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Synthesis and Characterization of Some New Organophosphonates and Their Adducts with Some Metal Salts

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The synthesis of the new monobasic organophosphonates $(C_2H_5O)RPO(OH)$, R=benzyl, benzoyl, or butanoyl group, by the hydrolysis of the neutral esters $(C_2H_5O)_2RPO$ is reported. The IR spectra of the new ligands showed that they were existed in solutions as dimers. The p*K*a values in 50% aqueous ethanol found to be 4.46, 3.98, and 3.48 for the benzyl, butanoyl, and benzoyl derivatives, respectively. These values were consistent with the calculated π-electron charge density. Solid complexes of the benzoylphosphonate with Pr, Eu, Er, and Co metal ions as well as the benzyl-Eu complex were isolated. The complex ratios were found to be 1:2 metal to phosphonate dimer. The octahedral arrangements were completed by the presence of a coordinated bidentate NO_3 group. Ionic properties of these complexes were ruled out from conductometric measurements. The IR spectra as well as the calculated π-electron charge density for the benzoyl complexes showed that the preference site for complex formation was from the carbonyl oxygen in contrast with the benzyl one where complexation through the phosphoryl group in addition to the hydroxyl oxygen.

It is well-established that the organophosphorus compounds of the type $(RO)_2PO(OH)$, $(RO)PO(OH)_2$, $(RO)R'PO(OH)$, $R'PO(OH)_2$, and $R'HPO(OH)$, where R and R′ are alkyl or aryl group, exist in dimeric forms.[1] These compounds were used as complexing agents for various transition and inner transition metal salts.[2] Neutral alkyl esters of phosphonic acid and phosphoric acid were also used in the formation of adducts with metal salts. However, isolation of crystalline compounds were generally not easily to perform.[3]

Here, we report the preparation of the new monobasic organophosphonates $(C_2H_5O)RPO(OH)$, R=benzyl, benzoyl, and butanoyl group as hydrolyzed products of the neutral esters $(C_2H_5O)_2RPO$. The IR spectra of these ligands and their complexes with some lanthanoid metals are also reported.

Experimental

The infrared spectra of the organophosphonates and their metal adducts were performed on a Perkin-Elmer infrared spectrophotometer Model 1430 with the use of KBr disc technique or in carbon tetrachloride solutions. Liquid film spectra (NaCl cell, 1.0 mm) were also carried out for the liquid ligands.

A Pye-Unicam pH-meter with expandable scale Model 290 Mk2 was used for the potentiometric titrations. It was connected to a Pye-Unicam glass combination electrode and was calibrated by using universal buffers.

The phosphonate ligands $(C_2H_5O)_2RPO$, R=benzyl, benzoyl, and butanoyl group, were purchased from Alfa Products, 99% purity, and were used without further purifications. Praseodymium, europium, erbium, and cobalt nitrates were supplied from British Drug Houses Ltd. Sodium hydroxide was of AnalaR grade. All the solvents used were purified by using the standard methods[4] and stored under nitrogen atmosphere.

Hydrolysis of the neutral phosphonates were carried out by using the following procedure:[5] The phosphonate reagent was mixed with aqueous sodium hydroxide solution in molar ratio of 1:6 (phosphonate:hydroxide). The mixture was stirred at 80 °C for 5 h in a sealed flask under nitrogen. The solution was left to cool and then shaked with benzene several times to remove the formed alcohol and any unhydrolyzed ester. The aqueous layer was separated and acidification with HCl was carried out to isolate the ligand in the acid form which was then extracted in benzene. The organic layer was separated and the acid was recovered by evaporating the benzene and any remaining alcohol by vacuum distillation.

The acid ionization constants of the new ligands were determined by titration of fixed amounts (20 ml) of

Table 1. The Acid Ionization Constants (pK_a's) and the Important Infrared Data of the New Organophosphonate Ligands

Ligand[a]	pK_a values (ethanol–water)		IR data[b] /cm^{-1}		
	50%	25%	$\nu_{OH(bond.)}$	$\nu_{P=O}$	$\nu_{C=O}$
$PhCH_2PO(OH)(OC_2H_5)$	4.46	3.95	2870(m)	1165(m)	—
$C_3H_6COPO(OH)(OC_2H_5)$	3.98	3.72	2880(vs)	1168(s)	1740(s)
$PhCOPO(OH)(OC_2H_5)$	3.48	3.18	2880(vs)	1170(s)	1718(s)

a) $PhCH_2$, benzyl; C_3H_6CO, butanoyl; PhCO, benzoyl. b) Liquid film spectra; m, medium; s, strong; vs, very strong.

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Table 2. The Analytical and Important Infrared Data of the New Complexes

Complex[a]	Mp/°C	Elemental analysis[b]				IR data/cm^{-1}[c]			
		%C	%H	%P	%N	$\nu_{OH(bond.)}$	$\nu_{P=O}$	$\nu_{C=O}$	ν_{NO_3}
Co-L_2NO_3	120—121	44.09 (44.32)	4.21 (4.34)	12.81 (12.70)	1.40 (1.44)	2922(vs)	1203(m), 1168(m)	1682(s)	1440(m), 1404(s), 1307(s), 1059(mw), 702(s)
Pr-L_2NO_3	123—125	40.76 (40.89)	3.93 (4.00)	11.79 (11.72)	1.25 (1.32)	2915(vs)	1205(m), 1167(mw)	1680(s)	1438(m), 1402(s), 1305(s), 1057(m), 702(s)
Eu-L_2NO_3	120—122	40.25 (40.46)	3.77 (3.96)	11.52 (11.59)	1.25 (1.31)	2925(vs)	1200(m), 1166(m)	1685(s)	1440(m), 1405(m), 1310(m), 1055(mw), 700(s)
Er-L_2NO_3	122—123	39.65 (39.89)	3.69 (3.91)	11.51 (11.43)	1.21 (1.29)	2900(vs)	1202(m), 1165(m)	1682(s)	1440(m), 1400(s), 1307(s), 1058(m), 705(s)
Eu-$L_2'NO_3$	131—133	42.53 (42.70)	4.78 (4.98)	12.11 (12.23)	1.28 (1.38)	2930(vs)	1175(s), 1100(s)	—	1462(s), 1377(m), 1310(m), 1035(m), 723(m)

a) L=benzoyl phosphonate dimer; L'=benzyl phosphonate dimer. b) Calculated values are given in parentheses. c) CCl_4 solutions; NaCl cell, 1.0 mm; vs=very strong, s=strong, m=medium, mw=moderately weak.

phosphonate solutions in 50 and 25% ethanol-water mixtures with standardized sodium hydroxide solutions at 25 °C. A stream of nitrogen gas was flushed through the solution during the titration. The pK_a values were computed by using the corrected pH values.[6] The results are given in Table 1.

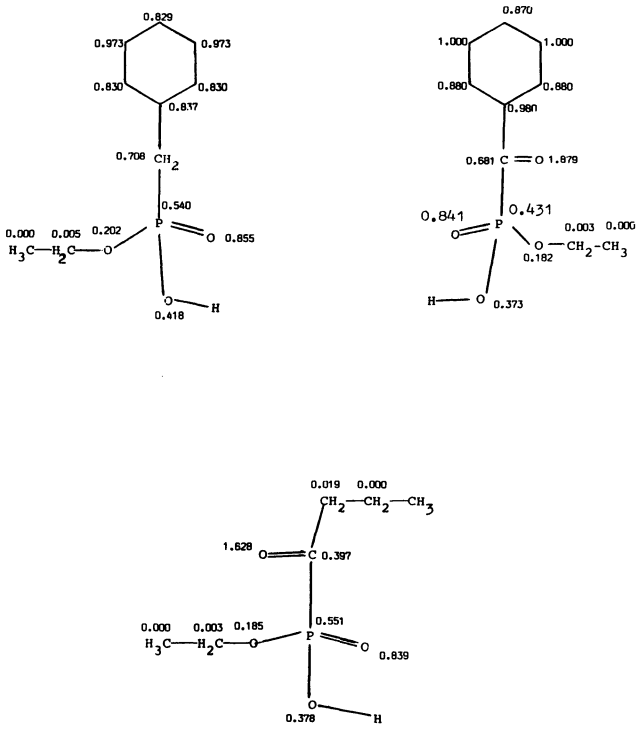
Solid complexes of the benzoyl phosphonate derivative with Co, Pr, Eu, and Er metal nitrates as well as the benzyl phosphonate with europium nitrate were synthesized by mixing equimolar amounts of both reagents with slight excess of the ligand in 50% aqueous ethanol and left to stand at room temperature for 24 h. (The benzyl complex took longer time ca. 40 h with the formation of white amorphous solid). White to pale yellow crystalline needles were isolated, washed with ethanol and left to dry under vacuum. Attempts to prepare the butanoyl analogous were unsuccessful; they decomposed above 0 °C. Elemental analysis were consistent with 1:2 adduct formations. Results for elemental analysis as well as melting points are given in Table 2.

Conductometric measurements were performed on a Griffin conductance bridge Model PJK-301. The conductance of 0.5 g metal complex dissolved in 50 ml of nitrobenzene or methylene chloride solvent was measured at different time intervals at 25 °C.

Results and Discussion

Hydrolysis of the organophosphonate compounds $RPO(OC_2H_5)_2$, R=benzyl, benzoyl, or butanoyl group, by sodium hydroxide solutions led to the formation of the monobasic $RPO(OH)(OC_2H_5)$ derivatives. The infrared spectra of these phosphonate compounds were measured from 4000—600 cm^{-1} in CCl_4 solutions or as a liquid film spectra. All the three compounds showed strong bands in the range of 2880 cm^{-1} (Table 1) which were indicative of the presence of bonded OH groups.[1,5,7] Dilute CCl_4 solutions did not show any stretching frequency due to free OH group. The phosphoryl region showed a lower field shift from the free P=O region as expected for bonding phosphoryl group.[7] Thus, these compounds would have dimeric structures with arrangements, presumably, similar to that proposed previously.[1]

The acid ionization constants of the phosphonate ligands were calculated from potentiometric titrations of known amounts of the phosphonate against standardized sodium hydroxide solutions. The pK_a values, listed in Table 1, clearly show that the acidity increases in the order benzyl<butanoyl<benzoyl derivative. This can be attributed to the effect of the R group on the electron density of the phosphorus atom and consequently on the ionization of the OH moiety. The π-electron densities on the different atoms of the three phosphonates, calculated by the use of simple HMO method,[8] are shown in Scheme 1. The π-electron density on the hydroxyl oxygen is decreased in the order benzyl>butanoyl≈benzoyl. This order is consistent with the order of increasing acidity and accounts for the closest pK_a values of both butanoyl and benzoyl derivatives, 3.98 and 3.48, respectively.



Scheme 1. The π-electron density on the different atoms of the benzyl-, benzoyl-, and butanoylphosphonate derivatives.

Addition of the new phosphonate ligands to solutions of Co(II), Pr(III), Eu(III), and Er(III) nitrates resulted in the formation of the corresponding metal complexes. The pH of the solutions was found to be decreased by time. Attempts to prepare the butanoyl metal complexes were unsuccessful due to their decomposition above 0 °C. The solid complexes were air stable white to pale yellow needle crystals (the benzyl derivative was amorphous solid). The elemental analysis, melting points, and the important IR data of the new complexes are listed in Table 2. The stoichiometry of these complexes were found to be 1:2 metal to phosphonate dimer. The formation of these complexes was accompanied by the release of two protons per one complex as found from solvent extraction and potentiometric analysis of these and other similar complexes.[9]

The infrared sectra of the new complexes in either CCl_4 solutions or in solid state (KBr disc technique) showed that two different types of phosphoryl groups present in the same spectrum. One of them was assigned to the P=O bonded to the OH group (hydrogen bonding) with about the same position as in case of the free ligand. The other has a position dependent on the type of the complex. In case of the benzyl complex, the second phosphoryl group showed lower field shift due to bonding to metal (donation to metal ion was stronger than hydrogen bonding). The interesting facet was the case of the benzoyl complexes. There, the second phosphoryl group showed upfield shift referred to unbonded P=O group, while the carbonyl stretching frequency exhibited a lower field shift. From Scheme 1, one can see that the carbonyl oxygen of the benzoylphosphonate derivative carried higher π-electron density than the phosphoryl oxygen. Thus, it can be concluded that the CO group of this ligand might be involved in the complex formation and donation from its site to the metal ion is predominant rather than from the phosphoryl oxygen. Recall that the synthesis of the benzylphosphonate complex, which has no CO group, took longer time and gave amorphous solid. It is not obvious that why the butanoyl derivative did not form stable complexes. Presumably, the presence of the phenyl group in the benzoyl derivative stabilized the complex formation.

The new complexes were found to be neutral species where a nitrate group was linked to the metal as a bidentate ligand. Effect of nitrate concentration on the extraction of these complexes in hexane revealed the presence of one NO_3 group in the complex sphere.[9] Also, the IR spectra of these complexes showed stretching frequencies attributed to such linkage,[7,10] Table 2. The formation of neutral complexes with the trivelent lanthanoid metal ions is obvious. In case of Co(II) complex it should be ionic. However, conductometric measurements for all cmplexes in nitrobenzene or CH_2Cl_2 solutions gave conductance due to nonelectrolyte materials which ruled out the presence of ionic nitrate. Two possibilities for the Co complex, thus, can be considered. First, the complex is very weak electrolyte where detection of conductance can not be observed. The second possibility is that cobalt in this complex existed with a formal +3 charge presumably due to delocalization of one of its electrons onto the ligand through the carbonyl moiety. The latter assumption does not seem unreasonable; heating the cobalt(II) semiquinone complex (Co_4(3,5-di-*t*-butylsemiquinone)$_8$) with bipyridyl resulted in the formation of the complex (3,5-di-*t*-butylcatecholato)-(3,5-di-*t*-butylsemiquinone)(bipyridyl)cobalt(III). The formation of Co(III) species was confirmed from an X-ray crystal structure determination of the complex.[11] Also, reaction of $Cr(CO)_6$ (zerovalent metal) with 1,2-chrysenequinone gave the semiquinone derivative Cr(chrysenesemiquinone)$_3$ with a formal +3 charge on the metal part.[12]

According to the available data the comlexes may have octahedral arrangements where the metal is linked to two ligands of the phosphonate dimer as well as a bidentate nitrate group. However, as a referee suggested, we can not rule out possibility of formation of rare earth complexes with higher coordination number than six. Here, the ligand dimer could act as a tridentate where it attached to the metal from a phosphoryl and a carbonyl group of one moiety and the OH group of the other moiety with the release of a proton.

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References

1) D. F. Peppared, J. R. Ferraro, and G. W. Mason, *J. Inorg. Nucl. Chem.*, **7**, 231 (1958). G. M. Kosolapoff and J. S. Powell, *J. Chem. Soc.*, **1950**, 3535.

2) E. G. Afonin and N. I. Pechurova, *Zh. Neorg. Khim.*, **32**, 1021 (1987); *Chem. Abstr.*, **107**, 108074u. C. M. Mikulski, P. Sanford, N. Harris, R. Rabin, and N. M. Karayannis, *J. Coord. Chem.*, **12**, 187 (1983). C. M. Mikulski, N. Harris, P. Sanford, F. J. Iaconianni, L. L. Pytlewski, and N. M. Karayannis, *J. Inorg. Nucl. Chem.*, **43**, 2753 (1981).

3) N. M. Karayannis, L. L. Pytlewski, and C. Owens, *J. Inorg. Nucl. Chem.*, **42**, 675 (1980). C. M. Mikulski, W. Henry, L. L. Pytlewski, and N. M. Karayannis, *J. Inorg. Nucl. Chem.*, **40**, 769 (1978).

4) J. A. Riddick, and W. B. Bunger, "Organic Solvents," 3rd ed, Wiley, New York (1970).

5) D. F. Peppard, J. R. Ferraro, and G. W. Mason, *J. Inorg. Nucl. Chem.*, **12**, 60 (1959).

6) A. Albert and E. P. Serjeant, "The Determination Of Ionization Constants," 2nd ed, Chapman and Hall, London (1971).

7) R. M. Silverstein, G. C. Bassler, and T. C. Morrill, "Spectrometric Identification of Organic Compounds," 4th ed, Wiley, New York (1981).

8) A. Streitwieser, "Molecular Orbital Theory For Organic Chemists," Wiley, New York (1961).

9) Details of these studies will be published elsewhere.

10) I. S. Ahuja, R. Singh, and C. P. Rai, *J. Mol. Struct.*, **49**, 201 (1978).

11) R. M. Buchanan and C. G. Pierpont, *J. Am. Chem. Soc.*, **102**, 4951 (1980).

12) R. M. Ramadan, W. H. Mahmoud, M. F. El-Shahat, and A. E. Attia, to be submitted for publication.