Inorganica Chimica Acta, 64 (1982) L97–L98

Reactions of Ethyl Dichlorophosphate with MCl_3 (M = Al, Cr) and UCl_4

NICHOLAS M. KARAYANNIS

Amoco Chemicals Corporation, Naperville, Ill. 60566, U.S.A.

LOUIS L. PYTLEWSKI

Department of Chemistry, Drexel University, Philadelphia, Pa. 19104, U.S.A.

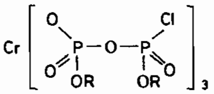
and CHESTER M. MIKULSKI

Department of Chemistry and Physics, Beaver College, Glenside, Pa. 19038, U.S.A.

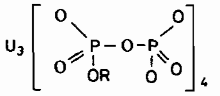
Received September 5, 1981

Previous studies at these laboratories established that during reactions of metal chlorides with diethyl chlorophosphate (decp; $(C_2H_5O)_2ClP{=}O$), at elevated temperatures, $M(ecp)_n$ complexes (ecp = ethyl chlorophosphate; $(C_2H_5O)ClPOO^-$) can be precipitated under rigorously anhydrous and inert conditions [1, 2]. Whereas, if these reactions are carried out in the presence of water by using, for instance, hydrated metal chlorides as starting materials, hydrolysis of the Cl–P bond occurs and $M(dep)_n$ complexes (dep = diethyl phosphate; $(C_2H_5O)_2POO^-$) are precipitated instead [1, 2]. We have more recently studied the corresponding reactions of ethyl dichlorophosphate (edcp; $(C_2H_5O)Cl_2P{=}O$) with metal chlorides. In many occasions ($M = Ti^{3+}, V^{3+}, Cr^{3+}$), the anhydrous metal chlorides do not dissolve in edcp, whilst in other cases ($M = Al^{3+}, U^{4+}$), the reaction between edcp and the anhydrous metal salt, under inert conditions, is rather violent, leading to the precipitation of rubber-like polymeric materials of uncertain nature. In view of these experimental difficulties we have limited our investigation to the reactions of edcp with hydrated metal chlorides. Thus far, well-defined products have been obtained for $M = Al^{3+}$, Cr^{3+} and U^{4+}. These products are described in the present letter.

Experimentally, all operations were performed in a dry-box (dry N_2 atmosphere). The hydrated metal chloride was suspended in excess neat edcp, and the temperature of the resulting mixture was raised at a rate of 2°/min. The salt dissolved in edcp at 50–70 °C, and heating was continued until precipitation occurred (at 90 °C for $M = Al^{3+}$; 111 °C for $M = Cr^{3+}$; and 119 °C for $M = U^{4+}$). The solid products analyzed as follows: $Al(dcp)(ecp)_2$ (where dcp is the dichlorophosphato ligand; Cl_2POO^-), white powder: found-(calcd.)%: Al 5.74(6.02); P 20.44(20.75); Cl 31.79-(31.66); C 10.45(10.73); H 2.50(2.25); CrL_3 (shown in (I) below), green powder: Cr 6.17(6.44); P 22.87-(23.04); Cl 12.96(13.19); C 18.15(17.87); H 3.93-(3.75); and $U_3L'_4$ (shown in (II) below), olive green powder: U 46.40(46.79); P 16.63(16.24); Cl 0.00; C 6.45(6.30); H 1.55(1.32).



(I)



(II)

(R = C_2H_5)

The formation of $Al(dcp)(ecp)_2$ may be attributed to initial formation of an $AlCl_3$ adduct with edcp [1, 2]. Eventually, one-third of the edcp ligands undergo the familiar deethylation reaction at elevated temperatures, yielding dcp and a mixture of C_2H_5Cl, HCl and $CH_2{=}CH_2$ [1–5]:

$$>\!AlCl + (C_2H_5O)Cl_2P{=}O \longrightarrow >\!Al(OOPCl_2) + C_2H_5Cl \qquad (1)$$

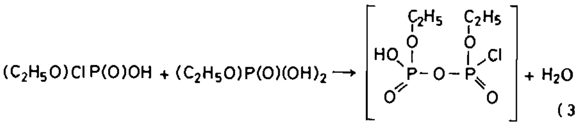
However, two-thirds of the edcp ligands are attacked by the water of hydration of $AlCl_3$ [1, 2, 6, 7], forming ecp and HCl:

$$(C_2H_5O)Cl_2P{=}O + H_2O \longrightarrow (C_2H_5O)ClP(O)OH + HCl \qquad (2)$$

$Al(dcp)(ecp)_2$ is stable in inert, dry atmosphere, but rapidly decomposes in the presence of moisture. It is generally insoluble in all common organic solvents, and is presumably a linear chainlike hexacoordinated polymer, characterized by triple bridges of bidentate mixed (dcp, ecp) ligands, coordinating through their two POO oxygens to adjacent Al^{3+} ions [8–10], *i.e.*, $[Al(dcp)(ecp)_2]_x$. The IR spectrum of the complex is consistent with the presence of two different ligands, as it shows doublets in both the $\nu_{POO,as}$ (1257vs, 1249vs) and $\nu_{POO,sym}$ (1140vs, 1133vs) regions, and a weak broad POO combination band at 1705 cm^{-1} [1, 4, 5, 11, 12]; furthermore, a doublet of very strong bands at 582, 576 cm^{-1} accounts for the ν_{P-Cl} mode of ecp and the $\nu_{P-Cl,as}$ vibration of dcp, while $\nu_{P-Cl,sym}$ of the latter ligand is probably associated with a medium absorption at 519 cm^{-1} [1, 13].

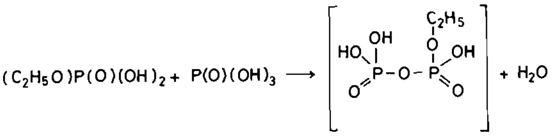
The reactions of $CrCl_3$ and UCl_4 with edcp led to formation of complexes with pyrophosphato ligands. Similar types of reactions have been previously observed during the interaction of triethyl phosphate [14], diisopropyl methylphosphonate [15] and triethyl or tri-n-butyl thiophosphate [16] with various metal halides. The reactions leading to the formation of the pyrophosphato ligands can be considered as proceeding as follows: For the Cr^{3+} complex, edcp is hydrolyzed to $(C_2H_5O)ClP(O)OH$

(see reaction 2); then part of this product is further hydrolyzed to yield $(C_2H_5O)P(O)(OH)_2$. Subsequently, a condensation reaction between the two hydrolysis products leads to the formation of the LH ligand of CrL_3 [14–18], *viz.*:



(3)

Likewise, $L'H_3$ is apparently produced by condensation between two products of the hydrolysis of edcp in the presence of UCl_4, namely $(C_2H_5O)P(O)(OH)_2$ and H_3PO_4:



(4)

Both CrL_3 and $U_3L'_4$ are stable in the atmosphere and insoluble in organic media. Pertinent characterization data: CrL_3: IR spectrum, cm^{-1}: $\nu_{POO,as}$ 1195 vs, $\nu_{POO,sym}$ 1085vs, $\nu_{P-O-P,as}$ 967s, $\nu_{P-O-P,sym}$ 730m, ν_{P-Cl} 555w, b [13–17]; solid-state (Nujol mull) electronic spectrum, nm: 450s, vb, 665ms, vb (approximate Dq = 1504 cm^{-1}); μ_{eff} = 3.63 μB (297 °K). $U_3L'_4$: IR spectrum, cm^{-1}: $\nu_{POO,as}$ 1179vs, $\nu_{POO,sym}$ 1082vs, $\nu_{P-O-P,as}$ 956vs, $\nu_{P-O-P,sym}$ 722 m; μ_{eff} = 2.79 μB (295 °K). The Cr^{3+} complex may be considered as a polymeric hexacoordinated species, in view of its insolubility in organic solvents and its relatively low magnetic moment [5, 19, 20]. Regarding the U^{4+} complex, which is also insoluble in organic media, its magnetic moment is normal for hexacoordinated, but clearly subnormal for octacoordinated U^{4+} [20–23]. Previous experience with U^{4+} organophosphato complexes [5, 24, 25] favors an octacoordinated polymeric configuration for the new complex.

The results of the present work seem to indicate that, depending on the metal ion present, reactions of metal chlorides with edcp in the presence of water of hydration, may lead to either deethylation and/or partial or complete dechlorination of edcp, following initial adduct formation between edcp and metal chloride. These interesting findings have prompted us to extend our studies to edcp reactions with the halides of various other metal ions; this work is currently underway and will be reported in the future.

References

1 C. M. Mikulski, N. M. Karayannis and L. L. Pytlewski, *J. Inorg. Nucl. Chem., 34,* 1215 (1972).
2 N. M. Karayannis, C. M. Mikulski and L. L. Pytlewski, *Inorg. Chim. Acta, Rev., 5,* 69 (1971).
3 V. Gutmann and K. Fenkart, *Monatsh. Chem., 99,* 1452 (1968); V. Gutmann and G. Beer, *Inorg. Chim. Acta, 3,* 87 (1969).
4 N. M. Karayannis, C. M. Mikulski, J. V. Minkiewicz, L. L. Pytlewski and M. M. Labes, *Inorg. Chim. Acta, 3,* 523 (1969).
5 C. M. Mikulski, N. M. Karayannis, M. J. Strocko, L. L. Pytlewski and M. M. Labes, *Inorg. Chem., 9,* 2053 (1970); *Inorg. Chim. Acta, 4,* 455 (1970).
6 R. F. Hudson and L. Keay, *J. Chem. Soc.,* 1859, 1865 (1960).
7 J. Epstein and D. H. Rosenblatt, *J. Am. Chem. Soc., 80,* 3596 (1958); J. Epstein and W. A. Mosher, *J. Phys. Chem., 72,* 622 (1968).
8 L. S. Smith, P. R. Newman, A. J. Heeger, A. F. Garito, H. D. Gillman and P. Nannelli, *J. Chem. Phys., 66,* 5428 (1977).
9 R. Cini, P. Orioli, H. D. Gillman and P. Nannelli, *Cryst. Struct. Commun., 8,* 621 (1979).
10 C. M. Mikulski, S. Chauhan, R. Rabin and N. M. Karayannis, *Inorg. Nucl. Chem. Lett., 17,* 195 (1981).
11 L. C. Thomas and R. A. Chittenden, *Spectrochim. Acta, 20,* 467, 489 (1964); *26A,* 781 (1970).
12 J. R. Ferraro, *J. Inorg. Nucl. Chem., 24,* 475 (1962).
13 R. A. Chittenden and L. C. Thomas, *Spectrochim. Acta, 21,* 861 (1965).
14 C. M. Mikulski, L. L. Pytlewski and N. M. Karayannis, *Z. anorg. allg. Chem., 403,* 200 (1974).
15 N. M. Karayannis, C. M. Mikulski, M. J. Strocko, L. L. Pytlewski and M. M. Labes, *Z. anorg. allg. Chem., 384,* 267 (1971); *Inorg. Chim. Acta, 5,* 357 (1971).
16 C. M. Mikulski, L. L. Pytlewski and N. M. Karayannis, *Inorg. Chem., 14,* 1559 (1975).
17 K. A. Andrianov and I. Ya. Manevich, *Zh. Neorg. Khim., 9,* 210 (1964); K. A. Andrianov, I. Ya. Manevich, Yu. A. Buslaev and E. I. Matrosov, *Zh. Neorg. Khim., 10,* 596 (1965); E. I. Matrosov, K. A. Andrianov, I. Ya. Manevich and Yu. A. Buslaev, *Izv. Akad. Nauk SSSR, Neorg. Mat., 1,* 464 (1965).
18 T. D. Smith, *J. Inorg. Nucl. Chem., 9,* 150 (1959).
19 J. C. Scott, A. F. Garito, A. J. Heeger, P. Nannelli and H. D. Gillman, *Phys. Rev., B, 12,* 356 (1975).
20 C. M. Mikulski, J. Unruh, R. Rabin, F. J. Iaconianni, L. L. Pytlewski and N. M. Karayannis, *Transition Met. Chem., 6,* 79 (1981).
21 B. Jezowska-Trzebiatowska and K. Bukietynska, in 'Theory and Structure of Complex Compounds', MacMillan, New York (1964), pp. 311–314.
22 G. A. Candela, C. A. Hutchinson and W. B. Lewis, *J. Chem. Phys., 30,* 246 (1959).
23 T. Yoshimura. C. Miyake and S. Imoto, *Bull. Chem. Soc. Japan, 47,* 515 (1971).
24 C. M. Mikulski, N. M. Karayannis and L. L. Pytlewski, *J. Inorg. Nucl. Chem., 36,* 971 (1974).
25 C. M. Mikulski, T. Tran, L. L. Pytlewski and N. M. Karayannis, *J. Inorg. Nucl. Chem., 41,* 1671 (1979).