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Continuous Process for Preparing Dialkyl Phosphites

A simple, cheap process is needed for commercial development of dialkyl phosphites, especially for insecticides and plasticizers. This proposed method may allow sale of these phosphites for as little as 50 cents a pound

RECENTLY, ORGANOPHOSPHORUS compounds have become increasingly important and considerable literature and patents covering them have appeared. They are versatile materials and have commercial value as, for example, insecticides, plasticizers, and flame retardants. A recent report (*6*) indicates their possibilities for future growth.

Dialkyl phosphites have been prepared by direct esterifications of phosphorous acid (*2*) and by reaction of white phosphorus with alcohols and oxygen (*10*). Usually, however, they are prepared by reaction of phosphorus trichloride and alcohols:

$$3ROH + PCl_3 \longrightarrow [(RO)_3P + 3HCl] \longrightarrow (RO)_2PHO + RCl + 2HCl$$

If cooling or solvent is not employed, hydrogen chloride degrades dialkyl phosphites at higher temperatures resulting from the exothermic reaction and significantly lowers yield:

$$\mathrm{RO)_2PHO} \xrightarrow{HCl} RCl + RO(HO)PHO \xrightarrow{HCl} (HO)_2PHO$$

This is particularly true for methyl and isopropyl esters. Therefore, the classical method of carrying out this reaction has been using low temperatures and/or solvents, and removing by-product hydrogen chloride by a current of inert gas or by evacuation, sometimes neutralizing the last traces with ammonia (*13–15*).

A continuous process (*5*) for preparing lower alkyl homologs uses evaporation of an internal coolant to remove heat of reaction and maintain a low reaction temperature. A method using liquid butane as a solvent and internal cooling agent has also been claimed (*3*). More recently a process involving a refluxing solvent for removing by-products and heat of reaction has been patented (*11*).

All these methods have the disadvantage of requiring low temperatures, a solvent, or a commercially unattractive procedure for removing hydrogen chloride. There are several indications that direct continuous reaction without solvent or cooling might be successful if sojourn time is short and heat of reaction (reaction temperature) is not too high.

For example, degradation rate of diisopropyl (*4*) and dibutyl (*12*) phosphites by hydrogen chloride is rapid but definitely finite and controllable. Hydrogen chloride can be stripped from dialkyl phosphites in systems under reduced pressure if temperature is increased gradually as concentration of hydrogen chloride is decreased and dialkyl phosphites can be successfully prepared in refluxing solvents. Such a direct, continuous reaction process has now been developed.

Briefly, this process consists of permitting the reagents to react in a spray nozzle, cooling the reaction product stream in the case of lower homologs, and removing low-boiling by-products from the liquid reaction product with a packed column stripper operated under reduced pressure. The process is autothermic—the reaction temperature is allowed to seek its own level and the heat of reaction is removed as latent and specific heat by the reaction products.

Under these reaction conditions, short exposure to hydrogen chloride at elevated temperature does not significantly decompose the dialkyl phosphite product; much heat of reaction and about two thirds of the hydrogen chloride are removed automatically. Because the liquid reaction-product stream is at elevated temperatures and still contains significant amounts of hydrogen chloride, decomposition following reaction must be avoided. This can be done by minimizing the holdup time between reaction and stripping, and for esters below butyl, by cooling the stream. Incorporating the reactor nozzle into the stripping column should be possible, but this

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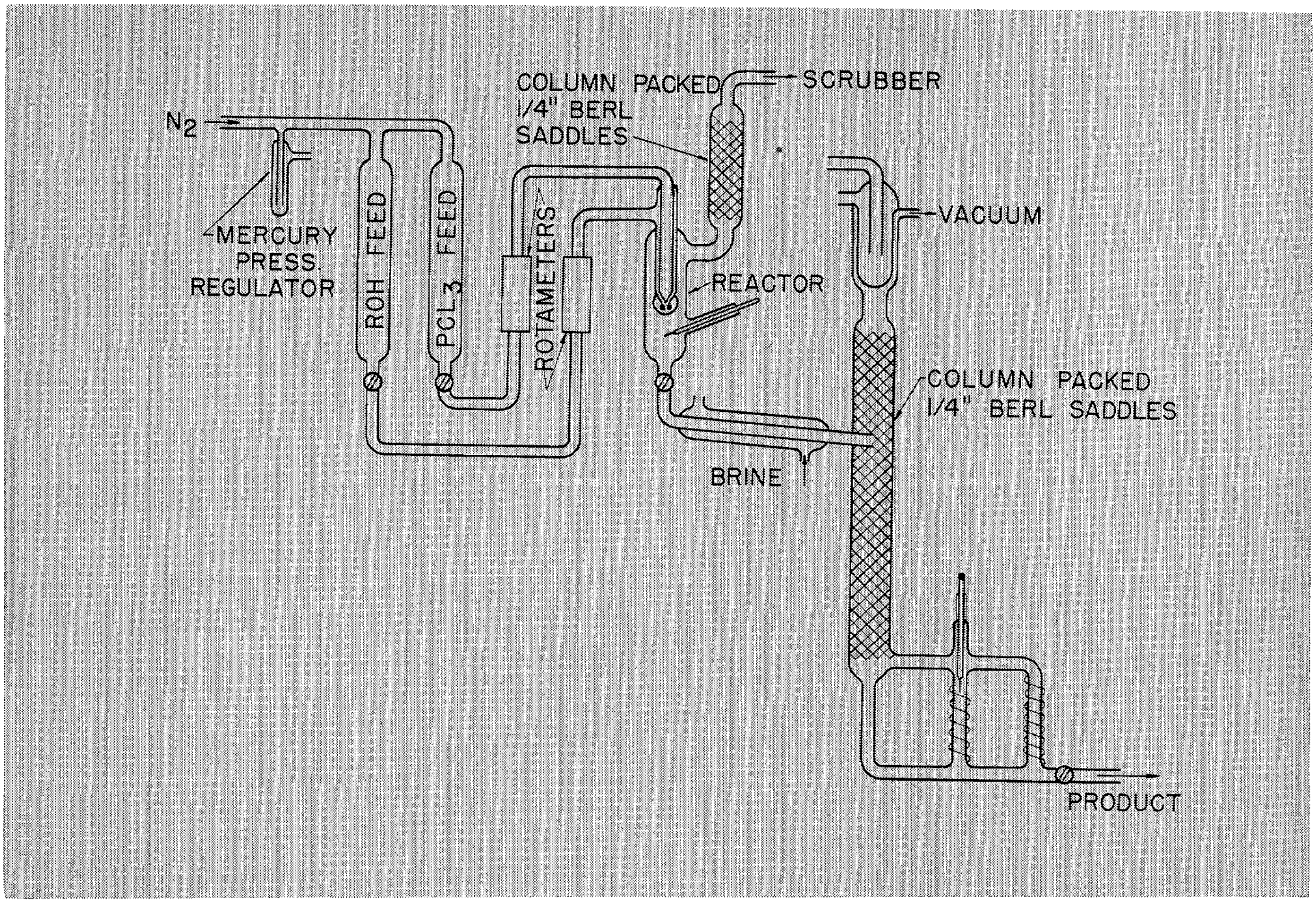

This laboratory apparatus was used for continuously preparing dialkyl phosphites in yields up to 98.5%

would greatly increase vapor load on the evacuating system.

Thus, the process presented here has three advantages—it is continuous, it requires no solvent, which permits greater capacity and easier recovery of by-product alkyl halide, and it minimizes or eliminates cooling. Products of high purity are obtained in good yield with relatively simple equipment.

Apparatus and Procedure

The feed system in the apparatus used consisted of two 1-liter burets under nitrogen pressure, which served as reservoirs for the reactants, and two rotameters to measure feed rates. All stopcocks in the feed lines were of the Teflon-coated, pressure type. The reactor consisted of a spray enclosed in a 40-mm. × 8-inch tube. The spray was constructed of 10-mm. glass tubing drawn to a 2-mm. opening at the tip with a 6-mm. tube similarly drawn and inserted concentrically. The tip of the feed tube was enclosed in a sparger-type envelope. A 50-mm. × 20-inch column packed with $^1/_4$-inch Berl saddles was used as an entrainment separator for the off-gas. A similar column, 36 inches long with a small thermosyphon reboiler, served as a stripper.

Procedure for all runs was basically the same. The reactants, phosphorus trichloride and alcohol, were fed to the reactor from the burets under slight positive nitrogen pressure. Feed rates were controlled both by rotameters and by periodically noting reactant level in the feed burets. Total reactants fed were calculated from specific gravities. The reactor was operated at atmospheric pressure and vented to a scrubbing tower to dispose of hydrogen chloride off-gas.

Liquid reaction products were removed from the reactor at a rate which maintained the minimum liquid level necessary for a seal in the take-off line. The crude product was then fed through a brine-cooled (about 0° C.) condenser to the stripper in those runs where the alcohol contained less than four carbon atoms, but was not cooled when higher molecular weight alcohols were used. During start-up, temperature of the reboiler was gradually increased until enough product had accumulated to reach equilibrium conditions, and the stripped product then removed continuously. The stripped product was batch distilled at reduced pressure through a column 12 inches long and packed with $^1/_4$-inch glass helices.

Results and Discussion

A summary of run data showing operating conditions and results obtained is given in Table I. Yields are good in most cases, but optimum conditions were not established for each product—this work was intended to demonstrate scope of the process rather than find the best conditions for any particular phosphite.

In general, these reactions proceeded smoothly. For dicyclohexyl phosphite, known to be unstable (*7*), the crude product could not be distilled in vacuo without decomposition. Increasing the number of carbon atoms tended to increase the reaction temperature slightly to a maximum at eight carbon atoms (Table I). Further increase in the molecular weight of the alcohol decreased reaction temperature. An increase in temperature with increasing carbon content of the alcohol was expected because of vaporization of less by-product alkyl halide. Decrease in reaction temperature with high molecular weight alcohols is probably caused by increased weight of alcohol fed to the reactor for the same number of moles.

Stripper pressure does not seem critical; however, it is believed that an optimum value of about 10 mm. of mercury should be maintained. Lower pressures cause excessive loss of product as vapor while higher pressures cause

Table I. Continuous Preparation of Dialkyl Phosphites

Run No.	Alcohol	G.	PCl_3, G.	Mole Ratio, ROH/ PCl_3	Duration of Run, Min.	Temp., ° C. Reactor	Temp., ° C. Stripper head	Temp., ° C. Reboiler	Stripper Pressure, Mm.	Crude Product, G.	Distilled Product, G.	% Yield, PCl_3 Basis	Product Analysis, % P Found	Product Analysis, % P Calcd.
1	Methyl	522	656	3.4	92	64–72	25–26	40–65	7–10	450.7	360.0	68.5	[a]	28.18
2		503	515	4.2	90	65–75	27–28	83–92	40–45	409.6	355.4	86.2	[a]	28.18
3		780	1070	3.1	193	64–85	20–25	63–69	10–12	733.4	663.0	77.4	[a]	28.18
4	Ethyl	1692	1297	3.8	240	74–79	23–24	49–83	10–18	1283.4	1232.8	95.0	22.36	22.42
5	Isopropyl	580	414	3.2	75		23–25	22–94	8–15	480	466	93.4	18.51	18.66
6		647	456	3.2	77	58–72	22–27	49–94	19	522.8	518.2	94.1	18.67	18.66
7		546	409	3.0	75	76–79	19–22	74–86	11–14	491.8	474.5	96.0	18.59	18.66
8		557	402	3.2	76	79–83	23–46	30–90	8–11	434.1	409	88.6	18.46	18.66
9		480	414	2.65	75	78–81	21–64	22–100	10–16	442	409	86.2	18.53	18.66
10		1120	815	3.2	150	81–83	23–50	22–91	10–12	945.3	904	92.6	18.61	18.66
11		700	468	3.4	75	74–80	19–21	83–90	11–13	546.9	529.4	93.4	18.72	18.66
12	*n*-Butyl	1190	655	3.3	120	82–87	19–25	108–113	12–16	967.0	881.0	95.4	15.89	15.95
13	1-Methylbutyl	662	356	2.9	79	82–93	23–24	83–118	7–8	538.5	376	65.0[b]	13.78	14.00
14	*n*-Hexyl	1400	490	3.8	130	90–93	28–47	92–165	10–13	1049.7	878.0	98.5	12.29	12.35
15	*n*-Octyl	1291	461	2.9	90	90–99	17–55	117–167	6–7	1187.0	924.8	90.5	10.05	10.01
16	2-Ethylhexyl	1250	448	2.9	74	98–107	19–41	119–145	6–7	1026.0	858.5	85.0	9.90	10.01
17	2-Butyloctyl	1050	258	3.0	50	80–94	62–101	114–220	6–23	928.5	637	82.0[c]	6.71	7.35
18	Tridecyl	670	154	3.0	75	65–82	42–83	70–200	7–8	627.0	348	68.0[d]	6.51	6.93
19	Cyclohexyl	899	521	2.5	101	73–84	21–26	97–182	8–18	490.0[e]				12.55
20		1535	667	3.2	135	78–83	23–25	79–125	7–10	1237.1				12.55
21		825	344	3.3	85	77–83	23–25	17–22	7–8	755.5				12.55
22		553	236	3.2	97	73–82	22–39	74–172	6–8	314.1		69.5	13.78[f]	12.55
23		520	222	3.2	100	73–78	22–39	65–182	7–9	239.5				12.55

[a] Checked by index of refraction.
[b] Low yield probably caused by incomplete stripping; crude analyzed 4.1% Cl^-. Phosphite distilled at 91–3° C. at 1 mm.
[c] Phosphite distilled at 215–20° C. at 1 mm.
[d] Enjay commercial oxo alcohol used. Phosphite distilled at 231–37° C. at 1 mm.
[e] Product decomposed on distillation.
[f] Analysis of crude stripped product.

product decomposition by elevation of temperature. Effectiveness of the stripper was indicated by a decrease in hydrogen chloride content from about 12 to 14% in the crude reaction mixture entering the stripper to 0.1 to 0.2% in the stripped products. In most cases, the stripped product was of high purity, yielding up to 97.5% of the crude as distilled product.

A slight excess of alcohol should be employed to ensure that localized excesses of phosphorus trichloride do not occur. A significant excess of phosphorus trichloride usually decreases yield, and sometimes causes decomposition evidenced by a yellow precipitate.

Decreased yields were obtained when the stripped product was allowed to reflux above the point of entry for the crude reaction product into the stripper column. The lowered yield in run 8 illustrates this effect. Loss in yield accompanying a high stripper head temperature may be attributed to increased degradation rate of product by hydrogen chloride at elevated temperatures (*4*). To maintain a low stripper head temperature when preparing lower homologs, crude reaction products were cooled before feeding to the stripper column.

Thermochemical data are being developed for organophosphorus compounds (*7*, *8*, *16*); but none is available either on, or for calculating a reliable heat of reaction for direct combination of alcohols and phosphorus trichloride to form dialkyl phosphites. Therefore, approximate thermochemical data were obtained for diisopropyl phosphite.

A Dewar flask calorimeter of the type described by Daniels, Mathews, and Williams (*9*) was employed. Heat of reaction for phosphorus trichloride and isopropyl alcohol was determined using a large excess of isopropyl alcohol as solvent, and the heat of solution for hydrogen chloride in isopropyl alcohol was determined at a comparable concentration. Heat of solution of hydrogen chloride in diisopropyl phosphite was determined at a concentration of about 0.5%; in these calculations, this value involves a slight error because the liquid reaction-product stream contained about 12% hydrogen chloride; accuracy, however, is adequate for the purpose at hand.

All determinations were made at 25° to 30° C. Duplicate values varied by 0.5 to 0.7 kcal. per mole. Slightly lower values (40 and 14.8 compared to 42 and 16.2, respectively) were observed for heats of reaction and of solution for hydrogen chloride in isopropyl alcohol when the commercial alcohol containing 1.5% water was dried to 0.04%.

Thermochemical Data

Heat of reaction, PCl_3 in large excess of iso-C_3H_7OH	**42.0 kcal./mole**
Heat of solution, HCl in	
iso-C_3H_7OH	**16.25 kcal./mole**
(iso-$C_3H_7O)_2PHO$	**10.7 kcal./mole**
Specific heat, (iso-$C_3H_7O)_2PHO$	**0.450 cal./° C.**

Using these values, heat of reaction may be estimated to conditions of the autothermic spray process. In the latter, as compared to conditions for determining heat of reaction, there will be no heat of solution for hydrogen chloride in isopropanol; but based on a 12% chloride content in the crude liquid reaction-mixture stream, there will be a heat of solution for $^2/_3$ mole of hydrogen chloride in diisopropyl phosphite; complete vaporization (6.3 kcal.) of by-prod-

Table II. Corrosion Tests

	Test Conditions						
Test Material	Medium	Temp., ° C.	Duration of Test, Hours	Weight Loss, G.	Penetration[a], Mils/Yr.	Specimen Appearance	Appearance of Media after Cooling
Hastelloy B, welded	**Reaction mixture**	25	455	0.0024	0.11	No visible corrosion	No change
SS 316, welded		25	474	3.7478	266.0	Attack on weld, serious intergranular corrosion	Black
SS 316, welded		100	475	0.0350	3.0	Weld visible, stained	Evaporated to grey-brown solid
Hastelloy B, welded		100	475	0.0386	7.1	Weld visible, etched corrosion	Evaporated to grey-brown solid
SS 316	**Crude DIPHP**	25	452	0.0012	<0.1	No visible corrosion	No change
SS 304, welded		25	452	0.0943	7.0	Stains, pits, intergranular corrosion; most corrosion due to vapor	Slightly green
Carbon steel, welded		25	452	1.4888	94.0	Serious corrosion; pits	Yellow-white solid present
Hastelloy B		100	475	0.0031	0.14	No visible corrosion	Amber solution
SS 316		100	452	0.0052	0.31	Upper, pitted; lower, stained; most corrosion due to vapor	Amber solution
SS 316, welded	**Distillation residue**	25	260	0	<0.1	Very slightly stained	No change
Hastelloy B, welded		100	259	0.0005	<0.1	Stained	Light brown solid
SS 316, welded		100	259	0.0052	0.68	Stained and light corrosion; most corrosion due to vapor	No change

[a] Calculated on the area showing the greatest attack; immersed area unless otherwise noted.

uct isopropyl chloride is assumed. Thus, $42.0-2\ (16.25)+{}^{2}/_{3}\ (10.7)-6.3=10.3$ kcal. per mole is the net heat of reaction under conditions of the autothermic process.

Heat of reaction may also be estimated from the observed operating temperature (about 85° C.) of the spray reactor and the specific heats of reactants and products. Thus,

$$3C_3H_7OH(l)\ 25^\circ + PCl_3(l)\ 25^\circ \longrightarrow (C_3H_7O)_2PHO(l)\ 85^\circ + C_3H_7Cl(g)\ 85^\circ + 2HCl(g)\ 85^\circ$$

gives 8.9 kcal. per mole based on reactants, or 11.9 kcal. per mole based on products, using specific heats of 0.67 calorie per mole for isopropyl alcohol, 0.20 for phosphorus trichloride, 0.45 for diisopropyl phosphite, 0.40 and 0.20 for isopropyl chloride liquid and gas, respectively, and 0.20 for hydrogen chloride.

These values are, of course, estimates. That calculated on the basis of reactants should be corrected for excess alcohol fed and that calculated from products should be corrected for the heat of solution for hydrogen chloride in the reaction product and incomplete volatilization of isopropyl chloride. The values do, however, substantiate that calculated from the experimental thermochemical data.

As materials of construction will be of concern with this as well as with any other process for dialkyl phosphites due to the presence of phosphorus trichloride, hydrogen chloride, and acids of phosphorus, preliminary corrosion test data were determined.

Several metals were evaluated by static immersion tests at room temperature and at 100° C. in samples of the process streams taken from diisopropyl phosphite runs—the reaction mixture prior to stripping, crude product as obtained from the stripper, and the distillation residue from batch distillation of crude phosphite. Test strips about 1 × 2 × $^{1}/_{4}$ inches with a hole $^{1}/_{4}$ inch in diameter were hung from glass hooks in such a way that they were approximately one half immersed in the liquid test medium. The samples tested at 100° C. were placed in an oil bath controlled to ±2° C. The containers were vented through a glass tube drawn to a capillary tip. Penetration rates were calculated on the basis of the most corroded area, which in several instances was the portion of the test piece exposed to vapor rather than the immersed area.

The data are shown in Table II. In the absence of localized attack, a penetration rate of less than 10 mils per year is considered satisfactory for most applications. Because of the loss of hydrogen chloride by volatilization and by reaction with the phosphite in the tests in reaction mixture at 100° C., the results only confirm the highly corrosive nature of the stream, and suggest the use of glass-lined construction for the reactor and stripping column. The much lower penetration rates observed in crude phosphite and in still residue attest to the efficiency of the stripping operation in removing hydrogen chloride without undue formation of acids of phosphorus. The applicability of metal construction for the stripper reboiler, where good heat transfer is desirable, and in the still is indicated.

Conclusions

Dialkyl phosphites may be prepared in yields up to 98.5% of theory by the autothermic process described.

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Literature Cited

(1) Arbuzov, A. E., Valitova, F. G., *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* **1952**, p. 801–8.
(2) Baker, A. A., Brown, J. H. (to Oldbury Electro-Chemical Co.), U. S. Patent **2,670,368** (Feb. 23, 1954).
(3) Bloch, H. S. (to Universal Oil Products Co.), *Ibid.*, **2,570,512** (Oct. 9, 1951).
(4) Campbell, C. H., Chadwick, D. H., *J. Am. Chem. Soc.* *77*, 3379 (1955).
(5) Chadwick, D. H. (to Monsanto Chemical Co.), U. S. Patent **2,661,364** (Jan. 15, 1952).
(6) *Chem. Eng.* **60**, No. 3, 126 (1953).
(7) Chernick, C. L., Skinner, H. A., *J. Chem. Soc.* **1956**, p. 1401.
(8) Chernick, C. L., Skinner, H. A., Mortimer, C. T., *Ibid.*, **1955**, p. 3936.
(9) Daniels, F., Mathews, J. H., Williams, J. W., "Experimental Physical Chemistry," 3rd ed., pp. 103–11, 344–5, McGraw-Hill, New York, 1941.
(10) Ernsberger, M. L., Hill, J. W. (to E. I. du Pont de Nemours & Co.), U. S. Patent **2,661,364** (Dec. 1, 1953).
(11) Gann, P. H., Heider, R. L. (to Monsanto Chemical Co.), *Ibid.*, **2,692,890** (Oct. 26, 1954).
(12) Gerrard, W., Whitbread, E. G. G., *J. Chem. Soc.* **1952**, p. 914.
(13) Hardy, E. E., Kosolapoff, G. M. (to Monsanto Chemical Co.), U. S. Patent **2,409,039** (Oct. 8, 1946).
(14) Kosolapoff, G. M., "Organophosphorus Compounds," p. 182, Wiley, New York, 1950.
(15) McCombie, H., Saunders, B. C., Stacey, G. J., *J. Chem. Soc.* **1945**, p. 380.
(16) Neale, E., Williams, L. T. D., *Ibid.*, **1954**, p. 2156; **1955**, p. 2485.

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