

Berry R S. Correlation of rates of intramolecular tunneling processes, with application to some group V compounds. *J. Chem. Phys.* 32:933-8, 1960.

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**This paper proposes a mechanism for intramolecular rearrangement of 5coordinate compounds of phosphorus and other 5coordinate species, by largeamplitude internal motions. It also introduces a scaling relation for estimating rates of intramolecular quantummechanical tunneling. [The SCI® indicates that this paper has been cited over 445 times since 1961]**

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"The first stimulus for this work was a puzzling experiment<sup>1</sup> that showed that the five fluorine atoms of PF<sub>5</sub> look equivalent in the fluorine nuclear magnetic resonance spectrum; this seemed inconsistent with the trigonalbipyramidal structure of the molecule. More generally, I wanted to reconcile the apparent paradox of the distinguishability of identical nuclei occupying inequivalent chemical sites. The reconciliation clearly lay in the possibility for rearrangement and exchange of the identical nuclei; the puzzle was finding whether there were real nontrivial examples in which the equivalence is established at a measurable rate. Phosphorus pentafluoride seemed to be exactly the right example. Could the rate of its rearrangement be estimated theoretically and tested in any way?

"There were two steps to answering that question, finding a mechanism and finding a way to estimate and rationalize the rate with the experimental data. The mechanism that seemed natural had been discussed by my research director, William Moffitt, and a graduate student classmate and friend, Felix T. Smith, as a possible rearrangement mechanism for the molecule ion CH<sub>5</sub><sup>+</sup>. Felix had showed me the process that converts a trigonal bipyramid into a square

pyramid, which then can return or move to either of two other 'rearranged' trigonal bipyramids. This mechanism is sometimes called 'Berry pseudorotation.' I did use the word 'pseudorotation' to describe the process because it is equivalent to a permutation of identical nuclei and a rotation of the molecule in space. It was first proposed, I believe, by Edward Teller and John A. Wheeler,<sup>2</sup> when they used moleculelike models to describe the dynamics of nuclei: they proposed that Ne<sup>20</sup> might be a rearranging trigonal bipyramid of five  $\alpha$  particles. I was unaware of the TellerWheeler work until Earl Muettterties showed my article to Wheeler, who then sent me their paper.

"Soon after my paper appeared, Mahler and Muettterties<sup>3</sup> examined the NMR spectra of substituted fluorophosphoranes. The results first suggested that my description of internal rearrangement in PF<sub>5</sub> was incorrect, and that the apparent equivalence arose from an accidental equality of the chemical shifts of the axial and equatorial fluorines. This finding turned me away from the problem somewhat, toward other subjects. However Muettterties' subsequent experiments soon showed that PF<sub>5</sub> and other phosphoranes do undergo pseudorotation.

"The idea was also applied soon to transition metal carbonyls; Cotton<sup>4</sup> has discussed that history. My paper began to be cited frequently as inorganic chemists found more and more examples of molecules that undergo ready intramolecular rearrangement. The pseudorotation mechanism became still better known when, in the mid 1960s, Frank Westheimer<sup>5</sup> and his coworkers showed its role in phosphate ester hydrolysis: 4coordinate phosphate adds a fifth group into a labile axial position, the now5coordinate phosphorus complex rearranges to put the new adduct into a stable equatorial position and an old group into a labile axial position; then the old group departs, leaving a newlysubstituted 4coordinate phosphate. The mechanism was conclusively demonstrated by experiments of Whitesides and Mitchell<sup>6</sup> in 1969. I myself recently reviewed the subject of nonrigid molecules from the viewpoint of a physical chemist or physicist."<sup>7</sup>

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4. Cotton F A. Fluxionality in organometallics and metal carbonyls. *J. Organometal. Chem.* 100:29-41, 1975.

5. Westheimer F H. Pseudorotation in the hydrolysis of phosphate esters. *Account. Chem. Res.* 1:70-8, 1968.

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