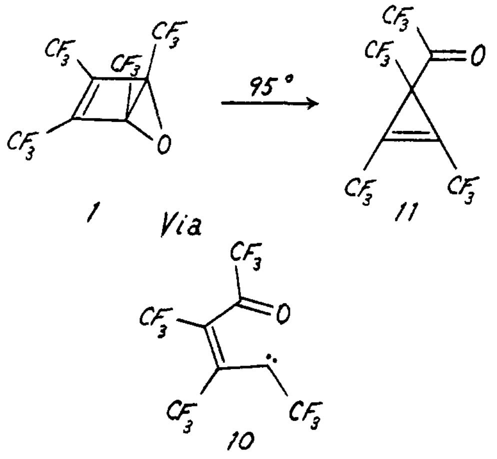
but it suffers irreversible change—quantitative aromatization[12]—only only under rather vigorous conditions ($t_{1/2}$ = 5 h at 160 °C[2,13]). In contrast, cyclobutadiene oxide **1** valence isomerizes cleanly by a different pathway at temperatures below 100 °C ($t_{1/2} \simeq$ 20 min at 95 °C), yielding the extremely stable cyclopropenyl ketone **11**.[3,14] We interpret this unexpected rearrangement of **1** in terms of fragmentation to carbene **10** followed by the amply precedented cyclization of a vinylcarbene to a cyclopropene.[15,16] For the parent heterocycle, cyclobutadiene oxide itself, one can estimate from strain and bond energies that formation of the carbene should be close to thermoneutral. Facile thermal access to a carbene from a ground state may be attributed here to relief of approximately 70-kcal/mol strain in two small rings[17] and the generation of a C–O π bond.[18] MNDO calculations[21] yield an energy difference of 17 kcal/mol between fully optimized cyclobutadiene oxide and the (singlet) carbene, *s-cis*-(*Z*)-2-buten-4-yliden-1-al. The dichotomous behavior of **1** and **2** on thermolysis is understandable on the basis that (1) the difference between single and double bond energies is more than 20 kcal/mol greater for C–O than for C–S[22] and (2) thiophene enjoys significantly greater aromatic stabilization than furan.[23]



The retro-Diels-Alder reaction of **9**, carried out in a flow apparatus, required temperatures approaching 200 °C, and thus gave ketone **11** unaccompanied by the presumed intermediate **1**. It was this discovery which stimulated us to synthesize **7**, whose fragmentation was expected to proceed under milder conditions by virtue of the greater stabilization energy of pyrrole as compared to furan.[23]

Kobayashi has shown that Dewar thiophene **2** is a talented dienophile which undergoes Diels-Alder addition to many unhindered dienes at ambient temperatures.[5] Competition experiments now reveal that its oxygen counterpart **1** reacts with furan at 25 °C *three orders of magnitude faster than* **2**. We ascribe the high reactivity of both dienophiles to low-lying LUMO's, which confer upon them cyclobutadienoid character.[24] Perhaps the more reactive **1** has the lower lying LUMO, as predicted by simple molecular orbital theory. The cycloaddition chemistry of **1** will be discussed more fully in a future report.

We plan to synthesize and study cyclobutadiene oxide itself.

Acknowledgment. We thank the National Science Foundation for generous support of this research.

Registry No. 1, 80326-57-4; **2**, 39091-73-1; **3**, 66008-14-8; **4**, 80326-58-5; **5**, 80326-59-6; **6**, 80326-60-9; **7**, 80326-61-0; **9**, 80326-62-1; **11**, 67705-04-8.

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[12] The corresponding aziridine (Dewar pyrrole) also aromatizes on heating, but automerization has not been detected. Kobayashi, Y.; Ando, A.; Kawada, K.; Kumadaki, I. *J. Org. Chem.* **1980**, *45*, 2966–2968.

[13] This appears to be another manifestation of the perfluoroalkyl effect. Lemal, D. M.; Dunlap, L. H., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 6562–6564.

[14] The assignments of ^{19}F NMR signals to the nonvinyl CF_3 groups in this compound were inadvertently switched in ref 3.

[15] Hartzler, H. In "Carbenes", Moss, R. A., Jones, M., Eds.; Wiley: New York, 1975; Vol. II, p 57ff.

[16] For a closely related example, see: Laganis, E. D.; Lemal, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 6634–6636.

[17] From the heat of isomerization of bicyclo[2.1.0]pent-2-ene to cyclopentadiene (47.8 kcal/mol), the strain energy of the former is almost 75 kcal/mol; about 10 kcal of this has been attributed to homoantiaromaticity.[19]

[18] Gordon, A. J.; Ford, R. A. "The Chemists' Companion, A Handbook of Practical Data, Techniques, and References", Wiley-Interscience: New York, 1972; p 113.

[19] Roth, W. R.; Klärner, F.-G.; Lennartz, H.-W. *Chem. Ber.* **1980**, *113*, 1818–1829.

[20] Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley-Interscience: New York, 1976; pp 273, 276.

[21] These were performed by R. Dave Mitchell and David Wirth at Columbia University, through the kind courtesy of Professor Ronald Breslow. See: Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 5558–5561 and references contained therein.

[22] Johnson, D. A. In "Sulfur in Organic and Inorganic Chemistry"; Senning, A., Ed.; Marcel Dekker: New York, 1972; Vol. 2, pp 58–60.

[23] Pihlaja, K.; Taskinen, E. In "Physical Methods in Heterocyclic Chemistry"; Katritzky, A. R., Ed.; Academic Press: New York, 1974; Vol. VI, pp 240–246.

[24] Antihomoaromaticity in bicyclo[2.1.0]pent-2-ene has been predicted[25] and recently documented.[19,26] Enhanced Diels-Alder reactivity is one of its manifestations.[19]

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Silver Ion Affinities of Alcohols As Ordered by Mass Spectrometry/Mass Spectrometry

S. A. McLuckey, A. E. Schoen, and R. G. Cooks*

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received August 24, 1981

Interest in gas-phase organometallic and inorganic complexes is at a high level[1] due to successful studies of intrinsic chemistry of organic ions[2] and the availability of laser desorption techniques for metal ion production.[3] The affinities of molecules for metal ions and the structures of the products of this interaction are key aspects of organometallic chemistry to which the technique of mass spectrometry/mass spectrometry (MS/MS)[4] should contribute. We now show that MS/MS can be used to order metal ion affinities for various ligands through the following sequence: (i) the metal ion is generated by laser desorption from the metal in the presence of the vaporized ligand(s); (ii) among the resulting products is the metal-bound dimer ion $(L_1 \cdots M \cdots L_2)^+$ (L = ligand, M = metal) which is mass selected; (iii) its structure is established by recording a collision-induced dissociation spectrum of fragment ions; (iv) finally, relative affinities of L_1 and L_2 for M^+ are assigned from the fragment intensity ratio $[L_1M^+]/[L_2M^+]$. We conclude inter alia that silver ion affinities depend upon the nature of the heteroatom in the ligand (ammonia solvates Ag^+ more strongly than does water) and upon polarizability and inductive effects which favor larger and more branched solvent molecules.

Consider the following data as an illustration of the basis for the method. An aluminum foil irradiated in the presence of diethylamine and isopropylamine by 1.06-μm radiation from a Nd:YAG laser in a combined chemical ionization/laser desorption

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[1] (a) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 455. (b) Holland, P. M.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 6174. (c) Armentrout, P. B.; Beauchamp, J. L. *Ibid.* **1981**, *103*, 784. (d) Kappes, M. M.; Staley, R. H. *Ibid.* **1981**, *103*, 1286. (e) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Ibid.* **1981**, *103*, 4360.

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Table I. Relative Fragment Ion Abundances from Silver-Bound Dimers[a, b]

fragment	$(CH_3OH)Ag^+$	$(C_2H_5OH)Ag^+$	$(n\text{-}C_3H_7OH)Ag^+$	$(i\text{-}C_3H_7OH)Ag^+$	$(n\text{-}C_4H_9OH)Ag^+$	$(t\text{-}C_4H_9OH)Ag^+$
$(CH_3OH)Ag^+$	1	2.9	4.9	6.2	9.4	15.8
$(C_2H_5OH)Ag^+$	0.34	1	1.7	2.1	3.6	5.7
$(n\text{-}C_3H_7OH)Ag^+$	0.20	0.59	1	1.2	1.8	3.2
$(i\text{-}C_3H_7OH)Ag^+$	0.16	0.47	0.83	1	1.6	2.6
$(n\text{-}C_4H_9OH)Ag^+$	0.11	0.29	0.55	0.62	1	1.7
$(t\text{-}C_4H_9OH)Ag^+$	0.063	0.18	0.31	0.37	0.59	1

[a] Numerator in abundance ratio shown in row at top, denominator in column at left. [b] In some cases ratios are an average of both indirect and direct measurements.

ion source[5] gave a mass spectrum which included ions with masses corresponding to the symmetrical species $(Et_2NH)_2Al^+$ and $(i\text{-}C_3H_7NH_2)_2Al^+$ as well as the unsymmetrical ion $(Et_2NH)Al(i\text{-}C_3H_7NH_2)^+$. Mass selection and dissociation of the last ion gave an MS/MS spectrum[6] with just two ions of greater than 10% relative abundance, *m/z* 100 (100%) corresponding to Et_2NHAl^+ and *m/z* 86 (20%) corresponding to $i\text{-}C_3H_7NH_2Al^+$. Arguing on the basis of earlier proton-bound dimer results,[7] the more facile loss of isopropylamine implies that the secondary amine has the higher affinity for the bridging ion Al^+, and the absence of other peaks in the MS/MS spectrum is consistent with a loosely bonded complex.[7] MS/MS spectra taken on the symmetrical dimer ions establish the assignment of loosely bonded structures; for example bis(diethylamino)aluminum cation (*m/z* 173) is expected and found to display but a single fragment ion (Et_2NHAl^+).

The relative rates of competitive unimolecular reactions (1 and 2) from a common species should under appropriate conditions[7] reflect the difference in activation energies for the competitive reactions. In addition, if reverse activation energies are negligible

$$L_1 \cdots M^+ \cdots L_2 \rightarrow L_1M^+ + L_2 \quad (1)$$

$$L_1 \cdots M^+ \cdots L_2 \rightarrow L_1 + L_2M^+ \quad (2)$$

or equal, the difference in the forward activation energies ($\Delta\epsilon^\circ$) will equal the difference in enthalpies of reaction[7] and in M^+ affinities, viz., $\Delta\epsilon^\circ = \Delta M^+$ affinity. Thus, a connection exists between peak heights in an MS/MS spectrum and the relative metal ion affinities of two ligands. These expectations have been confirmed in studies of proton-bound dimers; in these systems this kinetic method has been shown to be rapid, sensitive to small differences in proton affinities, easily implemented in conventional MS/MS instruments, applicable to impure samples, and to yield results in quantitative agreement (0.3 kcal mol^{-1}) with conventional equilibrium data. Quantitative measurements do require, however, that comparisons be made within a series of closely related ligands.

The remainder of this note is devoted to data for Ag^+ which show (i) analogous behavior of silver ion and proton-bound dimers in MS/MS and (ii) that qualitative ordering of silver ion affinities for alcohols is possible and that it yields self-consistent results. The MS/MS spectrum of the symmetrical silver-bound dimer ion of ammonia $[^{107}Ag(NH_3)_2^+]$ shows as the largest peak the loss of ammonia, yielding $AgNH_3^+$. The other major peak (*m/z* 107) corresponds to the loss of both ammonia molecules yielding $^{107}Ag^+$. This spectrum and those of the (dialkylamine)silver complexes, which are analogous, therefore indicates a loosely bound dimer of the general structure $(RH_2N \cdots Ag \cdots NH_2R)^+$. Minor fragmentations are observed for the amine complexes, and they may indicate contributions from covalently bonded structures which involve metal cation insertion.[8]

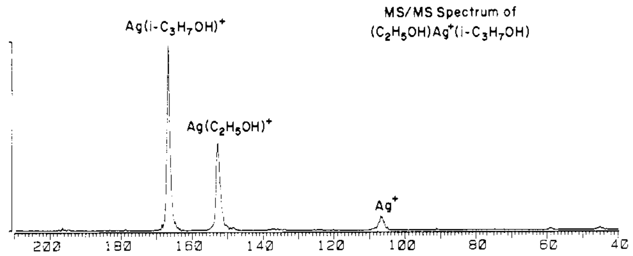

Figure 1. MS/MS spectrum of the silver-bound dimer ion consisting of ethanol and isopropanol as ligands (^{107}Ag selected). Major fragments are observed at *m/z* 167, 153, and 107.

Figure 1 shows a typical spectrum of an unsymmetrical silver-bound dimer ion consisting of ethanol and isopropanol as ligands. The peaks at *m/z* 167 and 153 correspond to the loss of ethanol and isopropanol, respectively. The peak at *m/z* 107 results from the loss of both ligands to yield $^{107}Ag^+$. The relative heights of the two largest peaks in the spectrum indicate that ethanol is more easily lost from the complex and hence has a lower silver cation affinity than isopropanol. The extremely simple kinetics of these systems are noteworthy.[9]

Table I lists abundance ratios for several silver fragment ions generated from alcohol adducts. The values were derived either from a direct comparison between the two alcohols (i.e., where the spectrum of the dimer consisting of the two alcohols was acquired) and/or by one or more indirect comparisons where the peak heights of the alcohols are compared via mutual comparison with a common ligand. For the compounds listed here, the indirect comparisons generally agree with the direct comparisons to within 15%. By comparing peak height ratios in any given column or row, relative silver ion affinities order as $t\text{-}C_4H_9OH > n\text{-}C_4H_9OH > i\text{-}C_3H_7OH > C_2H_5OH > CH_3OH$

Within this series silver cation affinities follow the order $C_4 > C_3 > C_2 > C_1$ with more highly branched alcohols showing a greater silver ion affinity within each group. Although accurate proton affinity values for several of these alcohols have not been obtained via conventional equilibrium measurements, due to competing reactions, similar trends occur except that the proton affinity of *i*-PrOH has been estimated to be larger than that of *n*-BuOH.[10] This work, however, shows that the silver cation affinity of the larger primary alcohol (*n*-BuOH) is greater than that of the smaller secondary alcohol (*i*-PrOH). The causes of such systematic variations in proton and metal ion affinity will likely not be evident until much more data are collected; this communication provides one method for obtaining these data.

The spectrum of the NH_3/H_2O adduct shows loss of H_2O to be five times more favored than loss of ammonia, indicating ammonia to have the higher silver ion affinity. This ratio would be expected to be much higher[7] if the difference in silver ion affinities is of the same magnitude as that of the proton affinitites (~32 kcal/mol[11]). For example, a similar ratio (4.9) is observed

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[5] Laser pulsed at 10 ns, power density ca. 5×10^7 W cm^{-2}, repetition rate 10 Hz, combined amine pressure ca. 0.1 torr. The source and experiment are described fully in: Zakett, D. Ph.D. Thesis, Purdue University, 1981. Compare also: Zakett, D.; Schoen, A. E.; Cooks, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 1295.

[6] Dissociation was by collision on air (10^{-3} torr) at 7 keV; mass analysis by electric sector scan. The MS/MS instrumentation (MIKES) and experimental procedure have been given elsewhere.[4b]

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[8] The behavior of covalently bonded organometallic ions in MS/MS has been reported in: Allision, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998. Compare also: Mueller, J.; Luedemann *Z. Naturforsch. B.* **1981**, *36(B)*, 74.

[9] By contrast, proton-bound dimers of alcohols display elimination of alkene or water as additional channels. See: Bomse, D. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 3292. Similar reactions occurring within the ion source with silver ion containing species are not precluded. However, that loosely bound metal-centered complexes are being sampled in this experiment is critical to this study. This method is not applicable where processes other than ligand loss are dominant.

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for the loss of methanol relative to *n*-propanol from the silver-bound dimer (Table I), but the difference in proton affinities for these two alcohols is only ~7 kcal/mol.[11] Absolute metal ion affinities are, in general, much smaller than the corresponding proton affinities[12,1a] due to a much smaller degree of covalency in the metal cation–ligand bond, particularly for closed-shell cations where electrostatic models have been successful at predicting metal ion affinities.[13,12b] Small metal ion affinity differences between H_2O and NH_3 relative to their proton affinity difference has also been observed for a number of metals.[12c] This has been explained for alkali metals as resulting from a greater transfer of charge from the metal ion to NH_3 than to H_2O.[12c] The tendencies of these bases for electron transfer to a proton are expected to have a more profound influence on their proton affinities,[14] resulting in an enhanced affinity for NH_3 relative to H_2O. The closed-shell silver cation is expected to behave similarly to the alkali metal cations, and these findings support this expectation although the relative degrees of covalent interaction, ionic interaction, and electron transfer cannot be obtained from the data. The difference in the tendency for electron transfer of methanol and *n*-propanol is likely to be much smaller than that of NH_3 and H_2O so that 7 kcal/mol represents an upper limit to the differences in the silver ion affinities of methanol and *n*-propanol, with the actual difference likely to be somewhat less.

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Registry No. CH_3OH, 67-56-1; C_2H_5OH, 64-17-5; *n*-C_3H_7OH, 71-23-8; *i*-C_3H_7OH, 67-63-0; *n*-C_4H_9OH, 71-36-3; *t*-C_4H_9OH, 75-65-0; Ag^+, 14701-21-4.

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MINDO/3-Based Transition-State Models for the Menschutkin Reaction. Iodomethylation of Alkylpyridines

Jimmy W. Viers* and John C. Schug*

Department of Chemistry, Virginia Polytechnic Institute
and State University, Blacksburg, Virginia 24061

Jeffrey I. Seeman*

Philip Morris Research Center
Richmond, Virginia 23261

Received August 21, 1981

The Menschutkin reaction of substituted pyridines has provided an important basis for the assessment of electronic and steric effects in organic chemical reactions.[1,2] A continuing challenge in the study of this important reaction is the elucidation of mechanistic information for systems which incorporate both nonadditive steric effects and subordinate electronic features.[3,4] Table I lists the rate constants for the iodomethylation of pyridines **1**–**21**.[4-6] We have recently shown[4] that the nonadditive part of the iodomethylation rate constants for **2**, **5**–**7**, and **11**–**13** were highly correlated with the molecular position of their 2-alkyl substituent. We now report a theoretical model for correlation of the relative rates of iodomethylation of a series of alkyl-substituted pyridines (**1**–**21**), ranging from the most reactive pyridine (toward iodomethane; 3,4-lutidine) to the least reactive (2,6-diisopropylpyridine) for which kinetic data are currently available. These alkylations, which span four orders of magnitude in rate, are simultaneously controlled by steric and electronic effects. We propose the hypothesis that a set of pyridine iodomethylation rate constants are determined by the relative interactions of CH_3^+–substrate pairs.

We have previously shown[4] that complete geometry optimization using the MINDO/3 program of Rinaldi[7] predicts appropriate trends in bond angles and lengths for pyridine and a series of analogous alkyl-substituted benzene derivatives, including the very sterically hindered *o*-di-*tert*-butylbenzene. The MINDO/3 algorithm has also been successfully used for the determination of the energetics of cations.[8] In addition, we have found that the MINDO/3 optimized geometry of the *N*-methylpyridinium cation compares favorably with the X-ray structure of *N*-methylpyridinium iodide.[9] We have further validated the use of MINDO/3 for these systems by obtaining an excellent correlation between experimental heats of reaction for a number of alkylpyridines and boron trifluoride reported by Brown et al.[10] and the MINDO/3 calculated heats of reaction for the analogous iodomethylation reactions.[11]

To provide a basis for correlating the relative rates, we constructed a model transition state (TS) for each substrate by placing the carbon atom of the CH_3^+ ion at a reasonable TS distance from the nitrogen atom. It is not possible to determine an appropriate $N\cdots CH_3^+$ separation (d_{NC_M}) for the model TS by considering the forward (methylation) reaction since the calculation does not show an activation barrier in the absence of solvent and a leaving group. The activation energy for the demethylation of *N*-methylpyridinium iodide is known[2a] (36.35 kcal/mol^{-1}), and by microscopic reversibility, it can be employed to determine the model TS. Starting from the optimized structure of *N*-methylpyridinium cation, we increased d_{NC_M}, optimizing all other geometric parameters at each separation. The energy difference between equilibrium cation and the model TS equalled 36.35 kcal/mol^{-1} when d_{NC_M} equalled 1.88 Å. This distance was then used for the entire series of alkylpyridines. Previous successful calculations of steric effects on S_N2 reactions showed that complete molecular relaxation was required in order to obtain meaningful changes in activation energies.[12] We therefore minimized the energy of the supermolecule with respect to *all* geometric parameters except the 1.88-Å $N\cdots CH_3$ distance.

For each compound, we calculated an energy difference ΔE between the completely optimized CH_3^+–substrate system and

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