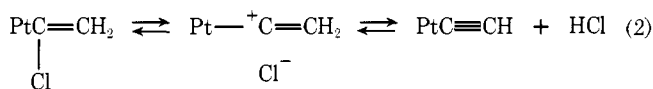


longer C_{α} -Cl bond distance in I, 1.809 (6) Å, is similar to the C_{sp^3} -Cl bond distance found in *tert*-butyl chloride, 1.828 (5) Å,¹¹ 1.807 (4) Å.¹² Furthermore, the observed Pt-C $_{\alpha}$ -Cl bond angle is smaller than expected while the Pt-C $_{\alpha}$ -C $_{\beta}$ angle is expanded toward linearity, in opposition to what would be expected from steric considerations. See paragraph at end of paper regarding supplementary material.

I dissolves in methanol to give *trans*-[Pt(CCl=CH₂)(COMe(Me))(PMe₂Ph)₂]⁺Cl⁻, IV-Cl, which in the presence of AgPF₆ (1 equiv) gives a stable hexafluorophosphate salt, IV-PF₆, as a white crystalline compound, mp 117–118 °C, $\nu_{str}(CCl=CH_2)$ 1570 cm⁻¹. Analogous reactions in MeOD lead to IV-Cl and IV-PF₆ in which the vinylic protons of the Pt-CCl=CH₂ moiety are *not* exchanged with deuterium atoms of the solvent. This is clearly evident from the ¹H NMR spectrum of IV-PF₆ which is shown in Figure 3. In particular the gem coupling of the vinylic protons is maintained.¹³

Detailed studies¹⁴ of the elimination of HCl from *trans*-PtX(CCl=CH₂)(PMe₂Ph)₂ in benzene and dichloromethane, where X = CCl=CH₂, -C≡CH, and -Cl, are consistent with sequence 2.



The present work also supports 2: the long C $_{\alpha}$ -Cl bond distance and the large Pt-C $_{\alpha}$ -C $_{\beta}$ angle in I are suggestive of a facile C $_{\alpha}$ -Cl heterolysis reaction. The observation that I reacts with MeOD to give IV-Cl/PF₆, in which reaction occurs at only one α -chlorovinyl ligand of I, indicates that the reactivity of the α -chlorovinyl ligand is very sensitive to the nature of the [L₂PtX] moiety to which it is bonded. It is reasonable to suppose that C $_{\alpha}$ -Cl heterolysis in IV-PF₆ is suppressed both by the positive charge on platinum and by the presence of the π -acceptor carbene ligand in the *trans*-position. At present we can only speculate on the relative importance of these factors. However, further work is in progress including a structural characterization of IV-PF₆.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant MPS 73-05016) for support of this work.

Supplementary Material Available: A listing of bond distances and bond angles (1 page). Ordering information is given on any current masthead page.

References and Notes

- (1) M. Hanack, *Acc. Chem. Res.*, **3**, 209 (1970).
- (2) R. A. Bell and M. H. Chisholm, *J. Chem. Soc., Chem. Commun.*, 181 (1974).
- (3) R. A. Bell and M. H. Chisholm, *J. Chem. Soc., Chem. Commun.*, 200 (1976).
- (4) NMR data for I in CD₂Cl₂,^b relative to Me₄Si = 0: $\delta(\text{PMe})$ 1.84 ppm, $^3J_{\text{Pt-H}} = 34.0$ Hz, $^2J + ^4J_{\text{P-H}} = 7.6$ Hz; $\delta(\text{trans-PtC}=\text{CH})$ 5.82 ppm, $^3J_{\text{Pt-H}} = 64.0$ Hz, $^4J_{\text{P-H}} = 2.2$ Hz; $\delta(\text{cis-PtC}=\text{CH})$ 4.71 ppm, $^3J_{\text{Pt-H}} = 24.0$ Hz, $^4J_{\text{P-H}} = 1.9$ Hz, $J_{\text{H-H}} = 0.6$ Hz (gem coupling).
- (5) $R = \frac{\sum |F_o - F_c|}{\sum |F_o|}$
- (6) $R_w = \frac{\sum w(F_o^2 - F_c^2)^2}{\sum wF_o^4}^{1/2}$
- (7) We are aware of only one other metal α -chlorovinyl structure, [1-chloro-2,2-bis(*p*-chlorophenyl)viny]bis(dimethylglyoximate)pyridinecobalt(III): D. A. Stotter, G. M. Sheldrick, and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 2124 (1975). This structure contains a vinylic C-Cl bond length of 1.803 (13) Å and angles about C $_{\alpha}$ similar to those of I. The cobaloxime complex did not react with Ag⁺ in water, but some evidence for solvolysis of the vinylic chloride was found in boiling methanol. D. A. Stotter, Ph.D. Thesis, 1974, Cambridge University and personal communication. The structure of I may also be compared with that reported for *trans*-PtCl(CH=CH₂)PEt₂(Ph)₂: C. J. Cardin, D. J. Cardin, M. F. Lappert, and K. W. Muir, *J. Organomet. Chem.*, **60**, C70 (1974), and that of *trans*-bis(isopropenyl acetylido)bis(triphenylphosphine)platinum(II): A. C. Villa, A. G. Manfredotti, and C. Guastini, *Cryst. Struct. Commun.*, **5**, 139 (1976).
- (8) R. C. Ivey and M. I. Davis, *J. Chem. Phys.*, **57**, 1909 (1972).
- (9) M. L. Unland, V. Weiss, and W. H. Flygare, *J. Chem. Phys.*, **42**, 2138 (1965).
- (10) J. N. Francis, A. McAdams, and J. A. Ibers, *J. Organomet. Chem.*, **29**, 131

(1970).

- (11) R. L. Hilderbrandt and J. D. Wieser, *J. Chem. Phys.*, **55**, 4648 (1971).
- (12) J. Hasse, H. D. Kamphusmann, and W. Zeil, *Z. Phys. Chem. (Frankfurt am Main)*, **55**, 225 (1967).
- (13) NMR data for IV-PF₆⁻ in CD₂Cl₂, δ relative to Me₄Si: $\delta(\text{PMe})$ 1.97 ppm, $^3J_{\text{Pt-H}} = 35.5$ Hz, $^2J + ^4J_{\text{P-H}} = 8.6$ Hz; $\delta(\text{PMe})'$ 2.00 ppm, $^3J_{\text{Pt-H}} = 35.5$ Hz, $^2J + ^4J_{\text{P-H}} = 8.6$ Hz; $\delta(\text{OMe})$ 5.07 ppm, $^4J_{\text{P-H}} = 6$ Hz; $\delta(\text{Me})$ 2.12 ppm, coupling obscured by PMe₂Ph group; $\delta(\text{trans-PtC}=\text{CH})$ = 6.19 ppm, $^3J_{\text{Pt-H}} = 60$ Hz, $J_{\text{H-H}} = 1.9$ Hz (gem); $\delta(\text{cis-PtC}=\text{CH})$ 5.30 ppm, $^3J_{\text{Pt-H}} = 23.5$ Hz, $J_{\text{H-H}} = 1.9$ Hz (gem); $\delta(\text{P-phenyl})$ 7.7–7.4 ppm.
- (14) R. A. Bell and M. H. Chisholm, results to be submitted for publication.

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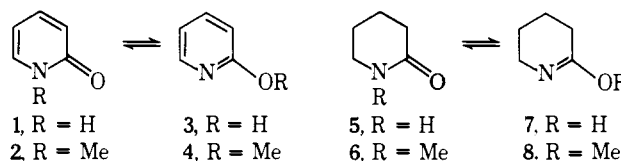
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Received April 20, 1976

Application of Ion Cyclotron Resonance Spectroscopic Gas-Phase Basicities to the Study of Tautomeric Equilibria¹

Sir:

Prototropic equilibria are sensitive to solvent and phase: their study is of considerable significance theoretically and experimentally.² Many spectroscopic and other methods are available for the study of such equilibria and quantitative data can be obtained provided detectable quantities (usually >5%) of both tautomers exist. However, the study of highly biased equilibria usually needs the basicity method, which depends on utilizing the relative pK_a values of suitable models (usually methyl derivatives) of each tautomer, cf. eq 1.² Unfortunately, simple



$$pK_T = pK(1) - pK(3) \approx pK(2) - pK(4) \quad (1)$$

application of the basicity method is restricted to aqueous solutions, although in conjunction with heat of solution data estimates of K_T can be made for equilibria in other solvents.³

Recently Beak⁴ has shown by uv and ir spectroscopy that 2- and 4-hydroxypyridine and some related compounds exist predominantly in the hydroxy form in the gas phase. For 2-hydroxypyridine (**1** \rightleftharpoons **3**) he obtained $\Delta H^\circ = 0.3 \pm 0.4$ kcal mol⁻¹ in favor of the hydroxy form **3**; for the related tetrahydro derivatives **5** \rightleftharpoons **7**, ΔH° is not determined directly, as the equilibrium content of **7** is not detectable, but using ΔH° for the equilibria⁵ of the methyl derivatives **2** \rightleftharpoons **4** and **6** \rightleftharpoons **8**, he estimated ΔH° (**5** \rightleftharpoons **7**) as ca. 7 kcal mol⁻¹ in favor of the oxo form **5**.

We wish to point out that gas-phase proton affinities, determined by pulsed ion cyclotron resonance (ICR) thermal proton transfer equilibria,^{6,7} offer a unique complementary approach. Data for the model compounds are collected in Table I: this indicates that **4** is more basic than **2** by $\Delta H^\circ = 2.1$ kcal mol⁻¹. However, the effect of O-methylation on the basicity of **3** is probably greater than the effect of N-methylation on the basicity of **1**. Thus, comparing H₂O \rightarrow MeOH \rightarrow Me₂O with NH₃ \rightarrow MeNH₂ \rightarrow Me₂NH indicates a differential effect on proton affinity (O > N) of 2.8 and 1.6 kcal mol⁻¹ for the first and second methylations, respectively.⁸ Comparison of ICR gas-phase basicities obtained in the present work with

Table I. Proton Affinities of Methyl Derivatives (**2**, **4**, **6**, and **8**)^a

Compd	Proton affinity, ^a kcal mol ⁻¹	Reference base used ^b
2	215.8	Pyridine; 2 is 0.9 kcal mol ⁻¹ weaker
4	217.9	<i>tert</i> -Butylamine; 4 is 1.0 kcal mol ⁻¹ stronger
6	214.9	Isopropylamine; 6 is 0.3 kcal mol ⁻¹ stronger
8	224.6	Diisopropylamine; 8 is 0.3 kcal mol ⁻¹ weaker

^a Based upon PA(NH₃) = 201.0 ± 2 kcal mol⁻¹ (ref 8 and 10); relative values are precise to ±0.2 kcal mol⁻¹; cf. ref 7 and 8. ^b Values given are Δ*G*[°] from direct equilibrium constant determinations.

the experimental Δ*H*[°] = -0.3 kcal mol⁻¹ obtained by Beak suggests that in the present series the differential methylation effect is in reasonable accord with the above figures,⁹ i.e., ~2.4 kcal mol⁻¹.

For the corresponding tetrahydro compounds we find that **8** is more basic than **6** by 9.7 kcal mol⁻¹; correcting this for the differential effect of O- vs. N-methylation indicates 7.3 kcal mol⁻¹ as the difference between **5** and **7**, in reasonable agreement with the value of 6.7 kcal mol⁻¹ deduced by Beak.

We believe that gas-phase basicities will be of considerable interest in the elucidation of prototropic equilibria in the gas phase, particularly in heavily biased cases.

Acknowledgment. This work was supported in part by a grant from the U.S. Public Health Service.

References and Notes

- Tautomeric Pyridines. Part 19. For part 18, see ref 3.
- For a survey see (a) J. Elguero, C. Marzin, A. R. Katritzky, and P. Linda, *Adv. Heterocycl. Chem.*, Supplement 1 (1976); (b) A. R. Katritzky and J. M. Lagowski, *Adv. Heterocycl. Chem.*, 1, 311 (1963).
- M. J. Cook, A. R. Katritzky, L. G. Hepler, and T. Matsui, *Tetrahedron Lett.*, 2685 (1976).
- (a) P. Beak and F. S. Fry, Jr., *J. Am. Chem. Soc.*, **95**, 1700 (1973); (b) P. Beak, F. S. Fry, Jr., J. Lee, and F. Steele, *ibid.*, **98**, 171 (1976).
- P. Beak, J. Bonham, and J. T. Lee, Jr., *J. Am. Chem. Soc.*, **90**, 1569 (1968).
- (a) M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **93**, 4314 (1971); (b) R. T. McIver, Jr., *Rev. Sci. Instrum.*, **41**, 555 (1970); (c) T. B. McMahon and J. L. Beauchamp, *ibid.*, **43**, 509 (1972); (d) W. G. Henderson, M. Taagepera, D. Holtz, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 4728 (1972).
- For a review, cf. R. W. Taft in "Proton Transfer Reactions", E. F. Caldin and V. Gold, Ed., Chapman and Hall, London, 1975, p 31.
- J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, submitted for publication.
- Unpublished results suggest that other groups may be more suitable than the methyl group in minimizing differential effects between oxygen and nitrogen. This matter is under further investigation.
- R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 1320 (1976).

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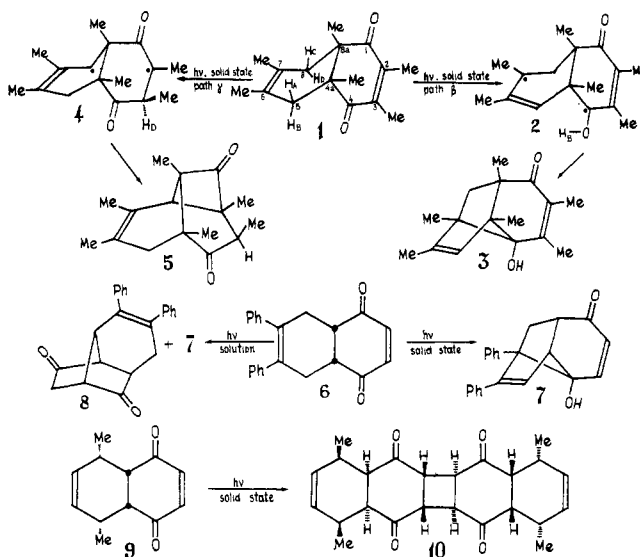
Received May 27, 1976

Intramolecular Photochemical Hydrogen Abstraction Reactions in the Solid State. Correlation with X-Ray Crystal Structure Data¹

Sir:

The correlation of solid state chemical reactivity with x-ray crystal structure data has provided valuable insight into a va-

Scheme I

**Table I.** Selected Angles and Nonbonded Distances in Adducts **1**, **6**, and **9** (Refer to Structure **1**)^a

Compound	Angles (deg) ^b			Distances (Å)	
	α	β	τ	H _B to O ₄	H _D to C ₃
1	60.0 (6)	61.4 (5)	0	2.47 (6)	2.89 (6)
6	62 (2)	67.9 (2)	3	2.46 (3)	3.05 (3)
9	61 (2)	72.8 (1)	c	c	d

^a The values in parentheses represent the standard deviation in the data. ^b α = Dihedral angle CH₃-C_{4a}-C_{8a}-CH₃ or H-C_{4a}-C_{8a}-H; β = dihedral angle C₄-C_{4a}-C_{8a}-C₈; τ = angle subtended by the O to H_B vector and its projection on the plane of the C₄ carbonyl group; cf. ref 8a. ^c Hydrogen B replaced by methyl. ^d Hydrogen D replaced by methyl.

riety of organic reaction types including (among others) 2 + 2 photodimerizations,² base-induced dehydrohalogenations,³ thermal rearrangements,⁴ azoalkane and diacyl peroxide photodecompositions,⁵ and the reaction of carboxylic acids with amines.⁶

In this paper we report the initial development of solid state structure-reactivity relationships in a class of organic reactions not yet studied in this way, namely, those involving intramolecular photochemical hydrogen atom abstractions. A study of this type was expected to provide evidence on five main points: (1) Over what distances can abstraction occur? (2) What is the preferred geometry for abstraction? (3) Can abstraction be facilitated relative to competing processes by "freezing" a reactant molecule in a favorable solid state conformation?⁷ (4) Will the products of such reactions in the solid state differ in type or amount from those obtained in solution due to crystal lattice restriction of rotation of the diradical intermediates involved? (5) Will changes in reaction molecularity be observed in going from studies in dilute solution to those in the solid state? We believe our results provide preliminary evidence on all five of these questions. In addition, the results are of relevance to the intramolecular hydrogen abstraction processes observed for carbonyl compounds upon electron impact (McLafferty rearrangement⁸) and anodic oxidation.⁹

The substrates chosen for study were the crystalline Diels-Alder adducts **1**, **6**, and **9** (Scheme I) whose solution phase photochemistry has recently been elucidated.^{1,10} In solution, two main reaction courses were identified as exemplified by the photoisomerization of **1** to **3** and **5**. These were (path β)