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Diarsenic Trioxide for Substituting Bridging Oxygen for Chlorine in Phosphorus Chlorides

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A preferential exchange of chlorines and bridging oxygens between phosphorus(III and V) chlorides and diarsenic trioxide was studied by adding diarsenic trioxide into phosphorus chlorides and then heating the mixtures at 50—60 °C with vigorous stirring under dried nitrogen (phosphorus(III) chlorides) or dried air (phosphorus(V) chlorides). ^{31}P NMR study showed that the exchange of chlorines and oxygens occurred between diarsenic trioxide and phosphorus trichloride, phosphoryl chloride, diethylphosphinic chloride, tetramethylphosphorodiamidic chloride, or diethylphosphinothioic chloride and that P–O–P bonds were formed in the products.

Diphosphorus trioxide is conventionally prepared by burning phosphorus under a reduced supply of oxygen. It is not easy to obtain pure diphosphorus trioxide by this method. One of us (J. R. Van Wazer) has pointed out the possibility of the exchange reaction of oxygen and halogen atoms for several pairs of different atoms. Among these exchange reactions, the enthalpy of the exchange between P–Cl and As–O bonds is the largest one, about 75 kJ/bond.[1] Therefore, we studied the exchange of oxygen and chlorine between diarsenic trioxide and several phosphorus(III and V) chlorides to investigate the formation of the P–O–P bond from the P–Cl bond.

Experimental

Materials. The diarsenic trioxide used in this study was purchased from J. T. Baker Chemical Co. and was ground for about 30 min by a miller, MIXER/MILL, made by Spex Co. Phosphorus trichloride, phosphoryl chloride, and carbon disulfide were Fisher Scientific Co. reagent grade. Phosphorus trichloride and phosphoryl chloride were distilled. Carbon disulfide was dried with calcium chloride and then distilled. Phenylphosphorous dichloride, diethylphosphinic chloride, diphenyl phosphorochloridate, tetramethylphosphorodiamidic chloride, and dimethylphosphinothioic chloride were purchased from Aldrich Chemical Co. and were used without any other purification. They were checked by ^{31}P NMR and gave the correct spectra.

^{31}P NMR Measurement. ^{31}P NMR measurements were carried out on Varian XL-100 spectrometer at 40.48 MHz. The chemical shifts in the phosphorus spectra are reported with respect to 85% phosphoric acid. In all cases, positive shifts were measured upfield.

Procedure. Diarsenic trioxide was added into a large excess of phosphorus(III) chloride in a three-necked round bottom flask under a stream of dried nitrogen. The mixtures were heated at 50—60 °C with vigorous stirring by using a hot-plate magnetic stirrer. The reaction mixtures were withdrawn at hourly intervals and analyzed for phosphorus compounds by the ^{31}P NMR instrument without any other solvent. The mixtures of diarsenic trioxide and a large excess of phosphorus(V) chloride were also reacted under dried air at 50—60 °C in the same way as that of the reaction of phosphorus(III) chloride. The progress of the reaction of the mixtures was checked by the same way as used for the reactions of phosphorus(III) chloride. The ^{31}P NMR analysis of the solid product in the system of phosphoryl chloride and diarsenic trioxide was also made by dissolving it in cold water.

Results and Discussion

As_2O_3–PCl_3 System. Typical NMR spectra of the reaction mixture are shown in Fig. 1. In the early stage of the reaction, the mixture gave a peak of PCl_3 at −220 ppm and unknown peaks at −183 and −193 ppm. The peak height of these unknown peaks did not change much with the passage of reaction time. Finally, the mixture gave a narrow peak of diphosphorus trioxide at −113 ppm and an unknown peak at −133 ppm. The intensity of these peaks increased as the reaction proceeded. The peak height of diphosphorus trioxide had a maximum; after

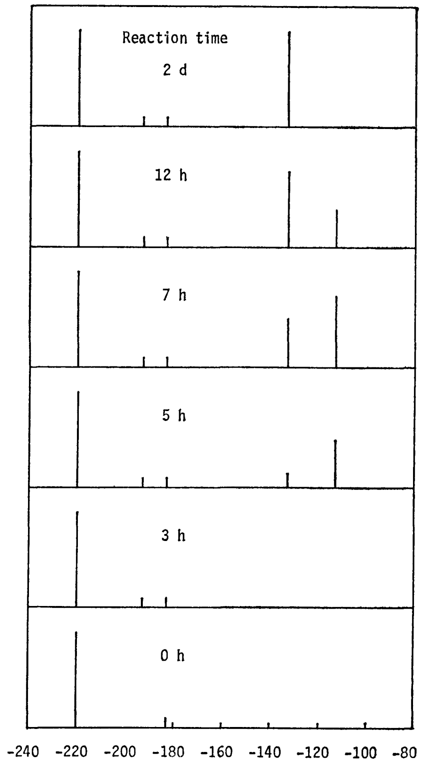


Fig. 1. ^{31}P NMR spectra of the reaction mixture of the As_2O_3–PCl_3 system.

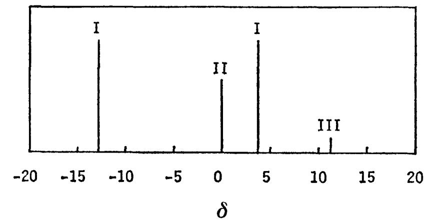


Fig. 2. ^{31}P NMR spectrum of the aqueous solution of the solid product of the As_2O_3–PCl_3 system.
I: Phosphonic acid, II: orthophosphoric acid, III: diphosphoric acid.

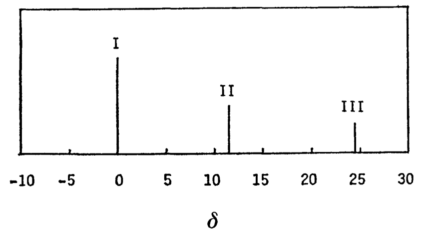


Fig. 3. ^{31}P NMR spectrum of the aqueous solution of the solid product of the As_2O_3–$POCl_3$ system.
I: Orthophosphoric acid, II: diphosphoric acid, III: *cyclo*-tetraphosphoric acid.

the maximum, it decreased gradually and finally disappeared. At this step of the reaction, the mixture gave a peak of phosphorus trichloride and unknown peaks at −133, −183, and −193 ppm. It was necessary to stir the reaction mixture vigorously to increase the rate of reaction. If the reaction mixture was stirred gently, it would take a much longer time to finish the reaction. When the reaction was stopped at the stage of maximum height of the ^{31}P NMR peak corresponding to diphosphorus trioxide, the reaction mixture contained a white precipitate. This precipitate was separated from the phosphorus trichloride solution by filtration and washed with phosphorus trichloride in a dry bag under nitrogen. Diphosphorus trioxide was obtained by a reduced distillation (667 Pa, 40 °C) of the phosphorus trichloride solution by using a trap cooled by Dry Ice–methanol; it had a melting point of around 23 °C and gave a narrow sharp ^{31}P NMR peak at −113 ppm. The yield of diphosphorus trioxide was about 35% relative to the amount of diarsenic trioxide used in this experiment. The liquid product in the trap gave boiling points of 75 and 130 °C at atmospheric pressure. The compound with a boiling point of 75 °C is unreacted phosphorus trichloride and that with a boiling point of 130 °C is arsenic trichloride. When the white precipitate was dissolved in cold water, a reddish brown precipitate was produced. The precipitate was filtered; the ^{31}P NMR spectrum of the filtrate is shown in Fig. 2. These peaks are due to phosphonic acid and ortho- and diphosphoric acids. The reddish brown precipitate was soluble in nitric acid and the solution gave the peak of phosphoric acid. So it could be concluded that the reddish brown precipitate is red phosphorus containing some phosphorus suboxides. Accordingly, the white precipitate mentioned above must be diphosphorus tetraoxide. Diphosphorus trioxide is oxidized very easily with oxygen, and the produced diphosphorus trioxide seems to be oxidized by slight amounts of oxygen in the reaction apparatus. It was difficult to prevent oxidation in the reaction apparatus used in this experiment. According to above results, one can write the following chemical equation for this reaction system:

$$\begin{tikzcd} 4PCl_3 + 2As_2O_3 \arrow[r, "(N_2)"] & P_4O_6 + 4AsCl_3. \arrow[d, "(O_2)"'] \\ & P_4O_8 \end{tikzcd}$$

Diphosphorus trioxide was extracted from diphosphorus tetraoxide with carbon disulfide by mixing the tetraoxide with carbon disulfide and stirring the mixture under nitrogen. It took a long time to extract (a few days). The peak at −133 ppm seems to be due to diphosphorus trioxide, since one peak of diphosphorus trioxide shifts easily from −113 ppm to −133 ppm in arsenic trichloride. Diphosphorus trioxide gives the same peak at −133 ppm in phosphorus trichloride and the change is very slow.[2)]

As_2O_3–$C_6H_5PCl_2$ System. The reaction mixture was brown in the initial stage of the reaction. The reaction mixture did not give any peak other than that of phenylphosphonous dichloride. The reaction was stopped at the reaction time of 15 h and the brownish solid product was separated by filtration. The solid product was insoluble in any solvent, so it was impossible to study the phosphorus compounds contained in the solid product by the ^{31}P NMR instrument.

As_2O_3–$POCl_3$ System. The reaction mixture did not show any ^{31}P NMR spectrum other than that of phosphoryl chloride at any reaction time. At the reaction time of 50 h, the reaction mixture was cooled and the ashy solid product was filtered in a dry bag. The solid product was insoluble in any solvent. When the product was dissolved in water, the aqueous solution gave the spectrum shown in Fig. 3. The aqueous solution of diphosphorus pentaoxide gives the same spectrum and diphosphorus pentaoxide is insoluble in any solvent. So the ashy solid product must be diphosphorus pentaoxide. The liquid part of the reaction mixture was distilled at atmospheric pressure. It gave products with boiling points of 108 and 130 °C; these are unreacted phosphoryl chloride and arsenic trichloride. Therefore, the following equation can be written for this reaction system:

$$4POCl_3 + 2As_2O_3 \longrightarrow P_4O_{10} + 4AsCl_3.$$

As_2O_3–$(C_2H_5)_2POCl$ System. Diarsenic trioxide was soluble in diethylphosphinic chloride. The dissolution reaction is highly exothermic. So diarsenic trioxide was added carefully to diethylphosphinic chloride; the temperature of the mixture did not go beyond 60 °C. About 3 g of diarsenic trioxide was dissolved completely in 12 cm^3 of diethylphosphinic chloride. The reaction system seemed to reach equilibrium in less than 1 h, because the ^{31}P NMR spectrum of the reaction mixture gave the same spectrum at any reaction time longer than 1 h. The ^{31}P NMR spectrum

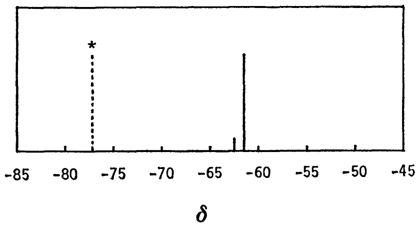


Fig. 4. Proton decoupled ^{31}P NMR spectrum of the reaction mixture of the As_2O_3–$(C_2H_5)_2POCl$ system at a reaction time of 1 h.
*: Diethylphosphinic chloride.

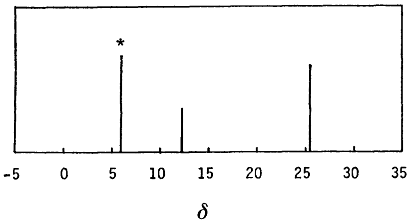


Fig. 5. ^{31}P NMR spectrum of the reaction mixture of the As_2O_3–$(C_6H_5O)_2POCl$ system at a reaction time of 15 h.
*: Diphenyl phosphorochloridate.

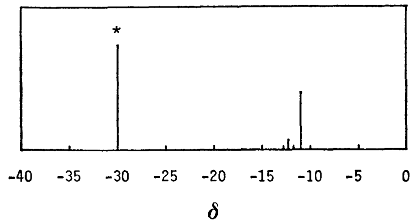


Fig. 6. Proton decoupled ^{31}P NMR spectrum of the reaction mixture of the As_2O_3–$[(CH_3)_2N]_2POCl$ system at a reaction time of 18 h.
*: Tetramethylphosphorodiamidic chloride.

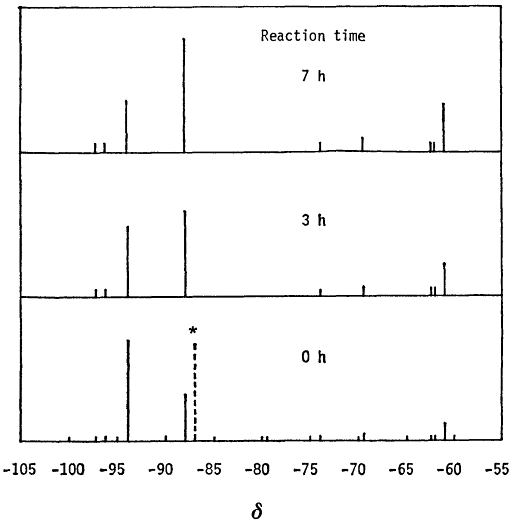


Fig. 7. Proton decoupled ^{31}P NMR spectrum of the reaction mixture of the As_2O_3–$(CH_3)_2PSCl$ system.
*: Dimethylphosphinothioic chloride.

of the reaction mixture at the reaction time of 1 h is shown in Fig. 4. The mixture gave a strong peak at −61.5 ppm. This peak seems to be due to diethylphosphinic anhydride, $(C_2H_5)_2\overset{O}{P}O\overset{O}{P}(C_2H_5)_2$. There are no ^{31}P NMR data about diethylphosphinic anhydride, but P(α) of $(C_2H_5)_2\underset{\alpha}{\overset{O}{P}}O\underset{\beta}{\overset{S}{P}}(C_2H_5)_2$ gives a ^{31}P NMR peak at −60 ppm.[3] Accordingly, a preferential exchange of oxygen and chlorine between diarsenic trioxide and diethylphosphinic chloride seems to take place in this reaction system. Another new peak at −62.5 ppm could not be identified. Arsenic trichloride was not obtained by distillation of the reaction mixture.

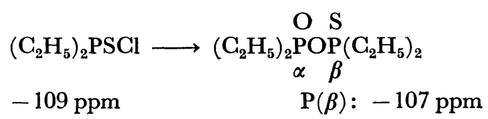
As_2O_3–$(C_6H_5O)_2POCl$ System. Diarsenic trioxide does not dissolve in diphenyl phosphorochloridate. As is shown in Fig. 5, the reaction mixture gave two new peaks at 12.2 and 25.6 ppm other than that of diphenyl phosphorochloridate. The intensity of the new peaks increased with reaction time. Tetraphenyl diphosphate, $(C_6H_5O)_2\overset{O}{P}O\overset{O}{P}(C_6H_5O)_2$, gives a ^{31}P NMR peak at 23.3 ppm,[3] so the new peaks do not come from tetraphenyl diphosphate. There are no ^{31}P NMR data for these new peaks.

As_2O_3–$[(CH_3)_2N]_2POCl$ System. Diarsenic trioxide did not dissolve in tetramethylphosphorodiamidic chloride. The reaction mixture gradually changed into an ashy color with the elapse of reaction time. The ^{31}P NMR spectrum of the reaction mixture is shown in Fig. 6 and a strong new peak appears at −11 ppm. The height of the new peak increased as the reaction proceeded. The data listed in Ref. 3 show that octamethyldiphosphoramide, $[(CH_3)_2N]_2\overset{O}{P}O\overset{O}{P}[(CH_3)_2N]_2$, gives a ^{31}P NMR peak at −11 ppm. It can be concluded that the exchange of oxygen and chlorine between diarsenic trioxide and tetramethylphosphorodiamidic chloride occurs in this reaction system. We could not find from where the other weak new peaks come. Arsenic trichloride was not obtained by distillation of the reaction mixture.

As_2O_3–$(CH_3)_2PSCl$ System. Diarsenic trioxide dissolves in dimethylphosphinothioic chloride and the reaction is highly exothermic. Diarsenic trioxide was added into dimethylphosphinothioic chloride so slowly that the temperature of the mixture did not go beyond 60 °C. As is shown in Fig. 7, just after mixing, the mixture gave two strong new peaks at −94 and −88 ppm and several weak peaks in the region below −95 ppm and the region between −61 and −80 ppm. The peak at −94 ppm decreased and the peak at −88 ppm increased as the reaction proceeded. There are no ^{31}P NMR data about dimethylphosphinothioic anhydride, but the data in Ref. 3 give these results:

$$\underset{-79.5\text{ ppm}}{(C_6H_5)_2PSCl} \longrightarrow \underset{-79.3\text{ ppm}}{(C_6H_5)_2\overset{S}{P}O\overset{S}{P}(C_6H_5)_2}$$

$$\underset{-98\text{ ppm}}{(CH_3)(C_2H_5)PSCl} \longrightarrow \underset{P(\beta):\ -98.1\text{ ppm}}{(CH_3)(C_2H_6)\underset{\alpha}{\overset{O}{P}}O\underset{\beta}{\overset{S}{P}}(CH_3)(C_2H_5)}$$



$$(C_2H_5)_2PSCl \longrightarrow (C_2H_5)_2\overset{O}{\underset{\alpha}{P}}O\overset{S}{\underset{\beta}{P}}(C_2H_5)_2$$

-109 ppm　　P(β): -107 ppm

The result of this reaction system is

$$(CH_3)_2PSCl \longrightarrow \text{Product.}$$

-87 ppm　　-88 ppm

The new peak at -88 ppm may come from dimethylphosphinothioic anhydride, $(CH_3)_2\overset{S}{P}O\overset{S}{P}(CH_3)_2$. The other new peaks could not be identified. Arsenic trichloride was not obtained by distillation of the reaction mixture.

References

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