Principles of Phosphorus Chemistry. XII. Isolated Oxygen–Sulfur Interchange Reactions

By Leo C. D. Groenweghe and John H. Payne

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Experiments have shown that sulfur and oxygen atoms bonded only to a single phosphorus atom will exchange between phosphorus compounds which have a total of four atoms directly attached to each phosphorus. The temperature and time required for this type of reorganization are comparable with those for exchange of halogens and alkoxy groups. Deviations from a completely random exchange are discussed in terms of electronegativities. Methods are described for making methylchloromethylphosphinic chloride, methylchloromethylthionophosphinic chloride and chloromethylthionophosphonic dichloride.

Work reported in five previous papers[1-3] of this series showed that compounds with two or more different monofunctional substituents, such as Cl, Br or OR groups, directly connected to the phosphorus atom can reorganize to give mixtures of phosphorus compounds. This reorganization is characterized by the fact that the substituents become more or less randomly distributed between the phosphorus atoms. This paper is concerned with the reorganization of sulfur and oxygen when these atoms are bonded only to the phosphorus atom in the "isolated" position (e.g., not forming a bridge between phosphorus atoms or between a phosphorus atom and another atom).

Experimental Section

The phosphorus oxychloride used in these experiments was redistilled from the Monsanto Commercial-grade product. The phosphorus oxybromide was purchased. The thiophosphoryl chloride was made from phosphorus trichloride and sulfur according to the method of Inorganic Syntheses.[4] Phenylthionophosphonic dichloride, $C_6H_5P(S)Cl_2$, was a commercial-grade product made by Eastman Kodak Chemical Company. Chloromethylphosphonic dichloride, $CH_2ClP(O)Cl_2$, was made by Monsanto Chemical Company on a pilot-plant scale and was redistilled before use. Methylthionophosphonic dichloride, $CH_3P(S)Cl_2$, and methylchloromethylphosphinic chloride, $CH_3(CH_2Cl)P(O)Cl$, were made in the laboratory. The former compound distilled at 67–70° and 50 mm. pressure, and the latter at 79–82° at 1 mm. All compounds were found to be better than 99% pure as analyzed by nuclear magnetic resonance (n.m.r.), except the phosphorus oxybromide, in which about 5% of phosphorus tribromide was detected. Since this was a relatively small amount of impurity which could be accounted for in our studies, the sample was used without further purification.[1]

Reorganization was carried out by weighing the desired proportions of two reagents (one with an "isolated" oxygen and the other with an "isolated" sulfur) and thoroughly mixing them. They were sealed in thick-walled Pyrex® tubes which were enclosed in short sections of iron pipe and heated in a furnace at 150 or 230°.

Preliminary tests indicated that equilibrium must be achieved within a few hours for mixtures heated at 230° and in about a day for mixtures heated at 150°. After the samples had been kept in the oven for 65 hr., the iron pipes containing them were taken out and allowed to cool in air before the glass tubes were removed. The samples then were analyzed and, after a second 65-hr. heating period, they were analyzed again. Several samples were heated for a third time at the same temperature and then cooled rapidly to room temperature in less than five minutes, and they were again analyzed. Since, in each case, all the analyses agreed, it can be concluded that the results obtained represent equilibrium values.

The quantitative analyses were performed by n.m.r. The P^{31} spectra were obtained by utilizing the intermediate-passage absorption-mode presentation. A Varian high-resolution spectrometer, Model No. V-4300B, was used with a 16.2 mc. radio frequency and a magnetic field of about 9395 gauss (Varian magnet Model No. V-4012-HR). The chemical shifts of the resonance peaks were determined by the tube-interchange technique and are reported in p.p.m. of the applied magnetic field using 85% H_3PO_4 as a standard (zero shift). Upfield shifts are denoted by a plus sign and downfield shifts by a minus sign.

The technique used for quantitative n.m.r. measurements is described in Paper V of this series.[1] However, it was found that it was not necessary to apply the correction for sweep non-linearity. This simplification was possible because the correction is appreciable only when the resonances of the compounds analyzed occur over large magnetic field shifts, such as 150 p.p.m., and in the only experiment where this is the case ($POBr_3 + PSCl_3$), the areas of the extreme peaks were so small that even a relative error of about 10% would not be larger than the absolute experimental error, which was estimated to be about 2 mole %. Furthermore, the equilibrium constants derived from these values agreed reasonably well with the previously found values (see Table II).

Results and Discussion

Experimental results obtained in this study are reviewed in Table I. In addition, two more systems were investigated: $(CH_3)_2POCl + (CH_3)_2P(S)-(S)P(CH_3)_2$ and $(C_2H_5O)_2P(O)CH_2Cl + (C_2H_5O)_3PS$. Neither of these, however, could be made to reorganize to interchange their "isolated" oxygen and sulfur before a considerable amount of side reactions occurred (at about 150°).

In all the reported experiments, a homogeneous liquid was obtained which gave only four resonance peaks in the n.m.r. spectrum, except for the experiments with methyl-chloromethylphosphinic chloride where a few extra small peaks indicated that some decomposition occurred, and with $POBr_3 + PSCl_3$ where eight previously identified peaks[1] were found. Since the chemical shifts of phosphoryl chloride and thiophosphoryl chloride are known[5] and the chemical shift of the phosphonic or phosphinic chlorides used is either known or could be determined, the fourth peak could be identified as the reagent phosphonic or phosphinic chloride in which the isolated oxygen or sulfur was replaced by an isolated sulfur or oxygen respectively. Furthermore, this identification could

(1) L. C. D. Groenweghe and J. H. Payne, J. Am. Chem. Soc., **81**, 6357 (1959).

(2) E. Schwarzmann and J. R. Van Wazer, ibid., **81**, 6366 (1959).

(3) J. R. Van Wazer and E. Fluck, ibid., **81**, 6360 (1959); L. C. D. Groenweghe, J. H. Payne and J. R. Van Wazer, ibid., **82**, 5305 (1960); E. Fluck, J. R. Van Wazer and L. C. D. Groenweghe, ibid., **81**, 6363 (1959).

(4) T. Moeller, H. J. Birch and N. C. Nielsen, "Inorganic Syntheses," Vol. IV, McGraw-Hill Book Co., New York, N. Y., 1953, p. 71.

(5) N. Muller, P. C. Lauterbur and J. Goldenson, J. Am. Chem. Soc., **78**, 3557 (1956).

TABLE I

EQUILIBRIUM OBTAINED FROM ISOLATED SULFUR–OXYGEN INTERCHANGE REACTIONS

Expt. no.	Molar ratio of reagents used	Reaction temp., °C.	Composition at equilibrium in mole %[a]				K_1[a]	$\Delta E\chi$[b]
			OPXYZ	SPXYZ	OPX'Y'Z'	SPX'Y'Z'		
1	$1CH_3PSCl_2 + POCl_3$	230	27	24	22	27	1.4	0.5
2	$1CH_3PSCl_2 + 3POCl_3$	230	59	18	16	6	1.2	.5
3	$1C_6H_5PSCl_2 + 1POCl_3$	230	27	21[c]	21[c]	30	1.8	.5
4	$1C_6H_5PSCl_2 + 3POCl_3$	230	59	16.5[c]	16.5[c]	8	1.7	.5
5	$1(CH_2Cl)POCl_2 + 1PSCl_3$	230	30	16	18	35	3.6	.5
6	$1CH_3(CH_2Cl)POCl + 1PSCl_3$	150[d]	35	11	10	43	13.5	1.0
7	$1POBr_3 + 1PSCl_3$[e]	230	..	..	..	..	..	..
	$POCl_2Br + PSCl_3$		11	4.3	20	17	2.2	0.2
	$POClBr_2 + PSCl_2Br$		20	17	15	20	1.6	.2
	$POBr_3 + PSClBr_2$		15	20	3.4	9	2.0	.2
	$POClBr_2 + PSCl_3$		11	4.3	15	20	3.4	.4
	$POBr_3 + PSCl_2Br$		20	17	3.4	9	3.1	.4
	$POBr_3 + PSCl_3$		11	4.3	3.4	9	6.7	.6

[a] The mixture at equilibrium contains the four compounds which appear in equation 1. The formulas OPXYZ and SPXYZ represent the compounds in this system with the greatest number of chlorines directly attached to the phosphorus; the K_1-values are computed accordingly. [b] Difference of the total Pauling's electronegativity of all atoms (except isolated oxygen or sulfur) directly connected to each of the two reagents as explained in text. [c] The n.m.r. resonances of $PSCl_3$ and $C_6H_5POCl_2$ could not be completely resolved. Since these compounds should be formed in equal amounts, the molar concentration was determined of the two species together. This concentration was divided by two to obtain the concentration of each individual species. [d] Decomposition resulted at 230°. Even at 150°, the reaction mixture is a black liquid and the n.m.r. analysis shows a few small extra peaks. [e] This mixture gives eight peaks because of reorganization of chlorines and bromines attached to the phosphorus; from the quantitative results, the six equilibria as shown could be studied.

be verified by the fact that the stoichiometry of the systems could not be made to agree with any other assignment. Thus the equilibria can be represented by the general equation

$$SPXYZ + OPX'Y'Z' \rightleftarrows OPXYZ + SPX'Y'Z' \quad (1)$$
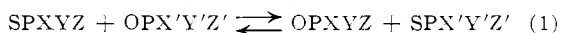
in which X, Y, Z, X', Y' and Z' represent either a halogen, an alkyl group or an aryl group, and in which OPXYZ and SPXYZ represent the molecules containing the largest number of chlorine atoms attached to the phosphorus. The equilibrium constants

$$K_I = \frac{[OPXYZ][SPX'Y'Z']}{[SPXYZ][OPX'Y'Z']} \quad (2)$$

are reported in Table I. These constants are similar to K_I reported in Paper IX of this series.[2]

Experiments 2 and 4 in this table were run to check whether or not the K_I's were truly constant. Since one of the components was present in a molar concentration of about 6% in either experiment, the quantitative data were not very accurate, and the K_I values calculated from these data are considered to check reasonably well with those of the corresponding values of experiments 1 and 3.

Since the four peaks obtained in the reaction mixtures of experiments 1 through 6 were identified as representatives of the four compounds in equation 1, it is obvious that the P–C bonds in these molecules did not reorganize to give molecules with more or less than one P–C bond as might be expected from previous reports.[1–3] Thus in experiment 1, molecules like $(CH_3)_2PSCl$ or $(CH_3)_3$-PO were not found. These results confirm the stability of the carbon-to-phosphorus bond toward reorganization, since all other atom-to-phosphorus bonds previously reported[1–3] by our Laboratory are found to reorganize at temperatures much lower than 230°. As a result, alkyl or aryl groups directly connected to the phosphorus atom can be used to label the phosphorus atom for reorganization studies. The chlorines in experiments 1

through 6 probably are reorganizing among themselves, but this will not result in the formation of additional compounds.

The situation is quite different in experiment 7, where the chlorine and bromine atoms reorganize to give the eight compounds which could be expected to form only by chlorine–bromine interchange reactions.[1] Four of these compounds result also from the reorganization of $POCl_3$ and $POBr_3$ and the other four from the system $PSCl_3$–$PSBr_3$. The two equilibrium constants determining the concentration of the compounds formed in each of these systems have been calculated,[1] and these figures are compared in Table II with the

TABLE II

COMPARISON OF EQUILIBRIUM CONSTANTS

Constant	Previously calcd.[1]	Found in system POBr₃–POCl₃–PSBr₃–PSCl₃
$K_{1,o} = \dfrac{[POCl_3][POClBr_2]}{[POCl_2Br]^2}$	0.406 ± 0.013	0.402
$K_{2,o} = \dfrac{[POCl_2Br][POBr_3]}{[POClBr_2]^2}$	$.341 \pm .012$	.308
$K_{1,s} = \dfrac{[PSCl_3][PSClBr_2]}{(PSCl_2Br)^2}$	$.297 \pm .012$	.290
$K_{2,s} = \dfrac{[PSCl_2Br][PSBr_3]}{[PSClBr_2]^2}$	$.419 \pm .019$	.383

same set of four corresponding constants calculated from the present POBr₃–POCl₃–PSBr₃–PSCl₃ system. Considering that the concentration of each of the components is on the average only half of its concentration in the separate systems POBr₃–POCl₃ and PSBr₃–PSCl₃, and therefore the relative error on the quantitative results can be expected to be about double, the fact that three out of four K values check within twice the standard error given for the separate systems is considered to show sufficiently good agreement.

Since the isolated oxygen–sulfur interchange reaction occurred in experiments 1 through 6 at temperatures as low as 150°, there is no reason to

believe that this reaction would not occur in experiment 7 in addition to the chlorine–bromine interchange. Because eight compounds are involved in the reaction product of this experiment, it is possible to write six equilibrium constants of the form expressed in equation 2. The values of these constants are given in Table I and are related to each other through the four equilibrium constants reported in Table II. In order to report these constants on a comparable basis, they are calculated for reaction 1 in which the compound in the reaction mixture having an isolated oxygen attached to the phosphorus and the largest amount of chlorines directly attached is put in the right side of the equation.

The value, $\Delta\Sigma\chi$, obtained by taking the total Pauling's electronegativity of X, Y and Z in equation 1 minus the total electronegativity of X', Y' and Z' ($\Delta\Sigma\chi$) is also entered in Table I. It is obvious for the six equilibria in experiment 7 that K_I increases with $\Delta\Sigma\chi$ and, as a matter of fact, when log K_I is plotted against $\Delta\Sigma\chi$, a straight line is obtained. The values obtained from experiments 5 and 6 also fit on this plot, but the other results do not. Generally, however, it can be concluded that there seems to be a trend for K_I to increase with $\Delta\Sigma\chi$. Furthermore, since all K_I values are greater than unity (representing completely random reorganization), it looks as if the isolated oxygen rather than sulfur prefers to be connected to the phosphorus directly attached to the greatest number of chlorines. This rule of thumb may well fail when fluorine atoms are present in the molecules, since their electronegativity is much higher.

The isolated oxygen–sulfur interchange reaction seems to occur whenever mixtures of quadruply connected phosphorus compounds containing "isolated" oxygen and sulfur are heated to the proper temperature, generally at least 150°. Since the equilibrium favors the formation of $POCl_3$, this reaction can be used advantageously for the preparation of thionophosphonic and phosphinic deriva-

tives in good yield from the corresponding oxy derivatives by using a slight excess of thiophosphoryl chloride. This is exemplified by the preparation of chloromethylthionophosphonic dichloride in a pressure vessel as reported in the preparative section. When the reorganization is attempted in an open flask, catalysts such as PCl_3 and $AlCl_3$ are necessary to obtain a satisfactory reaction rate at the resulting lower reaction temperature (see preparation of methylchloromethylthionophosphinic chloride).

Preparative Section

Methylchloromethylphosphinic Chloride.—The procedure outlined by M. T. Kabachnik and E. S. Shepeleva[6] has been modified by operating at atmospheric pressure. To 1011 g. of CH_3PCl_2 heated in a flask to reflux temperature, 328 g. of paraformaldehyde was added in small amounts through a nitrogen-protected feeding device. The reaction is exothermic. After addition had been completed, the reaction mixture was heated to 100° for an hour. Vacuum distillation produced 884 g. (70% yield based on CH_3PCl_2) of product with an n.m.r. chemical shift of -59.2 p.p.m. Agitation during the addition of the paraformaldehyde resulted in decreased yield.

Methylchloromethylthionophosphinic Chloride.—A 147-g. quantity of $CH_3(CH_2Cl)P(O)Cl$, 339 g. of $PSCl_3$ (100% excess) and catalytic amounts of PCl_3 and $AlCl_3$ (5 g. of each) were heated at 130–140° for 30 hr. in a 500-ml. flask fitted with an efficient fractionating column. Only those reaction products which distilled under 115° were collected. The residue was distilled under vacuum and 64 g. of pure colorless $CH_3(CH_2Cl)P(S)Cl$ (39% yield (identified by n.m.r., chemical shift = -84.9 p.p.m.) could be distilled at 68–70° and 3–4 mm. Another 23 g. of 90% pure product was collected at 70–83° and 3–4 mm.

Chloromethylthionophosphonic Dichloride.—An 839-g. quantity of $CH_2ClP(O)Cl_2$ and 1735 g. of $PSCl_3$ were heated in a 3-liter stainless steel autoclave for 72 hr. at 230°. Vacuum distillation yielded 700 g. of pure product (b.p. 65–66° at 9 mm.), corresponding to about 75% yield based on $CH_2ClP(O)Cl_2$. The n.m.r. chemical shift was -72.8 p.p.m.

(6) M. T. Kabachnik and E. S. Shepeleva, *Bull. Acad. Sci. U. S. S. R., Div. Chem. Sci. S. S. R.*, 862 (1953).

[Contribution from the Mass Spectrometry Section, National Bureau of Standards, Washington, D. C.]

Mass Spectrometric Study of Cyanogen and Cyanoacetylenes

By Vernon H. Dibeler, Robert M. Reese and J. L. Franklin[1]

Relative abundances and appearance potentials are reported for the principal ions in the mass spectra of cyanogen, cyanoacetylene, dicyanoacetylene and dicyanodiacetylene. Heats of formation of radicals and radical ions are calculated and the energetically probable ionization-dissociation processes are tabulated. Carbon–carbon and carbon–nitrogen bond dissociation energies are calculated for various ionized and neutral molecular species.

Introduction

Cyanogen may be considered as the initial member of an interesting series of compounds containing only carbon and nitrogen atoms and having the general structural formula

$$N\equiv C-(C\equiv C)_n-C\equiv N, \text{ where } n = 0, 1, 2, 3, \ldots[2]$$
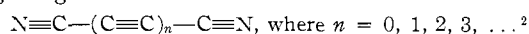
Unique bonding and structural arrangements of

these molecules result from the presence of conjugated triple bonds which are virtually unaffected by subsequent additions of triple bonds. Furthermore, their high endothermic heats of formation and very stable combustion products constitute a highly exothermic system and provide a means of achieving flame temperatures in the range of 5000 to 6000°K.[3]

(1) Guest worker from the Research and Development Division, Humble Oil and Refining Co., Baytown, Texas.

(2) A. J. Saggiomo, *J. Org. Chem.*, **22**, 1171 (1957).

(3) (a) J. B. Conway, W. F R. Smith, W. J. Liddell and A. V. Grosse, *J. Am. Chem. Soc.*, **77**, 2026 (1955); (b) A. D. Kirshenbaum and A. V. Grosse, *ibid.*, **78**, 2020 (1956).