

Gas-Phase Reactions of Transition-Metal Ions with Methyl Nitrite and Nitromethane

C. J. Cassady and B. S. Freiser*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. Received July 9, 1984

Abstract: The gas-phase reactions of Fe^+ , Co^+ , Ni^+ , Cu^+ , Rh^+ , Pd^+ , and Ag^+ with methyl nitrite and nitromethane were studied. The methyl nitrite chemistry is dominated by insertion of the metal ion into the weak $\text{CH}_3\text{O}-\text{NO}$ bond. This allows an opportunity to study differences in metal ion reactivity following formation of a common reaction intermediate, as opposed to differences due to initial bond insertion. Fe^+ , Co^+ , and Ni^+ give greater than 90% loss of NO, while Rh^+ and Pd^+ show a slight preference for NO. The large loss of NO is surprising since ligand displacement reactions give a relative binding order for Fe^+ , Co^+ , Ni^+ , and Rh^+ of $\text{CO} < \text{CH}_2\text{O} < \text{C}_2\text{H}_4 < \text{NO}$. This demonstrates that the ligand retained in a gas-phase ion-molecule reaction is not necessarily the species that forms the strongest bond to the metal ion in the absence of other ligands. Ligand displacement reactions bracket $D(\text{Fe}^+-\text{C}_2\text{H}_4) = 34 \pm 2$ kcal/mol $< D(\text{Fe}^+-\text{NO}) < D(\text{Fe}^+-\text{H}) = 58 \pm 2$ kcal/mol and $D(\text{Co}^+-\text{C}_2\text{H}_4) = 37 \pm 2$ kcal/mol $< D(\text{Co}^+-\text{NO}) < D(\text{Co}^+-\text{H}) = 52 \pm 2$ kcal/mol and also yield values of $D(\text{Ni}^+-\text{NO}) = 43 \pm 5$ kcal/mol and $D(\text{Rh}^+-\text{NO}) = 40 \pm 5$ kcal/mol. For Cu^+ and Ag^+ , exclusive loss of NO is observed, while ligand displacement reactions give a relative binding order of $\text{NO} < \text{CO} \lesssim \text{CH}_2\text{O} < \text{C}_2\text{H}_4$ for Cu^+ . Only Fe^+ , Co^+ , Rh^+ , and Pd^+ react with nitromethane. The majority of the nitromethane products appear to result from a metal-induced nitro-to-nitrite isomerization. For Fe^+ and Co^+ , a second mechanism which apparently involves the formation of a dioxygen-metal species is also observed. Collision-induced dissociation and secondary ion-molecule reactions with the neutral were used to probe ion structures providing insight into reaction mechanisms.

The reactions of gas-phase atomic metal ions with organic compounds have been the focus of many recent investigations involving ion cyclotron resonance spectrometry¹⁻⁴ and ion beam techniques⁵⁻⁷. These studies have provided fundamental information on the intrinsic reactivities of metal ions in the absence of complicating solvent effects. The transition-metal ions studied to date have been found to have reactivities which, as expected, are dependent on their electronic structure and, therefore, on their position in the periodic table. Studies involving alkanes have shown, for example, that for the first-row transition series, Ti^{+8} and V^{+9} react to cleave C-H bonds, while Sc^{+10} , $\text{Fe}^{+5,8,11,12}$, $\text{Co}^{+5,6,12}$ and $\text{Ni}^{+5,12-14}$ cleave both C-H and C-C bonds and Mn^{+7} , $\text{Cr}^{+7,15}$ and Cu^{+15} are unreactive. In addition to these broad generalizations, more subtle differences in metal ion reactivities also exist in moving across the periodic table.

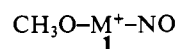
In an expansion of our previous study of the reactions of Co^+ with nitroalkanes and methyl nitrite,¹⁶ we present in this paper the results of a broader study of the reactions of nitromethane and methyl nitrite with a series of metal ions (Fe^+ , Co^+ , Ni^+ , Cu^+ , Rh^+ , Pd^+ , and Ag^+). Methyl nitrite is unique because it has a

Table I. Product Distributions for the Primary Reactions of Atomic Metal Ions with Methyl Nitrite

ion	products	relative abundance						
		Fe^+	Co^{+a}	Ni^+	Cu^+	Rh^+	Pd^+	Ag^+
MH^+	CH_2ONO	19	15	9	0	10	12	0
MCO^+	HNO , H_2	0	0	0	0	5	0	0
MOCH^+	NO , H_2	4	5	41	0	32	22	0
MOCH_2^+	HNO	5	5	8	86	6	11	100
MNO^+	OCH_3	2	5	9	0	10	45	0
MOCH_3^+	NO	70	70	33	14	0	5	0
MHNO^+	CH_2O	0	0	0	0	37	5	0

^a From ref 16.

very weak $\text{CH}_3\text{O}-\text{NO}$ bond (42 kcal/mol¹⁷) which dominates its chemistry both in solution and in the gas phase. Accordingly, all of the metal ions involved in this study should react by initial oxidative addition into this bond to form intermediate I. This



allows an opportunity to study differences in metal ion reactivity following formation of a common reaction intermediate, as opposed to differences due to the location of initial bond insertion.

The reactions of the seven metal ions with nitromethane, an isomer of methyl nitrite, are also presented in this paper. Since nitromethane contains no exceptionally weak N-O bond, the metal ions react in a dramatically different manner with this compound than they do with methyl nitrite. Nevertheless, the methyl nitrite chemistry provides insight into the mechanisms involved for nitromethane. The metal ions studied are all late transition metals, but they show interesting differences in reactivity going across a row or down a column in the periodic table.

Experimental Section

All experiments were performed with a prototype Nicolet FTMS-1000 which has previously been described in detail.¹⁸ 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 been

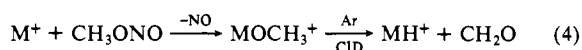
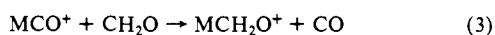
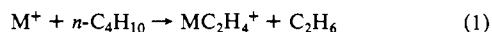
- (1) (a) Jacobson, D. B.; Freiser, B. S. *Organometallics* **1984**, *3*, 513. (b) Jacobson, D. B.; Byrd, G. D.; Freiser, B. S. *Inorg. Chem.* **1984**, *23*, 553. (c) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 1159.
- (2) Wronka, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 67.
- (3) Radecki, B. D.; Allison, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 946.
- (4) Uppal, J. S.; Staley, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3794.
- (5) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963.
- (6) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784.
- (7) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6501.
- (8) Byrd, G. D.; Burnier, R. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 3565.
- (9) Carlin, T. J.; Jackson, T. C.; Freiser, B. S. *J. Am. Chem. Soc.*, to be submitted for publication.
- (10) Tolbert, M. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 8117.
- (11) Allison, J.; Freas, R. B.; Ridge, D. B. *J. Am. Chem. Soc.* **1979**, *101*, 1332.
- (12) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5197.
- (13) Halle, L. F.; Hourlet, R.; Kappes, M. M.; Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6293.
- (14) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 736.
- (15) Byrd, G. D., Ph.D. Thesis, Purdue University, 1982.
- (16) Cassady, C. J.; Freiser, B. S.; McElvany, S. W.; Allison, J. J. *Am. Chem. Soc.* **1984**, *106*, 6125.

modified by drilling a 0.25-in.-diameter hole in one of the transmitter plates to allow irradiation by various light sources. Metal ions were generated by focusing the frequency doubled beam (530 nm) of a Quanta Ray Nd:YAG laser onto high-purity metal foils which were supported by the opposite transmitter plate. Details of the laser ionization experiment have been described elsewhere.^{19,20} Experimental conditions were adjusted to minimize complications due to excited-state metal ions.²¹ We cannot rule out the possibility, however, that some of the less abundant products arise from excited-state species.

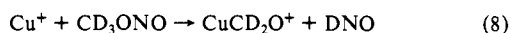
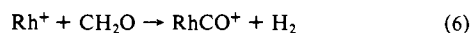
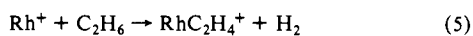
The distributions of primary product ions listed in Tables I and III are reproducible to $\pm 10\%$ absolute. The empirical formulas of all products were confirmed by using both deuterated and undeuterated reactants. In cases where a product has the same nominal mass as another product with both deuterated and undeuterated reagents (i.e., with CH_3ONO , CoNO^+ and CoOCH_2^+ are isobars, while with CD_3ONO , CoNO^+ and CoOCD^+ are isobars), the relative abundances of the products were determined by comparing peak intensities in both sets of data. The nature of the neutrals lost in the reactions listed in the tables and throughout the text is often unknown and structures other than those given may also be possible. Product distributions of subsequent reactions of the primary reaction products were determined by using swept double resonance ejection techniques²² to isolate the ions of interest.

Collision-induced dissociation (CID) experiments using FTMS have been described previously.^{12,14} Sample pressures were on the order of 1×10^{-7} torr, and the argon collision gas was on the order of 5×10^{-6} torr. Pressures were monitored with a Bayard-Alpert ionization gauge. The collision energy can be varied 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.²³

In ligand displacement experiments, ML^+ ($\text{L} = \text{CO}, \text{CH}_2\text{O}, \text{C}_2\text{H}_4$, and H) was generated by addition of a reagent gas into the vacuum chamber through a General Valve Corp. Series 9 pulsed solenoid valve.²⁴ The valve pulse, which was concurrent with a laser pulse to generate metal ions, filled the vacuum chamber to a maximum pressure of 10^{-5} torr and was pumped away by a high-speed 5-in. diffusion pump in ~ 250 ms. Swept double resonance techniques²² were then used to isolate the ML^+ ions, which were allowed to react with a static pressure of a second reagent gas ($\text{NO}, \text{CO}, \text{C}_2\text{H}_4$, or CH_2O) in the absence of complicating reactions with the initial reagent. For Fe^+, Co^+ , and Ni^+ , initial ML^+ species used in ligand displacement reactions were generated by reactions 1,¹² 2,^{15,25} 3,²⁶ and 4.²⁷ Initial RhL^+ species were generated via reactions



5,¹⁹ 6,²⁶ and 7,²⁶ while for Cu^+ displacement reactions, CuCD_2O^+ was formed by reaction 8.²⁶



Methyl nitrite and methyl nitrite- d_3 were prepared according to the literature.²⁸ All other chemicals were high-purity commercial samples

(19) Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 5944.

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

(21) Cassady, C. J.; Wise, M. B.; Freiser, B. S. *Int. J. Mass Spectrom Ion Phys.*, to be submitted for publication.

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

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(24) A detailed description of pulsed valve introduction of reagent gases in conjunction with FTMS can be found in: Carlin, T. J.; Freiser, B. S. *Anal. Chem.* **1983**, *55*, 571.

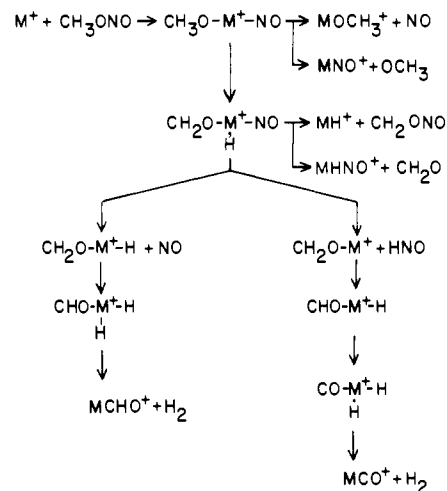
(25) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360.

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

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

Scheme I

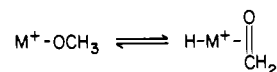


which were used as supplied except for multiple freeze-pump-thaw cycles to remove noncondensable gases.

Results and Discussion

Methyl Nitrite Primary Reactions. The primary reaction products observed for methyl nitrite are given in Table I. As expected, the first step in these reactions appears to be oxidative addition of the metal ion into the weak $\text{CH}_3\text{O}-\text{NO}$ bond to form intermediate **1**. Subsequent β -hydride shifts onto the metal, followed by elimination of various ligands, can explain all of the primary reaction products. While the same metal-insertion mechanism outlined in Scheme I can be invoked to explain the reactions of all of the metal ions with methyl nitrite, the final products vary dramatically, as is evident in Table I.

The structures of the product ions were probed by collision-induced dissociation and H/D exchange reactions. Formation of MH^+ and M^+ as the only CID product ions and observation of one H/D exchange with D_2 indicates that NiCOH^+ , RhCOH^+ , and PdCOH^+ have metal-hydride structures, $\text{M}(\text{CO})(\text{H})^+$, or are composed of $\text{M}(\text{COH})^+$ and $\text{M}(\text{CO})(\text{H})^+$ species in equilibrium. Since MCO^+ does not form as a CID product, this indicates that $D(\text{M}^+-\text{H}) > D(\text{M}^+-\text{CO})$ for $\text{M} = \text{Ni},^{29} \text{Rh}$, and $\text{Pd}.$ ³⁰ RhHNO^+ also undergoes CID to form RhH^+ and Rh^+ , implying that $D(\text{Rh}^+-\text{H}) = 42 \pm 3$ kcal/mol³⁰ $> D(\text{Rh}^+-\text{NO})$. The CID results, along with the observation of one H/D exchange with D_2 , indicate that the structure of this ion is $\text{Rh}(\text{H})(\text{NO})^+$ or that two equilibrating structures, $\text{Rh}(\text{HNO})^+$ and $\text{Rh}(\text{H})(\text{NO})^+$, are present. CID on FeOCH_3^+ , CoOCH_3^+ , and NiOCH_3^+ yields MH^+ in high efficiency, suggesting that $D(\text{M}^+-\text{H})^{29} > D(\text{M}^+-\text{CH}_2\text{O})$. NiOCH_3^+ undergoes three H/D exchanges with D_2 , while FeOCH_3^+ and CoOCH_3^+ do not react with D_2 . With ethene- d_4 ,³¹ however, all three first-row groups 8-10⁴³ MOCH_3^+ species give three H/D exchanges. These results suggest that these ions have equilibrating methoxy and hydrido-formaldehyde structures, **2**.



2

Structural studies also show that MCH_2O^+ does not have a metal-hydride structure, based on a lack of H/D exchange and the formation of only M^+ as a CID product.

Some interesting observations can be made from the data in Table I. For example, the first-row groups 8 and 9 ions Fe^+ and

(29) $D^\circ(\text{Fe}^+-\text{H}) = 58 \pm 5$ kcal/mol, $D^\circ(\text{Co}^+-\text{H}) = 52 \pm 4$ kcal/mol, and $D^\circ(\text{Ni}^+-\text{H}) = 43 \pm 2$ kcal/mol from ref 7.

(30) $D^\circ(\text{Rh}^+-\text{H}) = 42 \pm 3$ kcal/mol and $D^\circ(\text{Pd}^+-\text{H}) = 45 \pm 3$ kcal/mol from: Mandich, M. L.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 4403.

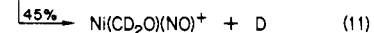
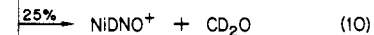
(31) Ethene- d_4 has been found to be a more facile H/D exchange reagent than D_2 ; however, C_2D_4 also adds ~ 30 kcal/mol more energy to the complex than does D_2 . Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 72.

Co⁺ react almost identically with methyl nitrite, while Ni⁺ reacts to give similar products as Fe⁺ and Co⁺ but in markedly different relative abundances. This differing reactivity of Ni⁺ from Fe⁺ and Co⁺ has also been observed with other organic species.^{12,13,32} For Fe⁺ and Co⁺, the major reaction product is M(H)(CH₂O)⁺, while for Ni⁺, the most abundant product is M(H)(CO)⁺. To aid in interpreting these results, bare Fe⁺, Co⁺, and Ni⁺ were reacted with CH₂O. Fe⁺ and Co⁺ were found to react slowly to form the condensation product, MCH₂O⁺, and the dehydrogenation product MCO⁺, in a ratio of ~1.0:0.05 (CH₂O:CO), which is also the approximate ratio of CH₂O to CO retention for Fe⁺ and Co⁺ in the methyl nitrite reactions. Ni⁺, however, reacts slowly with CH₂O to form NiCH₂O⁺ and NiCO⁺ in roughly a 1.0:1.0 ratio, which agrees well with the CH₂O to CO retention ratio for the methyl nitrite reactions. Dehydrogenation of CH₂O by Ni⁺ is surprising since Ni⁺ is typically the least reactive first-row groups 8–10 metal ion in the gas phase and the Ni⁺–H bond is considerably weaker than the Fe⁺–H and Co⁺–H bonds.²⁹

Another interesting feature of groups 8–10 metal ion reactivity with methyl nitrite is that there is very little retention of NO by the first-row metal ions while approximately 50% of the products from the second-row ions Rh⁺ and Pd⁺ retain NO. This is surprising since NO is a three-electron donor³³ and, therefore, would be expected to bind more strongly to the metal than two-electron donor ligands such as CO and CH₂O. Ligand-displacement reactions were performed to determine the relative binding order of NO, CO, and CH₂O to the groups 8–10 metal ions. As a reference, C₂H₄ displacement was also studied in these experiments since literature values of $D(M^+-C_2H_4)$ are available for the first-row groups 8–10 metals.^{34,35} For Fe⁺, Co⁺, Ni⁺, and Rh⁺, the relative binding order is CO < CH₂O < C₂H₄ < NO,³⁶ showing that NO is indeed the most strongly bound ligand of the four. In addition, displacement reactions with MH⁺ were performed to set an upper limit on M⁺–NO. No displacement of H by NO was observed for FeH⁺, indicating that $D(Fe^+-C_2H_4) = 34 \pm 2$ kcal/mol³⁵ < $D(Fe^+-NO) < D(Fe^+-H) = 58 \pm 2$ kcal/mol.⁷ For Co⁺, a small amount of displacement of H by NO was observed, indicating that $D(Co^+-NO)$ is close to $D(Co^+-H)$ and bracketing $D(Co^+-C_2H_4) = 37 \pm 2$ kcal/mol³⁴ < $D(Co^+-NO) < D(Co^+-H) = 52 \pm 2$ kcal/mol.⁷ For Ni⁺ and Rh⁺, NO displaces H, but at a rate that is roughly an order of magnitude slower than the displacement of C₂H₄ by NO. Loss of HNO to regenerate M⁺ also occurs, with M⁺ formation dominating over MNO⁺ formation. This slow displacement of H by NO suggests that $D(M^+-NO)$ for Ni and Rh are within ± 5 kcal/mol of $D(Ni^+-H) = 43 \pm 2$ kcal/mol⁷ and $D(Rh^+-H) = 42 \pm 3$ kcal/mol.³⁰ In addition, CID studies on RhHNO⁺ indicate that $D(Rh^+-NO) < D(Rh^+-H)$, while formation of M⁺–NO from methyl nitrite sets a lower limit of 38 kcal/mol³⁷ for $D(M^+-NO)$. Thus, we assign $D(Rh^+-NO) = 40 \pm 5$ kcal/mol and $D(Ni^+-NO) = 43 \pm 5$ kcal/mol.

There are several possible explanations for the preference of NO loss over CH₂O and CO loss in the methyl nitrite reactions. One possibility is that NO loss from intermediate **1** occurs prior to rearrangement of the methoxy to the hydrido-formaldehyde species. While $D(M^+-NO)$ is on the order of 40–50 kcal/mol,

$D(M^+-OCH_3)$ would be expected to be substantially higher based on $D(M^+-OH) \sim 70$ kcal/mol.³⁸ Although the M⁺–OCH₃ bond strength, and thus the exothermicity of the reaction, may play a role in NO loss in the primary reactions, it does not explain the loss of NO that also occurs in the subsequent reactions of ML_n⁺ species with methyl nitrite, which are discussed below. Another factor may be the nature of the NO ligand itself. Initial insertion of the metal into the CH₃O–NO bond could lead to an NO group with bent geometry which donates one electron,³³ and the lifetime of the intermediate may not be sufficient to allow rearrangement to the linear three electron donor geometry. Synergistic ligand effects may also be involved. For example, while both C₂H₄ and NO readily displace CD₂O from MCD₂O⁺ (M = Fe, Co, Ni), only C₂H₄ displaces CD₂O from FeOCD₃⁺, while NO does not react. For CoOCD₃⁺, a small amount of displacement of each of three ligands, D, OCD₃, and CD₂O, is observed with NO. NO reacts readily with NiOCD₃⁺, reactions 9 through 11, but dis-



placement of CD₂O by NO is not the dominant pathway. This suggests that the presence of other ligands around the metal has an effect on the relative binding energies of CD₂O and NO. In addition, other factors such as the ability of a ligand to delocalize charge³⁹ or to carry away excess energy may also aid in determining ligand loss. Overall, the methyl nitrite reactions serve to indicate that the ligand retained in a gas-phase ion-molecule reaction is not necessarily the species that forms the strongest bond to the metal ion in the absence of other ligands.

Another trend in the first-row groups 8–10 metal ion reactions is a decrease in the amount of MH⁺ formation in the order FeH⁺ > CoH⁺ > NiH⁺, which coincides with the order of $D(M^+-H)$ and, therefore, reaction exothermicity. Also, thermodynamic calculations show that MH⁺ formation to give CH₂O and NO as neutrals is endothermic for all three metals, implying that the neutral lost in these reactions is actually CH₂ONO.³⁷ In addition to being formed from intermediate **1**, it is also possible that some MH⁺ is the result of initial H–CH₂ONO insertion.

The reactivities of the second-row groups 8–10 transition-metal ions vary dramatically from those of the first-row ions. As noted previously, there is approximately a 1:1 ratio between retention of nitrogen-containing ligands and carbon-containing ligands by Rh⁺ and Pd⁺. In cases where the carbon–ligand bond is retained, the major product for Rh⁺ and Pd⁺ is M(H)(CO)⁺ rather than M(H)(CH₂O)⁺. Rh⁺ also readily dehydrogenates CH₂O with very little condensation, resulting in a RhCH₂O⁺:RhCO⁺ ratio of ~0.1:1.0, in accord with the CH₂O to CO retention ratio of 0.15:1.0 for the methyl nitrite reactions. Pd⁺, which reacts an order of magnitude slower with CH₂O than Rh⁺, gives a PdCH₂O⁺:PdCO⁺ ratio of ~1.0:1.0, while for the methyl nitrite reactions with Pd⁺ the ratio of CH₂O to CO retention is ~0.8:1.0.

Another interesting point about Rh⁺ and Pd⁺ reactivity with methyl nitrite is that although the major reaction pathway for both metals involves retention of NO, the most abundant product for Rh⁺ is Rh(H)(NO)⁺ while the major product for Pd⁺ is PdNO⁺. This result and others discussed below suggest that, in general, products resulting in a 12-electron configuration around the metal, such as Rh(H)(NO)⁺ and PdNO⁺, are more stable than products with 11- or 13-electron configurations, such as RhNO⁺ or Pd(H)(NO)⁺, respectively. This stability apparently arises due to 12-electron species having filled s and d shells.

The group 11 metal ions Cu⁺ and Ag⁺ react similarly with methyl nitrite, with Cu⁺ forming 86% CuOCH₂⁺ and 14% CuOCH₃⁺, while Ag⁺ forms 100% AgOCH₂⁺. This is in contrast

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

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

(34) $D^0(Co^+-C_2H_4) = 37 \pm 2$ kcal/mol from: Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6628.

(35) $D^0(Fe^+-C_2H_4) = 34 \pm 2$ kcal/mol and $D^0(Ni^+-C_2H_4) = 37 \pm 2$ kcal/mol from: Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7492.

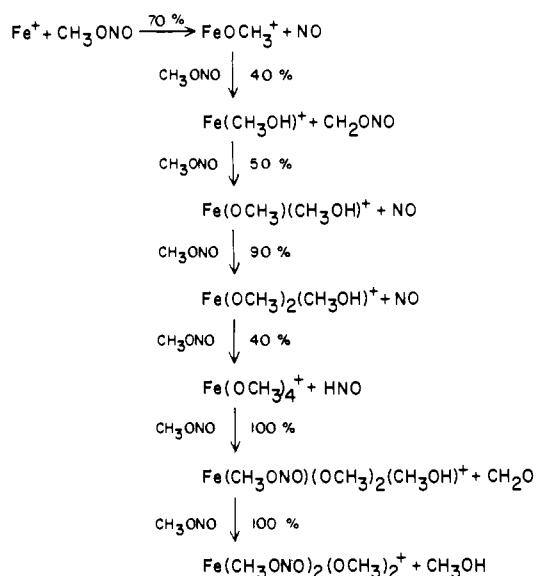
(36) There is a discrepancy in the literature between the bond strengths of C₂H₄ and CO to Fe⁺. The reported values are $D^0(Fe^+-C_2H_4) = 34 \pm 2$ kcal/mol (ref 35) and $D^0(Fe^+-CO) = 37.6$ kcal/mol (Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963). Ligand displacement reactions, however, show that C₂H₄ readily displaces CO from FeCO⁺ (this study and: Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 4808), indicating that $D^0(Fe^+-C_2H_4) > D^0(Fe^+-CO)$.

(37) Thermochemical information is taken from: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem., Ref. Data, Suppl.* **1**, **1977**, 6; and ref 17.

(38) $D^0(Fe^+-OH) = 73 \pm 3$ kcal/mol and $D^0(Co^+-OH) = 71 \pm 3$ kcal/mol from: Cassady, C. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 6176.

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

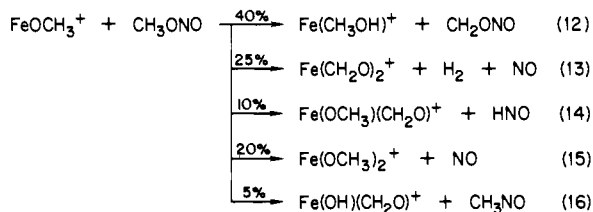
Scheme II



to the groups 8–10 metal ions where MOCH_2^+ is only a minor product. The reaction of Cu^+ with CH_2O , in which only a slow condensation to form CuCH_2O^+ is seen, agrees with the observation from the methyl nitrite reaction that Cu^+ does not dehydrogenate CH_2O . Ligand displacement reactions were also performed with Cu^+ , resulting in a ligand binding order of $\text{NO} < \text{CO} \lesssim \text{CH}_2\text{O} < \text{C}_2\text{H}_4$. (A small displacement of CH_2O by CO was observed, indicating that $D(\text{Cu}^+-\text{CO})$ is only slightly lower than $D(\text{Cu}^+-\text{CH}_2\text{O})$). This is in contrast to the groups 8–10 metal ions where NO is the most strongly bound of the four ligands. This may imply that NO is unable to serve as a three-electron donor to Cu^+ , which has a $4s^03d^{10}$ configuration, and must therefore donate only one electron with the end result being that NO is a more weakly bound ligand to Cu^+ than the two-electron donors CO , CH_2O , and C_2H_4 . This may also suggest that a configuration with 12 electrons around the metal, i.e., MCH_2O^+ , is more stable than a 13-electron configuration, i.e., MNO^+ and $\text{M}(\text{H})(\text{CH}_2\text{O})^+$, $\text{M} = \text{Cu}$ and Ag . In the case of the minor product CuOCH_3^+ , no H/D exchange is observed with either D_2 or C_2D_4 , suggesting that this ion has a metal-methoxy structure which does not rearrange to its hydrido-formaldehyde isomer.

Subsequent Reactions with Methyl Nitrite. Table II lists the subsequent reaction products generated when the primary products undergo further reactions with methyl nitrite. The first-row groups 8–10 metal ion products are very reactive with the neutral, undergoing up to eight subsequent reactions. As an example, the further reactions of the major ions formed from FeOCH_3^+ are outlined in Scheme II.

The secondary reactions of FeOCH_3^+ , reactions 12 through 16,



are typical of the reactions observed for the primary products of Fe^+ , Co^+ , and Ni^+ . The majority of the subsequent reactions appear to result from ML_n^+ insertion into the weak $\text{CH}_3\text{O}-\text{NO}$ bond followed by β -hydride shifts onto the metal and the elimination of various ligands. This mechanism, which is similar to that invoked in Scheme I for the primary reaction products, explains the products of reactions 12 through 15. The secondary product ions then undergo further reactions, again following the same mechanism. The most common reaction observed for Fe^+ and Co^+ species involves formally a hydrogen abstraction from

Table II. Primary and Subsequent Products of the Reactions of Atomic Metal Ions with Methyl Nitrite

product ^a	Fe ⁺	Co ⁺	Ni ⁺	Cu ⁺	Rh ⁺	Pd ⁺	Ag ⁺
MH ⁺	× ^b	×	×		×	×	
M(CO) ⁺					×		
M(CHO) ⁺	×	×	×		×	×	
M(CH ₂ O) ⁺	×	×	×	×	×	×	×
M(NO) ⁺	×	×	×		×	×	
M(CH ₃ O) ⁺	×	×	×	×		×	
M(HNO) ⁺					×	×	
M(CH ₃ OH) ⁺	×	×	×			×	
M(H)(CH ₃ OH) ⁺	×	×					
M(O)(CH ₃ O) ⁺	×						
M(OH)(CH ₃ OH) ⁺	×						
M(CO) ₂ ⁺					×		
M(CHO)(CO) ⁺		×	×				
M(CO)(NO) ⁺		×	×		×		
M(CHO)(NO) ⁺		×			×		
M(CH ₂ O)(CHO) ⁺	×	×	×		×		
M(CH ₂ O)(NO) ⁺		×	×			×	
M(NO) ₂ ⁺					×		
M(CH ₂ O) ₂ ⁺	×			×			
M(CH ₃ O)(CH ₂ O) ⁺	×	×	×	×			
M(CH ₃ ONO) ⁺					×	×	×
M(CH ₃ O) ₂ ⁺	×	×					
M(HNO) ₂ ⁺		×	×				
M(CH ₃ OH)(NO) ⁺		×	×			×	
M(CH ₃ OH)(CH ₃ O) ⁺	×	×					
M(CH ₃ OH) ₂ ⁺	×	×					
M(O)(CH ₃ O) ₂ ⁺	×						
M(OH)(CH ₃ OH) ₂ ⁺	×						
M(CH ₂ O)(NO) ₂ ⁺		×			×		
M(CH ₂ O) ₃ ⁺				×			
M(CH ₃ ONO)(CH ₂ O) ⁺	×	×					
M(CH ₃ ONO)(NO) ⁺			×			×	
M(CH ₃ O)(CH ₂ O) ₂ ⁺				×			
M(HNO) ₂ ⁺ (NO) ⁺		×					
M(CH ₃ O) ₂ (CH ₂ O) ⁺	×						
M(CH ₃ ONO)(CH ₃ OH) ⁺	×	×					
M(CH ₃ OH)(CH ₃ O) ₂ ⁺	×	×					
M(CH ₃ OH) ₂ (CH ₃ O) ⁺	×	×					
M(O)(CH ₃ ONO)- (CH ₃ OH) ⁺	×						
M(CH ₂ O) ₄ ⁺				×			
M(CH ₃ ONO)(NO) ₂ ⁺		×			×		
M(CH ₃ ONO) ₂ ⁺		×					
M(CH ₃ ONO)(CH ₃ O)- (CH ₂ O) ⁺	×						
M(CH ₃ ONO)(CH ₃ O) ₂ ⁺	×						
M(CH ₃ O) ₄ ⁺	×						
M(CH ₃ OH) ₂ (CH ₂ O) ₂ ⁺		×					
M(O)(CH ₃ ONO)(CH ₃ O) ₂ ⁺	×						
M(O)(CH ₃ ONO)- (CH ₃ OH) ₂ ⁺	×						
M(CH ₃ ONO)(CH ₃ O) ₂ - (CH ₂ O) ⁺	×						
M(CH ₃ ONO)(CH ₃ OH)- (CH ₃ O) ₂ ⁺	×						

^a In the formulas listed, ligands are grouped to aid in the examination of the data and are not meant to imply structure. ^b × indicates that this ion is formed in the reactions of the given metal ion.

CH_3ONO (loss of “ CH_2ONO ”) and the formation of a product ion that is 1 amu higher in mass than the original reactant ion. This process, exemplified by reaction 12, results in the formation of clusters of ions that are 1 amu apart, as shown in Figure 1. The product of reaction 12, FeCH_3OH^+ , undergoes CID to give only Fe^+ and does not H/D exchange suggesting a metal-methanol structure. CID and subsequent ion-molecule reactions with methyl nitrite indicate that the ions formed in this “clustering” process contain combinations of CO , CH_2O , OCH_3 , and CH_3OH ligands surrounding the metal.

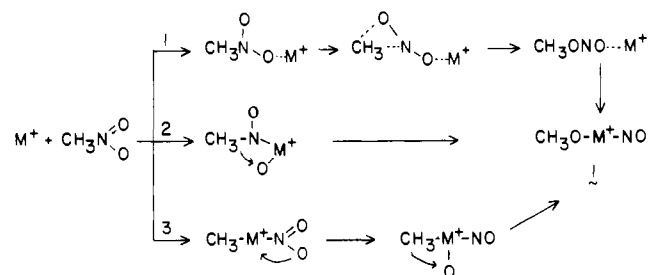
Reaction 16, which involves formally the abstraction of an oxygen from methyl nitrite by FeOCH_3^+ to generate $\text{FeO}_2\text{CH}_3^+$, does not occur with any of the other metals. CID on this ion yields FeOH^+ as the only product, suggesting that the structure is $\text{Fe}(\text{OH})(\text{CH}_2\text{O})^+$. In the subsequent reactions of this ion and its

Table III. Product Distributions for the Primary Reactions of Fe⁺ and Co⁺ with Nitromethane

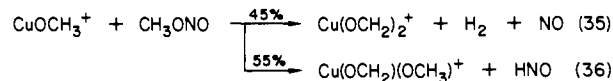
ion	products	rel abundance	
		Fe ⁺	Co ⁺ ^a
MH ⁺	CH ₂ NO ₂	4	2
MCH ₃ ⁺	NO ₂	2	0
MO ⁺	HCN, H ₂ O	7	17
MOH ⁺	CH ₂ NO	23	21
MOCH ⁺	NO, H ₂	0	2
MNCH ₃ ⁺	O ₂	2	0
MOCH ₂ ⁺	HNO	2	2
MNO ⁺	OCH ₃	0	2
MOCH ₃ ⁺	NO	57	40
M(OH) ₂ ⁺	HCN	3	6
MCHNO ⁺	H ₂ O	0	3
MCH ₂ NO ⁺	OH	0	3
MHNO ₂ ⁺	CH ₂	0	2

^a From ref 16.

Scheme III



to formally add HCO and CH₂O, reactions 35 and 36, and thus forms the same products as CuOCH₂⁺. Cu(OCH₂)₂⁺ and Cu-



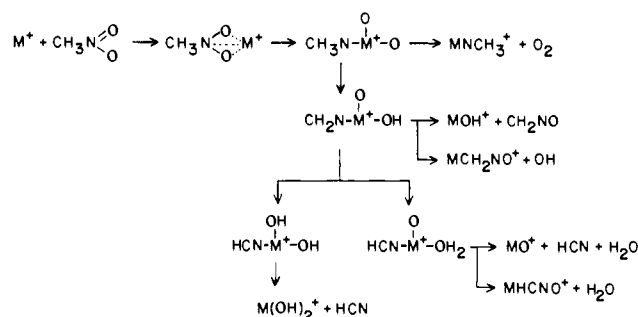
(OCH₂)(OCH₃)⁺ react with methyl nitrite to give Cu(OCH₂)₃⁺ and Cu(OCH₂)₂(OCH₃)⁺. These tertiary products react to form only Cu(OCH₂)₄⁺, an 18-electron species which does not react further with methyl nitrite. CID on the Cu(OCH₂)_n⁺ species yields consecutive loss of CH₂O.

In contrast to the CuL_n⁺ reactions, the Ag⁺ primary product ion AgOCH₂⁺ undergoes only displacement reaction 37. CID AgOCH₂⁺ + CH₃ONO → Ag(CH₃ONO)⁺ + CH₂O (37)

on this product ion yields Ag⁺ in high efficiency as the only product suggesting that the complex consists of an intact CH₃ONO bound to Ag⁺.

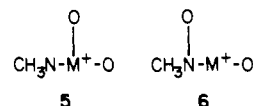
Fe⁺ and Co⁺ Reactions with Nitromethane. Of the first row transition metal ions studied, only Fe⁺ and Co⁺ react with nitromethane and their reactivities are very similar (Table III). The major reaction product for both metals is MOCH₃⁺, which is also the major product observed with methyl nitrite. In fact, for the nitromethane reactions, ~65% of the Fe⁺ products and ~48% of the Co⁺ products appear to result from nitrite intermediate 1 via the mechanism proposed in Scheme I. This suggests that a nitro-to-nitrite isomerization is occurring.¹⁶ As shown in Scheme III, there are two general pathways by which this isomerization may occur. The first involves the coordination of the M⁺ to an oxygen while the molecule isomerizes (reaction 1 in Scheme III), after which M⁺ inserts into the O-N bond to form intermediate 1. The second pathway involves insertion of the metal into an N-O or C-N bond followed by a rearrangement to form the nitrite intermediate 1 (reactions 2 and 3 in Scheme III), with no formation of the actual nitrite isomer. Both the N-O bond, at 75 kcal/mol,⁴⁰ and the C-N bond, at 61 kcal/mol,⁴¹ are weak relative to the typical C-C bond (ca. 88 kcal/mol⁴²) or C-H bond (ca.

Scheme IV



97 kcal/mol⁴²). Thus, it may be energetically feasible for either bond to be the target of a metal ion insertion.

Two major products, MO⁺ and MOH⁺, 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 IV, involves an intermediate with two oxygens bound to the metal, 5. Several factors point to this intermediate over a species with only one oxygen bound to the metal, structure 6. First, the formation



of the minor products MNCH₃⁺ (loss of O₂) and M(OH)₂⁺ (loss of HCN) indicate that at some point two oxygens must be bound to the metal. Second, although intermediate 6 seems reasonable, MO⁺ formation would presumably proceed by loss of CH₃NO, which is estimated to be endothermic by 26 kcal/mol for Fe⁺ and 30 kcal/mol for Co⁺³⁶ and, therefore, cannot occur. With intermediate 5, however, loss of HCN and H₂O by Scheme IV would be exothermic by 17 kcal/mol for Fe⁺ and 13 kcal/mol for Co⁺.³⁷ The fact that the ratio of MO⁺ to MOH⁺ is greater for Co⁺ than for Fe⁺ lends further support to intermediate 5 since formation of MO⁺ from 5 requires two β-hydride shifts, while MOH⁺ requires one, and Co⁺ appears to be a more facile β-hydrogen abstractor than Fe⁺.¹² If the mechanism involves intermediate 6, no β-hydride shifts are required to form MO⁺, while MOH⁺ requires one shift. By the same argument this predicts incorrectly that, compared to Co⁺, Fe⁺ should form more MO⁺ (relative to MOH⁺).

The major pathways for the reactions of Fe⁺ and Co⁺ with nitromethane (Schemes III and IV) require formation of an M⁺-O bond. Ni⁺ cannot react with nitromethane since the Ni⁺-O bond is ~20 kcal/mol weaker than the Fe⁺-O or Co⁺-O bonds,⁷ making Ni⁺-O formation (loss of HCN and H₂O) 8 kcal/mol endothermic.³⁷ Assuming that Cu⁺-O formation is also endothermic, this implies that D(Cu⁺-O) < 53 kcal/mol.

Insertion of M⁺ into the C-N bond, which is the weakest bond in nitromethane (61 kcal/mol⁴¹), results in only two very minor products (aside from a possible nitro-to-nitrite conversion route). For Fe⁺, reaction 38 appears to result from C-N insertion and



is ~9 kcal/mol exothermic for Fe⁺, but it is only ~1 kcal/mol exothermic for Co⁺³⁷ where it is not observed. For Co⁺, reaction 39, which results from a C-N insertion, is unusual since CH₂ is



a high-energy radical and its formation would require either an

(42) Weast, R. C., Ed. "Handbook of Chemistry and Physics", 55th ed.; CRC Press: Cleveland, 1974.

(43) The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

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

(41) Reference 17, p 1043.

Table IV. Product Distributions in Subsequent Reactions of the Primary Products of the $[\text{Fe}^+ + \text{CH}_3\text{NO}_2]$ Reaction ($\text{P} = \text{CH}_3\text{NO}_2$)

reactant ion	products		rel abundance
	ion	neutral(s)	
FeH^+	<i>a</i>		
FeCH_3^+	<i>a</i>		
FeO^+	$\text{Fe}(\text{OH})_2^+$	CHNO	80
	FeOP^+		20
FeOH^+	$\text{Fe}(\text{OH})_2^+$	CH_2NO	10
	$\text{Fe}(\text{OH})(\text{H}_2\text{O})^+$	CHNO	10
	$\text{FeCH}_2\text{NO}_2^+$	H_2O	20
	$\text{Fe}(\text{OH})\text{P}^+$		60
FeNCH_3^+	<i>a</i>		
FeOCH_2^+	<i>a</i>		
FeOCH_3^+	FeHP^+	CH_2O	100
$\text{Fe}(\text{OH})_2^+$	FeOP^+	H_2O	60
	$\text{Fe}(\text{OH})\text{P}^+$	OH	40
3rd Generation Reactions of Products Listed Above			
$\text{Fe}(\text{OH})(\text{H}_2\text{O})^+$	$\text{Fe}(\text{OH})\text{P}^+$	H_2O	100
$\text{FeCH}_2\text{NO}_2^+$	$\text{Fe}(\text{O})(\text{CH}_2\text{NO}_2)^+$	CH_3NO	80
	$\text{Fe}(\text{NO})\text{P}^+$	CH_2O	20
FeHP^+	$\text{Fe}(\text{OH})\text{P}^+$	CH_3NO	100
FeOP^+	$\text{Fe}(\text{OH})\text{P}^+$	CH_2NO_2	100
$\text{Fe}(\text{OH})\text{P}^{+b}$	$\text{Fe}(\text{OCH}_3)\text{P}^+$	HNO_2	25
	$\text{Fe}(\text{CH}_2\text{NO}_2)(\text{NO}_2)^+$	$\text{CH}_3, \text{H}_2\text{O}$	25
	$\text{Fe}(\text{CH}_2\text{NO}_2)\text{P}^+$	H_2O	25
	$\text{Fe}(\text{OH})\text{P}_2^+$		25

^a Due to low ion intensity, the further reactions of this ion could not be determined. ^b The $\text{Fe}(\text{OH})\text{P}^+$ reactions are much slower than the other subsequent reactions.

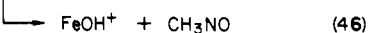
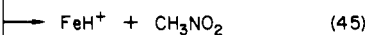
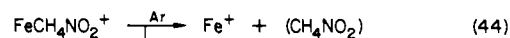
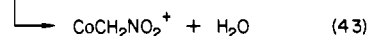
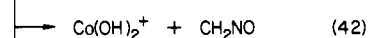
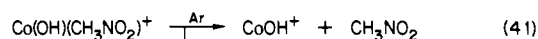
α -hydride shift onto Co^+ or a hydride shift onto an oxygen via a cyclic intermediate.¹⁶

Collision-induced dissociation experiments were performed on the three major products of the nitromethane reactions. As expected, for MO^+ and MOH^+ the only CID product was M^+ . MOCH_3^+ from nitromethane behaves in a manner similar to MOCH_3^+ formed from methyl nitrite, with a high efficiency formation of MH^+ at all energies and a small amount of M^+ at high energies. This ion also undergoes no H/D exchange with D_2 but undergoes three exchanges with ethene-*d*₄, again behaving identically with the ion formed from methyl nitrite. In addition, MOCH_3^+ reacts with nitromethane to displace CH_2O , reaction 40. These data again support an equilibration of methoxy and hydrido-formaldehyde structures, **2**, for MOCH_3^+ .

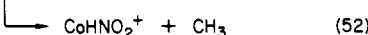
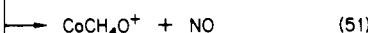
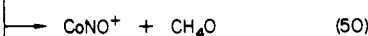
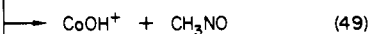
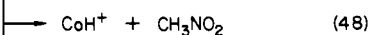
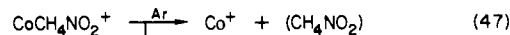


The primary products are very reactive with nitromethane. The subsequent reactions of the ions formed from Fe^+ are given in Table IV, while the reactions of the CoL_n^+ ions with nitromethane have been reported previously.¹⁶ The major difference in the subsequent reactions of the Fe^+ and Co^+ species is that the FeL_n^+ ions are less reactive than the CoL_n^+ ions. This is in contrast to the methyl nitrite reactions where just the opposite is true. For FeL^+ , the subsequent reactions essentially stop with the formation of $\text{Fe}(\text{OH})(\text{CH}_3\text{NO}_2)^+$, which then reacts away very slowly. $\text{Co}(\text{OH})(\text{CH}_3\text{NO}_2)^+$, however, reacts readily with nitromethane until the mass spectrum is eventually dominated by 5th generation reaction products such as $\text{Co}(\text{CH}_3\text{NO}_2)_3^+$. CoL_n^+ ions also have a greater tendency to lose OH than do FeL_n^+ ions. For example, in the reactions of CoOH^+ there is a 70% loss of OH, while only 15% of the FeOH^+ reactions involve loss of OH. This is surprising since the Co^+-OH bond is only ~ 2 kcal/mol weaker than the Fe^+-OH bond³⁹ and is apparently due to the ability of Co^+ to readily abstract β -hydrogens,¹² resulting in H_2O loss.

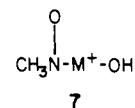
This tendency of $\text{Fe}(\text{OH})\text{L}_n^+$ to retain the hydroxy group is also seen in the CID spectra. For example, only one CID product, FeOH^+ , is seen for $\text{Fe}(\text{OH})(\text{CH}_3\text{NO}_2)^+$. For $\text{Co}(\text{OH})(\text{CH}_3\text{NO}_2)^+$ several products are observed, reactions 41 through 43, although CoOH^+ is the dominant product.¹⁶ $\text{FeCH}_4\text{NO}_2^+$ also gives FeOH^+ as the major CID product, reaction 46, with Fe^+ and FeH^+ as minor products. For $\text{CoCH}_4\text{NO}_2^+$, CoOH^+



is the major product, reaction 49, while several minor products are also present.¹⁶ Although CID does not confirm a structure



for $\text{MCH}_4\text{NO}_2^+$, the results suggest that the structure is **7**. The reaction of $\text{MCH}_4\text{NO}_2^+$ with nitromethane, which involves displacement of CH_3NO by CH_3NO_2 , also supports this structure.



Rh⁺ and Pd⁺ Reactions with Nitromethane. The second-row groups 9 and 10 metal ions Rh^+ and Pd^+ react with nitromethane to form MNO^+ , reaction 53. This reaction is slow relative to



the first-row group 8–10 metal ion reactions and has a rate constant on the order of 10^{-10} cm³ molecule⁻¹ s⁻¹; however, it does not appear to be caused by excited state metal ions since increasing the nitromethane pressure increases the extent of reaction and the addition of argon at pressures of 10^{-5} torr does not quench the reaction.²¹ This reaction yields a lower limit of $D(\text{M}^+-\text{NO})^{37} > 39$ kcal/mol for $\text{M} = \text{Rh}, \text{Pd}$. The mechanism of MNO^+ formation may be a nitro-to-nitrite rearrangement, similar to that proposed for Fe^+ and Co^+ , where NO is retained preferentially to OCH_3 .

Conclusion

The seven metal ions studied all react with methyl nitrite by oxidative addition of the metal ion into the weak $\text{CH}_3\text{O}-\text{NO}$ bond. The products resulting from this common intermediate, however, are dependent on the metal ion. The first row groups 8–10 metal ions Fe^+ , Co^+ , and Ni^+ give greater than 90% loss of the NO ligand, preferring to retain CH_3O , CH_2O , or CHO instead. The second-row ions Rh^+ and Pd^+ show a slight preference for the NO over the carbon-containing bases in the primary reactions, while their subsequent reactions are dominated by NO retention. The large loss of NO in these reactions is surprising since ligand displacement reactions give a relative binding order for Fe^+ , Co^+ , Ni^+ , and Rh^+ of $\text{CO} < \text{CH}_2\text{O} < \text{C}_2\text{H}_4 < \text{NO}$. In addition, NO does not displace H from FeH^+ or CoH^+ , bracketing $D(\text{Fe}^+-\text{C}_2\text{H}_4) = 34 \pm 2$ kcal/mol³⁵ $< D(\text{Fe}^+-\text{NO}) < D(\text{Fe}^+-\text{H}) = 58 \pm 2$ kcal/mol⁷ and $D(\text{Co}^+-\text{C}_2\text{H}_4) = 37 \pm 2$ kcal/mol³⁴ $< D(\text{Co}^+-\text{NO}) < D(\text{Co}^+-\text{H}) = 52 \pm 2$ kcal/mol.⁷ Also, slow displacements of H from NiH^+ and RhH^+ by NO suggest that $D(\text{Ni}^+-\text{NO}) = 43 \pm 5$ kcal/mol and $D(\text{Rh}^+-\text{NO}) = 40 \pm 5$ kcal/mol.

The carbon-containing primary products of the methyl nitrite reactions have either CH_2O or CO bound to the metal. The relative amounts of CH_2O and CO retained show an excellent correlation with the ability of the metal ion to dehydrogenate CH_2O .

The primary reactions also give some indication that 12 electron species may be more stable than species with 11 or 13 electrons around the metal. For example, $M(H)(NO)^+$ is the major Rh^+ product while MNO^+ is the most abundant Pd^+ product. Further evidence for the added stability of 12 electron configurations is given by the reactions of the group 11 ions Cu^+ and Ag^+ with methyl nitrite. These ions form primarily MCH_2O^+ , with no retention of NO. Ligand displacement reactions with Cu^+ give a relative binding order of $NO < CO \leq CH_2O < C_2H_4$, indicating that NO, which is the most strongly bound of the four ligands to groups 8-10 metals, is the least strongly bound ligand to Cu^+ . This may imply that NO cannot donate three electrons to the $4s^03d^{10}$ system of Cu^+ and must behave instead as a 1-electron donor.

Of the first-row transition-metal ions studied, only Fe^+ and Co^+ react with nitromethane. The majority of the products from these reactions appear to result from an intermediate similar to that invoked in the methyl nitrite reactions, implying that a metal-induced nitro-to-nitrite isomerization is occurring. The other major

product ions, MO^+ and MOH^+ , may result from a reaction pathway which involves the splitting of the nitro group resulting in an intermediate with two oxygens and a nitrogen bound to the metal.

The second row groups 9 and 10 transition-metal ions Rh^+ and Pd^+ react slowly with nitromethane to form MNO^+ . The production of this ion may also be the result of a nitro-to-nitrite isomerization with NO retention dominating over OCH_3 retention.

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Registry No. Fe^+ , 14067-02-8; Co^+ , 16610-75-6; Ni^+ , 14903-34-5; Cu^+ , 17493-86-6; Rh^+ , 20561-59-5; Pd^+ , 20561-55-1; Ag^+ , 14701-21-4; methyl nitrite, 624-91-9; nitromethane, 75-52-5.

Gas-Phase Reactions of Groups 8-10 Transition-Metal Ions with Nitroalkanes[†]

C. J. Cassady and B. S. Freiser*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. Received July 9, 1984

Abstract: Fe^+ , Co^+ , and Ni^+ exhibit a rich chemistry in their reactions with nitroalkanes. Oxidative addition of the metal ion into the C-N bond dominates the chemistry of Ni^+ . Fe^+ , however, preferentially attacks the stronger N-O and C-C bonds, while Co^+ reacts in a manner intermediate to Fe^+ and Ni^+ . An unusual reaction pathway for all three metals is an apparent nitro-to-nitrite isomerization. In addition, following C-C insertion, radical loss processes dominate over processes involving β -hydrogen abstraction. The structures of the reaction products were probed by collision-induced dissociation and secondary ion-molecule reactions with the nitroalkane. The effect of total pressure on these reactions was also studied. Evidence is presented for a long-lived (>1 ms) reaction intermediate of C-N insertion which undergoes stabilizing collisions in the presence of a relatively high pressure ($\sim 10^{-5}$ torr) of an inert gas.

Several recent studies¹ have shown that gas-phase transition-metal ions react with functionalized organic molecules predominantly by oxidative addition of the metal into the carbon-heteroatom bond. This is not surprising since this bond is typically weaker than either the C-C or the C-H bonds of the molecule and the resulting M^+-X bond is comparable to the M^+-R and M^+-H bonds that would result from C-C and C-H insertion.² Nitroalkanes, however, represent an interesting class of organic compounds because in addition to having a relatively weak C-NO₂ bond (~ 60 kcal/mol^{3a}), the N-O bond (~ 75 kcal/mol^{3b}) is also weak relative to the C-C (~ 88 kcal/mol⁴) and C-H (~ 97 kcal/mol⁴) bonds. In fact, in solution transition metals interact with nitroalkanes in the presence of a reducing agent not by cleavage of the C-N bond but instead by N-O cleavage which leads to amine formation.⁵ As discussed in the preceding paper in this journal, gas-phase groups 8-10 transition-metal ions react with nitromethane predominantly by cleavage of the N-O bond. In this study we expand upon the nitromethane results and upon our previous study of the reactions of Co^+ with nitroalkanes⁶ by presenting the results of a study of the reactions of the groups 8-10 transition-metal ions Fe^+ , Co^+ , and Ni^+ with nitroalkanes.

Experimental Section

All studies were performed on a Nicolet prototype FTMS-1000 Fourier transform mass spectrometer⁷ equipped with a laser ionization source to generate gas-phase atomic-metal ions.⁸ A brief description of

Table I. Product Distributions for the Primary Reactions of Fe^+ , Co^+ , and Ni^+ with Nitroethane

products		rel abundance ^a			intermediate structure
ion	neutral(s)	Fe^+	Co^{+b}	Ni^+	
MCH_3^+	CH_2NO_2	9	5	1	II
MO^+	CH_3CN, H_2O	5	2	0	V
MOH^+	C_2H_4NO	29	20	11	V
$MC_2H_3^+$	H_2, NO_2	2	14	4	I, III
$MC_2H_4^+$	HNO_2	0	3	4	I
MNO^+	C_2H_5O	2	3	6	VI
$M(OH)_2^+$	CH_3CN	13	4	0	V
MCH_3CN^+	$2OH$	0	0	4	V
$MC_2H_3O^+$	H_2, NO	4	5	7	VI
$MC_2H_4O^+$	HNO	6	10	4	VI
$MC_2H_5O^+$	NO	4	4	3	VI
$MHNO_2^+$	C_2H_4	3	12	44	I
$MC_2H_3NO^+$	H_2O	2	4	0	V
$MC_2H_4NO^+$	OH	4	5	3	V
$MCHNO_2^+$	CH_4	2	0	0	II
$MCH_2NO_2^+$	CH_3	10	7	9	II
$MCH_3NO_2^+$	CH_2	5	2	0	II

^aNitroethane pressure was 1×10^{-7} torr. ^bFrom ref 6.

the experiment has been given in the preceding paper in this journal which discusses our related study of the reactions of transition-metal ions

[†]The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

(1) (a) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360. (b) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998. (c) Byrd, G. D. Ph.D. Thesis, Purdue University, 1982.