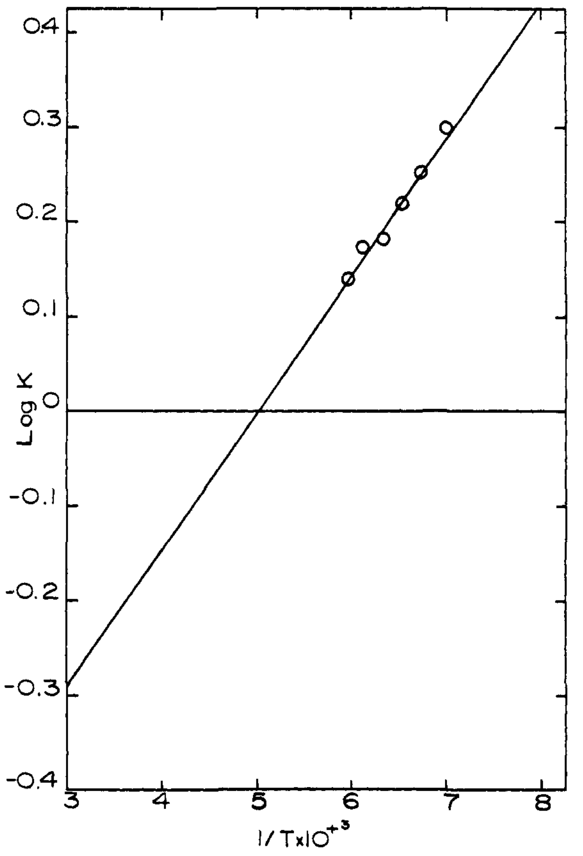

Figure 1. Log $K$ vs. $1/T$ for the equilibrium IIIa $\rightleftarrows$ IIIb in vinyl chloride. Values of $K$ were determined from $^{31}P$ nmr spectra.

I and II as standards, the signals are assigned to the equatorial (IIIb) and the axial (IIIa) conformers, respectively. Also, the upfield doublet had an area ratio of about 2:1 to the downfield, in accord with the equatorial–axial ratio found from the low-temperature $^{31}P$ spectrum. The overlap of the peaks, as well as some interference of the downfield signal with the ring $CH_2$ signals, prevented accurate determination of the variation of $K$ with temperature, but an approximate value (0.2) from extrapolation to room temperature supports the conclusion from the $^{31}P$ nmr experiment that the axial conformer predominates. Confirmation of the axial predominance is also found in the proximity of the time-averaged $J_{PH}$ value (3.0 Hz) at room temperature to that (3.2 Hz) of the "frozen" axial form IIIa.

As in the methylcyclohexanes,[13] axial methyl protons in the methylphosphorinane system are now seen to absorb downfield of equatorial ones When examined in benzene solution, tertiary 4-phosphorinanols show the opposite relation of $P$-methyl signals.[2,14] This may be explained on the basis of a deshielding effect associated with the OH group in aromatic solvents;[15] the effect is stronger on the equatorial methyl of the cis isomer[14] and causes a shift sufficient to place the signal slightly downfield of that of the axial methyl of the trans isomer.

The $\Delta G^{\ddagger}$ value for ring inversion calculated by the coalescence temperature method using the $^{31}P$ signals was 9.2 kcal/mol at −75°. This value is quite similar to that for inversion of the cyclohexane ring (10.5 kcal/mol at −67° [16]). Other thermodynamic functions for the conformational equilibrium in the two systems were considerably different, however. The $\Delta H°$ value, obtained from a van't Hoff plot, was small (−0.67 kcal/mol) and reflects the fact that 1,3 repulsive interactions are weaker than in cyclohexanes. Bond lengths and angles, as well as torsion angles, are quite different in the two systems; as noted elsewhere,[2,14] these differences can account for the diminution of the repulsive forces acting on a $P$-methyl group. The entropy change, calculated at −130°, was −3.3 eu. The combination of a small $\Delta H°$ value and a nonnegligible entropy difference between the isomers results in a substantial dependence of $\Delta G°$ on temperature and happens to be accompanied by a change in sign (at −130°, $\Delta G° = -0.20$; at 25°, $\Delta G° = +0.34$ kcal/mol). Thus the important conclusion is reached that, under these special circumstances for $\Delta H°$ and $\Delta S°$, the $\Delta G°$ value at room temperature does not reveal the true nature of the 1,3 interactions; the low-temperature studies imply, however, that these are repulsive, and that there is no need to invoke an explanation for the predominance of the axial form at room temperature on the premise of attractive interactions in this conformer. Such interactions may, however, be important in other systems, as has recently been discussed for the silacyclohexanes.[17]

All spectra were obtained on a Bruker HFX-10 spectrometer; $^{31}P$ spectra were obtained at 36.4 MHz and are referenced to external 85% $H_3PO_4$, while $^1H$ spectra were obtained at 90 MHz. For low-temperature work, 15% solutions of III were used; TMS was employed as lock in trimethylethylene and $CCl_2F_2$ in vinyl chloride. Mr. Antonio Castillo is thanked for his skilled technical assistance with these experiments.

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[14] H. E. Shook, Jr., and L. D. Quin, *ibid.*, **89**, 1841 (1967).

[15] P. V. Demarco, E. Farkas, D. Doddrell, B. L. Mylari, and E. Wenkert, *ibid.*, **90**, 5480 (1968).

[16] F. A. Bovey, F. P. Hood, III, E. W. Anderson, and R. L. Kornegay, *J. Chem. Phys.*, **41**, 2041 (1964).

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## The Equilibrium between 2-Hydroxypyridine and 2-Pyridone in the Gas Phase

*Sir:*

The equilibrium between 2-pyridone (**1**) and 2-hydroxypridine (**2**) is representative of a large number of protomeric equilibria which have been extensively investigated in solution[1] and are of interest to studies of thermodynamic stabilities and, for the heteroaromatic bases of the nucleic acids, to hypotheses about base pairings. It is clear that **1** is strongly favored over **2** in solution,[2] but some reservation has been expressed

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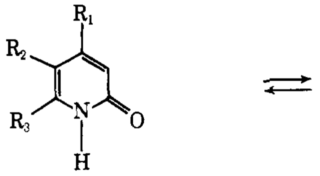
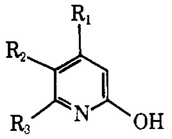
[1] A. Albert, "Heterocyclic Chemistry," Athlone Press, London, 1968, pp 369–375; A. R. Katritzky, *Chimia*, **24**, 134 (1970), and references cited therein.

[2] A. R. Katritzky and J. M. Lagowski, *Advan. Heterocycl. Chem.*, **1**, 347 (1963); R. H. Cox and A. A. Bothner-By, *J. Phys. Chem.*, **73**, 2465 (1969), and references cited therein.

about the fundamental significance of the position of this equilibrium under these conditions because of possible differential association or solvation for the tautomers,[3] and the quantitative validity of the classic p$K_a$ method, used to estimate the ratio of **2**:**1** as 2 ± 1 × $10^{-3}$ in aqueous solution at ambient temperatures,[4] has been questioned for the tautomerization of cytosine.[5] In the vapor phase, **2** has been reported to be the predominant tautomer by infrared[6] and mass spectrometric[7] analyses, but the question of whether these tautomers are in equilibrium in the gas phase appears to be open. In fact, the report that equilibrium for **3** and **4**, as measured by the relative intensities of NH and OH ir absorptions, is established only over a period of hours in the gas phase at 345–365° has been taken to suggest that the time and temperature invariant ratio[6,8] of *ca.* 2:1 for **2** to **1** at 160–300° could be that of a nonequilibrating mixture,[9] the composition of which is determined by the relative rates of vaporization of the tautomers.



**1**, $R_1 = R_2 = R_3 = H$
**3**, $R_1 = CH_3$; $R_2,R_3 = -(CH_2)_2-O-$



**2**, $R_1 = R_2 = R_2 = H$
**4**, $R_1 = CH_3$; $R_2,R_3 = -(CH_2)_2-O-$

$$K_{\text{vapor}} = [\mathbf{2}]/[\mathbf{1}] = 2.5 + 1.5$$

We have measured the uv spectra of *N*-methyl-2-pyridone (**5**), 2-methoxypyridine (**6**), and 2-hydroxypyridine–2-pyridone (**2**, **1**) in the gas phase at 120–140° using a heated cell with vacuum jacketed windows and a conventional spectrometer and find the ratio of **2** to **1** in the vapor over this temperature range to be 2.5 ± 1.5.[10] This ratio remains constant within these error limits over the temperature range 120–140°, while the absorbance increases by a factor of three over the same range, and this effect is reversible. Excess material is present as the melt during these measurements, the absorbance is stable for at least 8 hr, and the material can be recovered and shown to have ir, uv, and nmr spectra in solution characteristic of only **1**.

The invariance of the ratio of **2** to **1** coupled with the absorbance increase with increasing temperature rules out control of the gas phase ratio of **2** and **1** by selective vaporization and is consistent with a rapid equilibration of the tautomers in the gas phase, most likely *via* wall collisions, a process which has analogy in facile gas-phase enol-keto equilibria.[11,12] The ultraviolet spectra of **3–4** at 175° indicate a ratio greater than 10:1 in favor of **4**, provided that the solution spectra of the *N*- and *O*-methyl compounds corresponding to **3** and **4** are suitable models. In order to rationalize the discrepancy with earlier work,[8] it is probably significant that when **3–4** are heated to higher temperatures in our cell, extensive decomposition occurs although no change in the ratio of **3** to **4** is observed.

The fact that the equilibrium constant for the tautomeric ratio of **2**:**1** in the gas phase is in the opposite direction from that for the aqueous solution by three orders of magnitude, if p$K_a$ solution data are provisionally accepted,[4,5] has interesting implications. It establishes that the position of tautomeric equilibria for compounds of this type can, in fact, be controlled by the medium,[3] a result which is precedented by recent elegant studies of solution and gas-phase acidities[13] as well as by more modest solvent effects on other equilibria.[14,15] Clearly, attempts to understand the relative stabilities of tautomeric systems analogous to **1** and **2** must be consistent with gas-phase data; the recent quantum mechanical calculation which predicts that **1** is 12 kcal/mol[16] lower in chemical binding energy than **2** should be reevaluated.[17] Nonetheless, studies of solution equilibria in which solvent effects are cancelled by comparisons in a series should give reliable information about chemical binding.[3b,9,18] Finally, this demonstration that molecular environment can substantially affect the structure of tautomeric molecules should be of particular interest for studies of the base pairings, which are considered to control RNA transcription for protein synthesis and the replication of

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(3) (a) P. Beak, J. Bonham, and J. T. Lee, Jr., *J. Amer. Chem. Soc.*, **90**, 1569 (1968); (b) P. Beak and T. S. Woods, *Tetrahedron Lett.*, 775 (1972).

(4) A. Albert and J. N. Phillips, *J. Chem. Soc.*, 1294 (1956); S. F. Mason, *ibid.*, 674 (1958).

(5) G. C. Y. Lee, J. H. Prestey, and S. I. Chan, *J. Amer. Chem. Soc.*, **94**, 951 (1972).

(6) E. S. Levin and G. N. Rodionova, *Dokl. Akad. Nauk SSSR*, **164**, 584 (1965); **174**, 1132 (1967).

(7) T. Gronneberg and K. Undheim, *Org. Mass Spectrom.*, **6**, 823 (1972).

(8) E. S. Levin and G. N. Rodionova, *Dokl. Chem.* **189**, 900 (1969).

(9) M. J. Cook, A. R. Katritzky, P. Linda, and R. D. Tack, *J. Chem. Soc., Perkin Trans. 2*, 1295 (1972).

(10) It is assumed that the ratios of molar absorption coefficients for **1** and **2** are the same as those for **5** and **6**, respectively. The spectra will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-1700. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(11) R. Srinivasan and S. Cremer, *J. Phys. Chem.*, **69**, 3145 (1965); G. R. McMillan, J. G. Calvert, and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **86**, 3602 (1964).

(12) An alternative equilibration involving rapid proton transfer in the melt with equilibrium between the liquid and the vapor may seem more likely, but, in fact, vapor–liquid equilibrium is probably established slowly for an unstirred nonboiling liquid; E. Hala, J. Pick, V. Fried, and O. Vilim, "Vapor-Liquid Equilibrium," Part II, Pergamon Press, Oxford, England, 1958, Chapter 5.

(13) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **90**, 5636 (1968); E. M. Arnett, I. M. Jones, M. Taagepera, W. G. Henderson, J. L. Beauchamp, and R. W. Taft, *ibid.*, **94**, 4724 (1972); D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid.*, **94**, 4726 (1972), and references cited therein.

(14) R. J. Abraham, H. D. Banks, E. L. Eliel, O. Hofer, and M. K. Kaloustian, *ibid.*, **94**, 1913 (1972); A. Gordon and A. R. Katritzky, *Tetrahedron Lett.*, 2767 (1968), and references cited therein.

(15) A lack of dominant solvent effect has also been observed in some protomeric systems; *e.g.*, A. H. Lowery, C. George, P. D'Antonio, and J. Karle, *J. Amer. Chem. Soc.*, **93**, 6399 (1971); M. E. Remekamp, J. W. Paukstelis, and R. G. Cooks, *Tetrahedron*, 27, 4407 (1971). See, however, K. N. Houk, G. R. Newkome, and R. E. Duke, Jr., *J. Amer. Chem. Soc.*, in press.

(16) N. Bodar, M. J. S. Dewar, and A. J. Harget, *J. Amer. Chem. Chem. Soc.*, 92, 2929 (1970).

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DNA,[5,19,20] in that it suggests a possibly critical role for the molecular environment at the site of pairing in controlling the tautomeric structure of the nucleotide bases or base pairs. Additional information on the tautomeric ratio of **2** to **1** and related compounds is being sought by pressure and temperature studies in the gas phase.

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# *Book Reviews*

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**Characterization of Organometallic Compounds. Part II.** Edited by MINORU TSUTSUI (Texas A & M University). Wiley-Interscience, New York, N. Y. 1971. v + 877 pp. $19.95.

Part II of this volume contains four chapters, treating nuclear magnetic resonance (64 pp, 164 references), magnetic susceptibility, (41 pp, 43 references), electron spin resonance (170 pp, 1236 references), and preparation of $\sigma$-bonded organometallics of groups I–VA and group IIB (173 pp, 696 references). It is curious that only the shortest two of the four chapters really deal with characterization of organometallic compounds. Each chapter is discussed individually below.

"Nuclear Magnetic Resonance Spectroscopy of Organic Compounds," by R. Garth Kidd, is in the author's words "by no means exhaustive" and "should not be considered as a critical review of the literature" of the subject. Rather, this chapter is intended to show where the nmr technique can be of value in the study of organometallic compounds. This objective has been well accomplished by presentation of illustrations and discussion of spectral patterns, chemical shifts, and coupling constants for the proton magnetic resonance spectra of $\sigma$-bonded methyl, ethyl, phenyl, vinyl, and acetylenic organometallics and $\pi$-bonded ethylene, allyl, butadiene, cyclopentadienyl, arene, and alkyne complexes. Fluorine magnetic resonance spectra of fluoroalkyl, fluoroalkenyl and pentafluorophenyl derivatives are discussed. The nmr of $^{7}$Li, $^{27}$Al, $^{55}$Mn, $^{59}$Co, $^{119}$Sn, and $^{199}$Hg are briefly touched upon. Later sections of the chapter are devoted to kinetic processes in solution, where nmr has been so useful in the study of intermolecular exchanges of ligands and intramolecular rearrangements such as $\sigma$–$\pi$ interchange, encountered in allylic metal compounds, and the fluxional behavior of $\sigma$- and $\pi$-bonded complexes of cyclic olefins with metals. The author deliberately limits his coverage to diamagnetic molecules, and for these types of compounds he has presented a well-organized framework for obtaining a clear overview of the subject. The major deficiency of this chapter is the lack of treatment of the nmr of organometallic hydrido compounds.

"Magnetic Susceptibility: Characterization and Elucidation of Bonding in Organometallics," by L. N. Mulay and J. T. Dehn, discusses briefly the basic concepts and theory of diamagnetism and paramagnetism and experimental techniques for such measurements. This leads up to an attempt to make the point that diamagnetic susceptibility anisotropy, while difficult and time-consuming to measure, is a useful technique for obtaining structural interpretations and for testing the validity of certain molecular orbital descriptions. Specifically the magnetic anisotropy of ferrocene, ruthenocene, and osmocene is discussed and interpreted. Deliberately, only brief treatment of paramagnetism is given.

"Characterization of Organometallic Compounds by Electron-Spin Resonance," by F. J. Smentowski, is an exhaustive treatment of basic principles of esr and their applications to the study of rate processes, involving ion pairs in semiquinones and other aromatic radical anions. The ten pages devoted to organometallic compounds almost appear to be an afterthought to justify the title of the chapter. As a discussion of esr it is a compact and useful treatment of the subject and could stand alone as a book in itself, but it would have to go under a different title, for it really is not oriented to the organometallic chemist.

"Preparation, Physical Properties, and Reactions of Sigma-Bonded Organometallics," by W. T. Reichle, is a descriptive, primarily synthetic treatment of $\sigma$-bonded organometallics of main group elements. Though the editor's preface justifies its inclusion as dealing with compounds that "play significant roles in the analysis of other organometallic compounds," that point is hardly made in the chapter. Nevertheless, the chapter is thorough and well written. It covers the literature through 1966, with a few references in 1967. It will prove very useful to the organometallic chemists as well as to chemists in general.

All in all, the volume is one that will be an asset to the bookshelves of organometallic chemists and libraries, even though the distribution of its content is not entirely consistent with the title. Part I of this volume is much more directed to the intended subject.

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**The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results.** By HENRY F. SCHAEFER III (University of California at Berkeley). Addison-Wesley Publishing Co., Reading, Mass. 1972. x + 437 pp. $7.95.

It has been apparent for some time now that the available methods for the evaluation of the electronic properties of atoms and molecules from first principles through quantum mechanical calculation have reached a sufficient level of maturity that they now represent a significant and practical tool for the study of problems of real chemical interest. A number of computer programs for carrying out these so called *ab initio* calculations have been widely distributed, principally through the offices of the Quantum Chemistry Program Exchange located at the University of Indiana, and an ever-growing circle of scientists has been using them.

The nonspecialist who wants to carry out such a calculation has been faced with the lack of a single source of information as to the various formalisms which are currently in use, the proper choice of basis set for the molecule under consideration, and the accuracy which one can expect to get for a particular property from a given calculation.

This book fills this gap in a reasonably comprehensive fashion. It is organized about approximately fifty theoretical studies which both show the current state of the art of carrying out *ab initio* quantum chemical calculations and provide guidance for anyone who is embarking upon them.

The treatment of the various formalisms which are presently in use is descriptive rather than rigorous in that it is the physical content of each method rather than its formal mathematical derivation which is stressed. The book, however, references some 400 publications in the field, and the interested reader will easily find his way to the pertinent original papers if he so desires.

This is a useful book. Its focus is on methods, how to apply them, and what one can expect to get from them. It consistently avoids mathematical complexity, although the dust jacket claim that it is intended for "those students who have had only one quarter or one semester of introductory quantum mechanics" is probably overly optimistic. It would make a useful addition to the shelf of anyone interested in carrying out calculations of this type or in judging the likely accuracy of calculations carried out by others.

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