N indicated a composition Mo(IV) (total):CN^- of 1:3.96 with all C and N present as CN^-. It was demonstrated that the oxidation state of the aquomolybdenum remained (IV) by determination of the ratio of Fe(III) needed for oxidation of the molybdenum before and after reduction by Zn/Hg to Mo(III) (air-free techniques required). These results show that the solid obtained is a 1:1 adduct of aquo Mo(IV) and $Mo(CN)_8{}^{4-}$. Flame photometry revealed the presence of about one K^+ per aquo Mo(IV) indicating the possibility of one H^+ in the solid. Analysis figures were reproducible to ±5% for different samples and a ratio aquo Mo(IV):$Mo(CN)_8{}^{4-}$:CN^- of 1:1:8 was obtained in all cases. The solid is only stable for periods <3 hr. It is weakly acidic, a 1.25×10^{-3} *M* solution giving a pH of 3.08. The ir spectrum gives a broad ν(C═N) stretch at 2125 cm^{-1}. The lack of any shift compared to $K_4[Mo(CN)_8]$ indicates that CN^- bridging of the two molybdenum centers is probably absent.

Acknowledgment. We thank Dr. M. Lamache for a sample of molybdenum(IV) aquo ion, which gave identical behavior to our own. T.R. is grateful for the award of a Government of India National Merit Scholarship.

References and Notes

(1) P. Souchay, M. Cadiot, and M. Duhameaux, *C. R. Acad. Sci.*, **262**, 1524 (1966).
(2) P. Souchay, M. Cadiot, and B. Viossat, *Bull. Soc. Chim. Fr.*, **3**, 892 (1970).
(3) M. Ardon and A. Pernick, *J. Am. Chem. Soc.*, **95**, 6871 (1973).
(4) P. C. H. Mitchell, *Coord. Chem. Rev.*, **1**, 315 (1966).
(5) G. P. Haight, *Acta Chem. Scand.*, **15**, 2012 (1961).
(6) P. C. H. Mitchell, Ph.D. Thesis, University of Oxford, 1961.
(7) E. Wendling, *Bull. Soc. Chim. Fr.*, 437 (1965).
(8) M. C. Steele, *Aust. J. Chem.*, **10**, 367 (1957).
(9) H. M. Spittle and W. Wardlaw, *J. Chem. Soc.*, 792 (1929).
(10) W. Wardlaw and W. H. Parker, *J. Chem. Soc.*, 1311 (1925).
(11) M. Ardon and A. Pernick, *J. Am. Chem. Soc.*, **96**, 1643 (1974).
(12) See M. Lamache, *J. Less-Common Met.*, **39**, 179 (1975).
(13) M. Lamache-Duhameaux, *Rev. Chim. Miner.*, **5**, 1001 (1968).
(14) B. Viossat, *Rev. Chim. Miner.*, **9**, 737 (1972).
(15) J. F. Ojo, Y. Sasaki, R. S. Taylor, and A. G. Sykes, to be submitted for publication.
(16) H. H. Cady and R. E. Connick, *J. Am. Chem. Soc.*, **80**, 2426 (1958).
(17) A. Tiselius and S. Claesson, *Ark. Kemi, Mineral. Geol.*, **15** (No. 18) (1942); S. Claesson, *Ann. N.Y. Acad. Sci.*, **49**, 133 (1948).

Th. Ramasami, R. S. Taylor, A. Geoffrey Sykes*
Department of Inorganic and Structural Chemistry
The University, Leeds LS2 9JT, England

Received June 23, 1975

Intrinsic Acid-Base Properties of Molecules. Binding Energies of Li^+ to π- and n-Donor Bases

Sir:

The intrinsic basicity of a molecule B may be quantitatively specified by its binding energy to a reference acid in the gas phase. Proton binding energies (eq 1) have been obtained for a large number of organic and inorganic species,[1] providing one scale of molecule basicity. We wish to report the determination of the binding energies of 30 π- and n-donor bases to the reference acid Li^+ (eq 2) and the comparison of two scales of molecular basicity afforded by these results.

$$BH^+ \rightarrow B + H^+ \qquad \Delta H = D(B\text{-}H^+) \equiv PA(B) \quad (1)$$

$$BLi^+ \rightarrow B + Li^+ \qquad \Delta H = D(B\text{-}Li^+) \quad (2)$$

We have recently demonstrated that bimolecular reactions of alkali ions with certain alkyl halides lead to the formation of complexes of these species with molecules.[2] For example, Li^+ reacts with isopropyl chloride to form the complex of Li^+ with propylene (reaction 3). Transfer of Li^+ between molecules (reaction 4) is rapid allowing examination of the relative binding energies of Li^+ to various bases by use of trapped ion cyclotron resonance (ICR) techniques.[3,4]

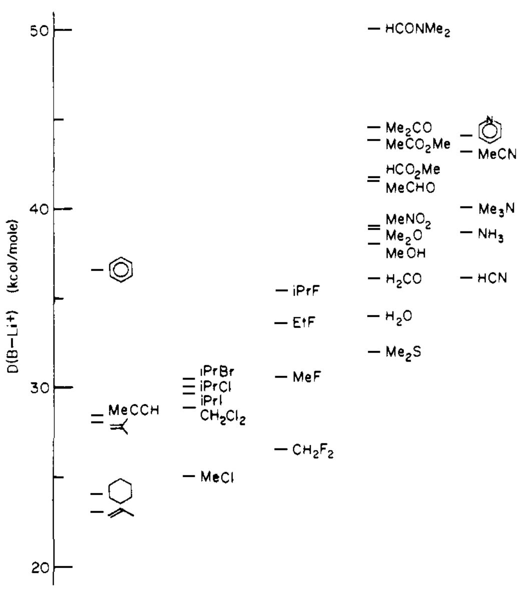

Figure 1. Binding energies of molecules to Li^+.

$$(CH_3)_2CHCl + Li^+ \rightarrow (CH_3CH{=}CH_2)Li^+ + HCl \quad (3)$$

$$B_1Li^+ + B_2 \rightleftharpoons B_1 + B_2Li^+ \quad (4)$$

Relative values of $D(B\text{-}Li^+)$ are quantitatively determined in cases where the free energy change for reaction 4 is sufficiently small (<3 kcal/mol) that equilibrium constants can be obtained.[1] A scale of Li^+ binding energies (Figure 1) has been constructed by combining the results of such determinations[5] and is referenced to experimental[6] and theoretical[7] values for $D(H_2O\text{-}Li^+) = 34$ kcal/mol. Relative to H_2O, reported values are estimated to be accurate to ±2 kcal/mol, with higher accuracy for smaller differences.

Several points may be noted in examining the data of Figure 1. Molecular binding energies of Li^+ are substantial even for a saturated species such as cyclohexane, $D(B\text{-}Li^+) = 24$ kcal/mol, and become quite large for aromatics, $D(C_6H_6\text{-}Li^+) = 37$ kcal/mol. $D(B\text{-}Li^+)$ increases with methyl substitution at the basic site in both π- (isobutene > propene) and n-donor bases (Me_2O > MeOH > H_2O, Me_3N > NH_3). Greater basicity toward Li^+ also results from increasing the size of the alkyl substituent (*i*-PrF > EtF > MeF). Compared to first-row species $D(B\text{-}Li^+)$ is smaller for second-row n-donor bases (MeCl < MeF, Me_2S < Me_2O).

These results may benefit theoretical approaches to the understanding of alkali ion interactions with molecules. The interaction potential has been described both at short distances where scattering results have been used to characterize the repulsive part of the potential[8] and at long distances where electrostatic terms dominate.[9] The present data describe the interaction at the equilibrium configuration. They provide quantification of the energetic changes associated with reactions in which alkali ions are involved both in the gas phase and solution and may be used to interpret the specific binding of alkali ions by polyfunctional molecules and in biological systems.[10] In addition, the data are directly applicable to the development of chemical ionization sources using alkali ions.[11]

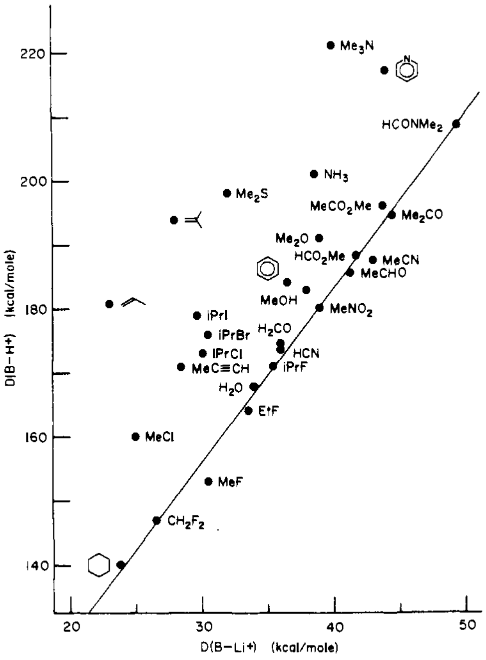

Figure 2. Comparison of two scales of gas phase basicity: binding energies of molecules to H^+, $D(B-H^+)$, and to Li^+, $D(B-Li^+)$.

Of particular interest is the comparison of the present data for Li^+ binding energies $D(B-Li^+)$ to proton affinities $D(B-H^+)$,[1,3,12] Figure 2. The data are consistent with the expectation that bonding to Li^+ is largely ionic while bonding to H^+ may also reflect strong covalent interactions. Many of the data fall near a line of slope 3 which intercepts the $D(B-H^+)$ axis at 70 kcal/mol for $D(B-Li^+) = 0$. The larger ionic bonding distances of second-row elements make them understandable exceptions. More dramatic is the comparison for alkenes: the intimate interaction afforded the proton in carbenium ions may be contrasted with the loose complex expected for Li^+. The different magnitudes of methyl substituent effects for the two reference acids also appear to reflect ionic contributions to the bonding of Li^+. Thus the dipole moments[13] NH_3 (1.47 D) > Me_3N (0.612 D) and H_2O (1.85 D) > MeOH (1.70 D) > Me_2O (1.30 D) as compared to CH_2O (2.33 D) < MeCHO (2.69 D) < Me_2CO (2.88 D) and HCN (2.98 D) < MeCN (3.92 D) are reflected in larger methyl substituent effects for $D(B-Li^+)$ in the latter series.

Acknowledgment. This research was supported in part by the Energy Research and Development Administration under Grant No. AT(04-3)767-8. The instrumentation used for these studies was funded by the National Science Foundation under Grant No. NSF-GP-18383.

References and Notes

(1) For leading references see 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); R. H. Staley and J. L. Beauchamp, *ibid.*, **96**, 6525 (1974); M. S. Foster and J. L. Beauchamp, *ibid.*, in press; M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., *ibid.*, **93**, 4314 (1971); D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid.*, **94**, 4726 (1972); **95** 2699 (1973); J. P. Briggs, R. Yamdagni, and P. Kebarle, *ibid.*, **94**, 5128 (1972); R. Yamdagni and P. Kebarle, *ibid.*, **95**, 3504 (1973).

(2) R. D. Wieting, R. H. Staley, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97**, 924 (1975).

(3) For a general review of ICR see J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).

(4) T. B. McMahon and J. L. Beauchamp, *Rev. Sci. Instrum.*, **43**, 509 (1972).

(5) For $HCONMe_2$ only a lower limit of 48 kcal/mol was established by the transfer experiments. The value indicated is suggested by the correlation of Figure 2.

(6) S. K. Searles, I. Džidić, and P. Kebarle, *J. Am. Chem. Soc.*, **91**, 2810 (1969); I. Džidić and P. Kebarle, *J. Chem. Phys.*, **74**, 1466 (1970).

(7) H. Kistenmacher, H. Popkie, and E. Clementi, *J. Chem. Phys.*, **59**, 5842 (1973); **61**, 799 (1974); P. A. Kollman and I. D. Kuntz, *J. Am. Chem. Soc.*, **94**, 9236 (1972); **96**, 4766 (1974).

(8) Y. S. Kim and R. G. Gordon, *J. Chem. Phys.*, **61**, 1 (1974); 60, 4323 (1974); J. Schaefer and W. A. Lester, Jr., *ibid.*, **62**, 1913 (1975); V. Staemmler, *Chem. Phys.*, **7**, 17 (1975); **1**, 27 (1973).

(9) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids", Wiley, New York, N.Y., 1964, p 941 ff.

(10) A. Pullman, *Int. J. Quantum Chem., Quantum Biol. Symp.*, **No. 1**, 33 (1974); A. Pullman and P. Schuster, *Chem. Phys. Lett.*, **24**, 472 (1974); H. Diebler, M. Eigen, G. Ilgenfritz, G. Maas, and R. Winkler, *Pure Appl. Chem.*, **20**, 93 (1969).

(11) F. H. Field in "Ion-Molecule Reactions", J. L. Franklin, Ed., Plenum, New York, N.Y., 1972, Chapter 6; R. V. Hodges and J. L. Beauchamp, submitted for publication.

(12) $D(B-H^+)$ values are based in part on recent unpublished results: J. F. Wolf, I. Koppel, R. W. Taft, R. H. Staley, and J. L. Beauchamp, to be submitted for publication.

(13) R. D. Nelson, Jr., D. R. Lide, Jr., and A. A. Maryott, "Selected Values of Electric Dipole Moments for Molecules in the Gas Phase", NSRDS-NBS 10, U.S. Government Printing Office, Washington, D.C., 1967.

(14) Camille and Henry Dreyfus Teacher-Scholar, 1971-1976.

Ralph H. Staley, J. L. Beauchamp* [14]
Contribution No. 5110, Arthur Amos Noyes Laboratory of
Chemical Physics
California Institute of Technology
Pasadena, California 91125

Received May 13, 1975

Nitrogen to Oxygen Isomerization of the Pentaammineruthenium(III) Glycine Ion

Sir:

During the course of our investigations into the interaction of amino acids and amino acid derivatives with the ruthenium ammine system, we observed a very facile isomerization of glycine as ligand from the N-bound to the O-bound form in pentaammineruthenium(III). This type of reaction has not been observed for the glycine complex of pentaamminecobalt(III).[1] Our observations on the pentaammineruthenium system are reported herein.

Pentaammineglycineruthenium(II) hexafluorophosphate was prepared by first reducing aquopentaammineruthenium(III) trifluoromethylsulfonate (0.075 *M*)[2] with zinc amalgam in an argon atmosphere. A tenfold excess of sodium glycinate was added to the reaction vessel. After 90 min the desired complex was precipitated as a yellow solid by acidifying with trifluoroacetic acid and adding an excess of ammonium hexafluorophosphate. The solid was filtered in air, washed with ethanol and ether, dried, and stored in a vacuum desiccator. Anal.[3] Calcd for $[(NH_3)_5Ru-NH_2CH_2COOH](PF_6)_2$: C, 4.36; N, 15.2; H, 3.63; Ru, 18.3. Found: C, 4.63; N, 15.4; H, 3.42; Ru, 18.3.

The electronic and infrared absorption spectra of this complex show the expected behavior for a "hexaammine" type of ruthenium(II) species.[4] The carboxylate stretch is clearly evident in the infrared spectrum at 1740 cm^{-1}. The cyclic voltammogram shows a reversible couple with E_f = 160 mV vs. NHE in 0.1 *M* trifluoroacetic acid to be compared to 120 mV measured for $(NH_3)_5RuNH_2CH_2C_6H_5{}^{2+}$ under the same conditions.[5] Oxidation of this species in acid media with a variety of oxidizing agents and reprecipitation with ammonium hexafluorophosphate produced a white solid (45% yield) which showed no -COOH stretching frequency in the infrared. The ultraviolet absorption spectrum of a typical reaction mixture before and after oxidation is shown in Figure 1. The peak at 288 nm has an extinction coefficient of 1.43×10^3 M^{-1} cm^{-1}, and is very similar in both position and intensity to known carboxylato complexes of pentaammineruthenium(III).[6] It should be noted that the isolated solid has an identical spectrum. The cyclic voltammogram shows behavior which is like that of carboxyla-