

conditions. By contrast, no NO could be detected in the effluent when NO₂ in the heated Au catalyst bed (400 °C) was mixed with alkanes, chlorinated alkanes, or water.

This redox process, which produces NO, has been coupled with a second redox reaction to allow for selective detection of the previously mentioned classes of reducing compounds with or without prior chromatographic separation.¹³ In such detectors the NO formed is subsequently allowed to react with ozone in the well-known redox reaction accompanied by chemiluminescence.¹⁰ Several inorganic compounds can also be oxidized by NO₂ in the presence of a catalyst. A different method of analysis in which carbon monoxide (rather than NO₂) is fed continuously in excess to a flowing gas stream, to allow the measurement of NO₂, has been reported by Bollinger, Sievers, Fahey, and Fehsenfeld.¹⁴ In the present study we have learned that, in the presence of NO₂ on gold catalysts, ammonia, hydrogen peroxide, carbon disulfide, sulfur dioxide, hydrogen sulfide, and hydrogen react to produce NO and thereby can also be detected by the redox chemiluminescence process.

From the experiments performed, it is clear that this redox reaction process can be used in either a continuous manner or in batch-type reactions to accomplish selective oxidation. The catalyzed redox reactions can be coupled with chemiluminescence detection in either continuous on-line sensors or as chromatographic detectors.^{13,15} Sensitivities of detection comparable to those of flame ionization detectors have been shown for the selected classes of compounds that can undergo catalyzed oxidation.^{13,16}

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Identification of Rb⁻ and Complexed Rb⁺ in Alkalides and Electrides by X-ray Absorption Spectroscopy (XANES and EXAFS)

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We recently synthesized a variety of novel salts that contain alkali-metal anions²⁻⁴ (alkalides) or trapped electrons (electrides).^{5,6} The counterions are alkali cations complexed with 18-crown-6, 15-crown-5, or [2.2.2]cryptand. Species identification and structural information, which are essential for understanding these new materials, are severely hampered by their thermal instability and poor crystal quality. In some cases, but not for complexed Rb⁺, alkali-metal NMR can be used to identify species.^{7,8} We

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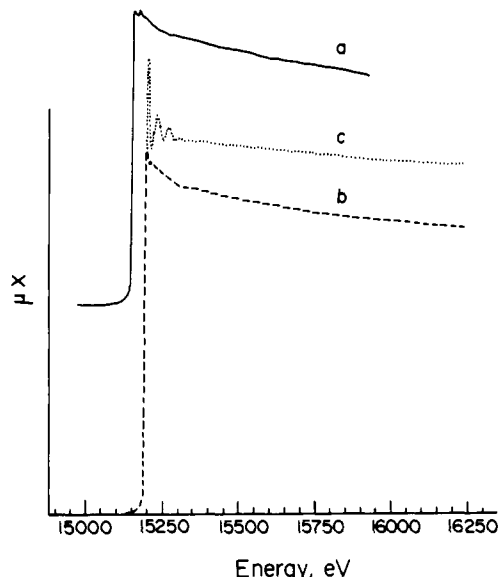


Figure 1. K-edge X-ray absorption spectra of (a) krypton gas,¹⁴ (b) Cs(18C6)₂-Rb⁻, and (c) Rb⁺(18C6)-Br⁻·2H₂O. Note that the Kr spectrum has been shifted horizontally. All three spectra have also been shifted vertically.

Table I. Relative Areas^a (*A*) of Rubidium K-Edge Absorption Threshold Resonances (Normalized to Edge Jump)

compound	<i>A</i> (pristine)	<i>A</i> (oxidized)
Rb ⁺ (18C6)-Br ⁻ ·2H ₂ O	25	
Rb ⁺ (18C6)-SCN ⁻	27	
Rb ⁺ (18C6)-Na ⁻	19	29
Cs ⁺ (18C6) ₂ -Rb ⁻	1	30
Rb ⁺ (18C6)-Rb ⁻	12	29
Rb ⁺ (18C6)-e ⁻ or Rb ⁺ (18C6) ₂ -Rb ⁻	14	27
Rb ⁺ (15C5) ₂ -Na ⁻	29	34
Rb ⁺ (15C5) ₂ -Rb ⁻	18	29
Rb ⁺ (18C6)-K ⁻ and/or K ⁺ (18C6)-Rb ⁻	10	29
Rb ⁺ (15C5) ₂ -K ⁻ and/or K ⁺ (15C5) ₂ -Rb ⁻	16	34
Rb ⁺ C222·e ⁻	21	
K ⁺ C222·Rb ⁻	3	26

^a Estimated accuracy: ±4 units.

report here the first X-ray absorption study of alkalides and electrides. Rubidium XANES and EXAFS with appropriate studies of model salts of known structure^{9,10} provide unequivocal identification of Rb⁻ and/or complexed Rb⁺.

Transmission measurements¹¹ at -50 °C were performed at CHESS¹² under strictly anaerobic conditions. After each measurement the alkalide or electride¹³ was allowed to react with air and the resulting oxide/hydroxide (decomposed sample) was measured again.

The X-ray absorption spectra of Cs⁺(18C6)₂-Rb⁻ and Rb⁺(18C6)-Br⁻·2H₂O are depicted in Figure 1. The energy of the K-edge absorption threshold of Rb⁻ is only 2 eV lower than that of complexed Rb⁺ salts (which have the same edge position as the decomposition product). Thus, as for some noble metal compounds,¹⁴ the relative rubidium edge positions are not good indicators of the formal oxidation states. However, the absorption threshold resonance ("white line"); which results from transitions to vacant bound excited states and is a measure of the density

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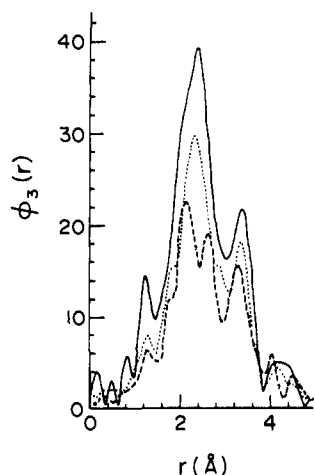


Figure 2. Fourier transforms of the rubidium K-edge transmission EXAFS for $\text{Rb}^+(18\text{C}6)\cdot\text{SCN}^-$ (—), $\text{Rb}^+(18\text{C}6)\cdot\text{Rb}^-$ (···), $\text{Rb}^+(18\text{C}6)\cdot\text{e}^-$ (---).

of such states,^{14,15} shows remarkable differences. The X-ray absorption spectrum of the rubidide $\text{Cs}^+(18\text{C}6)_2\cdot\text{Rb}^-$ (curve b) is very similar to that of Kr gas¹⁵ (curve a). The white line is virtually absent because of the low density of vacant bound excited states. Also, there is no discernible EXAFS, a result of the very large size of Rb^- (estimated radius 3.4 Å;¹⁶ nearest-neighbor distance ~ 5.5 Å). By contrast, $\text{Rb}^+(18\text{C}6)\cdot\text{Br}^- \cdot 2\text{H}_2\text{O}$ (curve c) shows a large white line and distinctive^{17,18} EXAFS, characteristic of Rb^+ .

The area A of the white line, normalized to unit edge jump, for all compounds studied, is given in Table I. On the one hand, the complexed rubidiums such as $\text{Rb}^+(18\text{C}6)\cdot\text{Br}^- \cdot 2\text{H}_2\text{O}$, $\text{Rb}^+(18\text{C}6)\cdot\text{SCN}^-$, $\text{Rb}^+(18\text{C}6)\cdot\text{Na}^+$, and $\text{Rb}^+(15\text{C}5)_2\cdot\text{Na}^+$ have the largest white lines with areas ranging from 20 to 30, very close to the range of 26 to 34 observed for the oxidized complexes. On the other hand, the rubidides $\text{Cs}^+(18\text{C}6)_2\cdot\text{Rb}^-$ and $\text{K}^+\text{C}222\cdot\text{Rb}^-$ have the smallest areas ($A = 1$ and 3, respectively). When both are present, e.g., $\text{Rb}^+(18\text{C}6)\cdot\text{Rb}^-$ and $\text{Rb}^+(15\text{C}5)_2\cdot\text{Rb}^-$, $A = 12$ and 18, respectively, roughly half the A values observed for the complexed rubidium systems, consistent with the fact that half of the rubidiums exist as Rb^+ . Finally, there are systems that are apparently mixtures. For example, $\text{RbK}(18\text{C}6)$, with an A value of 10 may be a mixture of $\text{Rb}^+(18\text{C}6)\cdot\text{K}^-$ and $\text{K}^+(18\text{C}6)\cdot\text{Rb}^-$ and $\text{RbK}(15\text{C}5)_2$ with $A = 16$ is probably a mixture of $\text{Rb}^+(15\text{C}5)_2\cdot\text{K}^-$ and $\text{K}^+(15\text{C}5)_2\cdot\text{Rb}^-$.

The spread of A values from 20 to 30 for complexed Rb^+ may be due to donation of electron density from the anion. Thus, the "protected" Rb^+ in $\text{Rb}^+(15\text{C}5)_2\cdot\text{Na}^+$ has $A = 29$ while for $\text{Rb}^+(18\text{C}6)\cdot\text{Na}^+$ $A = 19$. Also, within the 18C6 series, A decreases with decreasing ionization potential of the anions, $\text{SCN}^- \gtrsim \text{Br}^- > \text{Na}^- > \text{e}^-$.

Fourier transformed (FT) EXAFS¹⁷ for alkaliides with the $\text{Rb}^+(18\text{C}6)$ moiety are similar to those of the model compounds as illustrated in Figure 2 for $\text{Rb}^+(18\text{C}6)\cdot\text{SCN}^-$ (a), $\text{Rb}^+(18\text{C}6)\cdot\text{Rb}^-$ (b), and $\text{Rb}^+(18\text{C}6)\cdot\text{e}^-$ (c). In the former, Rb^+ is coordinated to six crown ether oxygens ($\text{Rb}-\text{O}$, 2.93–3.15 Å)⁹ and to two thiocyanate anions [$\text{Rb}-\text{N}(\text{S})$, 3.23 and 3.31 Å]. The FT shows a broad peak (phase-shift corrected) at 2.95 Å (Rb^+-O) that extends to 3.4 Å, thus masking the $\text{Rb}^+-\text{thiocyanate}$ peaks. A second peak at 3.95 Å corresponds to the $\text{Rb}^+ \cdots \text{C}$ distances. The FT for the rubidide, $\text{Rb}^+(18\text{C}6)\cdot\text{Rb}^-$ is very similar, with main

peaks at 2.95 Å (Rb^+-O) and 3.80 Å ($\text{Rb}^+ \cdots \text{C}$). The attenuation in the FT peaks from $\text{Rb}^+(18\text{C}6)\cdot\text{SCN}^-$ (a) to $\text{Rb}^+(18\text{C}6)\cdot\text{Rb}^-$ (b) results from dilution of the Rb^+ concentration (from 100% to 50%) and the absence of Rb^- EXAFS. The EXAFS of the other systems containing mixtures are also consistent with the presence of Rb^+ and Rb^- . The FT of the electride,¹⁹ $\text{Rb}^+(18\text{C}6)\cdot\text{e}^-$, in addition to the $\text{Rb}-\text{O}$ (2.7 Å) and $\text{Rb} \cdots \text{C}$ (3.8 Å) distances, has a peak at 3.4 Å which is tentatively assigned to $\text{Rb} \cdots \text{O}(\text{C})$ distances. The presence of this new peak, and the shifts of the $\text{Rb}-\text{O}$ and $\text{Rb} \cdots \text{C}$ peaks to lower distances, indicates a significant change in the local structure around Rb^+ .

In summary, the XANES and EXAFS results are fully consistent and can be used to differentiate between Rb^+ and Rb^- , thus providing new insights into the nature of alkaliides and electrides.

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(19) This salt could be the rubidide $\text{Rb}^+(18\text{C}6)_2\cdot\text{Rb}^-$.

Reductive Homologation of CO to a Ketene-carboxylate by a Low-Valent Organolanthanide Complex: Synthesis and X-ray Crystal Structure of $[(\text{C}_5\text{Me}_5)_4\text{Sm}_2(\text{O}_2\text{CCCO})(\text{THF})_2]_1$

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As part of our general investigation of low-valent lanthanide chemistry³ we reported that the divalent complex $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$ (I) reacts with CO at atmospheric pressure.⁴ The reaction was complex and separation of the many products formed has proven difficult. Multiple products are also formed when I reacts with CO at 90 psi, but under the proper conditions one product separates in crystalline form. We report here the structure of this remarkable product and discuss its implications in the areas of CO reduction⁵ and low-valent lanthanide chemistry.

Reaction of CO at 90 psi with $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$ (162 mg, 0.29 mmol) in 5 mL of THF in a 3-oz Fischer-Porter aerosol

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