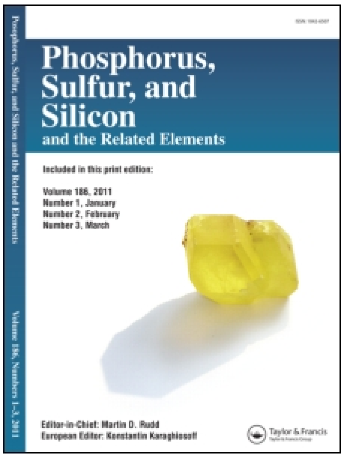

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ON THE INTERACTION BETWEEN HYPOPHOSPHOROUS ACID AND ALCOHOLS

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The esterification of hypophosphorous acid with alcohols, i.e. isopropanol, isobutanol, *n*-pentanol, *n*-octanol and 1,3-propylene glycol leads to the formation of the corresponding phosphonous acid esters in yields of up to 50%, in addition to the hypophosphorous acid esters. The compounds are characterized by their elemental analyses, infrared and ^{1}H NMR spectra. A mechanism of their formation is suggested.

The preparation of hypophosphorous acid esters via esterification with alcohols and azeotropic removal of the water formed is well known[1,2].

$$H_2P(O)OH + HOR \rightarrow H_2P(O)OR + H_2O \qquad (1)$$

The yields in these cases were determined on the basis of the amounts of water formed since the esters were found to be unstable.[1,2,3] For this reason they are not described as pure compounds. On distillation have been obtained up to 10% yields of pure esters which decompose even at 20°C within 15 min.[3]. The following decomposition path has been suggested:

$$ROP(O)H_2 \rightarrow (RO)_2P(O)H + PH_3 \qquad (2)$$

Our experimental data indicate that the amount of water evolved in the esterification reaction of hypophosphorous acid with alcohols exceeds the theoretical, while the reaction mixture remains acidic regardless of the amount of alcohol used, i.e. the pH value is below 3. The only reaction known to take place between hypophosphorous acid and alcohols is the esterification. The aim of the presented paper is to examine the interaction between hypophosphorous acid and alcohols, i.e. isopropanol, isobutanol, *n*-pentanol, *n*-octanol and 1,3-propylene glycol.

Titration with sodium hydroxide of the residue of the distillation of hypophosphorous isobutylate revealed the presence of the monoisobutyl ester of phosphorous acid. It seems likely that the decomposition of the hypophosphorous acid esters proceeds in accord with the following scheme:

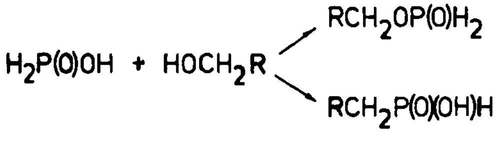
$$3\ ROP(O)H_2 \rightarrow (RO)_2P(O)H + RO(HO)P(O)H + PH_3 \qquad (3)$$

and not as given in References 1 and 2.

As can be seen from this scheme the esters lose phosphine which ignites in the presence of oxygen and also tends to explode. In our present studies we did not subject the reaction mixture to distillation. The esterification reaction is monitored and after evolution of 130% of the theoretical amount of water more water is introduced with a view of hydrolysing the hypophosphorous acid ester. It was expected that the main hydrolysis products formed would be hypophosphorous acid and alcohol. The inorganic compounds and the alcohol are water soluble while the organic products i.e. long-chain alcohols and possible organophosphorus compounds would be expected to remain in the toluene layer.

It was established that 50% of the phosphorus introduced in the system was present in the aqueous layer. The phosphorus-containing product was found to consist of hypophosphorous acid (90 to 93%), phosphorous acid (about 5%) and phosphorous acid monoester (3%). The ^{31}P NMR spectrum taken with 85% phosphoric acid as standard corroborate this observation. The spectrum shows a triplet in the ratio of 1:2:1 with a chemical shift of $\delta = -12.80$ ppm and $J\ ^{31}$(PH) of 563.96 Hz for hypophosphorous acid and a doublet with $\delta = -11.0$ ppm and $J\ ^{31}$(PH) = 674.44 Hz due to phosphorous acid ($(HO)_2P(O)H$).

The toluene layer is always acidic and contains phosphorus. A yellow oil remains after removing the solvent and excess alcohol. This residue was analysed by elemental analysis, acid number (see Table I), infrared and ^{1}H NMR spectra (see Table II). The data indicate that phosphonous acid is also formed. The interaction probably proceeds along the following lines:

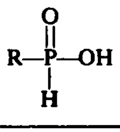


(4)

There are no data in the literature regarding this reaction pathway. The formation of a phosphorus-carbon bond has been observed in the reaction between hypophosphorous acid and poly(allyl alcohol)[4], glucose, cellulose and lignin[5,6] as the result of the isomerization undergone by the esters of hypophosphorous acid. It is pointed out that number of C—P bonds increases at higher temperatures, longer duration of the reaction and when there is a greater excess of hypophosphorous acid.

TABLE I

Properties of alkylphosphonous acids



$R-P(=O)(H)-OH$

R	n_D^{20}	P%		Acid number (mg KOH/g)		Yield
		found	calc.	found	calc.	%
$(CH_3)_2CH$	1.4372	28.1	28.4	508	514	41
$(CH_3)_2CHCH_2$	1.4388	25.3	25.4	447	560	48
$CH_3(CH_2)_4$	1.4410	22.3	22.8	400	412	50
$CH_3(CH_2)_7$	1.4482	16.9	17.6	311	319	48
$HO-(CH_2)_3$	1.4530	24.1	25.0	435	452	40

The acid number is the number of milligrams of potassium hydroxide required to neutralize 1 g of material.

TABLE II

^{1}H NMR data for alkylphosphonous acids

	Chemical shift, δ						Coupling constant, Hz					
Compound	$C\underline{H}_3$	$C\underline{H}$	$(C\underline{H}_2)_3$	$PC\underline{H}_2$	$PCH_2C\underline{H}_2$	$P\underline{H}$	$^3J_{CH_3CH_2}$	$^3J_{CH_3CH}$	$^3J_{CH_2CH_2}$	$^3J_{CHCH_2}$	$^2J_{PCH_2}$	J_{PH}
1	0.67	1.63	—	3.39	—	6.79	—	6.71	—	6.76	6.82	518.55
2	0.89	—	1.34	3.65	1.55	6.83	6.1	—	7.0	—	6.40	692.80
3	—	—	—	3.71	1.52	6.76	—	—	7.0	—	6.66	684.42

1. $(CH_3)_2CHCH_2P(O)(OH)H$; 2. $CH_3(CH_2)_3CH_2P(O)(OH)H$; 3. $HOCH_2CH_2CH_2P(O)(OH)H$.

TABLE III

^{1}H NMR data for compounds 8.I and 8.II after hydrolysis

	Chemical shift, δ							Coupling constant, Hz						
Comp	$C\underline{H}_3$	$C\underline{H}$	$(C\underline{H}_2)_3$	$PC\underline{H}_2$	$PCH_2C\underline{H}_2$	$POC\underline{H}_2$	$P\underline{H}$	$^3J_{CH_3CH_2}$	$^3J_{CH_2CH_2}$	$^3J_{CH_3CH}$	$^3J_{CHCH_2}$	$^2J_{PCH_2}$	$^3J_{OCH_2CH_2}$	$^3J_{OCH_2CH}$
1	0.89	—	1.34	3.65	1.55	—	6.83	6.0	7.0	—	—	6.40	—	—
2	0.89	—	1.34	—	—	4.05	6.78	6.0	—	—	—	—	7.0	—
3	0.67	1.63	—	3.39	—	—	6.79	—	—	6.71	6.76	6.82	—	—
4	0.95	1.92	—	—	—	3.82	6.75	—	—	7.0	—	—	—	7.0

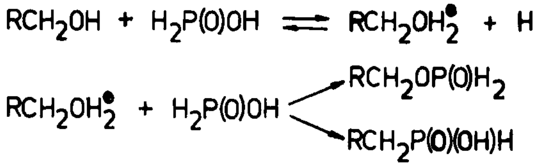
1. $CH_3(CH_2)_3CH_2P(O)(OH)H$; 2. $CH_3(CH_2)_3CH_2OP(O)(OH)H$; 3. $(CH_3)_2CHCH_2P(O)(OH)H$; 4. $(CH_3)_2CHCH_2OP(O)(OH)H$.

The phosphonous acid present in the reaction mixture can be envisaged to arise as the result of several reactions.

With the exception of the suggested isomerisation of the hypophosphorous acid esters,[4–6] unsupported by experimental data, evidence confirming this isomerisation could not be found in the literature. The presently obtained results corroborate the decomposition of the hypophosphorous acid esters to phosphine and dialkyl phosphite according to Scheme (3).

The following observations were made concerning the interaction between hypophosphorous acid with the olefin possibly formed *in situ* via the dehydration of the alcohol in the presence of mineral acid: the interaction between isobutanol and H_3PO_2 in the mixture indeed affords isobutene, determined by gas chromatographic comparison with an authentic sample. No addition product was detected on attempting to add isobutene to hypophosphorous acid under the reaction conditions, this addition should be expected to lead to the formation of tret.-butylphosphonous acid, however, the pmr spectrum does not support such a structure of the presently obtained phosphonous acids.

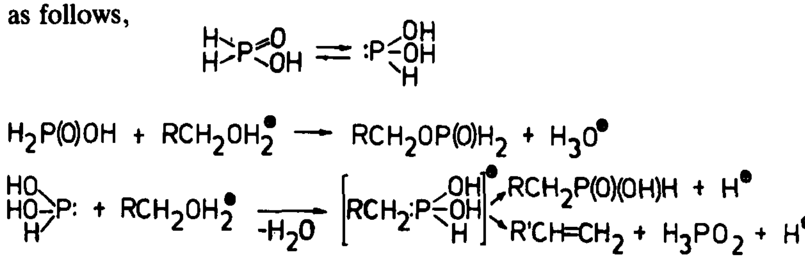
It is likely that the hypophosphorous acid protonates the alcohol which further reacts with the anion of the acid to give the ester or phosphonous acid:



$$RCH_2OH + H_2P(O)OH \rightleftharpoons RCH_2OH_2^{\oplus} + H_2P(O)\bar{O}|^{\ominus}$$

$$RCH_2OH_2^{\oplus} + H_2P(O)OH \longrightarrow \begin{cases} RCH_2OP(O)H_2 \\ RCH_2P(O)(OH)H \end{cases} \qquad (5)$$

The most likely way of formation of the olefin and the phosphonous acid is suggested as follows,



$$H_2P(=O)OH \rightleftharpoons :P(OH)_2H$$

$$H_2P(O)OH + RCH_2OH_2^{\oplus} \longrightarrow RCH_2OP(O)H_2 + H_3O^{\oplus} \qquad (6)$$

$$(HO)_2HP: + RCH_2OH_2^{\oplus} \xrightarrow[-H_2O]{} \left[RCH_2{:}P(OH)_2H\right]^{\oplus} \longrightarrow \begin{cases} RCH_2P(O)(OH)H + H^{\oplus} \\ R'CH{=}CH_2 + H_3PO_2 + H^{\oplus} \end{cases}$$

where $R = R'CH_2$.

The phosphonous acids cannot be purified by distillation[7] since they disproportionate to alkylphosphines and phosphonic acids according to the scheme:

$$RP(O)(OH)H \xrightarrow{t^\circ} RPH_2 + RP(O)(OH)_2 \qquad (7)$$

An attempt was made to distill the phosphonous acids synthesized in the reaction between H_3PO_2 and isobutanol and *n*-pentanol under a vacuum of about 2 millibars. In both cases a substance was obtained about 6% of the mixture, which according to ^1H NMR (see Table III) was an ester of the phosphonous acid, and a diester of phosphorous acid:

$$\underset{I}{RP(O)(OR)H} \qquad \underset{II}{ROP(O)(OR)H} \qquad (8)$$

On hydrolysis with water a mixture of phosphonous acid and a monoester of phosphorous acid was obtained in a ratio of 70:30; no ester of hypophosphorous acid was detected. The insignificant amount of phosphorous acid esters formed can be due to the decomposition of the esters of hypophosphorous acid according to Equation (3). The phosphonous acid esters probably arise from the interaction between the ester of hypophosphorous acid and the carbenium ion originating from the corresponding alcohol.

CONCLUSIONS

A. The interaction between hypophosphorous acid and alcohols affords also phosphonous acids.

B. This reaction is accompanied by dehydration of the alcohols.

C. The phosphonous acids most likely arise as the result of the interaction between the catalytically formed carbenium ion and the hypophosphorous acid enolate.

EXPERIMENTAL

Methods of Analysis. ^{1}H NMR spectra were determined on a "Tesla" BS 487 C (80 MHz) and "Bruker" WM (250 MHz) spectrometers as solutions in $CDCl_3$ with TMS as internal standard. ^{31}P NMR-spectra were recorded using a "Bruker" WM 250 spectrometer at 101.27 MHz (ref. 85% H_3PO_4). The IR spectra were run on a UR-20 instrument (Carl Zeiss Jena, GDR).

General Procedure for Conducting the Reaction between Hypophosphorous Acid and Alcohols. In a flask provided with a Dean-Stark apparatus are placed the alcohol or diol (0.25 mole), toluene (50 ml) and H_3PO_2 (0.1 mole) in the form of a 64.6% aqueous solution. The reaction is conducted under argon by refluxing the toluene-water azeotrope for 4–5 hrs during which time are separated 5.5 g (30% excess) of water. The reaction mixture is then cooled under argon to 50°C and washed repeatedly (4–5 times) with about 100 ml of water. From the separated toluene layer volatile products are removed under vacuum to give a yellow oil in a yield up to 50%, based on the hypophosphorous acid used. IR spectra: P=O 1190–1200 cm^{-1}, P—H 2375–2395 cm^{-1}.

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