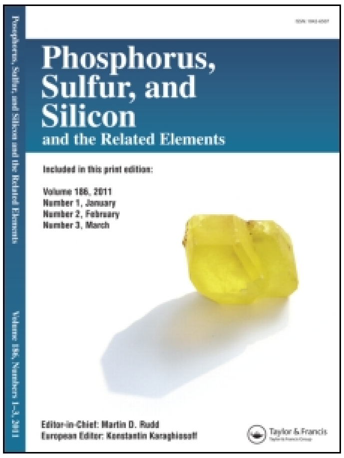

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STRUCTURES OF PHOSPHORUS-CONTAINING METAL AND AMMONIUM SALTS

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STRUCTURES OF PHOSPHORUS-CONTAINING METAL AND AMMONIUM SALTS

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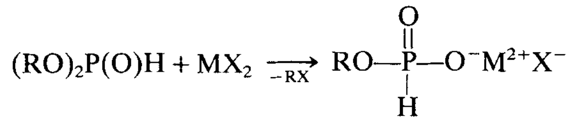
In order to test the proposal that phosphorus-containing metal salts exist as ion pairs, in contrast to ammonium salts which exist as free-ions, an investigation of their solution structure by means of ^{31}P and ^{1}H NMR spectroscopy was carried out. The presence of an ionic bond in the molecule of both salts causes a decrease of both the phosphorus chemical shift and the P–H coupling constant. The change of ^{31}P chemical shift and the P–H coupling constant depends on the type of the cation.

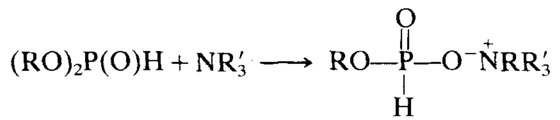
Key Words: Hydrogen phosphonates, ammonium, metal, salts, ions, ^{31}P NMR.

INTRODUCTION

Dialkyl hydrogenphosphonates are well known to react with metal salts to yield[1–3] phosphorus-containing metal salts (Equation 1). When dialkyl hydrogenphosphonates are reacted with tertiary amines, quaternary ammonium salts are obtained[4–8] (Equation 2). Both types of salt include an ionic bond in the molecules $P—O^-M^+$ and $P—O^-N^+$ respectively. Based on the experimental data of their reactivity,[7–11] we propose that the phosphorus-containing metal salts exist as ion pairs, in contrast to those of the ammonium ion which exists as free-ions.



$$(RO)_2P(O)H + MX_2 \xrightarrow[-RX]{} RO—\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{P}}—O^-M^{2+}X^- \qquad (1)$$



$$(RO)_2P(O)H + NR'_3 \longrightarrow RO—\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{P}}—O^-\overset{+}{N}RR'_3 \qquad (2)$$

RESULTS AND DISCUSSION

Metal and ammonium ion salts show significant differences in dealkylation and alkylation reactions. The phosphorus-containing metal salts (Equation 1) undergo dealkylation to produce oligomeric salts[9] (Equation 3).

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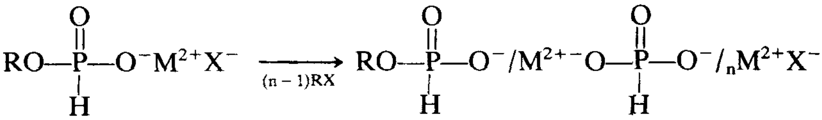
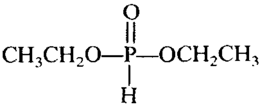
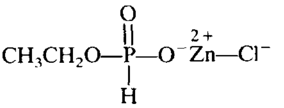
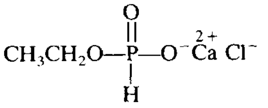
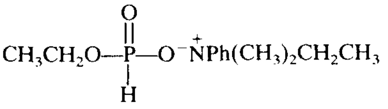
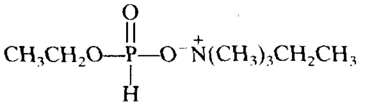
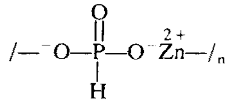
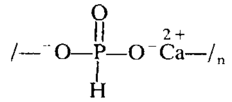


$$RO-\overset{O}{\overset{\|}{\underset{\underset{H}{|}}{P}}}-O^-M^{2+}X^- \xrightarrow[(n-1)RX]{} RO-\overset{O}{\overset{\|}{\underset{\underset{H}{|}}{P}}}-O^-/M^{2+}\,{}^-O-\overset{O}{\overset{\|}{\underset{\underset{H}{|}}{P}}}-O^-/_nM^{2+}X^- \qquad (3)$$

The ^{31}P-NMR spectra of the oligomeric salts (Equation 3) reveal (Table I) a signal at δ 2.49, doublet with $J_{PH} = 652$ Hz (Zn^{2+}); or at $\delta = -0.93$, doublet with $J_{PH} = 617$ Hz (Ca^{2+}). Such resonances are characteristic of the $^-OP(O)HO^-$ fragment. These data show that the second alkyl group has been displaced

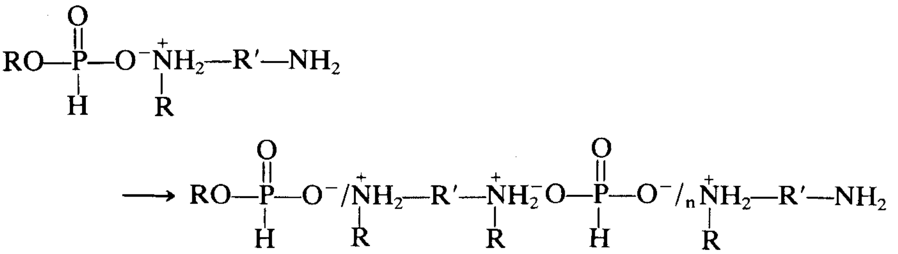
TABLE I

Data from ^{31}P NMR spectra of the phosphorus-containing metal and ammonium salts (DMSO-d_6)

Compounds	^{31}P Chemical shifts δ, ppm	$\Delta\delta$, ppm	Coupling constants, J, Hz		
			$^1J_{PH}$	Δ^1J_{PH}	$^3J_{PH}$
Monomeric salts					
 $CH_3CH_2O-\overset{O}{\overset{\|}{\underset{\underset{H}{|}}{P}}}-OCH_2CH_3$	d, 7.77	—	693	—	9.6
 $CH_3CH_2O-\overset{O}{\overset{\|}{\underset{\underset{H}{|}}{P}}}-O^-\overset{2+}{Zn}-Cl^-$	t, 4.84	2.93	663	30	8.1
 $CH_3CH_2O-\overset{O}{\overset{\|}{\underset{\underset{H}{|}}{P}}}-O^-\overset{2+}{Ca}\ Cl^-$	t, 0.28	7.49	609	84	8.9
 $CH_3CH_2O-\overset{O}{\overset{\|}{\underset{\underset{H}{|}}{P}}}-O^-\overset{+}{N}Ph(CH_3)_2CH_2CH_3$	t, 2.63	5.14	632	61	8.9
 $CH_3CH_2O-\overset{O}{\overset{\|}{\underset{\underset{H}{|}}{P}}}-O^-\overset{+}{N}(CH_3)_3CH_2CH_3$	t, 1.05	6.72	568	125	8.8
Oligomeric salts					
 $/-{}^-O-\overset{O}{\overset{\|}{\underset{\underset{H}{|}}{P}}}-O^-\overset{2+}{Zn}-/_n$	d, 2.49	5.28	652	41	—
 $/-{}^-O-\overset{O}{\overset{\|}{\underset{\underset{H}{|}}{P}}}-O^-\overset{2+}{Ca}-/_n$	d, −0.93	8.70	617	76	—

(Equation 3) to form the dianion HPO_3^{--}. This result shows that the second α-carbon atom of the alkoxy group on phosphorus takes part in the reaction with metal salts.

On the other hand, despite numerous synthetic attempts, such oligomeric salts are not obtained with alkylammonium salts (Equation 4).



$$RO-\overset{O}{\underset{H}{P}}-O^{-}\overset{+}{\underset{R}{N}}H_2-R'-NH_2 \longrightarrow RO-\overset{O}{\underset{H}{P}}-O^{-}/\overset{+}{\underset{R}{N}}H_2-R'-\overset{+}{\underset{R}{N}}H_2^{-}O-\overset{O}{\underset{H}{P}}-O^{-}/_{n}\overset{+}{\underset{R}{N}}H_2-R'-NH_2 \quad (4)$$

This result indicates that the second α-carbon of the alkoxy group of the monoalkylated product (Equation 2) is not attacked by tertiary amines. Furthermore it suggests that the electron density of the α-carbon atom of the alkoxy group of the monoalkylated product is significantly increased in comparison with the α-carbon atoms of the alkoxyl group of the metal salts and dialkyl hydrogenphosphonates. We propose that the type of cation in these salts determines the observed difference in their reactivity. To test this proposal a solution structural investigation by means of ^{31}P and ^{1}H NMR spectroscopy was carried out.

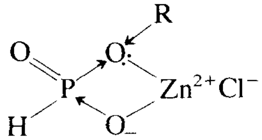
Examination of the ^{31}P NMR spectra (Table I) indicates that the presence of an ionic bond in the molecule of both types of salts induces a change in the ^{31}P chemical shifts. By comparison with the ^{31}P chemical shift of diethyl hydrogenphosphonate itself, the phosphorus chemical shifts of both salts are decreased. From the results obtained by ^{31}P NMR spectroscopy, it is apparent that the zinc cation causes a smaller decrease of the chemical shift when compared with those of the calcium and ammonium cations. On the other hand, increasing the degree of ionization causes a greater decrease in the chemical shift (see oligomeric salts, Table I). It should be noted that a decrease in the ^{31}P chemical shift of these salts depends on (1) the type of cation, and (2) the degree of ionization.

The factors that affect the ^{31}P chemical shift include (1) ionization,[12] (2) cation complexation,[13] (3) O—P—O bond angle,[14] (4) torsional angles,[15] (5) temperature,[16] and (6) solvent.[17] Each of these effects can induce changes in the ^{31}P chemical shift. Because the ^{31}P NMR spectra in our series of compounds were measured at the same temperature, and in the same solvent (DMSO-d_6), the changes in the ^{31}P chemical shifts of the metal and ammonium salts will be determined by the degree of ionization, by cation complexation, and by the O—P—O bond angle. The change in ^{31}P chemical shift in such cases may be treated by the following relationship[12] (Equation 5), where $\Delta\chi_O$, Δn_π and $\Delta\theta$ represent the change in the effective electronegativity of the

$$\Delta\delta = 180\,\Delta\chi_O - 147\,\Delta n_\pi - A\,\Delta\theta \qquad (5)$$

phosphoryl oxygens, the degree of occupation of the d-orbitals of the phosphorus atom, and the change of the O—P—O angle, respectively.

On the basis of the observed reactivity, and from these ^{31}P NMR spectroscopic data, we propose the following structure for the zinc salt:



Such a structure allows us to explain the observed reactivity at the α-carbon atom of the alkoxy group of the phosphorus-containing zinc salt (Equation 3). The formation of the coordinate bond between the oxygen atom of the alkoxy group and the zinc ion will accelerate the rate of the dealkylation reaction because of the attraction of the electron pair of the bond O ← R to the oxygen atom. The observed reactivity of the phosphorus-containing zinc salt confirms such a proposal. The results from the ^{31}P NMR spectra reveal that the electron density of the phosphorus atom of the zinc salt is not significantly increased. The formation of such a structure allows us to explain this phenomenon. The increased electron density at the phosphorus atom caused by this ionization, along with the presence of the negative charge at the oxygen atom, will be reduced by the imbalance of the $P \rightarrow O(R)$ bond due to the existence of the coordinate bond between the oxygen atom and the zinc ion. The change in the ^{31}P chemical shift for the phosphorus-containing zinc salt will depend on the change of O—P—O bond angle. The existence of the coordinate bond between the oxygen atom and the zinc will lead to a change in O—P—O bond angle, which will affect the phosphorus chemical shift.

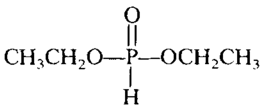
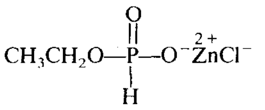
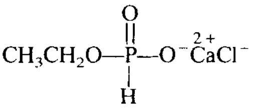
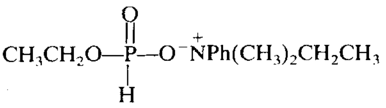
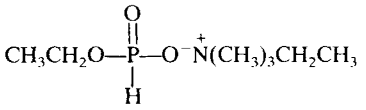
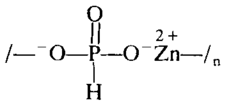
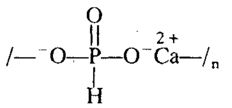
The ^{31}P chemical shift of the phosphorus-containing calcium salt is strongly decreased by comparison with that of the zinc salt. Whereas $\Delta\delta$ for zinc salt is 2.93 ppm, $\Delta\delta$ for the calcium salt is 7.49 ppm. This result indicates that the electron density of the phosphorus atom of the calcium salt is significantly increased. On the other hand, the phosphorus-containing calcium salt exhibits the same chemical reactivity as zinc salt in the dealkylation reaction. These shift data suggest that the electron density of the α-carbon atom of the alkoxy group of the calcium salt is similar to that of the α-carbon atom of the zinc salt. In the case of the calcium salt, since the ionic radius is larger (0.99 Å)[18] than that for zinc (0.74 Å), maybe the coordination between the oxygen atom and the calcium ion is different than for Zn^{2+}. The results obtained allow us to propose that the existence of a coordinate bond between the oxygen atom and the calcium ion will cause a decrease of electron density at α-carbon atom of the alkoxy group of the calcium salt, but that the donation from the oxygen atom to the calcium $P—O\!:\rightarrow Ca$ is weaker than is found with the zinc cation. Hence, the influence of the negative charge on the electron density of the phosphorus atom will be significantly different.

These results from ^{31}P NMR spectroscopy reveal that the ^{31}P chemical shifts of the phosphorus-containing metal salts depend on the nature of the interaction between the cation and anion, i.e. on the electrostatic energy of the interaction between the cation and anion. The anion will experience a greater positive charge, and thereby have a greater electrostatic interaction, when ion associated with Zn^{2+} as compared to Ca^{2+} because of the difference in the effective nuclear charges.

The ^{31}P chemical shifts of the phosphorus-containing ammonium salts are significantly decreased when compared to the chemical shifts of both diethyl hydrogenphosphonate itself and of the phosphorus-containing zinc salt. The

TABLE II

Data from ^{1}H NMR spectra of the phosphorus-containing metal and ammonium salts (DMSO-d_6)

	Chemical shifts, δ, ppm			Coupling constants, J, Hz		
Compounds	P—H	$POCH_2C\underline{H}_3$	$POC\underline{H}_2CH_3$	$^{1}J_{PH}$	$\Delta^{1}J_{PH}$	$^{3}J_{PH}$
Monomeric salts						
 $CH_3CH_2O-\overset{O}{\overset{\Vert}{\underset{H}{\underset{\vert}{P}}}}-OCH_2CH_3$	d, 6.81	t, 1.18	m, 3.92–4.00	692		9.8
 $CH_3CH_2O-\overset{O}{\overset{\Vert}{\underset{H}{\underset{\vert}{P}}}}-O^{-}\overset{2+}{Zn}Cl^{-}$	d, 6.68	t, 1.26	m, 3.85–3.96	663	29	7.4
 $CH_3CH_2O-\overset{O}{\overset{\Vert}{\underset{H}{\underset{\vert}{P}}}}-O^{-}\overset{2+}{Ca}Cl^{-}$	d, 6.64	t, 1.16	m, 3.85–3.96	613	79	7.4
 $CH_3CH_2O-\overset{O}{\overset{\Vert}{\underset{H}{\underset{\vert}{P}}}}-O^{-}\overset{+}{N}Ph(CH_3)_2CH_2CH_3$	d, 6.64	t, 1.26	m, 3.44–3.49[a]	631	61	7.6
 $CH_3CH_2O-\overset{O}{\overset{\Vert}{\underset{H}{\underset{\vert}{P}}}}-O^{-}\overset{+}{N}(CH_3)_3CH_2CH_3$	d, 6.62	t, 1.10	m, 3.54–3.68[b]	557	135	7.1
Oligomeric salts						
 $/\!-{}^{-}O-\overset{O}{\overset{\Vert}{\underset{H}{\underset{\vert}{P}}}}-O^{-}\overset{2+}{Zn}-/_{n}$	d, 6.77	—	—	679	13	—
 $/\!-{}^{-}O-\overset{O}{\overset{\Vert}{\underset{H}{\underset{\vert}{P}}}}-O^{-}\overset{2+}{Ca}-/_{n}$	d, 6.53	—	—	607	85	—

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[a] s, 2.97 ($\overset{+}{N}C\underline{H}_3$); t, 0.99 ($\overset{+}{N}CH_2C\underline{H}_3$); m, 3.52–3.68 ($\overset{+}{N}C\underline{H}_2CH_3$); m, 7.91–8.16 (phenyl).

[b] s, 2.97 ($\overset{+}{N}C\underline{H}_3$); t, 1.05 ($\overset{+}{N}CH_2C\underline{H}_3$); m, 3.52–3.68 ($\overset{+}{N}C\underline{H}_2CH_3$).

observed higher decrease of the ^{31}P chemical shift of the ammonium salts, as compared to that of the zinc salt, are likely due to differences in ion pairing interactions. The alkylammonium cation is usually considered as non-complexing, therefore the presence of negative charge at the oxygen atom will lead to an increase of electron density at the phosphorus atom. The absence of complexation between the cation and the oxygen atom of the alkoxy group will result in a significant increase in the electron density of the phosphorus and oxygen atoms. The increase of electron density at the oxygen atom and at the alkoxy group of the monoalkylated product will cause an increase in the electron density at the α-carbon atom of the alkyl group. As a result of this increased electron density, both the transesterification and alkylation reactions will be strongly hampered. The observed chemical reactivity of the phosphorus-containing alkylammonium salts[19] confirm this proposal.

The P—H coupling constants of the phosphorus-containing metal and ammonium salts also show variations with changing cation (Table II). Obviously the presence of the ionic bond in these salts causes a decrease in the P—H coupling constant, when compared to the P—H coupling constant of diethyl hydrogenphosphonate itself. The coupling constant (J_{PH}) of the zinc ion monomeric salt is greatest (663 Hz) when compared with that of calcium ion (609 Hz), arylammonium ion (632 Hz), and alkylammonium ion (568 Hz). Thus the zinc cation causes a smaller decrease in the P—H coupling constant. Sptiz *et al.*[20] carried out an investigation of the cation effects on one bond P—H coupling constant in phosphinate ions, and established that the coupling constant for the zinc cation is greater than that of calcium. These authors explained this difference on the basis of the fact that the zinc ion has a smaller ionic radius than does the calcium ion.

On the basis of our results, we consider that the electron density at the α-carbon atom of the alkoxy group of the phosphorus-containing metal salts is reduced appreciably by the existence of the coordinate bond between the oxygen atom of the alkoxy group and metal cation. On the other hand, such a coordinate bond does not exist in phosphorus-containing ammonium salts, and as a consequence the electron density at the α-carbon atom is not significantly altered. The relative reactivity of these type of salts to oligomerization reactions suggests that the alkylammonium salts exist as free-ions, and that the metal complexes are ion paired in solution.

EXPERIMENTAL SECTION

The phosphorus-containing monomeric and oligomeric salts were prepared[2,3,9] from commercial diethyl hydrogenphosphonate and either zinc or calcium chloride. The ammonium salts were prepared from commercial diethyl hydrogenphosphonate and dimethylaniline or trimethyl amine.[4,8] The ^{31}P and ^{1}H NMR spectra were obtained with samples dissolved in DMSO-d_6 using a Bruker AF 200 FT-NMR spectrometer operating at 81.02 MHz and 200.13 MHz respectively.

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