cupied molecular orbital, it may be that studies of ^{13}C SCS will provide a set of reactivity parameters measuring the ability of a substituent to alter the magnitudes of symmetry-imposed activation barriers.[12-14]

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(12) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1971.

(13) J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, *Accounts Chem. Res.*, **5**, 402 (1972).

(14) The explanation proposed by J. E. Baldwin and A. H. Andrist (*J. Amer. Chem. Soc.*, **93**, 3289 (1971)) for the existence of a linear correlation between electronic transition energies of a series of cyclic olefins and the activation energies for their thermal isomerizations can be viewed as perturbation of a parent olefin (π_{ii} remains constant) by various alkyl substituents ($\Delta\alpha_j$ is allowed to vary). It seems consistent with the approach proposed here, except for the specific probe chosen to monitor the magnitude of the perturbation imposed on the system.

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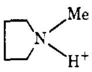
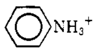
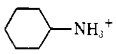
Regarding Heats of Solution of Gaseous Anilinium and Pyridinium Ions in Water and Intrinsic Basicities in Aqueous Solution[1]

Sir:

Accurate evaluation of the (relative) heats of solution ($-\Delta H_S°_{(BH^+)}$, kcal/mol) of NH_4^+ and of 20 aliphatic ammonium ions from the gas phase to dilute aqueous solution has recently shown[2] that there exist four nonoverlapping ranges, according to classical categories: NH_4^+, 84.0; primary ammonium, 75.0–78.0; secondary ammonium, 70.0–73.0; and tertiary ammonium, 62.0–65.0. The remarkably distinct increase in $-\Delta H_s°_{(BH^+)}$ values with increasing number of N–H protons in BH^+ was ascribed to predominant $NH^+ \cdots OH_2$ hydrogen bonding contributions of about 6–7 kcal.

We wish to report here that the results of a similar evaluation of the heats of solution of aromatic cations, *e.g.*, pyridinium and anilinium ions, follow the same scheme. Values of $-\Delta H_s°_{(BH^+)}$ are[3] (primary) $C_6H_5NH_3^+$, 76.0; (tertiary) $C_5H_5NH^+$, 64.0; and 4-CH_3-$C_5H_4NH^+$, 62.0. These results are of profound significance with respect to the extents of proton transfer equilibria in gas, aqueous, and other phases. Thus, the 20 kcal more exothermic heat of solution of $NH_4^+{}_{(g)}$ than $C_5H_5NH^+{}_{(g)}$ (due largely to the cationic hydrogen bonding) is the leading term accounting for the pronounced inversion in base strengths between the gas and aqueous phases;[4] C_5H_5N is about 11 powers of ten (in pK_A units) *more* basic than NH_3 toward $H^+{}_{(g)}$ but is about four powers of ten *less* basic than NH_3 toward $H^+{}_{(aq)}$.

Table I. Heats of Solution and Relative Gas- and Aqueous-Phase Acidities for Appropriate Pairs of Nitrogen Conjugate Acids Showing the Effects of Degree of Saturation[a]

Pair no.[b,c]	BH^+	$-\Delta H_s°_{(BH^+)}$[d]	$\delta_R \cdot \Delta G_i°_{(g)}$	$\delta_R \cdot \Delta G_i°_{(w)}$	$\delta_R \cdot \Delta H_i°_{(w)}$
1		73.0	−4.3	−3.88	−2.98
	$Me_2NH_2^+$	73.0	(0.0)	(0.00)	(0.00)
2		64.0	−8.3	−7.16	−4.25
		62.0	(0.0)	(0.00)	(0.00)
3		76.0	−9.6	−8.16	−7.19
		76.0	(0.0)	(0.00)	(0.00)

[a] Symbolism is as previously used except $\delta_R\Delta P$ refers to the standard thermodynamic property for ionization of the unsaturated BH^+ relative to the saturated member. Units are kcal/mol. [b] For pair 2, the "unsaturation effect" may be ascribed to effects of hybridization changes at N and C, *cf.* ref 8. [c] For pair 3, the "unsaturation effect" may be ascribed to a combination of inductive and resonance effects. According to an analysis of $\delta_R\Delta G_i°_{(w)}$ by Wepster, these effects contribute almost equally (1/2 each) to the total: B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **71**, 1171 (1952). [d] $-\Delta H_s°_{(BH^+)} = 84.0 - [\delta_R\Delta H_i°_{(g)} + \delta_R\Delta H_s°_{(B)} - \delta_R\Delta H_i°_{(w)}]$, which is eq 7 of ref 2a (with NH_3 the reference base). Values of $\delta_R\Delta H_i°_{(g)}$ have been obtained by us from the $\delta_R\Delta G_i°_{(g)}$ results from pulsed icr measurements in a trapped ion cell as described in ref 2a except values for ethylenimine and *N*-methylpyrrolidine are from ref 8. Values of $\delta_R\Delta H_s°_{(B)}$ and $\delta_R\Delta H_i°_{(w)}$ (as well as $\delta\Delta_R G_i°_{(w)}$ for aliphatic amines were taken from a recent tabulation by F. M. Jones III (Ph.D. Thesis, University of Pittsburgh, 1970). For pyridines, these values were obtained from L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Amer. Chem. Soc.*, **82**, 3828, 3831 (1960); for aniline $\delta_R P_i°$ values are from J. W. Larson and L. G. Hepler in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie Ed., Marcel Dekker, New York, N. Y., 1969, p 14; $\delta_R\Delta H_{s(B)}$ is from the heat of vaporization listed by J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970, p 283, and the heat of solution of liquid aniline in water obtained by Dr. J. F. Wolf; for cyclohexylamine $\delta_R\Delta H_{s(B)}$ is from the heat of vaporization estimated by the equation of Jones (*loc. cit.*, p 270) and the heat of solution of the liquid amine also obtained by Dr. Wolf.

Equally important is the comparison of base strengths for BH^+'s of the same or nearly the same $\Delta H°_{s(BH^+)}$. Simplification results from consideration of the effects of "degree of saturation" of carbon chains on base strength. Table I shows typical results for three representative pairs of nitrogen bases in the gas and aqueous phases. It is clearly evident that pairs of the same type, *i.e.*, with the same NH^+ and carbon numbers and similar frameworks, have very similar values of $\Delta H_s°_{(BH^+)}$, and, in turn, base strengths prevail in aqueous solution which are remarkably similar to those in the gas phase. The paired $\delta_R\Delta G_i°$ values for the relatively large effects of changing degrees of saturation are quantitatively only 10–20% smaller in water than in the gas phase. This result clearly indicates that there *are not* unusual (polarization or other) interactions associated with the different degrees of saturation of the carbon chain which are uniquely manifest in the gas phase. Instead, the large polarization and inductive effects which are frequently evident in the gas phase[2,5] may be masked almost completely in aqueous solution

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(1) This work was supported by the National Science Foundation.

(2) (a) E. M. Arnett, F. M. Jones, III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 4724 (1972); (b) D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid.*, **94**, 4726 (1972).

(3) For basis and references *cf.* footnote *d* of Table I.

(4) M. Taagepera, W. G. Henderson, R. T. C. Brownlee, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 1369 (1972); J. P. Briggs, R. Yamdagni, and P. Kebarle, *ibid.*, **94**, 5128 (1972).

(5) (a) W. G. Henderson, M. Taagepera, D. Holtz, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *ibid.*, **94**, 4728 (1972); (b) J. I. Brauman, J. M. Riveros, and L. K. Blair, *ibid.*, **93**, 3914 (1971).

basicities by nearly compensating solvation effects.[2a,6] The relatively small reduction factors of about 15% for the aqueous solvent which are shown in Table I are expected on the grounds that hydration of the free bases and their conjugate acids by hydrogen bonding somewhat reduces the apparent extents of proton transfer in aqueous solution as compared to the "complete" proton transfer of the gaseous reaction.[4,7]

The 2.0 kcal decrease in $-\Delta H_s{}^\circ{}_{(\mathrm{BH}^+)}$ shown by the 4-CH_3 substituent in pyridinium ion indicates that distant polar substituents exert relatively large effects upon the solvation of this cation. In fact, larger substituent effects, *e.g.*, for 4-CN or NO_2, might lead to a violation of the structural categorization of $-\Delta H_s{}^\circ{}_{(\mathrm{BH}^+)}$ values (in the pyridine as well as in other series). In any case, it is clear that the effects of 4-substituents on $-\Delta H_s{}^\circ{}_{(\mathrm{BH}^+)}$ for the pyridinium series may be a leading term in the previously reported[4] approximately 300% attenuation factor in base strengths between the gas phase and aqueous solution.

The results of Table I show also that the standard free energy charge, $\delta_R\Delta G_i{}^\circ{}_{(w)}$, is somewhat superior to the standard enthalpy change, $\delta_R\Delta H_i{}^\circ{}_{(w)}$, as an estimator of the intrinsic base strengths associated with the unsaturation effects behavior *in aqueous solution.* Several explanations for this type of result have been advanced.[9]

Acknowledgment. We are pleased to acknowledge the valuable assistance provided by Professor E. M. Arnett and Dr. J. F. Wolf in obtaining heats of solution of c-$C_6H_{12}NH_2$(l) and $C_6H_5NH_2$(l). We are also indebted to Professor D. H. Aue for communication of results prior to publication. Thanks are also due to Dr. W. G. Henderson for preliminary icr experiments with $C_6H_5NH_2$.

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(6) E. M. Arnett and J. F. Wolf, *J. Amer. Chem. Soc.*, **95**, 978 (1973), have found dramatic evidence for this point of view from very large alkyl substituent effects on the heat of protonation of the relatively poorly solvated $\gg PH^+$ and $>SH^+$ cations in fluorosulfuric acid.

(7) P. Love, R. B. Cohen, and R. W. Taft, *ibid.*, **90**, 2455 (1968).

(8) D. H. Aue, H. M. Webb, and M. T. Bowers, private communication.

(9) (a) L. G. Hepler, *J. Amer. Chem. Soc.*, **85**, 3089 (1963); J. W. Larson and L. G. Hepler, *J. Org. Chem.*, **33**, 3961 (1968); (b) L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1970, Chapter 12; (c) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p 70–73; (d) *cf.* also P. D. Bolton, K. A. Fleming, and F. M. Hall, *J. Amer. Chem. Soc.*, **94**, 1033 (1972); (e) E. M. Arnett and D. R. McKelvey in "Solute–Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 6.

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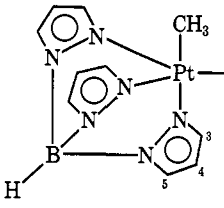
Five-Coordinate Acetylene, Allene, and Olefin Complexes of Platinum(II) Containing Polypyrazolylborate Ligands

Sir:

Several years ago Trofimenko discovered the polypyrazolylborate ions[1] and prepared many complexes demonstrating the unusually strong coordinating ability of this class of ligand.[2,3] As a ligand, the polypyrazolylborate ion is analogous to the cyclopentadienyl ion in the sense that each can be regarded as a tridentate, six-electron donor group, although the polypyrazolylborate metal complexes are generally much more stable. For example, the complex[4] $[HB(pz)_3]Cu(CO)$ is very air and heat stable while the analogous cyclopentadienyl complex[5] $(C_5H_5)Cu(CO)$ is very reactive.

Therefore it appeared to us that a tridentate polypyrazolylborate ligand might well stabilize five-coordinate complexes of platinum(II). We have prepared the insoluble complex $Pt(CH_3)[HB(pz)_3]$ which is probably polymeric with bridging pyrazolyl groups. The polymer is readily cleaved by a variety of acetylenes, olefins, and allenes to give the five-coordinate complexes I–III.



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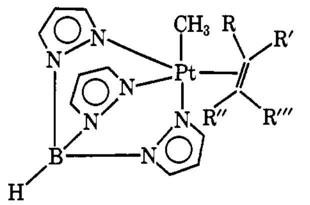
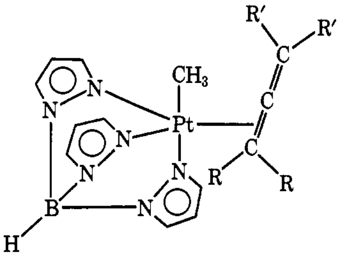


II



III

The acetylene complexes, I, with $CF_3C{\equiv}CCF_3$ and $(CH_3)O_2CC{\equiv}CCO_2(CH_3)$ show the expected nmr patterns for the platinum methyl and acetylene groups. The protons on the 4 positions of the pyrazolyl rings are easily assigned since they appear as triplets due to coupling with the 3-H and 5-H protons of the ring. They appear as two distinct resonances in the ratio of 2:1, consistent with (a) two equatorial and one axial pyrazolyl rings and (b) stereochemical rigidity of the hydrotris(1-pyrazolyl)borate ligand. Coupling between ^{195}Pt ($I = {}^1/_2$, 34% abundance) and the 4-H protons of both the equatorial and axial rings is observed thus confirming the tridentate nature of the polypyrazolylborate ion. The coupling constants J(Pt–H) are ≈ 10 and ≈ 3 Hz to the equatorial and axial 4-H protons which suggest that the group of highest trans influence[6] (*i.e.*, CH_3^-) is trans to the axial pyrazolyl group. The nmr spectrum of I with the unsymmetrical acetylene $C_6H_5C{\equiv}CCH_3$ shows three resonances which may be assigned to the 4-H protons indicating that the acetylene is not rotating and is constrained within the trigonal

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(1) S. Trofimenko, *J. Amer. Chem. Soc.*, **88**, 1842 (1966).

(2) S. Trofimenko, *Accounts Chem. Res.*, **4**, 17 (1971).

(3) S. Trofimenko, *Chem. Rev.*, **72**, 497 (1972).

(4) M. I. Bruce and A. P. P. Ostazewski, *J. Chem. Soc., Chem. Commun.*, 1124 (1972).

(5) F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **92**, 5114 (1970).

(6) For a review of the trans influence see T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, in press.