

Figure 3. Schematic cycle for the photosensitized reduction of  $\text{CO}_2$  to  $\text{CH}_4$ .

dynamically capable of reducing  $\text{CO}_2$  to  $\text{CH}_4$ . To account for the functions of the different components included in the system that leads to the reduction of  $\text{CO}_2$ , a laser flash photolysis study was performed (Figure 2). Flashing a system that includes  $\text{Ru}(\text{bpz})_3^{2+}$  and TEOA under an inert Ar atmosphere results in the trace displayed in Figure 2a. Namely, flashing of the system results in the formation of  $\text{Ru}(\text{bpz})_3^+$ . This photoproduct decays for ca. 80  $\mu\text{s}$ , as a result of back reaction with  $\text{TEOA}^{+}$ , and later is accumulated as a result of irreversible decomposition of the latter photoproduct. A similar trace is observed under a  $\text{CO}_2$  atmosphere, implying that  $\text{Ru}(\text{bpz})_3^+$  is unaffected by  $\text{CO}_2$  in the absence of the catalyst. Introduction of the Ru colloid to the  $\text{Ru}(\text{bpz})_3^{2+}$ -TEOA system under Ar atmosphere results upon flashing in the trace displayed in Figure 2b. It is evident that in the presence of the Ru colloid, the photoproduct  $\text{Ru}(\text{bpz})_3^+$  decays ( $\tau = 170 \mu\text{s}$ ), implying that electron transfer to the colloid occurs. We attribute this decay process to a charging process of the Ru colloid<sup>15</sup> by  $\text{Ru}(\text{bpz})_3^+$ . Even more interesting is the behavior of flash-photogenerated  $\text{Ru}(\text{bpz})_3^+$  in the presence of the Ru colloid and  $\text{CO}_2$  (Figure 2c). It can be seen that in the presence of these two components  $\text{Ru}(\text{bpz})_3^+$  rapidly decays and its lifetime is considerably shortened ( $\tau = 50 \mu\text{s}$ ), as compared to the system in the absence of  $\text{CO}_2$  or the system where the Ru colloid is excluded. These results clearly indicate that electron transfer from  $\text{Ru}(\text{bpz})_3^+$  is very rapid in the presence of the Ru colloid and  $\text{CO}_2$  together. This effect might be attributed to either improvement of the charging capability of the Ru colloid (via, for example, electron transfer from the colloid to adsorbed  $\text{CO}_2$ ), or to direct reduction of  $\text{CO}_2$  adsorbed to the metal colloid. Nevertheless, the decay curve of  $\text{Ru}(\text{bpz})_3^+$  in the presence of the Ru metal and  $\text{CO}_2$  shows a single exponential decay, and thus the first possibility is preferred. In view of these results, we suggest the schematic cycle presented in Figure 3 as a possible route for the photoreduction of  $\text{CO}_2$  to  $\text{CH}_4$ .

Previous studies have shown that  $\text{Ru}(\text{bpz})_3^{2+}$  can be effectively reduced by TEOA in ethanol.<sup>10</sup> Thus, we have studied the reduction of  $\text{CO}_2$  to methane using  $\text{Ru}(\text{bpz})_3^{2+}$  as sensitizer, TEOA as electron donor, and the Ru colloid in a mixture of  $\text{H}_2\text{O}$ -ethanol (2:1). The rate of  $\text{CH}_4$  formation is displayed in Figure 1b and corresponds to a quantum yield of  $\phi = 0.04\%$ . The higher quantum yield obtained under these conditions is mainly attributed to the effectiveness of  $\text{Ru}(\text{bpz})_3^+$  formation in this medium. Introduction of the Ru colloid to the photogenerated  $\text{Ru}(\text{bpz})_3^+$  in the water-ethanol mixture results in the evolution of  $\text{CH}_4$  and recovery of  $\text{Ru}(\text{bpz})_3^{2+}$ . These results are consistent with the previously described mechanistic cycle outlined in Figure 3. It should be noted that in the absence of  $\text{CO}_2$ , no  $\text{H}_2$  evolution is detected. Thus, the conversion to methane is not considered to proceed via hydrogenation of  $\text{CO}_2$  but rather via electron transfer to metal-activated  $\text{CO}_2$  followed by protonation. In the electrochemical reduction of  $\text{CO}_2$  to  $\text{CH}_4$ , it has been observed<sup>10</sup> that the Ru electrode undergoes partial oxidation by  $\text{CO}_2$  to form CO. In our system no CO formation is detected, yet such partial oxidative corrosion of the Ru colloid is not excluded.

In conclusion, we have demonstrated that the photosensitized reduction of  $\text{CO}_2$  to  $\text{CH}_4$  can be accomplished with photogenerated  $\text{Ru}(\text{bpz})_3^+$  in the presence of colloidal Ru. The functions of the metal colloid in this process clearly indicate that in the presence of  $\text{CO}_2$ , electron transfer from  $\text{Ru}(\text{bpz})_3^+$  to the colloid-associated  $\text{CO}_2$  is effective. Further experiments utilizing other catalysts and attempts to further characterize mechanistic aspects of the process are now under way in our laboratory.

## Neutral Gas-Phase Analogs of Condensed-Phase Post-Transition-Metal Cluster Ions: Laser Vaporization and Photoionization of Sn/Bi and Pb/Sb Alloys

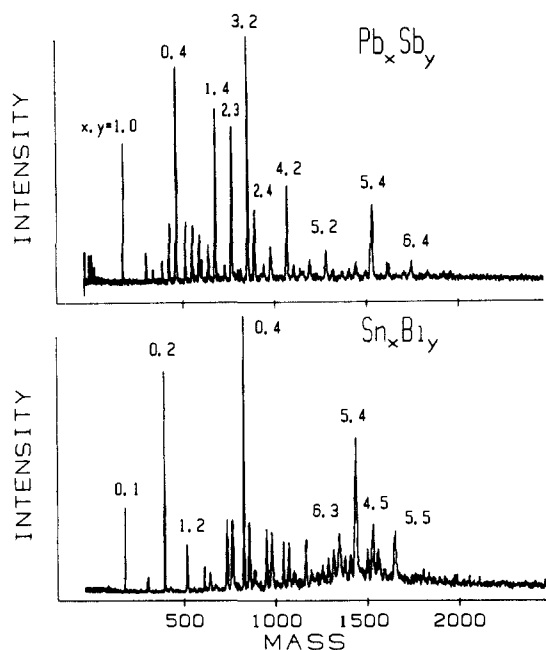
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The recent development of laser vaporization/molecular beam technology<sup>1</sup> has resulted in numerous studies of gas-phase metal cluster molecules.<sup>2</sup> Various experiments have examined the structures of diatomic<sup>3</sup> and triatomic<sup>4</sup> species, as well as size-dependent properties such as ionization potentials,<sup>5</sup> chemical reactivity,<sup>6</sup> and fragmentation.<sup>7</sup> Semiconductors<sup>8</sup> and other materials<sup>9</sup> have also been included in this growing area of research. Prior to the development of these rather exotic techniques, however, cluster systems had already been studied for many years in condensed phases. For example, borane,<sup>10,11</sup> carborane,<sup>10-12</sup> transition-metal carbonyl,<sup>13</sup> and post-transition-metal ion<sup>14-17</sup> cluster systems are well characterized. In general, condensed-phase clusters have limited volatility and are coordinatively saturated with external ligands so that detailed comparisons with bare-metal gas-phase species are not possible. However, ionic clusters of the post-transition elements ( $\text{Sn}_5^{2-}$ ,  $\text{Pb}_9^{4-}$ ,  $\text{Bi}_9^{5+}$ , etc.)<sup>15</sup> are ligand-free, consisting of charged metal polyhedral networks accompanied by counterions. These systems have been investigated extensively through NMR and X-ray diffraction experiments<sup>15</sup> and theoretical treatments using molecular orbital methods as well as less rigorous electron counting techniques.<sup>13,14</sup> In this report we describe the observation of neutral gas-phase counterparts to these condensed-phase ionic clusters. These results establish one of the few existing links between cluster research in these different environments.

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**Figure 1.** Time-of-flight mass spectra of clusters formed by laser vaporization of alloys in a pulsed supersonic nozzle source resulting from laser photoionization at 157 nm ( $F_2$  excimer laser;  $50 \mu\text{J}/\text{cm}^2$ ).

The structure and stability of post-transition-metal clusters show a strong similarity to those of carborane clusters.<sup>14-17</sup> Consequently, although detailed molecular orbital studies have been conducted,<sup>16,17</sup> many of the salient features of bonding in these systems are described by simple valence electron counting schemes.<sup>14,15</sup> In condensed phases stable electron configurations are achieved with multiply charged cluster species. Gas-phase experiments, however, produce primarily neutrals, and cluster elements must be specifically chosen to produce isoelectronic analogs of ionic species for comparison. Group 14 and 15 elements respectively are isolobal<sup>18</sup> to the BH and CH building blocks of carboranes, and therefore alloy clusters combining these elements provide the logical test cases for stable neutrals in the gas phase.

Figure 1 shows the laser-photoionization time-of-flight mass spectra of Sn/Bi and Pb/Sb clusters produced by excimer laser vaporization (248 nm; 30-40 mJ/pulse) of 1:1 alloys in a pulsed nozzle source<sup>1</sup> (1-mm orifice diameter; 6 atm of helium pressure). These spectra were obtained by using a photoionization wavelength of 157 nm in the limit of low laser power ( $50 \mu\text{J}/\text{cm}^2$ ). Intensities in these spectra are determined by the density of each size cluster formed in our experiment, by relative ionization efficiencies, and by the slowly varying mass spectral focusing function (optimized here for mass 1000 with approximate fwhm of 1500 amu). Cluster growth in our source occurs under collision-dominated near room temperature conditions, so that thermodynamic stability should have a strong influence on cluster abundances. We have also conducted laser wavelength and fluence dependent studies to elucidate fragmentation processes. Therefore, although we cannot rule out completely the presence of other cluster species not ionized under these conditions (because of higher ionization potentials), we believe the abundances shown in these spectra indicate the primary stable clusters formed.

In contrast to mass spectra of transition-metal cluster alloys,<sup>19</sup> the spectra shown here do not represent statistical combinations of the elements present. Of the more abundant species indicated, nearly all are even-electron molecules containing two or four atoms of antimony or bismuth. The apparent exceptions to this rule ( $X_3$  and  $X_5$  clusters) are especially stable *fragment ions* (also even-electron species). Under conditions of high laser power or longer ionization wavelength (193 nm), where multiphoton absorption

and fragmentation are important, these species dominate the spectra. The tetramers of antimony and bismuth are well-known stable species and dominate their respective pure component cluster distributions. Of the remaining abundant mass channels, several represent molecules related to condensed-phase clusters.  $\text{Pb}_3\text{Sb}_2$ , for example, is isoelectronic to the 5-atom 12-skeletal electron species  $\text{Sn}_5^{2-}$  and  $\text{Pb}_5^{2-}$  (trigonal bipyramid structures). More significantly, by far the largest features at higher mass for *both* alloys are the 9-atom 22-skeletal electron species,  $\text{Pb}_5\text{Sb}_4$  and  $\text{Sn}_5\text{Bi}_4$ , which are isoelectronic with the ions  $\text{Ge}_9^{4+}$ ,  $\text{Sn}_9^{4+}$ , and  $\text{Pb}_9^{4+}$  ( $C_{4v}$  uncapped square-antiprism structure), extensively studied in the condensed phase.<sup>15</sup>

The relationship between condensed-phase ionic clusters and gas-phase neutrals suggested by these data is significant. Structures of the ionic species have been measured, but spectroscopic studies of gas-phase clusters in molecular beams are plagued with difficulties and there are no detailed data for species larger than triatomics. Although there are no guarantees that structures of corresponding species will be the same, the known ionic data certainly provide a good "first guess" for gas-phase structures. In a more general way, researchers in both cluster media will likely benefit by recognizing the complementary kinds of information on metal cluster bonding available from these heretofore separate areas.

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**Note Added in Proof.** Similar results have recently been obtained for the Pb/Sb system by using inert gas condensation in an oven source with electron-impact ionization.<sup>20</sup>

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### Surprisingly Efficient Intramolecular Addition of Carbon Radicals to Carbonyl Groups: A Ready Route to Cycloalkanols<sup>1</sup>

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In the course of determining the structure of  $\alpha$ -caryophyllene by a process that involved the nitrite ester of a secondary alcohol (exemplified by I), Nickon and co-workers observed that the epimer (V) was produced, and it was concluded that the radicals II-IV were intermediates in the process.<sup>2</sup> Similar epimerization of alkoxy radicals II-IV have either been encountered or been invoked as intermediate steps in a number of instances,<sup>3-5</sup> and credence for the intermediacy of the aldehyde III comes from the fact that a label on the hydrogen of I is fully retained in the epimer IV and/or the products arising therefrom.<sup>3</sup>

The work of Walling and Padwa<sup>6</sup> on the  $\beta$ -scission of tertiary alkoxy radicals<sup>7-9</sup> provides an estimate of  $\Delta H = 5 \text{ kcal/mol}$  for

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