furnishes no clue as to the relative importance of these reactions to *in situ* build-up in the formation of the various radiocompounds which were found.)

Methanol presents a problem like that of carbon monoxide; the yields of both are essentially similar from the bromide and the sulfate targets. This may be an indication that methanol is formed from an oxygen free precursor, such as CH_2, in both crystals, though this is highly unlikely in view of the comparative yields of formic acid, etc. In the case of the sulfate target there is the possibility for protomethanolic precursors to be scavenged efficiently by oxygen to yield eventually less highly reduced activities; this would account for the low methanol yield from that target material.

A related situation seems to be reflected in the yields of urea and guanidine. In the presence of sulfate oxygen the amount of urea formed is increased, yet no appreciable quantity of guanidine was produced in the bromide case. In the sulfate lattice the N–CO–N skeleton, more or less embellished with hydrogen, apparently is more stable with respect to simpler combinations than is the N–CN–N skeleton in the ammonium bromide. Alternatively, the N–C–N part of the urea–guanidine skeleton may be effectively broken up in the halide matrix by hydrogen to yield methylamine or its precursors, while guanidine or protoguanidine formed in the sulfate may be hydrolyzed virtually completely to urea upon solution of the target. Considerable light undoubtedly would be shed upon situations of this type by experiments involving other solvents than water.

Effect of Pile Radiations.—In the foregoing discussion we have presumed that there is no sensible integrated effect of the pile flux of γ- and X-rays. A modest dependence of the retention of bromine in irradiated potassium bromate upon irradiation time has been observed,[6] and such effects may be of importance in the irradiation of ammonium sulfate. In the present situation the picture is complicated not only by the complexity of the apparent radiocarbon distribution, but also by the fact that we have no accurate information concerning the specific origins of any one compound, and so no way of determining from the data recorded above which or what part of any one might have resulted from radiation-induced reactions.

A simple calculation based on radiation dose, the terminal electron fraction of C^{14} in the target, and the assumption that g is 30 e.v. per ion pair, indicates that the chance for direct influence of radiation on the state of radiocarbon at the end of the irradiation is of the order of 0.001. This is an approximate lower limit for the occurrence of a radiation effect.

Gamma or X-ray induced events near a carbon should be expected to affect the final chemical state of that carbon; one must, however, decide what is meant by *near*. If we assume arbitrarily that a radiation-induced event occurring within a volume, about a carbon, containing 25 sulfate ions and 50 ammonium ions affects the final chemical state of the carbon, the chance that such influence occurs is roughly 0.3. This is an approximate upper limit for the occurrence of a radiation effect.

It seems likely that the steady state concentration of reactive species produced by the pile radiation flux is sufficiently large to be capable of exerting only secondary influence.

Acknowledgments.—We wish to express our thanks to Dr. J. D. Vaughan, who performed some of the preliminary experiments on this target material. This research was sponsored by the A. E. C.

[6] G. E. Boyd, J. W. Cobble and Sol Wexler, This Journal, **74**, 238 (1952).

Urbana, Illinois

[Contribution from the Department of Chemistry, Florida State University]

Isotopic Exchange Reactions of Phosphorus Pentachloride[1]

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The rate of exchange between phosphorus pentachloride and labeled chlorine in solvent carbon tetrachloride shows a difference in reactivity for the various chlorine atoms in the pentachloride molecule, three chlorine atoms reacting rapidly and two slowly. Chlorine, on addition to phosphorus trichloride, enters mainly into the equatorial positions; mercury attacking phosphorus pentachloride removes chlorine mainly from the equatorial positions. Mechanisms are proposed and an explanation for the difference in reactivities is suggested. In addition, the isotopic exchange reactions in carbon tetrachloride between chlorine and phosphorus oxychloride and between phosphorus trichloride-Cl^{36} and phosphorus pentachloride have been found to be measurably slow.

Introduction

In general, those compounds in which the central atom has a coördination number of five are quite unstable and not numerous,[3] so that information regarding their chemical characteristics and structural properties is relatively scarce and uncertain. Consequently, theoretical considerations of bond hybridization[4,5] are conjectural and unsatisfactory. Attempts to show a non-equivalence of atoms in such molecules as phosphorus pentachloride and phosphorus pentabromide by the use of isotopic

[1] Work performed on Contract No. AT-(40-1)-1317 with the Atomic Energy Commission.

[2] Abstracted from a dissertation presented by J. J. Downs for the degree of Doctor of Philosophy, August, 1954. Complete dissertation on file in Library, Florida State University.

[3] W. Huckel, "Structural Chemistry of Inorganic Compounds," translated by L. H. Long, Elsevier Publishing Co., Inc., New York, N. Y., 1950, p. 131.

[4] L. Pauling, "Nature of the Chemical Bond," 2nd Edition, Cornell University Press, Ithaca, N. Y., 1945, p. 92.

[5] R. Daudel, A. Bucher and H. Moureu, *Compt. rend.*, **218**, 917 (1944).

tracer methods have been reported.[6] These molecules exist in a trigonal bipyramid structure in the vapor[7] and in non-polar solvents[8] and it might be expected that chemical reactivity would depend upon the position of the atom in the molecule. In addition, in phosphorus pentachloride, the apical chlorines are farther (2.11 Å.) from the phosphorus atom than are the equatorial chlorine atoms (2.04 Å.).[8] However, in all reactions reported, complete equilibration of activity in all positions of the molecules was found, so that no conclusions pertinent to differing reactivities among positions could be drawn.

We have re-examined the homogeneous isotopic exchange reactions of phosphorus pentachloride in carbon tetrachloride solution. With an improved method of separation of reactants and a more rigorous exclusion of moisture we have found a dependence of exchange rate on position of exchange rate on position of exchanging chlorine atom.[9]

Experimental

Purification of Materials.—It soon became apparent in these experiments that hydrogen chloride, or substances, like water, which produce hydrogen chloride from the reactants had a powerful catalytic effect on the reaction. The following methods were selected with this in mind.

Chlorine, Mathieson Company, was further purified by passage in succession through an aqueous solution of potassium permanganate, dilute sulfuric acid, concentrated sulfuric acid, and a drying tower containing magnesium perchlorate.

Carbon tetrachloride, reagent grade, was purified by the method of Dickinson and Leermakers.[10] The boiling point was constant within 0.1° for individual distillations and in the range 76.6–76.9°. Radiochemical estimates of impurity showed less than 0.1% exchangeable chloride.

Phosphorus pentachloride, reagent grade, was used without purification for several runs and intensively purified in others. When used without further purification, a freshly opened bottle was handled in a dry-box atmosphere having a dew point of less than −20°. The purified material was prepared as follows: the material was sublimed at a temperature of 160–170° in a chlorine atmosphere into a previously weighed flask. The excess chlorine was displaced from the flask by dry nitrogen gas, the flask sealed and weighed, and all subsequent operations performed in the dry-box.

Phosphorus trichloride, analytical reagent, was purified in an all-glass apparatus by degassing, followed by two high vacuum distillations, one from room temperature into a −80° trap, the second from a trap at −40° into a −80° trap.

Phosphorus oxychloride, analytical reagent, was purified by a high vacuum sublimation into a trap cooled to −40°.

Hydrogen chloride, Mathieson Company, was dried by passing through magnesium perchlorate and used without further purification.

Syntheses.—Labeled chlorine and labeled phosphorus trichloride were both prepared by the same general method of high temperature equilibration of activity, between silver chloride-Cl^{36} and chlorine on the one hand,[11] and sodium chloride-Cl^{36} and phosphorus trichloride on the other.

Silver chloride, prepared from hydrochloric acid-Cl^{36},[12] was dried, then fused *in vacuo* to remove the last traces of moisture. In a Pyrex flask, the silver chloride and about a 200-fold molar excess of chlorine were heated to 450° for 12–16 hours at which time equilibration of activity was complete.

Sodium chloride-Cl^{36}, prepared from the neutralization of hydrochloric acid, was brought to dryness in a Pyrex flask. On a high vacuum system, the flask was evacuated, a known amount of phosphorus trichloride introduced, and the flask sealed off. After heating at 510° for 26 hours, the exchange was about 70% complete and the phosphorus trichloride was removed and used without further purification.

Analytical Procedures.—Chlorine concentrations in carbon tetrachloride solutions were determined by light absorption at 332 mμ[13] measured with a Beckman DU spectrophotometer. The phosphorus oxychloride impurity in some phosphorus pentachloride samples was estimated by the absorption due to the P=O stretching vibration at a wave number of 1290 cm.$^{-1}$[14] measured on a Perkin–Elmer Model 21 IR spectrophotometer. Preliminary experiments had shown a negligibly slow exchange between chlorine and phosphorus oxychloride under the conditions of our experiments, so we assumed that phosphorus oxychloride was the unexchangeable chlorine species present in the phosphorus pentachloride. Radiochemical estimates of the concentration of phosphorus oxychloride agreed well with the infrared results. Concentrations of all other materials were determined by direct weighing, except hydrogen chloride which was estimated by its volume at room temperature and pressure.

The chlorine-36 activity was determined by counting as thin layers of mercurous chloride in stainless steel planchets using a conventional scaling circuit and end-window Geiger tube. An experimentally determined self-absorption curve was used to correct for sample thickness. All samples were counted sufficiently long to assure a standard error of less than 1%. Activity balances were calculated for each run and always agreed within 5% which indicates that no appreciable reaction occurred between either reactant and the solvent carbon tetrachloride.

Experimental Procedures.—In general, separate solutions of reactants in carbon tetrachloride were prepared in the dry-box, then brought into the laboratory and all further operations were performed under the protection of drying tubes filled with magnesium perchlorate. For reactions at room temperature, solutions were mixed in an all glass apparatus; a few runs were attempted at 0° by mixing the solutions through a piece of Tygon tubing. Aliquots were taken at preselected times and the reactants separated by one of two methods. In those runs where we were mainly interested in exchange rates, chlorine (or phosphorus trichloride in one run) was evaporated from the aliquot by a rapid stream of nitrogen gas, leaving the phosphorus pentachloride behind. Under normal conditions, this process had a half time of about eight seconds and cannot have had a very great effect on the rate of the exchange reaction. In other runs, where we were interested in the loss of chlorine from the phosphorus pentachloride molecule, the aliquot was run into a pool of mercury stirred to a froth which reacted to give mercury chloride and a carbon tetrachloride solution of phosphorus trichloride.[15] Rapid separation of the two phases prevented further exchange. Standard chemical methods were used in each case to bring the chlorine in each fraction to mercurous chloride for counting.

Most runs were made at room temperature (24.5 ± 0.5°). A number of runs were attempted at 0°; invariably, the rate of reaction increased tremendously at the lower temperature due, we believe, to condensate moisture or the interaction of reactant chlorine with Tygon tubing (necessary for mixing reactants) to give hydrogen chloride. Reactions were carried out under the illumination of ordinary room (fluorescent) lights after preliminary experiments showed that such light did not affect the rate of reaction. No specific test was made for heterogeneity of reaction but a number of reaction vessels were used with comparable results, so we feel that the effect is small.

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[6] (a) W. Koskoski and R. D. Fowler, THIS JOURNAL, **64**, 850 (1942); (b) A. Polesitskii, M. Yashchenko and N. Baranchik, *Compt. rend. acad. sci. URSS*, **34**, 83 (1942); (c) J. Chatterjee, *J. Indian Chem. Soc.*, **19**, 49 (1942).

[7] M. Rouault, *Compt. rend.*, **207**, 620 (1938).

[8] Ref. 4, p. 109.

[9] J. Downs and R. E. Johnson, *J. Chem. Phys.*, **22**, 143 (1954).

[10] R. G. Dickinson and J. A. Leermakers, THIS JOURNAL, **54**, 3852 (1932).

[11] J. E. Willard, private communication.

[12] Received on allocation from the U. S. Atomic Energy Commission.

[13] A. I. Popov and J. J. Mannion, THIS JOURNAL, **74**, 222 (1952).

[14] L. W. Daasch and D. C. Smith, N. R. L. Report 3657, Naval Research Laboratory, Washington, D. C., 1950, p. 12.

[15] Similar to a method used by Koskoski and Fowler, ref. 6a. These authors found no appreciable exchange between the two chlorides.

To define more clearly the actual reaction taking place, we considered the other exchange reactions which might conceivably take place in our system. The exchange between chlorine and carbon tetrachloride at room temperature is known to be negligibly slow[16,17] and since phosphorus pentachloride does not lose activity in carbon tetrachloride solution, its exchange must be slow also. Similarly, the exchange between hydrogen chloride and phosphorus oxychloride is slow.[18] On the basis of an exchange run between labeled chlorine and phosphorus oxychloride, a minimum half-time of exchange of 500 hours was determined for reactant concentrations similar to those encountered in our reaction mixtures.

Results

PCl_5–Cl_2^* Exchange.—Since the phosphorus pentachloride contained a small (initially unknown) amount of phosphorus oxychloride, the infinite time value of the specific activity could not be directly determined. To calculate the fraction exchange, we used the expression[19]

$$1 - F = \frac{S_A - S_B}{S_{A_0} - S_{B_0}} \qquad (1)$$

which may be easily derived from other expressions for F and assuming conservation of activity. Because of the phosphorus oxychloride impurity, the McKay plot of log $(1 - F)$ *versus* time "tails off" at high F values as shown in Fig. 1. Estimation of the amount of impurity from the experimental data was used to correct the curve giving the typical straight line curve of a homogeneous exchange reaction.

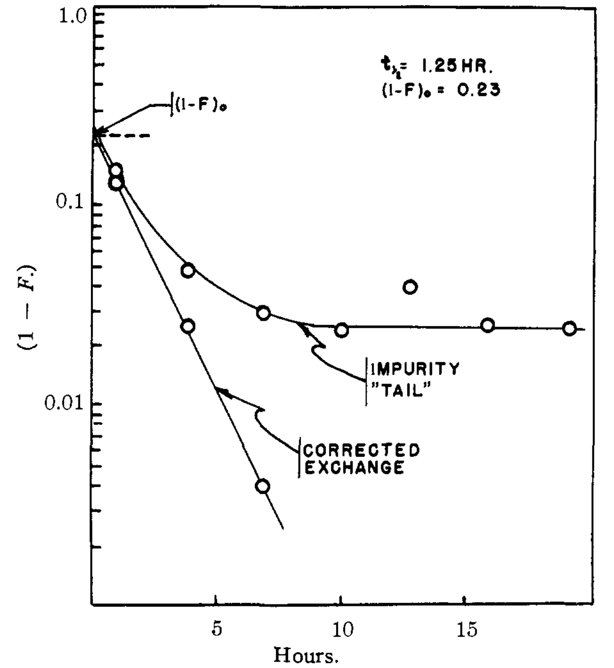

Fig. 1.—Log $(1 - F)$ *vs.* time for run 3.

Figure 1 also illustrates another striking feature of all exchange reactions run between phosphorus pentachloride and chlorine, *viz.*, an extrapolation of the experimental curve does not go to 0% exchange at zero time. While this may be due to a separation induced exchange, it is more likely that the exchange reaction is proceeding at two different rates. In view of the very large difference between the two rates, they may be considered separately. The initial, very rapid, exchange has reached completion by the time (usually less than a minute after mixing) the first experimental point is taken and the experimental points lie along the curve representing the following slow exchange. $(1 - F)_0$, the extrapolated value at zero time, would then be a function of the number of unexchanged chlorines in phosphorus pentachloride at zero time and the relative concentrations of chlorine and phosphorus pentachloride in the reacting mixture. The fraction, f, of chlorine atoms in phosphorus pentachloride involved in the initial exchange may be calculated from the general expression

$$f = F_0/[1 + Q\,(1 - F)_0] \qquad (2)$$

where Q represents the ratio of concentrations of the initially inactive species to the initially radioactive species, both in units of gram-atoms (say) of the exchangeable moiety per unit volume. We calculate Q in units of $5(PCl_5)/2(Cl_2)$ where parentheses represent concentrations in gram formula weights per liter.

Table I lists f values of reactions run over a sixfold change in concentration ratio and shows that, within the standard deviation of the mean listed, exactly three of the chlorines in phosphorus pentachloride are involved in the rapid exchange reaction. This, correlated with the structural arrangement of the chlorines in the phosphorus pentachloride molecule, makes it most reasonable to con-

Table I

Exchange Runs, PCl_5–Cl_2^*, Evaporative Quenching

Run	Concn. moles/l. × 10^2 PCl_5	Cl_2	$(1 - F)_0$	f	$t_{1/2}$, min.	$R_a \times 10^4$, moles/l./min.
			Using sublimed PCl_5			
3	2.07	4.14	0.23	0.598	75 ± 6	2.96 ± 0.49
5	1.19	2.36	.27	.544	61 ± 16	2.09 ± .55
6	1.08	4.33	.19	.724	170 ± 10	0.74 ± .04
			Using unsublimed PCl_5			
2	0.62	3.84	0.26	0.670	165 ± 15	0.46 ± 0.01
4	1.50	1.44	.15	.611	8.3 ± 3	17.8 ± 1.4
7	1.11	2.99	.18	.702	51 ± 11	2.44 ± 0.48
			Using PCl_3			
12	1.08	3.55	0.44	...[a]	40 ± 5	3.10 ± 0.38
13	1.09	2.81	.80	...[a]	36 ± 5	3.36 ± .46
			Miscellaneous runs			
1[b]	2.42	4.47	0.20	0.629	1.7 ± 0.5	152 ± 50
8[c]	1.61	1.89	.23	.517	5.5 ± 0.7	29.5 ± 3.7
9[c]	0.83	4.33	.35	.557	5.3 ± 1.3	18 ± 4
10[c]	1.03	5.21	.39	.511	1.5 ± 1.0	82 ± 50
11[d]	0.88	4.68	.32	.592	4.5 ± 1.5	24 ± 8
				Av. 0.605 ± 0.022		

[a] Run initiated by mixing PCl_3 and Cl_2^*; eq. 2 is invalid. [b] PCl_5 inadvertently exposed to moist air. [c] Run at 0°, exposed to Tygon tubing. [d] HCl added to reaction mixture, concentration 0.028 *M*.

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(16) G. K. Rollefson and W. F. Libby, *J. Chem. Phys.*, **5**, 569 (1937).

(17) F. J. Johnston, Thesis, University of Wisconsin, 1951.

(18) K. Clusius and H. Haimerl, *Z. physik. Chem.*, **51B**, 347 (1942).

(19) We shall use the same symbols throughout as are used in "Radioactivity Applied to Chemistry," A. C. Wahl and N. A. Bonner, Editors, John Wiley and Sons, Inc., New York, N. Y., 1951, Chap. 1. Here, the subscript A refers to chlorine, the subscript B to phosphorus pentachloride, hence S_{B_0} is zero in the present case.

clude further that the three chlorines are those occupying the equatorial positions in the molecule.

Little can be said concerning the kinetics of the rapid reaction. Exchange was complete within a time as short as 30 seconds; this implies a maximum half-time of reaction of about five seconds. Runs made in complete darkness also proceeded at an immeasurably fast rate; an atomic chlorine mechanism of exchange seems unlikely. Another possible mechanism for the exchange involves a very small dissociation of phosphorus pentachloride into phosphorus trichloride and chlorine in the presence of labeled chlorine. A test of exchange of phosphorus trichloride-Cl^{36} and phosphorus pentachloride in carbon tetrachloride gave a half-time of exchange of about an hour indicating either a negligible dissociation[20] or a very slow rate of dissociation or both. Furthermore, a dissociation mechanism would lead to the exchange of apical atoms at approximately the same rate as the equatorial atoms since the chlorines in phosphorus trichloride are equivalent. Perhaps the most reasonable mechanism is one in which an atom transfer process occurs between molecular chlorine and phosphorus pentachloride exclusively in the equatorial plane of the latter. This might take place through the formation of a complex similar to that formed between phosphorus pentachloride and iodine chloride.[21]

With respect to the kinetics of the slow exchange reaction, we had hoped that the exchange rates as determined from the McKay plot of each run would indicate a simple relationship between R, the exchange rate constant, and the concentrations of the reacting species. The concentrations of reactants can be varied over only a relatively small range; certain experimental conditions such as the low specific activity of chlorine-36 available, low solubility of phosphorus pentachloride, and the difficulty of determining the rate of the slow exchange as $(1 - F)_0$ approaches zero circumscribe the concentrations possible.

Table I shows values of R_a, the rate constant for exchange of apical chlorines only, calculated by the expression

$$R_a = \frac{\ln 2}{t_{1/2}} \times \frac{[0.4(\mathrm{PCl_5})][0.6(\mathrm{PCl_5}) + (\mathrm{Cl_2})]}{(\mathrm{PCl_5}) + (\mathrm{Cl_2})} \quad (3)$$

We have grouped the runs according to the amount of HCl believed present; it may be noted that in those runs in which the HCl concentration is high, the rate of exchange is rapid also. While a detailed analysis of the kinetic data is impossible, such a dependence rules out simple mechanisms. Thus an intramolecular rearrangement (which would be first order in phosphorus pentachloride alone) or a direct reaction between chlorine and apical chlorine atoms (which would be first order in chlorine and phosphorus pentachloride) are considered to be impossible.

PCl_5 Formation and Degradation.—When excess labeled chlorine is allowed to react with phosphorus trichloride in carbon tetrachloride solution, phosphorus pentachloride is formed rapidly by addition and the excess chlorine then enters into an exchange reaction with the phosphorus pentachloride. The same experimental conditions then exist as those described in the preceding section and we may calculate the fraction exchange by

$$1 - F = \frac{S_A - S_B}{S_{A_0} - 0.4S_{A_0}} \quad (4)$$

where S_{A_0} represents the specific activity of the chlorine fraction before any exchange has taken place. We are assuming that the addition process is much faster than the exchange between chlorine and phosphorus trichloride, or the exchange between chlorine and the apical atoms in phosphorus pentachloride, since the addition reaction gives the phosphorus pentachloride 0.4 times the specific activity of the chlorine. Extrapolation of the McKay plot curve to zero time again gives a value of $(1 - F)_0$ not equal to unity.

We imagine a process as follows to account for the initial exchange. Addition of labeled chlorine to phosphorus trichloride may introduce the label into the molecule in one or more of the following different ways

A. 1, Completely random addition, *i.e.*, an 0.4 probability to become an apical atom and an 0.6 probability to become an equatorial atom.

B. Simultaneous addition of both atoms to give: 1, both in equatorial positions; 2, both in apical positions; 3, one in an apical position, the other in an equatorial position.

C. Stepwise addition of the first atom to give a transitory particle (PCl_4) in which chlorines are indistinguishable followed by: 1, addition to an equatorial position; 2, addition to an apical position.

Immediately following the addition, the remainder of the labeled chlorine equilibrates activity rapidly with the equatorial atoms of the phosphorus pentachloride (no other exchange process having taken place up to this time) followed finally by the slow exchange of chlorine and apical chlorines giving the experimental curve. Table II gives $(1 - F)_0$ values calculated for each of the above possibilities and the $(1 - F)_0$ values observed in each of the two runs.

TABLE II

$(1 - F)_0$ VALUES, PCl_5 FORMATION AND DEGRADATION

			Run		
Case	12[a]	13[a]	D.1[b]	D.2[b]	D.3[b]
B-1	0.58	0.59	0.53	0.53	0.55
C-1	.40	.38	.29	.29	.33
A-1	.27	.25	.15	.15	.20
B-3	.20	.17	.05	.05	.10
B-2	.09	.07	..[c]	..[c]	..[c]
C-2	..[c]	..[c]	..[c]	..[c]	..[c]
Obs.	.44	.80	.40[d]	.38[d]	.26[d]

[a] Formation runs, original (PCl_3) = 0.0108 *f* in 12, 0.0109 *f* in 13; original (Cl_2) = 0.0463 *f* in 12, 0.039 *f* in 13. [b] Degradation runs, (PCl_5) = 0.0319 *f* in D-1 and D-2, 0.0322 *f* in D-3; (Cl_2) = 0.0277 *f* in D-1 and D-2, 0.0262 *f* in D-3. [c] Calculated values are negative. [d] Reaction quenched 5 min. after mixing for D-1 and D-2, after 10 minutes for D-3.

We may study the reverse reaction, the degradation of phosphorus pentachloride, by its reaction with mercury. If phosphorus pentachloride and labeled chlorine are mixed, then quickly react

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[20] A. I. Popov and N. E. Skelly, THIS JOURNAL, **76**, 3916 (1954).

[21] A. A. Kuz'menko and Ya. A. Fialkov, *Zhur. Obshchei Khim.*, **21**, 473 (1951).

with mercury, only the fast exchange of equatorial atoms can occur between the phosphorus pentachloride and chlorine before the mercury halts the exchange. The phosphorus trichloride produced in this reaction will have an activity depending upon, *inter alia*, the positions in the phosphorus pentachloride molecule from which chlorine atoms were removed by the mercury. The same possibilities obtain for removal as are listed above for addition with the obvious reversal of terms. Listed in Table II are the values of $(1 - F)_0$ calculated for the various possibilities and the observed values of $(1 - F)_0$ based on a single determination per run measured shortly after mixing reactants at times as indicated.

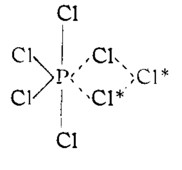
While the results are not clear cut, it is apparent that in the formation and degradation of phosphorus pentachloride, attack at the equatorial positions is favored. Whether one or more than one mechanism describes either reaction cannot be decided, but it seems certain that a large part of the time both atoms involved in the reaction are those in the equatorial positions.

Discussion

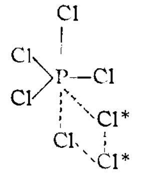
It seems likely that the difference in P–Cl bond length between apical and equatorial positions has little to do with the difference in chemical reactivity. Actually, the difference may be explained solely on the basis of a steric effect. If we postulate an equal Cl–Cl distance for all pairs of chlorine atoms in the molecule and assume some Cl_e–P bond length, then the 90° Cl_a–P–Cl_e arrangement requires a slightly longer Cl–P bond than does the 120° Cl_e–P–Cl_e arrangement. (Here Cl_e represents an equatorial atom and Cl_a an apical atom.) Since we believe that chlorine, exchanging with phosphorus pentachloride, enters only into the equatorial positions, we must now explain the rapid exchange of chlorine with the equatorial chlorine atoms and the very slow (if at all) exchange of chlorine atoms within the phosphorus pentachloride molecule *via* an intramolecular rearrangement.

Recently, Gillespie[22] has proposed possible orbital combinations which may describe bonding in third row elements. One such combination is a trigonal bipyramid having hybridized dp bonds extending in the apical directions and sp^2 bonds extending in the equatorial directions. A hybridization of orbitals such as this would mean a non-equivalence in terms of interconvertibility of position. While five points cannot assume equivalent positions on the surface of a sphere (disregarding the trivial cases where they occupy the same point or equidistant points on a great circle) it is not hard to imagine a transition state, perhaps caused by one or more vibrational modes in the phosphorus pentachloride molecule, in which equatorial and apical chlorine atoms exchange identities, but only if the bonding orbitals are sufficiently identical. We suspect non-identical hybrid orbitals due to lack of just such exchange.

The choice of an atom transfer mechanism for the rapid reaction between phosphorus pentachloride and chlorine leads to a similar conclusion. I and II represent two possible transition states,



I



II

where asterisks identify the chlorine molecule which has added to the phosphorus pentachloride. I leads to no exchange or to exchange of equatorial chlorine atoms only; II must give either no exchange or else simultaneous exchange of apical atoms and equatorial atoms, both disproved experimentally. Certainly the steric hindrance of a chlorine molecule attacking in the equatorial plane in I is no less than the hindrance in II, hence we must again conclude there are non-identical orbitals in the apical and equatorial bonds of phosphorus, as evidenced by different reactivities of the different positions.

The processes of formation and degradation of the phosphorus pentachloride molecule mainly through attack at the equatorial positions cannot be ascribed solely to a non-equivalence of orbitals. We expect chlorine to add mainly into the equatorial positions from considering the relative positions of chlorine atoms in the various molecules; it would be strange indeed to find it adding predominantly into the apical positions. On the other hand, in the degradation process, treated from a statistical standpoint, mercury should attack an apical atom almost as often as an equatorial atom and attack an apical–equatorial pair twice as readily as an equatorial–equatorial pair. From the fact that mercury does not, we must once again conclude a difference in hybridization of the orbitals.

We are happy to acknowledge the assistance given by the Air Reduction Company which donated the liquid nitrogen used in this work.

TALLAHASSEE, FLORIDA

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[22] R. J. Gillespie, *J. Chem. Soc.*, 1002 (1952).