen phosphonate and dimethyl methylphosphonate were extracted from the reaction mixture by diethyl ether. We tried to isolate products **9** and **10** but failed. The residual reaction mixture was then studied by ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy (Table 2).

CONCLUSION

The results obtained revealed that, during the reaction of dimethyl hydrogen phosphonate with urethane, two simultatious reactions occurred: an exchange reaction between the alkoxy groups of the two reagents and an alkylation of the urethane group. The interaction of dimethyl hydrogen phosphonate with acetanilide represents an alkylation of an amido group. The results indicate that the exchange and alkylation reactions can represent alternative mode of degradation of polyurethane waste products and for the modification of polyamides.

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