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Abstract

Full Text

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SAPONIFICATION AND TRANSESTERIFICATION OF FULL ESTERS OF PHOSPHOROUS ACID

It was shown by one of us ([1]) that the action of acidified water on full esters of phosphorous acid of the type $P(OR)_3$ is a typical catalytic reaction.

We studied the saponification by pure water of trimethyl, triethyl, tri-*n*-propyl, tri-*n*-butyl, and triphenyl phosphites. It was found that all the esters listed are readily saponified by pure water with the evolution of heat.

Pure water was obtained by secondary distillation of ordinary distilled water and had a specific electrical conductivity (at 25°) of $2.2 \cdot 10^{-6}$ $\text{ohm}^{-1} \cdot \text{cm}^{-1}$.

The saponification reaction is irreversible and does not depend on the mass of the reacting substances.

We studied (by the dilatometric method) the rate of saponification of the esters by pure water at equimolecular ratios.

The rate of saponification depends, above all, on the size of the radical entering into the composition of the ester. Thus, trimethyl phosphite is saponified 10 times faster than triethyl phosphite; 30 times faster than triphenyl phosphite; 90 times faster than tri-*n*-propyl phosphite; 200 times faster than tri-*n*-butyl phosphite—other conditions being equal.

In terms of the rate of saponification, they are arranged in the following sequence:

$$P(OCH_3)_3 > P(OC_2H_5)_3 > P(OC_6H_5)_3 > P(OC_3H_7\text{-n})_3 > P(OC_4H_9\text{-n})_3$$

Especially interesting is the difficult saponification of tri-*n*-propyl and tri-*n*-butyl phosphites in comparison with triphenyl phosphite. All experiments on the saponification of esters were carried out at a temperature of 25°. The results are given in Table 1.

Table 1

Reactions	Saponification time, min.: 25% of ester	Saponification time, min.: 50% of ester	Saponification time, min.: 75% of ester	Saponification time, min.: 100% of ester
$(CH_3O)_3P$+ H_2O	8	8-9	10	61
$(C_2H_5O)_3P$+ H_2O	68-75	81-82	90	240
$(n\text{-}C_3H_7O)_3P$+ H_2O	750-810	840-850	870	1110
$(n\text{-}C_4H_9O)_3P$+ H_2O	2010	2110	2140	2400
$(C_6H_5O)_3P$+ H_2O	245	265	285	~ 365

The rate of saponification also depends on the temperature at which the reaction is carried out. The influence of temperature on the rate of the saponification reaction is the usual one, as for most chemical reactions.

We studied the influence of the reaction product on the rate of saponification of esters, using triethyl phosphite as an example. To the initial mixture of equimolecular amounts

phosphite and water, various amounts of diethylphosphorous acid were added before the beginning of the experiment. All experiments were carried out at a temperature of 25°. The composition of the initial mixture was $(C_2H_5O)_3P + H_2O + x(C_2H_5O)_2POH$. The results are given in Table 2. As is seen from Table 2, preliminary addition of diethylphosphorous acid to the initial mixture accelerates the course of the reaction.

Table 2

x	Time of saponification, min.	Time of saponification, min.	Time of saponification, min.	Time of saponification, min.
x	25% ester	50% ester	75% ester	100% ester
0.000	68–75	81–82	90	240
0.002	23	32–33	45	100
0.050	up to 5	up to 5	7	50
0.200	–	–	–	11

Saponification of esters $P(OR)_3$, with the exception of triphenyl phosphite, is strongly slowed in the presence of small amounts of inorganic or organic bases, as is seen from Table 3.

Saponification of trimethyl phosphite in the presence of $1.9 \cdot 10^{-5}$ mol of caustic soda was slowed by 7-8 times, triethyl phosphite in the presence of $2.0 \cdot 10^{-5}$ mol

–by 2 times, tri-*n*-butyl phosphite in the presence of $2.1 \cdot 10^{-6}$ mol–by 3 times, and triethyl phosphite in the presence of 0.1 mol of pyridine–by 14 times.

Table 3

Reactions	Amount of base (in mol per 1 mol of ester)	Temperature, °C	Time of saponification, min.	Time of saponification, min.	Time of saponification, min.	Time of saponification, min.
Reactions	Amount of base (in mol per 1 mol of ester)	Temperature, °C	25% phosphite	50% phosphite	75% phosphite	100% phosphite
$(CH_3O)_3P + H_2O$	$1.9 \cdot 10^{-5}$ NaOH	0	450	660	840	1590
$(C_2H_5O)_3P + H_2O$	$2.0 \cdot 10^{-5}$ NaOH	25	139	156	183	437
$(C_2H_5O)_3P + H_2O$	$2.5 \cdot 10^{-5}$ NaOH	25	155	185	230	470
$(C_2H_5O)_3P + H_2O$	$2.0 \cdot 10^{-4}$ NaOH	25	450	490	515	680
$(C_2H_5O)_3P + H_2O$	0.1 C_5H_5N	50	240–250	250–255	255–260	~ 325
$(n\text{-}C_4H_9O)_3P + H_2O$	$2.1 \cdot 10^{-6}$ NaOH	50	150–170	170–173	180	220

Thus, the saponification rate decreases with increasing concentration of the base. Such slowing of the reaction is explained by removal from the reaction mass of the reaction catalyst–the free dialkylphosphorous acid–in the form of its salt with an organic base, or of a salt of monoalkylphosphorous acid with an inorganic base.

We also studied the saponification reaction of trialkyl phosphites in the medium of pyridine, acetone, dioxane, and alcohols. Of these solvents, only dioxane is practically indifferent.

Pyridine and acetone react with the reaction product, giving, respectively, the pyridine salt of dialkylphosphorous acid and an ester of α-oxyalkylphosphinous acid with acetone, and therefore the rate of saponification of the esters in their medium decreases accordingly. Thus, for example, saponification of triethyl phosphite in the presence of 0.2 mol of acetone is slowed by 21 times.

We also studied (by the refractometric method) the rate of saponification of triethyl and tri-*n*-propyl phosphites in dioxane medium.

Kinetic analysis of their saponification in dioxane medium shows that this reaction is complex and cannot be expressed either by the first-order equation

$$\frac{dx}{dt} = k(a - x),$$

or by the equation for autocatalytic reactions

$$\frac{dx}{dt} = kx(a - x).$$

The rate constants for saponification of triethyl phosphite in the medium of 1.5 and 3 mol of dioxane, and of tri-*n*-propyl phosphite in the medium of 4 mol of dioxane, calculated by the equation for second-order reactions

$$\frac{dx}{dt} = k(a - x)^2,$$

are constant over a considerable period of time. At the beginning and end of the reaction, deviations from constancy of the rate constants are observed.

Table 4

No.	Formula	B.p. (in °C at pressure, mm Hg)	n_D^{20}	d_4^{20}	MR, found	MR, calc.	P (in %), found	P (in %), calc.	Yield* (in %)
1	$(CH_3O)_2(n\text{-}C_3H_7O)P$	47–48/14	1,4165	0,9939	38,45	38,34	20,60; 20,75	20,36	78
2	$(CH_3O)_2(iso\text{-}C_5H_{11}O)P$	87–88/4	1,4305	0,9232	66,19	66,07	13,05; 13,05	13,11	–
3	$(CH_3O)(n\text{-}C_3H_7O)(iso\text{-}C_5H_{11}O)P$	75–76/5	1,4275	0,9389	57,62	56,83	15,00; 14,86	14,88	23
4	$(CH_3O)(C_2H_5O)(n\text{-}C_3H_7O)P$	60–61/45	1,4160	0,9732	42,84	42,98	18,70; 18,56	18,65	22
5	$(C_2H_5O)_2(n\text{-}C_3H_7O)P$	72–73/23	1,4150	0,9547	47,27	47,59	17,20	17,19	40
6	$(C_2H_5O)_2(iso\text{-}C_5H_{11}O)P$	83–84/7	1,4230	0,9357	56,71	56,83	15,13; 15,34	14,88	52

No.	Formula	B.p. (in °C at pressure, mm Hg)	n_D^{20}	d_4^{20}	MR, found	MR, calc.	P (in %), found	P (in %), calc.	Yield* (in %)
7	$(n\text{-}C_3H_7O)_2(iso\text{-}C_5H_{11}O)P$	94–96/5	1,4229	0,9223	66,07	66,07	13,29; 13,37	13,11	–
8	$(n\text{-}C_3H_7O)(n\text{-}C_4H_9O)_2P$	94–97/2	1,4242	0,9242	65,85	66,07	13,40; 13,22	13,11	–
9	$(n\text{-}C_4H_9O)_2(n\text{-}C_7H_{15}O)P$	142–143/3	1,4430	0,9030	84,58	84,54	10,71; 10,87	10,60	–
10	$(n\text{-}C_4H_9O)_2(n\text{-}C_7H_{15}O)P$	167–168/3	1,4497	0,9997	98,15	98,39	9,39; 9,36	9,26	61

* Yields are not given for products of side reactions.

Table 5

No.	Formula	B.p. (in °C at pressure, mm Hg)	n_D^{20}	d_4^{20}	MR, found	MR, calc.	P (in %), found	P (in %), calc.
1	$(CH_3O)(C_2H_5O)P(O)OH$	63–67/2	1,4120	1,0686	32,16	31,71	22,60; 22,80	22,43
2	$(CH_3O)(n\text{-}C_4H_9O)P(O)OH$	79–81/10	1,4170	1,0430	36,71	36,33	20,62	20,38
3	$(C_2H_5O)(n\text{-}C_3H_7O)P(O)OH$	97–99/24	1,4110	1,0354	36,48	36,33	20,21; 20,11	20,36
4	$(C_2H_5O)(iso\text{-}C_4H_9O)P(O)OH$	90–92/1	1,4071	1,0115	41,32	40,95	18,46; 18,64	18,66
5	$(C_2H_5O)(iso\text{-}C_5H_{11}O)P(O)OH$	96–98/4	1,4210	0,9964	45,87	45,56	17,43; 17,20	17,19
6	$(n\text{-}C_3H_7O)(n\text{-}C_4H_9O)P(O)OH$	101–103/3	1,4221	0,9988	45,75	45,56	17,00; 17,17	17,19
7	$(n\text{-}C_4H_9O)(n\text{-}C_7H_{15}O)P(O)OH$	151–152/2	1,4325	0,9481	64,71	64,04	12,80; 12,70	13,11

The saponification reaction of trialkyl phosphites without a solvent proceeds in a heterogeneous system. Therefore, kinetic analysis of this reaction did not give any definite results.

When trialkyl phosphites are saponified in an alcohol medium, the reaction proceeds rapidly with strong heating. However, not every alcohol can be used as a solvent, since when an alcohol whose radical differs from the radical of the phosphite is used, saponification is always accompanied by a side reaction—transesterification.

B. A. Arbuzov and V. S. Vinogradova ([2]) were the first to obtain a series of trialkyl phosphites with identical higher radicals by transesterification of triethyl phosphite with higher alcohols in the presence of a catalyst—phosphoric acid.

Dialkylphosphorous acids and alkali-metal alcoholates are catalysts for the transesterification of trialkyl phosphites with higher alcohols.

The synthesis of mixed phosphites of the type $(RO)_2(R'O)P$ and $(RO)(R'O)_2P$ was carried out by the method of partial transesterification of phosphite $P(OR)_3$, respectively with one and two moles of higher alcohols per mole of phosphite, in the presence of one of the two above-mentioned catalysts.

Mixed phosphites, on the first fractionation (Table 4, No. 1) under high vacuum, are obtained in good yields.

On repeated distillations, redistribution of radicals is observed. Phosphites with three different aliphatic radicals disproportionate especially readily (Table 4, Nos. 3 and 4: $(RO)(R'O)(R''O)P$), obtained by the method of partial transesterification of the mixed phosphite $(RO)_2(R'O)P$ with alcohols.

The physical constants of the esters synthesized by us for the first time are given in Table 4.

Mixed phosphites of the type $(RO)_2(R'O)P$ are readily saponified by slightly acidified water, forming the corresponding alcohols and mixed dialkylphosphorous acids. In their saponification, the light radical is always split off in the form of an alcohol. Here too, on repeated distillations, disproportionation is observed. The physical constants of some of the mixed dialkylphosphorous acids first isolated by this method are given in Table 5.

Mixed dialkylphosphorous acids have been obtained by a number of investigators by transesterification of diethyl phosphite with higher alcohols both in the absence of any catalysts ([3]) and with a catalyst—alkali-metal alcoholates ([4])—or with an acidic catalyst ([2]).

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.