We found that the net reaction of an excess of neptunium hexafluoride with sodium fluoride at 250° stopped with the formation of the 3:1 compound in the presence of an overpressure of about 146 torr of neptunium hexafluoride and 10 torr of fluorine. Therefore, the ratio of $p_{\mathrm{NpF_6}}/p_{\mathrm{F_2}}^{1/2}$ in the gas phase over $3\mathrm{NaF}\cdot\mathrm{NpF_5}$ necessary to initiate formation of the 1:1 compound, as expressed by eq 5, is greater than $K_p = (146/760)/(10/760)^{1/2} = 1.68\ \mathrm{atm}^{1/2}$.

The results of reaction of sodium fluoride with the hexafluorides of uranium, neptunium, and plutonium reflect the decreasing stability of the hexavalent state across this series of three actinide elements. In the reaction of uranium hexafluoride with sodium fluoride, the stable products are compounds of hexavalent uranium,[1-3] even though some reduction to pentavalent uranium occurs during thermal dissociation of the hexavalent compounds.[15] In the reaction of plutonium hexafluoride with sodium fluoride, plutonium undergoes autoreduction.[16,17] No evidence for a product of this reaction containing hexavalent plutonium has been presented. For the reaction of neptunium hexafluoride with sodium fluoride, Katz and Cathers[4] have reported the formation of a compound containing neptunium in the hexavalent state that readily undergoes reduction to a compound containing neptunium in a lower valence state. All of our observations indicate that, under the conditions described above, the reaction of neptunium hexafluoride with sodium fluoride proceeds with what appears to be direct autoreduction of neptunium and that a complex solid product involving hexavalent neptunium must be relatively unstable compared to $3\mathrm{NaF}\cdot\mathrm{NpF_5}$.

Acknowledgment.—The authors are indebted to Robert Schablaske and Ben Tani for X-ray powder diffraction analyses.

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Pentacoordinated Molecules. XII.[1,2] Correlation of Exchange Rates for Some Group V Pentahalide Molecules

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The height of the barrier restricting intramolecular exchange, postulated to be present in PF_5 and related trigonal-bipyramidal molecules, is computed using a vibrational potential function based on normal-coordinate analyses. The barrier height corresponds to a tetragonal pyramid. The latter structure is considered to represent the lowest energy path leading to exchange. Rate constants are calculated for tunneling through the barrier and for activation over the barrier. Although the calculated rates are lower than nmr data indicate, the relative ordering is in agreement with observations ($PF_5 > PClF_4 > PCl_5$). Application to other molecules is made as well as a brief discussion of exchange rates with regard to postulated trigonal-bipyramidal intermediates in substitution reactions.

An intramolecular exchange process has been postulated by Berry,[3] analogous to that established for ammonia, to explain the nmr equivalence of fluorine atoms in PF_5.[4,5] The F^{19} nmr spectrum of PF_5, usually studied below its boiling point of −85°, consists of a single fluorine resonance split into a doublet due to P–F coupling. The process involves an internal motion shown in Figure 1 which leaves the molecule in a rotated state compared to the original with equatorial and axial positions exchanged.

Examination of the gas-phase infrared spectrum at room temperature and liquid-phase Raman spectrum of PF_5 at −100°[6,7] shows a normal spectrum expected for a trigonal-bipyramidal molecule. A temperature-dependent study of gaseous PF_5 in the far-infrared[8] region between room temperature and −100° has not revealed any features assignable to the presence of an exchange process. Hence the presumed exchange process appears to take place at a rate faster than that detectable in the nmr measurements but slower than that which would affect line widths of vibrational bands.

An electron diffraction study by Hansen and Bartell[9] shows the expected nonequivalence of equatorial and axial bonds. A distance of 1.534 ± 0.004 Å was obtained for the $P\text{–}F_{eq}$ bond and 1.577 ± 0.005 Å was

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[1] Presented in part at the 155th National Meeting of the American Chemical Society, Division of Inorganic Chemistry, San Francisco, Calif., April 1968.

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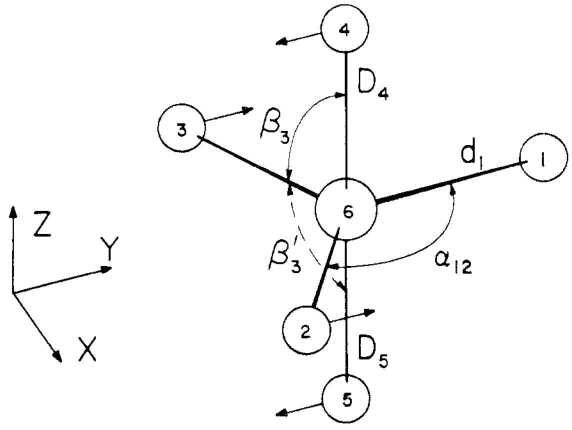

Figure 1.—Coordinates for a trigonal-bipyramidal molecule illustrating exchange.

obtained for the P–F_{ax} bond. It is possible, though highly improbable, that accidental magnetic equivalence of fluorine environments explains the nmr observations on PF_5 since related molecules have widely separated chemical shifts. Thus, in PCl_2F_3 (C_{2v} symmetry[10,11]) the chemical shift between equatorial and axial fluorine atoms is 109 ppm. In molecules like PCl_2F_3[10,11] and PH_2F_3[12,13] intramolecular exchange also has been reported on the basis of nmr measurements. In these cases the exchange is stopped by cooling the samples sufficiently. An appropriate low-temperature spectrum[10,13] is recorded in each case.

Consideration of the exchange process shown in Figure 1 leads to a double minimum potential function with the barrier height reached when the equatorial and axial atoms become equivalent in a tetragonal-pyramidal configuration. The purpose of the present paper is to calculate the barrier energies for certain trigonal-bipyramidal molecules from vibrational potential functions. With such information a rate of exchange may be determined and compared with experimental observations with the hope of obtaining some insight into the detailed mechanistic behavior inherent in an intramolecular exchange process.

Procedure

In the case of the ammonia molecule the barrier height restricting inversion has been determined by several investigators[14] from hyperfine splitting in the microwave spectrum and doubling in the infrared region. Lack of doubling in the infrared spectrum[6,7] of nonpolar PF_5 precludes following a similar procedure in this case. While the less symmetric molecules $PClF_4$ and PCl_2F_3 have low dipole moments, 0.78[15] and 0.68 D,[16] respectively, and an observable microwave spectrum,[17] no spectroscopic data showing exchange have been reported.

An alternate procedure based on a vibrational potential function was applied to the ammonia molecule by Costain and Sutherland.[14] The resulting barrier height was in close agreement with that derived from inversion splittings.[18] Since the vibrational spectra of all of the phosphorus chlorofluorides have been assigned[6,7,15,19] and normal-coordinate calculations have been performed,[20] the latter method is applicable in the present instance.

Examination of the eigenvector description of the normal modes using a valence force field reveals a mode appropriate for intramolecular exchange. This mode, associated with the lowest vibrational frequency in each case, is described principally as an axial bending motion with lesser amounts of equatorial bend and equatorial stretch contributing. The directions of the atom movements are consistent with those depicted in Figure 1.

By allowing the amplitude of such a motion to increase, a tetragonal pyramid may be formed. An energy is calculable for this configuration based on the expression governing the vibrational potential. Once the energy barrier is obtained, kinetic expressions may be applied to approximate an exchange rate. Alternately, the importance of quantum mechanical tunneling through the barrier may be determined and compared, for example, to a unimolecular rate

Other modes or combination of modes (Lissajous motions) also might provide suitable exchange coordinates. Thus, ν_{6a} which represents a high degree of in-plane equatorial bending[20] might be combined with ν_{7a}. Examination of several such cases led to barrier heights of unreasonable magnitude with $PClF_4$ as well as the other molecules considered. As discussed before[20] values of stretching force constants indicate that axial bonds are considerably weaker than equatorial P–F bonds. As a consequence, which the present calculations show, the low-frequency axial bending modes (Tables I and II) dominate in terms of relative amplitudes of motion compared to similar motions of the equatorial in-plane modes. The latter frequencies are comparatively higher and range around 500 cm^{-1} ± 10%.[6,20] Correspondingly, the associated amplitudes are much smaller when considering like atoms.

Actually the most favorable exchange coordinate is not represented by a single normal mode as might be inferred from above but may be more closely approximated by considering both the equatorial and axial bending motions expressed in symmetry coordinates S (defined below). The best combination of these two motions in a harmonic approximation is obtained by minimizing the potential function

$$V = {}^1/_2F_{66}S_6^2 + {}^1/_2F_{77}S_7^2$$

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TABLE I

CARTESIAN DISPLACEMENT COORDINATES (Å) FOR GROUND STATE OF AXIAL BENDING MODE[a]

Molecule D_{3h}	ν_7, cm^{-1}	Δy_1	$\Delta x_2 = -\Delta x_3$	$\Delta y_2 = \Delta y_3$	$\Delta y_4 = \Delta y_5$	Δy_6	$\Delta\beta_1$, deg
PF_5	(122)[b]	0.03069	0.00058	0.03170	−0.07126	0.02970	3.68
PCl_3F_2[c]	122	0.02212	−0.00032	0.02156	−0.07543	0.01785	3.40
PCl_5	100	0.02802	0.00180	0.03113	−0.05590	0.02463	2.11
$SbCl_5$	72	0.02146	0.00212	0.02513	−0.07088	0.02040	2.20

Molecule C_{2v}	ν_{7a}, cm^{-1}	Δy_1	$\Delta x_2 = -\Delta x_3$	$\Delta y_2 = \Delta y_3$	$\Delta y_4 = \Delta y_5$	Δy_6	$\Delta z_4 = -\Delta z_5$	$\Delta\beta_1$,[d] deg
$PClF_4$	144	0.02744	−0.00040	0.02621	−0.06700	0.01863	0.00000	3.13
CH_3PF_4	179	0.02692	0.00077	0.02875	−0.05966	0.02485	−0.00021	3.01
PCl_2F_3[c]	124	0.02136	0.00099	0.02480	−0.07372	0.02056	0.00000	3.44

[a] Coordinate directions and subscript numbering of atoms correspond to those shown in Figure 1. The entries represent classical turning point amplitudes. [b] For PF_5 122 cm^{-1} represents an assumed frequency. The ν_7 fundamental in this case has not been observed spectroscopically[8] but should lie somewhere near the corresponding frequency in related molecules. Hence the value taken is the same as that in PCl_3F_2. [c] Tetragonal pyramid in this case does not lead to exchange. [d] For C_{2v} molecules the unique atom or group in the equatorial plane resides at position 1 (Figure 1).

TABLE II

SYMMETRY FORCE CONSTANTS AND COORDINATES FOR THE ν_7 BENDING MODES[a]

D_{3h} Symmetry

	F_{55}	F_{66}	F_{77}	F_5
PF_5	5.55	0.785	0.0810	−0.1
PCl_5	2.49	0.349	0.104	−0.2
$SbCl_5$	2.20	0.160	0.0577	0.0
PCl_3F_2	2.33	0.978	0.0691	−0.5

	S_5	S_6	S_7
PF_5	0.001217	0.004961	−0.1721
PCl_5	0.004156	0.01599	−0.1346
$SbCl_5$	0.001292	0.01262	−0.1558
PCl_3F_2	0.005227	0.007476	−0.1842

C_{2v} Symmetry

	F_{11}	F_{22}	F_{5a5a}	F_{6a6a}	F_{7a7a}	F_{5a6a}
$PClF_4$	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
PCl_2F_3	2.17	4.95	4.79	0.598	0.0897	−0.2

	S_1	S_2	S_{5a}	S_{6a}	S_{7a}
$PClF_4$	−0.000312	0.0	0.01057	0.01560	−0.1483
CH_3PF_4	−0.000292	0.000299	0.002748	0.009231	−0.1464
PCl_2F_3	0.000994	0.0	0.001683	0.01019	−0.1633

[a] The F matrix elements are in units of 10^5 dyn cm^{-1}. The symmetry coordinates are in Å and represent values for the ground vibrational level.

where the subscripted F's are symmetry force constants. The condition on the angle in the tetragonal pyramid is obtained as $\sin \Delta\beta_1 = x/2(x + y)$, where $x = 3F_{66}d_1^2$ and $y = 1.5F_{77}d_1D_4$ for D_{3h} symmetry and $x = 3F_{66}d_2^2$ and $y = 1.5F_{77}D_4^2$ for C_{2v} symmetry. For the molecules to be discussed, the resultant barrier heights are lower on the average by only a few tenths kcal/mol than those obtained from use of the axial bending mode expressed in terms of normal coordinates.[21] Since the differences are slight compared to other approximations, especially the uncertainty of the magnitude expected for vibrational anharmonicity, the calculations to follow are outlined in terms of the single normal coordinate in order to maintain mathematical simplicity. When further spectroscopic information becomes available, a more detailed treatment may be warranted.

The molecules that will be treated are shown in Table I. All are trigonal bipyramids with fluorine atoms, when present, showing a preference for axial sites.[6,9,15,22] The axial bending frequencies listed in column two are of species e′ for trigonal bipyramids of D_{3h} symmetry and a_1 for those of C_{2v} symmetry. The part of the potential energy expression appropriate for vibrations of e′ species in terms of symmetry coordinates S is

$$2V = F_{55}S_5^2 + F_{66}S_6^2 + F_{77}S_7^2 + 2F_{56}S_5S_6 \quad (1)$$

The corresponding expression for the molecules of C_{2v} symmetry in Table I is

$$2V = F_{11}S_1^2 + F_{22}S_2^2 + F_{5a5a}S_{5a}^2 + F_{6a6a}S_{6a}^2 + F_{7a7a}S_{7a}^2 + 2F_{5a6a}S_{5a}S_{6a} \quad (2)$$

The procedure now will be described in more detail for $PClF_4$.

$PClF_4$.—A suitable set of symmetry coordinates[20] for vibrations of a_1 species is

$$S_1 = (\Delta d_1 + \Delta d_2 + \Delta d_3)/3^{1/2}$$

$$S_2 = (\Delta D_4 + \Delta D_5)/2^{1/2}$$

$$S_{5a} = (-2\Delta d_1 + \Delta d_2 + \Delta d_3)/6^{1/2}$$

$$S_{6a} = d_2(-2\Delta\alpha_{23} + \Delta\alpha_{12} + \Delta\alpha_{13})/6^{1/2}$$

$$S_{7a} = D_4(2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3 + 2\Delta\beta_1' - \Delta\beta_2' - \Delta\beta_3')/12^{1/2}$$

These symmetry coordinates are expressed in terms of internal coordinates where d and D refer to equatorial and axial bond distances, respectively, α refers to equatorial bond angles, and β and β' refer to axial bond angles. The meaning of the subscripts becomes apparent with reference to Figure 1.

A computer program previously developed[20] for normal-coordinate analyses of trigonal-bipyramidal molecules was modified to convert the normalized eigenvector descriptions of the normal modes from the above symmetry coordinates S to cartesian coordinates by suitable transformation matrices.

In the modification, eigenvectors were obtained by solution of the secular equation $|GF - E\lambda_k|l_k = 0$, where l_k is a column of the matrix l_{ik} giving the relation between the symmetry coordinates S and normal co-

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[21] In the case of PF_5 Hoskins and Lord[7] concluded that the efficiency of fluorine exchange along any normal coordinate will be significantly less than along the exchange coordinate, $Q_{ex} = S_{6a} + S_{7a}$.

[22] (a) L. S. Bartell and K. W. Hansen, *Inorg. Chem.*, **4**, 1777 (1965); (b) M. Rouault, *Ann. Phys.*, **14**, 78 (1940); (c) S. M. Ohlberg, *J. Am. Chem. Soc.*, **81**, 811 (1959).

ordinates Q. The eigenvector matrix l_{ik} was normalized to the ground-state vibrational energies to give the matrix L. By means of the transformation matrix U relating symmetry coordinates S and internal coordinates R, *i.e.*, $S = UR$, the relation between internal coordinates and normal coordinates is obtained as $R = U'LQ$. The expression for internal coordinates R in terms of cartesian coordinates C is $R = WC$. Using the latter transformation matrix W, cartesian coordinates are expressed in terms of normal coordinates by the relation $C = W^{-1}U'LQ$. Finally, the set of cartesian displacements for the ith normal mode Q_i is obtained by equating all normal coordinates, except Q_i, to zero.

The resulting displacements of the atoms in $PClF_4$ for the ground-state ν_{7a} bending vibration at 144 cm^{-1} are listed in Table I. For comparison, corresponding displacements are included for other molecules of interest along with the change in the internal coordinate $\Delta\beta_1$. The numbering of the atoms follows that shown in Figure 1. It is seen that this mode represents a suitable exchange coordinate.

Table II lists the makeup of the ν_{7a} vibration for $PClF_4$ in terms of the symmetry coordinates (normalized L matrix) as well as the values of the symmetry force constants that were used in the computation. The motion associated with the ν_{7a} frequency is seen to be represented largely by the axial bending symmetry coordinate, S_{7a}. Similar results of relative amplitudes were obtained for the other C_{2v} and D_{3h} trigonal bipyramids under consideration and are listed in Table II.

Multiplication of the ground-state ν_{7a} internal coordinates of $PClF_4$ by a suitable factor a chosen so that $\alpha_{12} = \beta_1$ yields a set of internal coordinates corresponding to a tetragonal pyramid. The angle β_1 in the tetragonal pyramid is 117.9° showing the magnitude of the displacements of the axial atoms from their assumed geometry of $\beta_1 = 90°$ for this coordinate. These internal coordinates give rise to a set of symmetry coordinates which may be substituted into eq 2 in order to calculate the height of the barrier restricting exchange. The energy of the tetragonal-pyramid configuration, V_{max}, can thus be expressed as a function of the factor a and the ground-state energy V_0

$$V_{max} = a^2 V_0 \tag{3}$$

However, it is expected that, as the amplitude of the motion 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. Thus, in place of a in (3), the quantity $a(1.02 - 0.02a)$ was used. 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 barriers are lowered by 25–40% compared to those based on the harmonic potential function. The resulting value V_{max} is 10.9 kcal/mol for $PClF_4$.

The potential energy curve with (Figure 2a (ii)) and without (Figure 2a (i)) the anharmonicity correction as a function of the displacement coordinate, H, is shown in Figure 2a for the normal vibration of $PClF_4$ leading to exchange. Similar calculations were performed on the other pentahalide molecules and the results are summarized in Table III. In the case of $PClF_4$ and PCl_2F_3, lacking the necessary structural information, angles of $\alpha = 120°$ and $\beta_1 = 90°$ were assumed for the ground-state structures. For CH_3PF_4 the observed[22a] angles were used ($\alpha_{12} = 122.2°$, $\beta_1 = 91.8°$). Figure 2b compares potential curves for $PClF_4$, CH_3PF_4, PF_5, PCl_5, and $SbCl_5$.

Table III

Calculated Energy Barriers Restricting Exchange

	Energy barrier, V_{max}, kcal/mol	H_{max}/H_0[a]
PF_5	7.6	7.630
PCl_3F_2	8.6	8.228
PCl_5	13.5	12.711
$SbCl_5$	9.4	12.381
$PClF_4$	10.9	8.570
CH_3PF_4	15.0	9.139
PCl_2F_3	8.5	8.077

[a] Ratio of the value of the tunneling coordinate for the tetragonal pyramid to that for the ground state of the trigonal bipyramid.

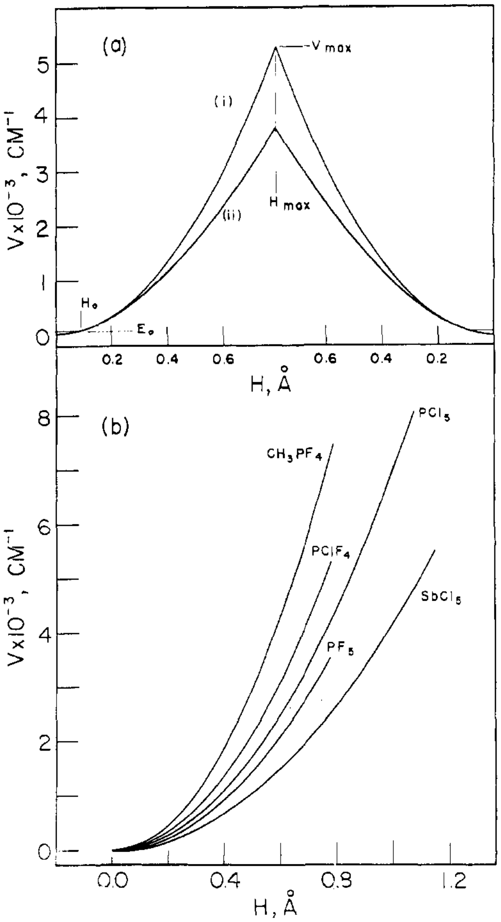

Figure 2.—Potential V as a function of the exchange coordinate H (a) for $PClF_4$ and (b) for PF_5, $PClF_4$, CH_3PF_4, PCl_5, and $SbCl_5$. In (a) the curve (i) is calculated from a harmonic potential and (ii) includes an anharmonic correction.

The displacement coordinate H is defined as $H = \Delta y(+) - \Delta y(-)$, where $\Delta y(+)$ refers to the change in the center of gravity of atoms moving in the positive y direction and $\Delta y(-)$ refers to the change in the center of gravity of atoms moving in the negative y direction during the execution of the vibration. Since the ν_{7a} vibration or ν_7 for D_{3h} molecules involves very little motion in the x and z directions (Table I), the definition of H is reasonable.

As the vibration involves no over-all change in the center of gravity, appropriate substitution shows that

$$H = -\Delta y_4\left[\frac{\sum m(-)}{\sum m(+)} + 1\right] \qquad (4)$$

where $\Sigma m(-)$ is the sum of the masses of the atoms moving in the negative y direction, $\Sigma m(+)$ is the corresponding sum for atoms moving in the positive y direction, and Δy_4 is the displacement of the cartesian coordinate y_4 associated with the bending vibration. For trigonal-bipyramidal molecules of D_{3h} and C_{2v} symmetry, $m_4 = m_5$, and for the particular symmetry species, $y_4 = y_5$; then $\Delta y(-)$ and Δy_4 are related by

$$\Delta y(-) = \frac{m_4\Delta y_4 + m_5\Delta y_5}{m_4 + m_5} = \Delta y_4$$

The potential V is calculated from eq 3 (modified to include the correction for anharmonicity discussed above) by considering incremental changes in H. The corresponding values of H from eq 4 result from changes in $\Delta\beta_1$ and, consequently, changes in Δy_4. The factor a corresponding to each value for H can be computed from the ratio of the H value to H_0 (H value for the ground state). From the resulting potential curve it is possible to compute the expected vibrational energy level splittings.

An expression for these tunneling frequencies for a double minimum potential has been derived by Dennison and Uhlenbeck.[23] They used the WKB approximation to the solution of the wave equation and applied the results to the inversion of ammonia.

If the tunneling motion consists predominantly of one normal vibrational mode, as is the case here (Table I), the energy level splitting of the nth vibrational level ΔE_n is given[23] by

$$\Delta E_n = \frac{h\nu}{\pi A_n} \qquad (5)$$

$$A_n = \exp\left\{\frac{4\pi}{h}\int_{H_{\max}}^{H_0} [2\mu(V - E_n)]^{1/2}\,\mathrm{d}H\right\} \qquad (6)$$

where ν is the vibrational frequency associated with the exchange process, H_0 is the value of H at which $V(H) = E_n = (n + {}^1/_2)h\nu$, and μ is the reduced mass for the vibration in grams per molecule.

As the derived expressions (eq 5 and 6) apply to a one-dimensional system, it is necessary to calculate a reduced mass μ along the tunneling coordinate H. Consideration of the cartesian displacements for the vibration gives the expression

$$\mu = \sum_{i=1}^{n} (m_i y_{ij}^2)/H_j^2$$

where the j subscript refers to the set of cartesian coordinates corresponding to a particular H value (μ is constant for all values of H).

By calculating the Boltzmann population of the various vibrational levels below the barrier (Figure 2a) at a particular temperature, a rate constant k_t for tunneling is obtained from the relation[24]

$$k_t = \frac{\sum_n \exp[-h\nu(n + {}^1/_2)/kT]\Delta E_n}{h\sum_n \exp[-h\nu(n + {}^1/_2)/kT]} \qquad (7)$$

This constant may be compared to the rate constant for activation over the barrier

$$k_c = (kT/h)\exp[-V_{\max}/RT] \qquad (8)$$

where $V_{\max}$, the barrier height, is in calories per mole. Both constants may be considered unimolecular rate constants.

The splittings ΔE_n and tunneling constants k_t were calculated by a computer program (TUNNEL) which evaluated expressions 5–7 at various temperatures. The integration in (6) was carried out numerically by Gregory's method[25] using the first and second terms.

The use of potential functions derived[20] from analysis of vibrational data leads to relatively small energy differences between a trigonal bipyramid and a tetragonal pyramid, *i.e.*, the energy barriers in Table III. It is clear that where exchange processes are possible, low barriers will be obtained only if the coordinate governing exchange has a low-frequency, 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 of phosphorus because of the apparent weakness of axial P–F bonds compared to equatorial P–F bonds.

In comparison with the ammonia molecule, where the barrier to exchange has been estimated by Manning[18] and others[14] to be about 6 kcal/mol, the most important quantities for ammonia are the low reduced mass leading to considerable vibrational amplitude and the smaller change in coordinates required to reach the barrier maximum (~13° change in the H–N–H angle). In ammonia the frequency governing the exchange is not especially low (950 cm^{-1}).

Listed in Table IV for $PClF_4$ and other pentahalide molecules are the length of the calculated tunneling coordinate $H_{\max}$, the reduced mass values μ, and calculated spectroscopic splittings for the ground and first excited vibrational states. In Table V are the calculated rate constants, k_c and k_t, based on the values of the barrier heights in Table III.

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TABLE IV

ESTIMATED SPECTROSCOPIC SPLITTINGS OF VIBRATIONAL LEVELS FOR PENTAHALIDE MOLECULES

Molecule	H_{max}, Å	μ, g/mol	ΔE_0, sec^{-1}	ΔE_1, sec^{-1}
PF_5	0.779	26.5	2.0×10^{-10}	3.2×10^{-8}
$PClF_4$	0.783	28.0	5.8×10^{-16}	1.2×10^{-13}
CH_3PF_4	0.792	26.2	3.3×10^{-20}	9.0×10^{-18}
PCl_5	1.077	46.9	1.1×10^{-46}	6.4×10^{-44}
$SbCl_5$	1.150	54.2	4.6×10^{-44}	2.4×10^{-41}

TABLE V

CALCULATED RATE CONSTANTS k_c AND TUNNELING RATE CONSTANTS k_t FOR PENTAHALIDE MOLECULES (SEC^{-1})

Molecule	Constant	100°K	200°K	300°K	400°K
PF_5	k_t	3.2×10^{-2}	4.3×10^{4}	8.3×10^{6}	1.2×10^{8}
	k_c	4.3×10^{-5}	1.9×10^{4}	1.7×10^{7}	5.6×10^{8}
$PClF_4$	k_t	1.5×10^{-7}	3.2×10	6.1×10^{4}	2.8×10^{6}
	k_c	3.1×10^{-12}	5.1	7.2×10^{4}	9.2×10^{6}
CH_3PF_4	k_t	2.9×10^{-13}	5.3×10^{-3}	1.7×10^{2}	3.6×10^{4}
	k_c	3.8×10^{-21}	1.8×10^{-4}	7.6×10	5.4×10^{4}
PCl_5	k_t	7.1×10^{-16}	7.4×10^{-3}	2.3×10^{2}	3.8×10^{4}
	k_c	5.3×10^{-18}	6.6×10^{-3}	8.5×10^{2}	3.3×10^{5}
$SbCl_5$	k_t	4.2×10^{-8}	8.3×10	1.1×10^{5}	3.6×10^{6}
	k_c	5.7×10^{-9}	2.2×10^{2}	8.7×10^{5}	6.0×10^{7}

Although the tunneling rate for the ground vibrational state of the mode governing exchange is calculated to be very small, for example, 5.8×10^{-16} sec^{-1} for $PClF_4$, the tunneling rate obtained by considering the population of higher harmonics and corresponding level splittings from (7) is much greater (7.2×10^4 sec^{-1} at room temperature for $PClF_4$). This is so, even though most of the molecules are in the ground vibrational level, because the increase in splittings associated with the higher levels more than compensates for the reduced population. Accordingly, the latter tunneling rate is temperature dependent and is the one used when making comparisons with observed kinetics of exchange processes.[26]

A tunneling rate for the ground-state vibrational level of PF_5 has been estimated as 3×10^6 sec^{-1} by Hoskins and Lord[7] based on Berry's potential curves.[3] One reason such a high value was obtained compared to that reported here, $\sim 10^{-10}$ sec^{-1} (Table IV), centers on the use of pyramidal NF_3 in their calculation. In using Berry's procedure, one has to assume a "reference" molecule if spectroscopic splitting is not known for any member of a related series.

Of the two sets of rates the tunneling rates k_t calculated from (7) are higher at 100°K and comparable at 200°K while the rates k_c dominate near room temperature and above in most instances. The ratio k_c/k_t becomes larger as the temperature increases. Hence, the rate of exchange should be governed by activation over the barrier rather than barrier penetration at all but the lower temperatures. Where the activated process is favored, then, the order of barrier energies will parallel the order of calculated exchange rates.

Comparison of either set of rates k_c or k_t at 200°K, the approximate temperature region of many of the nmr studies, leads to the conclusion that for the phosphorus halide molecules the rate of exchange decreases in the order $PF_5 > PClF_4 > PCl_5$ in agreement with experimental observations. The same ordering of rate constants is maintained at the other temperatures listed in Table V. The rate for PF_5, of course, is strongly dependent on the value assumed for the ν_7 frequency.

PF_5 shows nmr equivalence[4, 5] of fluorine atoms at the lowest temperatures studied.[27] In Table V k_t at $-73°$ is 4.3×10^4 sec^{-1}. The $PClF_4$ F^{19} spectrum begins to show broadening[27] at $-138°$ and complete broadening of the P–F doublet at $-157°$. An exchange rate comparable to the coupling constant of about 10^3 cps is inferred (k_t at $-73°$ is 3.2×10 sec^{-1}, Table V). In the case of PCl_5, it has been concluded[28] that results of tracer studies[29] rule out fast intramolecular exchange (Table V lists k_t at $-73°$ as 7.4×10^{-3} sec^{-1}). For CH_3PF_4 the calculation indicates a slower rate than that for $PClF_4$. However, the lowest temperature studied in the F^{19} nmr measurement was $-120°$ where no broadening was reported, only spectroscopic equivalence.[28] Thus, no comparison with $PClF_4$ is possible at present.

From the calculations considered here, it is not possible to compare exchange rates of more highly fluorinated molecules like PCl_2F_3 since no simple low-energy exchange coordinate suggests itself. To bring one or both of the axial fluorine atoms into an equivalent position with the equatorial fluorine atom would require considerable energy if it were accomplished by forming a trigonal bypyramid of D_{3h} symmetry. However, it is conceivable that a multistep process involving tetragonal pyramids may lead to a lower barrier than that expected from a single D_{3h} symmetry. Qualitatively, the observed exchange rate is lower for PCl_2F_3 than $PClF_4$. Below $-115°$ nonequivalence of fluorine atom environments is present in the case of PCl_2F_3.[10,11,28] An activation energy for the exchange of 6.5 ± 2 kcal/mol has been determined.[11]

Although the ordering of rates is, in general, in line with experimental observations, where comparisons can be made, the fact that these rates are lower than nmr measurements imply deserves comment. It may be that a larger "correction" for anharmonicity should be applied. However, this will not be known until the appropriate spectroscopic information becomes available.

The extension of axial bond angle deformations from 2.2–3.7° (Table I), calculated for the zero-point vibrational levels of these molecules, to about 28–29° required for exchange is certainly subject to considerable uncertainty. The excellent agreement, though somewhat fortuitous, between the calculated spectroscopic splittings and observed values that Costain and Sutherland[14] obtained when applying this method

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(26) For the ammonia molecule using the deformation vibration (950 cm^{-1}) as the basis for the exchange coordinate,[14] there are only two vibrational levels below the barrier maximum to consider. For the molecules discussed here having higher barriers (Table III) and much lower values (Table I) for normal vibrations (72–179 cm^{-1}), many levels exist below the barrier maximum from which molecules may tunnel. For ammonia, little temperature effect is present and the ground-state splitting represents the tunneling rate satisfactorily.

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

to ammonia lends some confidence to the general procedure. In ammonia, a relatively modest barrier height is calculated[14] as 2077 cm^{-1} (6.00 kcal/mol) in excellent agreement with Manning's potential[18] of 2076 cm^{-1} obtained without approximations. Similar agreement is not expected here since the uncertainty increases with the height of the barrier in the sense that the correction to the harmonic approximation applied in the present calculations becomes less justified.

Further, the observed rate data are obtained mainly from nmr measurements on the condensed state at reduced temperatures while the values in Table V are considered more appropriate for application to exchange processes in the gaseous state. In the condensed state there is evidence that intermolecular interaction serves to lower the barrier by allowing weakly held, short-lived solvation complexes or specifically oriented "collisional complexes" to be formed. Recent observations by Brownstein[30] of the temperature and concentration dependence of F^{19} nmr line widths of PF_5 in methylene chloride solution support such an intermolecular process for the intramolecular exchange. A specific example of a "collisional complex" thought to lower the exchange barrier in the condensed state has been reported[31] for SF_4, a pseudo-trigonal-bipyramidal molecule which undergoes exchange in the condensed state. At present though, it has not been determined[32,33] whether or not S–F bonds are broken during exchange in this case.

A suitable set of rate constants applicable to condensed state exchange processes is given in Table VI. An exchange rate inferred from nmr measurements on $PClF_4$ of about 10^3 cps at $-73°$ is used as a basis for constructing the table. A calculated energy barrier of 5.0 kcal/mol is then used to obtain rate constants at other temperatures. Applying a comparative reduction in the barrier heights based on the harmonic approximation leads to similar results for PF_5 and PCl_5. It is realized that condensed-state processes may vary from compound to compound (including varying sensitivity to foreign substances such as HF impurities) and may partially nullify the comparison of relative rates. The data in Table VI indicate that some influence on line widths of vibrational bands might be expected at room temperature and above for PF_5 and $PClF_4$ in the condensed state. However, no experiments have been reported under these conditions thus far.

On the basis of the rate constants in Table V, one might speculate that in the absence of intermolecular effects, such as in the gas state at sufficiently reduced pressures, exchange might be "stopped" in a molecule like $PClF_4$ or CH_3PF_4 at not too low a temperature. Observation of nonequivalence of fluorine atoms in PF_5 by nmr would be more difficult.

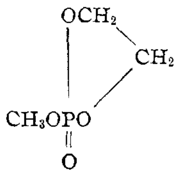
TABLE VI

CALCULATED CONDENSED-STATE RATE CONSTANTS FOR PENTAHALIDE MOLECULES (SEC^{-1})

	100°K	200°K	300°K	400°K
PF_5	9.4×10^4	8.8×10^8	2.2×10^{10}	1.2×10^{11}
$PClF_4$	2.7×10	1.5×10^7	1.5×10^9	1.6×10^{10}
PCl_5	4.7×10^{-5}	2.0×10^4	1.8×10^7	5.7×10^8

Often a trigonal bipyramid has been postulated as an intermediate in substitution reactions (*e.g.*, dissociation reactions of octahedral complexes or bimolecular reactions of tetrahedral or square-planar compounds) to explain the geometry and distribution of the products formed. The magnitude of the calculated exchange rates (Table V) 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 10^2–10^8 sec^{-1}. It seems altogether reasonable then that, in some of the studies, pseudorotations of trigonal-bipyramidal intermediates must be considered in accounting for product distribution. The main requirement must exist that the lifetime of the intermediate exceeds the exchange time.

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



Dennis and Westheimer[34] 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, $\sim 10^{-4}$ M^{-1} sec^{-1} at room temperature, is slow enough for exchange to occur.

Lastly, the low values calculated for the splittings of the ground-state vibrational levels in Table IV indicate that there is little chance of observing these spectroscopically. Much more favorable cases for the latter type of study would be the as yet unknown PH_4F and PH_5 molecules.

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