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Parallels in the Formation of Transition Metal-Amide Bonds in Solution and in the Gas Phase: An Ion Cyclotron Resonance Study of Cobalt Ion Chemistry with Amines

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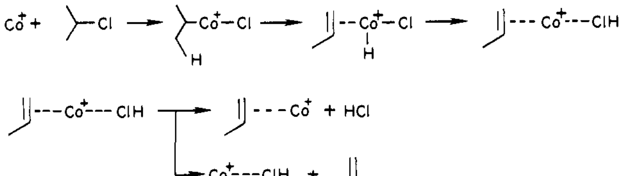
Abstract: A mechanistic study of the gas-phase ion-molecule reactions of ions of the type $Co(CO)_x^+$ (x = 0-2) and $CoNO(CO)_x^+$ (x = 0-3) with a number of primary, secondary, and tertiary amines is presented. Primary amines exhibit a chemistry with gaseous metal ions which parallels that observed for alkanes, rather than that observed for other polar compounds. This could be largely due to a weak Co^+-NH_2 bond which prohibits insertion of Co^+ into the polar C-N bond. Reactions of secondary and tertiary amines were used to elucidate the mechanisms of primary amines. Reactions occur in which intermediates involving secondary and tertiary amides are preferred over those involving primary amides. This behavior parallels the observed behavior of transition-metal amides in solution.

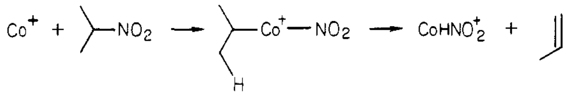
In the past 10 years, the area of gas-phase organometallic chemistry has been developed by a small number of research groups.[1] With use of ion cyclotron resonance (ICR) spectrometry, atomic ion-beam techniques and other mass spectrometric methods, the low pressure ion-molecule reactions of a variety of metal and metal-containing ions with a plethora of organic molecules have been characterized. Most of the metal centers studied to date have been first-row transition metals. Most of the organic molecules studied to date have been monofunctional species and alkanes. Early work in this area was done by using electron impact on volatile metal carbonyls to generate M^+ and $M(CO)_x^+$ ions whose chemistry with organic molecules was studied.[2] In most experiments of this type, the metal ions bound to one or more CO groups exhibited very simple chemistries, reacting almost exclusively by ligand substitution, and were considered to be an unnecessary complication. Hence, a variety of atomic ion sources were developed[3,4] and, recently, much emphasis has been placed on the characterization of the gas-phase chemistry of the "bare" +1 metal ions.

Essentially all saturated polar organic compounds that have been studied to date react with transition-metal centers such as Co^+ in the gas phase. The reaction frequently used to demonstrate a dominant mechanism in such gas-phase processes is the reaction of a transition-metal ion with isopropyl chloride.[5]

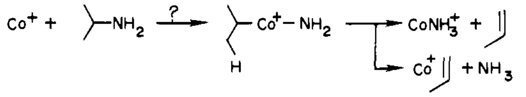


The mechanism shown above involves a metal insertion into the polar bond (here C-Cl) followed by a β-H shift.[6] Thus, the metal ion reacts with isopropyl chloride to form HCl and propene. These compounds then compete as ligands on the metal. Similarly, H_2O elimination is induced in alcohols via a mechanism involving insertion of the metal ion into a C-OH bond.[5]

We have been investigating the chemistry of metal ions with organic compounds containing C-N bonds. Nitroalkanes react with metal ions and exhibit products indicative of the mechanism described above, i.e., Co^+ appears to insert into the C-N bond of 2-nitropropane.[7]



Amines were expected to undergo similar reactions with metal ions. For example, the trend established from the reactions mentioned above suggests the following products in the reaction of Co^+ with isopropylamine:



However, products indicative of Co^+ insertion into the C-N bond of primary amines are *not* observed. Instead, cobalt ions react with primary amines to induce the elimination of H_2, small alkanes, and small alkenes. Such processes are also observed in the chemistry of Co^+ with alkanes.[4]

The reactions observed for amines were not completely unexpected. Müller studied the chemistry of metal-containing ions such as $C_6H_6V^+$ and $C_5H_5NiNO^+$ with diethylamine and dimethylamine and reported reaction products corresponding to the elimination of one or more molecules of hydrogen and the elimination of small hydrocarbons.[8,9]

In this work, the chemistry of the $Co(CO)_x^+$ (x = 0-2) and $Co(CO)_xNO^+$ (x = 0-3) ions formed by electron impact on $Co(CO)_3NO$ with primary, secondary, and tertiary amines is discussed. The failure to observe products resulting from Co^+ insertion into the $R-NH_2$ bond of primary amines will be discussed in light of the "elusive" nature of transition metal-NH_2 bonds in condensed phases.

The earliest examples of metal-amide bonds (early 1800's) involved the reaction of alkali metals with ammonia, e.g.[10]

$$Na + NH_3 \rightarrow NaNH_2 + {}^1/{}_2H_2$$

Transition-metal amides were not reported until the late 1950's. Work since then has largely been devoted to the amides of boron, silicon, and phosphorous.[10]

Transition-metal (covalent) primary amides ($M-NH_2$) are exceedingly rare; secondary amides (M-NHR) are moderately

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(1) Publications representative of the groups active in this area include the following: (a) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1736. (b) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Anal. Chem.* **1980**, *52*, 164. (c) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 1332. (d) Uppal, J. S.; Staley, R. H. *Ibid.* **1980**, *102*, 3794.

(2) Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 4924.

(3) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360.

(4) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784.

(5) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998.

(6) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1976**, *98*, 7445.

(7) McElvany, S. W.; Allison, J., unpublished results.

(8) Müller, J.; Goll, W. *Chem. Ber.* **1973**, *106*, 1129.

(9) Müller, J.; Holzinger, W.; Kalbfus, W. *J. Organomet. Chem.* **1975**, *97*, 213.

(10) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. "Metal and Metalloid Amides"; Ellis Horwood Limited: West Sussex, England, 1980.

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rare.[10] In condensed phases, tertiary amides of cobalt are by far the most common.[10] The increasing stability of amides with increasing N-alkyl substitution is not well understood. Apparently, unless there is some steric hindrance (contributing a "kinetic stabilization"), primary and secondary amides condense with loss of NH_3 or NH_2R to give species such as[10]

Also, certain metal amides may be difficult to isolate due to their ability to undergo reactions such as "β decompositions" to form species containing M–H bonds similar to those occurring for metal alkyls.[10]

Transition metal–tertiary amide bonds generally are considered to be moderately strong:[10]

$$\text{M–R} < \text{M–NRR}' < \text{MOR} < \text{MF}$$

Since this study utilizes gaseous Co^+, it is of interest to note that in solution amines are more likely to react to form amides when the central metal atom is in a low oxidation state.[10]

The results of this work will be discussed in light of these two condensed-phase observations: (1) covalent $M{-}NH_2$ bonds are not observed for transition metals; (2) N-alkyl substitution increases the stability of the metal–amide bond.

Experimental Section

All experiments were performed on an ion cyclotron resonance spectrometer of conventional design that was built at Michigan State University. The three-section ICR cell is 0.88 in. × 0.88 in. × 6.25 in. The source region is 2.00 in. long, the analyzer region is 3.75 in. long, and the collector is 0.50 in. long. Ions are formed in the source by electron impact with 70-eV electrons. The electron filament is emission regulated. The filament controller and plate voltage controller for the ICR cell were designed and constructed at MSU. The instrument is operable in the pulsed or drift ICR modes. Data in this paper were obtained under normal drift-mode conditions by using trapping voltage modulation and phase-sensitive detection. The marginal oscillator detector is based on the design of Warnick, Anders, and Sharp.[11] Ion cyclotron double resonance experiments[12] were performed to identify precursors of ion-molecule reaction products with use of a Wavetek Model 144 sweep generator as the secondary oscillator. The ICR cell is housed in a stainless steel vacuum system and is situated between the polecaps of a Varian 12 in. electromagnet (1.5-in. gap). The electromagnet is controlled by a Varian V-7800, 13 kW power supply and a Fieldial Mark I Magnetic Field Regulator.

The instrument is pumped by a 4-in. diffusion pump with a liquid nitrogen cold trap and an Ultek 20 L/s ion pump. Samples are admitted from a dual inlet (individually pumped by a 2-in. diffusion pump and liquid nitrogen cold trap) by Varian 951-5106 precision leak valves. Approximate pressures are measured with a Veeco RG 1000 ionization gauge.

Tricarbonylnitrosylcobalt(0) was obtained from Alfa Inorganics. Piperidine, pyrrolidine, tetrahydrofuran, diethyl ether, and isobutyl-, *n*-butyl-, *tert*-butyl-, diethyl-, and triethylamines were obtained from Chem-Service, Inc. Isopropyl- and ethylamines were obtained from the Eastman Kodak Co. The *n*-propylamine was obtained from Aldrich Chemical Co. Methylamine was purchased from Matheson Gas Co. Ethylamine-d_2 and tetrahydrofuran-d_8 were obtained from Norell Chemical Co, Inc. Ethylbutylamine was purchased from the Fluka Chemical Corp. All samples were degassed by multiple freeze–pump–thaw cycles and were used without further purification.

Data were acquired in the following manner. High- and low-pressure (1×10^{-5} torr vs. 1×10^{-6} torr) spectra of each compound were taken, and ion–molecule reaction products in the "amine alone" were determined. (The ion–molecule reaction products following electron impact on $Co(CO)_3NO$ have already been determined.[13]) Reported data are results of double resonance analysis of all product ions formed in 1:1 or 1:2 mixtures (by pressure) of $Co(CO)_3NO$ to amine, at a total pressure of 1×10^{-5} torr. Spectra were always taken to masses greater than 274 u, since the sum of the mass of $Co(CO)_3NO$ (173 u) plus the largest amine ($C_6H_{15}N$, 101 u) equals 274.

Results

The observed reactions for cobalt-containing ions with eight neutral primary amines are given in Table I, with branching ratios. With any organic compounds, a number of alkyl ions are formed which react with neutral $Co(CO)_3NO$. These reactions have been reported previously[5] (e.g., $C_3H_7^+$ reacts to eliminate CO from $Co(CO)_3NO$) and will not be reported here. A number of successive reactions of the *products* in Table I were observed, which were exclusively ligand-substitution processes. The reaction

$$\text{CoCO(amine)}^+ + \text{amine} \rightarrow \text{Co(amine)}_2^+ + \text{CO}$$

was observed for methylamine, ethylamine, and *n*-butylamine under the conditions of our experiments. A similar reaction

$$\text{Co(CO)NO(amine)}^+ + \text{amine} \rightarrow \text{CoNO(amine)}_2^+ + \text{CO}$$

was observed for methylamine and ethylamine.

Products formed in Table I also can react with $Co(CO)_3NO$. The reaction

$$\text{Co(amine)}^+ + \text{Co(CO)}_3\text{NO} \rightarrow \text{CoCO(amine)}^+ + \text{Co(CO)}_2\text{NO}$$

was observed in mixtures containing methylamine, ethylamine, isobutylamine, and *tert*-butylamine.

Branching ratios are assumed to be accurate within ±10%. Reported reactions are facile and occur within an order of magnitude of the collision frequency ($k \approx 1{-}10 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). An approximate lower limit for the rate constant for processes not observed is 5×10^{-11} cm^3 molecule $^{-1}$ s^{-1}.

Table II reports the reactions observed for the metal ions derived from $Co(CO)_3NO$ with diethylamine, diethyl ether, pyrrolidine, tetrahydrofuran, piperidine, ethylbutylamine, and triethylamine, in terms of the neutrals eliminated in each process. Branching ratios are included.

Labeled tetrahydrofuran was used to unambiguously identify the products since in the reactions of unlabeled tetrahydrofuran, loss of $\{H_2O + CO\}$ could not be distinguished from loss of C_2H_6O (C_2H_4 and CO both correspond to 28 u).

When working with metal carbonyls in such experiments, one must be cautious in interpreting results and suggesting product composition due to the possible C_2H_4/CO mass ambiguity. Following careful analysis of all precursors of each product, and by comparing products of similar compounds, the processes reported in Tables I and II represent a self-consistent set.

Experiments using labeled ethylamine confirmed several reactions observed in unlabeled ethylamine that are central to the interpretation of the data presented here.

$$\text{Co}^+ + \text{C}_2\text{H}_5\text{ND}_2 \rightarrow \text{Co(C}_2\text{H}_4\text{DN)}^+ + \text{HD}$$

$$\text{CoCO}^+ + \text{C}_2\text{H}_5\text{ND}_2 \rightarrow \text{CoC}_2\text{H}_5\text{ND}_2^+ + \text{CO}$$

$$\text{CoC}_2\text{H}_5\text{ND}_2^+ + \text{C}_2\text{H}_5\text{ND}_2 \rightarrow \text{Co(ND}_2\text{H)(C}_2\text{H}_5\text{ND}_2)^+ + \text{C}_2\text{H}_4$$

These results will be discussed below.

Discussion

The discussion will consist of four parts. Part A will discuss the formation of CoH as a neutral product and will present evidence indicating that metal-induced H_2 elimination from amines occurs with Co^+ insertion into an N–H bond as a first step. With this established, part B will discuss intermediates involving metal–amide bonds. It will approach the question "Why does Co^+ not insert into the $R{-}NH_2$bond"? Part C will be devoted to the reaction mechanisms for the observed processes involving primary amines in light of the principles established in part B. Part D will compare and contrast the reactions of cobalt and cobalt-containing ions with secondary amines and analogous oxygen-containing compounds (ethers).

(A) Reactions That Proceed via Intermediates Containing M–H Bonds. The data in Tables I and II suggest that attack of both the N–H and the α-C–H bonds by Co^+ occurs. Attack of the α-C–H leads to the loss of CoH neutral (forming the (amine–H)$^+$

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[11] Warnick, A.; Anders, L. R.; Sharp, T. E. *Rev. Sci. Instrum.* **1974**, *45*, 929.

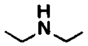
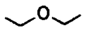
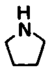
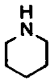
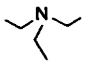
[12] Beauchamp, J. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 527.

[13] Weddle, G. H.; Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1977**, *99*, 105.

Table I. Summary of Reactions Observed for Primary Amines with Co^+-Containing Ions (Reactions Proceed via Indicated *Neutral Losses*)

	neutral reactant, $C_nH_{2n+2}NH_2$							
	n = 1	*n* = 2	*n* = 3		*n* = 4			
reactant ion	CH_3NH_2	$CH_3CH_2NH_2$	*n*-$C_3H_7NH_2$	*i*-$C_3H_7NH_2$	*n*-$C_4H_9NH_2$	*i*-$C_4H_9NH_2$	*sec*-$C_4H_9NH_2$	*t*-$C_4H_9NH_2$
Co^+	H_2 (0.47) CoH (0.53)	H_2 (0.15) CH_4 (0.26) CoH (0.59)	H_2 (0.09) $2H_2$ (0.09) C_2H_4 (0.40) CoH (0.42)	H_2 (0.52) CH_4 (0.24) CoH (0.24)	H_2 (0.15) $2H_2$ (0.04) CH_4 (0.04) C_2H_4 (0.14) C_2H_6 (0.12) C_3H_6 (0.08) C_3H_8 (0.14) CoH (0.20)	H_2 (0.09) $2H_2$ (0.04) CH_4 (0.17) $H_2 + CH_4$ (0.11) C_3H_6 (0.29) CoH (0.30)	H_2 (0.07) $2H_2$ (0.17) C_2H_4 (0.10) C_2H_6 (0.17) C_3H_6 (0.21) CoH (0.28)	CH_4 (1.0)
$CoCO^+$	CO (1.0)	H_2 (0.03) $H_2 + CO$ (0.11) CH_4 (0.06) CH_2CO (0.16) CO (0.65)	$H_2 + CO$ (0.06) $2H_2 + CO$ (0.04) $C_2H_4 + CO$ (0.49) CO (0.41)	$H_2 + CO$ (0.33) $CH_4 + CO$ (0.25) CO (0.42)	$H_2 + CO$ (0.50) $2H_2 + CO$ (0.12) $CH_4 + CO$ (0.08) $C_2H_4 + CO$ (0.16) $C_3H_6 + CO$ (0.04) CO (0.10)	H_2 (0.04) $H_2 + CO$ (0.23) CH_4 (0.05) $CH_4 + CO$ (0.27) $C_3H_6 + CO$ (0.17) CO (0.14)	H_2 (0.01) $H_2 + CO$ (0.32) $C_2H_4 + CO$ (0.20) $C_2H_6 + CO$ (0.20) CO (0.22) CoH (0.05)	$CH_4 + CO$ (0.48) CO (0.52)
$Co(CO)_2^+$	CO (0.51) 2CO (0.49)	CO (0.51) 2CO (0.49)	CO (0.39) 2CO (0.61)	$H_2 + 2CO$ (0.31) CO (0.41) 2CO (0.28)	CO (0.48) 2CO (0.52)	CO (0.38) 2CO (0.62)	CO (0.55) 2CO (0.45)	CO (0.34) 2CO (0.66)
	Substitution Reactions: $Co(CO)_xNO^+ + A \rightarrow Co(CO)_{x-a}NO(A)^+ + aCO$							
$CoCONO^+$	*a* = 1	*a* = 1	*a* = 1	*a* = 1	*a* = 1	*a* = 1	*a* = 1	*a* = 1
$Co(CO)_2NO^+$	*a* = 2	*a* = 1, 2	*a* = 2	*a* = 2	*a* = 2	*a* = 2	*a* = 2	*a* = 2
$Co(CO)_3NO^+$	*a* = 2	*a* = 2, 3	*a* = 3	*a* = 3	*a* = 2, 3	*a* = 2, 3	*a* = 2, 3	*a* = 2, 3

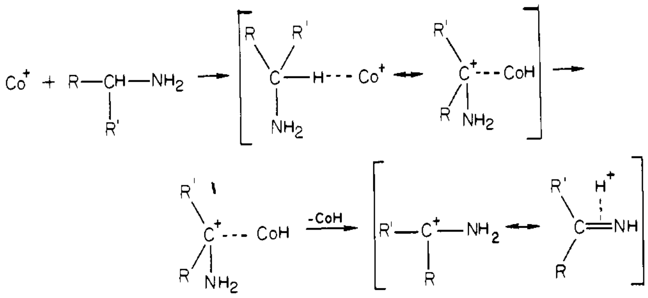
Table II. Reactions Observed for Secondary Amines, Tertiary Amines, and Analogous Ethers (Reactions Proceed via Indicated *Neutral Losses*)

	reactant neutral						
reactant ion							
Co^+	CoH (1.0)	C_2H_4 (0.30) C_2H_6 (0.01) C_2H_6O (0.45) CoH (0.24)	CoH (1.0)	H_2O (0.26) CH_2O (0.38) CoH (0.36)	$2H_2$ (0.11) CoH (0.89)	H_2 (0.10) C_2H_4 (0.08) C_2H_6 (0.18) C_3H_8 (0.19) CoH (0.45)	C_2H_4 (0.08) C_2H_6 (0.06) CoH (0.86)
$CoCO^+$	H_2 (0.14) $H_2 + CO$ (0.48) CO (0.38)	$C_2H_4 + CO$ (0.07) CO (0.93)	H_2 (0.52) CO (0.47)	$H_2O + CO$ (0.17) $CH_2O + CO$ (0.05) CO (0.78)	H_2 (0.11) $2H_2$ (0.03) $H_2 + CO$ (0.53) $2H_2 + CO$ (0.07) CO (0.26)	$H_2 + CO$ (0.65) $C_2H_4 + CO$ (0.18) CO (0.17)	$\left.\begin{matrix} C_2H_6 \\ CO + H_2 \end{matrix}\right\}$ (0.12) $C_2H_6 + CO$ (0.05) CO (0.06) CoH (0.77)
$CO(CO)_2^+$	CO (0.73) 2CO (0.27)	CO (1.0)	CO (0.48) 2CO (0.52)	CO (0.93) 2CO (0.07)	CO (0.61) 2CO (0.39)	CO (0.71) 2CO (0.29)	CO (0.48) 2CO (0.52)
	Substitution Reactions: $Co(CO)_xNO^+ + A \rightarrow Co(CO)_{x-a}NO(A)^+ + aCO$						
$CoCONO^+$	*a* = 1	*a* = 1	*a* = 1	*a* = 1	*a* = 1	*a* = 1	*a* = 1
$Co(CO)_2NO^+$	*a* = 2	*a* = 2	*a* = 2	*a* = 2	*a* = 2	*a* = 2	*a* = 2
$Co(CO)_3NO^+$	*a* = 3, 2	*a* = 2	*a* = 3, 2	*a* = 2	*a* = 2	*a* = 2, 3	N.R.[a]

[a] N.R. = no reaction observed.

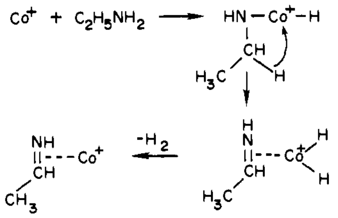
ion), while attack of the N–H bond apparently leads to H_2 elimination.

First consider the formation of CoH. Co^+ reacts with all of the compounds in Tables I and II (except *tert*-butylamine) to form CoH. Since this process occurs in the case of triethylamine (which contains no amine–hydrogen atom) and methylamine (which contains only an α-C–H bond), but not for *tert*-butylamine (which has no α-hydrogen atom), it is reasonable to assume that this reaction is predominately an α-hydride abstraction.



It is difficult to make thermodynamic conclusions based on this reaction type, since accurate thermodynamic data on the possible (amine–H)$^+$ ions are not available. Also, a number of bond strengths for Co–H have been proposed ranging from 40 to 70 kcal/mol, with no apparent consensus to date.[14] The driving force for the reaction may be the stability of the product ion, possibly a protonated amide.[15] Note also that *insertion* into the α-C–H bond is not *necessary* for hydride abstraction.

Table I shows that all of the primary amines studied (except *tert*-butylamine) react with Co^+ by elimination of H_2. In three cases two molecules of H_2 are eliminated. Very similar results, both in product type and distribution, are observed in the chemistry of Co^+ with alkanes.[4] For small amines, H_2 elimination is the predominant reaction mechanism. This work implies that H_2 elimination occurs following Co^+ insertion into the N–H bond. Using ethylamine as an example,



This mechanism and final product structure is suggested (and others refuted) by the following observations:

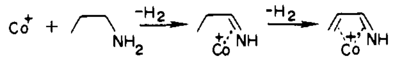
(1) H_2 elimination occurs in the reaction of Co^+ and methylamine in which only a C=N double bond can be formed.

(2) H_2 elimination is *not* observed for *tert*-butylamine. The proposed mechanism predicts this negative result since, following Co^+ insertion into the N–H bond, no β-H atom is available.

(3) Table II shows that H_2-elimination reactions occur for all secondary amines (which contain an N–H bond) but do not occur for triethylamine. *If* the elimination of H_2 occurs with insertion into the α-C–H bond as a first step, H_2 elimination (forming a C=C double bond) would be expected for triethylamine. Since this is not observed, this suggests that insertion into the N–H bond leads to H_2 elimination.

(4) Labeling experiments with $C_2H_5ND_2$ are consistent with the proposed mechanism. HD elimination predominates. Thus H_2 elimination from an amine produces an imine as opposed to other possible structures such as an ene-amine.

When the skeletal chain of the reacting amine consists of four or more atoms, elimination of 2 molecules of H_2 is observed. This results in a butadiene-like complex



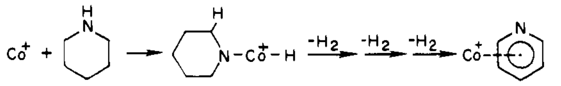
Similar products have been observed when Co^+ reacts with comparable neutral molecules. For example, it has been suggested that butane[4] and butene[16] react with transition-metal ions to form structure I, ketones[3] form structure II, diols[17] and ethers[18] form structure III.

(I)

(II)

(III)

In the case of piperidine, up to three molecules of hydrogen can be eliminated to form a metal–pyridine complex:



Thus we are confident that small amines react to a large extent through intermediates of the type $RNH\text{–}Co^+\text{–}H$, which leads to H_2 elimination.

(B) The Formation of Intermediates Involving Metal–Amide Bonds. Consider the following reactions:

$$Co^+ + C_2H_5NH_2 \rightarrow Co(C_2H_5N)^+ + H_2 \quad (1)$$

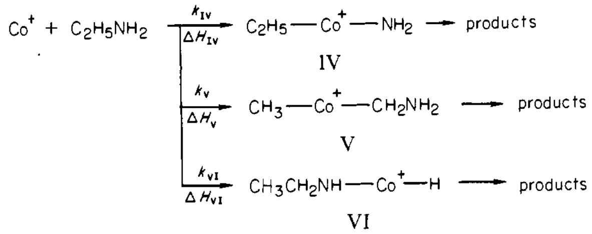
$$ \rightarrow Co(CH_3N)^+ + CH_4 \quad (2)$$

$$Co^+ + (C_2H_5)_3N \rightarrow Co(C_4H_{11}N)^+ + C_2H_4 \quad (3)$$

$$ \rightarrow Co(C_4H_9N)^+ + C_2H_6 \quad (4)$$

The reactions of ethylamine are typical of the primary and secondary amines. Products resulting from Co^+ insertion into N–H bonds (eq 1) and into C–C bonds (eq 2) are observed. No reactions appear to occur via initial insertion into the C–N bond. In contrast to this, triethylamine *does* form products indicative of Co^+ insertion into the C–N bond, eq 3 and 4.

With use of ethylamine as an example, the following scheme is proposed to explain the chemistry of Co^+ with amines.



We propose the following: (1) $k_{IV} < k_V$, k_{VI}; (2) $\Delta H_{IV} > \Delta H_V$, ΔH_{VI}; (3) as the extent of N-alkyl substitution increases, k_{IV} increases; and (4) $D(Co^+ - NH_2) < D(Co^+ - NHR) < D(Co^+ - NR_2)$. Intermediates IV and VI involve the formation of Co^+–N bonds. The structure of IV is a primary amide and VI is a secondary amide. Products formed through intermediate IV are not observed for primary amines whereas products formed through intermediates V and VI are observed. This suggests that k_{IV} is smaller than k_V and k_{VI}. Apparently, just as in solution the formation of secondary amides appears to be preferred over formation of primary amides. In the case of triethylamine, Co^+ insertion into the C–N occurs through a tertiary amide intermediate:

$$Co^+ + (C_2H_5)_3N \rightarrow C_2H_5\text{—}Co^+\text{—}N(C_2H_5)_2 \rightarrow \text{products}$$

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[14] See, for example: Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1736. Connor, J. A. In "Topics in Current Chemistry. No. 71. Inorganic Chemistry/Metal Carbonyl Chemistry"; Boschke, F. L., Ed.; Springer-Verlag: New York, 1977.

[15] Consider CH_3NH_2. While the exact structure of the hydride abstraction product ion, CH_4N^+, is not known, a protonated amide would represent a stable product. Available thermochemical data suggest that CH_4N^+ is a highly stable ion.[19]

[16] Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6624.

[17] Huang, S. K.; Allison, J., unpublished results.

[18] Huang, S. K.; Allison, J., *Organometallics* **1983**, *2*, 883.

Products from this intermediate are observed.

Why is k_{IV} slow, i.e., why does Co^+ not insert into the C–N bond of primary and secondary amines competitive with other insertion processes? The *overall* reaction

$$Co^+ + C_2H_5NH_2 \rightarrow CoC_2H_4^+ + NH_3 \qquad (5)$$

is exothermic. The reaction

$$Co^+ + C_2H_5I \rightarrow CoC_2H_4^+ + HI \qquad (6)$$

occurs at thermal energies[5] and gives an upper limit on the heat of formation of the ionic product, $\Delta H_f(CoC_2H_4^+) < 275$ kcal/mol.[19] *Less* energy is required to form ethylene from ethylamine than from ethyl iodide, and available thermodynamic data indicate that reaction 5 should be at least 8 kcal/mol *more* exothermic than (6).[19]

In terms of the Arrhenius form of rate constants, $k(T) = A \exp(-E_a/RT)$, a slow rate can have a geometric or energetic basis. since analogous reactions of metal ions with saturated polar organic compounds are facile *and* because Co^+ readily inserts into the C–N bond of tertiary amines, it seems unlikely that k_{IV} is small as a result of a constraint on the encounter geometry (i.e., the preexponential factor). If the *overall* reaction is exothermic, there may be an activation energy barrier to products indicative of this insertion. This barrier may be the formation of intermediate IV. (A large *entropic* barrier is unlikely since there seems to be no such barrier for other insertion processes.)

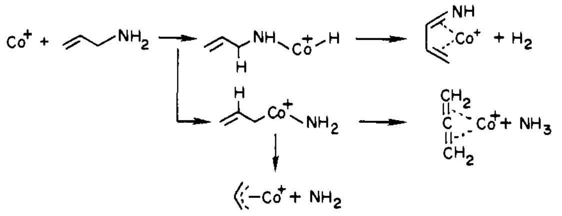
In the insertion process

$$M^+ + AB \rightarrow (AMB)^+$$

the sum of the strengths of the two bonds formed, (M^+–A) and (M^+–B) (or more accurately, (M^+–A) and (AM^+–B)), must be greater than the strength of the A–B bond which is broken for the process to be exothermic.

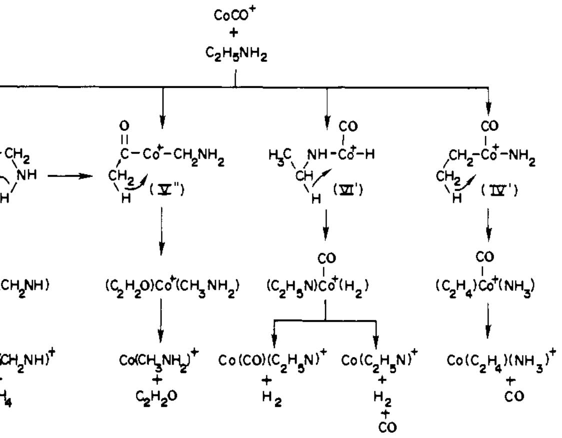
Consider the reaction of Co^+ with CH_3NH_2. Less energy is required to break the C–N bond (79.7 kcal/mol) than the N–H bond (94.6 kcal/mol).[19] If Co^+ did insert into the C–N bond, the Co^+–CH_3 bond which is formed has a bond strength of 61 kcal/mol.[20] If the insertion does not occur, it may be inferred that $D(Co^+ - NH_2)$ must be less than 18.7 kcal/mol (this assumes that $D(Co^+ - CH_3) \approx D(NH_2Co^+ - CH_3)$ and $D(Co^+ - NH_2) \approx D(CH_3Co^+ - NH_2)$). The Co^+ ion does apparently insert into the *stronger* N–H bond. Making similar assumptions and using $D(Co^+ - H) = 52$ kcal/mol,[20] insertion implies $D(Co^+ - NHCH_3) > 42.6$ kcal/mol.

There *is* a primary amine in which Co^+ insertion into the C–N bond is observed. The following reactions occur for Co^+ and allylamine:[21]



Since the Co^+–allyl bond *alone* is stronger than the C–N bond in allylamine,[21] insertion could occur even if the Co^+–NH_2 bond is very weak. A Co^+–NH_2 bond strength of less than 19 kcal/mol is *unusually* weak, but may correlate with the elusive nature of primary metal amides in condensed phases.

Scheme I



It is also interesting to note that in the series $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$, the strength of the C–N bond increases from 77 to 89 kcal/mol.[19] Despite this, Co^+ inserts into the C–N bond of triethylamine. This may be interpreted as an indication of an increasing metal–amide bond strength as the extent of N-alkyl substitution increases. With use of the same assumptions above, an *approximate lower bound* on the Co^+–$N(C_2H_5)_2$ bond strength can be given as 59 kcal/mol. (Thus, the solution observation that $D(M - R) < D(M - NRR')$ may also be true in the gas phase.)

A very interesting series of reactions is observed in studies involving ethylamine (and confirmed in labeling experiments):

$$CoCO^+ + C_2H_5NH_2 \rightarrow Co(C_2H_7N)^+ + CO \qquad (7)$$

$$Co(C_2H_7N)^+ + C_2H_5NH_2 \rightarrow Co(NH_3)(C_2H_5NH_2)^+ + C_2H_4 \qquad (8)$$

By what is formally considered to be the ligand-substitution process, a complex between Co^+ and ethylamine is formed in reaction 7. The further reactions of a product ion have been useful in gaining insights into its structure.[5] The further reaction of the product in (7), reaction 8, implies that the product of (7) exists as:

$$\underset{\text{VII}}{(C_2H_4)Co^+(NH_3)}$$

Structure VII would be formed via an intermediate such as IV, which apparently *is not* formed when Co^+ reacts with ethylamine. Here, however, the reactant is $CoCO^+$. This seemingly contradictory set of reactions can be understood by considering the complete set of processes which occur between $CoCO^+$ and $C_2H_5NH_2$. These are shown in Scheme I (omitting, for simplicity, hydride abstraction).

Assume that all four intermediates shown in Scheme I are formed (this assumption will be justified). A variety of groups are attached to Co^+ before the dissociation to final products occurs. Previous work indicates that the bond strength between Co^+ and a variety of ligands takes the following order:[13,22]

$$NH_3 > C_2H_4 > CO > H_2, CH_4$$

Thus, in each reaction sequence in Scheme I, the more weakly bound ligands are lost to form the final products. The product formed via intermediate IV′ contains two strongly bound ligands, NH_3 and C_2H_4, which are retained, while CO is lost. Thus the $Co^+(C_2H_7N)$ ion formed has the structure $Co(C_2H_4)(NH_3)^+$. Other possible structures for $Co^+(C_2H_7N)$ such as $Co^+(C_2H_5N)(H_2)$ and $Co^+(CH_3N)(CH_4)$ would not be expected since the intermediates through which they would be formed would lose H_2 or CH_4 rather than retain these electron-poor ligands.

Thus, $CoCO^+$ reacts with ethylamine to form $Co(C_2H_4)(NH_3)^+$ which reacts further in (8) by a simple ligand substitution in which

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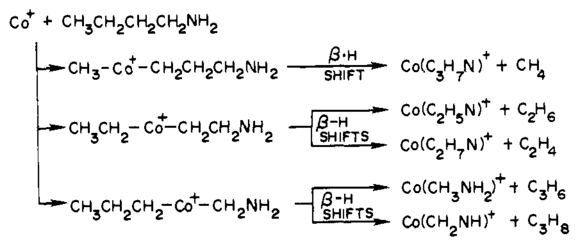
[19] Bond strengths and other thermodynamic values calculated by using the data from Franklin et al. and Rosenstock et al.: Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Herron, J. T.; Draxl, K. *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.* **1969**, 26. Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, 6. In cases where conflicting thermodynamic data have appeared in the literature, the authors have had to decide which values are most valid.

[20] Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6501.

[21] Lombarski, M.; Allison, J. *Int. J. Mass. Spectrom. Ion Phys.* **1983**, *49*, 281.

[22] Lombarski, M.; Tsarbopoulos, A.; Allison, J., unpublished results.

Scheme II



a second molecule of ethylamine displaces the more weakly bound C_2H_4 from the metal center.

The question that remains to be answered is, why would $CoCO^+$ form an intermediate such as IV′ in Scheme I (i.e., insert into the C–NH_2 bond) when Co^+ does not? We propose that the bonds formed in IV′ are stronger than those in IV, i.e., $CoCO^+$ forms stronger bonds to –C_2H_5 and/or –NH_2 than does Co^+. This concept is proposed on the basis of two observations:

(1) This is true for the bond between a metal and CO. $D(MCO^+ - CO) > D(M^+ - CO)$ for similar first-row transition-metal ions where M = Fe, Ni, and Cr and for M = W.[19]

(2) Comparison of the chemistry of Co^+ and $CoCO^+$ with primary and secondary amines supports this concept. Co^+ reacts with primary amines by elimination of H_2 via insertion into N–H. As we move from ethylamine to diethylamine the N–H bond being attacked becomes stronger by 15 kcal/mol.[19] No reaction is observed for Co^+ with diethylamine (except hydride abstraction); however, H_2 elimination occurs when $CoCO^+$ reacts with diethylamine. This suggests that higher energy intermediates can be formed with $CoCO^+$ than with Co^+.

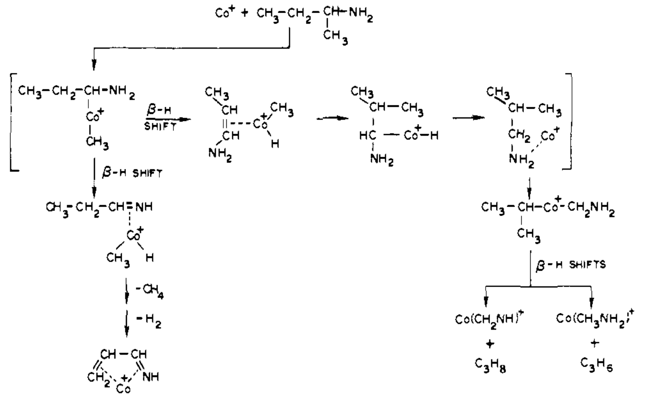
Thus, the sum of the bonds formed in IV′ is larger than the C–N bond strength in ethylamine, and the insertion becomes energetically accessible. This also supports the general concept of the thermodynamic inaccessibility of intermediate IV.

Obviously, until the RCo^+–NH_2 bond strengths are accurately determined, a precise evaluation of the thermodynamic influence on insertion into such C–N bonds by Co^+ cannot be made. Nonetheless, these experiments certainly indicate that the Co^+–NH_2 bond may be very weak, and $D(Co^+ - NR_2)$ is largely dependent on the extent of N-alkyl substitution.

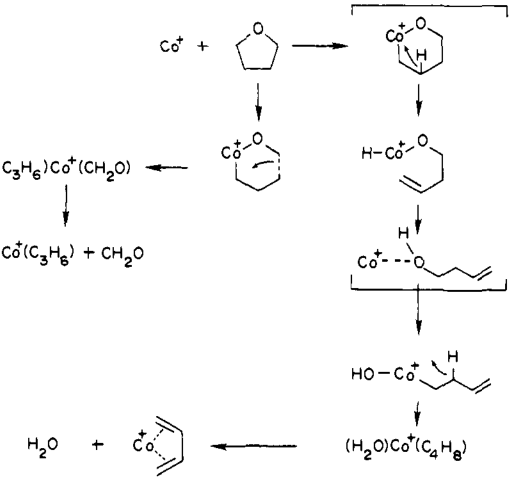
(C) Reaction Mechanisms—Primary Amines. In addition to molecular hydrogen elimination reactions, primary amines react with Co^+ by eliminating small alkanes and alkenes. These reactions presumably proceed through initial metal insertions into C–C bonds and strongly parallel the reactions observed for alkanes of similar skeletal structures.[4] In the eight primary amines studied, all of the skeletal bond strengths (C–C and C–N) are within ±4 kcal/mol of each other.[19] If we assume that the Co^+–CH_3 bond strength[20] is typical of a Co^+–alkyl bond, insertion into *every* C–C bond of each compound is energetically accessible, and products following all possible insertions of this type are observed. For example, most of the primary amines react with Co^+ to form $Co(CH_3NH_2)^+$. The implied mechanism is shown in Scheme II for *n*-butylamine. Also shown in Scheme II are the other processes which follow Co^+ insertion into C–C bonds. Note that β-H's can shift from either a carbon or nitrogen which is β to the metal following insertion.

sec-Butylamine is unique because it reacts with Co^+ by the elimination of both CH_4 *and* H_2 and also reacts to form $Co(CH_3NH_2)^+$, which would *not* be predicted. Loss of CH_4 and H_2 is reasonable and occurs following the sequence shown in Scheme III. Also shown is a proposed pathway leading to the formation of $Co(CH_3NH_2)^+$ in which Co^+ induces the isomerization of *sec*-butylamine to isobutylamine as a first step. Similar isomerization steps have been reported previously.[23]

Scheme III



Scheme IV



Also reported in this study are the reactions observed for the $Co(CO)_x^+$ and $Co(CO)_xNO^+$ ions with amines. As the number of CO's present on the metal center increases, the observed chemistry with monofunctional compounds follows (almost exclusively) simple ligand substitutions, in which one or more CO's are displaced by an organic molecule.[5] $CoCO^+$ and, to a lesser extent, $Co(CO)_2^+$ react by both ligand substitution and reactions which parallel those observed for the bare metal ion. One unique reaction occurs for ethylamine. The mixture of $Co(CO)_3NO$ and ethylamine, when subject to electron impact, produces $Co(CH_3NH_2)^+$. This product would not be expected in the reaction of Co^+ with ethylamine because insertion of Co^+ into the C–C bond to form this product would result in the elimination of CH_2, which would require an amount of energy not normally available in such reactions. Ion cyclotron double resonance indicates that Co^+ was not the precursor of $Co(CH_3NH_2)^+$, rather $CoCO^+$ was. We believe this to be an example of active participation of the CO ligand in the reaction, as is indicated in Scheme I (intermediate V′). With "CoCO" insertion into the C–C bond, a β-H atom becomes available to shift, with elimination of CH_2CO, a relatively low-energy neutral molecule. Thus, one advantage of working with metal carbonyls in such experiments is to occasionally observe active participation of ligands on a metal center in the process of "rearranging" an organic molecule.[21]

(D) The Chemistry of Metal Centers with Secondary Amines and Ethers. The products observed in the chemistry of Co^+ with amines are much different from those observed with alcohols. Oxygen is a very good "director" for the site of metal attack in the organic molecule; only insertion into the C–OH bond occurs. For example, isopropyl alcohol reacts by H_2O elimination but not by CH_4 or H_2 elimination pathways as does isopropylamine. (It is interesting to note that Ni^+ reacts with ethanol to give an H_2O-elimination product *and* an H_2-elimination product[5]. In light of the discussion presented here, H_2 elimination may occur via an intermediate such as C_2H_5O–Ni^+–H.)

These differences are also observed in secondary amines and analogous ethers. Diethylamine and pyrrolidine only react to eliminate H_2, consistent with the fact that the metal center can insert into the N–H bond of each compound and form a favored

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(23) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1978**, *100*, 163.

tertiary amide intermediate. Diethyl ether and tetrahydrofuran react to form products indicative of exclusive Co^+ insertion into the C–O bond. The processes leading to the formation of products for Co^+ and tetrahydrofuran are indicated in Scheme IV. H_2O elimination is shown to occur by first inducing the isomerization of the ether to an ene-ol. Following Co^+ insertion into the C–O bond of tetrahydrofuran, there may be attack of the carbon which is bonded to the β carbon to facilitate CH_2O elimination.

Also included in Table II are the products formed for ethylbutylamine, which appear to be typical H_2 and small-hydrocarbon eliminations. Finally, triethylamine reacts to form products analogous to diethyl ether. Co^+ readily inserts into the polar C–N bond of triethylamine.

Conclusions

The polar C–N bond in primary and secondary amines is not as susceptible to attack by transition-metal ions, as are similar polar bonds. The amine nitrogen is not a strong "directing" group for the metal. Amine reactions closely parallel alkane reactions. Co^+ reacts with the alkyl chain in larger primary amines as well as reacting by insertion into the N–H bond. The reason for failure of Co^+ to insert into the $R-NH_2$ bond may be due to the weak Co^+-NH_2 bond. There are considerable parallels in condensed phases which indicate that primary amide complexes are not easily formed.

Studies of this type involving gas-phase organometallic chemistry under mass spectrometric conditions are providing chemists with a unique view of the interaction of metal centers with organic molecules. Molecules representative of *all* of the basic organic functional groups have not yet been studied. The work done to date indicates that metal ions react in specific ways with organic molecules. Reaction products reflect functional group and structure. Thus, such work is also done to investigate the possibility of using metal ions as chemical ionization (CI) reagents. This concept has been pointed out previously. Reactions such as

$$CoCO^+ + M \rightarrow CoM^+ + CO$$

are common and provide molecular weight information. Table I shows that, in the case of the butylamines, reaction products carry very specific structural information. Thus, this work further supports the concept that metal ions can be used as CI reagents.

Acknowledgments are made to (1) the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation, for support of the construction of the ion cyclotron resonance spectrometer at MSU, (2) Russ Guyer and Martin Raab for their expertise in the construction of the mechanical and electronic components of the ICR (respectively), (3) the NSF for partial support of this work under Grant CHE-8023704, and (4) The Dow Chemical Company Foundation for partial support of this work.

Registry No. $Co(CO)_3NO$, 14096-82-3; Co^+, 16610-75-6; $CoCO^+$, 28963-35-1; $Co(CO)_2{}^+$, 28963-34-0; $Co(CO)NO^+$, 61816-95-3; $Co(CO)_2NO^+$, 61816-96-4; $Co(CO)_3NO^+$, 52309-13-4; CH_3NH_2, 74-89-5; $CH_3CH_2NH_2$, 75-04-7; *n*-$C_3H_7NH_2$, 107-10-8; *i*-$C_3H_7NH_2$, 75-31-0; *n*-$C_4H_9NH_2$, 109-73-9; *i*-$C_4H_9NH_2$, 78-81-9; *sec*-$C_4H_9NH_2$, 13952-84-6; *t*-$C_4H_9NH_2$, 75-64-9; $CH_3CH_2NHCH_2CH_3$, 109-89-7; $CH_3CH_2OCH_2CH_3$, 60-29-7; $CH_3CH_2CH_2CH_2NHCH_2CH_3$, 13360-63-9; $(CH_3CH_2)_3N$, 121-44-8; pyrrolidine, 123-75-1; tetrahydrofuran, 109-99-9; piperidine, 110-89-4.

Vertical Excited States and Magnetic Circular Dichroism Spectrum of Allene

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Abstract: Large-scale ab initio calculations of the excited singlet states of allene are reported. Excellent agreement between optical absorption data and calculated vertical transition energies and oscillator strengths is noted. The experimental magnetic circular dichroism (MCD) spectrum has no dispersive signals characteristic of degenerate excited states. We find all degenerate states to have small magnetic moments and large *B* terms, and thus would have nondispersive MCD line shapes. Calculated MCD parameters provide a novel interpretation of the MCD spectrum in the 180–155-nm region.

Allene (1,2-propadiene) is the most primitive of the cumulenes. The molecular point group in the ground-state geometry is D_{2d}. Electronic excited states of ^1E symmetry are therefore susceptible to Jahn–Teller distortion as are the ^2E states of the positive ion. There is general agreement that the highest occupied molecular orbital is a π orbital of e symmetry; one would therefore expect that a number of low-lying excited electronic states of ^1E symmetry should exist. The magnetic circular dichroism (MCD) of allene has been measured by Fuke and Schnepp[1] in the 200–155-nm region in both the gas phase and perfluorohexane (PFH) solution. Remarkably, no disperisve signals, i.e., no *A* terms, are observed. An *A* term is the talisman of a degenerate electronic state in this experiment.[2] Baker and Turner[3] and Thomas and Thompson[4] have measured the photoionization spectrum of allene and observed two peaks of 10.02 and 10.58 eV in the first ionization band; they have assigned these peaks as the Jahn–Teller split components of the ^2E state of the molecular ion. This is a Jahn–Teller splitting of more than half an electronvolt. Robin[5] has interpreted the optical absorption spectrum of allene in terms of the components of Jahn–Teller split ^1E excited electronic states of Rydberg character. The two Rydberg series are assumed to converge to the two separate ionization limits, 10.02 and 10.58 eV. Fuke and Schnepp interpret the absence of A terms as evidence of the destruction of degeneracy through Jahn–Teller splitting in all excited ^1E states.

In a previous theoretical study of the MCD spectrum of cyclopropane[6] (a molecule whose D_{3h} molecular point group admits similar effects and whose ionization spectrum also exhibits a doubly

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[1] Fuke, K.; Schnepp, O. *Chem. Phys.* **1979**, *38*, 211.

[2] Stephens, P. J. *Annu. Rev. Phys. Chem.* **1974**, *25*, 201; *J. Chem. Phys.* **1970**, *52*, 3489.

[3] Baker, C.; Turner, D. W. *Chem. Commun.* **1969**, 480.

[4] Thomas, R. K.; Thompson, H. T. *Proc. R. Soc. London, Ser. A* **1974**, *339*, 29.

[5] Robin, M. B. "Higher Excited States of Polyatomic Molecules"; Academic Press: New York, 1975; Vol. 2, pp 199–202.

[6] Goldstein, E.; Vijaya, S.; Segal, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 6198.

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