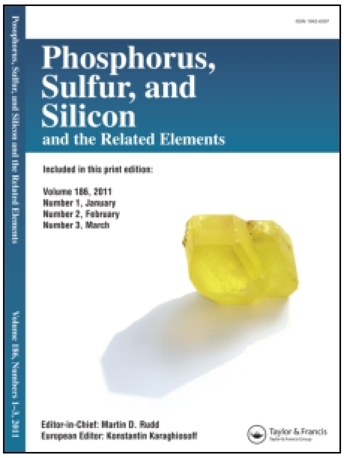

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INTRAMOLECULAR EXCHANGE IN PHOSPHORUS PENTAHALIDE MOLECULES

Robert R. Holmes[a]; Rose Mary Deiters[a]
[a] Department of Chemistry, University of Massachusetts, Amherst, Massachusetts

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INTRAMOLECULAR EXCHANGE IN PHOSPHORUS PENTAHALIDE MOLECULES[1]

ROBERT R. HOLMES and SR. ROSE MARY DEITERS
Department of Chemistry, University of Massachusetts,
Amherst, Massachusetts 01002

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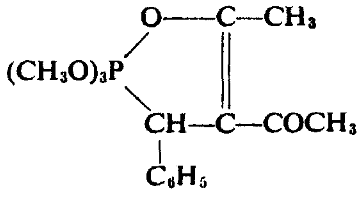
Pseudorotation of a trigonal-bipyramidal intermediate has been postulated recently by a number of investigators[2–5] concerned with various aspects of phosphorus chemistry. We wish to report results defining the requirements for such a process for phosphorus pentahalide molecules (known to undergo intramolecular exchange) and provide useful criteria in analyzing possible related situations. What is being considered here is a process analogous in some respects to the inversion occurring in the ammonia molecule.[6] In the case of trigonal-bipyramidal molecules an internal vibration is thought to lead to exchange of equatorial and axial positions, leaving the molecule rotated compared to its original state (Figure 1). This type of process was first postulated by Berry[7] to rationalize the appearance of equivalent fluorine environments in the ^{19}F nmr spectrum[8] of trigonal-bipyramidal PF_5. Nmr studies have now revealed examples of several trigonal-bipyramidal phosphorus compounds, PCl_2F_3,[9,10] PH_2F_3,[11] $(CH_2H_5)_2NPF_4$,[10b] and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which have been shown to undergo exchange. In each case, a low-temperature pattern consistent with a non-exchanging structure transforms on increasing the temperature to a pattern showing averaging of fluorine atom magnetic environments with retention of P—F spin coupling.

Detailed considerations[12] of a vibrational exchange (pseudorotation), using a potential function[13] based on complete assignments of ir and Raman spectra,[14] show that a tetragonal pyramid provides the lowest energy path leading to exchange. Actually only part of the potential function need be considered in the calculation, since the internal motions expected to lead to exchange, *i.e.*, vibrations involving predominantly equatorial or axial bending motions, belong to the same symmetry

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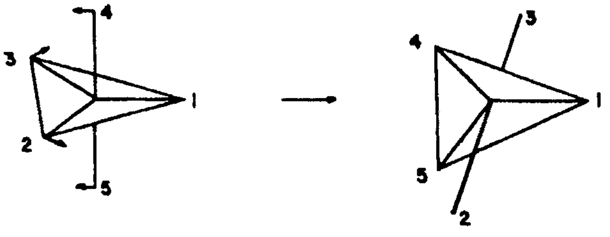


FIGURE 1 Pseudorotation.

class (e′ modes for D_{3h} molecules and a_1 modes for molecules of C_{2_v} symmetry). The resulting normal coordinate calculations show, analogous to that for the ammonia molecule,[15] that one normal mode dominates the exchange process for each of the pentahalide molecules considered here. This mode is the axial bending mode, a relatively low-frequency vibration with considerable amplitude in the ground vibrational state. The bending frequency, when the axial groups are fluorine atoms, has been observed[13,14,16] to lie in the range 120–190 cm^{-1}. The eigenvector description (L matrix) (obtained by solution of the secular equation $|GF - E\lambda_k|L_k = 0$) shows that this normal mode is primarily made up of an axial bending coordinate with small contributions from equatorial bending and stretching coordinates.[17]

By allowing the amplitude of such a motion to increase, a tetragonal pyramid is formed (Figure 2). However, it is expected that as the amplitude of the motion

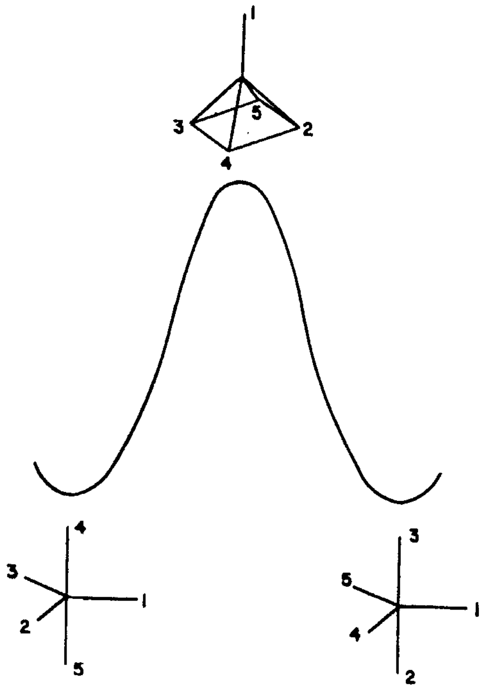


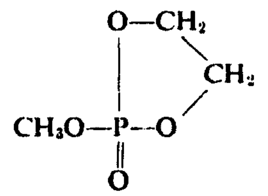
FIGURE 2 Potential well for trigonal bipyramids of type MX_5 and MX_4Y.

increases anharmonicity should become increasingly more important. In the absence of detailed information, a correction amounting to 2% initially and then increasing slowly as the barrier maximum is approached was considered reasonable for vibrations of molecules of the type discussed. This procedure introduces a cubic and quartic term into the calculations and results in greater corrective effects for molecules having the larger barrier heights. The "corrected" barrier energies (Table I) range from 25 to 40% lower than those computed from the harmonic potential function.

Consideration of tunneling through the barrier and reaction over the barrier lead to the conclusion that for these molecules the latter process assumes importance at all but the lowest temperatures. Table II lists the symmetry force constants used, and Table I compares unimolecular rate constants, approximated as $(KT/h)e^{-\Delta E/RT}$, for several trigonal-bipyramidal molecules. A *relative* ordering in agreement with rates ascertained from nmr[8,18] and exchange data[19] is seen. The rates should be regarded as upper limits, since effects of "collisional complexes" which may serve to reduce the barrier height, especially in solution, have not been considered.

The magnitude of the calculated exchange rates (Table I) for trigonal-bipyramidal molecules as heavy as $SbCl_5$ at room temperature and above (where most kinetic processes have been studied) lies in the range 10^2 to 10^8 sec^{-1}. It seems altogether reasonable then that, in some mechanistic studies, pseudorotations of trigonal-bipyramidal intermediates must be considered in accounting for product distribution. The main requirement exists that the lifetime of the intermediate exceeds the exchange time.

In fact, in the hydrolysis of cyclic phosphate esters, for example



Dennis and Westheimer[20] postulate a pseudorotation of the trigonal-bipyramidal intermediate to account for the products formed. In their case, relatively light atoms are involved, and the reaction rate, $\sim 10^{-4}$ sec^{-1} $(mol/l.)^{-1}$ at room temperature, is slow enough for exchange to occur.

However, it is clear that for the molecules under consideration pseudorotation

TABLE I

Calculated Energy Barriers and Rate Constants (sec^{-1}) for Pentahalide Molecules

	Energy barrier, kcal/mol	−73°	27°	127°	Obsd exchange data (condensed state)	Ref
PF_5	7.6	2.0×10^4	1.7×10^7	5.6×10^8	Appreciable at −160° by ^{19}F nmr	8[a]
$PClF_4$	10.9	5.1	7.2×10^4	9.2×10^6	P–F doublet broadened at −157°	*a*
CH_3PF_4	15.0	1.8×10^{-4}	7.6×10^1	5.4×10^4	Appreciable at −120° by ^{19}F nmr	10a
PCl_5	13.5	6.6×10^{-3}	8.5×10^2	3.3×10^5	Exchange not detected	10a[b]
$SbCl_5$	9.4	2.2×10^{-3}	8.7×10^5	6.0×10^7	Exchange not detected	

[a] R. P. Carter, Jr., and R. R. Holmes, *Inorg. Chem.*, **4**, 738 (1965). [b] J. Downs and R. E. Johnson, *J. Chem. Phys.*, **22**, 143 (1954).

TABLE II

Symmetry Force Constants (10^5 dyn cm^{-1}) for Calculation of Exchange Barriers

	D_{3h} Symmetry			
	F_{55}	F_{66}	F_{77}	F_{56}
PF_5	5.55	0.785	0.0864	−0.1
PCl_5	2.49	0.349	0.104	−0.2
$SbCl_5$	2.20	0.160	0.0577	0.0

	C_{2v} Symmetry					
	F_{11}	F_{22}	$F_{5a\,5a}$	F_{6a6a}	F_{7a7a}	$F_{5a\,6a}$
$PClF_4$	10.44	5.34	1.90	0.612	0.121	−0.5
CH_3PF_4	5.40	3.96	3.74	0.798	0.161	0.0

is possible only because the coordinate governing exchange has a low frequency and large amplitude motion (hence a correspondingly small force constant) associated with a molecule of comparatively low reduced mass. The latter conditions may apply for these trigonal-bipyramidal molecules because of the apparent weakness of axial bonds compared to equatorial bonds.

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17. Many possibilities of suitable exchange coordinates were considered such as combinations of normal modes. In all cases considerably higher barriers resulted compared to that discussed here except that about the same barriers were obtained by minimizing the symmetry coordinates S_6 and S_7.
18. See Table I, footnote *a*.
19. See Table I, footnote *b*.
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