165. *Interaction of Hydrogen Halides and* n-*Butyl Phosphites.*

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Rates of dealkylation of three *n*-butyl esters of phosphorous acid by means of hydrogen halides have been determined in ethereal solution and in absence of ether. It is shown that the rates for a given ester are with respect to the hydrogen halides in the order $HI > HBr \gg HCl$, and for a given halide are with respect to the three esters in the order $P(OR)_3 \gg PHO(OR)_2 > PHO(OH)(OR)$. The possibility of studying such systems by kinetic methods was also investigated. The results have an important bearing on the understanding of the course of interaction of inorganic non-metallic halides and alcohols.

Rates of stepwise dehalogenation of non-metallic inorganic halides and rates of stepwise dealkylation of the corresponding esters by hydrogen halides must be known in order to give detailed descriptions of reaction sequences in alcohol–inorganic non-metallic halide systems. A superimposed factor is the degree of reactivity of the alcoholic carbon atom, and useful progress cannot be made without recognising at least a rough classification into alcohols such as butan-1-ol and octan-2-ol of " ordinary " reactivity and those such as 1-phenylethanol and *tert.*-butyl alcohol which have a very much more reactive alcoholic carbon atom. Successive replacement of chlorine in phosphorus trichloride by alkoxyl, $PCl_2{\cdot}OR$, $PCl(OR)_2$, $P(OR)_3$, followed by dealkylation, $P(OR)_3 + HCl \longrightarrow PHO(OR)_2 + RCl$, appears to constitute the reaction sequence mainly, if not entirely, responsible for the formation of such alkyl chlorides as 1-chlorobutane and 2-chloro-octane (Gerrard, *J.*, 1940, 218, 1464; 1944, 85) under what may be termed ordinary experimental conditions. That the hydrogen atom in the so-called dialkyl hydrogen phosphites is attached to the phosphorus atom is supported by observations on vibrational spectra (Meyrick and Thompson, *J.*, 1950, 225), and the esters are therefore dialkyl phosphonates. The ready removal of one alkyl group from the trialkyl phosphite may therefore be correlated with the basic function of the lone pair of electrons on the phosphorus atom, a structural detail missing in four-covalent phosphorus systems and in boron and silicon systems (Gerrard and Lappert, *J.*, 1951, 1020, 2545; Gerrard and Woodhead, *J.*, 1951, 519).

Phosphorus tribromide–alcohol and phosphorus tri-iodide–alcohol systems tend to follow the same reaction sequences; but dealkylation of the dialkyl hydrogen phosphite is rapid enough to be effective in ordinary reaction times, and furthermore, there are signs that alkyl halide is also formed by other reactions involving the hydrogen halide (Gerrard, *J.*, 1945, 848; Berlak and Gerrard, *J.*, 1949, 2309). It must be emphasised that for more reactive alcohols (*e.g.*, *tert.*-butyl alcohol and 1-phenylethanol) the aforementioned sequences have not yet been clearly discerned; *e.g.*, *tert.*-butyl alcohol rapidly gives the alkyl chloride and phosphorous acid in practically 100% yield.

We have now examined the interaction of hydrogen halides with *n*-butyl phosphites for two reasons—to obtain more precise information about relative rates of reaction, and to explore possibilities of applying the kinetic method to the further study of alcohol–phosphorus trihalide systems. Data for ethereal solutions at 25° are summarised in the table, the initial esters being tributyl phosphite and dibutyl hydrogen phosphite (phosphonate). Hydrogen chloride removed one butyl group from the tri-ester in a time during which removal of alkyl group from the product (di-ester) was not perceptible. Dealkylation of the di-ester proceeded very slowly, and this explains why the preparation of the hydrogen phosphite in accordance with the equation $3BuOH + PCl_3 = RCl + PHO(OBu)_2$ is practicable. Although the removal of one alkyl group from the tri-ester was rapidly effected by hydrogen bromide at −10° without observed incursion of further dealkylation, a plot of the data for the much slower dealkylation of the di-ester at 25° clearly shows that the removal of a second alkyl group (dealkylation of the product, mono-ester) proceeded to an observable extent soon after the beginning of the experiment. We estimate that dealkylation of the di-ester by hydrogen bromide proceeds 9 times as fast as that of the mono-ester under equivalent conditions.

Comparison of dealkylation rates expressed as the number of alkyl groups per mol. of n-*butyl phosphites removed in the stated time.*

Ester	Molality	HX	Molality	Time	No. of alkyl groups removed
Tri-	0·10	HCl	0·10	5 hours	0·5
Di-	0·50	HCl	1·00	1290 „	1·0
„	0·65	„	1·3	1260 „	1·0
Tri-	0·20	HBr	0·20	3 min.	1·0 (at −11°)
„	0·075	„	0·10	2 „	1·0 (at −10°)
Di-	0·25	„	0·50	3 hours	1·0
				126 „	1·9
„	0·10	„	0·20	6 „	1·0
				224 „	1·96
„	1·02	„	0·39	1·3 „	0·38
Di-	0·025	HI	0·05	2 „	1·0
„	0·04	„	0·08	1 hour	0·9
				2 hours	1·2

We examined our data with a view to calculating specific rates, but concluded that study over a much more extensive field of conditions is necessary before precise statements can be made about the details of mechanism. This study is being continued.

Experiments performed with the reagents in absence of ether support the observations already described. The di-ester exothermally absorbed 1 mol. of hydrogen chloride, evolving approximately 4260 cal./mole; but dealkylation proceeded slowly, 0·5 mol. of alkyl group being removed during 4 days, and 0·75 mol. during 30 days. Furthermore, as dealkylation progressed, so the mixture was able to absorb more hydrogen chloride. This seems to show a ready initial interaction between the di-ester and halide not involving the final attachment of chlorine to the alkyl group. The mono-ester, on formation by dealkylation of the di-ester, can form a similar association with hydrogen chloride. Now, the tri-ester rapidly absorbed 2 mols. of hydrogen chloride exothermally, and after 10 days 1-chlorobutane was isolated in 39·6% yield. Similarly, the tri-ester and hydrogen bromide afforded 1-bromobutane in 72% yield after 2 days, whereas after 24 hours the corresponding reagents gave 1-iodobutane in 82·1% yield.

We conclude that the rates for a given ester are with respect to hydrogen halides in the order $HI > HBr \gg HCl$, and for a given halide are with respect to the three esters in the order $P(OR)_3 \gg PHO(OR)_2 > PHO(OH)(OR)$, and that the data now submitted contribute to the correlation of experimental conditions, relative proportions of reagents, and nature and amounts of products in the alcohol–phosphorus trihalide system.

EXPERIMENTAL

Rate of Interaction of Hydrogen Halides and n-*Butyl Phosphites in Ethereal Solution.*—Tri-*n*-butyl phosphite, d_4^{20} 0·9200 (Found : P, 12·8. Calc. for $C_{12}H_{27}O_3P$: P, 12·4%), and di-*n*-butyl hydrogen phosphite, b. p. 124—126°/20 mm. (Found : P, 15·8. Calc. for $C_8H_{19}O_3P$: P, 16·0%), were prepared as described by Gerrard (*loc. cit.*). An ethereal solution of the hydrogen halide and the ester was kept in a thermostat, and samples were removed after the specified intervals of time. This was done by the slight application of pressure through a calcium chloride guard tube to the surface of the solution in the reaction flask. The sample was received in a tube (11·46 ml.) fitted with two taps. Halide ion was determined in the aqueous extract of each sample by Volhard's method. To prepare the solution, dry hydrogen halide was passed into anhydrous ether, the approximate concentration of the solution determined, and ether added to give approximately the concentration required; the actual concentration was then determined, the initial concentration, for the purpose of the experiment, being calculated by allowing for the volume change when the ester was added. The results are given in the following tables.

0·100 Molal tri-ester, 0·102 molal HCl at 25°.

Time, hours	0·25	0·5	0·75	1	1·5	2·5	3	4	5
HCl reacted, mole/l. × 10^4	56	96	132	173	244	340	386	457	518

0·50 Molal di-ester, 1·00 molal HCl at 25°.

Time, hours	48	234	523	691	859	1070	1290	1644
HCl reacted, mole/l. × 10^2	4	16	30	37	40	46	50	54

(When initial molality of HCl was 1·297, and that of the ester was 0·65, 0·64 mol./l. of HCl reacted in 1260 hours.)

0·200 Molal tri-ester, 0·204 molal HBr at −11°.

Time, min.	1	2	3	7	10	20
HBr reacted, mole/l. × 10^3	170	187	193	200	202	204

0·075 Molal tri-ester, 0·10 molal HBr at −10°.

Time, min.	0·5	1	2	3	5	10	60
HBr reacted, mole/l. × 10^3	44	65	72	74	74	75	75

[In 2 min. over 97% of the HBr corresponding to the reaction $HBr + P(OR)_3 \longrightarrow RBr + PHO(OR)_2$ had disappeared, but even after 60 min., the loss of HBr did not perceptibly exceed the amount required for that reaction, even though HBr was available for further attack on the hydrogen phosphite.]

0·25 Molal di-ester, 0·502 molal HBr at 25°.

Time, hours	0·5	1	1·5	2	2·5	3·5	4·5	6	8	30	54	78	126
HBr reacted, mole/l. × 10^3	98	155	190	211	237	266	282	298	333	409	442	455	475

0·10 Molar di-ester, 0·208 molal HBr at 25°.

Time, hours	0·5	1	1·5	2	2·5	3	3·5	5
HBr reacted, mole/l. × 10^3	18	36	46	52	59	70	74	88
Time, hours	6	55	80	106	152	224	272	320
HBr reacted, mole/l. × 10^3	95	166	176	179	189	196	198	199

1·02 Molal di-ester, 0·386 molal HBr at 25°.

Time, min.	15	35	50	65	80
HBr reacted, mole/l. × 10^3	193	290	335	375	380

0·025 Molal di-ester, 0·05 molal HI at 25°.

Time, min.	20	40	60	80	100	120	140	160	180	200	220
HI reacted, mole/l. × 10^4	74	125	162	167	222	250	255	259	287	269	287

(By the time the equivalent of one alkyl group had been removed there was a serious liberation of free iodine.)

0·04 Molal di-ester, 0·08 molal HI at 25°.

Time, min.	20	40	60	80	100	120	140	160
HI reacted, mole/l. × 10^4	168	270	354	387	410	480	499	504

[When the initial molality of di-ester was 0·015, and that of HI 0·03, the molality of the latter fell to 0·015 (corresponding to one alkyl group) in 4 hours.]

Interaction of Di-n-*butyl Hydrogen Phosphite and Hydrogen Halides in the Absence of Ether.*— The ester was weighed in a vessel fitted with a tube through which the hydrogen halide could be passed. The vessel was put into a thermostat (25°) and fitted with a trap kept at −10°. The gas was passed for the time stated, and the vessel and the trap were re-weighed. The contents were mixed with water, and the halide ion was estimated by Volhard's method.

Dry hydrogen chloride was passed into 2·2545 g. of ester for 15 minutes; the gain in weight of the reaction vessel was 0·4155 g., and that of the trap, 0·0160 g. Determination of chloride ion showed the presence of 0·4225 g. of hydrogen chloride. The amount of gas absorbed, but not permanently lost, is very nearly that required by the equimolar ratio (Calc.: 0·4242 g.). The total increase in weight of 1·862 g. of ester after the gas had been passed for 6 hours was 0·3490 g., and the weight of hydrogen chloride present was, by titration, 0·3480 g. Again these weights correspond to an equimolar ratio.

It was noticed that when the gas was passed into the uncooled ester, there was a sudden rise in temperature, and the amount of heat evolved was estimated by adding a copper cylinder (5·62 g.) (at 100°) to 5·242 g. of ester in a specially constructed apparatus, the original temperature of which was 17·6°. The rise in temperature of the vessel and contents was 11·1°. Therefore the heat capacity of the vessel and ester was 3·43 cal./degree. The rise in temperature when hydrogen chloride was passed into 5·25 g. of ester was 33·6°, and this corresponds to 4260 cal./g.-mol. of ester.

Observations on the passage of dry hydrogen bromide into the ester are recorded below :

Time, min.	Wt. of ester, g.	Increase in wt. of trap, g.	Increase in wt. of vessel, g.	Wt. of HBr (by titrn.), g.	Wt. of HBr reacted, g.	Removal of one R group, %
20	0·8425	0·1205	0·4770	0·4664	0·1311	37
50	1·1610	0·0820	0·6550	0·4573	0·2797	58
85	0·7885	0·0910	0·5265	0·4083	0·2092	64

The absorption of hydrogen iodide was so quick that the rate could not be followed. The amount absorbed appeared to correspond with the removal of both butyl groups.

In order to study the interaction with hydrogen chloride over a longer period, a different technique was devised. The stated weight of the ester in a tube was saturated with hydrogen chloride, the tube was sealed, and the weight of gas absorbed determined. A number of such tubes were placed in a thermostat at 25°, and each tube was opened under a solution of silver nitrate after the stated interval of time. Chloride ion was determined by Volhard's method, and the results are recorded in the following table.

Time, days	Wt. of ester, g.	Wt. of HCl, g.	Wt. of HCl left, g.	Fraction of HCl reacted	Time, days	Wt. of ester, g.	Wt. of HCl, g.	Wt. of HCl left, g.	Fraction of HCl reacted
1	0·4965	0·0870	0·0781	0·10	11	0·5245	0·0910	0·0257	0·72
2	0·4290	0·0770	0·0610	0·21	14	0·5815	0·1020	0·0367	0·64
4	0·6605	0·1185	0·0582	0·51	21	0·6555	0·1185	0·0343	0·71
7	0·5470	0·0950	0·0354	0·63	30	0·5760	0·1010	0·0254	0·75

Isolation of the Alkyl Halides.—Hydrogen chloride (1·3555 g.) was rapidly absorbed by 4·6160 g. of the tri-ester, and this weight corresponds with almost 2 g.-mol. of the gas to 1 g.-mol. of the ester (Calc. : 1·43 g. HCl). The temperature rose rapidly to 35° despite attempts at cooling. It appears therefore that dealkylation of the first group was proceeding, and we were left with the molecular proportion of hydrogen chloride merely absorbed. After the capped absorption vessel had been at 25° for 24 hours, hydrogen chloride was again passed, but there was no further increase in weight. After a further 4 days at 25°, there was an increase in weight of 0·3280 g. when hydrogen chloride was again passed. 1-Chlorobutane (2·035 g., 39·8% yield, considering the three butyl groups), b.p. 76—78° (Found : Cl, 38·0. Calc. : Cl, 38·4%), was obtained from the reaction mixture after it had stood at 25° for a further 5 days.

In a similar way 4·609 g. of the tri-ester absorbed 4·3815 g. of hydrogen bromide during two days, and the reaction mixture separated into two layers. The top layer was soluble in water, and from the bottom layer, 1-bromobutane (5·49 g., 72%), b. p. 100—101° (Found : Br, 58·0. Calc. : Br, 58·4%), was isolated.

The amount of hydrogen iodide absorbed rapidly rose to 3 mols. for one mol. of the tri-ester. After 24 hours at 25°, the mixture had separated into two layers. From the bottom one, 1-iodobutane (4·88 g., 82·1%) (Found : I, 68·2. Calc. : I, 69·0%) was obtained.

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