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REACTIONS OF DIETHYL TRICHLOROMETHYLPHOSPHONATE WITH METALLIC ZINC

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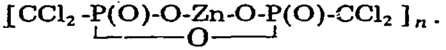
Summary

Complexes of tetrachloroethylenediphosphonic acid tetraethyl ester and diethyl trichloromethylphosphonate (DETCMP) with $ZnCl_2$ are shown to be formed in the reaction of DETCMP with metallic zinc. The complexes undergo dealkylation and condensation reactions leading to the formation of zinc polypyrophosphonate:



$[\mathrm{CCl_2{-}\underbrace{P(O){-}O{-}Zn{-}O{-}P}_{O}(O){-}CCl_2}]_n$.

Alcoholic solvents cause an increase of reaction rate.

Introduction

Complexes of phosphonic esters with salts of di-, tri- and tetra-valent metals have recently been the subject of interest, both from the theoretical aspect of structural investigation [1—12] and because of their possible industrial application [12, 13].

Complex formation of diethyl trichloromethylphosphonate (DETCMP) with zinc salts has not been investigated up to now. Kleimenov, Sanin and coworkers [12] only noticed that diesters of trichloromethylphosphonic acid react with metallic iron to form an alkyl chloride and a polymeric organophosphorus compound containing iron, but the authors did not explain the mechanism of the respective steps of reaction.

Discussion

We have observed that diethyl trichloromethylphosphonate reacts unexpectedly easily with metallic zinc, the reaction occurring even at room temperature in methanol or ethanol solutions. When the reaction was carried out under reflux in either of these alcohols a fairly rapid decrease in the amount of zinc suspended in the reaction mixture was observed irrespective of the molar ratio of zinc and DETCMP used for the reaction. After the solvent and other volatiles

TABLE 1

REACTION PRODUCTS OF DETCMP WITH METALLIC ZINC

Molar ratio DETCMP/Zn	Concentration of DETCMP in methanol (mol/l)	Reaction temperature (°C)	Reaction time (h)	Analysis of the product		
				n_D^{20}	Zn (%)	Total Cl [a] (%)
4/1	0.5	65	3	1.4528	5.9	22.7
2/1	0.5	65	7	1.4554	11.4	15.1
1/2	0.5	65	3		24.3	16.3

[a] The Cl content was determined by the method described by Gefter [14].

had been removed by means of distillation, the products of the reaction included from 0.5% to 25% Zn, depending on the amount of Zn powder used (Table 1).

It has been found that the reaction products contain chloride ion, the amount of which is dependent on the zinc content of the products. The chloride content corresponded to a molar ratio of $n(\mathrm{Cl})/n(\mathrm{Zn}) \leqslant 2/1$. This ratio decreased with increase of the temperature or the reaction time (Table 2).

Infrared measurements on gaseous reaction products indicated the presence of ethyl chloride, with traces of diethyl ether. It has been found that ethyl chloride is formed rapidly when the reaction products are heated, dechloralkylation reaching its maximum rate at 170—180° (thermogravimetry). Slow formation of ethyl chloride was also observed when the reaction products were stored at room temperature for several months. Evolution of C_2H_5Cl was accompanied by a decrease in chloride content of the reaction products irrespective of the reaction time and temperature. The appearance of IR absorption bands in the range 845—850 cm^{-1} and 660 cm^{-1} indicated the presence of P—O—P bonds in the main reaction products.

DETCMP was also treated with zinc powder in non-polar solvents (petroleum ether, benzene, carbon tetrachloride). In these solvents, at temperatures of 60—70°, even when excess zinc powder was used and after prolonged reaction time not more than 1.5% Zn was present in the reaction products. When no solvent was used the reaction occurred rapidly only at elevated temperatures (120°), the reaction products containing up to 12.1% zinc and not more than 3% chloride. The low chloride content is explained because there is rapid evolution of ethyl chloride from the reaction mixture when no solvent is present.

Crofts [15] discovered that DETCMP does not react with ethanol. The ester was recovered unchanged after boiling in ethanol for 4 h. $CCl_3P(O)(OC_2H_5)$-

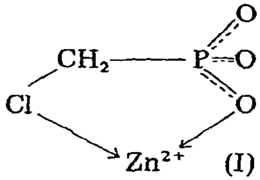
TABLE 2

INFLUENCE OF THE REACTION TIME AND TEMPERATURE ON THE MOLAR RATIO $n(\mathrm{Cl})/n(\mathrm{Zn})$ IN THE PRODUCTS OF THE REACTION OF DETCMP WITH METALLIC ZINC

Molar ratio $n(\mathrm{DETCMP})/n(\mathrm{Zn})$	Reaction temperature (°C)	Reaction time (h)	Analysis of the products		
			Cl^- (%)	Zn (%)	$n(\mathrm{Cl}^-)/n(\mathrm{Zn})$
2/1	65	0.5	9.8	9.4	1.92 /1
2/1	65	7.0	9.4	11.4	1.52 /1
2/1	65	9.0	8.5	11.6	1.35 /1
2/1	120 [a]	4.0	3.0	12.1	0.465/1
2/1	180 [a]	1.0	1.8	13.9	0.238/1

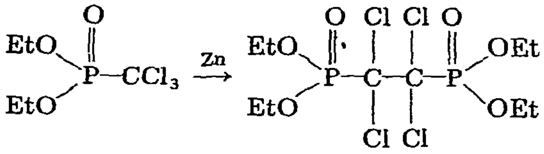
[a] The reaction was carried out without any solvent (non-solvent reaction process).

OH was formed only after prolonged refluxing (10 hours or longer) of a solution of DETCMP in alcohol [16]. Therefore, we consider that the difference between the reactions in alcohol and in non-polar solvents is caused mainly by strong solvation of the substrates and of the products of the reaction with alcohol. Some workers have observed the formation of hydrogen bonds between trichloromethylphosphonic acid [17] and its diesters [18] and alcohols. This suggests partially ionic nature of the reaction of a chloromethyl group with zinc to form zinc chloride, solvated by alcohol and complexed by organophosphorus compounds present in the reaction system. The complexes formed have a rather complicated structure, as has been pointed out by Karayannis [8] in his studies on the reaction of zinc chloride with phosphonic acid esters. In their numerous papers [1—8] Karayannis and coworkers proved that dealkylation of complexes of methylphosphonic acid diesters with metal chlorides occurred when these complexes were heated. The structures of the products obtained depend on the nature of the metal, and particularly on its valency and coordination number. Extremely complicated structures were formed when zinc chloride was used because the zinc ions catalyse the hydrolysis of the alkyl groups to yield P—OH groups. These condense at high temperatures to form pyrophosphonate systems as described by Matrosov [9]. Tridot and coworkers [10] investigated the complexes of chloromethylphosphonic acid with zinc cations and proved the formation of a complex of structure (I).


(I)

On the basis of our present investigations and previous papers [1—19] concerning the complexes of metal salts with phosphonic acids and their esters, we suggest that the following reactions take place when metallic zinc is introduced into a solution of DETCMP.

(1). Condensation reaction:



(2). Formation of a mixture of complexes with the simultaneous dealkylation of these complexes:

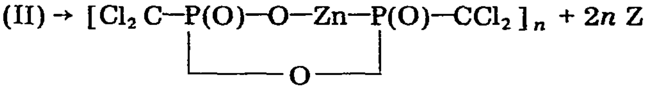
$$X([CCl_2{-}P(O)(OEt)_2]\cdot ZnCl_2\cdot[(EtO)_2P(O){-}CCl_2])_n Y \rightarrow$$

$$\rightarrow X[CCl_2{-}P(O)(OEt){-}O{-}Zn{-}O{-}P(O)(OEt){-}CCl_2]_n Y + 2n\ C_2H_5Cl$$

(II)

$(X = (EtO)_2P(O)CCl_2{-};\ Y = (EtO)_2P(O)CCl_2{-}$ or $Cl{-};\ n = 1, 2, \ldots)$.

(3). Condensation to pyrophosphonic systems:



$$\text{(II)} \rightarrow [\mathrm{Cl_2C{-}P(O){-}O{-}Zn{-}P(O){-}CCl_2}]_n + 2n\,\mathrm{Z}$$

(Z is a mixture of $(C_2H_5)_2O$ and C_2H_5Cl, due to the catalytic effect of HCl and Zn^{2+} on the condensation reaction [1, 8]).

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