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Reactions of Alkali Metal Iodides with Diisopropyl Methylphosphonate

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Alkali metal iodides dissolve in diisopropyl methylphosphonate (DIMP) and react at elevated temperatures (70-120°C) to yield isopropoxy methylphosphonato (IMP) M^I (M = Li, Na, K) complexes and a mixture of isopropyl iodide, HI and propene. Li(IMP) was isolated in crystalline form. This complex redissolves in the reaction mixture at 125°C, while the Na^I and K^I analogs are soluble in the reaction mixture and were not obtained in crystalline form. Solutions of M(IMP) in the reaction mixture yield metal hydrogen methylphosphonate (M(MPH)), possibly through reaction with HI. M(MPH) is subsequently condensed to the corresponding metal pyromethylphosphonate (M_2(PMP); M = Li, Na, K), which is precipitated in crystalline form. Li(IMP) and the M_2(PMP) complexes were characterized by means of infrared and conductance studies. Possible structures for these compounds are discussed.

Introduction

Interactions of neutral phosphonate or phosphate esters with metal di-, tri-, tetra- and penta-halides at elevated temperatures lead to the precipitation of polynuclear phosphonato or phosphato complexes of the corresponding mono- or di-acidic phosphoryl compounds.[1-7] Formation of these products is accompanied by evolution of methyl halide, in the cases of methoxy-substituted phosphoryl compounds,[2,5] or a mixture of alkyl halide, alkene and hydrogen halide, in the cases of esters with higher alkoxy alkyls.[3,4] Alkali metal chlorides are generally insoluble in neutral phosphonate and phosphate esters, even at elevated temperatures, but the corresponding iodides dissolve slowly in these esters at temperatures higher than 50 °C. It was found that, unlike the halides of tri- to penta- valent metal ions,[3-5] alkali metal iodides react with diisopropyl methylphosphonate to yield the corresponding metal pyromethylphosphonates as final products. The present paper deals with our studies of these reactions.

Experimental Section

Anhydrous metal iodides were generally utilized during the present study, but it was established that the interaction of DIMP with either anhydrous or hydrated LiI leads to the same final products. The MI (M = Li, Na, K, Rb, Cs) is suspended in excess DIMP (*ca.* 5 ml of DIMP per 0.2 g of metal salt). Dissolution of the salt is effected by warming the mixture at 50°C for 10-15 min. The temperature of the resulting solution is subsequently increased at a rate of *ca.* 2°C/min. In the case of LiI, the yellow solution starts reacting at 85°C. The volatile products evolved are isopropyl iodide, HI and propene, which were collected and identified as previously described.[4] At 100°C a crystalline white solid is precipitated, which is filtered, thoroughly washed with acetone and ether and dried over $CaCl_2$ in an evacuated desiccator. Analysis of this compound corresponds to the formula $(C_3H_7O)CH_3P(O)OLi$ (isopropoxy methylphosphonato Li (Li(IMP)), *i.e.*: % Found (% Calcd): Li 4.59 (4.82), C 33.16 (33.36), H 6.77 (7.00), P 21.51 (21.50). During another experiment, Li(IMP) was allowed to remain under the supernatant liquid and the temperature was increased at the rate mentioned above. At *ca.* 125°C Li(IMP) is completely dissolved, probably with decomposition, and a new white compound is precipitated at *ca.* 150°C. Analytical data for this compound and the Na and K analogs described below, in combination with infrared evidence (*vide infra*), led us to the conclusion that the alkali metal pyromethylphosphonates[8] (M_2(PMP)) are formed under these conditions.

Analysis of Li_2(PMP): Li7.23 (7.47), C 13.30 (12.92), H 3.47 (3.25), P 32.84 (33.32).

NaI and KI yield under the same experimental conditions the white M_2(PMP) compounds at tempe-

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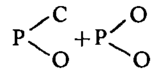
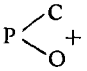
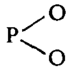
Table I. Infrared Spectra of Alkali Metal Isopropoxy Methylphosphonates and Pyromethylphosphonates (cm^{-1})[a]

Li(IMP)	Assignments for M(IMP) Compounds [b]	Intermediate of NaI-DIMP Reaction	Assignments for M$_2$(PMP) Compounds [c]	Na$_2$(PMP)	Li$_2$(PMP)	K$_2$(PMP)
1690w	POO(combination)	1660w				
1318s	PCH$_3$	1307s	PCH$_3$	1300s	1311s	1300s
1200vs 1189vs 1173vs 1144m 1092vs 1069vs	POO(antisymmetric)+ >CH–O–P+ POO(symmetric)	1220vs 1185vs 1142sh 1110m 1102m 1079s	POO(antisymmetric)+ POO(symmetric)	1195vs,b 1107s 1060m	1192vs 1168vs 1111vs 1052m	1199vs 1189vs 1112vs 1056m
1012vs	P–O–(C)	1000s				
910s	PCH$_3$	969s 949sh 892s 875sh	PCH$_3$+ P–O–P(antisymmetric)	960s 945sh 888s 875s	975sh 935s 900m 880s	955sh 940s 919s 902sh 880s 865s
790s 735m	P–C	777s 753s	P–C	780s 749s	790s 760s	772s 740s
		629m	P–O–P(symmetric)	636s	660s	629s
565sh 526s 498sh 450m 412m 370m-s 348sh 325sh	P–O–i–Pr(?) M–O  M–O	548s 519s 498s 450s,b 318m	  M–O+ ν_{Ligand}	550s 498s 465s,b 370vw 350vw	532s 492s 430s 362m 341m 300w,b	545s 502sh 482s 458sh 448s 368vw 320vw
278w	ν_{Ligand}	272s 260s	M–O+ ν_{Ligand}	275m-s 262sh	273m 262sh	277m 259m-s

Abbreviations: s: strong, m: medium, w: weak, v: very, b: broad, sh: shoulder. [a] POH and H$_2$O bands are generally absent in the above spectra. [b] Based on the assignments of Refs. 8, 16, 17, 21 and J. R. Ferraro, D. F. Peppard and G. W. Mason, *J. Inorg. Nucl. Chem., 19,* 811 (1963). [c] Based on the assignments of Refs. 8 and 16. Note: In M(IMP)$_3$ complexes, the most characteristic IR bands occur as follows: ν_{POO} (antisymmetric), 1172-1120 cm^{-1}; ν_{POO} (symmetric), 1088-1060 cm^{-1}; metal-sensitive bands: 2-3 absorptions at 565-290 cm^{-1}.[3,5]

ratures higher than 180°C, without precipitation of the corresponding M(IMP) complexes as intermediates.

Analyses: % Found (% Calcd): Na$_2$(PMP): Na 20.81 (21.09), C 11.45 (11.02), H 3.07 (2.77), P 28.23 (28.42); K$_2$(PMP): K 30.68 (31.25), C 10.04 (9.60), H 2.23 (2.42), P 24.48 (24.76).

Tests for iodine in the alkali metal compounds reported above were negative. In an attempt to isolate an intermediate of the NaI-DIMP interaction, the reaction was interrupted at 140°C and the mixture cooled at 0°C. A yellow solid was obtained in this way, which gave the following analysis: Na 17.61, C 19.33, H 4.27, P 23.46, I 7.88. The M$_2$(PMP) compounds and the latter product were filtered, washed with acetone and ether and dried over CaCl$_2$ in an evacuated dessiccator. RbI and CsI in excess DIMP did not form any solid product when heated at temperatures exceeding 250°C.

Li(IMP) and the M$_2$(PMP) compounds do not melt or decompose at temperatures up to 300°C. They are insoluble in hydrocarbons (n–heptane, cyclohexane, benzene), halocarbons (CH$_2$Cl$_2$, CHCl$_3$, CCl$_4$) and acetone, but dissolve readily in water and a number of polar organic solvents (methanol, pyridine).

Nujol mull infrared spectra (Table I, Figures 1, 2) and electrolytic conductance measurements of the alkali metal compounds reported were obtained by methods previously described.[3-5] The electrical conductivities of 5 × 10^{-4}N aqueous solutions of these compounds at 25°C are as follows (Λ_{eq} in Ω^{-1} equiv.$^{-1}$ cm^2): Li(IMP) 59; Li$_2$(PMP) 67; Na$_2$(PMP) 94; K$_2$(PMP) 100.

Discussion

Infrared Studies. The IR spectrum of Li(IMP) is characteristic of isopropoxy methylphosphonato metal complexes.[3-6] The ν_{POO} (antisymmetric) mode is split into two bands (1200 and 1189 cm^{-1}) (Table I, Figure 1). A similar splitting of this mode has been observed in the spectrum of di–n–butoxyphosphato Li.[9] The ν_{POO} (symmetric) mode is also split into at least two bands (1092 and 1069 cm^{-1}). On the other hand, comparison of the low frequency IR spectrum if Li(IMP) (Table I, Figure 2) to those of M(PMP)$_3$ complexes involving covalent metal to phosphonate bonds,[3,5] reveals the presence of two bands at 526

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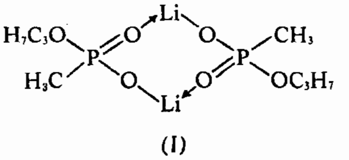
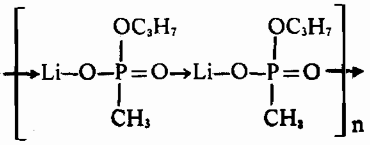
[9] T. D. Smith, *J. Inorg. Nucl. Chem., 9,* 150 (1959).

and 370 cm^{-1}, which are most probably due to ν_{Li-O}. It should be noted, in this connection, that Li^I salts, dissolved in oxygen- or nitrogen- ligands, exhibit a low-frequency band attributable to the Li$^+$ ion vibration in a cage of solvent molecules and, in some cases, the anionic group.[10] In tetrahydrofuran (THF) solution this band occurs at 413-373 cm^{-1}, and in dimethyl sulfoxide (DMSO) at 425-424 cm^{-1}.[10] The corresponding vibrations of the Na$^+$ and K$^+$ ions occur at: Na$^+$: in THF, 198-184 cm^{-1}, in DMSO, 203-194 cm^{-1}; K$^+$: in THF, 142 cm^{-1}.[10] Li^I shows a greater tendency to form covalent bonds than Na^I and K^I.[11] The conductance of Li(IMP) in water, which is low for a 1:1 electrolyte, is also in favor of the presence of covalent LiO bonds. The fact that at least two metal-sensitive bands are present in the IR spectrum of Li(IMP) suggests that both oxygens of the (i–C_3H_7-O)CH_3POO group are coordinated to the metal ion.[3-5] This is also suggested by the splittings of the ν_{POO} bands, which may be attributed to the presence of inequivalent P–O bonds,[12,13] or simply to crystal lattice effects. Uncoordinated P=O groups[13] are rather unlikely to be present in the Li^I complex, since the highest frequency band in the phosphoryl stretch region (1200 cm^{-1}) lies 10 cm^{-1} lower in energy than $\nu_{P=O}$ in free IMP.[14] Possible structural formulae for Li(IMP), based on the above discussion, are the following:



(I)

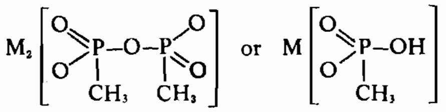


$$\left[\rightarrow Li-O-\overset{OC_3H_7}{\underset{CH_3}{P}}=O\rightarrow Li-O-\overset{OC_3H_7}{\underset{CH_3}{P}}=O\rightarrow\right]_n$$

(II)

A monomeric structure, involving a four-membered chelate ring, may be ruled out, since it would involve equivalent P–O bonds.[15] The dimeric structure (I) and the oligomeric structure (II) would be consistent with the ν_{POO} splittings observed[13] and more compatible with the bonding angles.

The analytical data of the higher temperature products might be attributed to either of the following formulae:



$$M_2\left[O_2\underset{CH_3}{P}-O-\underset{CH_3}{P}O_2\right] \text{ or } M\left[O_2\underset{CH_3}{P}-OH\right] \quad (M=Li, Na, K).$$

Infrared evidence (Table I, Figures 1, 2) clearly demonstrates that these compounds contain P–O–P groups[8,16] and that bands attributable to P–OH modes[17] are absent. The spectra of the above compounds are, in fact, very similar to those of metal pyromethylphosphonates reported by Matrosov *et al.*,[8] and band assignments (down to 400 cm^{-1}) were made on the basis of this work. Below 400 cm^{-1} metal-sensitive bands are observed. The Li^I complex exhibits three

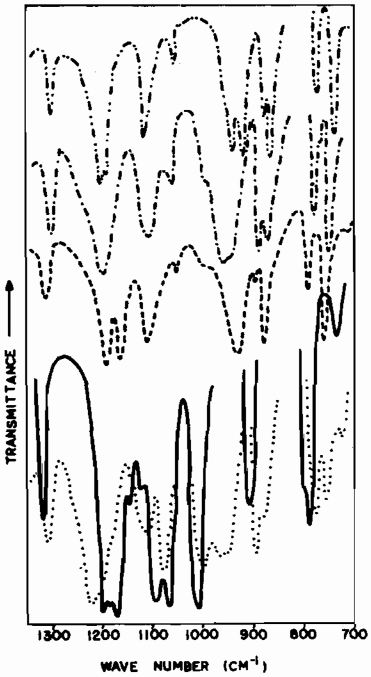


Figure 1. Infrared spectra (1350-700 cm^{-1}) of: (——), Li(IMP); (- - -), Li$_2$(PMP); (——), Na$_2$(PMP); (—·—), K$_2$(PMP); (. . .), NaI-DIMP reaction intermediate.

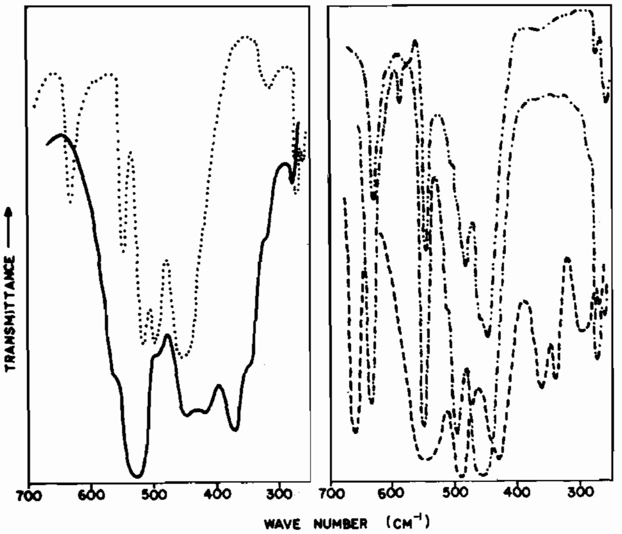


Figure 2. Infrared spectra (700-250 cm^{-1}) of: (——), Li(IMP); (- - -), Li$_2$(PMP); (——), Na$_2$(PMP); (—·—), (K$_2$(PMP); (. . .), NaI-DIMP reaction intermediate.

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(10) W. F. Edgell, J. Lyford, IV, R. Wright, W. Risen, Jr., and A. Watts, *J. Amer. Chem. Soc.*, **92**, 2240 (1970).

(11) See, for example: W. H. Zachariasen, *J. Am. Chem. Soc.*, **62**, 1011 (1940); V. Armithalingham and V. M. Padmanabhan, *Acta. Chryst.*, **11**, 986 (1958); R. J. Capwell. K. H. Rhee, and K. S. Seshadri, *Spectrochim. Acta*, **24A**, 955 (1968).

(12) G. H. Dahl and B. P. Block, *Inorg. Chem.*, **6**, 1439 (1967).

(13) J. J. Pitts, M. A. Robinson, and S. I. Trotz., *J. Inorg. Nucl. Chem.*, **30**, 1299 (1968); **31**, 3685 (1969).

(14) E. Gryszkiewicz-Trochimowski, J. Quinchon, and M. Bousquet, *Bull. Soc. Chim. France*, 1645 (1962); J. Quinchon, M. LeSech, and E. Gryszkiewicz-Trochimowski, *ibid.*, 169.

(15) L. S. Mayants and E. I. Matrosov, *Izv. Akad. Nauk SSSR, Neorg. Mat.*, **1**, 546 (1965).

(16) L. C. Thomas and R. A. Chittenden, *Spectrochim. Acta*, **20**, 467, 489 (1964); **21**, 1905 (1965).

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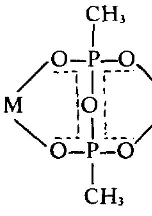
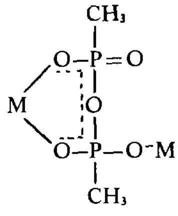
bands at 362-300 cm^{-1}, while the Na^{I} and K^{I} compounds do not show strong absorption in this region, but exhibit single metal-sensitive bands below 280 cm^{-1} (Na 275 cm^{-1}, K 259 cm^{-1}). The assignment of the latter two bands as ν_{M-O} (M=Na, K) is reasonable, since the ionic vibration of Na$^+$ and K$^+$ in solvents with comparable coordinating ability occurs at substantially lower wavenumbers.[10] The conductances of these compounds in aqueous solution are generally lower than those corresponding to 2:1 electrolytes of these metal ions (*vide supra*).

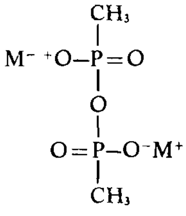
Possible structures of these compounds[9,18,19] are given below:



(III)



(IV)



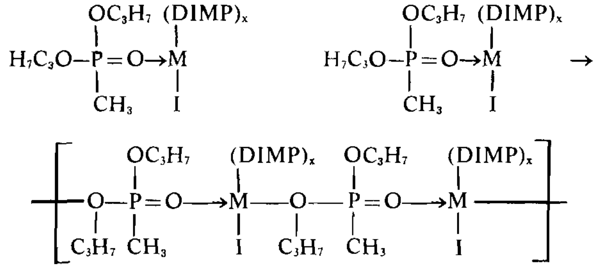
(V)

Li$_2$(PMP) has most probably structure (III) in view of the presence of several metal-sensitive bands in its IR spectrum and its low conductance. It should be noted that the positions of the P–O–P (antisymmetric) bands in the metal pyromethylphosphonates reported are in favor of chelated rather than ionic structures.[18] In fact, this mode, which occurs at *ca.* 940 cm^{-1} in pyroalkylphosphonates,[16] shows positive shifts in the new complexes (Table I, bands at 975-935 cm^{-1}). Similar trends in metal complexes of octamethylpyrophosphoramide have been attributed to the presence of chelate rings.[18]

Although Na^{I} and K^{I} form usually ionic compounds, a number of complexes of these metal ions have been reported and characterized.[18-20] In view of the significantly higher conductances of M$_2$(PMP) (M=Na, K) relative to Li$_2$(PMP) and the occurrence of single metal sensitive bands in the spectra of the former compounds, structure (IV) appears to be the most probable for the Na^{I} and K^{I} pyromethylphosphonates.

Finally, the intermediate isolated during the NaI-DIMP reaction is essentially a mixture of Na(IMP) and Na$_2$(PMP). Absorptions attributable to both these complexes are, in fact, observed in the IR spectrum of this product (Table I). The higher frequency band in the $\nu_{P=O}$ and ν_{POO} (antisymmetric) region occurs at 1220 cm^{-1}. This band may be due to either ν_{POO} (antisymmetric)[21] or the presence of uncoordinated $\nu_{P=O}$.[13] The fact that Na(I) dialkoxyphosphato compounds exhibit ν_{POO} (antisymmetric) at considerably higher frequencies than their Li(I) analogs,[21] is in favor of the former assignment. The mixture exhibits P–O–(C) and P–O–P bands as well as metal sensitive bands attributable to both Na(IMP) (318 cm^{-1}) and Na$_2$(PMP) (272 cm^{-1}) (Table I). The presence of iodine in this product is discussed in the follwong section.

Nature of the Reactions. Adducts of alkali metal salts with phosphoryl ligands in molar ratios ranging from 1:1 to 1:5 have been either identified in solution[22] or isolated in crystalline form and characterized.[23] The mechanism of formation of M(IMP) complexes most probably involves DIMP adduct formation and subsequent elimination of isopropyl iodide, *via* an intermediate involving coordination of alkoxy oxygens to the metal ions:[2-5]



$$\rightarrow 2M(IMP) + 2i\text{–}C_3H_7I + 2xDIMP$$

A simpler mechanism, involving a nucleophilic attack of I$^-$ on an isopropyl group of DIMP, leading to the formation of isopropyl iodide and (IMP)$^-$, may also be considered as possible. The isopropyl halide produced is partially dehydrohalogenated in the presence of the complex metal halide residue.[3,24]

Metal pyromethylphosphonates are produced during the thermal condensation of metal hydrogen methylphosphonates.[8] The presence of iodine in the NaI–DIMP reaction intermediate is probably indicative of the participation of iodide ions in the dealkylation of the isopropoxy methylphosphonato group of M(IMP). It has already been reported that M(IMP)$_3$ or M(IMP)$_4$ complexes dissolve with decomposition in dilute mineral acids (HCl, HNO$_3$ *etc.*).[3-5] Since the M(IMP) complexes are soluble in the reaction mixture, production of metal hydrogen methylphosphonates might be attributed to interaction of M(IMP) with the hydrogen iodide liberated during the dehydroiodination of isopropyl iodide:[25,26]

$$MO(O)PCH_3(O\text{–}i\text{–}C_3H_7) + HI \rightarrow MO(O)PCH_3OH + i\text{–}C_3H_7I$$

The metal hydrogen methylphosphonate formed loses water at higher temperatures (150-200 °C) to yield M$_2$(PMP):[8,9]

$$2MO(O)PCH_3OH \rightarrow M_2(PMP) + H_2O$$

In conclusion, reaction of DIMP with alkali metal iodides at elevated temperatures leads initially to the formation of M(IMP) complexes. The distinguishing feature of these compounds, as opposed to M(IMP)$_3$ and M(IMP)$_4$,[3,5] is that they either remain in solution after their formation (Na, K), or are precipitated and redissolved in the reaction mixture at higher tempe-

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(26) R. F. Hudson and D. C. Harper, *J. Chem. Soc.*, 1356 (1958).

ratures (Li, cf. experimental section). In the hexacoordinated $M(IMP)_3$ and octacoordinated $M(IMP)_4$ polynuclear complexes,[3,5] the high coordination number of the central metal ions and effective shielding by the bulky ligand groups (3 or 4 per metal ion) may be considered as responsible for the resistance of these compounds to attack by water, DIMP and all common organic solvents.[3,5] The M(IMP) complexes involve one IMP group per metal ion and, if a certain degree of covalency is assumed for the metal-to-ligand bond, a low coordination number. The alkali metal ion is, thus, accessible for interaction with the various components of the reaction mixture (*e.g.*, DIMP, C_3H_7I).[27,28] The solvated species formed in this way decomposes to yield metal hydrogen methylphosphonate, which subsequently undergoes a condensation reaction to form M_2(PMP).

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