

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[†]

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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

[†]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.

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

(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.

Table II. Distributions for the Primary Reactions of Fe⁺, Co⁺, and Ni⁺ with 1-Nitropropane

products		rel abundance ^a			intermediate structure
ion	neutral(s)	Fe ⁺	Co ⁺ ^b	Ni ⁺	
C ₃ H ₇ ⁺	MNO ₂	9	12	35	I
MCH ₃ ⁺	C ₂ H ₄ NO ₂	1	2	0	II
MOH ⁺	C ₃ H ₆ NO	21	15	6	V
MC ₂ H ₅ ⁺	CH ₂ NO ₂	1	0	2	II
MNO ⁺	C ₃ H ₇ O	0	2	6	VI
MOCH ₃ ⁺	C ₂ H ₄ NO	6	0	0	IV, VI
MOCH ₄ ⁺	C ₂ H ₃ NO	2	0	0	IV
M(OH) ₂ ⁺	C ₃ H ₅ N	5	0	0	V
MC ₃ H ₅ ⁺	H ₂ , NO ₂	2	10	8	I, III
MC ₃ H ₆ ⁺	HNO ₂	0	4	3	I
MC ₂ H ₄ O ⁺	HCN, H ₂ O	0	0	3	V
MCH ₂ NO ⁺	C ₂ H ₅ O	2	0	0	VI
MHNO ₂ ⁺	C ₃ H ₆	3	21	20	I
MC ₃ H ₅ O ⁺	H ₂ , NO	9	14	3	VI
MC ₃ H ₆ O ⁺	HNO	4	6	4	VI
MC ₃ H ₇ O ⁺	NO	2	1	0	VI
MCH ₂ NO ₂ ⁺	C ₂ H ₅	20	2	3	II
MCH ₃ NO ₂ ⁺	C ₂ H ₄	2	1	3	II
MC ₃ H ₄ NO ⁺	H ₂ , OH	4	0	0	V
MC ₃ H ₆ NO ⁺	OH	2	0	0	V
MC ₂ H ₄ NO ₂ ⁺	CH ₃	3	8	3	II
MC ₂ H ₅ NO ₂ ⁺	CH ₂	2	2	1	II

^a 1-Nitropropane pressure was 1 × 10⁻⁷ torr. ^b From ref. 6.**Table III.** Product Distributions for the Primary Reactions of Fe⁺, Co⁺, and Ni⁺ with 2-Nitropropane

products		rel abundance ^a			intermediate structure
ion	neutral(s)	Fe ⁺	Co ⁺ ^b	Ni ⁺	
C ₃ H ₇ ⁺	MNO ₂	20	17	33	I
MCH ₃ ⁺	C ₂ H ₄ NO ₂	6	2	0	II
MOH ⁺	C ₃ H ₆ NO	28	18	6	V
MNO ⁺	C ₃ H ₇ O	1	2	4	VI
MC ₃ H ₅ ⁺	H ₂ , NO ₂	2	6	8	I
MC ₃ H ₆ ⁺	HNO ₂	1	3	2	I
MC ₂ H ₄ O ⁺	HCN, H ₂ O	0	0	2	V
MCH ₂ NO ⁺	C ₂ H ₅ O	2	0	0	VI
MHNO ₂ ⁺	C ₃ H ₆	9	16	24	I
MC ₃ H ₅ O ⁺	H ₂ , NO	6	11	3	VI
MC ₃ H ₆ O ⁺	HNO	6	7	6	VI
MC ₃ H ₇ O ⁺	NO	5	3	0	VI
MCH ₂ NO ₂ ⁺	C ₂ H ₅	2	2	1	II
MCH ₃ NO ₂ ⁺	C ₂ H ₄	3	2	2	II
MC ₂ H ₄ NO ₂ ⁺	CH ₃	6	8	6	II
MC ₂ H ₅ NO ₂ ⁺	CH ₂	3	3	3	II

^a 2-Nitropropane pressure was 1 × 10⁻⁷ torr. ^b From ref. 6.with nitromethane and methyl nitrite.⁹

Results and Discussion

The primary products for the reactions of Fe⁺, Co⁺, and Ni⁺ with nitroethane, the nitropropanes, and the nitrobutanes are listed in Tables I–VI. To aid in elucidating reaction mechanisms, the

(2) See for example Table X1 on *D*(M⁺–L) for L = H, CH₃, and O in: Martinho Simoes, J. A.; Beauchamp, J. L. *Chem. Rev.*, in press.

(3) (a) Patai, S., Ed. "The Chemistry of Amino, Nitroso, and Nitro Compounds and their Derivatives", Part 2; Wiley: New York, 1982; p 1043. (b) Pepekina, V. I.; Matyushin, Y. N.; Lebedev, Y. A. *Izv. Akad. Nauk, SSSR Ser. Khim.* 1974, 8, 1707.

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

(5) March, J. "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure", 2nd ed.; McGraw-Hill: New York, 1977; pp 1125–1126 and references therein.

(6) Cassady, C. J.; Freiser, B. S.; McElvany, S. W.; Allison, J. *J. Am. Chem. Soc.* 1984, 106, 6125.

(7) (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.

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

(9) Cassady, C. J.; Freiser, B. S. *J. Am. Chem. Soc.*, preceding paper in this issue.

Table IV. Product Distributions for the Primary Reactions of Fe⁺, Co⁺, and Ni⁺ with 1-Nitrobutane

products		rel abundance ^a			intermediate structure
ion	neutral(s)	Fe ⁺	Co ⁺ ^b	Ni ⁺	
C ₄ H ₉ ⁺	MNO ₂	18	38	40	I
MOH ⁺	C ₄ H ₈ NO	10	8	1	V
MC ₂ H ₄ ⁺	C ₃ H ₅ NO ₂	1	2	0	II
MNO ⁺	C ₄ H ₉ O	1	0	3	VI
MOCH ₃ ⁺	C ₃ H ₆ NO	7	0	0	IV, VI
M(OH) ₂ ⁺	C ₄ H ₇ N	7	0	0	V
MC ₃ H ₅ ⁺	CH ₄ NO ₂	1	2	9	II
MC ₂ H ₇ ⁺	CH ₂ NO ₂	2	0	2	II
MC ₃ H ₈ ⁺	CHNO ₂	3	0	1	II
MC ₂ H ₆ O ⁺	C ₂ H ₄ NO	3	0	0	VI
MHNO ₂ ⁺	C ₄ H ₈	2	10	10	I
MC ₄ H ₆ ⁺	H ₂ , HNO ₂	3	3	3	I
MC ₄ H ₇ ⁺	H ₂ , NO ₂	4	6	8	I
MC ₄ H ₈ ⁺	HNO ₂	1	1	2	I
MC ₃ H ₆ O ⁺	HCN, H ₂ O	2	1	2	V
MCH ₂ NO ₂ ⁺	C ₃ H ₇	11	2	0	II
MC ₄ H ₅ O ⁺	2H ₂ , NO	3	3	5	VI
MC ₄ H ₆ O ⁺	H ₂ , HNO	3	1	2	VI
MC ₄ H ₇ O ⁺	H ₂ , NO	8	3	2	VI
MC ₄ H ₈ O ⁺	HNO	3	2	1	VI
MC ₂ H ₄ NO ₂ ⁺	C ₂ H ₅	2	3	4	II
MC ₂ H ₅ NO ₂ ⁺	C ₂ H ₄	1	14	3	II
MC ₄ H ₈ NO ⁺	OH	2	0	2	V
MC ₃ H ₆ NO ₂ ⁺	CH ₃	2	1	0	II

^a 1-Nitrobutane pressure was 1 × 10⁻⁷ torr. ^b From ref. 6.**Table V.** Product Distributions for the Primary Reactions of Fe⁺, Co⁺, and Ni⁺ with 2-Nitrobutane

products		rel abundance ^a			intermediate structure
ion	neutral(s)	Fe ⁺	Co ⁺ ^b	Ni ⁺	
C ₄ H ₉ ⁺	MNO ₂	57	30	69	I
MCH ₃ ⁺	C ₃ H ₆ NO ₂	3	0	0	II
MOH ⁺	C ₄ H ₈ NO	18	7	3	V
MNO ⁺	C ₄ H ₉ O	0	0	2	VI
MC ₃ H ₅ ⁺	CH ₄ NO ₂	0	1	2	II
MC ₃ H ₇ ⁺	CH ₂ NO ₂	0	2	1	II
MC ₃ H ₈ ⁺	CHNO ₂	0	0	1	II
MHNO ₂ ⁺	C ₄ H ₈	0	14	7	I
MC ₄ H ₆ ⁺	H ₂ , HNO ₂	3	4	2	I
MC ₄ H ₇ ⁺	H ₂ , NO ₂	6	14	5	I
MC ₄ H ₈ ⁺	HNO ₂	0	3	1	I
MC ₃ H ₆ O ⁺	HCN, H ₂ O	0	1	1	V
MC ₄ H ₅ O ⁺	2H ₂ , NO	0	3	0	VI
MC ₄ H ₆ O ⁺	H ₂ , HNO	0	2	0	VI
MC ₄ H ₇ O ⁺	H ₂ , NO	4	5	1	VI
MC ₄ H ₈ O ⁺	HNO	3	4	1	VI
MC ₄ H ₉ O ⁺	NO	2	3	0	VI
MC ₂ H ₄ NO ₂ ⁺	C ₂ H ₅	3	5	3	II
MC ₃ H ₆ NO ₂ ⁺	CH ₃	1	2	1	II

^a 2-Nitrobutane pressure was 1 × 10⁻⁷ torr. ^b From ref. 6.

reactions of Fe⁺, Co⁺, and Ni⁺ with 1-butyl nitrite were also studied, with the reaction products listed in Table VII. For several primary products, empirical formulas other than those listed are also possible. Based on a consideration of all of the data, however, we feel that the formulas given 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. Insertion into the C–NO₂ bond is represented by structure I, while C–C and C–H insertion are represented by structures II and III, respectively. Insertion into the N–O bond gives structure IV. In addition, based on the nitromethane reactions,⁹ structure V, a dioxygen-metal species, is a likely reaction intermediate. This intermediate may form by either an α-oxygen shift from intermediate IV or a concerted process involving initial coordination of the metal to all three atoms in the nitro group. Another prominent intermediate is VI, a nitrite intermediate resulting from a nitro-to-nitrite isomerization which is also proposed in the nitromethane reactions.^{6,9} Table VIII gives the contribution of each

Table VI. Product Distributions for the Primary Reactions of Fe⁺, Co⁺, and Ni⁺ with 2-Nitro-2-methylpropane

products		rel abundance ^a			intermediate structure
ion	neutral(s)	Fe ⁺	Co ⁺ ^b	Ni ⁺	
C ₄ H ₉ ⁺	MNO ₂	87	80	84	I
MCH ₃ ⁺	C ₃ H ₆ NO ₂	3	2	0	II
MOH ⁺	C ₄ H ₈ NO	3	3	1	V
MC ₃ H ₃ ⁺	CH ₆ NO ₂	0	0	1	I, II
MC ₃ H ₅ ⁺	CH ₄ NO ₂	0	0	1	I, II
MHNO ₂ ⁺	C ₄ H ₈	0	2	2	I
MC ₄ H ₇ ⁺	H ₂ , NO ₂	3	5	4	I
MC ₄ H ₈ ⁺	HNO ₂	0	1	1	I
MC ₄ H ₉ ⁺	NO ₂	1	1	0	I
MC ₃ H ₆ O ⁺	CH ₃ NO	0	2	2	VI
MC ₄ H ₈ O ⁺	HNO	1	1	1	VI
MC ₄ H ₉ O ⁺	NO	2	1	0	VI
MC ₃ H ₆ NO ₂ ⁺	CH ₃	0	2	3	II

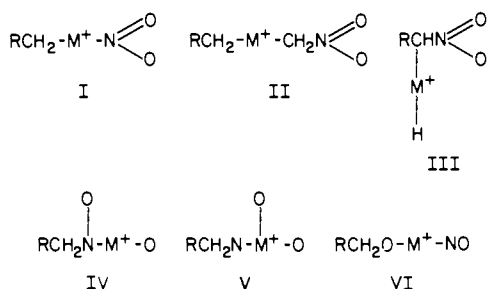
^a2-Nitro-2-methylpropane pressure was 1×10^{-7} torr. ^bFrom ref 6.

Table VII. Product Distributions for the Primary Reactions of Fe⁺, Co⁺, and Ni⁺ with 1-Butyl Nitrite

products		rel abundance ^a		
ion	neutral(s)	Fe ⁺	Co ⁺ ^b	Ni ⁺
C ₄ H ₉ ⁺	MONO	3	3	11
MNO ⁺	C ₄ H ₉ O	0	0	15
MOCH ₃ ⁺	C ₃ H ₆ NO	28	0	0
MC ₃ H ₅ ⁺	H ₂ , CH ₂ ONO	0	6	12
MC ₃ H ₇ ⁺	CH ₂ ONO	3	0	0
MC ₄ H ₆ ⁺	H ₂ , HNO ₂	3	4	0
MCH ₂ NO ₂ ⁺	C ₃ H ₇	2	23	31
MC ₄ H ₅ O ⁺	2H ₂ , NO	2	28	19
MC ₄ H ₆ O ⁺	H ₂ , HNO	3	6	0
MC ₄ H ₇ O ⁺	H ₂ , NO	30	21	6
MC ₄ H ₈ O ⁺	HNO	9	7	6
MC ₄ H ₉ O ⁺	NO	15	2	0
MC ₂ H ₄ NO ₂ ⁺	C ₂ H ₅	2	0	0

^a1-Butyl nitrite pressure was 1×10^{-7} torr. ^bFrom ref 6.

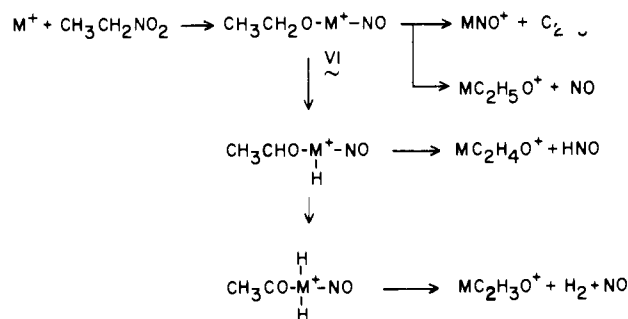
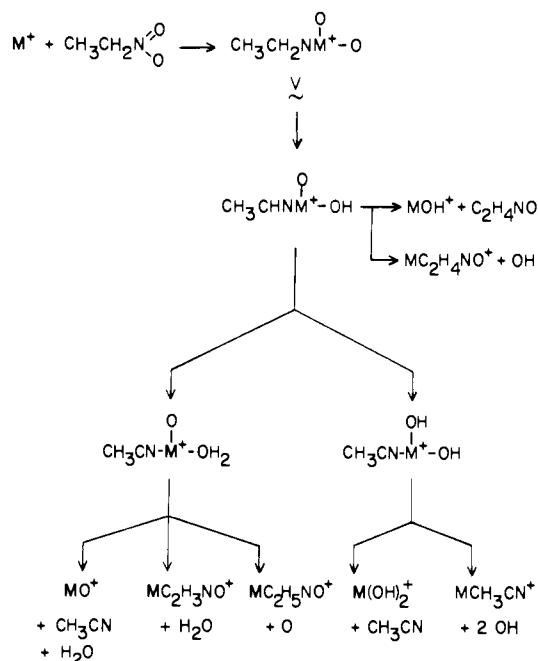
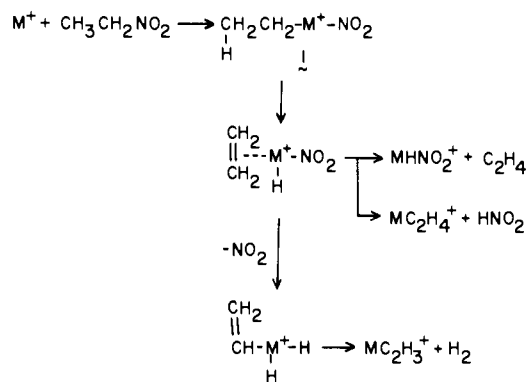
intermediate to the reactions of Fe⁺, Co⁺, and Ni⁺ with the nitroalkanes studied.



Nitroethane. In the nitromethane reactions,⁹ intermediates V and VI dominate for Fe⁺ and Co⁺, while Ni⁺ does not react. With nitroethane, however, all three metals react and in addition to V and VI other intermediates also play a role in the chemistry, as shown in Table I.

The major nitromethane reaction pathway,⁹ which involves a nitro-to-nitrite isomerization producing intermediate VI, is also present in the nitroethane reactions but is not the dominant reaction pathway. This mechanism, shown in Scheme I, accounts for approximately 20% of the products from each of the three metal ions. The major products of this mechanism result from loss of combinations of H₂ with NO or HNO, as suggested by the 1-butyl nitrite reactions (Table VII). A small amount of MNO⁺ formation occurs in the order FeNO⁺ < CoNO⁺ < NiNO⁺. This is also the order of MNO⁺ formation observed in the methyl nitrite reactions.⁹

The other major nitromethane mechanism,⁹ which involves intermediate V and possibly intermediate IV, is also present in the nitroethane reactions. Scheme II gives a mechanism for

Scheme I**Scheme II****Scheme III**

nitroethane product formation from V. The dominance of this mechanism for Fe⁺ and Co⁺ reacting with nitroethane over the nitro-to-nitrite isomerization mechanism, which dominates with nitromethane, suggests that the isomerization pathway becomes less favorable with increasing alkyl chain length. As seen from Table VIII, the participation of intermediate V in the nitroethane reactions decreases in the order Fe⁺ > Co⁺ > Ni⁺. This is also the order of decreasing strength of the M⁺-O bond¹⁰ and thus is expected to be the order of decreasing exothermicity for intermediate V formation. For Ni⁺, which has a Ni⁺-O bond that is 23 kcal/mol weaker than the Fe⁺-O bond,¹⁰ reaction via in-

(10) $D^\circ(\text{Fe}^+\text{-O}) = 68 \pm 3$ kcal/mol, $D^\circ(\text{Co}^+\text{-O}) = 65 \pm 3$ kcal/mol, and $D^\circ(\text{Ni}^+\text{-O}) = 45 \pm 4$ kcal/mol from: Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6501.

Table VIII. Intermediate Distributions in the Reactions of Fe⁺, Co⁺, and Ni⁺ with Nitroalkanes

nitroalkane	intermediate	rel abundance ^a		
		Fe ⁺	Co ⁺ ^c	Ni ⁺
nitromethane ^b	I	2	2	0
	II			
	IV or V	32	44	0
	VI	66	54	0
nitroethane	I	5	29	52
	II	26	14	10
	IV or V	53	35	18
	VI	16	22	20
1-nitropropane	I	14	47	66
	II	29	15	12
	IV or V	40	15	9
	VI	17	23	13
2-nitropropane	I	32	42	67
	II	20	17	12
	IV or V	28	18	8
	VI	20	23	13
1-nitrobutane	I	28	58	63
	II	23	24	19
	IV or V	21	9	5
	VI	28	9	13
2-nitrobutane	I	66	65	74
	II	7	10	12
	IV or V	18	8	6
	VI	9	17	8
2-nitro-2-methylpropane	I	91	89	91
	II	3	4	5
	IV or V	3	4	3
	IV	3	3	1

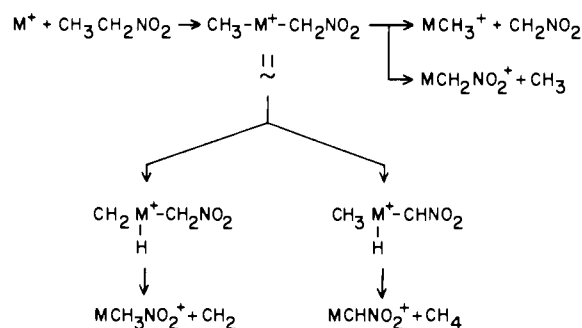
^a Nitroalkane pressure was 1×10^{-7} torr. ^b From ref 9 ^c From ref 6.

intermediate V is only a minor pathway with all of the nitroalkanes studied.

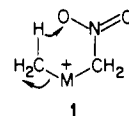
Oxidative addition of the metal ion into the C–N bond, intermediate I, results in only 2% of the nitromethane products,⁹ but it occurs to a greater extent in the nitroethane reactions. As seen in Scheme III, the major product from this reaction pathway is MHNO₂⁺. Production of this ion is unfavorable with nitromethane since an α-hydride shift and the loss of the high-energy-fragment CH₂ would be required. For nitroethane, however, the presence of β-hydrogens and the formation of C₂H₄ as the leaving group make this a much more thermodynamically favorable pathway. With a bond dissociation energy of 59 kcal/mol,^{3a} the C–N bond is by far the weakest bond in nitroethane. The order of increasing participation of intermediate I in the nitroethane reactions is Fe⁺ < Co⁺ < Ni⁺, with Ni⁺ showing a strong preference for insertion into this weak bond.

MC₂H₃⁺, which at 14% is the second most abundant product of the Co⁺ reactions, may form via intermediate I as shown in Scheme III. In addition, some formation of this ion may result from oxidative addition into a C–H bond, intermediate III, followed by a β-hydride shift and elimination of either H₂ and NO₂ or H₂O and NO. Loss of "H₂NO₂" is also the dominant process in the reactions of linear nitroalkanes with Rh⁺,¹¹ an ion which is known to favor C–H bond insertion in reactions with alkanes.⁸ The formation of this ion from nitroethane sets a lower limit of $D(M^+-C_2H_3) > 96$ kcal/mol,¹² assuming H₂ and NO₂ loss or $D(M^+-C_2H_3) > 60$ kcal/mol for H₂O and NO loss.

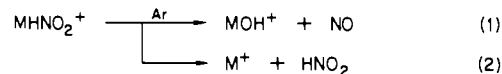
Insertion into the C–C bond of nitroethane, depicted in Scheme IV, accounts for 26% of the Fe⁺ products, 14% of the Co⁺ products, and 10% of the Ni⁺ products. It is interesting that following formation of II, loss of CH₃ to form MCH₂NO₂⁺ ap-

Scheme IV

pears to be slightly more favorable than CH₂NO₂ loss to form MCH₃⁺, which suggests that $D(M^+-CH_2NO_2) > D(M^+-CH_3)$. The minor product MCH₃NO₂⁺ is unusual, and its formation requires either an α-hydride shift or transfer of H to the nitro group via cyclic intermediate 1.⁶

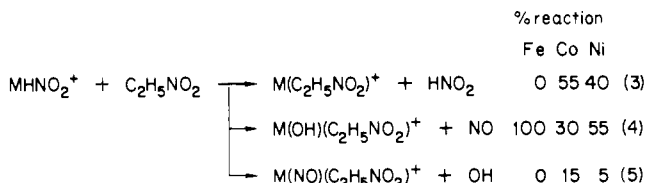


Collision-induced dissociation (CID) experiments were performed on major primary products of the nitroethane reactions. As expected, FeOH⁺ and CoOH⁺ dissociate to form Fe⁺ and Co⁺, respectively, with no MH⁺ or MO⁺ formation. FeO₂H₂⁺ dissociates to give FeO⁺ at low energies and FeOH⁺ at higher energies, suggesting a dihydroxide structure, Fe(OH)₂⁺. CoC₂H₃⁺ forms CoH⁺ and Co⁺, with CoH⁺ formation starting at slightly lower energies. Both NiHNO₂⁺ and CoHNO₂⁺ undergo CID by reactions 1 and 2, with M⁺ generated at slightly higher energies



than MOH⁺. No MNO⁺ forms, indicating that $D(M^+-NO) < D(M^+-OH)$ ¹³ for Co and Ni. The absence of MH⁺ and MNO₂⁺ is evidence against a hydrido-nitro structure. However, CID does not provide unequivocal evidence for whether the ion structure is M(HNO₂)⁺ or M(OH)(NO)⁺ since only 49 kcal/mol¹² is required to split HNO₂ into NO and OH and more than enough energy for this cleavage is imparted to the ion during CID.

The primary product ions undergo many further reactions with nitroethane. In some cases these secondary reactions can aid in the elucidation of ion structures. While CID was unsuccessful in probing the structure of MHNO₂⁺, displacement of NO and OH in reactions 3 through 5 points to an M(OH)(NO)⁺ structure.



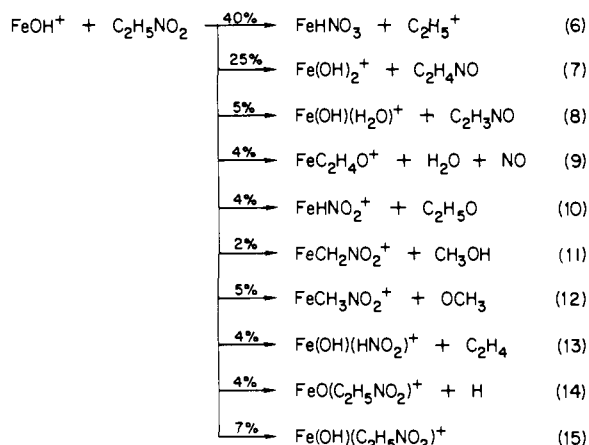
The secondary and subsequent reactions also aid in characterizing the metal's reactivity. The secondary FeL⁺ reactions, for example, reflect the trend of Fe⁺ to undergo a myriad of reactions with nitroalkanes. This is clearly demonstrated by the secondary reactions 6 through 15 of FeOH⁺, the major Fe⁺ primary product. In these reactions N–O and C–N insertions dominate.

The formation of alkyl ions as a major secondary product, reaction 6, is also seen in the reactions of other ML⁺ species with

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

(12) 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 3a.

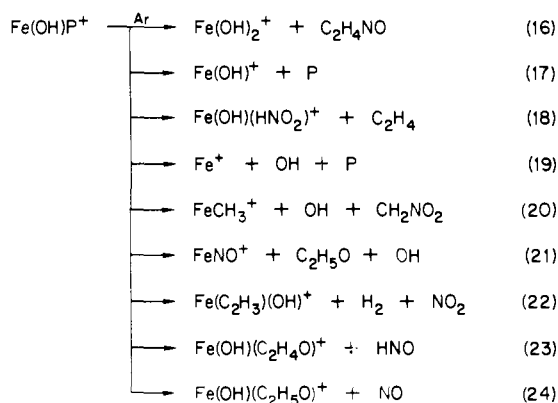
(13) $D^0(Fe^+-OH) = 73 \pm 3$ kcal/mol and $D^0(Co^+-OH) = 71 \pm 3$ kcal/mol from: Cassady, C. J.; Freiser, B. S. *J. Am. Chem. Soc.* 1984, 106, 6176.



nitroalkanes and has been observed in studies involving other organic molecules,¹⁴ as well. This reaction is quenched by the presence of $\sim 10^{-5}$ torr of argon,¹⁵ but exposing FeOH^+ to a high-pressure argon pulse prior to allowing it to react with nitroethane has no effect. This suggests that the addition of argon stabilizes a long-lived reaction intermediate of C–N insertion, as discussed later in this paper. The presence of argon is observed to have only a minor effect on the metal-containing product ions.

While there are many small primary and secondary products formed by the reaction of Fe^+ with nitroethane, after a reaction time of approximately 1 s the mass spectrum is dominated by Fe(OH)P^+ (P = nitroethane). At longer reaction times $\text{Fe(OH)}_2\text{P}^+$, Fe(OH)P_2^+ , and $\text{Fe(OH)}_2\text{P}_2^+$ dominate, with very little loss of the OH ligand occurring in the subsequent reactions. Fe(NO)P^+ , $\text{Fe(NO}_2\text{)P}^+$, Fe(NO)P_2^+ , and $\text{Fe(NO}_2\text{)P}_2^+$ are also major products in the mass spectrum at longer reaction times, but little formation of FeP^+ , FeP_2^+ , and FeP_3^+ is observed.

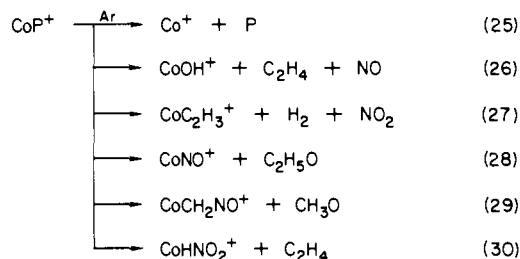
CID on the subsequent products of the Fe^+ reactions yields a menagerie of products but gives little structural information. For example, CID on Fe(OH)P^+ results in ten products, reactions 16 through 24. Reaction 16 dominates at all energies, while reactions 17 and 18 are also major processes, and reactions 19 through 24 occur only at higher energies. These data say little except to indicate that the $\text{Fe}^+\text{--OH}$ bond¹³ is the strongest bond in the ion.



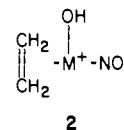
The primary products from Co^+ are also very reactive. For example, CoOH^+ reacts with nitroethane at $\sim 10^{-7}$ torr to form 60% C_2H_5^+ and eight small products in a manner similar to that of the FeOH^+ reactions, with the C_2H_5^+ intensity again dependent on pressure. In addition, Co(OH)P^+ is a dominant ion in the mass spectrum at reaction times approaching 1 s, just as Fe(OH)P^+ dominates for the Fe^+ reactions. The Co(OH)L^+ ions, however, have a much greater tendency to lose OH than do Fe(OH)L^+ ions. This OH loss occurs primarily via H_2O loss following a β -hydride

shift onto the metal and appears to dominate for Co^+ due to its enhanced ability to abstract β -hydrogens,¹⁶ rather than due to any differences in the $\text{Fe}^+\text{--OH}$ and $\text{Co}^+\text{--OH}$ bond strengths.¹³ CoP^+ , CoP_2^+ , and CoP_3^+ are also major ions in the mass spectrum at longer trapping times, while these ions are almost totally absent for Fe^+ as a consequence of the inability of Fe^+ to lose OH once it is bound. Other prominent products of the subsequent Co^+ reactions are Co(NO)P^+ , $\text{Co(NO}_2\text{)P}^+$, $\text{Co(OH)}_2\text{P}^+$, Co(OH)P_2^+ , Co(NO)P_2^+ , and $\text{Co(NO}_2\text{)P}_2^+$.

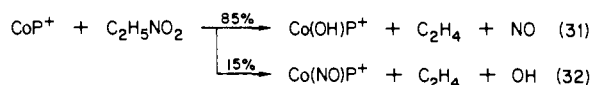
CID on CoL^+ species also gives a large number of products. For example, CID on Co(OH)P^+ yields $\text{Co(OH)(HNO}_2\text{)}^+$ as the major low-energy product, Co(OH)_2^+ as the second most abundant product, and nine minor high-energy products similar to those observed for Fe(OH)P^+ . CoP^+ dissociates to give CoOH^+ at low energies and Co^+ at higher energies as the major products, reactions 25 and 26, while reactions 27 through 30 are low-abundance processes. The products formed by CID on CoP^+ are also



the major primary products of the reaction of Co^+ with nitroethane. Although CID does not confirm a structure, it suggests

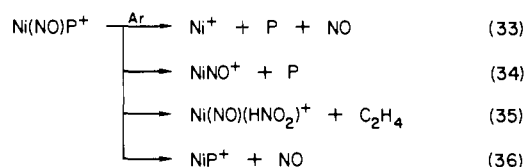


the possibility of **2** as the CoP^+ structure. The reactions of CoP^+ with nitroethane, reactions 31 and 32, also support this structure.



In the subsequent reactions of NiL^+ with nitroethane, fewer reaction channels are present than with FeL^+ and CoL^+ . In addition to the major products noted for FeL^+ and CoL^+ , many smaller products are also present for these species. For NiL^+ , however, virtually the only secondary ions observed are NiP^+ , Ni(OH)P^+ , Ni(NO)P^+ , NiP_2^+ , Ni(OH)P_2^+ , and NiP_3^+ . There is also a trend toward increasing the amount of MP^+ and M(NO)P^+ formed with $\text{Fe}^+ < \text{Co}^+ < \text{Ni}^+$.

As was the case with FeL^+ and CoL^+ , CID on NiL^+ species yields a large number of products. Ni(OH)P^+ dissociates to give $\text{Ni(OH)(HNO}_2\text{)}^+$ (loss of C_2H_4) as the major low-energy product, with nine high-energy, low-efficiency processes also occurring. No Ni(OH)_2^+ forms, which may indicate that the $\text{Ni}^+\text{--OH}$ bond is considerably weaker than the $\text{Fe}^+\text{--OH}$ and $\text{Co}^+\text{--OH}$ bonds. Ni(NO)P^+ dissociates in a relatively uncomplicated manner, with only four processes occurring, reactions 33 through 36. Loss of



C_2H_4 , reaction 35, is the major low-energy process, while NiNO^+ formation dominates over NiP^+ formation at high energies and Ni^+ forms only at the highest energies. CID and ion–molecule reactions 37 through 39 say little about the structure of Ni(NO)P^+ except to suggest that at least one NO is present as an intact ligand. CID on NiP^+ results in the formation of several products,

(14) Carlin, T. J.; Freiser, B. S., unpublished results.

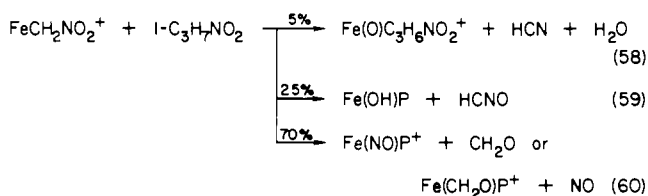
(15) Exposure to pulsed or static pressures on the order of 10^{-5} torr has been found to thermalize laser-generated excited-state metal ions within 500 ms. Cassidy, C. J.; Wise, M. B.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Phys.*, to be submitted for publication.

Table IX. Effect of Pressure on the Primary Product Distribution of the Reaction of Ni⁺ with 2-Nitrobutane

products		rel abundance at these pressures (in torr) ^a				
ion	neutral(s)	1 × 10 ⁻⁷	5 × 10 ⁻⁷	1 × 10 ⁻⁶	5 × 10 ⁻⁶	1 × 10 ⁻⁵
C ₄ H ₉ ⁺	NiNO ₂	68	54	37	4	2
NiOH ⁺	C ₄ H ₈ NO	3 (10) ^b	3 (7)	3 (5)	2 (2)	1 (1)
NiNO ⁺	C ₄ H ₉ O	2 (8)	3 (7)	5 (7)	7 (7)	7 (7)
NiC ₃ H ₅ ⁺	CH ₄ NO ₂	2 (6)	2 (4)	2 (4)	2 (2)	1 (1)
NiC ₃ H ₇ ⁺	CH ₃ NO ₂	1 (2)	1 (1)	2 (3)	1 (1)	1 (1)
NiC ₃ H ₈ ⁺	CHNO ₂	1 (4)	1 (3)	2 (3)	1 (1)	1 (1)
NiHNO ₂ ⁺	C ₄ H ₈	7 (22)	11 (25)	14 (23)	15 (16)	11 (11)
NiC ₄ H ₆ ⁺	H ₂ , HNO ₂	2 (6)	2 (5)	2 (4)	3 (3)	4 (4)
NiC ₄ H ₇ ⁺	H ₂ , NO ₂	5 (15)	9 (19)	13 (21)	26 (28)	31 (32)
NiC ₄ H ₈ ⁺	HNO ₂	1 (4)	2 (3)	2 (3)	3 (3)	3 (3)
NiC ₃ H ₆ O ⁺	HCN, H ₂ O	1 (4)	1 (3)	2 (3)	2 (2)	1 (1)
NiC ₄ H ₇ O ⁺	H ₂ , NO	1 (2)	1 (2)	1 (1)	1 (1)	1 (1)
NiC ₄ H ₈ O ⁺	HNO	1 (4)	2 (4)	2 (3)	3 (3)	2 (2)
NiC ₂ H ₄ NO ₂ ⁺	C ₂ H ₅	3 (8)	5 (10)	8 (12)	18 (19)	22 (23)
NiC ₄ H ₈ NO ⁺	OH	1 (3)	2 (4)	3 (5)	8 (8)	8 (8)
NiC ₃ H ₆ NO ₂ ⁺	CH ₃	1 (2)	1 (3)	2 (3)	4 (4)	4 (4)

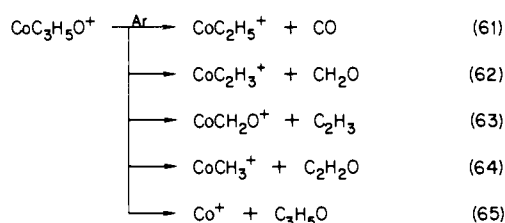
^a 2-Nitrobutane was present at 1 × 10⁻⁷ torr in all experiments. Argon was added to obtain the desired total pressure. The reaction time was 300 ms. ^b Values in parentheses are the relative product abundances (to 100%) neglecting C₄H₉⁺.

higher energies, with reaction 55 dominating. These results, combined with secondary reactions 58 through 60, suggest that the ion may have an Fe(NO)(CH₂O)⁺ structure. CoC₃H₅⁺

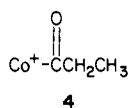


undergoes CID in a manner characteristic of an allyl-Co⁺ complex¹⁸ to give CoC₃H₃⁺ as the major low-energy product and Co⁺ as the major high-energy product, with CoCH₃⁺ also forming at higher energies. The formation of this ion from 1-nitropropane sets a lower limit of $D(\text{Co}^+-\text{C}_3\text{H}_5^+) > 78$ kcal/mol,¹² assuming H₂ and NO₂ elimination. This agrees well with the previously reported value of $D(\text{Co}^+-\text{C}_3\text{H}_5) > 74$ kcal/mol.¹⁸ If the neutrals lost are H₂O and NO, this lower limit is $D(\text{Co}^+-\text{C}_3\text{H}_5) > 34$ kcal/mol.¹²

Collision-induced dissociation on CoC₃H₅O⁺ results in five products, as shown in reactions 61 through 65, with CoCH₃⁺ as the major product at all energies studied.⁶ The only secondary



product in the reaction of CoC₃H₅O⁺ with 1-nitropropane is Co(C₃H₅O)(OH)⁺, suggesting that no easily displaced ligand is present. These results point to structure 4, which most probably results from the loss of H₂ and NO from intermediate VI.



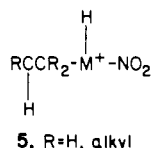
As with nitroethane, the primary products from nitropropane are very reactive with the neutral. The same general trends in the sequence of reactions noted for nitroethane also occur with nitropropane and with nitrobutane, as well. CID on the major ions gives an abundance of products but provides little structural information.

Nitrobutane. The reactions of Fe⁺, Co⁺, and Ni⁺ with 1- and 2-nitrobutane and 2-nitro-2-methylpropane are given in Tables IV–VI, respectively. The same reaction pathways observed for nitroethane and nitropropane also occur with the nitrobutanes. However, C₄H₉⁺ is the major product for each of the three metal ions. Formation of C₃H₇⁺ also occurs in the nitropropane reactions, but to a more limited extent. The formation of alkyl ions, which has also been observed in the reactions of gas-phase metal ions with other R–X species,¹⁴ is highly dependent on total pressure. Table IX shows the effect of argon pressure on the reaction of Ni⁺ with 2-nitrobutane, demonstrating that increasing the pressure results in a decrease in the amount of alkyl ion formation. Surprisingly, subjecting the laser-generated metal ions to an argon pulse, which raises the pressure to a maximum of ~10⁻³ torr and pumps away within ~500 ms, and then allowing the metal ions to react with a nitroalkane at 10⁻⁷ torr has no effect on the reaction. This indicates that the pressure dependence of product intensities is not due to the buffer gas cooling down excited-state metal ions,¹⁵ but rather it leads to the alternative conclusion that a long-lived (>1 ms) reaction intermediate of C–N insertion is undergoing stabilizing collisions with the buffer gas. In general, as would be expected, formation of alkyl ions is most prevalent for Ni⁺, which preferentially attacks C–N bonds. Assuming that alkyl ion formation is exothermic, as these experiments seem to indicate, the neutral product must be MNO₂.¹⁹ The 1-nitrobutane reactions set a lower limit of $D(\text{M}-\text{NO}_2) > 60$ kcal/mol for all three metal ions, with $\Delta H_f(\text{MNO}_2) < 48$ kcal/mol.¹²

Addition of a buffer gas at relatively high pressures is also observed to have a small, but noticeable, effect on the metal-containing products as well, although no products are observed to appear or disappear with increasing pressure. The relative product distributions of the Ni⁺ reactions show the most marked pressure dependence, with the Co⁺ reactions exhibiting a small pressure effect, while little pressure dependence is seen in the Fe⁺ reactions. The most notable pressure effects can once again be seen in Table IX. These include an increase in NiC₄H₇⁺ formation (loss of H₂ and NO₂) relative to NiHNO₂⁺ formation (loss of C₄H₈), suggesting that intermediate 5 is collisionally stabilized at higher pressures, thus allowing a second β-hydride shift to occur resulting in loss of H₂ and NO₂ as opposed to NiHNO₂⁺ formation. Also, the ratio of OH retention to OH loss products, i.e., NiOH⁺ and NiC₄H₈NO⁺, changes with pressure and an increase

(19) In the reaction leading to C₄H₉⁺ from 1-nitrobutane, formation of Co + NO₂ as neutral products is ~60 kcal/mol endothermic, while CoO + NO formation is also ~60 kcal/mol endothermic. The values for Fe and Ni are similar. All thermochemical information is taken from ref 12, except $\Delta H_f(\text{CoO}) = 74$ kcal/mol which is derived by using $D(\text{Co}-\text{O}) = 87 \pm 4$ kcal/mol from: Grimley, R. T.; Burns, R. P.; Inghram, M. G. *J. Chem. Phys.* **1966**, *45*, 4158; Smoes, S.; Mandy, F.; Auwera-Mahieu, A.; Drowart, J. *Bull. Soc. Chim. Belg.* **1972**, *81*, 45.

in C–C insertion products (such as $\text{NiC}_2\text{H}_4\text{NO}_2^+$) is observed for Co^+ and Ni^+ with increasing pressure.



1-Butyl Nitrite. The reactions of Fe^+ , Co^+ , and Ni^+ with 1-butyl nitrite, Table VII, aid in interpreting the nitroalkane data. In particular these reactions demonstrate that insertion of the metal into the weak O–NO bond ($D(\text{C}_4\text{H}_9\text{O–NO}) = 42 \text{ kcal/mol}^{20}$) of larger alkyl nitrites (intermediate VI) results primarily in loss of combinations of H_2 with NO or HNO. Ni^+ also reacts with 1-butyl nitrite to form NiNO^+ , but the analogous ions are not observed for Fe^+ and Co^+ . Oxidative addition of the metal into the weak O–NO bond does not totally dominate the 1-butyl nitrite reactions. Cleavages of this bond results in 59% of the Fe^+ products, 64% of the Co^+ products, and 46% of the Ni^+ products. Insertion into the stronger $\text{C}_4\text{H}_9\text{–ONO}$ bond accounts for 6%, 7%, and 11% of the Fe^+ , Co^+ , and Ni^+ products, respectively. Carbon–carbon bond cleavage is also a major process, resulting in 7% of the Fe^+ products, 29% of the Co^+ products, and a surprising 43% of the Ni^+ products. For Co^+ and Ni^+ , the C–C bond attacked is the $\text{C}_3\text{H}_7\text{–CH}_2\text{ONO}$ bond, with formation of MCH_2ONO^+ dominating over MC_3H_7^+ . The abundance of these products for Ni^+ and Co^+ may indicate that they result from O–NO insertion followed by a cleavage of the carbon chain, as opposed to initial C–C insertion. This alternate mechanism is supported by the fact that Rh^+ , an ion which reacts with alkanes almost exclusively by C–H insertion,⁸ reacts with 1-butyl nitrite to give 45% C–C cleavage products.¹¹

An ion at m/z 87 accounts for the remaining 28% of the Fe^+ products. This ion readily undergoes three H/D exchanges with C_2D_4 , indicating that it is FeOCH_3^+ as opposed to the isobar FeHNO^+ . This ion is also observed in the reactions of Fe^+ with 1-nitropropane and 1-nitrobutane and again can arise from mechanisms involving either initial C–C or O–NO insertion.

Conclusion

Fe^+ , Co^+ , and Ni^+ exhibit a rich chemistry in their reactions with nitroalkanes. Insertion of the metal ion into the C–NO₂ bond, which is the weakest bond in nitroalkanes, dominates the chemistry of Ni^+ . Fe^+ , however, attacks the stronger N–O and C–C bonds, forming an abundance of products. Co^+ reacts in a manner which is intermediate to Fe^+ and Ni^+ . An unusual aspect of these reactions is that following C–C insertion the major pathway for product formation is the elimination of radicals as opposed to the elimination of stable molecules following β -hydride abstractions by the metal.

Another unusual aspect of the reactions of groups 8–10 metal ions with nitroalkanes is the formation of products that seem to result from a nitrite intermediate. This process, which dominates in the reactions of Fe^+ and Co^+ with nitromethane as discussed in the preceding paper of this journal,⁹ accounts for ~10–20% of the products of the reactions of Fe^+ , Co^+ , and Ni^+ with larger nitroalkanes and appears to involve a metal-induced nitro-to-nitrite isomerization. Such isomerizations have previously been observed in solution, where they are induced by thermal²¹ or photochemical²² means and involve an NO₂ dissociation from the alkyl group followed by a recombination. They have also been observed in the gas phase, in the electron impact mass spectra of many aromatic²³ and some aliphatic²⁴ nitro compounds, where they arise due to charge/radical sites in the molecule.

A major pathway in the reactions with nitropropane and nitrobutane is the generation of alkyl ions. These ions decrease in intensity when relatively high pressures of an inert gas are added to the system but are not affected by a high-pressure pulse of gas prior to the reaction. This indicates that they are not formed by excited-state metal ions,¹⁵ but rather, the pressure dependence may be due to the buffer gas stabilizing a long-lived (>1 ms) reaction intermediate of C–N insertion. Formation of alkyl ions is most prevalent for Ni^+ , which preferentially attacks C–N bonds in its reactions with nitroalkanes. In general, relative abundances of metal-containing products vary little with pressure, with the greatest effect again seen for Ni^+ . This same pressure dependence is also observed in the secondary reactions of the primary product MOH^+ . Further studies of the effect of pressure on gas phase metal ion reactions are currently underway in our laboratory.

Acknowledgement is made to the Division of Chemical Sciences in the Office of Basic Energy Sciences in the United States Department of Energy (DE-AC02-80ER10689) for supporting this research and the National Science Foundation (CHE-8100039) for providing funds for continued support of the FTMS. In addition, one of us (C.J.C.) thanks Phillips Petroleum for providing fellowship support.

Registry No. Fe^+ , 14067-02-8; Co^+ , 16610-75-6; Ni^+ , 14903-34-5; nitroethane, 79-24-3; 1-nitropropane, 108-03-2; 2-nitropropane, 79-46-9; 2-nitropropane, 79-46-9; 1-nitrobutane, 627-05-4; 2-nitrobutane, 600-24-8; 2-nitro-2-methylpropane, 594-70-7; 1-butyl nitrite, 544-16-1.

(20) Reference 3a, p 1075.

(21) Reference 3a, Part I, pp 434–441 and references therein.

(22) Reference 3a, Part I, pp 214–216 and references therein.

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

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