1 h. The usual workup afforded 1.1 g (45% based on BTMSA) of a mixture consisting of **2** (85%), **1** (10%), and an unidentified 1:1 adduct of NBD and BTMSA (5%) (by GC analysis). The spectral data of **2** (IR, NMR) were obtained with the mixture and corrected for the contribution of **1**. **2**: IR (neat) 3057 (m), 3017 (m), 2950 (s), 2927 (sh), 2900 (s), 2845 (m), 1535 (m), 1440 (w), 1405 (w), 1248 (s), 1048 (m), 854 (sh), 835 (vs), 752 (s), 708 (m), 690 (m), 682 (m), 643 (m), 630 (w) cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.14 (dm, $J_{1,2} = 5.0$, $J_{2,5} = 1.2$ Hz, H-2), 5.89 (dd, $J_{5,6} = 3.6$ Hz, H-5), 5.86 (m, H-7), 5.68 (m, H-8), 3.27 (dm, $J_{1,6} = 11$ Hz, H-6), 2.83 (dddd, $J_{1,6} = 11$ Hz, $J_{1,9'} = 6.8$, $J_{1,9} = 8.5$, $J_{1,2} = 5$ Hz, H-1), 2.61 (dm, $J_{9,9'} = 15.6$, $J_{9,1} = 8.5$ Hz, H-9), 2.14 (ddq, $J_{9',8} = 2.3$, $J_{9',7} = 2.3$ Hz, H-9′), 0.12 (s, 9 H), 0.02 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 140.84 (d), 135.71 (d), 135.00 (s), 134.56 (s), 131.82 (d), 131.58 (d), 43.23 (d), 40.42 (t), 36.26 (d), 1.08 (q); ^{29}Si NMR ($CDCl_3$) δ −4.57, −4.66; MS *m/z* (relative intensity) 262 ($M^{+}\cdot$, 1), 247 (5.5), 231 (1.6), 174 (10.1), 173 (13), 159 (14.3), 145 (3.5), 131 (3), 73 (100), 59 (14.5), 45 (12.3).

Preparation of 8,9,10,11-Tetrakis(trimethylsilyl)tricyclo[5.2.2.0^{2,6}]undeca-3,8,10-triene (3). A. Crude compound **2** (1.2 g, 4.5 mmol), BTMSA (0.76 g, 4.4 mmol), Et_2AlCl (2 mL of the 1.0 M solution), and $TiCl_4$ (1 mL of the 0.1 M solution) were mixed under cooling to −78 °C and then rapidly warmed to 60 °C under vigorous stirring. After 1 h at 60 °C the mixture was diluted with benzene (10 mL), washed with water, and dried with sodium sulfate. The solvents were evaporated in vacuo at 40 °C, a fraction distilling at 80–100 °C (0.2 g) was separated, and the residue was sublimed onto a cold finger at 100 °C to yield 1.2 g of a crystalline material which was further purified by double recrystallization from ethanol; mp 72–73 °C. The liquid distillation product contained mainly **1** and **2** and traces of another 1:1 BTMSA–NBD adduct (*m/z* 262 ($M^{+}\cdot$), trimethylsilylindene (*m/z* 188 ($M^{+}\cdot$)), bis(trimethylsilyl)indene (*m/z* 260 ($M^{+}\cdot$)), and bis- and tetrakis(trimethylsilyl)benzenes (*m/z* 222 ($M^{+}\cdot$), 366 ($M^{+}\cdot$)), according to GC–MS. Anal. Calcd for (**3**): C, $C_{23}H_{44}Si_4$ (**3**): C, 63.80; H, 10.24. Found: C, 63.75; H, 10.12. **3** IR (KBr pellet) 3048 (w), 3041 (w), 2978 (m), 2952 (s), 2927 (m), 2900 (m), 2843 (w), 1523 (w), 1438 (w), 1407 (w), 1248 (s), 1083 (m), 1004 (w), 988 (w), 973 (m), 933 (m), 834 (vs), 752 (s), 716 (m), 690 (m), 681 (m), 635 (m), 544 (w), 513 (w), 457 (w), 423 (w), cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.41 (dm, $J_d = 5.6$ Hz, 1 H), 5.35 (dm, $J_d = 5.6$ Hz, 1 H), 4.27 (d, $J = 3.0$ Hz, 1 H), 4.25 (d, $J = 2.9$ Hz, 1 H), 2.51 (m, 1 H), 2.02–2.27 (m, 2 H), 1.68 (dm, $J_d = 15.2$ Hz, 1 H), 0.17 (s, 9 H), 0.16 (s, 9 H), 0.14 (s, 9 H), 0.12 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 157.65 (s), 157.47 (s), 156.83 (s), 153.79 (s), 133.02 (d), 131.53 (d), 53.98 (d), 53.09 (d), 52.41 (d), 40.28 (d), 36.77 (t), 1.45 (q), 1.32 (q, 2C), 1.23 (q); ^{29}Si NMR ($CDCl_3$) δ −8.23, −8.29, −8.89, −9.29; MS *m/z* (relative intensity) 432 ($M^{+}\cdot$, 0.05), 353 (16), 352 (31), 351 (84), 335 (33), 293 (20), 263 (30), 247 (6), 155 (5), 152 (4), 145 (3), 73 (100), 59 (6), 45 (14).

B. A mixture of **1** (0.8 g, 1.8 mmol) and BTMSA (0.38 g, 2.2 mmol) was treated with the same amount of the catalyst as under A. This procedure afforded the liquid fraction (0.2 g) and a solid (0.6 g) which gave 0.45 g of **3** after recrystallization from ethanol.

C. Treating NBD (1 mL) and BTMSA (2 mL) with the in situ prepared catalyst under the conditions described for the preparation of either **1** or **2** yielded a mixture from which **3** was isolated by vacuum sublimation. The yield of **3** was 0.5 g when the reaction was run at 20 °C and 0.8 g at 60 °C.

Preparation of 1,2,4,5-Tetrakis(trimethylsilyl)benzene (4). Compound **3** (0.3 g) was heated in vacuo in a 20-mL ampule at 190 °C for 2 h. Cyclopentadiene and dicyclopentadiene were evaporated in vacuo at 40 °C, and the crystalline residue was twice crystallized from ethanol to give 0.23 g (90%) of **4**: mp 169–171 °C (lit.[17] 173 °C); IR (KBr pellet) 3076 (w), 2947 (s), 2897 (m), 1405 (w), 1268 (sh), 1247 (s), 1178 (m), 1087 (m), 835 (vs), 756 (s), 693 (m), 678 (m), 644 (m), 632 (m), 500 (m), 441 (m), 433 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.39 (s, 36 H), 8.00 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 144.75 (s), 141.50 (d), 1.83 (s); ^{29}Si NMR ($CDCl_3$) δ −2.90; MS *m/z* (relative intensity) 366 ($M^{+}\cdot$, 44), 351 (90), 335 (47), 263 (44), 247 (8), 205 (5), 152 (13), 73 (100), 45 (18).

Isomerization of 1 to 2. Compound **1** (0.5 g) was mixed with Et_2AlCl (2 mL of the 1.0 M solution) and $TiCl_4$ (1 mL of the 0.1 M solution) at −78 °C, and the mixture was rapidly warmed to 60 °C. After workup a mixture of $C_{15}H_{26}Si_2$ isomers was obtained which was identical by GC–MS with that described for the preparation of **2**. Isomerization of **2** (1.1 g) under conditions used for the preparation of **1** (1 h at 20 °C) yielded only the unchanged starting compound in 80% yield.

Registry No. **1**, 101652-96-4; **2**, 101652-97-5; **3**, 101652-98-6; **4**, 17156-61-5; BTMSA, 14630-40-1; NBD, 121-46-0; Et_2AlCl, 96-10-6; $TiCl_4$, 7550-45-0.

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Gas-Phase Chemistry of Transition-Metal-Containing Anions with Nitroalkanes and *n*-Butyl Nitrite

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The gas-phase ion/molecule reactions of iron-, cobalt-, and chromium-containing anions with a series of nitroalkanes and *n*-butyl nitrite are reported here. A mechanism is proposed in which the anion reacts by a charge-transfer mechanism which results in the cleavage of C–NO_2 and N–O bonds, leading to intermediates of the type $RM(CO)_xNO_2^-$ and $RNOM(CO)_xO^-$. These intermediates may then fragment or rearrange further. If charge transfer is the first mechanistic step leading to the observed products, the exothermicity of the charge transfer may determine the number of reaction pathways which are thermodynamically accessible. Thus, on the basis of the observed chemistry of alkyl halides, alcohols, bromochloroalkanes, chloro alcohols, and nitroalkanes, an ordering of the electron affinities of the organometallic reactant species studied here is reported.

Introduction

Recently, the gas-phase ion/molecule chemistry of $Fe(CO)_{3,4}^-$, $Cr(CO)_{3-5}^-$, $Co(CO)_{2,3}^-$, and $CoNO(CO)_{1,2}^-$ with a series of *n*-chloroalkanes, *n*-alcohols, 1,*n*-bromochloroalkanes, and 1,*n*-chloroalcohols was reported.[1] In the chloroalkane reactions, all products could be explained via the formation of a metal insertion/charge transfer intermediate 1. Ligand displacement, chlorine abstraction, and

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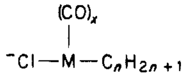
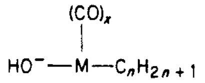


$$^{-}Cl-\overset{(CO)_x}{\overset{|}{M}}-C_nH_{2n+1}$$

1

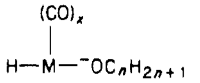
HCl abstraction processes were observed. In these reactions, groups bound to the metal which had positive electron affinities, i.e., those onto which the charge could be extensively delocalized (e.g., Cl), appeared to be preferentially retained.

Alcohols reacted via metal insertion/charge transfer intermediates **2** and **3**, which correspond to attack of the C–O and O–H bonds. The observed trends in chemistry



$$HO^{-}-\overset{(CO)_x}{\overset{|}{M}}-C_nH_{2n+1}$$

2



$$H-\overset{(CO)_x}{\overset{|}{M}}-{}^{-}OC_nH_{2n+1}$$

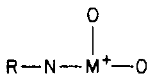
3

were rationalized in terms of the energy released in the electron transfer step, which suggested the following order in electron affinities (EA): EA($Cr(CO)_3$) < EA($Co(CO)_2$) < EA(CoCONO) < EA($Co(CO)_3$) < EA($Fe(CO)_3$). The only known electron affinity in this series is that of $Fe(CO)_3$ (41.5 kcal/mol).[2]

This work focuses on the chemistry of the same set of iron-, cobalt-, and chromium-containing anions with a series of nitroalkanes and *n*-butyl nitrite. The chemistry of transition-metal- and metal-containing *cations* with these compounds have been previously reported.[3-5] Ions such as Co^+ reacted with nitroalkanes by inserting into C–N, N–O, and C–C bonds. Two rearrangement-type intermediates, **4** and **5**, were also suggested as being formed

$R-O-M^+-NO$

4



$$R-N-\overset{O}{\overset{|}{M^+}}-O$$

5

early in the metal ion–nitroalkane interactions. Ions such as $Co(CO)_2^+$ only reacted with nitroalkanes by ligand substitution processes such as reaction 1. The Co^+ ion reacted with *n*-butyl nitrite by inserting into C–O, C–C, and RO–NO bonds.

$$Co(CO)_2^+ + CH_3NO_2 \rightarrow CoCO(CH_3NO_2)^+ + CO \qquad (1)$$

On the basis of these previous studies, we would predict that metal-containing anions should react with nitroalkanes by attack of the C–N and N–O bonds. The relatively high electron affinities of NO_2 (53 kcal/mol) and O (33.7 kcal/mol) also suggest that intermediates due to attack of these bonds will be formed. (The pertinent electron affinities for this study are listed in Table I.)

Table I. Pertinent Electron Affinities (EA, kcal/mol)[a]

anion (M^-)	EA(M), kcal/mol	ref
Fe^-	3.8	2
$Fe(CO)^-$	29.1	2
$Fe(CO)_2^-$	28.1	2
$Fe(CO)_3^-$	41.5	2
$Fe(CO)_4^-$	55.3	2
Co^-	15.3	6
Cr^-	15.4	7
CrO_2^-	55.3	8
H^-	17.4	9
CO_2^-	-13.8	10
O^-	33.7	11
HO^-	42.2	12
H_2O^-	0.00	13
n-$C_4H_9O^-$	43.8	14
CH_3^-	26	15
$C_2H_5^-$	23	15
$C_3H_7^-$	16	15
$C_4H_9^-$	15	15
$C_2H_4^-$	-35.7	16
$C_3H_5^-$	12.5	17
$CH_3NO_2^-$	9.2	18
NO^-	0.5	19
HNO^-	7.8	20
NO_2^-	53	21
$C_2H_5N^-$	43	22

[a] Electron affinity is defined as ΔH for the reaction $M^- \rightarrow M + e^-$

Experimental Section

All experiments were performed on an ion cyclotron resonance (ICR) mass spectrometer of conventional design (used in the "drift mode") which was constructed at Michigan State University and is described elsewhere.[23] Positive ion (70-eV) electron-impact mass spectra were obtained to determine the purity of the samples. The ICR was then configured to detect negative ions[1] for the present study. All chemicals used in this work were high-purity commercial samples which were used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensable gases.

The reactant metal-containing anions were formed by low-energy electron impact on $Co(CO)_3NO$ (to form $Co(CO)_2^-$, $CoCONO^-$, $Co(CO)_3^-$, and $Co(CO)_2NO^-$), $Fe(CO)_5$ (to form $Fe(CO)_3^-$ and $Fe(CO)_4^-$), and $Cr(CO)_6$ (to form $Cr(CO)_3^-$, $Cr(CO)_4^-$, and $Cr(CO)_5^-$) as described previously.[1] Ion/molecule reactions and precursors were identified by using double-resonance techniques. Reported data are results of product ions formed in a 1:1 mixture (by pressure) of the metal carbonyl to organic compound, at a total pressure of approximately 1×10^{-5} torr. Spectra were always taken to masses greater than the sum of the molecular weight of the metal carbonyl and the organic compound. The branching ratios listed in Tables II–V are accurate to within ±10%. In some cases empirical formulas other than those listed may also be possible for the product ions, however, we believe those listed are the most reasonable on the basis of observed reaction trends for the series of nitroalkanes and the reactions

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Table II. Reactions of Iron-Containing Anions with *n*-Nitroalkanes and 2-Methyl-2-nitropropane

reaction			intermediate structure	branching ratios				
				n = 1	*n* = 2	*n* = 3	*n* = 4	*n* = 4 ($(CH_3)_3CNO_2$)
$Fe(CO)_3^- + C_nH_{2n+1}NO_2$	→	$Fe(CO)C_nH_{2n+1}NO_2^- + 2CO$		9	23	13	7	35
	→	$Fe(CO)_2C_nH_{2n+1}NO_2^- + CO$		15	10	7	3	
	→	$FeC_nH_{2n+1}NO^- + CO_2 + 2CO$	I′, III′	42	(8)[a]	21	20	65
	→	$Fe(CO)C_nH_{2n+1}NO^- + CO_2 + CO$	I′, III′	19	16	8	4	
	→	$FeH_2O^- + C_nH_{2n-1}NO + 3CO$	III		19	7	18	
	→	$Fe(CO)H_2O^- + C_nH_{2n-1}NO + 2CO$	III		6	6	14	
	or	$FeNO_2^- + C_nH_{2n+1} + 3CO$	II					
	→	$Fe(CO)NO^- + C_nH_{2n+1} + CO_2 + CO$	III′	4				
	→	$Fe(CO)HNO^- + C_nH_{2n} + CO_2 + CO$	III′		(8)	25	32	
	→	$FeC_nH_{2n-1}NO^- + H_2O + 3CO$	I	7				
	or	$Fe(CO)C_nH_{2n+1}^- + NO + CO_2 + CO$	III′					
	→	$Fe(CO)C_nH_{2n-1}NO^- + H_2O + 2CO$	I, III		18	13	2	
	or	$Fe(CO)_2C_nH_{2n+1}^- + NO + CO_2$	III′					
	→	$Fe(CO)_3O^- + C_nH_{2n+1}NO$	I	4				
	or	$Fe(CO)_2C_nH_{2n}NO^- + OH + CO$	I					
$Fe(CO)_4^- + C_nH_{2n+1}NO_2$	→	NR[b]						

[a] Values in parentheses are the sum of branching ratios for isobaric product ions. [b] NR indicates the ion did not undergo any reactions.

Table III. Reactions of Cobalt-Containing Anions with *n*-Nitroalkanes and 2-Methyl-2-nitropropane

reaction			intermediate structure	branching ratios				
				n = 1	*n* = 2	*n* = 3	*n* = 4	*n* = 4 ($(CH_3)_3CNO_2$)
$Co(CO^-)_2^- + C_nH_{2n+1}NO_2$	→	$CoC_nH_{2n+1}NO_2^- + 2CO$		6	(11)[a]			
	→	$Co(CO)C_nH_{2n+1}NO_2^- + CO$		13	14	7	9	
	→	$Co(CO)_2O^- + C_nH_{2n+1}NO$	I	32	37	28	32	50
	→	$CoC_nH_{2n+1}NO^- + CO_2 + CO$	I′, III′	36	7	17	*b*	
	→	$CoH_2O^- + C_nH_{2n-1}NO + 2CO$	III		9	13	20	
	→	$CoHNO^- + C_nH_{2n} + CO_2 + CO$	III′		19	7	10	
	→	$CoHNO_2^- + C_nH_{2n} + 2CO$	II		3	5	9	
	→	$Co(CO)HNO_2^- + C_nH_{2n} + CO$	II		(11)	12	20	50
	→	$CoC_nH_{2n-1}NO^- + H_2O + 2CO$	I	13	*b*	11	*b*	*b*
	or	$Co(CO)C_nH_{2n+1}^- + NO + CO_2$	III′					
$CoCONO^- + C_nH_{2n+1}NO_2$	→	$Co(NO)C_nH_{2n+1}NO_2^- + CO$		13	7	6	10	
	→	$CoCONO(O)^- + C_nH_{2n+1}NO$	I	12	12	10	9	
	→	$CoNO(O)^- + C_nH_{2n+1}NO + CO$	I	53	46	54	52	
	or	$Co(CO)H_2O^- + C_nH_{2n-1}NO + NO$	I					
	→	$CoH_2O_2^- + C_nH_{2n-1}N + CO + NO$	IV	8	7	11	9	
	→	$Co(CO)(NO)NO_2^- + C_nH_{2n+1}$	II	14	28	19	20	100
$Co(CO)_3^- + C_nH_{2n+1}NO_2$	→	NR[c]						
$Co(CO)_2NO^- + C_nH_{2n+1}NO_2$	→	NR[c]						

[a] Values in parentheses are the sum of branching ratios for isobaric product ions. [b] These product ions are expected, but no double-resonance response is observed due to interference from electron impact fragments of $Co(CO)_3NO$. [c] NR indicates the ion did not undergo any reactions.

of the other metal anions.

Results and Discussion

Reactions of *n*-Nitroalkanes. The ion/molecule reaction products and their branching ratios for the reactions of iron-, cobalt-, and chromium-containing anions with the series of 1-nitro-*n*-alkanes (*n*-nitroalkanes) (n = 1–4) are listed in Table II, III, and IV, respectively. It is interesting to note that the number of different products observed for $Fe(CO)_3^-$, $Co(CO)_2^-$, and $Cr(CO)_3^-$ (8, 9, and 17 products, respectively) correlates with the order of electron affinities suggested for these metal-containing species from the alkyl halide and alcohol reactions ($EA(Cr(CO)_3) < EA(Co(CO)_2) < EA(Fe(CO)_3)$). This suggests that, when a greater amount of energy is released in the charge-transfer process for the metal species with lower electron affinities, a larger variety of products is observed.

Substitution of the neutral nitroalkane for one to three CO ligands (parent substitution) is observed for the reactive (i.e., non-17 electron) metal-containing anions for all three metals studied (reaction 2). The nitroalkanes displace one or two CO ligands in the reaction of $Fe(CO)_3^-$ and $Co(CO)_2^-$, but all three CO ligands are lost in the parent substitution products with $Cr(CO)_3^-$. This trend correlates well with the suggested ordering of electron affinities (and thus exothermicity of the charge-transfer process) of the three metal species mentioned previously. Thus, a metal insertion/charge transfer mechanism may account for the parent substitution products. In the chloroalkane and alcohol reactions, the parent substitution product structure presumably does *not* consist of an intact organic molecule as a ligand but was predicted to result from metal insertion/charge transfer into the C–functional group bond. This was proposed to be due to the negative electron affinity of the neutral molecule and due to the fact that all of the products observed could be formed through this common intermediate. In contrast, the electron affinity of the neutral nitroalkanes is positive (e.g., $EA(CH_3NO_2)$ = 9.2 kcal/mol, suggesting that the parent substitution product structure may consist of either an intact nitroalkane bound to the metal or a metal insertion type structure.

$$M(CO)_x^- + C_nH_{2n+1}NO_2 \rightarrow M(CO)_{x-a}C_nH_{2n+1}NO_2^- + aCO \quad (2)$$

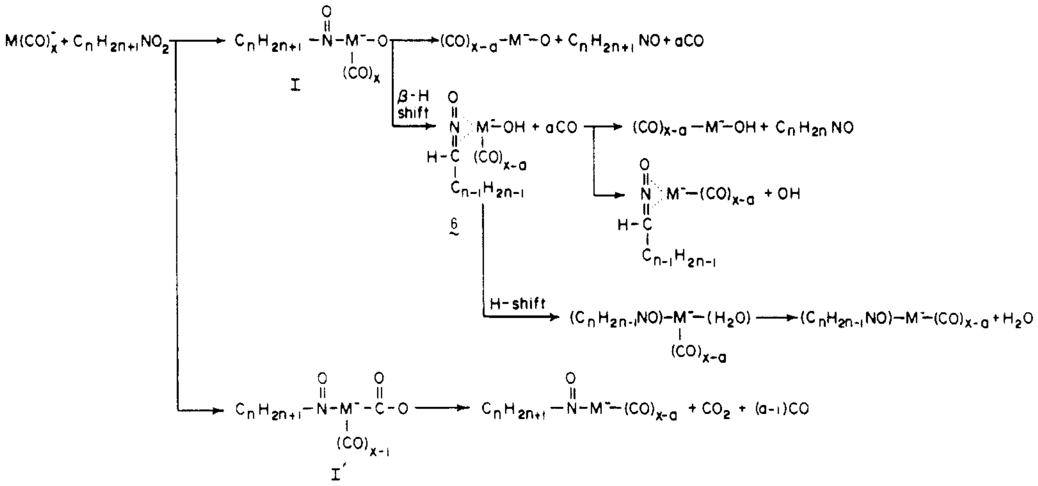
Two metal insertion structures may be predicted for the reactions of nitroalkanes with metal-containing anions. Intermediate I results from metal insertion into the N–O

Table IV. Reactions of Chromium-Containing Anions with *n*-Nitroalkanes and 2-Methyl-2-nitropropane

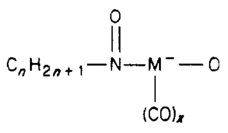
reaction			intermediate structure	branching ratios $n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 4$ ($(CH_3)_3CNO_2$)
$Cr(CO)_3^- + C_nH_{2n+1}NO_2$	→	$CrC_nH_{2n+1}NO_2^- + 3CO$		13	6	2	4	4
	→	$Cr(CO)_2O^- + C_nH_{2n+1}NO + CO$	I, III	18	11	4	4	3
	→	$Cr(CO)_3O^- + C_nH_{2n+1}NO$	I	20	25	18	22	22
	→	$Cr(CO)_2OH^- + C_nH_{2n}NO + CO$	I	4	(5)[a]	(4)	3	
	→	$Cr(CO)_3OH^- + C_nH_{2n}NO$	I	3	3	2	(4)	4
	→	$CrC_nH_{2n+1}NO^- + CO_2 + 2CO$	I′, III′	1	4	(4)	2	7
	→	$Cr(CO)NO^- + C_nH_{2n+1} + CO_2 + CO$	III′	1	4	3	2	
	→	$Cr(CO)C_nH_{2n+1}O^- + NO + 2CO$	III	5	(5)	1	(4)	
	→	$CrO_2^- + C_nH_{2n+1}N + 3CO$	IV	11	8	10	7	
	→	$Cr(CO)O_2^- + C_nH_{2n+1}N + 2CO$	IV	3	3	3	3	
	→	$Cr(CO)_2O_2^- + C_nH_{2n+1}N + CO$	IV					49
	→	$CrO_2H^- + C_nH_{2n}N + 3CO$	IV	5	7	5	4	
	→	$CrO_2H_2^- + C_nH_{2n-1}N + 3CO$	IV	10	20	33	30	
	→	$Cr(CO)NO_2^- + C_nH_{2n+1} + 2CO$	II					3
	→	$Cr(CO)_2NO_2^- + C_nH_{2n+1} + CO$	II	3	4	4	6	8
	→	$CrHNO_2^- + C_nH_{2n} + 3CO$	II			4	3	
	→	$CrH_2NO_2^- + C_nH_{2n-1} + 3CO$				4	2	
	→	$CrH_4NO_2^- + C_nH_{2n-3} + 3CO$				3	4	
	→	$CrC_nH_{2n-1}NO^- + H_2O + 3CO$	I	3				
	or	$Cr(CO)C_nH_{2n+1}^- + NO + CO_2 + CO$	III′					
$Cr(CO)_4^- + C_nH_{2n+1}NO_2$	→	$CrC_nH_{2n+1}NO_2^- + 4CO$				9		
	→	$Cr(CO)C_nH_{2n+1}NO_2^- + 3CO$		49	80	58	100	
	→	$Cr(CO)_3O^- + C_nH_{2n+1}NO + CO$	I	38	20	11		
	→	$Cr(CO)_3OH^- + C_nH_{2n}NO + CO$	I			22		
	→	$CrC_nH_{2n+1}NO^- + CO_2 + 3CO$	I′, III′	13				100
$Cr(CO)_5^- + C_nH_{2n+1}NO_2$	→	NR[b]						

[a] Values in parentheses are the sum of branching ratios for isobaric product ions. [b] NR indicates the ion did not undergo any reactions.

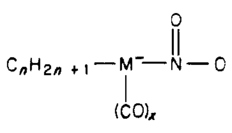
Scheme I



bond. This structure is predicted to be stable due to the relatively high electron affinity of O (33.7 kcal/mol). The electron affinity of $C_nH_{2n+1}NO$, however, is not known. The electron affinities of NO_2 (53 kcal/mol) and C_nH_{2n+1} (~20 kcal/mol) suggest that intermediate II (C–N insertion) would also be stable. In this discussion, structures


$C_nH_{2n+1}-\overset{\overset{\displaystyle O}{\|}}{N}-\underset{\underset{\displaystyle (CO)_x}{|}}{M^-}-O$

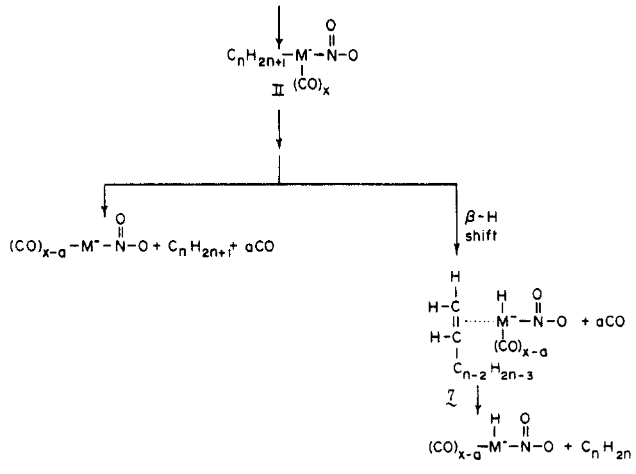
I


$C_nH_{2n+1}-\underset{\underset{\displaystyle (CO)_x}{|}}{M^-}-\overset{\overset{\displaystyle O}{\|}}{N}-O$

II

will be depicted with the negative charge on the metal center for simplicity. However, charge transfer/charge delocalization over the various ligands present is assumed to occur as in the alkyl halide and alcohol reactions.

Scheme II

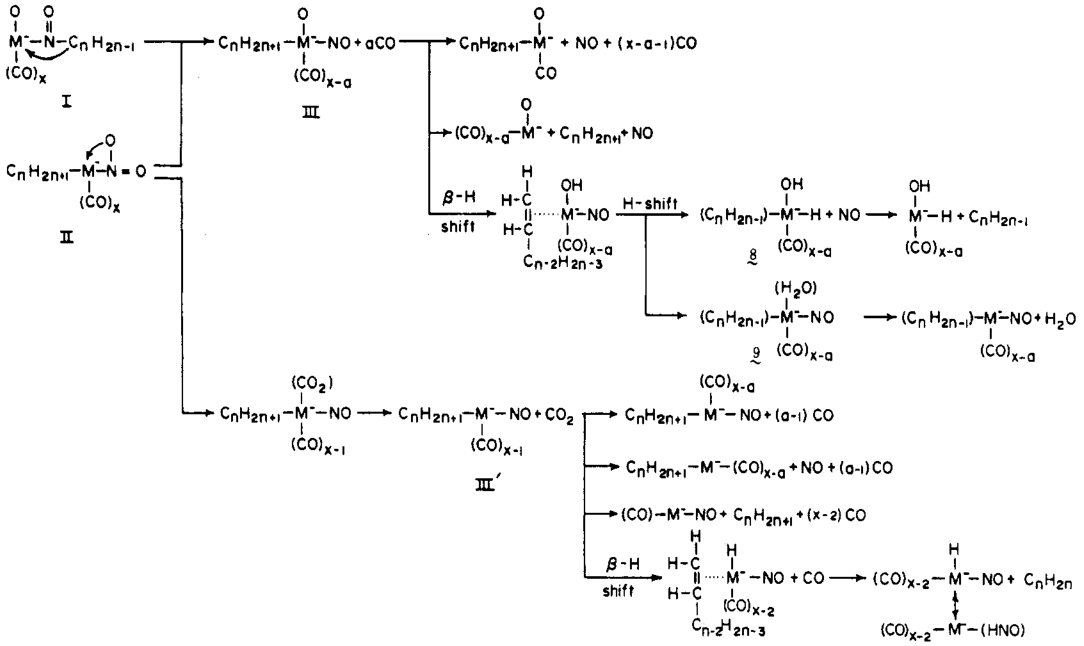


The proposed intermediate structures which lead to the various product ions are also listed in Tables II–IV. The mechanisms for the formation of product ions from intermediates I and II are shown in Schemes I and II, respectively. A large number of products, however, do not result from intermediates I and II. These products appear

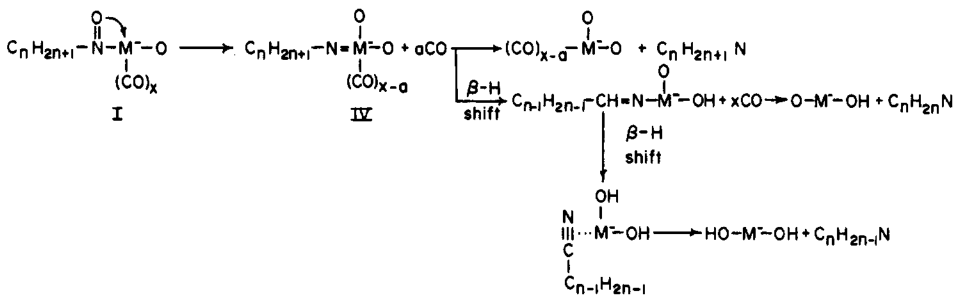
Table V. Reactions of Iron-, Cobalt-, and Chromium-Containing Anions with *n*-Butyl Nitrite (C_4H_9ONO)

reactions			intermediate structure	branching ratios					
				$Fe(CO)_3^-$	$Co(CO)_2^-$	$CoCONO^-$	$Co(CO)_3^-$	$Cr(CO)_3^-$	$Cr(CO)_4^-$
$M(CO)_x(NO)_y^- + C_4H_9ONO$	→	$M(CO)C_4H_9ONO^- + (x-1)CO$							100
	→	$MC_4H_9ONO^- + xCO + yNO$		59	20	62	100	6	
	or	$M(CO)_2HNO_2^- + C_4H_8 + (x-2)CO$	B						
	→	$M(CO)HNO_2^- + C_4H_8 + CO$	B		8				
	→	$M(CO)_3NO^- + C_4H_9O$	A	9					
	→	$M(CO)C_4H_9O^- + NO + (x-1)CO$	A		21			4	
	→	$M(CO)_2C_4H_9O^- + NO + (x-2)CO$	A	19				12	
	→	$M(CO)_2C_4H_8O^- + HNO + CO$	A	13				5	
	→	$MNOC_4H_8O^- + HNO + CO$	A			38			
	→	$M(CO)HNO^- + C_4H_8O + CO$	A		51				
	→	$M(CO)_2C_4H_7O^- + H_2 + NO + CO$	A					34	
	→	$M(CO)_2C_4H_6O^- + H_2 + HNO + CO$	A					13	
	→	$M(CO)_2C_4H_5O^- + 2H_2 + NO + CO$	A					16	
	→	$M(CO)_3NO_2^- + C_4H_9\cdot$	B					10	

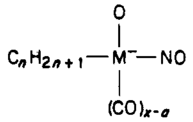
Scheme III



Scheme IV

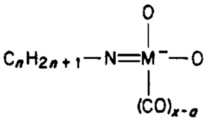


to result from intermediates III and IV as shown in Schemes III and IV, respectively. In intermediate III, the



$$C_nH_{2n+1}-\overset{\overset{\displaystyle O}{|}}{\underset{\underset{\displaystyle (CO)_{x-a}}{|}}{M^-}}-NO$$

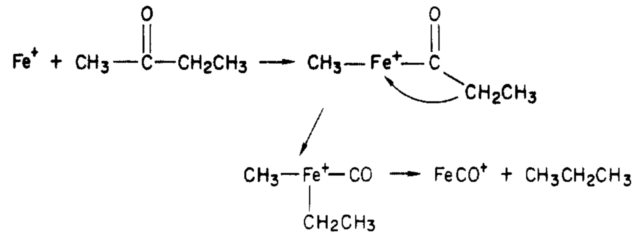
III



$$C_nH_{2n+1}-N=\overset{\overset{\displaystyle O}{|}}{\underset{\underset{\displaystyle (CO)_{x-a}}{|}}{M^-}}-O$$

IV

nitroalkane exists as *three* ligands (C_nH_{2n+1}, NO, and O) on the metal. Intermediate III may result from rearrangement of intermediate I (N–O insertion) through an alkyl migration as shown in Scheme III. An analogous process has been observed in the reactions of Fe^+ and ketones[20] (reaction 3). Intermediate III may also be formed from intermediate II as a result of the oxygen shifting onto the metal center (Scheme III). Several products observed in the reactions of nitroalkanes result from an intermediate in which both oxygens are present on the metal as shown in intermediate IV. Intermediate



(3)

IV may be formed from intermediate I as shown in Scheme IV. A similar intermediate was suggested in the reactions of Co^+ with nitroalkanes.[3]

Products Resulting from Intermediate I. Once intermediate I is formed (Scheme I), it may undergo a ligand loss process to form $M(CO)_{x-a}O^-$. This product is observed for metal-containing anions containing all three of the metals studied. The retention of the O ligand is expected since it has a relatively high electron affinity (33.7 kcal/mol) (EA($C_nH_{2n+1}NO$) is not known). This product may also be formed through intermediate III (Scheme III) with the loss of the NO and alkyl (C_nH_{2n+1}) ligands. Note that the electron affinities of the two ligands which are lost (0.5 and ~20 kcal/mol, respectively) are less than the electron affinity of O which is retained. In some cases, however, the formation of $M(CO)_{x-a}O^-$ *cannot* proceed through intermediate III due to the larger number of ligands which would be present on the metal in intermediate III compared to intermediate I; i.e., in intermediate III the nitroalkane exists as three ligands on the metal but in intermediate I it exists as only two ligands. For example, $Cr(CO)_2O^-$ may proceed through intermediate III since only five ligands would be present on the metal at any one time. The product $Cr(CO)_3O^-$ cannot result from intermediate III since it would be formed via an intermediate with six ligands on the metal which would violate the 18 electron rule.

The corresponding product ion $M(CO)_{x-a}C_nH_{2n+1}NO^-$ (i.e., *loss* of O) is observed for $Fe(CO)_3^-$, $Co(CO)_2^-$, $Cr(CO)_3^-$, and $Cr(CO)_4^-$ (n = 1–4). This product is *not* predicted to result from intermediate I since it would require loss of the oxygen ligand which has a relatively high electron affinity. The active participation of carbonyl ligands in the metal insertion process has been suggested in both positive and negative metal ion reactions. If the metal anion *and* one of the carbonyl ligands inserts into the N–O bond, intermediate I′ (Scheme I) may be formed. In this structure, the oxygen is never a ligand on the metal but instead combines with CO to form a CO_2 ligand on the metal. The CO_2 ligand, which has a *negative* electron affinity (−13.8 kcal/mol), is then lost. This product ion may also result from an intermediate similar to intermediate III. If the oxygen in intermediate II shifts onto a CO ligand instead of the metal, then, again, a CO_2 ligand is formed. The CO_2 ligand is then lost to yield intermediate III′ as seen in Scheme III.

A β-H may shift onto the metal in intermediate I to yield structure **6** (Scheme I). The O and H ligands on the metal may exist as a single OH ligand (EA(O) = 33.7 kcal/mol, EA(H) = 17.4 kcal/mol, and EA(OH) = 42.2 kcal/mol) as shown in structure **6**. The electron affinities suggest that O and H may exist as either one or two ligands on the metal. Structure **6** may proceed through a ligand loss process to yield $M(CO)_{x-a}OH^-$ (retention of OH, for $Cr(CO)_3^-$) or $M(CO)_{x-a}C_nH_{2n}NO^-$ (loss of OH, for the reactant $Fe(CO)_3^-$). Since these products (formation of an OH ligand) are observed for nitromethane (n = 1), they *cannot* proceed through intermediate III since *no* β-H's are present when n = 1.

A second hydrogen may shift onto the metal in structure **6** to produce an H_2O ligand (EA(H_2O) = 0.0 kcal/mol), which is lost to yield the product ion $M(CO)_{x-a}C_nH_{2n-1}NO^-$. This product is observed for metal-containing anions from all three metal carbonyl compounds as seen in Tables II–IV. The formation and subsequent loss of H_2O may suggest that O and H are present as a single OH ligand on the metal prior to the second β-H shift. Since this ion is observed for nitromethane (n = 1), then it must proceed through intermediate I and *not* from intermediate III (similar to the above argument). In one case, $Fe(CO)C_nH_{2n-1}NO^-$, this product ion is *not* observed for n = 1 but only for n = 2–4. Therefore, this ion may result from either intermediate I or III (Scheme III) but note that the ion $Fe(CO)_2C_nH_{2n+1}^-$ (loss of NO_2) is isobaric with this product ion.

Products Resulting from Intermediate II. We propose that the product ions $M(CO)_{x-a}NO_2^-$ and $M(CO)_{x-a}HNO_2^-$ are formed through intermediate II (C–N insertion) as shown in Scheme II. Once intermediate II is formed, the alkyl ligand may be lost to form $M(CO)_{x-a}NO_2^-$ since the electron affinity of C_nH_{2n+1} is less than the electron affinity of NO_2. This ion may also be formed through intermediate III, but NO_2 then exists as two ligands (O and NO) on the metal. The electron affinities of O and NO suggest that the product ion resulting from intermediate II delocalizes the negative charge more than in intermediate III, and thus $M(CO)_{x-a}NO_2^-$ presumably is formed through intermediate II. Note that a product ion at m/z 102 is observed for n = 2–4 but *not* for n = 1 (Table II). One possible structure for this ion is $FeNO_2^-$ which may be formed through intermediate II. This structure, however, would be expected to occur for n = 1 also. Another possible structure is $FeCO(H_2O)^-$ which may be formed through intermediate III. This ion would *not* be predicted to occur for n = 1 due to the absence of β-H's. Also note that all three carbonyls would be lost in the formation of $FeNO_2^-$ but only one or two carbonyls are lost in the formation of $Cr(CO)_{x-a}NO_2^-$ (Table IV). The loss of all three carbonyl ligands is unexpected in the formation of $FeNO_2^-$ since the reactions of $Cr(CO)_3^-$ are always more exothermic than $Fe(CO)_3^-$ (the charge transfer/delocalization process is more exothermic since EA($Cr(CO)_3$) < EA($Fe(CO)_3$)). Therefore, $FeNO_2^-$ is probably *not* the correct assignment for the m/z 102 product ion, with $FeCO(H_2O)^-$ being the more probable assignment.

The product ion $M(CO)_{x-a}HNO_2^-$ is observed for $Co(CO)_2^-$ and $Cr(CO)_3^-$ with the n-nitroalkanes ($n \geq 2$). This suggests a mechanism in which a β-H shifts onto the metal in intermediate II to yield structure **7** (Scheme II). The alkene formed is then lost due to it's negative electron affinity (e.g., EA(C_2H_4) = −35.7 kcal/mol). The two remaining ligands (H and NO_2) both have positive electron affinities over which the negative charge can be delocalized.

Products Resulting from Intermediate III. The product ions $M(CO)C_nH_{2n+1}O^-$ and $M(CO)_{x-a}O^-$ may be formed through intermediate III by loss of NO or NO and C_nH_{2n+1} ligands, respectively as seen in Scheme III. The ligands which are lost (NO and C_nH_{2n+1}) both have lower electron affinities than the O ligand which remains on the metal. Two H shifts may occur in intermediate III to yield either structure **8** or **9** in Scheme III. Structure **8** loses the C_nH_{2n-1} ligand to yield the product ion $M(CO)_{x-a}H_2O^-$ which is observed for $Fe(CO)_3^-$ and $Co(CO)_2^-$ with the nitroalkanes ($n \geq 2$). The electron affinity data suggests that H_2O (0.0 kcal/mol) exists as OH (42.2 kcal/mol) and H (17.4 kcal/mol) ligands in order to delocalize the charge as shown in structure **8**. Structure **9** results from the formation of an H_2O ligand which is then lost to yield $M(CO)_{x-a}C_nH_{2n-1}NO^-$ which was discussed previously. The C_nH_{2n-1} ligand has a positive electron affinity (e.g., EA(C_3H_5) = 12.5 kcal/mol).

Several products result from intermediate III′ (i.e., following the loss of O as CO_2) as seen in Scheme III. The loss of the NO ligand from intermediate III′ yields $M(CO)_{x-a}C_nH_{2n+1}^-$ which is observed for metal-containing anions from all three metals studied. This corresponds to a net loss of NO_2 from the nitroalkane. Although it is more straightforward to lose NO_2 from intermediate II (C–N insertion), this process is *not* predicted since EA(NO_2) > EA(C_nH_{2n+1}); i.e., it is expected that, as in the other reactions, the ligand with the lower electron affinity would be lost. If this product is formed through III′, however, the NO_2 is lost as CO_2 and NO which have low or negative electron affinities (−13.8 and 0.5 kcal/mol, respectively). The loss of C_nH_{2n+1} from intermediate III′ yields the product ion $M(CO)NO^-$ which is observed for $Cr(CO)_3^-$ and $Fe(CO)_3^-$. When $n \geq 2$ for the *n*-nitroalkanes, a β-H may shift onto the metal in intermediate III′ to yield $M(CO)_{x-2}HNO^-$ with loss of the corresponding alkene which is formed as seen in Scheme III. Note that HNO may exist as one ligand on the metal (EA(HNO) = 7.8 kcal/mol) or as H (EA(H) = 17.4 kcal/mol) and NO (EA(NO) = 0.5 kcal/mol).

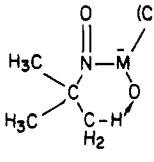
Products Resulting from Intermediate IV. All of the reaction products observed for $Fe(CO)_3^-$ and $Co(CO)_2^-$ may be explained through intermediates I, II, or III. Approximately 45% of the products from $Cr(CO)_3^-$ result from intermediate IV (Scheme IV) in which two oxygen ligands are present on the metal. The electron affinities of the ligands present in intermediate IV (EA(O) = 33.7 kcal/mol and EA(C_2H_5N) = 43 kcal/mol) suggest that this structure should be stable. Loss of the $C_nH_{2n+1}N$ ligand yields the product $M(CO)_{x-a}O_2^-$. This is *not* expected if the electron affinities of the two ligands are considered (i.e., EA($C_nH_{2n+1}N$) > EA(O)). If the electron affinity of the CrO_2 species (55.3 kcal/mol) is considered, then the $C_nH_{2n+1}N$ ligand *is* expected to be lost since it has a lower electron affinity. The product ions MO_2H^- and $MO_2H_2^-$ result from one and two β-H shifts from intermediate IV, respectively, as seen in Scheme IV. It is interesting to note that products resulting from intermediate IV occur almost exclusively for $Cr(CO)_3^-$. Since $Cr(CO)_3^-$ is predicted to have the lowest electron affinity of the metal-containing anions studied, the largest amount of energy released in the charge-transfer (delocalization) process would occur for $Cr(CO)_3^-$. Therefore, a relatively large amount of energy appears to be required to form intermediate IV from intermediate I since it is only formed by $Cr(CO)_3^-$.

Reactions of 2-Methyl-2-nitropropane. The reactions of the metal-containing anions from $Fe(CO)_5$, $Co(CO)_3NO$, and $Cr(CO)_6$ with 2-methyl-2-nitropropane are also included in Tables II, III, and IV, respectively. The 2-methyl-2-nitropropane appears to be less reactive than the corresponding 1-nitrobutane with only two products observed for $Fe(CO)_3^-$ and $Co(CO)_2^-$ and eight products for $Cr(CO)_3^-$.

The only product ion observed for $Fe(CO)_3^-$ besides the parent substitution product is $FeC_nH_{2n+1}NO^-$ (loss of O) resulting from either intermediate I′ or III′. If this product is formed through intermediate III′, the formation of $Fe(CO)HNO^-$ would be expected since β-H's are present and it is the largest product observed for 1-nitrobutane. This product is *not* formed, suggesting that $FeC_nH_{2n+1}NO^-$ is formed through intermediate I′. The other products expected from intermediates I and I′ are only minor products for 1-nitrobutane and were not detected for 2-methyl-2-nitropropane.

The two products formed from the reaction of $Co(CO)_2^-$ with 2-methyl-2-nitropropane are $Co(CO)_2O^-$ from intermediate I and $Co(CO)HNO_2^-$ from intermediate II. This is consistent with the fact that these are the only two products observed from these two intermediates for the *n*-nitroalkanes. Also, there are β-H's available to shift in intermediate II for 2-methyl-2-nitropropane to produce $Co(CO)HNO_2^-$ (isobutene elimination).

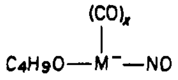
The reaction of $Cr(CO)_3^-$ with 2-methyl-2-nitropropane yields the product ions $Cr(CO)_2O^-$ and $Cr(CO)_3O^-$ from intermediate I and $CrC_nH_{2n+1}NO^-$ from intermediate I′. The product ion $Cr(CO)_{x-a}OH^-$ seen in the reaction of 1-nitrobutane is *not* expected in the 2-methyl-2-nitropropane reactions since there are *no* β-H's present in intermediate I with 2-methyl-2-nitropropane. A small amount of $Cr(CO)_3OH^-$ is observed, however, which may proceed by a H shift through a six-member ring intermediate as shown in structure **10**.



10

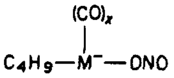
The largest product formed through intermediate IV in the 1-nitrobutane reactions is $CrO_2H_2^-$. In the 2-methyl-2-nitropropane reactions, however, there are *no* β-H's present in intermediate IV, and thus, the only product resulting from intermediate IV is $Cr(CO)_2O_2^-$. The product ion $Cr(CO)_{x-a}NO_2^-$ is formed through intermediate II in the reactions of 2-methyl-2-nitropropane. Although β-H's are available to shift to produce $Cr(CO)_{x-a}HNO_2^-$, these β-H's are terminal hydrogens for 2-methyl-2-nitropropane. The lack of *terminal* β-H shifts is not unexpected since the terminal β-H's in the reaction of nitroethane do *not* shift to yield $Cr(CO)_{x-a}HNO_2^-$ (Table IV).

Reactions of *n*-Butyl Nitrite. The ion/molecule reaction products and branching ratios for the reactions of *n*-butyl nitrite (C_4H_9ONO) with iron-, cobalt-, and chromium-containing anions are listed in Table V. In the corresponding positive ion reactions of *n*-butyl nitrite,[3] the majority of the products resulted from metal insertion into the relatively weak RO–NO bond (42 kcal/mol).[24] Metal insertion into the C–O bond also appeared to occur. All of the products observed for *n*-butyl nitrite with the metal-containing anions appear to proceed through two intermediates. Intermediates A and B (nitrite intermediates) result from metal insertion into the weak O–NO bond and the C–O bond, respectively.



$C_4H_9O\text{—}\overset{(CO)_x}{\overset{|}{M^-}}\text{—}NO$

A



$C_4H_9\text{—}\overset{(CO)_x}{\overset{|}{M^-}}\text{—}ONO$

B

Intermediate A may lose the C_4H_9O ligand to yield $M(CO)_xNO^-$ or lose the NO ligand to yield $M(CO)_{x-a}C_4H_9O^-$ as shown in Scheme V. The electron affinity data (EA(C_4H_9O) = 43.8 kcal/mol and EA(NO) = 0.5 kcal/mol) suggest that the loss of C_4H_9O should not occur. The loss of C_4H_9O *is* a minor process and is only observed for $Fe(CO)_3^-$, whereas the loss of NO is extensive

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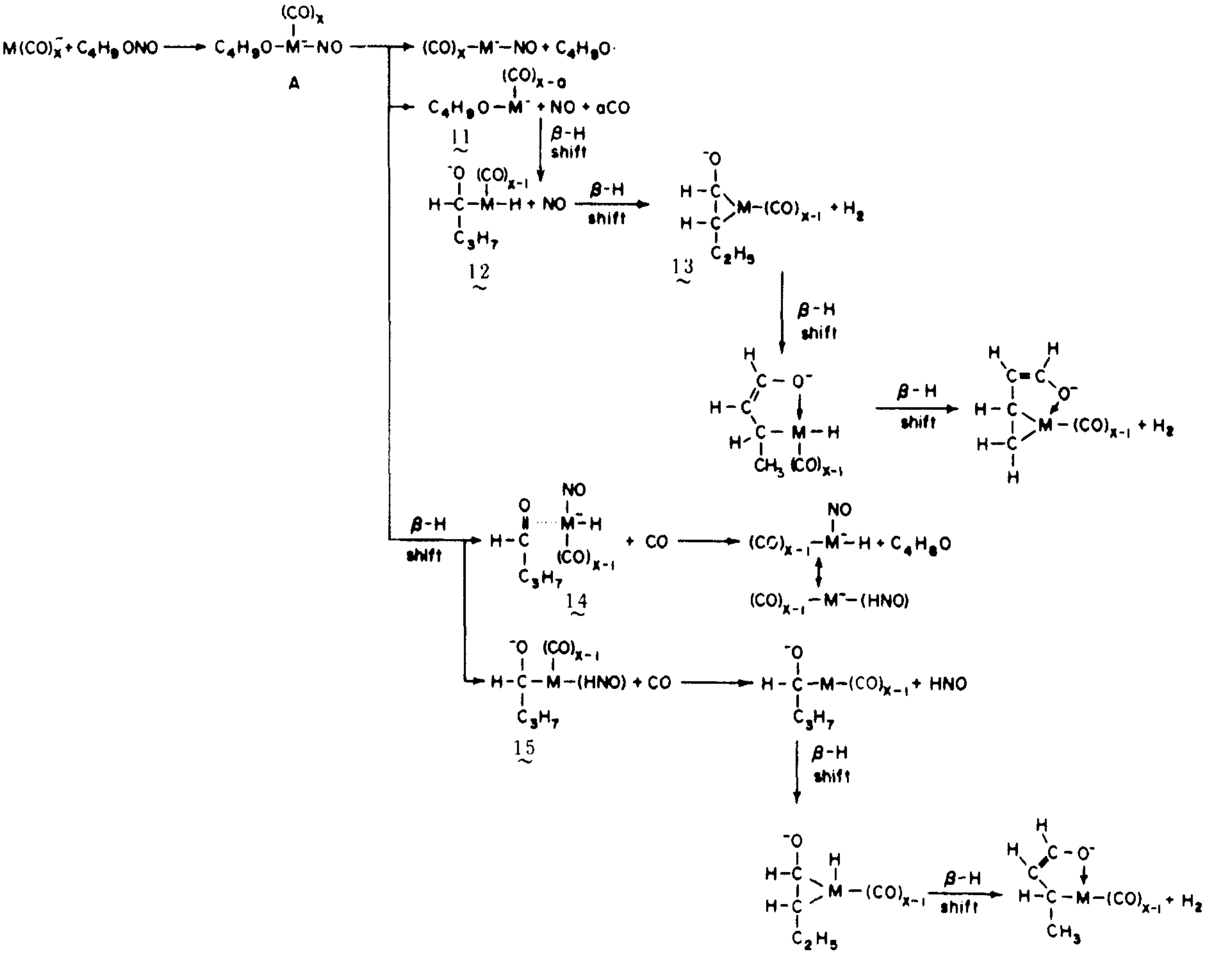
[24] Batt, L.; Robinson, G. N. *The Chemistry of Amino, Nitroso, and Nitro Compounds and their Derivatives*; Patai, S., Ed.; Wiley: New York, 1982; Part 2, p 1075.

Scheme V



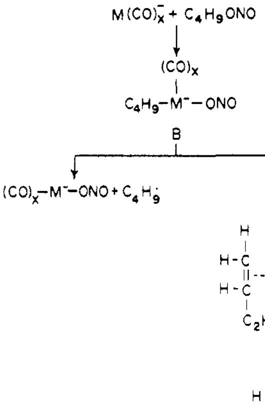
(~20% of the observed products) and is observed from all three metal-containing anions.

The chemistry of $Cr(CO)_3^-$ with *n*-butyl nitrite is unique in that, following the loss of NO (structure 11, Scheme V), further elimination of molecules of H_2 occurs. A similar process was also reported with *n*-butyl alcohols, again only for $Cr(CO)_3^-$. This supports the proposal that an alkoxy group is present when molecules of H_2 are eliminated. A β-H may shift onto the metal in 11 to yield structure 12 in which the metal is bonded to the carbon and the charge is moved onto the oxygen. This mechanism is identical with that proposed in the reactions of *n*-alcohols. Another β-H may shift with loss of H_2 to yield structure 13 (loss of NO and H_2). The metal may continue to move down the alkyl chain in a similar manner to eliminate a second H_2 molecules as seen in Scheme V. There appears to be no thermodynamic advantage for the elimination of H_2 molecules but presumably occurs to dispose of excess energy.

A β-H may shift onto the metal in intermediate A to yield structures 14 and 15. In 14, the charge remains on the metal with the formation of an aldehyde which is lost to yield $M(CO)_{x-1}HNO^-$. Note that two structures are possible (HNO, or NO and H as ligands) for this product ion as shown in Scheme V. In structure 15, the metal is bonded to the carbon with the negative charge being transferred to the oxygen, analogous to 11. The HNO ligand which is formed may be lost due to it's low electron affinity. This product ion reacts further to lose a molecule of H_2 to yield $Cr(CO)_2C_4H_6O^-$ (loss of HNO and H_2) as shown in Scheme V.

The remaining two products may be explained through intermediate B (C–O insertion) (Scheme VI). The alkyl radical C_4H_9 in intermediate B may be lost to yield $M(CO)_xONO^-$ The product ion $M(CO)_{x-a}HONO^-$ is formed as a result of a β-H shift in intermediate B followed by loss of the 1-butene ligand which is formed.

Scheme VI



Insights into the Metal Insertion/Charge Transfer Mechanism. A comment should be made on the failure of anions to insert into C–C and C–H bonds, processes which are observed for transition-metal cations. The lack of reactivity of such bonds may be related to the mechanism by which the insertion intermediates are formed. There are at least two possible explanations for the lack of C–C and C–H activation in the reactions of metal-containing anions with organic molecules. The first involves the stability of the three metal insertion intermediates following insertion into C–C, C–H, and C–X bonds as shown in structures 16, 17, 18, respectively. On the basis

$$R'{-}M^-{-}R''X \qquad H{-}M^-{-}R'''X \qquad R{-}M^-{-}X$$

16 17 18

Scheme VII

of the reactions observed for alcohols,[1] alkyl halides,[1] and nitroalkanes, the formation of intermediates containing electronegative ligands appears to be important. Thus, structure 18 (C–X insertion, X = functional group) is assumed to be more stable than structures 16 and 17 due to the relatively high electron affinity of the functional group, X, leading to greater charge delocalization. (This analysis contains a number of assumptions; e.g., without charge delocalization, all of the metal–ligand σ bonds in 16–18 are of approximately the same energy.) The second explanation for failure of anions to insert into C–C and C–H bonds may be that metal insertion occurs via a complexation/charge transfer/fragmention sequence, as shown in Scheme VII; i.e., charge transfer occurs *prior* to metal insertion. In order to differentiate between these two processes, one must determine when in the mechanistic sequence the charge-transfer process occurs. The latter process can be considered analogous to the dissociative electron capture process which occurs during low energy electron impact.

The electron-impact negative ion mass spectra of the organic molecules studied here and in our previous work[1] are consistent with a mechanism in which the charge-transfer process occurs *prior* to the formation of bonds to the metal. For example, the negative ion mass spectra of alkyl chlorides[25] at high electron energies (>50 eV) include Cl^- and several alkyl fragment ions (e.g., C_2H^-, C_2^-, and CH^-). At lower electron energies, however, the only ion present in the mass spectrum is Cl^-; i.e., electron attachment to RCl leads to the unstable RCl^- which dissociates to form Cl^- and R·. This parallels the metal insertion/charge transfer process in which the $R–Cl^-$ bond is broken in close proximity to the metal such that $M–Cl^-$ and M–R bonds can be formed. Note that the metal anion is shown in Scheme VII to approach perpendicular to the R–X bond. Such an approach is required to avoid anion–dipole repulsions while getting the metal close to the functional group for charge transfer to occur. Such an approach geometry also "sets up" the complex so that, following charge transfer and bond cleavage, M, X, and R are in sufficiently close proximity to allow for the M–X and M–R interactions. The major negative ions present in the 90-eV electron-impact mass spectra of alcohols[26] are $(M-H)^-$, OH^-, and O^-. The formation of the ion/radical pairs ($(M-H)^-$ and H·) and (OH^- and R·) parallels metal insertion/charge transfer into the O–H and C–OH bonds of *n*-alcohols, respectively. The predominant negative ions in the low-energy (4.5-eV) electron-impact mass spectra of nitroalkanes[27] are NO_2^-, O^-, and CN^-. At higher energies more alkyl and rearrangement type ions are present. The formation of the ion/radical pairs (NO_2^- and R·) and (O^- and RNO·) in the electron-impact process again suggests that the charge-transfer process may occur prior to the metal insertion into the $R–NO_2$ and N–O bonds of nitroalkanes.

Thermodynamic calculations[28] for the dissociative electron capture process (reaction 4) yield values for ΔH_4 of $\sim$−6 kcal/mol for X = Cl, $\sim$−15 kcal/mol for X = Br, and $\sim$+48 kcal/mol for X = OH. These results correlate

$$RX + e^- \rightarrow R\cdot + X^- \qquad (4)$$

well with the preference for site of attack which was observed in the chemistry of the bifunctional organic molecules.[1] For example, metal insertion/charge transfer into the R–Br bond was preferred over the C–Cl bond in 1,*n*-bromochloroalkanes, and C–Cl insertion occurs preferentially over C–OH insertion in 1,*n*-chloroalcohols. These trends may be predicted by the exothermicity of the dissociative electron capture process in reaction 4.

A similar analysis of the formation of RO^- and H· from *n*-alcohols, i.e., a process similar to metal insertion/charge transfer into the O–H bond, yields a value of $\Delta H_4 = \sim+60$ kcal/mol which is approximately 12 kcal/mol more endothermic than for the formation of OH^- and R·. This would suggest preference for metal insertion/charge transfer into the R–OH bond over the O–H bond of *n*-alcohols. The opposite trend, however, was observed in the chemistry of *n*-alcohols with metal-containing anions. This may reflect the effect which the energies of the various bonds which are *formed* (e.g., M–OH, M–R, RO–M, and M–H) have on the preference of attack by the metal anions in the metal insertion/charge transfer process.

Conclusions

The general mechanism proposed in the reactions of metal-containing anions with alkyl halides and alcohols[1] has been successfully applied to the reactions of nitroalkanes. The metal insertion/charge transfer (delocalization) process occurs exclusively at the functional group (i.e., no C–C or C–H insertion). The nitroalkane reactions parallel the alcohol reactions in complexity relative to the chloroalkane reactions, since the NO_2 and OH functional groups both *contain* bonds which are also attacked. The nitroalkane reactions are unique in that several products appear to result from intermediates which are formed by rearrangement of the initial metal insertion intermediate. The electron affinity data available allow one to predict the ligands which are bound to the metal and are lost in the reactions. The same ligand effects are observed in the reactions of nitroalkanes as in alkyl halides and alcohols (e.g., 17-electron species are unreactive) including the possibility of active participation of the carbonyl ligands in the reaction mechanisms.

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Registry No. $Fe(CO)_3^-$, 53221-56-0; $Co(CO)_2^-$, 99632-76-5; $Cr(CO)_3^-$, 53221-59-3; CH_3NO_2, 75-52-5; $C_2H_5NO_2$, 79-24-3; $C_3H_7NO_2$, 108-03-2; $C_4H_9NO_2$, 627-05-4; C_4H_9ONO, 544-16-1; 2-methyl-2-nitropropane, 594-70-7.

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