REACTION OF PHOSPHORUS TRICHLORIDE WITH CARBOXYLIC ACIDS

L. A. Valitova, E. V. Popova,
Sh. N. Ibragimov, and B. E. Ivanov

UDC 542.91:543.422.
25:547.1'118

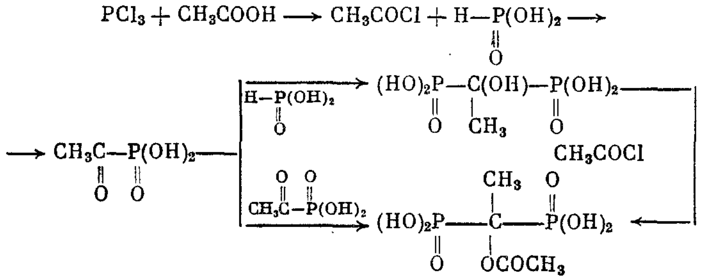
The reaction of phosphorus trichloride with a number of monobasic carboxylic acids has been studied and the optimum ratio of reactants for the yield of acid chlorides has been established. Based on analysis and the data from ^{31}P NMR spectroscopy of the phosphorus-containing products from this reaction it is shown that at 40-50°C a mixture of P—H acids having a predominant content of pyrophosphorous acid is formed.

Studies into the reaction of acetic acid with phosphorus trichloride were commenced at the end of the last century [1] and have continued up to the present. Interest in it arises from the unique complex-forming properties of 1-hydroxyethylidenediphosphonic acid (HEDA), the final phosphorus-containing products from this reaction.

Numerous patents give different variants for the optimization of this process and indicate that it takes place through the stage of the formation of an oligomer, the hydrolysis of which leads to HEDA [2]. To identify the intermediate labile phosphorus-containing products leading to the oligomer various physicochemical methods of investigation are used, especially ^{31}P NMR. In [3] a number of condensed products from HEDA have been studied by TLC and ^{31}P NMR and the paths of their mutual transitions have been demonstrated. In [4] the formation of phosphorous acid and its acid chlorides was established in a solution of PCl_3 at −20°C in propionic acid and evidence of their existence at 0°C has also been given [5].

The doublet signals δP 2.3 ppm, J_{P-H} = 744.6 Hz and δP = 3.9 ppm J_{P-H} = 769.0 Hz are assigned by them to the mono- and dichlorophosphorous acids respectively.

According to [1, 6-8] the reaction of PCl_3 with acetic acid takes place through the stage of phosphorous acid formation followed by its reaction with acetyl chloride



However, the paths for the formation of the oligomers are not clear from this scheme, while in the ^{31}P NMR spectra of the reaction mixtures at 40-50°C phosphorous acid has not been established in appreciable amounts [9].

This paper is devoted to the study of the initial stages of the reaction of PCl_3 with carboxylic acids under conditions preceding the formation of the oligomer.

A detailed study of the reaction of phosphorus trichloride with a number of monobasic carboxylic acids, including C_7-C_9 fractions of synthetic fatty acids (FSFA) (50°C 5 h) showed that, depending on the ratio of the reactants and the acid radical, the yield of the reaction products varies. For a reactant ratio (PCl_3:RCOOH) of 1:3 the anhydrides of the carboxylic acid and the acids themselves were separated from the upper layer besides acyl halides. With a change in the ratio of phosphorus trichloride to carboxylic acid in

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A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 428-432, February, 1990. Original article submitted December 7 1988.

0568-5230/90/3902-0366$12.50 © 1990 Plenum Publishing Corporation

TABLE 1. Reaction of Phosphorus Trichloride with Carboxylic Acids

R	Ratio of reactants PCl_3:RCOOH	Yield of acid chloride, %	Still yield, %	Residue after distilling off acid chloride, %
CH_3	1 : 2	56.4	24.3	2,4
	1 : 2,14	54.15	25.5	3,5
	1 : 3	40.5	29.5	10,5
C_2H_5	1 : 2	57.9	19.4	2,1
	1 : 2,2	51,0	15,8	4.0
	1 : 3	46,4	22.9	18,0
C_3H_7	1 : 2	67,0	17,8	2.4
	1 : 3	49.3	16,0	16,9
C_4H_9	1 : 2	66.4	16.5	1.9
	1 : 2,2	67.5	17,05	3,0
	1 : 3	48.7	16,6	22,0
C_8H_{17}	1 : 2,14	73.0	12.5	4.45
	1 : 3	54.7	11.8	21,4
FSFA C_7-C_9	1 : 2	63.0	14,0	9.0
	1 : 3	49.0	5.6	25.0
$C_{11}H_{23}$	1 : 3	54.9	9.8	22,9

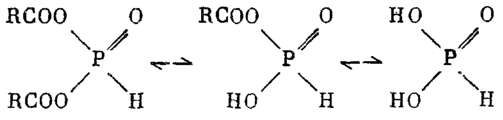
TABLE 2. Characteristics of the Products from the Reaction of Still Residues (PCl_3 + RCOOH) with Propylene Oxide

R	Still, g	Consumption of propylene oxide, g	n_D^{20}	^{31}P NMR		Found, %		
				δP ppm	J_{P-H}, Hz	C	H	P
CH_3	18,2	35,3	1,4565	+10	724,4	42,49	8,42	10,14
C_3H_7	4,55	10,15	1,4570	+9	724	43,5	8.59	11,79
C_8H_{17}	11,5	24,0	1,4580	+9	724	42,14	8,13	11,28
FSFA C_7-C_9	5,7	11,8	1,4585	+9	724	41,08	7,97	15,04

the direction of a decrease in the latter the yield of acid chloride was increased, while the amount of anhydride and acid was lowered. The ratio 1:2 or 1:2.2 (Table 1) can be considered as the optimum for the yield of acid chloriode.

The phosphorus-containing products comprising the lower layer (we shall subsequently refer to them as still residues) were separated from the acid chloride layer and studied by ^{31}P NMR spectroscopy.

In all cases two doublet signals were established having δP −4 ppm, J_{P-H} = 785.4 Hz (principal) and δP +8 ppm, J_{P-H} = 734.4) Hz (an impurity, at 40-50°C). We assigned them previously [9] to di- (I) and monoacetyl (II) phosphites respectively for the example of the reaction of PCl_3 with acetic acid, where their possible existence in the form of the equilibrium mixture



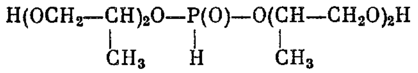
(I) (II) (III)

was postulated.

The initial formation of acetoxy derivatives in the reaction being discussed and not phosphorous acid, as suggested by the authors of [1, 6-8], seemed to us to be the more likely direction for the formation of the oligomeric products. The possibility of the existence of acetyl phosphites as independent compounds is not excluded in the literature [10, 11].

The addition of H_3PO_3 to the lower phosphorus-containing layer did not alter the general picture of the ^{31}P NMR spectrum and in a weak field led to the appearance of a broadened doublet signal having δP +8 ppm, J_{P-H} = 714.0 Hz.

However, on studying the reaction of the phosphorus-containing still residues with propylene oxide it was noted that in the ^{31}P NMR spectra of the products obtained the signal having δP −4 ppm and $J_{P\text{-}H}$ = 785.4 Hz disappeared. The propyloxylated still residues from the action of any of the carboxylic acids used with PCl_3 had similar data for elemental analysis and n_D^{20} while in the ^{31}P NMR spectra there was only one doublet signal having δP +9 ppm, $J_{P\text{-}H}$ = 724 Hz (Table 2), which indicated the absence of an effect of the carboxylic acid radical on the composition of the products formed. For the propyloxylation of phosphorous acid a product having the same characteristics in the ^{31}P NMR spectrum is obtained, while according to the data from elemental analysis it had a higher content of carbon and corresponded to the product from the addition of four molecules of propylene oxide. The IR spectroscopic data do not contradict the structure (IV)

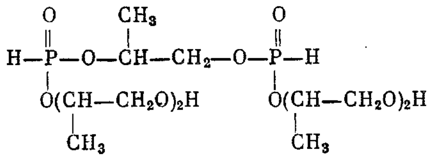


$$\mathrm{H(OCH_2{-}\underset{CH_3}{C}H)_2O{-}\underset{H}{P}(O){-}O(\underset{CH_3}{C}H{-}CH_2O)_2H}$$

(IV)

The phosphorus-containing still residues also reacted vigorously with compounds having a labile hydrogen atom (water, alcohols, CH_3COOH, HCl) with the evolution of a considerable amount of heat and the appearance in the ^{31}P NMR spectrum of a signal characteristic of phosphorous acid (δP +6 ppm, $J_{P\text{-}H}$ = 693.6 Hz).

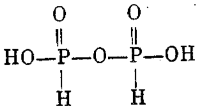
According to the data from elemental analysis the phosphorus-containing lower layer from the reaction of lauric acid with PCl_3 contained only traces of chlorine and carbon (~1%) and corresponded to pyrophosphorous acid, while in the products from its propyloxylation approximately 5 moles of propylene oxide were consumed for each molecule. The penetration of one molecule of propylene oxide through the pyrophosphate bond, which is characteristic of anhydrides [12], probably takes place



$$\mathrm{H{-}\underset{O(\underset{CH_3}{C}H{-}CH_2O)_2H}{\overset{O}{\overset{\|}{P}}}{-}O{-}\overset{CH_3}{C}H{-}CH_2{-}O{-}\underset{O(\underset{CH_3}{C}H{-}CH_2O)_2H}{\overset{O}{\overset{\|}{P}}}{-}H}$$

(V)

Structures of such a type are capable of further reactions under harsher conditions. All the facts presented above enable us to assign one of the doublet signals in the ^{31}P NMR spectrum having δP −4 ppm and $J_{P\text{-}H}$ = 785.6 Hz to pyrophosphorous acid

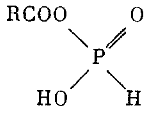


$$\mathrm{HO{-}\underset{H}{\overset{O}{\overset{\|}{P}}}{-}O{-}\underset{H}{\overset{O}{\overset{\|}{P}}}{-}OH}$$

(VI)

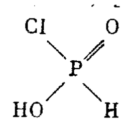
In the literature another spin−spin interaction constant is presented for this compound, although the doublet signal in the ^{31}P NMR spectrum is given in the same region [13].

A certain deviation between the values found from elemental analysis of the propyloxylated still residues (Table 2) and the calculated values ($C_{15}H_{34}O_{10}P_2$, C 41.30; H 7.80; P 14.20%) is possibly associated with an impurity of another P−H acid (^{31}P NMR: δP +8 ppm, $J_{P\text{-}H}$ = 734.4 Hz) which can be assigned with equal probability to both the structure of the acetoxy derivative (VII) [8] and the acid chloride (VIII) [5]



(VII)

or



(VIII)

Thus, in the reaction of carboxylic acids with PCl_3 mixtures of P—H acids with a predominant content of pyrophosphorous acid are formed as the initial phosphorus-containing products.

EXPERIMENTAL

The ^{31}P NMR spectra were recorded on a KGU-4 instrument having a working frequency of 10.2 Hz relative to 85% H_3PO_4. The IR spectra were recorded on a Specord-75 IR spectrometer (KBr). The solvents used were dehydrated.

Reaction of PCl_3 with Acetic Acid. To 54 g (0.9 mole) CH_3COOH 41.25 g (0.3 mole) PCl_3 was added in portions with mixing. The exothermic effect was 2-3°C. After 2 h mixing at 45-50°C two layers separated out. The lower layer, 28.1 g (29.5%), was washed three times with dry petroleum ether and evaporated under vacuum. ^{31}P NMR: δP +8 ppm, J_{P-H} = 734.4 Hz (impurity) and δP —4 ppm, J_{H-P} = 785.4 Hz. On distilling the upper layer was isolated: 38.6 g (40.5%) acetyl chloride, bp 52-53°C, n_D^{20} 1.3870, 8.3 g (8.7%) of acetic anhydride, bp 58-60°C (50 mm), n_D^{20} 1.3890, and 4.8 g (5%) acetic acid, bp 116-118°C, n_D^{20} 1.3710, cf. [15].

The experiments with the other carboxylic acids were conducted similarly. Mixing time was 4-5 h at 40-50°C. The lower phosphorus-containing layer was washed with dry petroleum ether and vacuum distilled on a rotary evaporator (1 h, 40°C, 10-20 torr).

Reaction of PCl_3 with Propionic Acid. From 66.6 g (0.9 mole) CH_3CH_2COOH and 41.25 g (0.3 mole) PCl_3 was isolated: 24.65 g (22.9%). ^{31}P NMR: δP —4 ppm, J_{P-H} = 785.5 Hz (principal); δP +8 ppm, J_{P-H} = 734.4 Hz (impurity).

On distilling the upper layer was isolated: 50 g (46.4%) C_2H_5COCl, bp 73-75°C, n_D^{20} 1.4040 and 19.4 g (18%) $(C_2H_5CO)_2O$, bp 64-67°C (17 mm), n_D^{20} 1.4030 [15].

Reaction of PCl_3 with Butyric Acid. From 58.86 g (0.6 mole) $CH_3(CH_2)_2COOH$ and 27.5 g (0.2 mole) PCl_3 was isolated 13.8 g (16%) of the lower layer, n_D^{20} 1.4670, ^{31}P NMR: δP —4 ppm, J_{P-H} = 785.4 Hz (principal); δP +8 ppm, J_{P-H} = 734.6 Hz (impurity). On distilling the upper layer was isolated: 42.6 g (49.3%) C_3H_7COCl, bp 46-47°C (100 mm), n_D^{20} 1.4130. Found: Cl 33.75%. Calculated for C_4H_7OCl: Cl 33.65%; 9.1 g (10.54%) $(C_3H_7CO)_2O$, bp 80-83°C (12 mm), n_D^{20} 1.4130. Found: C 60.62; H 8.92%. Calculated for $C_8H_{14}O_3$: C 60.76; H 8.86%. 4.2 g (4.9%) C_3H_7COOH, bp 63-67°C (10 mm), n_D^{20}1.4020.

Reaction of PCl_3 with Pentanoic Acid. From 61.28 g (0.6 mole) C_4H_9COOH and 27.5 g (0.2 mole) PCl_3 was isolated: a lower layer 14.7 g (16.6%), ^{31}P NMR: δP —4 ppm, J_{P-H} = 785.4 Hz; δP +8 ppm, J_{P-H} = 734.4 Hz (impurity). On distilling the upper layer was isolated: 43.25 g (48.7%) C_4H_9COCl, bp 64-66°C (98 mm), n_D^{20} 1.4200, 12.6 g (14.2%) $(C_4H_9CO)_2O$, bp 116-118°C (15 mm), n_D^{20} 1.4205; 5.7 g (6.4%) C_4H_9COOH, bp 93-95°C (17 mm), n_D^{20}1.4072, cf. [14].

Reaction of PCl_3 with Nonanoic Acid. From 94.92 g (0.6 mole) $CH_3(CH_2)_7COOH$ and 27.5 g (0.2 mole) PCl_3 was isolated: a lower layer 14.5 g (11.8%), n_D^{20} 1.4680. On distilling the upper layer: 67 g (54.7%) $CH_3(CH_2)_7COCl$, bp 108-110°C (20 mm), n_D^{20} 1.4385 and 14.9 g (12.2%) $(C_8H_{17}CO)_2O$, bp 131-134°C (0.08 mm), n_D^{20} 1.4320.

Reaction of PCl_3 with Lauric Acid. From 180 g (0.9 mole) $C_{11}H_{23}COOH$ and 41.25 g (0.3 mole) PCl_3 was isolated: 21.75 g (9.8%) of a lower layer, δP —4 ppm, J_{P-H} = 785.4 Hz. Found: H 3.65; P 41.82%. Calculated for $H_4P_2O_5$: H 2.75; P 42.46%. On distilling the upper layer: 121.4 g (54.9%) $C_{11}H_{23}COCl$, bp 68-70°C (0.7 mm), n_D^{2} 1.4460. Found: Cl 16.00%. Calculated for $C_{12}H_{23}OCl$: Cl 16.25%. 63.7 g (28.8%) of crystals $(C_{11}H_{23}CO)_2O$ containing $C_{11}H_{23}COOH$ impurity. The results of experiments on the reaction of PCl_3 with the carboxylic acids for other ratios of the reactants are presented in Table 1.

Reaction of Still Residue (PCl_3 + CH_3COOH) with α-Propylene Oxide. To 18.2 g of still residue 44 g of propylene oxide was added through a reflex condenser over the course of 5 h (until there was a neutral reaction). The reaction mixture was cooled after adding each portion (exothermic effect up to 50-60°) with cold water. The reaction was terminated by heating for 1-1.5 h at 60-80°C. After vacuum distillation on a rotary evaporator (1 h, 50°C, 15 torr) was isolated: 53.5 g of a colorless viscous product, n_D^{20} 1.4565, δP +10 ppm, J_{P-H} = 724.4 Hz. The product is soluble in toluene, acetone, alcohol, and benzene. Found: C 42.49; H 8.42; P 10.14%. Calculated for $C_{15}H_{34}O_{10}P_2$: C 41.28; H 7.80; P 14.22%.

Reaction of Still Residue (PCl_3 + C_7-C_9 FSFA) with Propylene Oxide. To 5.7 g of still residue 17.2 g of propylene oxide was added in portions with cooling by cold water. Then the mixture was maintained at 63-67°C for 2 h. After removing the readily volatile products under vacuum (1 h, 40°C, 10 torr) 17.5 g of viscous colorless product was isolated: n_D^{20} 1.4585, δP +9 ppm, J_{P-H} = 724 Hz. The product is soluble in acetone, benzene, and toluene: Found: C 41.08: H 7.97; P 15.04%. Calculated for $C_{15}H_{34}O_{10}P_2$: C 41.28; H 7.80; P 14.22%.

Subsequent experiments on phosphorus-containing still residues (PCl_3 + RCOOH) with propylene oxide were conducted similarly. The results of these experiments are presented in Table 2.

Reaction of Phosphorous Acid with Propylene Oxide. From 3.1 g H_3PO_3 and 16.2 g propylene oxide was obtained 13 g propyloxylated H_3PO_3: n_D^{20} 1.4530, δP +9 ppm, J_{P-H} = 724.4 Hz. The product is soluble in acetone, toluene, benzene, and CCl_4. Found: C 45.86; H 8.69; P 9.30%. Calculated for $C_{12}H_{27}O_7P$: C 45.86: H 8.60; P 9.87%. IR spectrum (KBr, ν, cm^{-1}): 3380 (OH), 2420 (PH), 1220 (P=O), 1070, 980 (P—O—C).

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