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Oxidizing Alkoxylation of Phosphine  
in Alcoholic Solutions of Iodine

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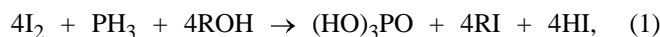
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**Abstract**—Oxidizing alkoxylation of  $\text{PH}_3$  to trialkyl phosphates was performed in pyridine-alcoholic solutions of iodine. The optimal conditions of the reaction were found.

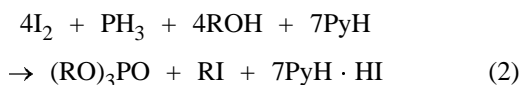
The reaction of  $\text{PH}_3$  with  $\text{I}_2$  was studied in detail in [1, 2]. Iodine solutions are widely used for gas treatment to remove  $\text{PH}_3$  [3] and for phosphine analysis [4]. Hypophosphorous, phosphorous, or phosphoric acids are formed depending on  $\text{I}_2/\text{PH}_3$  ratio [1–3].

Reaction of  $\text{PH}_3$  with  $\text{I}_2$  in alcohols has not been studied [5]. We found that alcoholic solutions of  $\text{I}_2$  rapidly oxidize  $\text{PH}_3$  at 25–70°C into phosphoric acid:



where R is Me, Et, Bu, Am, and Oct.

In pyridine-alcoholic solutions,  $\text{I}_2$  oxidizes  $\text{PH}_3$  into trialkyl phosphate:



with the formation of a white precipitate of pyridine hydroiodide. Reaction (2) quantitatively yields trialkyl phosphates, which are widely used in extraction of rare earth elements and preparation of polymers [6]. Due to the high rate and high selectivity, the new reaction (2) can be used for utilization of  $\text{PH}_3$  contained in exhaust gases from phosphorus plants [3]. In this work, we studied reactions (1) and (2) by IR and  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR spectroscopy, gas chromatography, potentiometry, and the differential kinetic method.

#### EXPERIMENTAL

Oxidizing alkoxylation of  $\text{PH}_3$  in alcoholic solutions of iodine was studied in a flow-type installation equipped with a vigorously shaken isothermal re-

actor, a unit for redox potential measurement, and supply and sampling of gaseous, solid and liquid reagents and products, a gasometer with an Ar- $\text{PH}_3$  mixture, and a rheometer for measuring the gas flow rate. The reactor volume was 150 ml, and that of supplied liquid, 10 ml. The relative error of measurements of the uptake rate and the volume of the converted  $\text{PH}_3$  was within 8–10%. The reactor was charged with alcohol (or alcohol-pyridine mixture) and iodine, purged with Ar, the shaker was switched on, the redox potential measurement was started, and then the Ar- $\text{PH}_3$  gas mixture was supplied into the reactor. The rate of the gas mixture supply was controlled so as to obtain the constant  $\text{PH}_3$  concentration at the outlet ( $\sim 1$  Pa). During the experiment, the redox potential, the rate of  $\text{PH}_3$  uptake  $w$  ( $\text{mol l}^{-1} \text{min}^{-1}$ ), and the amount of  $\text{PH}_3$  taken up  $Q$  (M) were continuously measured, and the compositions of the liquid and gas phases were analyzed at regular intervals. The experiment was continued until the  $\text{PH}_3$  uptake ceased. The rate of oxidizing alkoxylation of phosphine (2) was determined from the consumption of  $\text{PH}_3$  and alcohol and the accumulation of trialkyl phosphate and alkyl iodide. The concentrations of the reaction components were varied depending on particular alcohol as follows (M): 0.4–1.2 ( $\text{I}_2$ ), 0.0–22.2 (ROH), 0.0–12.4 (PyH), and  $p_{\text{PH}_3}$  ( $1.6\text{--}4.0 \times 10^{-3}$  Pa). The temperature  $T$  was 25–70°C.

Phosphine was prepared by acid decomposition of  $\text{Zn}_3\text{P}_2$ . Gases ( $\text{PH}_3$  and Ar) were dried over granulated NaOH. Alcohols were purified by distillation from CaO, and pyridine by distillation from Na metal. Analytically pure iodine was used without additional purification. The  $\text{I}_2$  concentration was determined titrimetrically [8].

## Redox alkoxylation of phosphine in alcoholic solutions of iodine

Solution composition, M			$p_{\text{PH}_3} \times 10^{-3}$ , Pa	$T, ^\circ\text{C}$	$Q_{\text{PH}_3}$ , M	$\text{I}_2/\text{PH}_3$	$(\text{RO})_3\text{PO}$ , M	Yield of $(\text{RO})_3\text{PO}$ , %
$\text{I}_2$	PyH	RON						
BuOH								
0.8	12.4	–	2.3	25	0.3	3	–	–
0.8	12.4	–	1.4	70	0.3	3	–	–
0.4	–	10.9	1.1	25	0.1	4	0.002	1.0
0.8	–	10.9	0.7	70	0.2	4	0.002	1.0
0.8	1.2	9.8	2.3	25	0.2	4	0.2	100.0
0.8	1.2	9.8	1.4	70	0.2	4	0.2	100.0
0.8	2.5	8.7	1.4	70	0.2	4	0.2	100.0
0.8	5.0	6.5	1.4	70	0.2	4	0.2	100.0
0.8	7.4	4.3	1.4	70	0.2	4	0.2	100.0
0.8	9.9	2.2	1.4	70	0.2	4	0.1	64.0
0.8	11.2	1.1	1.4	70	0.2	4	0.2	82.0
0.4	1.2	9.8	2.0	50	0.1	4	0.1	100.0
0.8	2.5	8.7	2.0	50	0.2	4	0.2	100.0
1.2	5.0	6.5	2.0	50	0.3	4	0.3	100.0
OctOH								
0.4	1.2	5.7	2.3	50	0.1	4	0.1	100.0
0.8	2.5	5.0	2.3	50	0.2	4	0.2	100.0
AmOH								
0.4	1.2	8.3	2.0	50	0.1	4	0.1	100.0
EtOH								
0.4	1.2	15.4	2.0	50	0.1	4	0.1	100.0
MeOH								
0.4	1.2	22.2	2.0	50	0.1	4	0.1	100.0

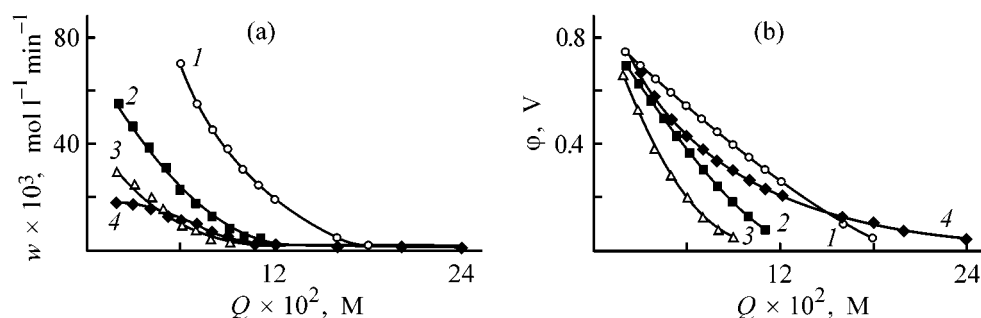
The chromatographic analysis of  $\text{PH}_3$  in the initial gas mixture was performed on an LKhM-8 MD chromatograph equipped with a heat conductivity detector and a steel column packed with Porapak Q at  $100^\circ\text{C}$  at a helium flow rate of  $12 \text{ ml min}^{-1}$ . Unreacted phosphine was determined colorimetrically [9]. The stationary redox potential of alcoholic solutions of  $\text{I}_2$  was continuously measured with a pH-121 millivoltmeter, using calomel and platinum electrodes, with a ground-glass stopper wetted with KCl solution as an electrolytic junction [10].

The chromatographic analysis of alcohols, pyridine, alkyl iodides, and organic products was performed on a 3700 chromatograph with a flame-ionization detector and a  $3.0 \text{ m} \times 3.0 \text{ mm}$  steel column packed with Chromaton-N-AW-DMCS impregnated with PEG-20M (10%). The column temperature was programmed from 100 to  $200^\circ\text{C}$  at a carrier gas (argon) flow rate of  $30 \text{ ml min}^{-1}$ .

Inorganic phosphates were determined colorimetrically in the form of vanadomolybdophosphate on an FEK-56 PM in 4-cm cells relative to water at 370 nm [8].

Trialkyl phosphates were recovered by vacuum distillation at 1–10 mm Hg after separation of the  $\text{PyH} \cdot \text{HI}$  precipitate by decanting. The products obtained were identified by the boiling point, refractive index, and IR and  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR spectra.

The IR spectra in the  $400\text{--}4000 \text{ cm}^{-1}$  range were recorded on a Specord IR-75 spectrometer with KBr windows. The  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR spectra were registered on a Bruker WP-80 spectrometer [31.44 MHz ( $^{31}\text{P}$ ) and 20.55 MHz ( $^{13}\text{C}$ )]. The main physicochemical constants of the isolated products agreed well with reference data [11]. In the  $^{31}\text{P}$  NMR spectra, the signal at  $\delta$  from  $-0.3$  to  $-0.9$  ppm relative to 85%  $\text{H}_3\text{PO}_4$  corresponds to the chemical shift of trialkyl phos-



**Fig. 1.** (a) Conversion and (b) potentiometric curves of phosphine uptake by iodine solution. ( $w$ ) Rate of phosphine uptake, ( $\phi$ ) potential, and ( $Q$ ) amount of phosphine taken up.  $c_{I_2}$  (M): (1, 4) 0.8; and (2, 3) 0.4.  $c_{Py}$  (M): (1) 0, (2, 3) 1.2, and (4) 12.4.  $c_{BuOH}$  (M): (1) 10.9, and (2) 9.8; (3)  $c_{OctOH}$  5.7; (4) No alcohol.  $p_{PH_3} \times 10^{-3}$  (Pa): (1) 1.6, (2, 4) 3.3, and (3) 4.0.  $T$  ( $^{\circ}C$ ): (1) 70, (2, 3) 50, and (4) 25.

phates [12]. The IR spectra of the trialkyl phosphates obtained coincided with those of the reference samples and contained characteristic bands of P=O ( $\nu = 1260\text{--}1285\text{ cm}^{-1}$ ) and P-O-C ( $\nu = 1020\text{--}1045\text{ cm}^{-1}$ ) groups [13]. The  $^{13}C$  NMR spectra of the products contained signals with chemical shifts  $\delta(CH_3) = 19.5 \pm 0.5$ ,  $\delta(CH) = 29.5 \pm 0.5$ , and  $\delta(CH_2) = 73.6 \pm 0.5$  ppm, characteristic of trialkyl phosphates.

**The  $PH_3\text{--}I_2\text{--}ROH$  system.** The alcoholic solution of  $I_2$  is fairly stable at  $20\text{--}70^{\circ}C$ . The  $I_2/I^-$  redox potential was constant for a long time (30 min). The  $I_2$  concentration did not change, and no products of alcohol oxidation with iodine were detected [14]. Introduction of  $PH_3$  into this solution is accompanied by a cathodic shift of the redox potential  $\phi$  from 0.8 to 0.1 V because of the decrease in the  $I_2$  concentration due to reaction (1). In the course of  $PH_3$  uptake by iodine alcoholic solution,  $I_2$  is reduced to  $RI$  and  $HI$ , and  $PH_3$  is oxidized to phosphoric acid by Eq. (1). The yield of organic phosphates is 1–2% (see the table). The  $W\text{--}Q$  conversion and  $\phi\text{--}Q$  potentiometric curves are descending (Figs 1a, 1b, curves 1). The alcoholic solution of iodine eliminates from  $Ar\text{--}PH_3$  mixtures even trace amounts of  $PH_3$  ( $< 10$  Pa). The  $PH_3$  uptake stops only when  $I_2$  is completely reduced and, correspondingly, the reddish brown alcoholic solution of  $I_2$  is decolorized.

**The  $PH_3\text{--}I_2\text{--}ROH\text{--}PyH$  system.** The pyridine-alcoholic solution of  $I_2$  is fairly stable at  $20\text{--}70^{\circ}C$ . The redox potential of the  $I_2/I^-$  couple remains constant for 30–40 min. During this time, the  $I_2$  concentration is also unchanged, and products of alcohol and pyridine oxidation by iodine do not appear. Introduction of  $PH_3$  into the pyridine-alcoholic solution of  $I_2$  is accompanied by uptake of  $PH_3$ , decrease in the  $I_2$  concentration, and cathodic shift of the redox potential from 0.7 to 0.05 V (Fig. 1). During the ex-

periment, the initial reddish brown solution of  $I_2$  is decolorized, and a white precipitate of  $PyH \cdot HI$  is formed. The uptake of  $PH_3$  by the pyridine-alcoholic solution is accompanied by the oxidizing alkoxylation of  $PH_3$  (2) with the formation of trialkyl phosphates in high yields (see table). The table illustrates the effect of the temperature and concentration of iodine, phosphine, pyridine, and alcohol on the trialkyl phosphate yield. Under the optimal conditions, the yield is 100%. The increase in  $PyH$  concentration in the alcoholic solution of  $I_2$  from 1.2 to 7.4 M does not affect the tributyl phosphate (TBP) yield. At the pyridine concentration of 9.9 M, the TBP yield decreases to 64%. The pyridine solution of  $I_2$  takes up  $PH_3$ , and a yellow precipitate of, probably,  $P_2I_4$  is formed [15], with no organophosphorus compounds detected in the solution. The effect of alcohol on reaction (2) was studied at the optimal  $[PyH]/[I_2]$  ratio close to the stoichiometric ratio. The character of conversion and potentiometric curves of  $PH_3$  uptake by pyridine-alcoholic solutions of  $I_2$  are similar to those for alcoholic solutions of  $I_2$ . The rate of reaction (2) grows with increasing concentration of  $I_2$  and  $PH_3$ , temperature, and alcohol acidity and decreases with accumulation of  $PyH \cdot HI$  (Fig. 1).

## CONCLUSION

At  $20\text{--}70^{\circ}C$ , pyridine-alcoholic solutions of  $I_2$  rapidly take up  $PH_3$  from gas mixtures with selective formation of trialkyl phosphates. The optimal conditions of this reaction are  $T = 25\text{--}50^{\circ}C$ ,  $p_{PH_3} = (1.4\text{--}2.3) \times 10^{-3}$  Pa, and  $c_{I_2} = c_{PyH} = 10\text{--}30$  wt% (the remainder is ROH).

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