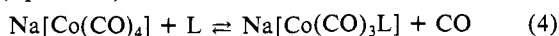


actions (eq 4 and 5). The stoichiometry and the reversibility of



L = maleic anhydride, dimethyl maleate (DM),
dimethyl fumarate (DF)

these reactions were established by gas evolution and IR spectral measurements. Selective conversions of $\text{Na}[\text{Co}(\text{CO})_4]$ and L into $\text{Na}[\text{Co}(\text{CO})_3\text{L}]$ ¹⁸ at 1:1 molar ratio or into $\text{Na}[\text{Co}(\text{CO})_2\text{L}_2]$ ¹⁹ at 1:2 molar ratio were realized by using UV irradiation or thermolysis at reflux, respectively. The Li^+ and K^+ salts of $[\text{Co}(\text{CO})_4]^-$ react similarly to $\text{Na}[\text{Co}(\text{CO})_4]$. By contrast, $\text{PPN}[\text{Co}(\text{CO})_4]^-$ does not react with the aforementioned olefins under comparable thermal conditions.

The IR spectra of these $\text{Na}[\text{Co}(\text{CO})_3\text{L}]$ and $\text{Na}[\text{Co}(\text{CO})_2\text{L}_2]$ olefin complexes show metal carbonyl absorptions shifted to higher frequencies compared with those of $\text{Na}[\text{Co}(\text{CO})_4]$. This indicates substantial cobalt-to-olefin π back-donation. Consistently, the C=O stretching frequencies of the olefins move to lower values upon ligation.

The ¹H and ¹³C NMR spectra in CD_2Cl_2 or CDCl_3 solution reveal expected changes in the chemical shifts of the olefins upon coordination.²⁰ Interestingly and significantly, however, there is a doubling (with equal intensity) of signals for each of the otherwise equivalent H and C nuclei. This effect may be attributed to the coordination of the counterion to only one carbonyl group of each olefin in forming a tight ion pair in these solvents. Preliminary X-ray crystallographic results show that the Na^+ ion in $\text{Na}[\text{Co}(\text{CO})_2(\text{DF})_2]\cdot\text{THF}$ is surrounded by the THF oxygen and by one oxygen atom from each of four COOMe groups of different dimethyl fumarate ligands belonging to two anions. By contrast, the NMR spectra of $\text{Na}[\text{Co}(\text{CO})_2\text{L}_2]$ in D_2O show only one signal for each kind of H and C nucleus which also has a normal chemical shift for coordinated olefins. Here, solvent separated ion pairs are probably present.

Studies are in progress to delineate the scope of substitution reactions of $[\text{Co}(\text{CO})_4]^-$ and other metal carbonyl anions and to explore the chemistry of the substituted anionic products.

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Registry No. DM, 624-48-6; DF, 624-49-7; $\text{Na}[\text{Co}(\text{CO})_4]$, 14878-28-5; P(OPh)₃, 101-02-0; P(O-*n*-Bu)₃, 102-85-2; PPh₃, 603-35-0; P(*n*-Bu)₃, 998-40-3; maleic anhydride, 108-31-6.

(18) E.g., a THF solution (50 mL) of equimolar amounts (8.6 mmol) of $\text{Na}[\text{Co}(\text{CO})_4]$ and dimethyl maleate in a quartz Schlenk tube was irradiated under Ar with 254-nm lamps in a Rayonet reactor for 5 days at 25 °C. Concentration to 12 mL and crystallization at -78 °C afforded 3.51 g (77%) of orange crystals of $\text{Na}[\text{Co}(\text{CO})_3(\text{DM})]\cdot 3\text{THF}$: mp ~ 25 °C; IR (THF) 1997 (s), 1918 (vs), 1904 (vs) 1706 (s) cm^{-1} ; ¹H NMR (CD_2Cl_2 , 250 MHz) δ 3.92 (d, $J = 15$ Hz, 1 H, CH), 3.68 (m, 12 H, CH₂), 3.60 (s, 3 H, Me), 3.35 (s, 3 H, Me), 2.77 (d, $J = 15$ Hz, 1 H, CH), 1.82 (m, 12 H, CH₂); ¹³C NMR (CD_2Cl_2 , 63 MHz) δ 177.1 (COO), 176.2 (COO), 67.7 (CH₂), 51.0 (Me), 50.2 (Me), 48.8 (CH), 41.5 (CH), 25.4 (CH₂). Anal. Calcd for $\text{C}_{21}\text{H}_{32}\text{CoNaO}_{10}$: Co, 11.20. Found: Co, 11.51.

(19) E.g., a THF solution (30 mL) of $\text{Na}[\text{Co}(\text{CO})_4]$ (8.5 mmol) and dimethyl fumarate (17.7 mmol) was refluxed under Ar for 24 h. Concentration to 15 mL and filtration of the slurry at 25 °C gave 3.98 g (94%) of orange crystals of $\text{Na}[\text{Co}(\text{CO})_2(\text{DF})_2]\cdot\text{THF}$: IR (THF) 1998 (s), 1946 (s), 1731 (vw), 1701 (sh), 1692 (s), 1657 (w) cm^{-1} ; ¹H NMR (CDCl_3 , 250 MHz) δ 3.93 (d, $J = 9.4$ Hz, 2 H, CH), 3.76 (t, 4 H, CH₂), 3.59 (s, 6 H, Me), 3.47 (s, 6 H, Me), 2.73 (d, $J = 9.7$ Hz, 2 H, CH), 1.84 (q, 4 H, CH₂); ¹H NMR (D_2O , 250 MHz) δ 4.02 (s br, 4 H, CH₂), 3.90 (s, 12 H, Me), 3.68 (s, 4 H, CH), 2.16 (s br, 4 H, CH₂); ¹³C NMR (CDCl_3 , 63 MHz) δ 210.1 (CO), 177.9 (COO), 177.5 (COO), 67.9 (CH₂), 50.9 (Me), 50.3 (Me), 48.6 (CH), 41.5 (CH), 25.6 (CH₂); ¹³C NMR (D_2O , 63 MHz) δ 178.5 (COO), 67.8 (CH₂), 51.5 (Me), 45.1 (CH), 25.2 (CH₂). Anal. Calcd for $\text{C}_{18}\text{H}_{24}\text{CoNaO}_{11}$: C, 43.38; H, 4.85; Co, 11.82. Found: C, 42.91; H, 4.83; Co, 11.60.

(20) (a) Pregosin, P. S.; Kunz, K. W. ³¹P and ¹³C NMR of Transition Metal Phosphine Complexes; Springer-Verlag: New York, 1979; pp 141-142. (b) Churchill, M. R.; Fetinger, F. C.; Rees, W. M.; Atwood, J. D. *J. Organomet. Chem.* **1986**, 301, 99-108.

Uranyl Ion As a Probe of the Conduction Plane of β'' Alumina

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The fast ion conductor, sodium β'' alumina, is well known for its transport properties and rich ion exchange chemistry.¹ The latter aspect has led to the synthesis of a number of compounds which possess interesting transport and optical properties.²⁻⁴ In this communication we present the first report of the ion exchange of a luminescent molecule, the uranyl ion, and show that it is a sensitive probe of the sites and the interaction of ions in the conduction plane of β'' alumina.

The structure of the β'' aluminas is anisotropic with a strong two-dimensional character. The conduction planes are loosely packed regions that contain the mobile cation (i.e., Na^+ in sodium β'' alumina) and O^{2-} (see Figure 1). Alternating with the conduction planes are dense regions, called spinel blocks, composed of Al^{3+} and O^{2-} in close-packed arrangements. The large vacancy concentration in the conduction plane leads to high ionic mobilities in two dimensions. The sodium ions in the plane occupy sites of distorted tetrahedral (C_{3v}) symmetry known as Beavers-Ross (BR) sites. A second site in the conduction plane which possesses octahedral symmetry is known as the mid-oxygen (mO) site. Although the β'' alumina exchange chemistry permits a wide range of monatomic ions to be introduced, the incorporation of complex ions or molecules in the conduction plane is rare. Water is readily incorporated, and various hydration effects have been studied by vibrational spectroscopy.⁵

The luminescence spectrum of the uranyl ion in β'' alumina is shown in Figure 2. Single crystals of sodium β'' alumina ($2 \times 2 \times 0.2$ mm) were prepared by the flux evaporation technique.⁶ The exchange process, uranyl-sodium, was accomplished by immersing the precursor single crystals in sodium nitrate melts containing either 0.2% or 2% uranyl nitrate. The crystals were held in the melt between 2 and 18 h at 350 °C. A maximum of 4% of the sodium ions was replaced by uranyl ions. X-ray diffraction results indicate that the β'' alumina structure was retained without any significant change in lattice parameters from the parent crystal.⁷ The spectra were obtained at 10K by excitation at 351 nm with an Ar⁺ laser. The spectrum shows the signature Franck-Condon progression in the symmetric O-U-O stretch with a frequency of 860 cm^{-1} and the origin at 19 840 cm^{-1} . A second progression (the primed labels) is also observed with the same frequency but with an origin at about 19 560 cm^{-1} . When the concentration of the uranyl ion is varied, the positions of the primed and unprimed peaks remain fixed, but the relative intensities change.

The origin of the vibronic progression in the luminescence spectra of uranyl compounds changes as a function of the environment.^{8,9} Two extremes are shown in Figure 2 for comparison

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- (1) Dunn, B.; Farrington, G. C. *Solid State Ionics* **1983**, 9, 10, 223.
- (2) Saltzberg, M. A.; Davies, P. K.; Farrington, G. C. *Mat. Res. Bull.* **1986**, 21, 1533.
- (3) Barrie, J. D.; Dunn, B.; Stafsudd, O. M.; Farrington, G. C. *Solid State Ionics* **1986**, 18/19, 677.
- (4) Jansen, M.; Alfrey, A.; Stafsudd, O. M.; Dunn, B.; Yang, D. L.; Farrington, G. C. *Optics Lett.* **1984**, 9, 119.
- (5) Bates, J. B.; Wang, J. C.; Dudney, N. J.; Brundage, W. E. *Solid State Ionics* **1983**, 9/10, 237.
- (6) Briant, J. L.; Farrington, G. C. *J. Solid State Chem.* **1980**, 33, 385.
- (7) The lattice parameters of the exchanged crystal did not vary significantly from those of the Na^+ β'' alumina. The *a* axis parameter was 5.626 Å and the *c* axis parameter was 33.597 Å.
- (8) Brittain, H. G.; Perry, D. L. *J. Phys. Chem.* **1980**, 80, 2630.
- (9) Reisfeld, R.; Eyal, M.; Jorgensen, C. K. *Chem. Phys. Lett.* **1986**, 132, 252.

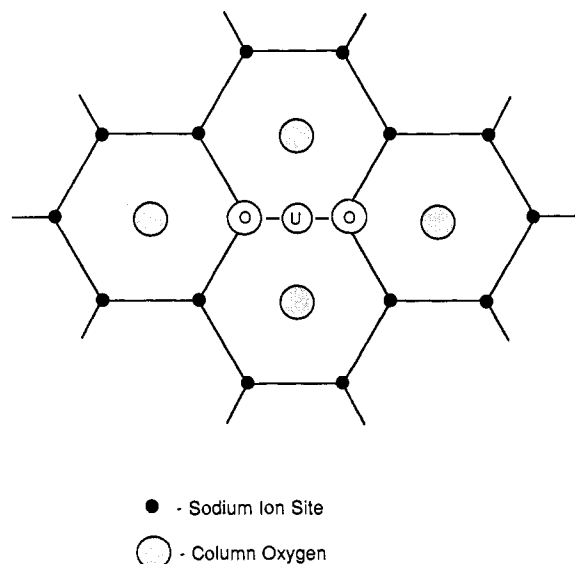


Figure 1. Schematic of the conduction plane of Na^+ β'' alumina showing the proposed position of the uranyl ion relative to those of the column oxygens and the sodium ion sites.

with the spectrum in β'' alumina. First, the spectrum of the uranyl ion in an ionic crystal (uranyl nitrate, Figure 2 middle) has its origin at $21\,083\text{ cm}^{-1}$. It consists of a series of sharp zero-phonon lines with phonon wings. The spacing between the vibronic peaks is approximately 860 cm^{-1} . Similar sharp line spectra were obtained from other uranyl salts. The narrow lines are indicative of a relatively small range of different sites. Second, the spectrum of the uranyl ion in a silica matrix formed by the sol-gel technique is shown at the bottom of Figure 2.¹⁰ The spectral origin is $20\,330\text{ cm}^{-1}$, and the vibronic spacing is also 860 cm^{-1} . The broader bands in this spectrum are indicative of a larger range of sites in the gel than in the crystal. Control experiments were also carried out to determine the spectrum of uranyl ions in a sodium nitrate matrix from the melt. Relatively broad bands with an origin at $18\,208\text{ cm}^{-1}$ were observed. From these results it is clear that the spectrum of the uranyl ion can shift by several 1000 cm^{-1} as a function of changes in the environment and that the spectrum of the uranyl ion in the β'' alumina environment is distinctly different from those obtained from crystals or the melt.

The spectrum of the uranyl ion in the β'' alumina consists of the superposition of the spectra of uranyl ions in at least two different environments. The 280-cm^{-1} energy separation between the two sets of peaks is small compared to the environmental shifts in the examples given above and suggests that the sites in the alumina are only subtly different. The widths of the peaks show that there is significant inhomogeneity within a given site. Further evidence for multiple sites is provided by lifetime measurements. At 77 K , a multiexponential decay was observed with principal components of 74 and $55\ \mu\text{s}$.

The most likely position of the uranyl ion in the conduction plane of β'' alumina is shown in Figure 1. The uranyl ion fits between the column oxygens in the conduction plane. Electrostatic considerations suggest that the uranium atom is situated on a mid-oxygen site and that the covalently bonded oxygens are on adjacent BR sites. The distance between adjacent sodium sites is about $3.2\ \text{\AA}$ while the O–O distance in the uranyl ion is about $3.4\ \text{\AA}$. The uranyl ion is thus perturbed by the environment but the O–U–O unit is intact, and, as a result, the vibrational frequency is almost unchanged. The breadth of the uranyl peaks in β'' alumina may arise from two contributions. First, the uranyl ion may exhibit a distribution of slight displacements from precise centering over the mid-oxygen site. Small displacements of this type have been shown previously in the β'' aluminas from the X-ray diffraction studies of Thomas et al.¹¹ In addition, the linear uranyl

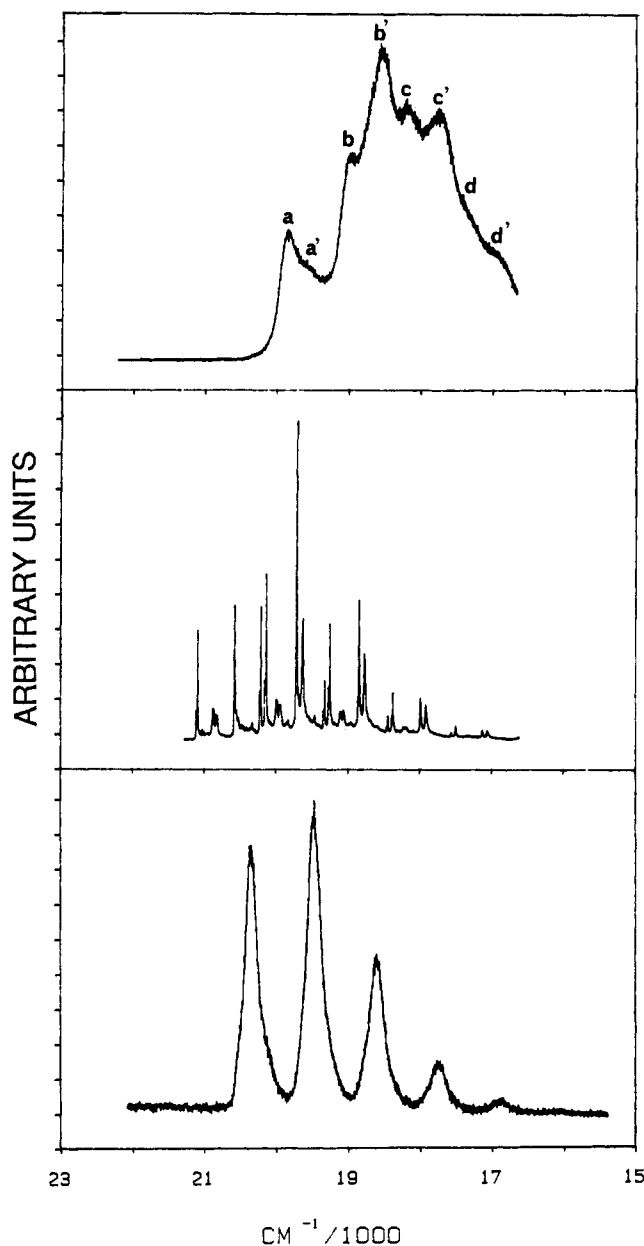


Figure 2. Luminescence spectra of the uranyl ion at 10 K in β'' alumina (top), in uranyl nitrate (middle), and in silica formed by the sol-gel method (bottom).

ions could also be tilted with respect to the conduction plane. It is known, for example, that adjacent sodium ion sites are displaced, on an alternating basis, slightly above and below the conduction plane.

Distinct types of electrostatic environments will arise from the distribution of the nearest neighbor sodium ions around the uranyl site. The most probable distribution will consist of four sodium ions in their usual BR sites. The unprimed peaks in Figure 2 could arise from uranyl ions in the environment. The second most probable distribution would consist of three sodium ions in the BR sites. This distribution could cause the 280-cm^{-1} shift observed in Figure 2. The probabilities of other distributions of sodium atoms are much lower. The small shoulder at $20\,200\text{ cm}^{-1}$ in Figure 2 may be evidence for a nonzero concentration of UO_2^{2+} in such an environment.

In summary, we find that β'' alumina is able to incorporate uranyl ion by ion exchange processes. In view of its size, it is somewhat surprising that such a species is mobile in the conduction

(10) The silica matrix was formed by the method of Sakka and Kamiya (Sakka, S.; Kamiya, K. *J. Non-Cryst. Solids*, **1980**, *42*, 403).

(11) Carillo-Cabrera, W.; Thomas, J. O.; Farrington, G. C. *Solid State Ionics* **1983**, *9/10*, 245.

plane of sodium β'' alumina. Nonetheless, the luminescence spectra show that not only is the uranyl ion incorporated in the conduction plane but also that it is a sensitive probe of the environment in the conduction plane. This result suggests that it may be feasible to use various molecules to probe the local structural environment of solid ionic conductors and provide greater insight concerning the structure/property relationship in these materials.

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Activation of Nitric Oxide by Dimeric Cobalt Ions in the Gas Phase

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Transition-metal clusters containing nitrosyl ligands are the focus of increasing interest due to their rich and diverse chemistry compared with binary carbonyl compounds.^{1,2} For example, the nitrosyl ligand is susceptible to electrophilic attack,^{3,4} reduction with molecular hydrogen,^{4,5} and deoxygenation yielding nitrido clusters.⁶⁻⁸ This latter process results in the conversion of CO to CO₂ by oxygen transfer, process 1. The mechanisms of these



oxygen transfers are quite speculative. For example, oxide transfer may proceed by (1) initial dissociation of a CO ligand followed by insertion of NO yielding a nitrido-oxide cluster with subsequent oxide transfer to free CO or (2) by a concerted oxide transfer to a coordinated CO from an intact NO ligand resulting in CO₂ elimination.⁷ Gas phase ion techniques, however, may provide unique insights into the above process. In this communication the formation of cobalt-cluster-nitrido cations in the gas phase by oxide transfer to carbon monoxide from cobalt cluster nitrosyls is described.

All experiments were performed on a Nicolet FTMS-1000 Fourier transform mass spectrometer equipped with a 5.08-cm cubic-trapping cell immersed in a 3.0-T magnetic field.⁹ The theory, instrumentation, and methodology of conventional ion cyclotron resonance (ICR)^{9,10} and Fourier transform mass spec-

(1) Badhuri, S.; Johnson, B. F. G.; Lewis, J.; Watson, D. J.; Zucarro, C. *J. Chem. Soc., Dalton Trans.* **1979**, 557.

(2) For recent reviews on nitrosyl-metal clusters, see: (a) Gladfelter, W. L. *Adv. Organomet. Chem.* **1985**, *24*, 41 and references cited therein. (b) Adams, R. D.; Horvath, I. T. *Prog. Inorg. Chem.* **1985**, *33*, 127. (c) Eisenberg, R.; Hendricksen, D. E. *Adv. Catal.* **1979**, *79*. (d) McCleverty, J. A. *Chem. Rev.* **1979**, *79*, 53. (e) Caulton, K. G. *Coord. Chem. Rev.* **1975**, *14*, 317. (f) Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339.

(3) (a) Stevens, R. E.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1982**, *104*, 645. (b) Legzdins, P.; Nurse, C. R.; Rettig, S. J. *Ibid.* **1983**, *105*, 3727.

(4) Gladfelter, W. L. *Organometallic Compounds: Synthesis, Structure, and Reactivity*; Shaprio, B. L., Ed.; Texas A&M University Press: College Station, TX, 1983; p 281.

(5) (a) Johnson, B. F. G.; Lewis, J.; Mace, J. M. *J. Chem. Soc., Chem. Commun.* **1984**, 186. (b) Smieja, J. A.; Stevens, R. E.; Fjare, D. E.; Gladfelter, W. L. *Inorg. Chem.* **1985**, *24*, 3206.

(6) Collins, M. A.; Johnson, B. F. G.; Lewis, J.; Mace, J. M.; Morris, J.; McPartlin, M.; Nelson, W. J. H.; Puga, J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1983**, 689.

(7) (a) Fjare, D. E.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 1572. (b) Fjare, D. E.; Gladfelter, W. L. *Ibid.* **1984**, *106*, 4799.

(8) Feasey, N. D.; Knox, S. A. R. *J. Chem. Soc., Chem. Commun.* **1982**, 1062.

(9) A complete description of the instrument will appear in a later publication.

(10) For reviews on ICR, see: (a) Beauchamp, J. L. *Ann. Rev. Phys. Chem.* **1971**, *22*, 527. (b) Lehman, T. A.; Bursley, M. M. *Ion Cyclotron Resonance Spectrometry*; Wiley-Interscience: New York, 1976.

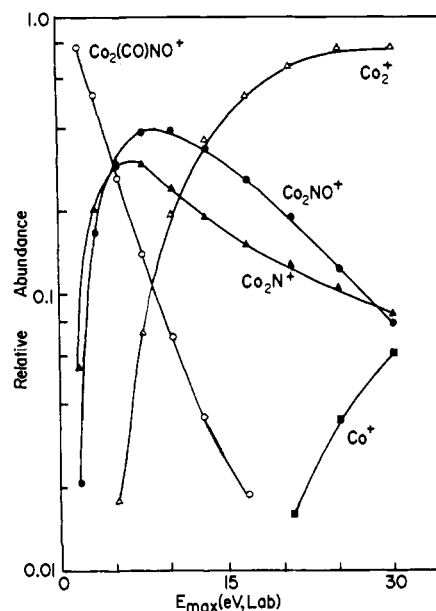
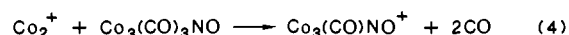
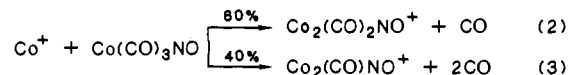


Figure 1. Variation of ion abundances as a function of kinetic energy for dissociation of collisionally activated Co₂(CO)NO⁺ with argon as the collision gas at a pressure of 1 × 10⁻⁵ Torr. The relative ion intensities are taken as a fraction of the initial Co₂(CO)NO⁺ intensity (no excitation). The sum of ion abundance totals slightly less than unity at high kinetic energy due to ion ejection from the cell.

trometry (FTMS)¹¹ have been discussed at length elsewhere. The cobalt-cluster cations were generated by rapid condensation of fragment ions (formed from electron impact on Co(CO)₃NO) with Co(CO)₃NO.¹² For example, Co₂(CO)₂NO⁺, Co₂(CO)NO⁺, and Co₃(CO)NO⁺ are formed by reactions 2-4. The highly unsat-



urated clusters, Co₂NO⁺ and Co₃NO⁺, were generated by collisional activation (CA)^{13,14} of Co₂(CO)₂NO⁺ and Co₃(CO)NO⁺ which were subsequently isolated by swept double resonance ejection techniques.¹¹ Argon was used as the target gas for collisional activation at a pressure of 1 × 10⁻⁵ Torr and also serves to collisionally cool the daughter ions prior to studying their reactivity. Co(CO)₃NO was admitted into the vacuum chamber via a pulsed solenoid inlet valve¹⁵ allowing it to be removed from the chamber within 500 ms permitting these studies to be performed without complicating side reactions with Co(CO)₃NO.

The variation of ion abundances as a function of kinetic energy for dissociation of collisionally activated Co₂(CO)NO⁺ is illustrated in Figure 1 with facile elimination of CO and CO₂ observed, processes 5 and 6. This is in stark contrast to the binary metal-carbonyls which yield exclusively facile elimination of the

(11) For reviews on FTMS methodology, see: (a) Comisarow, M. B. *Adv. Mass Spectrom.* **1980**, *8*, 1698. (b) Ghaderi, S.; Kulkarni, P. S.; Ledford, E. B.; Wilkins, C. L.; Gross, M. L. *Anal. Chem.* **1981**, *53*, 428. (c) Gross, M. L.; Rempel, D. L. *Science (Washington, D.C.)* **1984**, *226*, 26. (d) Marshall, A. G. *Acc. Chem. Res.* **1985**, *18*, 316.

(12) For a detailed description of the condensation reactions for ionized Co(CO)₃NO, see: Fredeen, D.-J. A.; Russell, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 1860. See, also: Weddle, G. H.; Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1977**, *99*, 105.

(13) Cooks, R. G. *Collision Spectroscopy*; Plenum Press: New York, 1978.

(14) For discussions on collisional activation involving FTMS, see: (a) McIver, R. T., Jr.; Bowers, W. D. *Tandem Mass Spectrometry*; McLafferty, F. W., Ed.; John Wiley and Sons: New York, 1983; p 287. (b) Burnier, R. C.; Cody, R. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 7436. (c) Jacobson, D. B.; Freiser, B. S. *Ibid.* **1983**, *105*, 736, 7484.

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