A solution was investigated to determine whether exchange with HF could be detected. It contained 0.100 M $Al(NO_3)_3$, 0.350 M NaF and 1.10 M HNO_3. From Brosset and Orring's equilibrium quotients one calculates that the solution should have contained fluorine atoms distributed roughly as follows: 1 as HF, 1.3 as AlF_3 and 1 as AlF_2^+. Only a single broad resonance was observed at $\sigma_B = 3.3$ whereas a blank with aluminum nitrate omitted gave $\sigma_B = 11$ for HF. Either the estimated HF concentration is much too high or the HF resonance is greatly broadened and not observed, since the position of the resonance does not at all correspond to the calculated weighted average of the resonances of HF and the aluminum fluoride complexes. If the latter case holds, the exchange time of fluoride ion between the complexes and HF must be greater than 5×10^{-4} second.

If it is assumed that the relaxation time T_1 for the aluminum in the aluminum fluoride complexes is much shorter than for aluminum ion, a lower limit to the exchange time for aluminum may be set from the half-width of the resonance. This value is, of course, also a lower limit for T_1 of aluminum ion. It is approximately 0.004 second for the solutions of Table III.

Additional information on rates comes from the work of Brosset and Orring[1] who reported measurable slowness in the formation of AlF^{++} in solutions containing aluminum, ferric and fluoride ions at roughly 10^{-3} M concentrations. It may be concluded that under these conditions the net transfer of a fluoride ion from a ferric ion to an aluminum ion is slow, the reaction requiring an hour to approach completion. Assuming that the fluoride was added last in their experiment it may also be concluded that fluoride ion reacts very rapidly with ferric ion, and more rapidly than with aluminum ion.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FLORIDA STATE UNIVERSITY]

Isotopic Exchange Reactions between Phosphorus Trichloride and Phosphorus Pentachloride[1]

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A measurable exchange of isotopically labeled phosphorus and chlorine has been observed between phosphorus trichloride and phosphorus pentachloride in carbon tetrachloride solution. The exchange rates are the same within experimental error and the reaction is first order in phosphorus pentachloride and zero order in phosphorus trichloride. The reactions were studied over a temperature range from 0.1 to 50.0° and the activation energy has been determined. The catalytic effect of hydrogen chloride on the chlorine exchange was investigated.

Introduction

It has been shown[3] that a dimeric compound of antimony pentachloride exists, and represents an important path for the exchange of antimony between the trichloride and pentachloride. In the line of a general examination of the isotopic exchange reactions of the Group V halides, we have measured the kinetics of the exchanges of phosphorus and chlorine between phosphorus trichloride and phosphorus pentachloride. We find no evidence for a corresponding complex in the phosphorus system and the exchanges proceed *via* a simple dissociative mechanism.

Experimental

Materials.—Phosphorus trichloride, phosphorus pentachloride, chlorine, carbon tetrachloride and hydrogen chloride were treated as described previously.[4]

Phosphorus trichloride-P^{32} was prepared from red phosphorus which had been neutron irradiated at the Oak Ridge National Laboratory. Chlorine of normal isotopic ratio was added to the phosphorus suspended in boiling phosphorus trichloride.[5] The product mixture was purified as described previously and sealed in small ampules until used. The activity of a sample decayed with a half time of 14.5 days, observed for P^{32} is 14.3 days.[6] This latter figure was used to correct for radioactive decay.

Phosphorus trichloride-Cl^{36} was prepared from red phosphorus of normal isotopic ratio and chlorine-Cl^{36}. Hydrogen chloride-Cl^{36}, received on allocation from the Atomic Energy Commission, was converted to silver chloride-Cl^{36}. This was exchanged at 450° in a sealed Pyrex bulb with a large excess of chlorine gas. The labeled chlorine was removed and allowed to react with a slight excess of red phosphorus in a sealed Pyrex bulb at about 100°. The product was diluted with inactive phosphorus trichloride and purified and stored as described above.

Separate solutions of the reactants (phosphorus trichloride-P^{32} and phosphorus pentachloride in one series of runs, phosphorus trichloride-Cl^{36} and phosphorus pentachloride in another series) in carbon tetrachloride were prepared inside a dry box by breaking the appropriate ampules in the solvent and diluting to a known volume. Recovery of the glass of the ampule and weighing allowed us to calculate the solution concentrations. As a check, aliquots of the

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[2] Texas Instruments, Inc., Dallas, Texas.

[3] (a) F. B. Barker and M. Kahn, THIS JOURNAL, **78**, 1317 (1956); (b) V. Gutmann, *Monatsh.*, **82**, 473 (1951).

[4] J. J. Downs and R. E. Johnson, THIS JOURNAL, **77**, 2098 (1955).

[5] "Inorganic Syntheses," W. C. Fernelius, Ed., Vol. II, McGraw-Hill Book Co., New York, N. Y., 1946, p. 145.

[6] J. M. Hollander, I. Perlman and G. T. Seaborg, *Rev. Mod. Phys.*, **25**, 469 (1953).

solutions were hydrolyzed and analyzed for total acid and results agreed within experimental error.

Procedures.—Known quantities of reactant solutions were mixed inside the dry box and the mixtures pipetted into small Pyrex bulbs. The bulbs were temporarily capped with rubber hose stoppers, removed from the dry box, lightly evacuated, and sealed. The bulbs were placed in a constant temperature (±0.01°) bath at one of the three temperatures to be removed at pre-selected times.

In the phosphorus labeled series, the bulb was removed from the bath, cracked open, and the sample washed into a 40-ml. centrifuge tube using both carbon tetrachloride and water for rinsing the bulb. The sample was stirred for 10 minutes, the water removed from the carbon tetrachloride, and the P(V) precipitated from the aqueous solution as magnesium ammonium phosphate using a standard method.[7] The filtrate contains the main part of the P(III) though some is coprecipitated with the P(V). After separation, the magnesium ammonium phosphate was dissolved in a little acid and reprecipitated. After separation of the second precipitation, the combined filtrates contained essentially all of the P(III). The magnesium ammonium phosphate was redissolved in a little acid and one-ml. aliquots from each fraction were taken for radioactivity determinations. Each sample was counted as a liquid in a shallow Pyrex dish under an end window GM tube with a conventional scaler.

In the chlorine labeled series, the samples were hydrolyzed in a similar manner for only 3 minutes and the wash water then removed from the carbon tetrachloride. Preliminary experiments showed that about 99% of the phosphorus trichloride was hydrolyzed in 3 minutes and only about 50% of the phosphorus pentachloride. Also, the water-induced exchange of activity was small and constant. The carbon tetrachloride solution then contained only phosphorus pentachloride; this was extracted by prolonged hydrolysis, the chlorine precipitated by a standard method as silver chloride, and counted as described by Kahn.[8] The zero time fraction of exchange, averaged for 19 chlorine exchange runs, was 0.22 ± 0.02 which gives an indication of the reliability of the separation method.

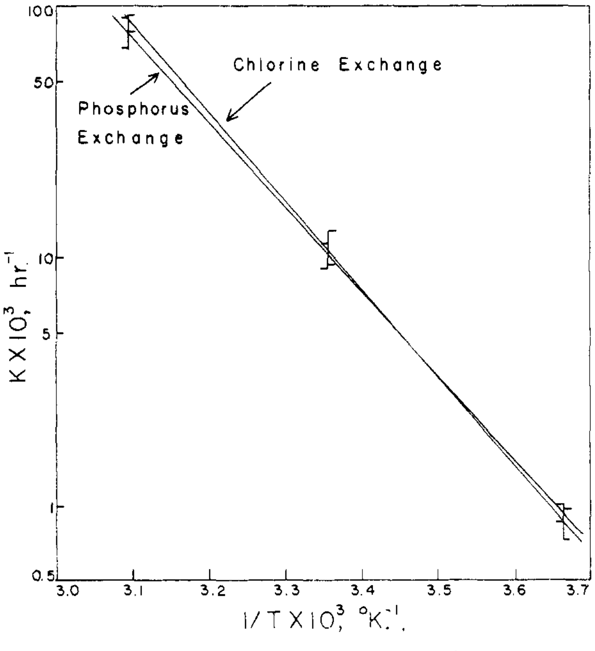

Fig. 1.—The temperature dependence of the specific rate constants. Fiducial limit marks to the right indicate error in chlorine exchange experiments, to the left in phosphorus exchange experiments. The activation energies are the same within the limits of the experimental error.

In the phosphorus series, to calculate F, the fraction exchange, we used

$$1 - F = \frac{S_{\mathrm{PCl_3}} - S_{\mathrm{PCl_5}}}{S_0} \tag{1}$$

which averages the exchange rates of the phosphorus trichloride and pentachloride. Here, S is the specific activity and S_0 represents the initial specific activity of the phosphorus trichloride. The fraction of exchange in the chlorine series was based upon the specific activity of the pentachloride fraction. In both series, zero time exchanges as high as 25% were noted which is due to incomplete separation but plots of log (1 − F) *vs.* time gave straight lines. R, the exchange rate constant, was calculated by the appropriate equation

$$R_{\mathrm{p}} = \frac{(\mathrm{PCl_3})(\mathrm{PCl_5})}{(\mathrm{PCl_3}) + (\mathrm{PCl_5})} \times \frac{\ln(1 - F)}{t} \tag{2a}$$

or

$$R_{\mathrm{Cl}} = \frac{3(\mathrm{PCl_3})5(\mathrm{PCl_5})}{3(\mathrm{PCl_3}) + 5(\mathrm{PCl_5})} \times \frac{\ln(1 - F)}{t} \tag{2b}$$

where parentheses indicate concentrations in moles $\mathrm{l.}^{-1}$ and t is time. Activity balances in the phosphorus series agreed within 5%.

The addition of a small amount of molecular oxygen had no catalytic effect on the rate of either exchange nor did the rate change with the intensity of illumination nor in the presence of a ten-fold increase in glass surface. Small amounts of water or hydrogen chloride had no catalytic effect on the phosphorus exchange but both increased the rate of the chlorine exchange. The water presumably hydrolyzed a portion of the reactants and produced hydrogen chloride. Exploratory runs showed a very rapid exchange of activity between hydrogen chloride and phosphorus pentachloride in carbon tetrachloride solution and a moderate rate of exchange between hydrogen chloride and phosphorus trichloride.

Results and Discussion

The results obtained from the exchange reactions are given in Table I. The specific rate constant, k, is calculated on the basis of

$$R = k(\mathrm{PCl_5}) \tag{3}$$

where the concentration is expressed in g. atoms $\mathrm{l.}^{-1}$ of the exchanging species and time is expressed in hours.

The values of k are averaged and listed in Table II. In Fig. 1, k for each exchange is plotted against the reciprocal of the absolute temperature. The experimentally determined average activation energy is 15.9 ± 0.1 kcal./mole for the first-order reaction.

From the data, it appears that the reaction is homogeneous, first order, and non-catalyzed by light. The experimental data are represented by the rate law

$$R = 4.48 \times 10^9 \exp\left(\frac{-15900}{RT}\right)(\mathrm{PCl_5}) \tag{4}$$

where R is in units of g. atoms $\mathrm{l.}^{-1}\,\mathrm{hr.}^{-1}$. A reasonable mechanism is represented by the slow dissociative equilibrium of phosphorus pentachloride

$$\mathrm{PCl_5} = \mathrm{PCl_3} + \mathrm{Cl_2} \tag{5}$$

Discussion

The striking similarity of the results of the phosphorus and chlorine exchanges indicates that the same mechanism is operating in both cases, to the exclusion of other exchange paths. Attempts to measure the dissociation of phosphorus pentachloride have proved unsuccessful[9] but the exchange

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[7] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 1st ed., The Macmillan Co., New York, N. Y., 1948, p. 391.

[8] M. Kahn, *et al.*, *Nucleonics*, **13**, No. 5, 58 (1955).

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

TABLE I

RESULTS OF EXCHANGE EXPERIMENTS

Temp., °C.	Concn., mole/l. × 10^2 PCl_5	PCl_3	$T_{1/2}$, hr.	Specific rate constant $k \times 10^3$, hr.$^{-1}$
	Phosphorus exchange			
0.10	0.97	1.30	418	0.95
	0.97	2.59	475	1.06
	1.69	7.09	744	0.75
	2.12	3.54	427	1.02
			Av.	0.94 ± 0.09
25.00	0.37	0.51	62.7	6.4
	.47	2.10	44.6	12.7
	.59	0.91	40.7	10.3
	.63	0.96	63.4	6.6
	.63	0.96	59.9	7.0
	.74	0.51	28.7	9.9
	.80	1.68	46.7	10.0
	.94	2.46	51.9	9.7
	.95	2.46	41.1	12.2
	1.02	0.98	42.1	8.1
	1.02	0.98	24.3	14.0
	1.04	1.37	32.1	12.3
	1.04	2.73	47.2	10.6
	1.04	4.10	42.1	13.1
	1.39	1.89	74.1	6.0
	1.41	2.10	30.4	13.6
	1.48	0.51	19.9	8.9
	1.81	6.07	79.9	6.7
	1.85	0.51	14.1	10.6
	1.85	0.51	9.8	15.3
	1.85	0.51	10.8	13.8
	2.12	3.54	33.4	13.0
			Av.	10.1 ± 1.5
50.00	0.91	1.56	6.08	72.0
	0.94	0.53	4.33	57.8
	1.10	0.76	2.95	96.0
	1.16	2.77	6.24	78.3
	1.24	1.88	4.38	95.4
	1.82	1.56	3.77	84.9
	2.32	1.38	3.72	69.5
			Av.	79 ± 13
	Chlorine exchange			
0.10	0.49	0.55	260	1.07
	0.97	3.82	589	0.83
	1.35	1.37	260	1.01
	1.35	2.74	561	0.68
	2.70	1.37	154	1.05
	3.41	1.64	203	0.76
	4.38	0.55	88	0.55
			Av.	0.85 ± 0.14
25.00	0.86	1.43	36.8	9.4
	0.86	2.85	43.7	10.5
	1.08	1.46	30.2	10.3
	1.18	0.85	13.7	15.4
	1.18	1.71	26.4	12.2
	1.18	2.56	37.0	10.6
	1.18	3.42	39.6	11.1
	1.25	4.32	63.9	7.3
	1.38	3.34	42.4	9.7
	1.53	1.95	22.4	14.0
	1.54	1.78	16.0	17.7
	1.54	1.78	16.2	17.5
	1.57	3.66	34.8	11.6
	1.57	3.66	38.1	10.6
	1.73	2.85	27.5	12.5
	2.16	1.46	26.6	7.5
	3.24	1.46	24.0	6.1
	4.32	1.46	15.4	7.6
			Av.	11.2 ± 2.2
50.00	1.37	1.31	2.73	92.2
	2.74	1.31	1.72	90.2
	4.11	1.31	1.48	75.4
			Av.	86 ± 6

TABLE II

AVERAGE SPECIFIC RATE CONSTANTS

Temp., °C.	Specific rate constant $k \times 10^3$, hr.$^{-1}$
0.10	0.90 ± 0.08
25.00	10.6 ± 1.4
50.00	82 ± 6

probably proceeds with only a very small dissociation.

The dissociative mechanism would also allow the exchange of elemental chlorine with phosphorus pentachloride; such an exchange has been shown to have a much more rapid rate than the exchanges reported here.[4] The increase in rate of the chlorine exchange reaction can be attributed to one or more additional, rapid exchange paths which would effectively mask the dissociative mechanism. We note, for example, that the chlorine–phosphorus pentachloride exchange is strongly catalyzed by hydrogen chloride. We find a rapid hydrogen chloride–phosphorus pentachloride exchange and postulate a rapid hydrogen chloride–chlorine exchange to account for the catalysis. The hydrogen chloride catalysis found in the present work is much less marked because of the relatively slow rate of exchange of hydrogen chloride and phosphorus trichloride.

Finally, we might consider the phosphorus trichloride-Cl^{36} exchange experiments of the present work and ask whether the chlorine which exchanges will appear preferentially in one of the positions (apical or equatorial) of the phosphorus pentachloride. The three chlorines in phosphorus trichloride are equivalent so the label is evenly distributed. Chlorine adds mainly to become equatorial atoms in the phosphorus pentachloride and seems to be removed mainly from the same position so there probably would not be any non-equivalence of chlorine atoms. Our experimental results agree with this supposition.

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