JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

© Copyright 1984 by the American Chemical Society

VOLUME 106, NUMBER 21 OCTOBER 17, 1984

Gas-Phase Reactions of Co^+ and $Co(ligand)_n{}^+$ with Nitroalkanes

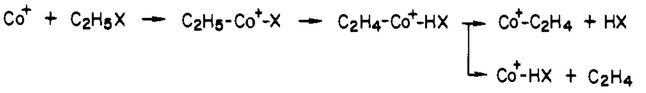
C. J. Cassady,[†] B. S. Freiser,*[†] S. W. McElvany,[‡] and J. Allison*[‡]

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, and the Department of Chemistry, Michigan State University, East Lansing, Michigan 48824-1322. *Received March 28, 1984*

Abstract: The gas-phase chemistry of Co^+ and ions of the type $Co(ligand)_n{}^+$ with a series of nitroalkanes is presented. Also, for comparison, reactions of methyl nitrite and 1-butyl nitrite are included. The Co^+ ion reacts with nitroalkanes by inserting into C–H, C–C, C–N, and N–O bonds. Many nitroalkane products can be best explained via a "nitrite-like" intermediate—possibly indicating a metal-induced nitro-to-nitrite isomerization. Collision-induced dissociation analysis of (i) primary reaction products and (ii) products of subsequent reactions is used to suggest product ion structures. With ligands present on the metal, dramatic changes of reactivity are observed. While nitroalkanes react by simple ligand displacement with $Co(ligand)_n{}^+$ typical of monofunctional alkanes, alkyl nitrites exhibit a much richer chemistry, more typical of multifunctional organic molecules.

In recent years there has been a growing interest in the study of the gas-phase reactions of atomic metal and metal-containing ions with organic molecules. Studies of these reactions using ion cyclotron resonance (ICR) spectrometry[1] and ion beam techniques[2] yield information on the activation of bonds in organic molecules by metal ions in the absence of complicating solvent effects. Thermodynamic, kinetic, and mechanistic information concerning the intrinsic organometallic and coordination chemistry of metal ions can be obtained from these studies. Also, the specific chemistry of metal ions with organic molecules is the basis for a new approach to chemical ionization mass spectrometry.[3,4]

An important area of interest has been the study of the interaction of metal ions with organic molecules containing specific functional groups. In addition to studies of the reactions of a variety of metal ions with alkanes,[2,5] the reactions of transition-metal ions with organic species such as alkyl halides,[1b,6] alkenes,[1c,7] alcohols,[6] amines,[3] aldehydes,[3,9,10] ketones,[3,9,10] carboxylic acids,[3,10] esters,[3,10] ethers,[9,10] sulfides,[11,12] and mercaptans[12] have also been studied. As an example of the types of reactions that have been observed, the reactions of Co^+ with several C_2H_5X species are given in Table I. With the exception of ethylamine, the major reaction pathway for all of these compounds involves insertion of the metal ion into the relatively weak C–X bond as the first mechanistic step. A β-H shift from the alkyl ligand may then occur, forming $Co(C_2H_4)(HX)^+$ which then dissociates by competitive ligand loss as seen in reaction 1. For the reactions of Co^+ with complex functional groups, such as carboxylic acids, insertion into the C–X bond is still a major reaction pathway, but some cleavage of bonds within the functional group also occurs.[3]



$$Co^+ + C_2H_5X \rightarrow C_2H_5\text{-}Co^+\text{-}X \rightarrow C_2H_4\text{-}Co^+\text{-}HX \rightarrow \begin{cases} Co^+\text{-}C_2H_4 + HX \\ Co^+\text{-}HX + C_2H_4 \end{cases} \qquad (1)$$

Table I. Listing of the Neutrals and Ions Resulting from the Reactions of Co^+ with Various Monosubstituted Ethanes

$Co^+ + C_2H_5X \rightarrow A^+ +$ neutral

X	A^+	neutral	rel %	ref
H	no reaction			5d
CH_3	$CoC_2H_4{}^+$	CH_4	31	5d
	$CoC_3H_6{}^+$	H_2	69	
I	$CoC_2H_4{}^+$	HI	78	6
	CoI^+	C_2H_5	11	
	$CoHI^+$	C_2H_4	11	
OH	CoH_2O^+	C_2H_4	13	6
	$CoC_2H_4{}^+$	H_2O	87	
SH	$CoC_2H_4{}^+$	H_2S	70	12
	$CoSH^+$	C_2H_5	7	
	CoH_2S^+	C_2H_4	23	
NH_2	$CoC_2H_5N^+$	H_2	15	8
	$CoCH_3N^+$	CH_4	26	
	$C_2H_6N^+$	CoH	59	
$\overset{O}{\overset{\|}{C}}CH_3$	$CoCO^+$	C_3H_8	8	10
	$CoC_2H_4{}^+$	C_2H_4O	24	
	$CoC_2H_4O^+$	C_2H_4	52	
	$CoC_3H_4O^+$	CH_4	11	
	$CoC_4H_6O^+$	H_2	5	
$\overset{O}{\overset{\|}{C}}OH$	CoH_2O^+	C_3H_4O	36	10
	$CoC_2H_4{}^+$	CH_2O_2	37	
	$CoCH_2O_2{}^+$	C_2H_4	5	
	$CoC_3H_4O^+$	H_2O	21	
	$CoC_3H_4O_2{}^+$	H_2	1	
$O\overset{O}{\overset{\|}{C}}H$	$CoC_2H_4{}^+$	CH_2O_2	36	10
	$CoCH_2O_2{}^+$	C_2H_4	64	

[†] Purdue University.
[‡] Michigan State University.

Table II. Listing of Neutrals and Ions Resulting from the Primary Reactions of Co^+ with Nitromethane and Methyl Nitrite

$$Co^+ + \text{reactant} \rightarrow CoR^+ + \text{neutral(s)}$$

		CH_3NO_2		CH_3ONO	
CoR^+	neutral(s)	rel %	intermediate structure	rel %	intermediate structure
$CoHNO_2^+$	CH_2	2	I	0	
CoH^+	CH_2ONO	2	III, E	15	C, E
CoO^+	HCN, H_2O	17	IV, V	0	
$CoOH^+$	CH_2NO	21	IV, V	0	
$Co(OH)_2^+$	HCN	6	IV, V	0	
$CoCH_2NO^+$	OH	3	IV, V	0	
$CoCHNO^+$	H_2O	3	IV, V	0	
$CoNO^+$	CH_3O	2	E	5	E
$CoOCH_3^+$	NO	40	E	70	E
$CoOCH_2^+$	HNO	2	E	5	E
$CoOCH^+$	H_2, NO	2	E	5	E

Table III. Listing of Ions and Neutrals Resulting from the Primary Reactions of Co^+ with Nitroethane

$$Co^+ + C_2H_5NO_2 \rightarrow CoR^+ + \text{neutral(s)}$$

CoR^+	neutral(s)	intermediate structure	rel %
$CoHNO_2^+$	C_2H_4	I	12
$CoC_2H_4^+$	HNO_2	I	3
$CoC_2H_3^+$	H_2, NO_2	I, III	14
$CoCH_3^+$	CH_2NO_2	II	5
$CoCH_2NO_2^+$	CH_3	II	7
$CoCH_3NO_2^+$	CH_2	II	2
CoO^+	CH_3CN, H_2O	IV, V	2
$CoOH^+$	C_2H_4NO	IV, V	20
$Co(OH)_2^+$	CH_3CN	IV, V	4
$CoC_2H_4NO^+$	OH	IV, V	5
$CoC_2H_3NO^+$	H_2O	IV, V	4
$CoNO^+$	C_2H_5O	E	3
$CoC_2H_5O^+$	NO	E	4
$CoC_2H_4O^+$	HNO	E	10
$CoC_2H_3O^+$	H_2, NO	E	5

Table IV. Listing of Neutrals and Ions Resulting from the Primary Reactions of Co^+ with Nitropropane

$$Co^+ + C_3H_7NO_2 \rightarrow CoR^+ + \text{neutral(s)}$$

$$Co^+ + C_3H_7NO_2 \rightarrow R'^+ + \text{neutral(s)}$$

			rel %	
CoR^+ or R'^+	neutral(s)	intermediate structure	1-$C_3H_7NO_2$	2-$C_3H_7NO_2$
$C_3H_7^+$	$CoNO_2$	I	12	17
$CoHNO_2^+$	C_3H_6	I	21	16
$CoC_3H_6^+$	HNO_2	I	4	3
$CoC_3H_5^+$	H_2, NO_2	I, III	10	6
$CoCH_3^+$	C_2H_4, NO_2	II	2	2
$CoC_2H_4NO_2^+$	CH_3	II	8	8
$CoC_2H_5NO_2^+$	CH_2	II	2	3
$CoCH_2NO_2^+$	C_2H_5	II	2	2
$CoCH_3NO_2^+$	C_2H_4	II	1	2
$CoOH^+$	C_3H_6NO	IV, V	15	18
$CoNO^+$	C_3H_7O	E	2	2
$CoC_3H_7O^+$	NO	E	1	3
$CoC_3H_6O^+$	HNO	E	6	7
$CoC_3H_5O^+$	H_2, NO	E	14	11

A logical extension of this area, which has been receiving recent interest, is the study of the effect of various ligands on metal ion reactivity. Although this work is still in its infancy, preliminary studies have shown that the presence of a ligand may lead to new reaction mechanisms as well as enhance or deactivate the bare metal ion.[1a,4,8,13]

As a continuation of our work in this area, the results of a study of the reactions of Co^+ with some aliphatic nitro compounds are presented here. In addition, reactions involving CoL^+ generated as primary products from the interaction of Co^+ with nitroalkanes as well as $Co(CO)_x^+$ ($x = 0$–2) and $Co(CO)_xNO^+$ ($x = 0$–3) generated by electron impact on $Co(CO)_3NO$ are presented.

Experimental Section

The experiments involving the bare metal ion, Co^+, were carried out by using a prototype Nicolet FTMS-1000 which has been previously described in detail.[14] The mass spectrometer is equipped with a 5.2-cm cubic trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.9 T. The cell has a 0.25-in.-diameter hole in one of the transmitter plates to allow various light sources access to the inside of the cell. Co^+ was generated by focusing the frequency-doubled beam (530 nm) of a Quanta Ray Nd:YAG laser onto a high-purity cobalt foil which was supported by the opposite transmitter plate. Details of the laser ionization experiment have been described elsewhere.[5b,9] Laser ionization can produce ions in excited states, and while steps are taken to minimize their presence,[15] the formation of minor products from excited Co^+ cannot be completely ruled out.

The distributions of primary product ions listed in Tables II–V are reproducible to within ±10% absolute for the major products and ±5% absolute for the minor products. Product distributions of subsequent reactions of the Co^+ primary reaction products were determined by using swept double resonance techniques[16] to isolate the ions of interest.

The CID experiments were performed by using the FTMS. Sample pressures were on the order of 1×10^{-7} torr, and the argon target gas was on the order of 1×10^{-5} torr. Pressures were monitored with a Bayard-Alpert ionization gauge. Details of the CID experiments have been described previously.[5c,d,14b] The collision energy can be varied

---

(1) Publications representative of the groups active in this area include the following: (a) Huang, S. K.; Allison, J. *Organometallics* **1983**, *2*, 883. (b) Jones, R. W.; Staley, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3794. (c) Jacobson, D. B.; Freiser, B. S. *Ibid.* **1983**, *105*, 7484. (c) Wronka, J.; Ridge, D. P. *Ibid.* **1984**, *106*, 67.

(2) (a) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784. (b) Armentrout, P. B.; Beauchamp, J. L. *Ibid.* **1981**, *103*, 6628. (c) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963.

(3) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Anal. Chem.* **1980**, *52*, 1641.

(4) Lombarski, M.; Allison, J. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *49*, 281.

(5) (a) Byrd, G. D.; Burnier, R. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 3565. (b) Byrd, G. D.; Freiser, B. S. *Ibid.* **1982**, *104*, 5944. (c) Jacobson, D. B.; Freiser, B. S. *Ibid.* **1983**, *105*, 736. (d) Jacobson, D. B.; Freiser, B. S. *Ibid.* **1983**, *105*, 5197. (e) Allison, J.; Freas, R. B.; Ridge, D. P. *Ibid.* **1979**, *101*, 1332.

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

(7) (a) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6624. (b) Allison, J.; Ridge, D. P. *Ibid.* **1977**, *99*, 35.

(8) Radecki, B.; Allison, J. *J. Am. Chem. Soc.* **1984**, *106*, 946.

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

(10) Byrd, G. D. Ph.D. Thesis, Purdue University, West Lafayette, IN, 1982.

(11) Carlin, T. J.; Wise, M. B.; Freiser, B. S. *Inorg. Chem.* **1981**, *20*, 2743.

(12) Carlin, T. J. Ph.D. Thesis, Purdue University, West Lafayette, IN, 1983.

(13) (a) Allison, J.; Huang, S. K.; Lombarski, M.; McElvany, S. W.; Radecki, B.; Tsarbopoulos, A., American Society for Mass Spectrometry Meeting, Boston, 1983. (b) Tsarbopoulos, A.; Allison, J. *Organometallics* **1984**, *3*, 86.

(14) (a) Cody, R. B.; Freiser, B. S *Int. J. Mass Spectrom. Ion Phys.* **1982**, *41*, 199. (b) Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96.

(15) Cassady, C. J.; Freiser, B. S., unpublished results.

(16) (a) Comisarow, M. B.; Grassi, V.; Parisod, G. *Chem. Phys. Lett.* **1978**, *57*, 413. (b) Marshall, A. G.; Comisarow, M. B.; Parisod, G. *J. Chem. Phys.* **1979**, *71*, 4434. (c) Parisod, G.; Comisarow, M. B. *Adv. Mass Spectrom.* **1980**, *8*, 212.

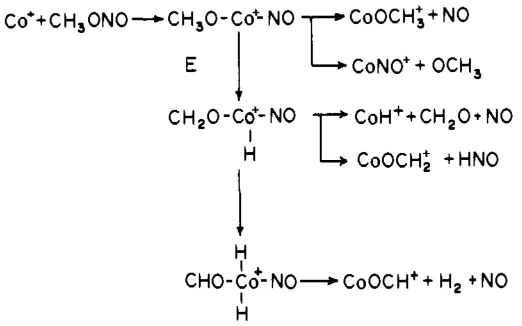
Table V. Listing of the Neutrals and Ions Resulting from the Primary Reactions of Co^+ with Nitrobutane and Butyl Nitrite

$$Co^+C_4H_9NO_2 \rightarrow CoR^+ + \text{neutral(s)}$$

$$Co^+ + C_4H_9NO_2 \rightarrow R'^+ + \text{neutral(s)}$$

			rel %				
CoR^+ or R'^+	neutral(s)	intermediate (nitro)	$1\text{-}C_4H_9NO_2$	$2\text{-}C_4H_9NO_2$	$(CH_3)_3CNO_2$	intermediate (nitrite)	$1\text{-}C_4H_9ONO$
$C_4H_9{}^+$	$CoNO_2$	I	38	30	79	A	2
$CoHNO_2{}^+$	C_4H_8	I	9	13	2		0
$CoC_4H_8{}^+$	HNO_2	I	1	3	1	A	1
$CoC_4H_7{}^+$	H_2, NO_2	I, III	6	13	5		0
$CoC_4H_6{}^+$	H_2, HNO_2	I	3	4	0	A	4
$CoCH_3{}^+$	$C_3H_6NO_2$	II	0	0	2		0
$CoC_3H_6NO_2{}^+$	CH_3	II	1	2	2		0
$CoC_2H_4NO_2{}^+$	C_2H_5	II	3	5	1		0
$CoC_2H_5NO_2{}^+$	C_2H_4	II	14	1	1		0
$CoC_2H_4{}^+$	$C_2H_5NO_2$	II	2	0	0		0
$CoCH_2NO_2{}^+$	C_3H_7	II	2	1	0	B	23
$CoC_3H_7{}^+$	CH_2NO_2	II	2	2	0		0
$CoC_3H_5{}^+$	CH_4, NO_2	II	2	1	0	B	6
$CoOH^+$	C_4H_8NO	IV, V	7	7	3		0
$CoC_4H_9O^+$	NO	E	1	3	1	E	2
$CoC_4H_8O^+$	HNO	E	2	4	1	E	7
$CoC_4H_7O^+$	H_2, NO	E	3	5	0	E	21
$CoC_4H_6O^+$	H_2, HNO	E	1	2	0	E	6
$CoC_4H_5O^+$	$2H_2$, NO	E	2	3	0	E	27
$CoC_3H_6O^+$	CH_3NO	E	1	1	2	E	1

Scheme I



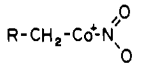
typically between 0 and 100 eV. The spread in ion kinetic energies is dependent on the total average kinetic energy and is approximately 35% at 1 eV, 10% at 10 eV, and 5% at 30 eV.[17]

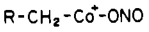
The studies of the reactions of cobalt-containing ions formed by electron impact on tricarbonylnitrosylcobalt(0) were performed on an ion cyclotron resonance spectrometer of conventional design which has previously been described in detail.[8] Ion/molecule reactions and precursors were identified by using double resonance techniques. Reported data are results of product ions formed in a 1:1 mixture (by pressure) of $Co(CO)_3NO$ to nitroalkane, at total pressures between 5×10^{-6} and 1×10^{-5} torr. Spectra were always taken to masses greater than 276 amu, since the sum of the mass of $Co(CO)_3NO$ (173 amu) and the largest nitroalkane ($C_4H_9NO_2$, 103 amu) equals 276.

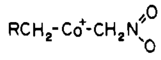
Methyl nitrite and methyl-d_3 nitrite were prepared according to the literature.[18] All other chemicals were high-purity commercial samples which were used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensible gases.

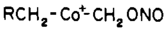
Results and Discussion

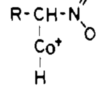
Primary Reactions. The primary products for the reactions of Co^+ with nitroalkanes are listed in Tables II–V. As an aid in elucidating reaction mechanisms, the reactions of Co^+ with methyl nitrite and 1-butyl nitrite were also studied, with their reaction products being given in Tables II and V, respectively. In the experiments with nitromethane and methyl nitrite, the empirical formulas of all the products were confirmed by using both deuterated and undeuterated reagents. For several products from the larger nitroalkanes, empirical formulas other than those listed may also be possible for the products. On the basis of a consideration of all of the data, however, including (i) subsequent ion/molecule reactions of the primary products with the nitroalkanes, (ii) collision-induced dissociation results, (iii) the reactions of Co^+ with other nitroalkanes, and (iv) the reactions of other metal ions with nitroalkanes,[15] we believe the formulas listed are the most reasonable. Also listed in the tables is the probable structure of the reaction intermediate that leads to the formation of each product. Structure I results from Co^+ insertion into the $C\text{-}NO_2$ bond. Structures II and III (which are possible intermediates suggested by the observed reactions of Co^+ with amines[8]) are products of metal insertion into the C–C and C–H bonds, respectively. Insertion of Co^+ into the N–O bond, which has a bond strength[19] of 75 kcal/mol, leads to intermediate IV. An analogous set of insertion isomers for Co^+ with alkyl nitrites are also given (structures A–E). Throughout this paper, intermediates which follow from nitroalkanes will be labeled by I–V, and intermediates from alkyl nitrites will be labeled A–E.

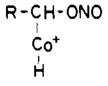

I

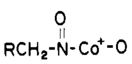

A

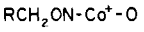

II

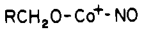

B


III


C


IV


D


E

As will be discussed below, some products from the reaction of nitroalkanes with Co^+ can be most easily explained via intermediates A–E, suggesting that either a nitro-to-nitrite isomeri-

---

(17) Huntress, W. T.; Mosesman, M. M.; Elleman, D. D. *J. Chem. Phys.* **1971**, *54*, 843.

(18) Hartung, W. H.; Crossley, F. "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol. II, pp 363–364.

(19) Pepekin, V. I.; Matyushin, Y. N.; Lebedev, Y. A. *Izv. Akad. Nauk. Am. SSR, Ser. Khim. Nauk.* **1974**, *8*, 1707.

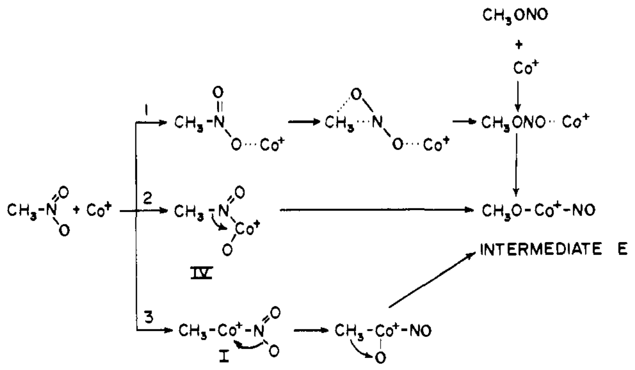
zation occurs or, in some other mechanistic step, a "nitro intermediate" is converted to a "nitrite intermediate".

Nitromethane and Methyl Nitrite. From the data in Table II, two interesting points are evident about the reactions of Co^+ with nitromethane. First, in comparison with the reactions of Co^+ with other monosubstituted methanes, nitromethane chemistry is considerably richer, having a large number of products. Methane[2], methyl alcohol,[6] and methylamine[8] have been found to be unreactive with Co^+, while methyl bromide,[6] methyl chloride,[6] and methyl mercaptan[12] each give only one to two products, in contrast to the reaction with nitromethane which yields three major products and seven minor products. Second, the products are not those that might be expected on the basis of C–N bond insertion, but appear to result primarily from insertion into the N–O bond.

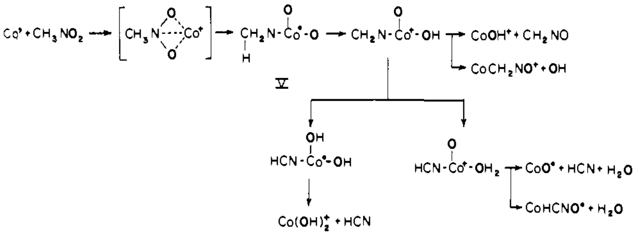
In order to explain the reaction products, it is useful to compare the results for nitromethane with those for methyl nitrite. Both compounds are observed to yield the same major primary product, $CoOCH_3^+$, as well as having four minor products in common.

There is one distinguishing feature of methyl nitrite chemistry that affects both its solution and gas-phase chemistry. This is a very weak CH_3O–NO bond. With a bond-dissociation energy of 42 kcal/mol,[20] this bond is considerably weaker than the typical C–C bond (ca. 88 kcal/mol[21]), the C–H bond (ca. 97 kcal/mol[21]), the nitromethane C–N bond (61 kcal/mol[22]), or the N–O bond (75 kcal/mol[19]). Thus, one would expect that the reactions of Co^+ with methyl nitrite would involve oxidative addition into the weak O–N bond, giving the insertion intermediate E. As shown in Scheme I, the formation of E followed by a β-H shift onto the metal can explain all of the products of the methyl nitrite reaction. Products resulting from the possible intermediates A and D are not observed, possibly due to the relatively strong bonds which would have to be broken. It is interesting that the NO group, which is a three-electron donor[23] and has been found to bond strongly to Co^+ in the gas phase,[24] is lost preferentially to the OCH_3 group. Since the initial insertion into the O–N bond leads to an NO group which donates only one electron, the lifetime of the intermediate may not be sufficient to allow rearrangement to the linear three-electron donor complex geometry. Of relevance is a study of Walton et al.[25] using secondary ion mass spectrometry (SIMS) on $[Cr(NO)(CNCMe_3)_5]PF_6$ and several other similar complexes. It was found that while initial fragmentation occurs via loss of isocyanide ligands, after the third isocyanide ligand is lost, the fourth ligand lost is exclusively NO. No ions corresponding to $Cr(NO)(CNCMe_3)^+$ or $Cr(NO)^+$ were observed. Their rationale for this observation was that while initial ligand loss from large ions is determined by relative bond strengths, in smaller ions the ability of a ligand to delocalize charge becomes an important factor in ligand loss. Other factors such as synergistic ligand effects and the ability of a ligand to carry away excess energy may also play a role in ligand loss.

Scheme II

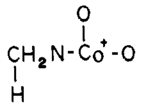


Scheme III



In the reactions of Co^+ with nitromethane, products are observed due to intermediates predicted from *both* the nitro and nitrite functional groups. An intramolecular RNO_2 to RONO isomerization is observed in the electron impact (EI) mass spectra of many aromatic nitro compounds[26] and in a few aliphatic nitro compounds.[27] Such an isomerization can also occur thermally[28] or photochemically.[29] However, EI-induced isomerizations arise due to charge/radical sites in the molecule, and thermal and photochemical isomerizations are believed to occur by an NO_2 dissociation from the alkyl group followed by a recombination. It seems likely in the case of Co^+ reacting with nitromethane that the metal assists in such a nitro-to-nitrite isomerization. Possible mechanisms for the nitro-to-nitrite conversion are presented in Scheme II. There are two general pathways in which this conversion may occur. The first involves the coordination of Co^+ to an oxygen while the molecule isomerizes (reaction 1 in Scheme II). Once the nitrite isomer is formed, Co^+ inserts into the O–N bond to give intermediate E. The other possibilities involve participation of the metal (reactions 2 and 3 in Scheme II) by initial N–O or C–N insertion. Note that the actual nitrite isomer is not formed in these mechanisms, but only the metal-insertion intermediate (E) typical of nitrites is formed.

Two major products, CoO^+ and $CoOH^+$, and several minor products are seen in the nitromethane reactions which are not present in the methyl nitrite reactions. The most probable mechanism for the formation of these products, Scheme III, involves an intermediate with two oxygen atoms bound to the metal, intermediate V. One fact suggesting the formation of this intermediate as opposed to a species with only one oxygen bound to the metal, intermediate IV, is that CoO^+ formation from IV would involve loss of CH_3NO. This process would be approximately 30 kcal/mol endothermic.[30] The formation of CoO^+ from V with loss of HCN and H_2O is 13 kcal/mol exothermic. Also, the formation of the minor product $Co(OH)_2^+$ (or $Co(O)(H_2O)^+$) indicates that, at some point, two oxygen atoms must be bound to the metal.



$\underset{H}{\underset{|}{C}}H_2N\text{-}\overset{O}{\overset{|}{Co^+}}\text{-}O$

V

Collision-induced dissociation experiments were performed on the major primary reaction products of Co^+ with nitromethane. As expected, the products CoO^+ and $CoOH^+$ lost O and OH,

---

(20) Batt, L.; Robinson, G. N. "The Chemistry of Amino, Nitroso, and Nitro Compounds and their Derivatives"; Patai, S.; Ed.; Wiley: New York, 1982; Part 2, p 1075.

(21) West, R. C., Ed. "Handbook of Chemistry and Physics", 55th ed.; Chemical Rubber Publishing Co.: Cleveland, 1974.

(22) Reference 20, p 1043.

(23) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Interscience: New York, 1972; pp 713–719.

(24) Weddle, G. H.; Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1977**, *99*, 105.

(25) Pierce, J. L.; Wigley, D. E.; Walton, R. A. *Organometallics* **1982**, *1*, 1328.

(26) (a) Bursey, M. M.; McLafferty, F. W. *J. Am. Chem. Soc.* **1966**, *88*, 5023. (b) Meyerson, S.; Puskas, I.; Fields, E. K. *Ibid.* **1966**, *88*, 4974. (c) Westwood, R.; Williams, D. H.; Yeo, A. N. H. *Org. Mass. Spectrom.* **1970**, *3*, 1485. (d) Beyon, J. H.; Bertrand, M.; Cooks, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 1739.

(27) Nibbering, N. M. M.; deBoer, Th. J. *Org. Mass Spectrom.* **1970**, *3*, 487.

(28) Reference 20, Part I, pp 434–441 and references therein.

(29) Reference 20, Part I, pp 214–216 and references therein.

(30) Thermochemical information is taken from ref 20 and Rosenstock et al.: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl.* **1977**, *1*, 6.

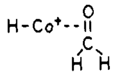
Table VI. Ions and Neutrals Formed in Subsequent Reactions of the Primary Products of the [$Co^+ + CH_3NO_2$] Reaction ($P = CH_3NO_2$)

$CoR^+ + CH_3NO_2 \rightarrow CoR'^+ +$ neutral

CoR^+	CoR'^+	neutral	rel %
CoO^+	$Co(OH)_2^+$	HCNO	40
	$Co(CH_2NO_2)^+$	OH	30
	CoP^+	O	15
	$CoOP^+$		15
$CoOH^+$	$Co(OH)(H_2O)^+$	HCNO	10
	$Co(CH_2NO_2)^+$	H_2O	40
	CoP^+	OH	20
	$CoHP^+$	O	10
	$Co(OH)P^+$		20
$CoOCH^+$	*a*		
CoH^+	*a*		
$CoNO^+$	NR[b]		
$CoOCH_2^+$	CoP^+	CH_2O	100
$CoOCH_3^+$	$CoHP^+$	CH_2O	100
$Co(OH)_2^+$	$CoOP^+$	H_2O	75
	$Co(OH)P^+$	OH	25
$CoCHNO^+$	$CoOP^+$	HCN	100
$CoCH_2NO^+$	$Co(OH)P^+$	HCN	100
$CoHNO_2^+$	$Co(OH)P^+$	NO	100
3rd Generation (Subsequent Reactions of Products Listed Above)			
$Co(OH)(H_2O)^+$	$Co(OH)P^+$	H_2O	100
$CoCH_2NO_2^+$	$Co(NO)P^+$	CH_2O	100
CoP^+	$CoOP^+$	CH_3NO	10
	$Co(OH)P^+$	CH_2NO	70
	$CoHP^+$	CH_2NO_2	20
$CoHP^+$	$Co(OH)P^+$	CH_3NO	100
$CoOP^+$	$Co(OH)P^+$	CH_2NO_2	70
	$Co(OCH_2)P^+$	HNO_2	10
	$Co(CH_2NO_2)P^+$	OH	5
	CoP_2^+	O	15
$Co(OH)P^+$	$Co(OCH_3)P^+$	HNO_2	10
	$Co(CH_2NO_2)P^+$	H_2O	80
	$Co(OH)P_2^+$		10
4th Generation (Subsequent Reactions of 3rd Generation Reactions)			
$Co(OCH_2)P^+$	*a*		
$Co(OCH_3)P^+$	$Co(OCH_3)(CH_2)P^+$	HNO_2	100
$Co(NO)P^+$	$Co(CH_2NO_2)P^+$	HNO	30
	CoP_2^+	NO	30
	$Co(NO)P_2^+$		40
$Co(CH_2NO_2)P^+$	$Co(CH_2)(CH_2NO_2)P^+$	HNO_2	50
	$Co(CH_2NO_2)P_2^+$		50
CoP_2^+	$Co(CH_2)P_2^+$	HNO_2	50
	CoP_3^+		50
$Co(OH)P_2^+$	$Co(CH_2NO_2)P_2^+$	H_2O	100
5th Generation (Subsequent Reactions of 4th Generation Reactions)			
$Co(OCH_3)(CH_2)P^+$	*a*		
$Co(NO)P_2^+$	*a*		
$Co(CH_2)(CH_2NO_2)P^+$	*a*		
$Co(CH_2)P_2^+$	*a*		
$Co(CH_2NO_2)P^+$	NR		
CoP_3^+	NR		

[a] Further reactions of this ion could not be determined. [b] NR indicates that this ion did not undergo any further reactions within the time scale (10 s) of this experiment.

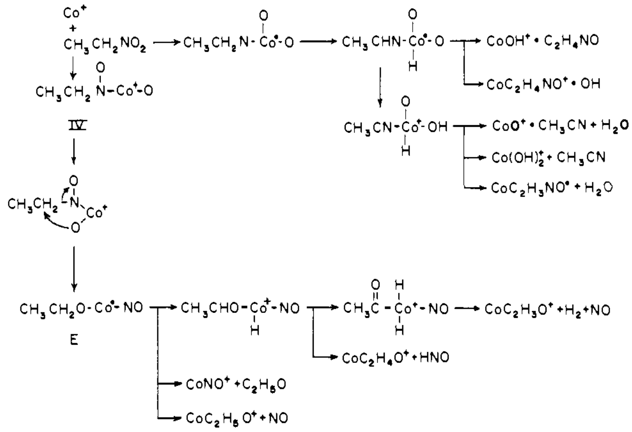
respectively, to form Co^+ as the only CID product. $CoOCH_3^+$ lost CH_2O to form CoH^+ exclusively with high-CID efficiency. Deuterium exchange experiments to probe for metal hydride character, i.e., a structure such as



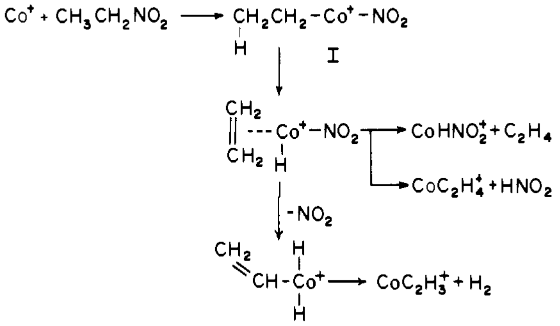
$$H{-}Co^+{\cdots}\overset{O}{\underset{H\ \ H}{\overset{\|}{C}}}$$

proved inconclusive. No deuterium exchange was observed. Lack of deuterium exchange yields no information since FeH^+, an ion of obvious metal hydride character, does not undergo deuterium exchange. CoH^+, however, undergoes deuterium exchange slowly, and NiH^+ exchanges with deuterium readily.[31] Although $CoOCH_3^+$ does not react with D_2, $NiOCH_3^+$, formed in the reaction of Ni^+ with methyl nitrite, was found to undergo one deuterium exchange.[15] This indicates that $NiOCH_3^+$ has a hydride structure and most probably $CoOCH_3^+$ has a similar structure based on the facile loss of CH_2O when activated, as well as the displacement of CH_2O when $CoOCH_3^+$ reacts with CH_3NO_2 (Table VI) and other Lewis bases.

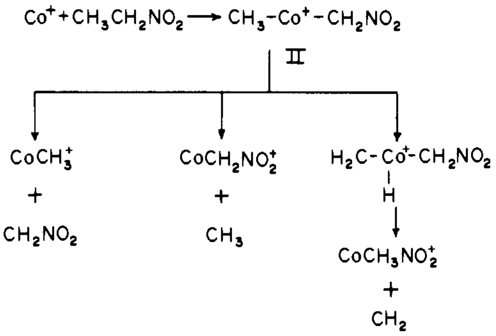
Scheme IV



Scheme V



Scheme VI



Nitroethane. For the reaction of Co^+ with nitroethane (Table III), the majority (57%) of the primary products are analogous to those present in nitromethane (note that, as in the case of nitromethane, some products are best explained via the "nitrite-like" intermediate, E). Scheme IV suggests a mechanism for forming these products starting with intermediate IV.

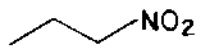
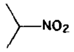
Carbon–nitrogen bond insertion (intermediate I) is also an important process in the nitroethane reaction. In Scheme V, a mechanism is proposed that includes insertion of Co^+ into the C–N bond followed by a β-H shift onto the metal. This mechanism could account for the formation of $CoC_2H_4^+$ and $CoHNO_2^+$, which are 15% of the total primary product intensity.

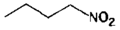
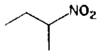
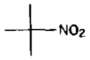
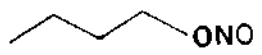
Carbon–carbon bond insertion (intermediate II) also appears to occur and results in 14% of the products, including $CoCH_3^+$, $CoCH_2NO_2^+$, and $CoCH_3NO_2^+$. The proposed C–C bond in-

---

[31] Carlin, T. J.; Sallans, L.; Cassady, C. J.; Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 6320.

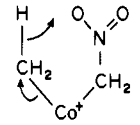
Table VII. Reaction Products of CoL_n^+ with Nitroalkanes and Alkyl Nitrites

reactant	P (parent)			
	CH_3NO_2	$C_2H_5NO_2$		
$CoCO^+$	$CoP^+ + CO$	$CoP^+ + CO$	$CoCOHNO_2^+ + C_3H_6$ (0.10) $CoCOC_2H_3^+ + H_2 + CH_2NO_2$ (0.12) $Co(C_3H_7O)^+ + NO + CO$ (0.09) $CoP^+ + CO$ (0.69)	$CoCOHNO_2^+ + C_3H_6$ (0.25) $CoHNO_2^+ + CO + C_3H_6$ (0.10) $CoC_3H_7O^+ + NO + CO$ (0.30) $CoC_2H_4NO_2^+ + CH_3 + CO$ (0.15) $CoP^+ + CO$ (0.20)
$Co(CO)_2^+$	$CoCOP^+ + CO$	$CoCOP^+ + CO$ (0.75) $CoP^+ + 2CO$ (0.25)	NR	NR
$CoNO^+$	NR	NR	NR	NR
$CoCONO^+$	$CoNOP^+ + CO$	$CoNOP^+ + CO$	$CoNOP^+ + CO$	$CoNOP^+ + CO$
$Co(CO)_2NO^+$	$CoNOP^+ + 2CO$ (0.66) $CoCONOP^+ + CO$ (0.34)	$CoNOP^+ + 2CO$ (0.74) $CoCONOP^+ + CO$ (0.26)	$CoNOP^+ + 2CO$	$CoNOP^+ + 2CO$
$Co(CO)_3NO^+$	$CoCONOP^+ + 2CO$	$CoCONOP^+ + 2CO$	$CoCONOP^+ + 2CO$	$CoCONOP^+ + 2CO$

reactant	P (parent)			
				
$CoCO^+$	$CoC_2H_4NO_2^+ + C_2H_5 + CO$ (0.18) $CoC_2H_5NO_2^+ + C_2H_4 + CO$ (0.35) $CoC_4H_9O^+ + CO + NO$ (0.05) $CoC_4H_7O^+ + CO + NO + H_2$ (0.03) $CoC_4H_5O^+ + NO + 2H_2 + CO$ and/or $CoCOC_3H_5^+ + CH_2NO_2 + H_2$ (0.04) $CoP^+ + CO$ (0.35)	$CoCOC_4H_8^+ + HNO_2$ (0.04) $CoHNO_2^+ + C_4H_8 + CO$ (0.11) $CoC_4H_7^+ + CO + NO_2 + H_2$ (0.07) $CoC_2H_4NO_2^+ + C_2H_5 + CO$ (0.16) $CoC_2H_5NO_2^+ + C_2H_4 + CO$ (0.12) $CoC_4H_9O^+ + CO + NO$ (0.12) $CoC_4H_7O^+ + CO + NO + H_2$ (0.05) $CoC_3H_6NO_2^+ + CO + CH_3$ (0.18) $CoC_4H_8O^+ + CO + HNO$ (0.05) $CoC_4H_8NO_2^+ + CO + H$ and/or $CoCOC_2H_4NO_2^+ + C_2H_5$ (0.05) $CoP^+ + CO$ (0.05)	$CoHNO_2^+ + C_4H_8 + CO$ (0.12) $CoC_4H_9O^+ + CO + NO$ (0.22) $CoC_3H_6NO_2^+ + CO + CH_3$ (0.47) $CoC_4H_8NO_2^+ + CO + H$ and/or $CoCOC_2H_4NO_2^+ + C_2H_5$ (0.19)	$CoC_2H_4NO_2^+ + C_2H_5 + CO$ (0.07) $CoC_4H_9O^+ + CO + NO$ (0.07) $CoC_4H_7O^+ + CO + NO + H_2$ (0.29) $CoC_3H_6NO_2^+ + CO + CH_3$ (0.12) $CoCH_2NO_2^+ + CO + C_3H_7$ (0.20) $CoC_4H_8O^+ + CO + HNO$ (0.11) $CoC_4H_8NO_2^+ + CO + H$ and/or $CoCOC_2H_4NO_2^+ + C_2H_5$ (0.06) $CoCOC_4H_8NO_2^+ + H$ (0.04) $CoP^+ + CO$ (0.04)
$Co(CO)_2^+$	$CoCOP^+ + CO$	$CoCOC_4H_8^+ + CO + HNO_2$ (0.13) $CoC_4H_9O^+ + NO + 2CO$ (0.25) $CoC_2H_4NO_2^+ + 2CO + C_2H_5$ (0.06) $CoCOP^+ + CO$ (0.56)	$CoC_3H_6NO_2^+ + CH_3 + 2CO$ (0.75) $CoC_4H_8NO_2^+ + 2CO + H$ and/or $CoCOC_2H_4NO_2^+ + C_2H_5 + CO$ (0.25)	$CoC_4H_8NO_2^+ + 2CO + H$ and/or $CoCOC_2H_4NO_2^+ + C_2H_5 + CO$ (0.13) $CoCOC_4H_7O^+ + CO + NO + H_2$ (0.11) $CoCOC_4H_9O^+ + CO + NO$ (0.53) $CoCOC_4H_8NO_2^+ + CO + H$ and/or $Co(CO)_2C_2H_4NO_2^+ + C_2H_5$ (0.18) $CoP^+ + 2CO$ (0.05)

$CoNO^+$	NR	NR	NR	$CoNOCH_2NO_2^+ + C_3H_7$
$CoCONO^+$	$CoNOP^+ + CO$	$CoNOP^+ + CO$ (0.59) $CoNOC_2H_4NO_2^+ + CO + C_2H_5$ (0.41)	$CoNOC_3H_6NO_2^+ + CO + CH_3$	$CoNOCH_2NO_2^+ + C_3H_7 + CO$
$Co(CO)_2NO^+$	$CoNOP^+ + 2CO$ (0.83) $CoCONOP^+ + CO$ (0.17)	$CoNOP^+ + 2CO$ (0.90) $CoCONOP^+ + CO$ (0.10)	$CoCONO(NO_2)^+ + CO + C_4H_9$ (0.35) $CoNOP^+ + 2CO$ (0.65)	$CoNOC_4H_8O^+ + 2CO + HNO$ (0.10) $CoNOC_4H_9O^+ + 2CO + NO$ (0.10) $CoCONOC_4H_8O^+ + CO + HNO$ (0.02) $CoCONOC_2H_3NO_2^+ + C_2H_6 + CO$ (0.07) $CoCONOC_2H_4NO_2^+ + C_2H_5 + CO$ (0.17) $CoCONONO_2^+ + CO + C_4H_9$ and/or $CoNOC_2H_4NO_2^+ + 2CO + C_2H_5$ (0.31) $CoNOC_3H_6NO_2^+ + 2CO + CH_3$ (0.09) $CoNOP^+ + 2CO$ (0.14)
$Co(CO)_3NO^+$	$CoCONOP^+ + 2CO$	$CoCONOP^+ + 2CO$	$CoCONOP^+ + 2CO$	$CoCONOC_4H_8O^+ + 2CO + HNO$ (0.08) $CoCONOC_4H_9O^+ + 2CO + NO$ and/or $CoCONOC_2H_3NO_2^+ + C_2H_6 + 2CO$ (0.14) $CoCONOC_2H_4HO_2^+ + 2CO + C_2H_5$ (0.24) $CoCONOP^+ + 2CO$ (0.34) $CoNOP^+ + 3CO$ (0.20)

sertion mechanism is given in Scheme VI. The minor product, $CoCH_3NO_2^+$, is interesting since it results from the loss of CH_2. Methylene is also formed in the reaction leading to $CoHNO_2^+$ from nitromethane. This process is unusual since CH_2 is a high-energy radical and would require either an α-H shift onto Co^+ or alternatively onto an oxygen via a cyclic intermediate:



The second most abundant product (14%) of the nitroethane reaction, $CoC_2H_3^+$, could result from oxidative addition into a C–H bond (intermediate III) followed by a β-shift and loss of H_2. This loss of H_2 is then followed by a cleavage of the C–N bond and the loss of NO_2, as shown in Scheme VII. This mechanism is reasonable since Co^+ is observed to insert readily into C–H bonds of small alkanes[2a,5d] and because the dominant process in the reactions of nitro compounds with Rh^+,[15] which favors C–H bond insertion,[5b] is the loss of H_2 and NO_2. An alternate pathway leading to the formation of $CoC_2H_3^+$ via intermediate I is shown in Scheme V.

Collision-induced dissociation experiments were performed on the three major nitroethane products. Again, not surprisingly, CID on $CoOH^+$ formed only Co^+ and no CoH^+. For $CoHNO_2^+$, reactions 2 and 3 occurred, with the formation of Co^+ resulting at higher CID energies. No $CoNO^+$ was formed, placing an upper

$$CoHNO_2^+ \xrightarrow{Ar} CoOH^+ + NO \qquad (2)$$

$$\longrightarrow Co^+ + HNO_2 \qquad (3)$$

limit of $D(Co^+\text{–}NO) < D(Co^+\text{–}OH) = 71 \pm 3$ kcal/mol.[32] The ion/molecule reactions discussed below also agree with this conclusion. In addition, the absence of CoH^+ and $CoNO_2^+$ is evidence against a hydrido–nitro structure. This splitting of the HNO_2 group during CID does not give any information on whether the $CoHNO_2^+$ ion is actually $Co(HNO_2)^+$ or $Co(OH)(NO)^+$ since only 49 kcal/mol are required to form NO and OH from HNO_2,[30] and more than enough energy is imparted to the ion during the CID process for this cleavage to occur. Displacement of NO by CH_3NO_2 (Table VI), however, provides evidence for the hydroxy structure. CID experiments were also performed on the $CoC_2H_3^+$ ion, leading to the products CoH^+ and Co^+ from the losses of C_2H_2 and C_2H_3, respectively.

Nitropropane. Table IV shows that, within the limits of experimental error, the two nitropropanes react with Co^+ identically. The formation of these products can be explained by using the mechanisms evoked in the nitroethane reactions. The dominant process again involves cleavage of the N–O bond, with isomerization to structure E still playing an important role. However, the C–N insertion intermediate I is beginning to play a more important role in the chemistry than it did with the smaller nitroalkanes. The loss of C_2H_5 and C_2H_4 from 2-nitropropane cannot be easily explained and may arise from a metal-induced isomerization of 2-nitropropane to 1-nitropropane. Similar metal-induced isomerizations have been previously described.[8]

CID on $CoOH^+$ and $CoHNO_2^+$ formed from 1-nitropropane yielded the same spectra as those formed from nitromethane. The ion believed to be formed by either C–H or C–N insertion, $CoC_3H_5^+$, underwent CID to give three products, as shown in reactions 4–6. The major product at low collision energies was $CoC_3H_3^+$, while the major product at higher energies was Co^+. These results are characteristic for an allyl–Co^+ complex.[33]

$$CoC_3H_5^+ \xrightarrow{Ar} CoC_3H_3^+ + H_2 \qquad (4)$$

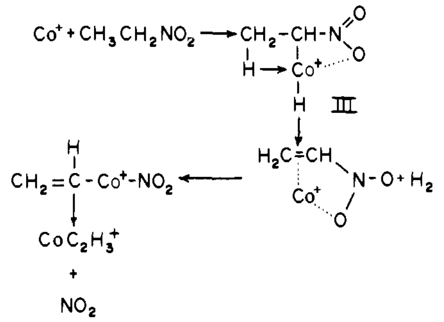
$$\longrightarrow CoCH_3^+ + C_2H_2 \qquad (5)$$

$$\longrightarrow Co^+ + C_3H_5 \qquad (6)$$

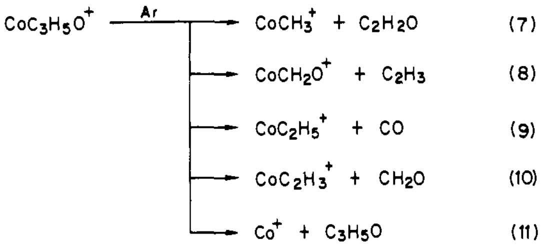
---

(32) Cassady, C. J.; Freiser, B. S. *J. Am. Chem. Soc.*, in press.

Scheme VII

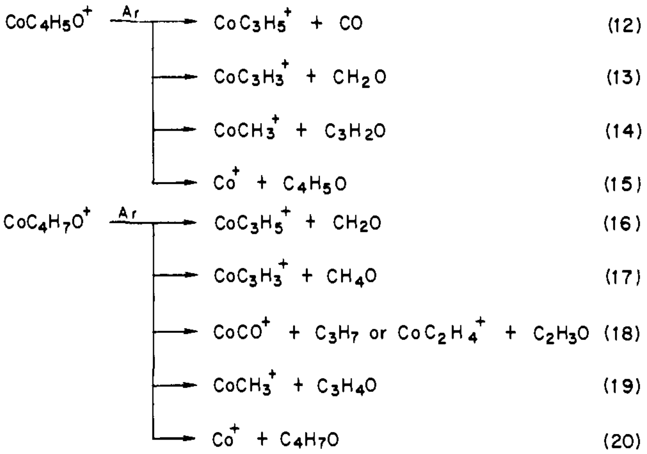


Collision-induced dissociation was also performed on $CoC_3H_5O^+$, an ion most probably resulting from the loss of H_2 and NO from intermediate E. This ion dissociates to form five products, reactions 7–11, with $CoCH_3^+$ being the major product.



$$CoC_3H_5O^+ \xrightarrow{Ar} CoCH_3^+ + C_2H_2O \qquad (7)$$
$$\rightarrow CoCH_2O^+ + C_2H_3 \qquad (8)$$
$$\rightarrow CoC_2H_5^+ + CO \qquad (9)$$
$$\rightarrow CoC_2H_3^+ + CH_2O \qquad (10)$$
$$\rightarrow Co^+ + C_3H_5O \qquad (11)$$

A comparison of these results to the CID data obtained from $CoC_4H_5O^+$ and $CoC_4H_7O^+$ formed from 1-butyl nitrite provides some useful information in determining how the loss of H_2 from structure E occurs. The dissociations that occur in the CID of $CoC_4H_5O^+$ and $CoC_4H_7O^+$ are given in reactions 12–15 and 16–20, respectively. In both cases the major low-energy product



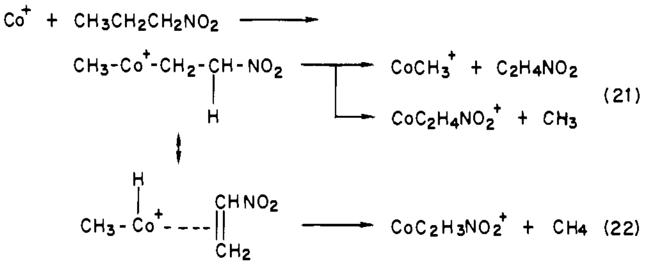
$$CoC_4H_5O^+ \xrightarrow{Ar} CoC_3H_5^+ + CO \qquad (12)$$
$$\rightarrow CoC_3H_3^+ + CH_2O \qquad (13)$$
$$\rightarrow CoCH_3^+ + C_3H_2O \qquad (14)$$
$$\rightarrow Co^+ + C_4H_5O \qquad (15)$$
$$CoC_4H_7O^+ \xrightarrow{Ar} CoC_3H_5^+ + CH_2O \qquad (16)$$
$$\rightarrow CoC_3H_3^+ + CH_4O \qquad (17)$$
$$\rightarrow CoCO^+ + C_3H_7 \text{ or } CoC_2H_4^+ + C_2H_3O \qquad (18)$$
$$\rightarrow CoCH_3^+ + C_3H_4O \qquad (19)$$
$$\rightarrow Co^+ + C_4H_7O \qquad (20)$$

is $CoC_3H_5^+$ and the two major high-energy products are $CoCH_3^+$ and Co^+. The low energy loss of CO from $CoC_4H_5O^+$ and CH_2O from $CoC_4H_7O^+$ suggests that both hydrogens involved in the β-H shifts to form H_2 come from the carbon α to the oxygen (see Scheme IV).

Nitrobutane. The reactions of Co^+ with three nitrobutane isomers are given in Table V. Products resulting from the proposed nitro-to-nitrite rearrangement are still present in these reactions; however, as the length of the carbon chain increases, C–C bond insertion products (structure II) become more prominent. Carbon–carbon insertion can account for 26% of the 1-nitrobutane products, 12% of the 2-nitrobutane products, and 6% of the 2-methyl-2-nitropropane products. In the case of 2-methyl-2-nitropropane, all of the C–C bonds are terminal. Co^+ has been found to be selective against insertion into terminal C–C bonds.[2a,5d] The only major difference in the C–C bond cleavage reactions of the three nitrobutanes with Co^+ is that $CoC_2H_5NO_2^+$ is a major product with 1-nitrobutane but only a minor product with 2-nitrobutane and 2-methyl-2-nitropropane. This product probably results from insertion of Co^+ into the middle C–C bond of the 1-butyl group followed by a β-H shift onto the Co^+ and the loss of C_2H_4. This cannot occur with a 2-methyl-2-propyl group without prior rearrangement of the alkyl chain.

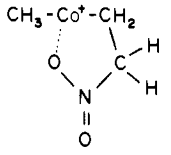
Insertion into the C–N bond (intermediate I) also appears to be a major process in the reactions of Co^+ with the nitrobutanes. In addition to the products $CoHNO_2^+$, $CoC_4H_5^+$, and $CoC_4H_6^+$ which can result from a C–N insertion similar to that shown in Scheme V, the major product in the reactions of each of the nitrobutanes with Co^+ is $C_4H_9^+$. This charge migration product is also seen to a limited extent in the reactions of Co^+ with the nitropropanes. The reaction leading to $C_4H_9^+$ is apparently not dissociative charge transfer, since this would be exceedingly endothermic (~60 kcal/mol for 1-nitrobutane). Thus, the neutral products are *not* Co and NO_2. The combination of CoO + NO as neutral products is also highly endothermic. If the product is $CoNO_2$, the results for 1-nitrobutane suggest $D(Co\text{–}NO_2) \geq 60$ kcal/mol and $\Delta H_f(CoNO_2) \leq 48$ kcal/mol.[34] The prominence of C–N insertion seen for 2-methyl-2-nitropropane may result from the fact that all C–C bonds are terminal, which hinders C–C bond insertion,[2a,5d] and the fact that steric factors may hinder a nitro-to-nitrite isomerization.

An interesting aspect of the reactions of Co^+ with nitropropane and nitrobutane is the loss of neutral radicals as opposed to stable neutral molecules. For example, in the reaction of 1-nitropropane with Co^+, following insertion into the terminal C–C bond, a β-shift and loss of CH_4 (reaction 22) would be expected. However,



$$Co^+ + CH_3CH_2CH_2NO_2 \longrightarrow CH_3\text{-}Co^+\text{-}CH_2\text{-}\underset{H}{CH}\text{-}NO_2 \longrightarrow CoCH_3^+ + C_2H_4NO_2;\ CoC_2H_4NO_2^+ + CH_3 \qquad (21)$$
$$CH_3\text{-}\overset{H}{Co^+}\text{---}\|(CHNO_2, CH_2) \longrightarrow CoC_2H_3NO_2^+ + CH_4 \qquad (22)$$

reaction 21 is actually observed. One possible explanation for the lack of this β-H shift is that, upon insertion of Co^+ into the C–C bond, coordination may also occur to an oxygen of the nitro group, producing a stable complex in which the β-H's are *geometrically inaccessible* to the metal.



Subsequent Reactions of the Primary Products. The primary products for the reactions of Co^+ and nitroalkanes react further with the neutral nitroalkanes. Up to five subsequent reactions may occur after the formation of the primary products. To illustrate the complexity of these reaction sequences, Table VI lists all of the reactions of the primary products for the simplest case, nitromethane.

Some interesting observations can be made from the data in Table VI. For example, with the $CoOCH_3^+$ ion the only secondary reaction observed is (23), which involves displacement of CH_2O. This supports the conclusion drawn from the CID results that this species has a $Co(H)(CH_2O)^+$ structure.

$$CoOCH_3^+ + CH_3NO_2 \rightarrow Co(H)(CH_3NO_2)^+ + CH_2O \qquad (23)$$

---

(33) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 1159–1160.

(34) All values calculated from data obtained in ref 30 except D(Co–O) = 87 ± 4 kcal/mol which was obtained from Grimley et al. and Smoes et al.: (a) Grimley, R. T.; Burns, R. P.; Inghram, M. G. *J. Chem. Phys.* **1966**, *45*, 4158. (b) Smoes, S.; Mandy, F.; VanderAvwera-Mahieu, A.; Drowart, J. *Bull. Soc. Chim. Belg.* **1972**, *81*, 45.

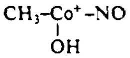
It is also interesting that the other major nitromethane products (CoO^+ and $CoOH^+$) do not react with nitromethane to form "nitrite-like" rearrangement products. Other than reactions to form $CoOP^+$ and $CoOHP^+$ ($P = CH_3NO_2$), the only reactions of these ions involve either the gain of H_2O (loss of HCNO) or the loss of H_2O, OH, or O. These products could result from an initial insertion of $CoOH^+$ and CoO^+ into the N–O bond of nitromethane. Again, the loss of radicals, as opposed to stable neutral molecules, is observed in many of the subsequent reactions of the primary products.

Many of the subsequent reactions involve formal extraction of O, OH, or H_2O from nitromethane. Even the $CoHP^+$ ion ($P = CH_3NO_2$) formed from reaction 23 rapidly reacts with nitromethane to form $Co(OH)P^+$. The ion $Co(OH)P^+$ also comes from several other sources and dominates the mass spectrum after trapping times of about 1 s. This ion then reacts away slowly with the dominant process being the loss of H_2O. The loss of OH from all of the ions is less favorable than the loss of H_2O, while the loss of O is even more unfavorable than the loss of OH.

Collision-induced dissociation experiments were performed on the two major secondary reaction products of the nitromethane reactions, $CoHP^+$ and $Co(OH)P^+$. For $CoHP^+$, reactions 24–29 were observed, with reaction 26 dominating at low energy and reaction 24 dominating at higher energies. Reactions 27–29 are

$$\begin{aligned} Co(H)(CH_3NO_2)^+ &\xrightarrow{Ar} Co^+ + CH_4NO_2 && (24)\\ &\longrightarrow CoH^+ + CH_3NO_2 && (25)\\ &\longrightarrow CoOH^+ + CH_3NO && (26)\\ &\longrightarrow CoNO^+ + CH_4O && (27)\\ &\longrightarrow CoCH_4O^+ + NO && (28)\\ &\longrightarrow CoHNO_2^+ + CH_3 && (29) \end{aligned}$$

only minor pathways at all energies. Although these CID data do not confirm a structure for the ion, they do leave open the possibility that $CoHP^+$ has a structure such as



$$CH_3\text{–}\underset{\displaystyle OH}{\underset{|}{Co^+}}\text{–}NO$$

This structure is also consistent with the further reactions of the $CoHP^+$ ion (Table VI), which imply the presence of an OH group in the ion.

For the dissociation of the major secondary product, $Co(OH)P^+$, three products were observed, as shown in reactions 30–32. By

$$\begin{aligned} Co(OH)(CH_3NO_2)^+ &\xrightarrow{Ar} CoOH^+ + CH_3NO_2 && (30)\\ &\longrightarrow Co(OH)_2^+ + CH_2NO && (31)\\ &\longrightarrow CoCH_2NO_2^+ + H_2O && (32) \end{aligned}$$

far the dominant product at all energies was $CoOH^+$, and this is an indication of the strength of the Co^+–OH bond.

The subsequent reactions observed with nitroethane parallel those discussed above for nitromethane (with the exception of $CoOH^+$, discussed below). The ion $Co(OH)P^+$ ($P = CH_3CH_2NO_2$) is still dominant at trapping times around 1 s. Other major ions are CoP^+, $Co(NO)P^+$, $Co(C_2H_4NO_2)P^+$, CoP_2^+, $Co(OH)P_2^+$, and $Co(NO)P^+$. At trapping times of 5 s and longer $Co(C_2H_4NO_2)P_2^+$ and CoP_3^+ are essentially the only ions present. The reactions of the ions $CoC_2H_3^+$ and $CoCH_2NO_2^+$, which do not have analogues in the nitromethane reactions, are given in (33) and (34). Reaction 35 gives the subsequent reactions of $CoHNO_2^+$ which is only a minor product in the nitromethane reactions.

$$\begin{aligned} CoC_2H_3^+ + CH_3CH_2NO_2 &\xrightarrow{50\%} CoP^+ + C_2H_3\\ &\xrightarrow{50\%} CoHP^+ + C_2H_2 && (33) \end{aligned}$$

$$\begin{aligned} CoCH_2NO_2^+ + CH_3CH_2NO_2 &\xrightarrow{20\%} Co(OH)P^+ + CHNO\\ &\xrightarrow{80\%} Co(NO)P^+ + CH_2O && (34) \end{aligned}$$

$$\begin{aligned} CoHNO_2^+ + CH_3CH_2NO_2 &\xrightarrow{50\%} CoP^+ + HNO_2\\ &\xrightarrow{30\%} Co(OH)P^+ + NO && (35)\\ &\xrightarrow{20\%} Co(NO)P^+ + OH \end{aligned}$$

For the $CoOH^+$ ions formed from nitroethane and the large nitroalkanes, only approximately 20% of the secondary reaction products can be obtained from N–O insertion similar to that observed for the reaction of $CoOH^+$ with nitromethane. Instead, the major reaction pathway for the reaction of $CoOH^+$ with larger nitroalkanes is the formation of alkyl ions, apparently the result of insertion into the C–N bond. These ions then react rapidly with the nitroalkane to form protonated nitroalkane ions, as shown in reactions 36 and 37. In reaction 36, the neutrals formed are

$$CoOH^+ + CH_3CH_2NO_2 \rightarrow C_2H_5^+ + CoHNO_3 \quad (36)$$

$$C_2H_5^+ + CH_3CH_2NO_2 \rightarrow CH_3CH_2NO_2H^+ + C_2H_4 \quad (37)$$

not Co and HNO_3 since this reaction would be 93 kcal/mol endothermic.[35] Due to the lack of heat of formation values, no other thermodynamic calculations could be made regarding other possible neutral loss products. The ion $CoCH_3^+$ is also observed to react with larger nitroalkanes to form primarily alkyl ions, while several other ions do so to a limited extent.

Collision-induced dissociation experiments were carried out on CoP^+ and $Co(OH)P^+$ (P = nitroethane). For the CID of CoP^+, the two major products were $CoOH^+$ and Co^+, while $CoC_2H_3^+$, $CoNO^+$, $CoHNO_2^+$, and $CoC_2H_4O^+$ were minor products. This formation of $CoOH^+$ again indicates the strength of the Co^+–OH bond. While the CID spectrum provides little definitive structural information, the fragments do resemble the primary reaction products of Co^+ with nitroethane. CID spectra of $Co(OH)P^+$ from nitroethane yield the major products $Co(OH)_2^+$ and $Co(OH)_2(NO)^+$ and the minor products Co^+, $CoNO^+$, $Co(C_2H_3)(OH)^+$, $CoCH_3^+$, $CoOH^+$, $CoHNO_2^+$, $CoC_2H_5O^+$, $CoC_2H_4NO_2^+$, and CoP^+.

The further reactions of the primary products of the nitropropane and nitrobutane reactions with the neutral are again similar to those observed for nitromethane. The same major reaction channels occur. CID experiments on secondary ions from nitropropane gave an assortment of products similar to those in the nitroethane CID experiments.

Ligand Effects. Table VII lists the products observed for the reactions of the electron-impact fragments of $Co(CO)_3NO$ with the series of nitroalkanes and 1-butyl nitrite. The results in Table VII can be evaluated in a number of ways to supply information concerning "ligand effects". These include (1) identification of changes in the chemistry of a metal center when *one* ligand is added (i.e., compare the chemistry of Co^+ with CoL^+), (2) identification of "vertical trends" in the table (i.e., mechanistic changes due to the *number* of ligands on the metal), and (3) identification of "horizontal trends" (i.e., changes in the chemistry related to increases in the alkyl chain length of the organic reactant).

General Trends

Small Nitroalkanes. The reactions observed for the C_1–C_3 nitroalkanes are typical for metal-containing ions, ML_n^+, in their chemistry with monofunctional organic compounds in the following ways: (1) The bare metal ion reacts to form the largest variety of products.[8] (2) The organic rearrangement processes observed for $CoCO^+$ are similar to those observed for Co^+.[1a,4,8,13] (3) In direct contrast with the carbonyl ligand, an NO ligand *deactivates* the metal center[1a,4,8,13] (note that no products are observed for

---

[35] Calculated from thermochemical information obtained in ref 30 and 32.

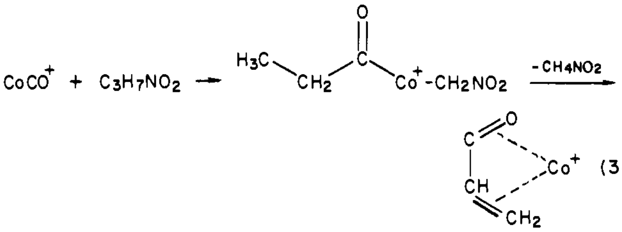
$CoNO^+$ except with 1-butyl nitrite). (4) As the *number* of ligands present on the metal ion increases, ligand-substitution reactions predominate.[8] In substitution processes, nitroalkanes displace two carbonyls from $Co(CO)_3NO^+$, while 1-butyl nitrite displaces up to three carbonyls. The implications is that $D(Co^+{-}RONO) > D(Co^+{-}RNO_2)$.

Larger Nitroalkanes. In contrast to the smaller nitroalkanes, the larger nitroalkanes react with CoL_n^+ not only by substitution but by bond cleavage processes. In this trend, butyl nitrite bond cleavages/rearrangements occur for all CoL_n^+ ions, even $Co(CO)_{2,3}NO^+$. Such reactivity is typically observed for multifunctional organic molecules.[1a,13,14]

Also, a "horizontal trend" can be seen. As the length of the alkyl chain increases ($C_1 \rightarrow C_4$), more reactions involving C–C insertions (intermediate II) are observed. Previous work suggests that the probability of reactions involving intermediate I should be greater for secondary and tertiary nitroalkanes than for primary nitroalkanes.[2a] This is apparently the case as shown in Tables V and VII.

The reactions discussed in this work tend to involve intermediates in which two orbitals are required on the metal (e.g., reaction 21) or reactions which require three orbitals on the metal (e.g., reactions 1 and 22). It is no surpise that such reaction products disappear when ligands are added to the metal. Reactions requiring three metal orbitals occur for Co^+, in some cases for $CoCO^+$, and rarely for the other metal-containing species in Table VII. Reactions requiring two orbitals on the metal (as opposed to three orbitals) seem to dominate (in addition to substitution reactions) when the reactant metal center has two or more ligands present, as would be expected.

Nitropropanes. There are many similarities in the reactions observed for Co^+ and $CoCO^+$ with nitropropane, and some major differences as well. The products $CoHNO_2^+$ (loss of C_3H_6 through intermediate I) and $CoC_3H_7O^+$ are formed from both Co^+ and $CoCO^+$. Both Co^+ and $CoCO^+$ insert into C–C bonds; however, $CoCO^+$ preferentially attacks the $C_2H_5{-}CH_2NO_2$ bond. Following this insertion, Co^+ *loses* the C_2 fragment while $CoCO^+$ *retains* the C_2 fragment. This may imply active participation in the reaction by the carbonyl group leading *not* to a type II intermediate but to the $CoCO^+$ insertion intermediate shown in (38).[8] There are a number of possible neutral losses, (CH_3NO_2 + H) or (CH_2NO_2 + H_2), which would generate the butadiene-like metal complex. Thus, one effect of the CO ligand appears to be an active involvement of the ligand in the reaction.[8]



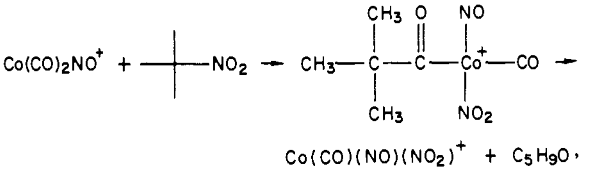
(38)

In most cases, CO is not involved in the reaction directly but appears to be a "spectator" on the metal.[13b] Even spectator ligands can influence product distributions, in cases where cleavage of the $M^+{-}CO$ bond competes with processes involving eliminations from the organic species. An example of this is seen in the case of 2-nitropropane. The Co^+ ion reacts to form $CoC_3H_5O^+$ by elimination of NO and H_2. This reaction also occurs for $CoCO^+$; however, there appears to be two possible processes following NO elimination: loss of H_2 from C_3H_7O or loss of CO from the metal. In the case of $CoCO^+$ with 2-nitropropane, the loss of NO followed by the loss of CO (to form $CoC_3H_7O^+$) predominates; however, H_2 vs. CO eliminations frequently appear to be competitive processes.

Nitrobutanes. The outstanding feature in Table VII regarding the nitrobutanes is the "vertical trends"—i.e., changes in the chemistry of the metal center as the *number* of ligands on the metal increases, in particular for 2-nitrobutane and 2-methyl-2-nitropropane.

For 2-nitrobutane, the predominant reaction intermediate changes as the number of ligands increases. Co^+ reacts through intermediates I, II, IV, and E. With one or two carbonyls present on the metal, reactions are observed via intermediates analogous to I, II, and E; $CoCONO^+$ only induces organic bond cleavage through an intermediate analogous to II. Note that only *one* C–C bond is attacked by $CoCONO^+$. This may correspond to attack of the weakest bond (since in the corresponding alkane, isopentane, the weakest C–C bond[36] is the $C_2H_5{-}C_3H_7$ bond). Presumably, there are not a sufficient number of orbitals available on the metal following C–C insertion of $CoCONO^+$ to assist in a β-H shift; thus, $C_2H_5\cdot$ is lost. Similar studies with amines show analogous results.[8]

The 2-methyl-2-nitropropane reactions also show a variety of interesting changes as the number of ligands increases. Intermediate structures I, II, III, and E lead to the products observed for 2-methyl-2-nitropropane. Structures II and III predominate when more ligands are present on the metal (e.g., $Co(CO)_2^+$). Insertion into the $C{-}NO_2$ bond (structure I) appears to be inhibited due to steric effects of the ligands present on the metal and the bulky 2-methyl-2-propyl group. Thus, the remaining options for the metal are insertion *only* into bonds such as C–C and C–H. The loss of H (from C–H insertion) is more prominent when the number of ligands present on the metal ion increases. The reaction of $Co(CO)_2NO^+$ produces $CoCONO(NO_2)^+$ with a loss of CO and C_4H_9. At first, one may predict a Co^+ insertion into the C–N bond (structure I) as the intermediate. This intermediate is not possible for several reasons. The cobalt ion already has three ligands present, which does not leave enough empty metal orbitals for metal insertion to occur. If the insertion *did* occur, there are many β-H's available to shift and produce a strong HNO_2 ligand. No products, however, are observed resulting from a β-H shift. A possible intermediate structure leading to the product ion $CoCONO(NO_2)^+$ is shown in the structure below.



(39)

The suggested intermediate corresponds to insertion of the $CoCO^+$ group into the $C{-}NO_2$ bond of the nitroalkane. In this intermediate there are no H atoms which are on a carbon which is β to the metal that could shift to produce the HNO_2 ligand. Also, there are no empty orbitals on the metal to assist in any rearrangement of the molecule. Thus, the only product ion observed is $CoCONO(NO_2)^+$ with the loss of C_4H_9CO as one ligand.

In summary, several typical ligand effects have been observed in reactions of nitroalkanes. Products which require three or more empty orbitals on the metal are seen to be repressed or disappear as the number of ligands on the metal increases. Reactions occurring at branched sites are favored over unbranched sites. Steric effects were observed with 2-methyl-2-nitropropane when ligands were added to the metal ion. Intermediates in which the ligands must be actively involved in the insertion are seen. Also, when a ligand is present on the metal, several options for reaction mechanisms (such as competition between loss of CO and H_2) are available.

Acknowledgement is made by C.J.C. and B.S.F. to the Division of Chemical Sciences, Office of Basic Energy Sciences, United States Department of Energy (DE-AC02-80ER10689), for supporting this research and to the National Science Foundation (CHE-8002685) for providing funds to purchase the FTMS. S.W.M. and J.A. acknowledge the National Science Foundation

---

(36) Bond strengths in isopentane may be calculated from data obtained in Cox and Pilcher and McMillen and Golden: (a) Cox, J. D.; Pilcher, G. "Thermochemsitry of Organic and Organometallic Compounds"; Academic Press: New York, 1970. (b) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

J. Am. Chem. Soc. **1984**, *106*, 6135–6139

(CHE-8023704) and the Dow Chemical Company Foundation for support of this work. Also, one of us (C.J.C.) thanks Phillips Petroleum for Fellowship Support.

Registry No. CH_3NO_2, 75-52-5; CH_3ONO, 624-91-9; $C_2H_5NO_2$, 79-24-3; $C_3H_7NO_2$, 108-03-2; 1-$C_4H_9NO_2$, 627-05-4; 1-C_4H_9ONO, 544-16-1; 2-$C_3H_7NO_2$, 79-46-9; 2-$C_4H_9NO_2$, 600-24-8; 2-$CH_3CCH_3NO_2CH_3$, 594-70-7; Co^+, 16610-75-6; $CoCO^+$, 28963-35-1; $Co(CO)_2{}^+$, 28963-34-0; $CoNO^+$, 87616-10-2; $CoCONO^+$, 61816-95-3; $Co(CO)_2NO^+$, 61816-96-4; $Co(CO)_3NO^+$, 52309-13-4.

Ion–Solvent Molecule Interactions in the Gas Phase. The Potassium Ion and Me_2SO, DMA, DMF, and Acetone

Jan Sunner and Paul Kebarle*

Contribution from the Chemistry Department, University of Alberta, Edmonton, Alberta, Canada T6G 2G2. *Received January 23, 1984*

Abstract: Measurements of the gas-phase equilibria $K^+(L)_{n-1} + L = K^+(L)_n$ where K^+ is the potassium ion and L = dimethyl sulfoxide, *N,N*-dimethylacetamide, *N,N*-dimethylformamide, and acetone with a high-pressure mass spectrometer lead to the corresponding thermomechemical data $\Delta H^\circ_{n-1,n}$, $\Delta G^\circ_{n-1,n}$, and $\Delta S^\circ_{n-1,n}$. The observed stability order of the 1:1 complexes K^+L is the following: Me_2SO (25), DMA (24), DMF (23), $MeOC_2H_4OMe$ (23), $NH_2C_2H_4NH_2$ (19), Me_2CO (19), MeCN (18), $C_6H_5NH_2$ (16), Et_2O (15), pyridine (15), Me_2O (13), Me_3N (13), $MeNH_2$ (13), C_6H_6 (12), NH_3 (12), H_2O (11), where the numbers give the value for $-\Delta G^\circ_{0,1}$ in kcal/mol. Ab initio (4–31G) calculations were performed for the complex K^+Me_2SO. These show that the bonding is largely electrostatic. The major contribution to this bonding is due to the large S–O bond dipole. K^+ lines up with the S–O bond (dipole) in the most stable structure. The higher solvation $(n - 1,n)$ steps for Me_2SO, DMA, and DMF are quite similar. These compounds form a much more strongly bonded inner shell with K^+ than H_2O; however, the solvation of the inner-shell cluster $K^+(L)_i$ in these solvents is much less favorable than that for $K^+(H_2O)_i$ in water. This compensating effect leads to only slightly higher single-ion solvation K^+ energies in Me_2SO, DMA, and DMF than in H_2O. The gas-phase equilibria measurements for DMA and DMF led to somewhat curved van't Hoff plots for the higher $(n - 1,n)$ equilibria. A theoretical analysis shows that this is probably due to unimolecular dissociation of the corresponding clusters in the vacuum of the mass analysis system. This effect reduces the accuracy of the data.

Measurements of the gas-phase equilibria 1 and 2 for M^+ = alkali cations and X^- = halide anions and the solvent molecules L = H_2O and acetonitrile were reported earlier from this laboratory.[1-4] Measurements of the equilibrium constants $K_{n-1,n}$ for

$$M^+L_n{}^{-1} + L = M^+L_n \qquad (1)$$

$$X^-L_{n-1} + L = X^-L_n \qquad (2)$$

(1) and (2) at different temperatures with a pulsed electron beam high pressure mass spectrometer lead via van't Hoff plots to the corresponding stepwise solvation energies $\Delta H^\circ_{n-1,n}$ and $\Delta G^\circ_{n-1,n}$. These data provide useful insights into the solvation of the above ions in liquid solutions of the solvents.

Dimethyl sulfoxide (Me_2SO), *N,N*-dimethylacetamide (DMA), *N,N*-dimethylformamide (DMF), and acetone are important dipolar aprotic solvents much used in laboratory and industrial synthetic practice. The study of these solvents represents a natural extension of our previous work. The $\Delta G^\circ_{0,1}$ and the $\Delta H^\circ_{0,1}$ energies represent the binding energies in the 1:1 complexes between the ion K^+ and the ligand L. Comparison with data for various other ligands measured earlier[5,6] establishes useful Lewis basicity orders in the absence of a solvent. In this respect DMA and DMF are particularly interesting since they contain elements of peptide-type bonding which is of interest in biophysical chemistry[7] and design of ion-selective electrodes.[8]

The present paper deals only with the results for positive ions. The companion paper[9] which gives results for the negative halide ions deals also with the relative solvation of positive and negative ions in protic and aprotic solvents and the synthetic utility of dipolar aprotic solvents for reactions involving negative ions.

Experimental Section

Apparatus. The apparatus was essentially the same as that used earlier.[3] The potassium ions were produced by thermionic emission from a filament painted with potassium salt. The filament is inside the ion source which contains gas, generally in the 0.5–3-torr range. The gas may be the neat solvent vapor or a mixture of a major, buffer gas (CH_4) containing a small fraction of the solvent vapor. The ions drift under the influence of electric fields into the field-free reaction chamber. At the bottom of the reaction chamber there is a narrow slit ~15 μm by 1 mm through which gas and ions escape into the evacuated mass analysis region. The ions are separated with a magnetic field and detected with an ion-counting system.

Results and Effects due to Unimolecular Decomposition of Ions. Equilibrium constants were determined from expression 3 where I_n are the detected counts/time of ions, K^+L_n, and P_L is the known partial pressure of the solvent vapor. The equilibrium constants were measured

$$K_{n-1,n} = \frac{I_n}{I_{n-1}} P_L \qquad (3)$$

at different constant temperatures. For any given temperature, measurements at different ligand pressures were performed. Typically the pressure ratio of CH_4-to-ligand vapor was equal to 10, and the pressure of the ligand was changed from 0.05 to 0.3 torr. At very low ligand concentrations the observed $K_{n-1,n}$ tended to decrease, particularly for low *n* cluster equilibria. In special experiments the K^+ supply to the reaction chamber was pulsed, so that the residence time of the ions could be determined. These experiments showed that the low-pressure falloff of the equilibrium constants was due to slow kinetics in the approach to equilibrium. Selecting only ions with long residence time one observed no falloff for $K_{n-1,n}$ at low P_L. Typical results for the pulsed and unpulsed experiments are given in Figure 1. A gradual falloff of *K* with an

---

[1] Dzidic, I.; Kebarle, P. *J. Phys. Chem.* **1970**, *74*, 1466.

[2] Arshadi, M.; Yamdagni, R.; Kebarle, P. *J. Phys. Chem.* **1970**, *74*, 1975.

[3] Davidson, W. R.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 6125.

[4] Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1971**, *94*, 2940.

[5] Davidson, W. R.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 6133.

[6] Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445.

[7] (a) Rao, C. N. R. In "Metal-Ligand Interactions in Organic Chemistry and Biochemistry"; Pullman, B., Goldblum, N., Eds.; B. Reidel Publishing: Holand, **1977**. (b) Balasubramanian, D.; Mishra, B. C., ref 7a. (c) Noelken, M. E. *Biochemistry*, **1970**, *9*, 4122. Lothan, N. *J. Phys. Chem.* **1973**, *77*, 242. (d) Truter, M. R. "Structure and Bonding"; Dunitz, J. D., et al., Eds.; Springer: New York, 1973; Vol. 16.

[8] Corongiu, G.; Clementi, E.; Pretch, E.; Simon, W. *J. Chem. Phys.* **1979**, *70*, 1266.

[9] Magnera, T. L.; Caldwell, G.; Sunner, G.; Ikuta, J.; Kebarle, P. *J. Am. Chem. Soc.*, following paper in this issue.

0002-7863/84/1506-6135$01.50/0