Pseudorotation in XPF$_4$[1]

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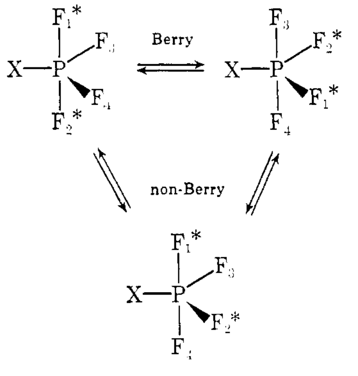
Abstract: The temperature dependence of the ^{31}P nmr spectra of $(CH_3)_2NPF_4$ (**1**), $ClPF_4$, and CH_3PF_4 has been examined. The interchange of axial and equatorial fluorines in $(CH_3)_2NPF_4$ and $ClPF_4$ follows the permutational scheme expected for Berry pseudorotation; *viz.*, both axial and equatorial fluorine atoms interchange at the same time. The rate of pseudorotation of **1** is independent of the concentration of **1** but is catalyzed by THF and $(CH_3)_2O$. The free energy of activation for pseudorotation of **1** in $CHCl_2F$ is $\Delta G^{\ddagger} = 8.8 \pm 0.2$ kcal/mol at $-85°$, and for $ClPF_4$ in $CHCl_2F$ is $\Delta G^{\ddagger} \simeq 4.2 \pm 0.3$ kcal/mol at $-177°$. Combination of these rates with data obtained by others indicates that the relative rates of pseudorotation of compounds having the composition XPF_4 increases in the order $(CH_3)_2N < SR, H < Cl < CH_3, F$. A new procedure has been developed which permits calculation of the influence of an intermediate present in low concentration along the pseudorotation coordinate for **1** on its spectrum. This procedure establishes that the influence of a single intermediate in equilibrium with two ground states can in general be described exactly by incorporation of only one further operator, called the "transfer operator" A, into the usual Kaplan–Alexander equation of motion of the nuclear spin system. Application of this procedure to the spectrum of **1** indicates that even if a square pyramid were an intermediate along the pseudorotation coordinate, it would not be possible to detect it by nmr line shape analysis at presently accessible spectral resolution.

The polytopal[5] exchange of ligands around pentacoordinate phosphorus has been extensively studied,[6-8] both because this class of intramolecular interchange reactions provides experimentally tractable examples of the fluxional behavior that is an important characteristic of many pentacoordinate inorganic complexes[9,10] and because pentacoordinate phosphorus compounds are believed to be intermediates in many biological processes involving phosphate esters.[11] Substances having the composition XPF_4 have been subjected to particularly detailed study for four reasons. First, these compounds are easily synthesized, purified, and manipulated. Second, the combination of ^{31}P and ^{19}F nmr spectroscopy with other physical techniques makes it possible to define the ground state geometry of these substances as trigonal bipyramidal, with the substituent X in an equatorial position.[9,12,13] Third, the polytopal exchange reactions of many of these compounds occur at rates that are convenient for study by magnetic resonance techniques. Finally, the observation that ^{19}F–^{31}P coupling is preserved during these exchange reactions guarantees their intramolecularity (although not their unimolecularity, *vide infra*).

Recent interest in these polytopal exchanges has centered on questions of the details of their mechanisms. One elementary problem in establishing a mechanism is that of defining the permutational scheme that describes the process by which the four fluorine atoms interchange; the influence of the fifth ligand, X, and of the solvent on the energetics of this process is also of obvious interest. For XPF_4 compounds having trigonal bipyramidal ground state geometry, there are only two classes of permutational isomerizations that are distinguishable by nmr: (13)(24) and (13)(2)(4).[8]



(1)

Mechanistically, the first of these corresponds to a process in which the two axial fluorine atoms interchange

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(4) National Science Foundation Predoctoral Fellow, 1971–1973.

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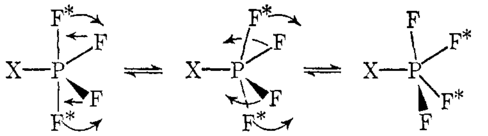
(10) (a) P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, **94**, 5271 (1972); (b) P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *ibid.*, **93**, 4701 (1971).

(11) T. C. Bruice and S. Benkovic "Bioorganic Mechanisms," Vol. 2, W. A. Benjamin, New York, N. Y., 1966, pp 1–109; F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968); F. Ramirez, *ibid.*, **1**, 168 (1968); S. J. Benkovic and K. J. Schray in "The Enzymes," 3rd ed, Vol. VII, P. D. Boyer, Ed., Academic Press, New York, N. Y., 1973, Chapter 6; F. H. Richards and H. W. Wycoff, *ibid.*, Vol. IV, 1971, Chapter 4; J. H. Young, J. McLick, add E. F. Korman, *Bioorg. Chem.*, **3**, 1 (1974).

(12) E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, **20**, 245 (1966).

(13) References to representative studies using other physical techniques are contained in these articles: ir and Raman, R. R. Holmes, *Accounts Chem. Res.*, **5**, 296 (1972); B. J. Dalton, *J. Chem. Phys.*, **54**, 4745 (1971); L. C. Hoskins and R. C. Lord, *ibid.*, **46**, 2402 (1967); J. Brickmann, *Ber. Bunsenges. Phys. Chem.*, **75**, 747 (1971); electron diffraction, L. S. Bartell and K. W. Hansen, *Inorg. Chem.*, **4**, 1775, 1777 (1965).

simultaneously with the two equatorial fluorines;[14] the second corresponds to a process in which one axial and one equatorial fluorine interchange, while the remaining axial and equatorial fluorines remain in their positions. Throughout this paper, we will refer to any process belonging to the former class by the phrase "Berry permutation" for want of a better term and to processes belonging to the latter class by "non-Berry permutation." In so doing, we wish to emphasize the distinction between the permutational character of the pseudorotation and its detailed physical mechanism. Berry's original discussion of the mechanism of the process responsible for the averaging of the axial and equatorial ^{19}F chemical shifts of PF_5 included a description of one specific reaction coordinate. For a substance of composition XPF_4 pseudorotating by this mechanism, fluorine interchange would occur by a process which carried the molecule from a trigonal bipyramid to a square pyramid of C_4 local symmetry through intermediate structures of C_2 symmetry.[15,16] This reaction coordinate of course results in the simultaneous interchange of both pairs of axial and equatorial fluorine atoms. Subsequently, other reaction coordinates that also result in the same permutation of fluorine nuclei have been suggested to be responsible for pseudorotation in derivatives of phosphorus(V).[17] Only two points concerning these several mechanistic suggestions are directly pertinent to this paper. First, no experiment has so far been carried out or proposed that can distinguish between them for compounds of the structure XPF_4. Second, it is not obvious that they all differ from one another by more than the amplitudes of zero-point bending vibrations of P–F bonds. If they do not, it is questionable whether any experiment is capable of distinguishing between them. Regardless, magnetic resonance spectroscopy is capable of establishing experimentally the one of two possible permutational schemes that characterizes the pseudorotation of a particular XPF_4 compound, and in what follows any process that interchanges both axial and equatorial fluorines simultaneously will be referred to as a "Berry permutation," without implying further details of its mechanism.



(2)

The research described in this paper had several objectives. First, this work refines the data, briefly presented previously,[14] which served as the basis for the conclusion that pseudorotation in $(CH_3)_2NPF_4$ (**1**) followed a Berry permutation, and extends the nmr technique developed for this purpose to $ClPF_4$ to ensure that this conclusion was not restricted to **1**. Second, it examines the influence of solvent and concentration on the pseudorotation of **1**. This effort seemed particularly worthwhile in light of suggestions that pseudorotation in a number of related compounds may involve bimolecular processes.[18] Finally, it attempts to define conditions and techniques with which it might be possible to detect a square pyramidal intermediate along the pseudorotational coordinate, if one were present. Theoretical calculations have offered no indication that such an intermediate should be present,[7] and in fact none was detected. Nonetheless, the techniques used in this effort are instructive in defining the circumstances in which such an intermediate might be detected by magnetic resonance techniques and of possible use in other, related, problems.

Results and Discussion

$(CH_3)_2NPF_4$ (**1**) was prepared by reaction of phosphorus pentafluoride with trimethyl(dimethylamino)silane,[19] or by formation and thermal decomposition of the adduct of phosphorus pentafluoride and dimethylamine[20]; it was purified by bulb-to-bulb distillation on a Pyrex vacuum line. Although normal techniques in the manipulation of air- and water-sensitive compounds were used in preparing nmr samples of **1**, no heroic measures were taken to exclude trace hydrolysis, because subsequent studies indicated that any fluoride or hydrogen fluoride catalyzed contribution to the pseudorotation was negligible (*vide infra*). Phosphorus nmr spectra were taken in spinning 5-mm tubes using pulse methods, with proton broad-band decoupling to eliminate ^1H–^{31}P spin–spin coupling. The residual ^{31}P line width (typically 8 Hz at the coalescence temperature) may be due in part to unresolved ^{14}N–^{31}P coupling. Typical spectra are shown in Figure 1. The decrease in the intensity of the lines in going from right to left in the experimental spectra is an artifact; the the pulse amplifier used in these experiments was not capable of producing a uniform power distribution over the broad frequency range required to cover the entire phosphorus spectrum.

The spectroscopic technique used to distinguish between the correlated and anticorrelated nuclear motions characterizing Berry and non-Berry permutations is now standard[10,14,21] and will only be summarized here; a detailed qualitative discussion has been constructed for the closely related spin system provided by the five protons of the allyl groups of tetrakis(η^3-allyl)zirconium(IV).[22] The line shapes of the central three

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(14) H. L. Mitchell and G. M. Whitesides, *J. Amer. Chem. Soc.*, **91**, 5384 (1969).

(15) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

(16) It is interesting, although not necessarily pertinent to any discussion of reaction coordinates, that the ν_7 normal vibrational mode for PF_5 apparently corresponds to the motion implied by eq 2: H. Selig, J. Holloway, J. Tyson, and H. H. Claassen, *J. Chem. Phys.*, **53**, 2559 (1970).

(17) I. Ugi, D. Marquarding, H. Klusacek, and P. Gillespie, *Angew. Chem., Int. Ed. Engl.*, **9**, 703 (1970); I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Famirez, *Accounts Chem. Res.*, **4**, 288 (1971); F. Ramirez and I. Ugi, *Advan. Phys. Org. Chem.*, **9**, 26 (1971). J. I. Musher, *J. Amer. Chem. Soc.*, **94**, 5662 (1972). A clear statement of the problems to be faced in defining a detailed molecular mechanism for pseudorotation of a five-coordinate compound has been presented.[10a]

(18) R_3PF_2: T. A. Furtsch, D. S. Dierdorf, and A. T. Cowley, *J. Amer. Chem. Soc.*, **92**, 5759 (1970). SF_4, ClF_4, BrF_5: E. L. Muetterties and D. W. Phillips, *ibid.*, **79**, 322 (1957); C. V. Berney, *J. Mol. Struct.*, **12**, 87 (1972); R. A. Frey, R. L. Redington, and A. L. Khidir Aljibury, *J. Chem. Phys.*, **54**, 344 (1971); I. W. Levin and W. C. Harris, *ibid.*, **55**, 3048 (1971); E. L. Muetterties and W. D. Phillips, *ibid.*, **46**, 2861 (1967).

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(20) D. H. Brown, G. W. Fraser, and D. W. A. Sharp, *Chem. Ind. (London)*, 367 (1964); *J. Chem. Soc. A*, 171 (1966).

(21) A related treatment has been presented for the epr spectrum of PF_4: P. W. Atkins, *Mol. Phys.*, **13**, 37 (1967). For a discussion of the use of alternating line width effects to study motional correlation in epr spectroscopy, see P. D. Sullivan and J. R. Bolton, *Advan. Magn. Resonance*, **4**, 39 (1970).

(22) J. K. Krieger, J. M. Deutch, and G. M. Whitesides, *Inorg. Chem.*, **12**, 1535 (1973).

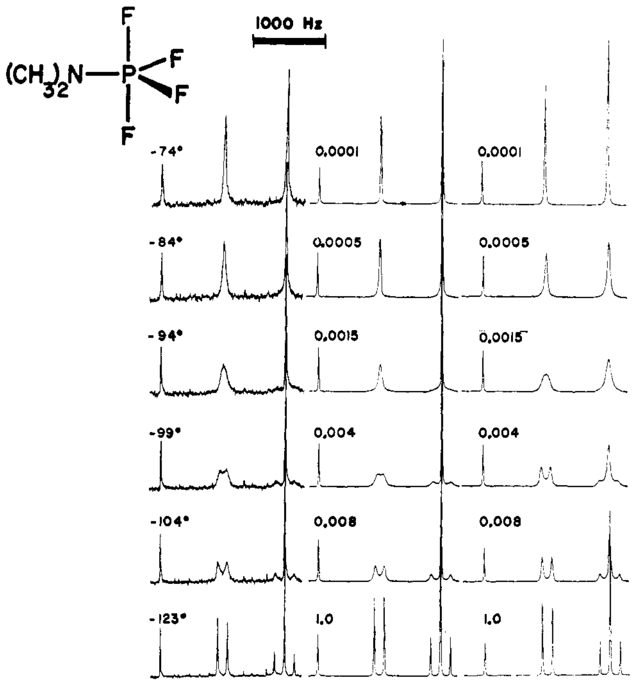

Figure 1. Comparison of ^{31}P nmr spectra (36.4 MHz), 40% v:v in 20% $(CH_3)_2O$ and 40% $CHCl_2F$ of $(CH_3)_2NPF_4$ with spectra calculated for Berry and non-Berry permutations, confirm that pseudorotation follows the former.

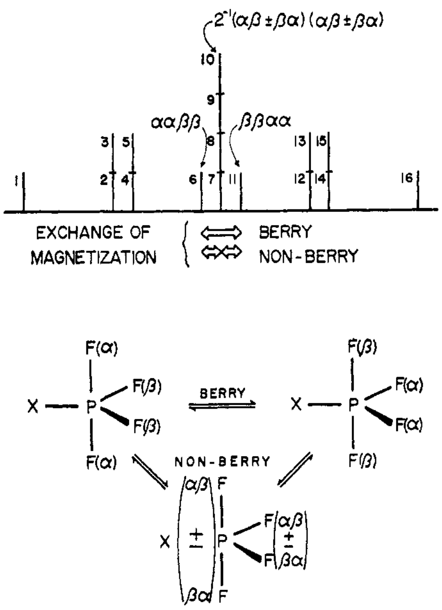

Figure 2. Assignment of ^{31}P transitions of **1** to fluorine spin configurations. The assignments given are approximate; the correct wave functions are listed in eq 3.

lines of the ^{31}P spectrum of **1** contain sufficient information to distinguish Berry and non-Berry permutations (Figure 2). The transition labeled 6 in this figure can, to a good approximation, be considered to be due to a phosphorus nucleus in the characteristic magnetic field provided by two axial fluorines in α-spin states and two equatorial fluorines in β-spin states; transition 11 can be interpreted similarly.[23] Transitions 7–10 are due to phosphorus bonded to pairs of axial and equatorial fluorines, each characterized by $(\alpha\beta + \beta\alpha)$ or $(\alpha\beta - \beta\alpha)$ spin configurations (that is, to simplify slightly, by one axial and one equatorial fluorine in α-spin states and one axial and one equatorial fluorine in β-spin states). The phosphorus line shapes in the region of intermediate exchange rate are determined by the way in which magnetization is transferred between these lines by the pseudorotation. Berry permutation clearly interchanges $\alpha\alpha\beta\beta$ and $\beta\beta\alpha\alpha$ magnetic environments around the phosphorus nucleus and results in transfer of magnetization between transitions 6 and 11; it does not transfer magnetization between either transition 6 or transition 11 and transitions 7–10. Non-Berry permutation results in exchange of magnetization between transitions 6 and 7–10 and between 7–10 and 11 but not directly between 6 and 11. Hence, if the interchange of axial and equatorial fluorines occurs by Berry permutation, lines 6 and 11 should broaden and coalesce to a single line under the line composed of the degenerate transitions 7–10, while this latter line remains sharp; if the interchange occurs by non-Berry permutation, all three of the central lines should broaden and coalesce in the region of intermediate exchange rates.[24] The observed spectra clearly conform to the line shape behavior expected for Berry permutation. The calculated spectra included in Figure 1 were obtained using procedures described previously,[12] using the following parameters (in Hz) to calculate the required eigenfunctions of the spin Hamiltonian: $\nu_a - \nu_e = 1430$, $J_{P-a} = 778$, $J_{P-e} = 915$, $J_{aa} = 10$, $J_{ae} = 62$, $J_{ee} = 50$.

Equation 3 gives the fluorine nuclear spin eigenfunctions describing the spin configurations responsible for transitions 6–11 in the phosphorus spectrum; eq 4 and 5 are the kinetic exchange matrices for these transitions assuming Berry and non-Berry permutations. Each of these matrices is symmetrical around its principal diagonal; only the upper half is given. In both Berry and non-Berry permutations, **K** matrix elements between the blocks corresponding to transitions 1–5, 6–11, and 12–16 are zero. Note in particular that there is a very small, nonzero, matrix element between transitions 6 and 10 in the Berry schemes, indicating small but finite transfer of magnetization between these transitions during Berry permutation. This element reflects slight mixing of the $\alpha\alpha\beta\beta$ and $2^{-1}(\alpha\beta + \beta\alpha)\cdot(\alpha\beta + \beta\alpha)$ symmeterized basis functions. Although its magnitude is sufficiently small that it has negligible effect on line shapes in first order considerations, it is one limitation to a scheme designed to test for a square pyramidal intermediate along the pseudorotation coordinate (*vide infra*).

Having established that Berry permutation is responsible for the dynamic line shape behavior of **I**, we examined briefly the influence of concentration and medium on the rate of pseudorotation; the results of these experiments are summarized in Table I. Be-

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(23) Discussion of this problem in terms of the symmetrized wave functions $\alpha\alpha\beta\beta$, $\beta\beta\alpha\alpha$, and $2^{-1}(\alpha\beta \pm \beta\alpha)(\alpha\beta \pm \beta\alpha)$ is approximate to the extent that these functions are slightly mixed in the true eigenfunctions for the problem. However, the extent of this mixing, defined by the coefficients of eq 3, is small and can be neglected in qualitative discussion.

(24) Similar arguments are presented for other transitions in the spectrum of **1** in ref 14. Note that Table I of this paper contains a formal error: the final spin configurations given for non-Berry permutations for ϕ_7 and ϕ_8 should be $\phi_7 = (1/4)[\phi_6 + \phi_8 + \phi_9 + \phi_{11}]$ and $\phi_8 = (1/4)[\phi_6 + \phi_8 + \phi_9 + \phi_{11}]$. This change has no influence on the calculated line shapes for the non-Berry mechanism, since it involves only the transfer of magnetization within degenerate transitions. This matter is discussed in detail in ref 22.

$$\begin{pmatrix} \psi_6 \\ \psi_{10} \\ \psi_8 \\ \psi_9 \\ \psi_7 \\ \psi_{11} \end{pmatrix} = \begin{pmatrix} 0.9992 & -0.0401 & 0 & 0 & -0.0001 & 0.0009 \\ & 0.9983 & 0 & 0 & -0.0002 & -0.0429 \\ & & -1.0000 & 0.0002 & 0 & 0 \\ & & & 1.0000 & 0 & 0 \\ & & & & -1.0000 & 0 \\ & & & & & 0.9991 \end{pmatrix} \begin{pmatrix} \alpha\alpha\beta\beta \\ 2^{-1}(\alpha\beta + \beta\alpha)(\alpha\beta + \beta\alpha) \\ 2^{-1}(\alpha\beta + \beta\alpha)(\alpha\beta - \beta\alpha) \\ 2^{-1}(\alpha\beta - \beta\alpha)(\alpha\beta + \beta\alpha) \\ 2^{-1}(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha) \\ \beta\beta\alpha\alpha \end{pmatrix} \tag{3}$$

$$\tau\mathbf{K}_{\text{Berry}} = \begin{array}{c} \\ 6 \\ 7 \\ 8 \\ 9 \\ 10 \\ 11 \end{array} \begin{array}{c} \begin{array}{cccccc} 6 & 7 & 8 & 9 & 10 & 11 \end{array} \\ \begin{pmatrix} -1.0 & 0 & 0 & 0 & 0.0075 & 0.9924 \\ & 0 & 0 & 0 & 0 & 0 \\ & & -1.0 & 1.0 & 0 & 0 \\ & & & -1.0 & 0 & 0 \\ & & & & -0.0152 & 0.0075 \\ & & & & & -1.0 \end{pmatrix} \end{array} \tag{4}$$

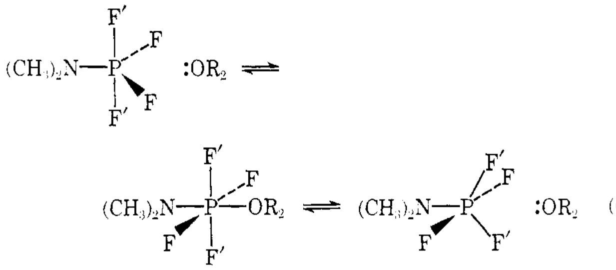
$$\tau\mathbf{K}_{\text{non-Berry}} = \begin{array}{c} \\ 6 \\ 7 \\ 8 \\ 9 \\ 10 \\ 11 \end{array} \begin{array}{c} \begin{array}{cccccc} 6 & 7 & & 9 & 10 & 11 \end{array} \\ \begin{pmatrix} -0.9983 & 0.2715 & 0.2488 & 0.2491 & 0.2289 & 0 \\ & -0.7499 & 0 & 0 & 0.2507 & 0.2278 \\ & & -0.7497 & 0.2500 & 0.0019 & 0.2480 \\ & & & -0.7503 & 0.0019 & 0.2483 \\ & & & & -0.7551 & 0.2718 \\ & & & & & -0.9979 \end{pmatrix} \end{array} \tag{5}$$

Table I. Rates and Free Energies of Activation for Pseudorotation of $(CH_3)_2NPF_4$

Sample composition (vol %)					
$(CH_3)_2NPF_4$	$CHCl_2F$	Other	Rate[a] (10^{-1} sec^{-1})	$\Delta G^{\ddagger}$,[b] kcal/mol	Temp,[b] °C
10	90		2.1	9.0 ± 0.4	−83
50	50		2.9	8.8 ± 0.2	−84
50	50	CsF[c]	3.5	8.8 ± 0.2	−86
20	40	40 Et_2O, CsF[c]	3.0	8.8 ± 0.3	−91
20	60	20 $(CH_3)_2O$	12	8.4 ± 0.2	−101
40	40	20 $(CH_3)_2O$	35	8.0 ± 0.2	−104
20	40	40 $(CH_3)_2O$	81	7.8 ± 0.2	−89
20	40	40 $(CH_3)_2O$, CsF[c]	105	7.7 ± 0.2	−112
20	40	40 THF	60	7.6 ± 0.3	−111

[a] Rates are estimated at −98°. These rates were estimated by interpolation from the Arrhenius plot for the compound of interest. [b] Values of $\Delta G^{\ddagger}$ are reported at the temperature indicated in the column headed Temp. These temperatures are *not* the coalescence temperature; they are the average of the extreme temperatures used in calculating $\Delta G^{\ddagger}$. [c] Solid cesium fluoride was present in the sample tube to scavenge fluoride ion.

cause only a relatively small number of spectra were taken in the intermediate exchange region for each sample, separation of $\Delta G^{\ddagger}$ into $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ does not yield significant data.[25] Nonetheless, the relative rates and the values of $\Delta G^{\ddagger}$ reported in the table are believed to be accurate. Three interesting conclusions emerge from these data. First, changing the concentration of **1** by a factor of 5 has no detectable influence on the rate of pseudorotation.[26] Hence, proposals for pseudorotation of **1** involving dimeric intermediates can be discarded.[27] Second, addition of solid cesium fluoride to solutions of **1** to scavenge fluoride ion has no influence on the pseudorotation rate. Thus, pseudorotation is not catalyzed by fluoride or hydrogen fluoride. Third, additions of high concentrations of basic, sterically unhindered ethers (THF, $(CH_3)_2O$) to solutions of **1** do significantly accelerate pseudorotation; diethyl ether, a less basic, more hindered, substance apparently does not influence the rate.[28] A number of mechanisms can be envisioned by which this catalysis might take place. The most straightforward is the reaction sequence represented by eq 6; attack of the



(6)

nucleophile between the two fluorines in the equatorial plane, with formation of an adduct having D_4 symmetry (assuming rapid rotation of both the dimethylamino

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(25) Arrhenius plots are reasonably linear, but the scatter in values of $\Delta S^{\ddagger}$ among comparable runs in Table I is larger than anticipated for accurate data. A representative plot is included in the Experimental Section.

(26) The rate of pseudorotation of $(C_2H_5)_2NPF_4$ has previously been shown to be concentration independent: E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, 3, 1298 (1964).

(27) J. I. Musher, *Tetrahedron Lett.*, 1093 (1973).

(28) Related solvent effects have been observed in other connections; *cf* E. J. Panek and G. M. Whitesides, *J. Amer. Chem. Soc.*, **94**, 8768 (1972); T. L. Brown, *Accounts Chem. Res.*, **1**, 23 (1968); F. A. Settle, M. Haggerty, and J. F. Eastham, *J. Amer. Chem. Soc.*, **86**, 2076 (1964), and references cited in each. The complex association constants implied by these data do not correlate with either dipole moment [A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963] or with pK_a [E. M. Arnett and C. Y. Yu, *J. Amer. Chem. Soc.*, **82**, 4999 (1960); N. C. Deno and J. D. Turner, *J. Org. Chem.*, **31**, 1969 (1966)].

group and the coordinated ether moiety around the nitrogen–phosphorus and oxygen–phosphorus bonds). Loss of the ether moiety from the adduct could be accompanied either by reversion to starting material or with equal probability by movement of F_1 and F_2 to form a new trigonal plane. The result of this latter mode of decomposition is a Berry permutation.[29,32]

$ClPF_4$ and CH_3PF_4. A wide variation in the rate of pseudorotation has been observed for XPF_4 compounds: the coalescence temperature for **1** is *ca.* −40°; PF_5 itself shows no evidence of line broadening at the lowest temperatures that have been obtained without it crystallizing from solution;[33] static spectra of various $RSPF_4$,[34] of HPF_5,[35] and possibly of $ClPF_4$[36] have been obtained at intermediate temperatures. We have reexamined the low temperature spectra of $ClPF_4$ and CH_3PF_4[38] with two purposes: to try to provide information that would be useful in rationalizing the influence of the substituents X on the rate of pseudorotation of XPF_4 compounds and to test whether the Berry permutation established for **1** is peculiar to a PF_4 moiety bearing a dimethylamino group or characterizes several members of this class of compounds. Chlorotetrafluorophosphorane was prepared by gas phase reaction between **1** and anhydrous hydrogen chloride.[39] Pure samples of $ClPF_4$ crystallized from Freon solutions at temperatures around −160° and were unsatisfactory for very low temperature work. The sample finally used to obtain static spectra was crude material, purified after synthesis only by two nonfractionating bulb-to-bulb distillations to remove salts and nonvolatile materials. This sample (Figure 3) consisted of *ca.* 35% $ClPF_4$, 55% OPF_3, and 10% a mixture of other materials (PF_5,[40] PF_3Cl_2) from the preparation. This mixture could be cooled to *ca.* −185° before freezing. Comparison of the observed line shapes with those calculated for Berry and non-Berry permutations again indicates that the former dominates; these comparisons were carried out by matching line shapes for the 2–5 transitions, since the 6 and 11 transitions are not resolved at the lowest temperatures obtained. The distinction between mechanisms is best seen simply by comparing the height and width of the 7–10 transition in experimental and calculated spectra, since all three sets of spectra were normalized to the same amplitude for the 1 and 2–5 transitions. The temperature dependence of the spectra leads to an estimate of $\Delta G^{\ddagger} = 4.2 \pm 0.3$ kcal/mol at −177°; as previously, decomposition of this number into $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is not significant.

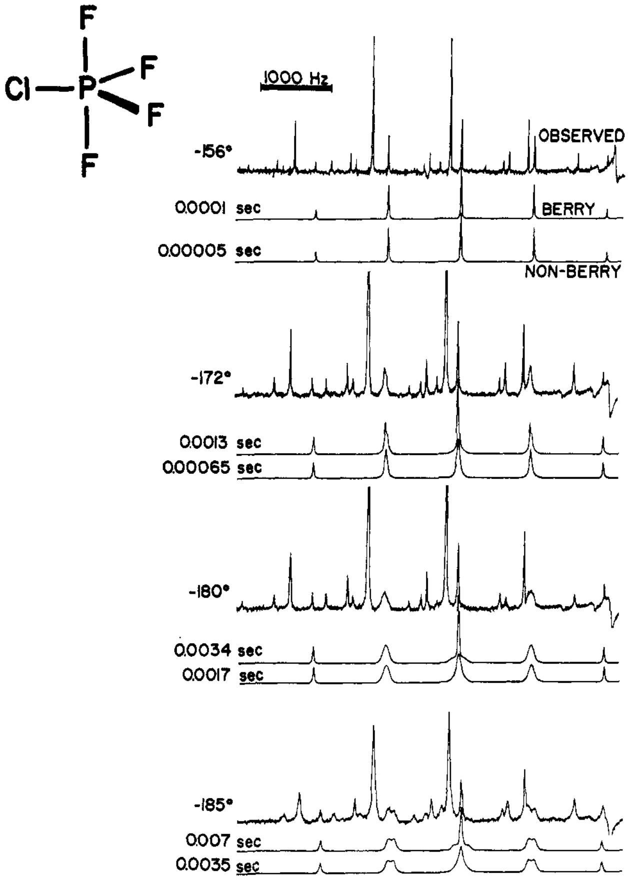

Figure 3. Continuous wave ^{31}P spectra (40.487 MHz) of $ClPF_4$ as a function of temperature, together with spectra calculated for Berry and non-Berry permutations. The major peaks of the spectra are due to OPF_3. Several peaks on the right-hand side of the spectra are distorted by overlap with center-band signals.

Efforts to slow the pseudorotation of CH_3PF_4[41] were not successful, because of its low solubility at low temperature. Efforts to increase the solubility by using solutions containing OPF_3 (Figure 4) resulted in spectra that showed no evidence of line broadening at −177°;[42]

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[29] The importance of pseudorotation in the biological hydrolysis of phosphate esters is presently unclear.[11,30] In an instance involving "adjacent" attack and, presumably, pseudorotation, it is interesting to speculate that the pseudorotation might be water catalyzed.[31] Although the trigonal bipyramid likely to be an intermediate in a biological hydrolysis would be less electrophilic than 1, water (or hydroxide ion) is less hindered than dimethyl ether, and water is present in high concentration.

[30] For evidence suggesting that the second step in cleavage of RNA by ribonuclease involves "in-line" rather than "adjacent" attack and that pseudorotation is not important in this process, see D. A. Usher, D. I. Richardson, and F. Eckstein, *Nature (London)*, **228**, 663 (1970).

[31] This possibility has also been mentioned by Musher[27] and by P. Gillespie, F. Ramirez, I. Ugi, and D. Marquarding, *Angew. Chem., Int. Ed. Engl.*, **12**, 91 (1973).

[32] A number of other mechanisms can be drawn that would have the same permutational result as the mechanism represented by eq 6. In the absence of additional experimental data, it is not useful to enumerate them.

[33] Estimates of the barrier to pseudorotation in PF_5 range from *ca.* 4 kcal/mol up.[6,7] See also H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953); R. R. Holmes, L. S. Couch, and C. J. Hora, *Chem. Commun.*, 175 (1974).

[34] S. C. Peake and R. Schmutzler, *Chem. Commun.*, 1662 (1968); *J. Chem. Soc. A*, 1049 (1970).

[35] A. H. Cowley and R. W. Braun, *Inorg. Chem.*, **12**, 491 (1973).

[36] R. P. Carter, Jr., and R. R. Holmes, *Inorg. Chem.*, **4**, 738 (1965), report the ^{19}F spectrum of $ClPF_4$ to be "completely broadened" at −157°. These authors were not able to obtain an accurate coalescence temperature, or to observe a static spectrum. Nonetheless, since the temperature at which this broadening was reported to occur is not far from the coalescence temperature observed in this work, the barrier to pseudorotation estimated[37] from their observations (*ca.* 5 kcal/mol) is in satisfactory agreement with that obtained here (*vide infra*).

[37] R. R. Holmes and R. M. Deiters, *Inorg. Chem.*, **7**, 2229 (1968).

[38] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963). Pseudorotation in $(CH_3)_3CPF_4$ is rapid at −100°: M. Fild and R. Schmutzler, *J. Chem. Soc. A*, 2359 (1970).

[39] R. Rogowski and K. Cohn, *Inorg. Chem.*, **7**, 2193 (1968). A superior procedure is that of W. B. Fox, D. E. Young, R. Foester, and K. Cohn, *Inorg. Nucl. Chem. Lett.*, **7**, 861 (1971).

[40] Incorrect values reported for the ^{31}P chemical shift of PF_5 have been corrected by L. Maier and R. Schmutzler, *Chem. Commun.*, 961 (1969).

[41] Methyltetrafluorophosphorane was prepared by gas phase reaction between PF_5 and $(CH_3)_4Sn$: P. M. Treichel and R. A. Goodrich, *Inorg. Chem.*, **4**, 1424 (1965).

[42] The observation that essentially indistinguishable spectra were obtained, how be it at higher temperatures, using Freon solvents, suggests that the CH_3PF_4 does not complex with OPF_3. E. L. Muetterties and W. Mahler, *Inorg. Chem.*, **4**, 119 (1965), have provided evidence that CH_3PF_4 is not a particularly strong Lewis acid.

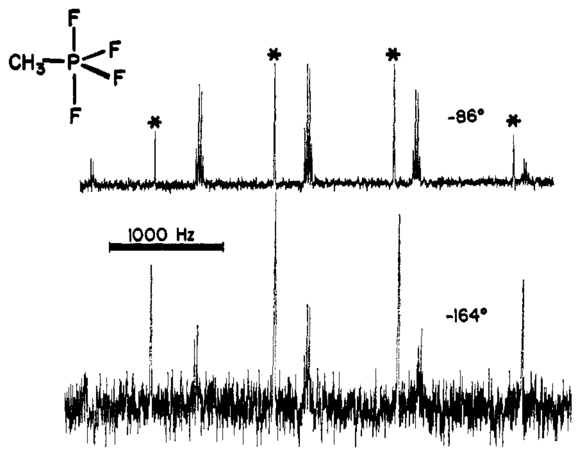

Figure 4. Continuous-wave ^{31}P spectra (40.487 MHz) of CH_3PF_4. The sharp superimposed quartet whose lines are marked with asterisks is due to OPF_3.

spectra at lower temperatures could not be obtained. Although no barrier height for pseudorotation can be obtained from these data, it seems unlikely that this barrier is higher than that for $ClPF_4$.

Two useful conclusions emerge from these data. First, it appears that the Berry permutation inferred to occur in **1** is not unique to amine-substituted PF_4 moieties, since the pseudorotation of $ClPF_4$ has the same permutational character. Second, the height of the barrier to pseudorotation of XPF_4 depends on the substituent X in a way that is not immediately rationalizable: $(CH_3)_2N$ > SR,[34] H[35] > Cl > CH_3, F. The slow pseudorotation of R_2NPF_4 and $RSPF_4$ has been suggested to reflect P–X π-bonding.[43] However, X = H is clearly out of place in this listing if the pseudorotation barrier is determined primarily by π-bonding, and the finite, if low, barrier observed for $ClPF_4$ is possibly surprising, in light of the cylindrical P–Cl π-bonding possible in this substance.

Attempts to Detect a Square Pyramidal Intermediate in the Pseudorotation of 1 Using Nmr Line Shape Analysis. A number[17] of reaction coordinates are compatible with the permutational scheme established for pseudorotation of the XPF_4 compounds studied here. Most of these coordinates will be exceedingly difficult to distinguish experimentally. One possible path for pseudorotation that is, in principle, amenable to experimental investigation is one involving a square or tetragonal pyramid as an intermediate. Molecular orbital studies do not suggest an energy minimum in the Berry pseudorotation coordinate corresponding to a square pyramidal intermediate; however, the calculated difference in energy between trigonal bipyramidal and square pyramidal intermediates of PF_5 is relatively small (0.7–10 kcal/mol),[7] and an intermediate of this type in the pseudorotation of **1** cannot be excluded on the basis of presently available evidence. Further, examination of the temperature dependence of the nmr spectra of arylbis(4,4′-dimethyl-2,2′-biphenylene)phosphoranes suggests that the pseudorotation of these substances involves intermediates.[44]

Examinations of the ^{31}P, ^{1}H, and ^{19}F nmr spectra of **1** at its low temperature limit give no hint of a square pyramidal species in solution. This result is, however, uninformative for two reasons: first, without knowing what the chemical shifts of a square pyramidal isomer of **1** might be, it is difficult to look for it, particularly since it may be present at only a fraction of the concentration of the trigonal bipyramidal form; second, since there may be a large discrepancy between the concentrations of square pyramidal and trigonal bipyramidal conformers, the resonances of the former may be broadened much more seriously than the latter by their interconversion. Thus, the apparent "slow-exchange limit" for the trigonal bipyramidal form might be far from the "slow-exchange limit" for a square pyramidal isomer.

Phosphorus line broadening in the intermediate exchange region for **1** can be thought to result from transfer of magnetization between lines. Any contribution to this transfer from a square pyramidal intermediate present in low concentration can be separated roughly into a part resulting from the difference in ^{31}P chemical shift between the trigonal bipyramid and the square pyramid and a part reflecting differences in the ^{19}F chemical shifts and in the phosphorus–fluorine (and possibly fluorine–fluorine) coupling constants in the two. Assuming the difference in ^{31}P chemical shifts between trigonal bipyramidal and square pyramidal forms to be large, the first part is difficult both to estimate and to detect experimentally; it will influence the widths of all of the lines approximately equally and is troublesome to distinguish from viscosity broadening. We have examined the feasibility of detecting a square pyramidal intermediate in pseudorotation through its contribution to differential line broadening of the ^{31}P resonances, reflecting only differences in the ^{16}F chemical shifts and ^{19}F–^{31}P and ^{19}F–^{19}F coupling constants of the trigonal bipyramidal and square pyramidal forms. We conclude that the magnitude of line broadening expected to result from an intermediate square pyramid is not detectable, at resolutions currently attainable experimentally. We nonetheless summarize the procedure used in reaching this conclusion, both to establish that techniques other than nmr line shape analysis will be required to detect intermediates along the pseudorotation coordinate for **1** and because this procedure provides an alternative to the commonly used density matrix formalism that is both appealing in the ease with which it can be understood physically and potentially attractive for other applications.[45]

The spectral basis on which the hope of detecting a square pyramid was founded is the peculiarity of **1** that the Berry permutational process results in rapid transfer of magnetization between lines 6 and 11 but only very slow transfer between these transitions and transition 7–10 (Figure 2). In contrast, an intermediate square pyramid *will*, in principle, require magnetization to be transferred between line 6 and lines 7–10 (*vide infra*). Thus, a square pyramidal intermediate might be detected through its influence on the shape of the 7–10 transition, since it would broaden a resonance that would otherwise be predicted to remain sharp. The calculation that follows connects the length of time **1**

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[43] E. L. Muetterties, P. Meakin, and R. Hoffman, *J. Amer. Chem. Soc.*, **94**, 5674 (1972), have discussed the importance of P–N π-bonding in determining the barrier to pseudorotation of compounds having the composition $(R_2N)_2PF_3$.

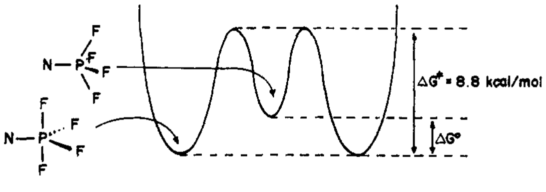
[44] D. Hellwinkel, *Chimia*, **22**, 488 (1968); G. M. Whitesides, M. Eisenhut, and W. M. Bunting, *J. Amer. Chem. Soc.*, **96**, 5398 (1974).

[45] Intermediates present in low concentrations have been detected previously using related techniques; *cf.* R. W. Krelick and S. I. Weissman, *J. Amer. Chem. Soc.*, **84**, 306 (1962); **88**, 2645 (1966).

would spend in a hypothetical square pyramid with the resulting broadening of lines 6–10.

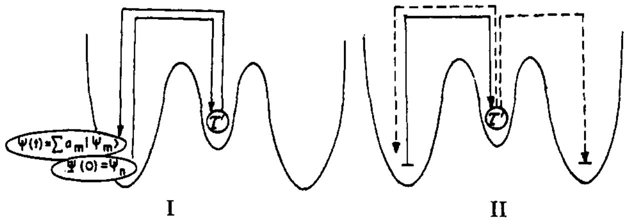
The reaction coordinate assumed as the basis for this calculation is simple; a trigonal bipyramidal molecule of **1**, described by a nuclear spin wave function $|\Psi(t)\rangle$, is originally in a nuclear spin configuration $|\psi\rangle$ that is one of the eigenfunctions of the trigonal bipyramidal Hamiltonian $\mathcal{H}_{TB}$. At time $t = 0$ this molecule undergoes an instantaneous transition to a square pyramidal conformation and spends a period of time τ' in this conformation, before returning to its original or pseudorotated trigonal bipyramidal ground state. The assumed pseudorotation coordinate incorporates the observed pseudorotational barrier ($\Delta G^{\ddagger} = 8.8$ kcal/mol, Table I and Scheme I). We would like to know the probability that the molecule will be in a state, $|\Psi\rangle = |\psi_m\rangle$, different than the one in which it started, after spending time in the square pyramidal conformation and returning to the ground state. If we know how this probability varies with the lifetime of the intermediate, we can estimate the rate constant for transfer of magnetization between the lines of the spectrum of the trigonal bipyramid and the shape of the spectrum, as a function of this lifetime.

Scheme I. Pseudorotation Coordinate for **1** Incorporating a Square Pyramidal Intermediate



We solve this problem in two stages. First, we consider a simplified case (I, Scheme II) in which a molecule of **1** undergoes a transition to the square pyramidal conformation, spends a mean time, τ', in that conformation, and then returns to the original (*not* the pseudorotated) trigonal bipyramidal ground state. The mean lifetime of **1** in the hypothetical intermediate square pyramidal conformation, τ', is related to its mean lifetime, τ, in the trigonal bipyramidal ground state by eq 7; $\Delta G°$ is the difference in energy between the square pyramid and trigonal bipyramid. This case gives a clear, physically interpretable, picture of the time development of $|\Psi(t)\rangle$ during the excursion through the square pyramidal conformation and indicates the time scale required for the square pyramidal intermediate to influence the line shapes. We then consider the real problem (II): transition from the ground state trigonal bipyramid to the square pyramid, a pause for a mean time, τ', in this conformation, and return with equal probabilities to either the original or pseudorotated ground state. The manipulations for the exact solution of this problem are described in Appendix I; the remarkably simple solution to this problem (eq 18 and 19 below) incorporates the results of the simpler calculation in a physically interpretable manner.

Scheme II. Reaction Types Considered in Calculating the Effect of an Intermediate on the Spectrum of **1**



$$\tau_{SP}/\tau_{TB} = \tau'/\tau = \exp(-\Delta G°/RT) \qquad (7)$$

The problem presented by case I is that of describing the influence of the excursion through the square pyramidal conformation on the nuclear spin wave function for **1**, $|\Psi(0)\rangle$. Since $|\Psi(0)\rangle = |\psi_m\rangle$ is not an eigenfunction of the Hamiltonian $\mathcal{H}_{SP}$ for the square pyramidal geometry, it will evolve during the time the molecule spends as a square pyramid according to the time-dependent Schrödinger equation (eq 8). The eigenfunction $|\psi_n\rangle$ of $\mathcal{H}_{TB}$ can be expanded as a linear combination of the eigenfunctions of $\mathcal{H}_{SP}$, $|\phi_j\rangle$, and the exponential evaluated in terms of the eigenvalues of $\mathcal{H}_{SP}$, E_j (eq 9). Immediately after the molecule has returned to the trigonal bipyramidal conformation, the coefficient of $|\psi_m\rangle$ in $|\Psi\rangle$ will be given by eq 10 and the probability that the molecule will be in the state $|\psi_m\rangle$ is given by the square of this coefficient (eq 11);[46] note that the basis sets $\{|\psi_n\rangle\}$ and $\{|\phi_j\rangle\}$ are constructed to be real. Assuming that the return from square pyramidal to trigonal bipyramidal geometry will occur by a first-order process with rate constant $k = 1/\tau'$, an expression analogous to eq 6 can be written for a collection of molecules by integration (eq 12). The summations over j and k refer to the same set of states (*viz.*, the eigenfunctions of $\mathcal{H}_{SP}$); thus, terms containing the energy differences in eq 12 may be simplified as indicated by eq 13, and eq 12 may be conveniently rewritten and manipulated as a sum of diagonal and off-diagonal terms (eq 14).

$$|\Psi(0)\rangle = |\psi_n\rangle \text{ at } t = 0 \qquad (8a)$$

$$|\Psi(t)\rangle = e^{-i\mathcal{H}_{SP}t}|\psi_n\rangle \text{ at } t = t \qquad (8b)$$

$$|\Psi(t)\rangle = \sum_j \exp(-i\mathcal{H}_{SP}\, t)|\phi_j\rangle\langle\phi_j|\psi_n\rangle \qquad (9a)$$

$$= \sum_j \exp(-iE_jt)|\phi_j\rangle\langle\phi_j|\psi_n\rangle \qquad (9b)$$

$$\langle\psi_m|\Psi(t)\rangle = \sum_j \exp(iE_jt)\langle\psi_m|\phi_j\rangle\langle\phi_j|\psi_n\rangle \qquad (10)$$

$$\overline{|\langle\psi_m|\Psi(t)\rangle|}^2 = \sum_j\sum_k \exp(-i(E_j - E_k)t) \times \langle\psi_m|\phi_j\rangle\langle\phi_j|\psi_n\rangle\langle\psi_m|\phi_k\rangle\langle\phi_k|\psi_n\rangle \qquad (11)$$

$$\overline{|\langle\psi_m|\Psi(\tau)\rangle|}^2 = \int_0^\infty dt(1/\tau')\exp(-t/\tau')\langle\psi_m|\Psi(t)\rangle^2 = \sum_j\sum_k[1 + i\tau'(E_j - E_k)]^{-1} \times \langle\psi_m|\phi_j\rangle\langle\phi_j|\psi_n\rangle\langle\psi_m|\phi_k\rangle\langle\phi_k|\psi_n\rangle \qquad (12)$$

$$\sum_j\sum_k[1 + i\tau'(E_j - E_k)]^{-1} = (1/2)\sum_j\sum_k\{[1 + i\tau'(E_j - E_k)]^{-1} + [1 - i\tau'(E_j - E_k)]^{-1}\} = \sum_j\sum_k[1 + \tau'(E_j - E_k)^2]^{-1} \qquad (13)$$

$$\overline{|\langle\psi_m|\Psi(\tau')\rangle|}^2 = \sum_j\sum_k[1 + \tau'^2(E_j - E_k)^2]^{-1} \times \langle\psi_m|\phi_j\rangle\langle\phi_j|\psi_n\rangle\langle\psi_m|\phi_k\rangle\langle\phi_k|\psi_n\rangle \qquad (14a)$$

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[46] For related developments of similar equations, see ref 33 and L. H. Piette and W. A. Anderson, *J. Chem. Phys.*, **30**, 899 (1959).

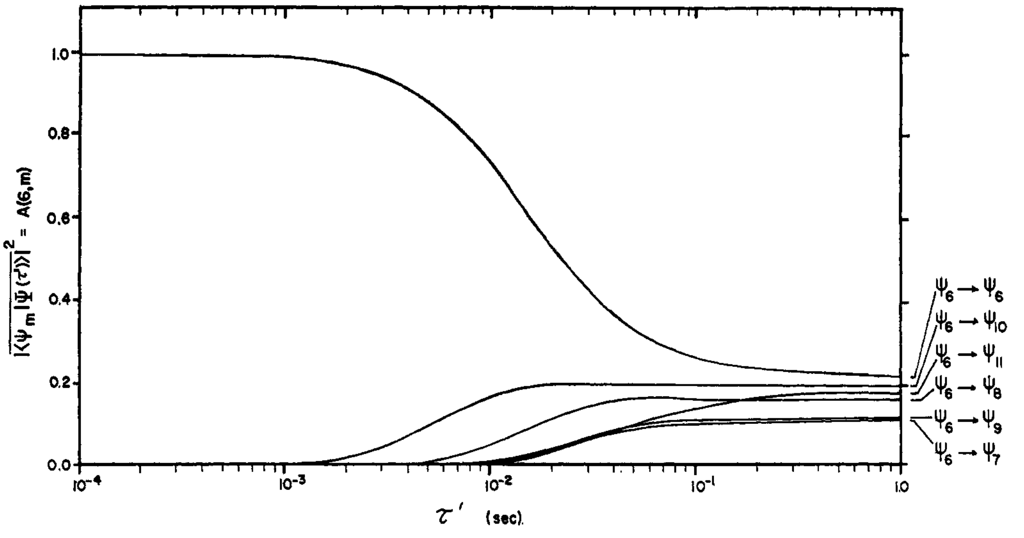

Figure 5. $\overline{|\langle \psi | \Psi(\tau') \rangle|}^2 = A(6, m)$ as a function of τ'; $\Psi(0) = \psi_6$. The meaning of the symbols is discussed in the text.

$$\overline{|\langle\psi_m|\Psi(\tau')\rangle|}^2 = \sum_j \langle\psi_n|\phi_j\rangle^2\langle\phi_j|\psi_m\rangle^2 + 2\sum_j\sum_k[1 + \tau'^2(E_j - E_k)^2]^{-1} \times \langle\psi_m|\phi_j\rangle\langle\phi_j|\psi_n\rangle\langle\psi_m|\phi_k\rangle\langle\phi_k|\psi_n\rangle \quad (14b)$$

Equation 14 gives the probability, $\overline{|\langle\psi_m|\Psi(\tau')\rangle|}^2$, that a sample of molecules that jumps from a trigonal bipyramidal conformation having nuclear spin wave function $|\psi_n\rangle$ to a square pyramidal conformation, and then returns to the trigonal bipyramidal conformation with the first-order rate constant $1/\tau'$, will end in the nuclear spin state $|\psi_m\rangle$. The rate at which the transition from $|\psi_n\rangle$ to $|\psi_m\rangle$ is accomplished clearly depends strongly on the terms $\tau'^2(E_j - E_k)^2$ in the denominator of eq 14; the energies are in turn a function of coupling constants and chemical shifts differences among the nuclei of the spin system being examined. Note, however, that in this instance they do not depend on the ^{31}P chemical shift difference between square pyramidal and trigonal bipyramidal conformations.

Values for $\langle\psi_m|\Psi(\tau')\rangle$ were calculated as a function of τ' using the magnetic parameters for **1** and values estimated for a square pyramidal conformation;[47] details of the calculation are summarized in the Experimental Section. The results of these calculations are summarized in Figure 5 for the starting state $|\Psi(0)\rangle = |\psi_6\rangle$, the wave function giving rise to transition 6 of the ^{31}P spectrum (Figure 2 and eq 3). In this figure, for example, the probability that a molecule originally in ψ_6 will be in ψ_{10} after spending τ' sec in a square pyramidal conformation is given by the coefficient $A(6,10)$ along the line designated $\psi_6 \rightarrow \psi_{10}$. The important conclusion from this figure is that, for the parameters assumed for a square pyramid, a molecule of **1** would have to spend longer than 10^{-3} sec in the square pyramidal conformation before the probability that this stay would result in a transition from ψ_6 to ψ_7, ψ_8, ψ_9, or ψ_{10} would become significant.

This conclusion, is, of course, only suggestive, since eq 14 describes the effect of conversion of trigonal bipyramid to square pyramid and return to the (nonpseudorotated) trigonal bipyramid (I of Scheme II). Further, it offers no indication of the manner in which the data of Figure 5 should be used to calculate line shapes. We have considered explicitly the more complex but realistic combination of processes outlined in II of Scheme II. The details of these calculations are presented in Appendix I; the conclusion of these calculations is summarized here.

The calculated dnmr spectra of **1**, presented in Figure 2, and of most dnmr spectra of interconverting species, rests on the solution of eq 15,[10,22] where **K**, the "kinetic

$$\frac{\partial\rho_n(t)}{\partial t} = -\alpha_n\rho_n(t) + \frac{1}{\tau}\sum_m K_{nm}\rho_m(t) \qquad (15)$$

exchange matrix," describes the exchange of magnetization between resonances resulting from the pseudorotation. In the special case presented by **1**, in which there is no mixing of phosphorus and fluorine spin wave functions, the elements of **K** can be defined very simply.[22]

$$\psi_{\text{after}} = \mathbf{R}\psi_{\text{before}} \qquad (16)$$

$$K_{nm} = R_{nm}R_{mn} - \delta_{nm} = K_{nm} \qquad (17)$$

Here, *e.g.*, the matrix **R** describes the way in which a fluorine spin wave function ψ_{before} is transformed into ψ_{after} by the nuclear permutation characteristic of the pseudorotation; δ_{nm} is the Kronecker delta. The calculations of Appendix I lead to the conclusion that the effect of inclusion of a low-concentration square pyramidal intermediate along the reaction coordinate for pseudorotation of **1** can be described by an equation of the same form as eq 15 but having a new kinetic exchange matrix $\tilde{\mathbf{K}}$.

$$\frac{\partial\rho_n(t)}{\partial t} = -\alpha_n\rho_n(t) + \frac{1}{2\tau}\sum\tilde{K}_{nm}\rho_m(t) \qquad (18)$$

The elements of this matrix, $\tilde{K}$, are defined by eq 19 (*cf.* eq 24A–26A in Appendix I).

$$\tilde{K}_{nm} + \delta_{nm} = \sum_q A(n,q)[K_{qm} + \delta_{qm}] + [A(n,m) - \delta_{nm}] \quad (19a)$$

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[47] For a hypothetic square pyramidal conformation of **1**, the following values were assumed (Hz): $J_{\text{FF(trans)}} = 20$; $J_{\text{FF(cis)}} = 60$; $J_{\text{PF}} = 846$. These values are based on the assumption that J_{FF} increases with decreasing F–P–F angles; *cf.* ref 34 and M. F. C. Hewson, S. C. Peake, and R. Schmutzler, *Chem. Commun.*, 1454 (1971).

$$A(n,m) = \overline{|\langle\psi_n|\Psi(\tau)\rangle|}^2, \quad |\Psi(0)\rangle = |\psi_m\rangle \qquad (19b)$$

The index q runs over all fluorine wave functions ψ_q that have the same value of F_z;[48] for **1**, we are interested in those spin configurations giving rise to lines 6–11. Equations 18–19 thus provide a method of incorporating the probabilities $\overline{|\langle\psi_m|\Psi(\tau')\rangle|}^2$ obtained using eq 14 and the elements of the **K** matrix calculated previously (eq 4–5) for a pseudorotation coordinate *not* having an intermediate into a quantitative calculation of the line shape of **1** pseudorotating by an exchange coordinate having a square pyramidal intermediate.

Equation 19 was used to generate rate constants $\tilde{K}_{nm}$ for transfer of magnetization between ^{31}P lines of **1**: for example, insertion of values of $K_{n,m}$ from eq 4 into eq 19 yields the expression for $\tilde{K}_{6,10}$ in eq 20; values for

$$\tilde{K}_{6,10} = 0.0075A(6,6) + 1.9848A(6,10) + 0.0075A(6,11) \qquad (20)$$

the $A(n,m)$ were taken from the data used to prepare Figure 5. The conclusion from these calculations of the elements of the **K** matrix appropriate to a pseudorotation coordinate incorporating a square pyramidal intermediate is that the magnitude of the leakage of magnetization between line 6 and lines 7–10 of the experimental spectrum would not become large enough to detect experimentally until the concentration of the intermediate became $\gtrsim 0.5\%$ that of the trigonal bipyramidal ground state. Table II gives relative values of the rate constants of magnetization transfer $2\tau\tilde{K}_{6,m}$, for pseudorotation occurring with a square pyramidal intermediate, as a function of τ'/τ, the ratio of the lifetimes (and concentrations) of the intermediate and ground state. Thus, at $\tau'/\tau = 0.003$, the relative exchange broadening of each of the components of transition 10 will be only ~6% ($\tilde{K}_{6,10}/\tilde{K}_{6,11}$) of that of transition II. Broadening of this magnitude would not be detectable under the conditions of our experiments. For $\tau'/\tau = 0.01$, the corresponding relative broadening would be ~40% and would be easily detectable; however, this concentration of intermediate is bordering on that which could be detected directly.

Table II. Representative Rate Constants for Magnetization Transfer by Pseudorotation Involving a Square Pyramidal Intermediate, as a Function of τ'/τ, the Ratio of Lifetimes for Square Pyramid and Trigonal Bipyramid

τ'/τ	$2\tau\tilde{K}_{6,6}$	$2\tau\tilde{K}_{6,7}$	$2\tau\tilde{K}_{6,8}$	$2\tau\tilde{K}_{6,9}$	$2\tau\tilde{K}_{6,10}$	$2\tau\tilde{K}_{6,11}$
0	−1.0	0	0	0	0.0075	0.9924
0.00001	−1.0056	0.0004	0.0004	0.0004	0.0180	0.9868
0.003	−1.0453	0.0032	0.0035	0.0035	0.0556	0.9474
0.01	−1.2107	0.0312	0.0325	0.0325	0.3302	0.7841
0.1	−1.5721	0.2131	0.2649	0.2649	0.4006	0.4271

We conclude from these calculations that it will not be possible to detect a square pyramidal intermediate along the pseudorotation coordinate for **1** by examination of differential line broadening in the intermediate exchange region without much improved experimental line shapes. Regardless, the *method* developed during this investigation is one of potential utility in dnmr investigations of other types of interconversions involving intermediates, particularly those in which the magnetic parameters characterizing the intermediate differ markedly from those in the ground state(s). In essence, for successful application of this method, the time evolution of the wave function of the nuclear spin system during the time spent in the intermediate must be such that it permits magnetization transfer between resonances of the ground state that are magnetically isolated in the absence of the intermediate. Circumstances favoring this behavior include an intermediate having higher nuclear spin symmetry than the ground state, a first-order spectrum in the ground state, and large differences in the magnitudes of the coupling constants and chemical shifts in the ground state and the intermediate.

Experimental Section

General Methods. Standard vacuum line techniques were used in preparing and manipulating tetrafluorophosphoranes.[49] Phosphorus nmr spectra of **1** were taken with a Bruker HFX-90 spectrometer operating at 36.4 MHz and locked on ^{19}F, using Digilab Models 400-2 pulse generator, 410 C pulse amplifier, and 50-80 proton broad-band decoupler. Temperature measurement was accomplished using a Digitek digital thermometer, with thermocouple positioned 0.5-cm below the bottom of the nmr tube. The thermocouple and thermometer were calibrated against standard methanol or ethylene glycol samples. Spectra of PF_5, $ClPF_4$, and CH_3PF_4 were obtained using a Varian HA-100 spectrometer operating at 40.5 MHz. The V-6040 variable temperature unit was modified to allow the cooling nitrogen gas to be used at elevated pressures and high flow rates; temperatures as low as −190° could be obtained.[50] Temperatures were measured using the same procedure and apparatus described above. All ^{31}P spectra on this instrument were taken in unlocked HR mode; sweeps were calibrated with a Hewlett-Packard Model 5245L counter.

Calculations of exchange-broadened line shapes were performed at the M.I.T. Information Processing Center using the program EXCHSYS.[22,51] A representative Arrhenius plot used to obtain $\Delta G^{\ddagger}$ is given in Figure 6. Calculations involving eq 13 were carried out by expressing $|\psi\rangle$ and $|\phi\rangle$ in terms of simple product functions $|\chi\rangle$ using LAOCN3[52] and taking advantage of the fact that the inverse and transpose of $\mathbf{H}_{\mathrm{SP}}$ and $\mathbf{H}_{\mathrm{TB}}$ are equal; $\mathbf{H}^{-1} = \bar{\mathbf{H}}$.

$$\psi = \mathbf{H}_{\mathrm{TB}}\chi = \mathbf{H}_{\mathrm{TB}}\mathbf{H}^{-1}{}_{\mathrm{SP}}\phi = \mathbf{D}\phi$$

$$\phi = \mathbf{H}_{\mathrm{SP}}\chi = \mathbf{H}_{\mathrm{SP}}\mathbf{H}^{-1}{}_{\mathrm{TB}}\psi = \bar{\mathbf{D}}\psi$$

Equation 10 can then be written in terms of the matrix elements d_{ij} of $\mathbf{D} = \mathbf{H}_{\mathrm{TB}}\mathbf{H}^{-1}{}_{\mathrm{SP}}$ and $\tilde{\mathbf{D}}$, using the relation $d_{ij} = \bar{d}_{ji}$. The eigenvalues E_i were also obtained from LAOCN3.

$$\overline{|\langle\psi_k|\Psi(\tau)\rangle|}^2 = \sum\sum[1 + \tau^2(E_m - E_n)^2]^{-1}d_{km}d_{mg}d_{nk}d_{gn}$$

Acknowledgments. Without the assistance of Mr. James Simms and Dr. John Fleming in the modification of nmr spectrometers, this work would not have been possible. Dr. Jeanne Krieger provided extensive assistance with the computer programs.

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(48) In a complex spin system, particularly one in which the nucleus whose resonances are being observed is tightly coupled to the nuclei that are exchanging, eq 18 will still hold, but the relation between $\tilde{\mathbf{K}}$ and **R** will be more complex than that given by eq 19.

(49) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1967.

(50) Details of these modifications are described in the Ph.D. Thesis of H. L. Mitchell, Massachusetts Institute of Technology, Cambridge Mass., 1969.

(51) This program is based on the program LAOCN3,[52] and local line shape programs KMATRX and EXCNMR.[53] See also G. M. Whitesides, S. L. Regen, J. B. Lisle, and R. Mays, *J. Phys. Chem.*, **76**, 2871 (1972).

(52) A. A. Bothner-By and S. M. Castellano, in "Computer Programs for Chemistry," Vol. I, D. F. DeTar, Ed., W. A. Benjamin, New York, N. Y., 1968.

(53) J. K. Krieger, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1971; J. B. Lisle, B.S. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1969; J. K. Krieger, unpublished work.

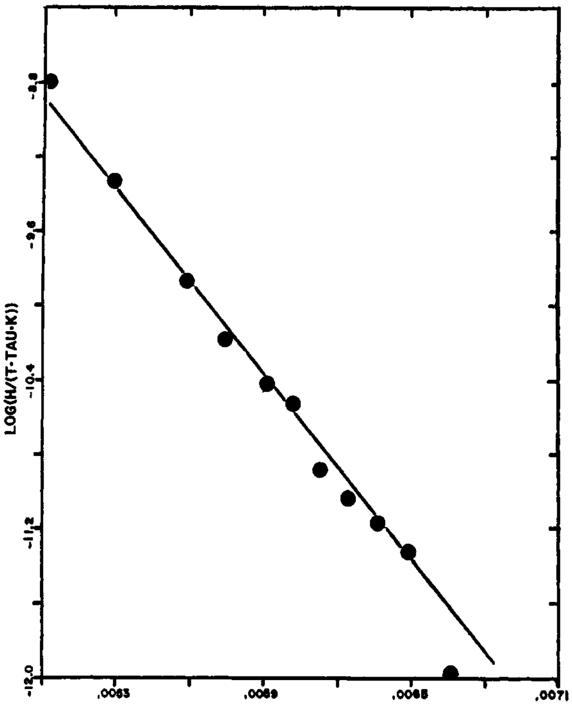


Figure 6. Arrhenius plot for pseudorotation of **1** in a solution consisting of (v : v) **1** (40%), $CHCl_2F$ (40%), and $(CH_3)_2O$ (20%).

Appendix

The interchange of two principal species in a dnmr problem may take place by way of an intermediate. If the concentration of the intermediate is comparable to that of the principal species, it must be included in the calculation explicitly as a third species; if its concentration is very small, it is usually neglected completely. In the original treatment of the dnmr behavior of **1**,[14] the possibility of a square pyramidal intermediate between trigonal bipyramidal ground states was recognized but ignored. Here we develop a quantitative but approximate procedure for calculating the influence of such an intermediate on the spectrum in the intermediate exchange region. This treatment establishes that it is possible to calculate most of the effects of the intermediate on the spectra of the principal species by a simple modification of the **K** matrix used to describe the exchange of magnetization in the absence of the intermediate. As such, the treatment is of value both in providing an alternative and physically illuminating method of describing the effect of an intermediate on magnetization exchange and in appreciably simplifying certain types of calculations. The discussion given here is applied to the specific problem presented by **1**; the principle of this treatment is broadly applicable.

The question of the role of an intermediate may be addressed using any one of several alternative (and equivalent) formalisms. Here we employ the formalism of the stochastic line shape theory introduced by Kubo[54] and Johnson.[55] The stochastic line shape approach is particularly suitable for the problem under consideration because it permits the simple and direct introduction of the "steady state" approximation for the intermediate square pyramidal form. In the stochastic line shape theory each conformation is characterized by a different spin Hamiltonian; in contrast, the conventional Kaplan–Alexander theory of chemical exchange employs a single spin Hamiltonian, and an exchange operator is introduced that permutes the individual spins in the spin wave functions consistent with the different conformations.[10,22,56]

We first consider the two-site case where the molecule is assumed to undergo conformation changes with a rate τ^{-1} between the two equivalent sites—the two trigonal bipyramids interconvertible by pseudorotation—characterized by spin Hamiltonians $\mathcal{H}_1$ and $\mathcal{H}_2$, respectively. We denote by $\rho_1(t)$ [$\rho_2(t)$] the spin density matrix of the system at time t given that the molecule is in conformation 1 [2] and solve the set of coupled equations, 1A and 2A.[55] In these we ignore the terms $\rho(t)/T_2$ introduced to account for spin–lattice relaxation effects on the line widths (that is, the "slow-exchange" line widths). These terms can be incorporated directly into the final equations. These equations contain a restriction to an equilibrium constant of unity between the two sites which can easily be relaxed.

$$\frac{\partial\rho_1(t)}{\partial t} = -i[\mathcal{H}_1,\rho_1(t)] + \frac{1}{\tau}\rho_2(t) - \frac{1}{\tau}\rho_1(t) \qquad (1A)$$

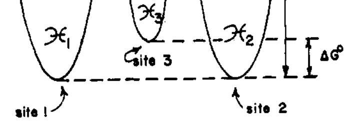
$$\frac{\partial\rho_2(t)}{\partial t} = -[H_2,\rho_2(t)] + \frac{1}{\tau}\rho_1(t) - \frac{1}{\tau}\rho_2(t) \qquad (2A)$$

We wish to compare the two-site case with a three-site case in which a third site—a square pyramid—characterized by Hamiltonian $\mathcal{H}_3$ is assumed to lie at an intermediate position along the reaction coordinate. The appropriate set of stochastic equations for this three-site case is given in eq 3A–5A, where $\rho_3(t)$ signifies the spin density matrix at time t assuming the molecule is in the intermediate conformation 3. The rate constant $[\tau']^{-1}$ is that describing the return of the intermediate state to the ground state conformations 1 and 2. According to our picture of the reaction profile, $\tau'_{SP} = \tau_{TB}\exp[-\Delta G^\circ/RT]$ and $\tau \gg \tau'$. Our calculation of the effect of the third site consists of obtaining an approximate expression for $\rho_3(t)$ from eq 5A and substituting this expression into eq 3A and 4A to obtain an effective two-site case than can be compared with eq 1A and 2A.

$$\frac{\partial\rho_1(t)}{\partial t} = -i[\mathcal{H}_1,\rho_1(t)] + \frac{1}{\tau'}\rho_3(t) - \frac{1}{\tau}\rho_1(t) \qquad (3A)$$

$$\frac{\partial\rho_2(t)}{\partial t} = -i[\mathcal{H}_2,\rho_2(t)] + \frac{1}{\tau'}\rho_3(t) - \frac{1}{\tau}\rho_2(t) \qquad (4A)$$

$$\frac{\partial\rho_3(t)}{\partial t} = -i[\mathcal{H}_3,\rho_3(t)] + \frac{1}{\tau}[\rho_1(t) + \rho_2(t)] - \frac{2}{\tau'}\rho_3(t) \qquad (5A)$$



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[54] R. Kubo in "Fluctuation, Relaxation, and Resonance in Magnetic Systems," D. ter Haar, Ed., Oliver and Boyd, London, 1962.

[55] C. S. Johnson, Jr., *J. Chem. Phys.*, **41**, 3277 (1964).

[56] J. I. Kaplan, *J. Chem. Phys.*, **28**, 278 (1958); **29**, 462 (1958); S. Alexander, *ibid.*, **37**, 967, 974 (1962); **38**, 1787 (1963); **40**, 2741 (1964).

The exact solution for $\rho_3(t)$ is eq 6A; this solution

$$\rho_3(t) = \exp[-i\mathcal{H}_3 t]\rho_3(0)\exp[+i\mathcal{H}_3 t]\exp[-2t/\tau'] + \frac{1}{\tau}\int_0^t \mathrm{d}s \exp[-i\mathcal{H}_3 s][\rho_1(t - s) + \rho_2(t - s)] \times \exp[+i\mathcal{H}_3 s]\exp[-2s/\tau'] \quad (6A)$$

may be verified by differentiation. From eq 3A and 4A we see that except for oscillatory terms $\rho_1(t)$ and $\rho_2(t)$ will decay on a time scale τ^{-1}. However, the integral in eq 6A contains a factor $(\tau')^{-1}$ which has a much faster time decay. Accordingly we may replace $\rho_1(t - s)$ and $\rho_2(t - s)$ in eq 6A by $\rho_1(t)$ and $\rho_2(t)$ and incur an error of order (τ/τ'). Furthermore since we are interested in the steady state effect of the intermediate, we neglect the effect of the initial condition by setting $\rho_3(0)$ equal to zero in eq 6A and extending the upper limit on the integral to infinity. The resulting approximate expression for the steady state value of $\rho_3(t)$ is

$$\rho_3(t) = \frac{\tau'}{2\tau}A[\rho_1(t) + \rho_2(t)] \quad (7A)$$

where the effect of the operator A on an arbitrary operator, θ, is

$$A\theta(t) = \frac{2}{\tau'}\int_0^\infty \exp\left[-\frac{2s}{\tau'}\right]\exp[-i\mathcal{H}_3 s]\theta(t) \times \exp[+i\mathcal{H}_3 s]\mathrm{d}s \quad (8A)$$

We note that if $\tau' \to 0$, $A \to 1$. If we substitute the approximate expression for $\rho_3(t)$ into eq 3A and 4A, we obtain an *effective two-site case* for comparison with eq 1A and 2A.

$$\frac{\partial\rho_1(t)}{\partial t} = -i[\mathcal{H}_1,\rho_1(t)] + \frac{1}{2\tau}A\rho_2(t) - \frac{1}{2\tau}(2 - A)\rho_1(t) \quad (9A)$$

$$\frac{\partial\rho_2(t)}{\partial t} = -[\mathcal{H}_2,\rho_2(t)] + \frac{1}{2\tau}A\rho_1(t) - \frac{1}{2\tau}(2 - A)\rho_2(t) \quad (10A)$$

The difference between this expression for the effective two-site problem and the customary two-site expression (eq 1A and 2A) is the presence of the *transfer operator* A and the factors of (1/2) appearing on the right hand side of eq 9A and 10A. These latter factors of (1/2) are irrelevant; they simply exhibit, as is well known from analogous cases in chemical kinetics, the fact that explicit treatment of an intermediate in the steady state approximation reveals an additional factor of (1/2) which indicates the available two pathways. The transfer operator A is the source of the new physics in the line shape analysis. In the limit $\tau' \to 0$, which corresponds to an infinitely short lifetime for the intermediate $A\theta(t) \to \theta(t)$ so that eq 9A–10A reduce precisely to the two-site problem (eq 1A and 2A).

Before proceeding we wish to translate these results obtained from the stochastic line shape formalism to the perhaps more familiar Kaplan–Alexander formalism.[56] In the Kaplan–Alexander formalism one relates $\rho_1(t)$ and $\rho_2(t)$ as well as $\mathcal{H}_1$ and $\mathcal{H}_2$ by an exchange operator R, *viz.*

$$R\rho_1(t)R = \rho_2(t) \qquad R\rho_2(t)R = \rho_1(t) \quad (11A)$$
$$R\mathcal{H}_1R = \mathcal{H}_2 \qquad R\mathcal{H}_2R = \mathcal{H}_1$$

With use of the operator R both eq 1A and 2A reduce to the single expression (12A), where $R\rho(t)R$ denotes

$$\frac{\partial\rho}{\partial t} = -i[\mathcal{H},\rho(t)] + \frac{1}{\tau}[R\rho(t)R - \rho(t)] \quad (12A)$$

the density matrix "after exchange," $\rho(t)$ is the density matrix "before exchange," and $\mathcal{H}$ is the spin Hamiltonian that characterizes the system. Applying the operator R to the left and right hand side of either equation 9A or 10A leads to the single expression 13A

$$\frac{\partial\rho}{\partial t} = -i[\mathcal{H},\rho(t)] + \frac{1}{2\tau}AR\rho(t)R - \frac{1}{2\tau}(2 - A)\rho(t) = -i[\mathcal{H},\rho(t)] + \frac{1}{2\tau}[AR\rho(t)R - \rho(t)] + \frac{1}{2\tau}[A\rho(t) - \rho(t)] \quad (13A)$$

if one assumes that the transfer operator A commutes with the exchange operator R; that is, $R[A\theta(t)]R = A[R\theta(t)R]$. This assumption is indeed justified for the case under consideration since the conformation corresponding to $\mathcal{H}_3$, *i.e.*, the square pyramidal, lies symmetrically between the two sites 1 and 2 and hence $R\mathcal{H}_3R = \mathcal{H}_3$. Thus eq 13A, when compared with eq 12A, exhibits in the Kaplan–Alexander language the effect of the presence of a short-lived intermediate along the exchange reaction coordinate.

The various terms in the modified Kaplan–Alexander equation (13A) can be interpreted physically. In the conventional two-site Kaplan–Alexander expression (eq 12A), the term $R\rho(t)R$ describes the density matrix $\rho(t)$ after exchange has taken place; thus, $R\rho(t)R - \rho(t)$ is the *change* in ρ due to the exchange. The term $R\rho(t)R$ results from the substance of interest passing over the barrier separating the two sites; $\rho(t)$ is the (unchanged) term resulting if it stays in its original site. In the Kaplan–Alexander equation (13A) modified to take into account an intermediate, the term $(2\tau)^{-1}\cdot[AR\rho(t)R - \rho(t)]$ describes the change in the density matrix resulting from transitions from the ground state (site 1) to the intermediate (site 3), a pause of mean duration τ', and continuation over the second barrier back to the alternative ground state (site 2). The term $(2\tau)^{-1}[A\rho(t) - \rho(t)]$ describes the corresponding change in ρ due to a transition from site 1 to site 3, a pause of duration τ', and return to site 1. Thus, in the particular problem provided by **1**, the first term describes conversion of trigonal bipyramidal to square pyramidal conformations, followed by return to the pseudorotated trigonal bipyramid, while the second describes conversion of trigonal bipyramid to square pyramid, followed by reversion of the original, *non*pseudorotated, trigonal bipyramid.

Explicit calculations can be carried out with the modified Kaplan–Alexander expression eq 13A in an analogous manner to the conventional expression eq 12A once the Hamiltonian $\mathcal{H}_3$ and an intermediate lifetime τ' are specified. The operator equation (eq 13A) can of course be written in matrix form.

The effects to be expected in the modified Kaplan–Alexander procedure can be illustrated by consideration of the XPF_4 system. The phosphorus resonances of these molecules reflect fluorine spin configurations, but there is no mixing of phosphorus and fluorine wave functions. Accordingly, only the fluorine spin eigenfunctions need be explicitly considered, and the matrix form of the density matrix equations (12A or 13A) are simplified. Here and below $|\psi_n\rangle$ are the fluorine spin eigenfunctions of $\mathcal{H}_{\text{TB}}$, the spin Hamiltonian for the trigonal bipyramidal ground state of **1**, and ρ_n is the corresponding element of the density matrix between corresponding eigenfunctions of $\mathcal{H}_{\text{TB}}$ that *include* the phosphorus spins but differ *only* in the phosphorus spin configuration (eq 14A). With this notation, the con-

$$\rho_n(t) = \langle \alpha_P\psi_n|\rho(t)|\beta_P\psi_n\rangle \qquad (14\text{A})$$

ventional Kaplan–Alexander equation (12A) has the matrix form

$$\frac{\partial\rho_n(t)}{\partial t} = -\alpha_n\rho_n(t) + \frac{1}{\tau}\sum_m K_{nm}\rho_m(t) \qquad (15\text{A})$$

where $\alpha_n = i(\omega_n - \omega) + (1/T_2)_n$, the ω_n is the frequency of the phosphorus lines, ω is the observing frequency, and K_{nm} are elements of the kinetic exchange matrix; in the special cases covered by eq 14A, the elements of the kinetic exchange matrix have the particularly simple form of eq 16A, where the R_{nm} define the influence of the

$$K_{nm} = R_{nm}R_{mn} - \delta_{nm} = K_{mn} \qquad (16\text{A})$$

permutation of nuclear indices on the fluorine spin eigenfunctions of $\mathcal{H}_{\text{TP}}$ by ψ (after interchange) = $\mathbf{R}\psi$ (before interchange),[22] and δ_{nm} is the Kronecker delta: $\delta_{nm} = 1$ if $n = m$; $\delta_{nm} = 0$ if $n \neq m$. Similarly, the modified Kaplan–Alexander equation (eq 13A) has the matrix form

$$\frac{\partial\rho_n(t)}{\partial t} = -\alpha_n\rho_n(t) + \frac{1}{2\tau}\sum_{q,m}A(n,q)R_{qm}R_{mq}\rho_m(t) - \frac{2}{2\tau}\rho_n(t) + \frac{1}{2\tau}\sum_m A(n,m)\rho_m(t) \qquad (17\text{A})$$

The matrix $A(n,m)$ arises from the transfer operator A when taking the matrix elements in the basis set $\{\psi_n\}$ of the operator equation. Explicitly this matrix is given by eq 18A, where $\mathcal{H}_3$ is the spin Hamiltonian of the intermediate (square pyramidal) conformation. Equation 18A can be expanded in terms of the eigenfunctions

$$A(n,m) = \frac{2}{\tau'}\int_0^\infty \mathrm{d}s\, \exp[-2s/\tau']\langle\psi_n| \times \exp(-i\mathcal{H}_3 s)|\psi_m\rangle\langle\psi_m| \exp(+i\mathcal{H}_3 s)|\psi_n\rangle \qquad (18\text{A})$$

$|\phi_j\rangle$ of $\mathcal{H}_3$ (eq 19A). Comparison of eq 19A with eq

$$A(n,m) = \sum_j\sum_k\left[1 + \left(\frac{\tau'}{2}\right)^2(E_j - E_k)^2\right]^{-1} \times \langle\psi_n|\phi_j\rangle\langle\phi_j|\psi_m\rangle\langle\psi_m|\phi_k\rangle\langle\phi_k|\psi_n\rangle \qquad (19\text{A})$$

13a in the body of the text establishes that these equations are identical, except for the trivial factor for two: τ' (eq 13a) = $\tau'/2$ (eq 19A). Thus, for $|\Psi(0)\rangle = |\psi_m\rangle$

$$A(n,m) = \overline{|\langle\psi_n|\Psi(\tau')\rangle|^2} \qquad (20\text{A})$$

The interpretation of the $A(n,m)$ as probabilities of passing from state m to state n with an excursion to the intermediate square pyramidal form is discussed in the body of the paper. The important properties of $A(n,m)$ follow from this interpretation: (1) $A(n,m)$ is real; (2) $A(n,m) = A(m,n)$; (3)

$$\sum_m A(n,m) = \sum_n A(n,m) = 1$$

Note that $A(n,m)$ depends only on the nuclear spin energy levels E_j of the intermediate and on the lifetime τ' of the intermediate; it does not depend on the energy levels of the ground state.

The matrix $A(n,m)$ describes the way in which the magnetization transfer between lines is modified by introduction of an intermediate along the reaction coordinate. It is possible to incorporate these terms into an *effective* kinetic exchange matrix $\tilde{\mathbf{K}}$ having a form analogous to the familiar expression 15A; $\tilde{\mathbf{K}}$ is defined by eq 21A, and comparison of eq 15A and 17A leads to the equivalent identifications 22A and 23A. Note that as $\tau' \rightarrow 0$, $A(n,q) \rightarrow \delta_{nq}$ and $\tilde{K}_{nm} \rightarrow K_{nm}$. Equations 21A + 23A make it possible to calcu-

$$\frac{\partial\rho_n(t)}{\partial t} = -\alpha_n\rho_n(t) + \frac{1}{2\tau}\sum_m \tilde{K}_{nm}\rho_m(t) \qquad (21\text{A})$$

$$\tilde{K}_{nm} = \sum_q A(n,q)R_{qm}R_{mq} - 2\delta_{nm} + A(n,m) \qquad (22\text{A})$$

$$\tilde{K}_{nm} + \delta_{nm} = \sum_q A(n,q)[K_{qm} + \delta_{qm}] + [A(n,m) - \delta(n,m)] \qquad (23\text{A})$$

late in a quantitative (but approximate) way the effect on the spectrum of an intermediate which is present in small amounts. It is remarkable and useful that eq 21A has the same form as eq 15A; in particular, the same computational techniques and computer programs used with the latter equation can be employed with the former.

We conclude with a brief discussion of the physical interpretation of the effective kinetic exchange matrix $\tilde{\mathbf{K}}$. In the conventional Kaplan–Alexander expression (eq 15A) in the site approximation appropriate to XPF_4, the quantity $\tau^{-1}K_{nm}$ ($n \neq m$) denotes the rate of magnetization transfer from line m to line n. Furthermore since the intensities, I^+ of all the phosphorus resonances are equal, eq 24A (which states that magnetization is conserved by the dynamic process) can be replaced for **I** by 25A.

$$\sum_m I^+{}_m K_{nm} = 0 = \sum_m I^+K_{mn} \qquad (24\text{A})$$

$$\sum_m K_{nm} = 0 = \sum_m K_{mn} \qquad (25\text{A})$$

The quantity

$$\tau^{-1}K_{nn} = -\tau^{-1}\sum_{m\neq n}K_{mn}$$

refers to the net rate of magnetization transfer out of the state n to all other states. The expression (eq 15A) may be rewritten

$$\frac{\partial\rho_n(t)}{\partial t} = i\omega\rho_n(t) + \frac{1}{\tau}\sum_{m\neq n}K_{nm}\rho_m(t) - \frac{1}{\tau}\left[\sum_{m\neq n}K_{mn}\right]\rho_n(t) \qquad (26\text{A})$$

From the definition of the effective kinetic exchange matrix $\tilde{K}_{nm}$ (eq 23A), we find that $\tilde{K}_{nm} = \tilde{K}_{mn}$ and

$$\sum_m \tilde{K}_{nm} = 0 = \sum_m \tilde{K}_{mn} \qquad (27\text{A})$$

Accordingly eq 21A may be rewritten in an analogous form

$$\frac{\partial\rho_n(t)}{\partial t} = i\omega\rho_n(t) + \frac{1}{\tau}\sum_{m\neq n}\tilde{K}_{nm}\rho_m(t) - \frac{1}{\tau}\Big[\sum_{m\neq n}\tilde{K}_{mn}\Big]\rho_n(t) \quad (28\text{A})$$

and $\tau^{-1}\tilde{K}_{nm}$ again interpreted as the rate of magnetization transfer from line m to line n. From eq 23A we see that $\tilde{K}_{nm}$ ($n \neq m$) may be expressed as

$$\tau^{-1}\tilde{K}_{nm} = \sum_{q\neq m} A(n,q)\frac{K_{qm}}{\tau} + \frac{A(n,m)}{\tau}[K_{mm} + 1] + \frac{A(n,m)}{\tau} \quad (29\text{A})$$

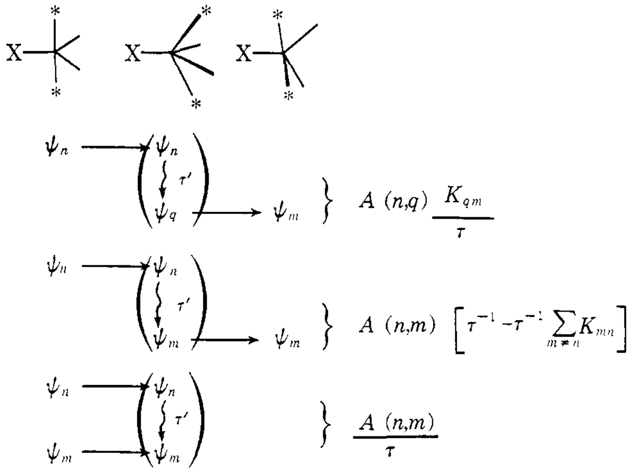
or by use of eq 24A

$$\tau^{-1}\tilde{K}_{nm} = \sum_{q\neq n} A(n,q)\frac{K_{qm}}{\tau} + A(n,m) \times \Big[\tau^{-1} - \tau^{-1}\sum_{m\neq n} K_{mn}\Big] + \tau^{-1}A(n,m) \quad (30\text{A})$$

This equation states that the rate of magnetization transfer from line m to line n ($m = n$) is made up of three contributions, each referring to a different mechanism. These mechanisms are perhaps most easily understood by reference to a diagram (Scheme IA).

The first term describes the system, initially in state ψ_n and giving rise to line n, going to the intermediate conformation to state ψ_q with probability $A(n,q)$ and then proceeding to the final state of interest ψ_m with rate $\tau^{-1}K_{qm}$ characteristic of the rate of transfer magnetization from line q to line m. The second term describes the system going to the intermediate, undergoing a transition during its residence in the intermediate conformation to state ψ_m with probability $A(n,m)$ and then proceeding on to ψ_m of the pseudorotated product. The third term describes the system going to the intermediate, undergoing a transition during its residence in the intermediate conformation to state m with probability $A(n,m)$ and then returning to its original, nonpseudorotated conformation without passing over the barrier.

Scheme IA



There are several important points to note about the difference between $\tilde{K}_{nm}$ and K_{nm}. First for short $[\tau']^{-1}$ where our analysis is valid, the difference between $\tilde{K}_{nm}$ and K_{nm} does not depend on the fractional population between the stable and intermediate conformations. The effect depends exclusively on the residence time in the intermediate state τ' and on the splitting of the magnetic levels in that state. Second, the dominant difference between $\tilde{K}_{nm}$ and K_{nm} can arise from any one of the three contributions in eq 30A. All this is required is for $A(n,m)$ to differ appreciably from unity. Presumably this circumstance can be most easily realized for a paramagnetic intermediate. Third, in the case of a completely degenerate rearrangement, $K_{nm} = 0$ and the conventional analysis would predict no line broadening; the modified theory predicts a broadening $\tilde{K}_{nm} = 2A(n,m)$ ($n \neq m$) as expected. Finally we note that, while our analysis has been restricted to the simple site magnetization picture appropriate to XPF_4, our development is quite general. In particular the result displayed in eq 14A for the modified Kaplan–Alexander expression is in a form appropriate for application to other systems of chemical interest.