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 $\mu J/cm^2$).

The structure and stability of post-transition-metal clusters show a strong similarity to those of carborane clusters.[14–17] Consequently, although detailed molecular orbital studies have been conducted,[16,17] many of the salient features of bonding in these systems are described by simple valence electron counting schemes.[14,15] 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[18] 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[1] (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 $\mu J/cm^2$). 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,[19] 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. Pb_3Sb_2, for example, is isoelectronic to the 5-atom 12-skeletal electron species $Sn_5{}^{2-}$ and $Pb_5{}^{2-}$ (trigonal bipyramid structures). More significantly, by far the largest features at higher mass for *both* alloys are the 9-atom 22-skeletal electron species, Pb_5Sb_4 and Sn_5Bi_4, which are isolectronic with the ions $Ge_9{}^{4-}$, $Sn_9{}^{4-}$, and $Pb_9{}^{4-}$ (C_{4v} unicapped square-antiprism structure), extensively studied in the condensed phase.[15]

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.

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.[20]

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Surprisingly Efficient Intramolecular Addition of Carbon Radicals to Carbonyl Groups: A Ready Route to Cycloalkanols[1]

Ray Tsang* and Bert Fraser-Reid*

*Department of Chemistry
Paul M. Gross Laboratory, Duke University
Durham, North Carolina 27706*

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In the course of determining the structure of α-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.[2] Similar epimerization of alkoxy radicals II–IV have either been encountered or been invoked as intermediate steps in a number of instances,[3–5] 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.[3]

The work of Walling and Padwa[6] on the β-scission of tertiary alkoxy radicals[7–9] provides an estimate of $\Delta H = 5$ kcal/mol for

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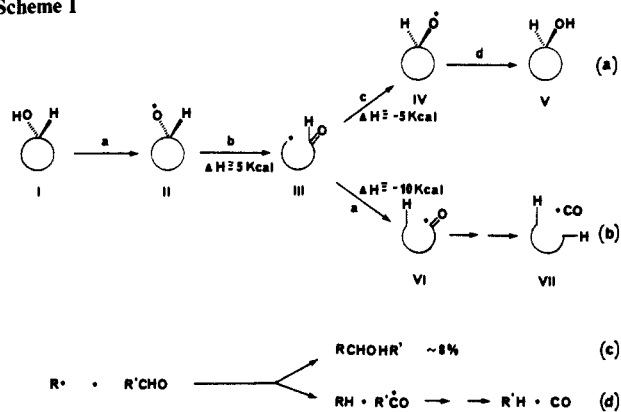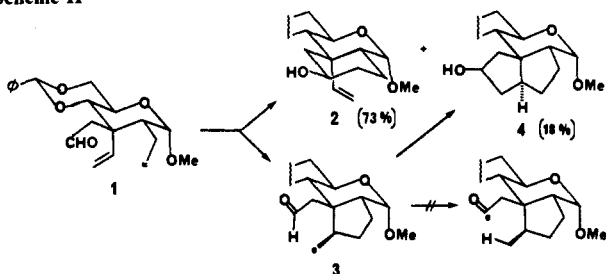(6) Walling, C.; Padwa, A. J. Am. Chem. Soc. 1963, 85, 1593.
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Scheme I

Scheme II

Table I. Reaction of Carbon-Centered Radicals with Carbonyl Groups[a]

[a] In a typical reaction the radical was generated by treating a 0.032 M solution of the iodide in benzene with 1 equivalent of n-Bu$_3$SnH and a catalytic amount of AIBN under reflux in an argon atmosphere. The yields quoted are after chromatographic isolation.

Scheme III

step b, which therefore suggests that the reverse process, i.e., step c, is favorable. However, the synthetic potential of step c is undermined by a second competitive, exothermic avenue, step e, a process for which ΔH is approximately −10 kcal/mol. Not surprisingly, therefore, Maruyama and co-workers found that intermolecular radical additions to aldehydes (Scheme Ic) yielded only approximately 8% of secondary alcohols, the principal products being hydrocarbons RH and R′H.[10] On the basis of those studies, the reaction course III → VI → VII might therefore be expected to prevail, particularly where an entropically favorable transition state can be realized in step e. Nevertheless, as part of a study on radical isomerization of oxepanes, Flies, Laland, and Maillard investigated the radical cyclization of 6-chlorohexanal and isolated several products, including 10% of cyclohexanol.[11]

Our interest in this area of chemistry was triggered by our investigation of a serial radical cyclization procedure in which we observed that cyclization of radical **1** afforded the cyclohexanol **2** in 73% yield (Scheme II).[12] This high chemical yield was particularly remarkable in light of the attractive alternative option leading to the cyclopentane **3**. Thus, in spite of the unfavorable thermochemistry predicted by the data in Scheme Ia,b, the generally low yields for step c in the aforementioned epimerization precedents,[2–5] and the poor prospect based on the work of Maruyama (Scheme Ic,d)[10] and Flies,[11] the intramolecular radical addition to a carbonyl group appeared to promise a ready, unexplored route to cycloalkanols. In this paper, we report that this seemingly contrathermodynamic process is indeed of synthetic value—certainly for the synthesis of some fused-ring systems.
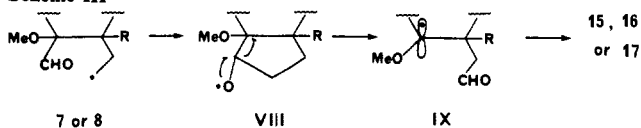
The test substrates **5–12** were conveniently prepared from carbohydrate precursors by procedures which will be described elsewhere. As shown in entries a and b of Table I, the trans- and cis-fused products **13** and **14** were obtained in high yields which, combined with the case of **2**, indicate the synthetic generality of the procedure for the preparation of cyclohexanols. Compounds **7–9** were used to address the possibility of cyclopentanol formation
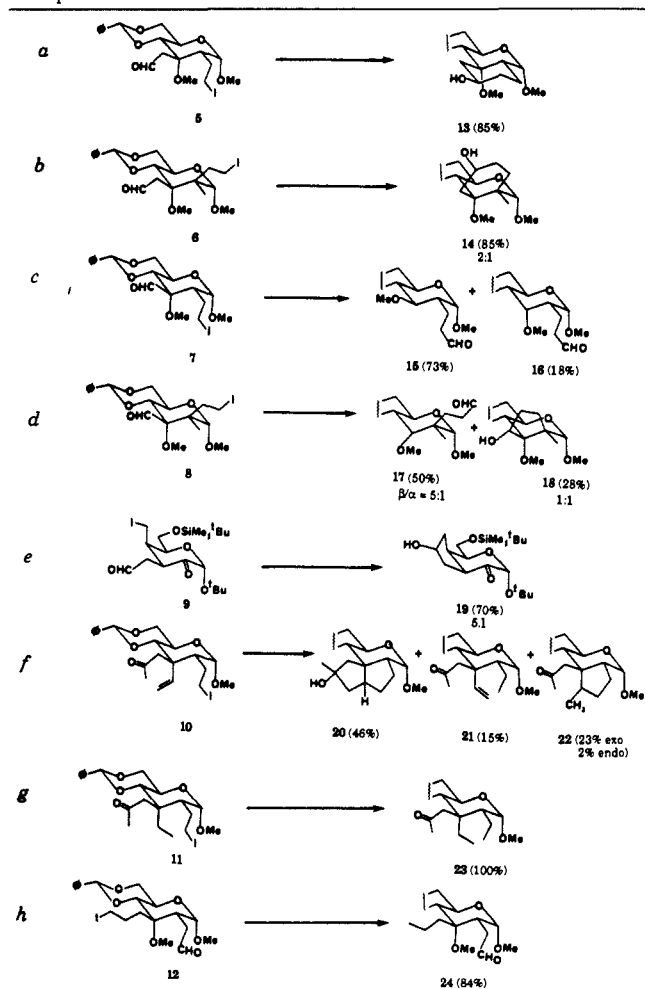
and the results in entries c and d indicate only modest isolation of the cis-fused product **18**, the preferred pathway being for translocation of the aldehydo group leading to **15–17**[13,14] (Scheme III).

The contrasting reaction courses in entries a/b vs. c/d are in keeping with the observations of Walling and Padwa on the relative ease of β-scission in cyclohexyl and cyclopentyl tertiary alkoxy radicals.[6] The former were found to be of the same order as acyclic systems, whereas the latter opened more readily by approximately 6.5 kcal/mol. In addition to these ring strain effects, β-scission of the alkoxy intermediate VIII leads to the highly stabilized oxymethyl radical IX. The overiding influence of the latter factor may be judged by the absence of aldehyde translocation products during the formation of **4** and **19** where the corresponding β-scission would have merely regenerated a primary radical.

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The ketone 11 (entry f) was next examined and in contrast to the corresponding aldehyde 1, a cyclohexanol was not obtained, the preferred reaction course being that of serial radical cyclization leading to 20 as the principal product. Accordingly, when this preferred pathway was removed by saturation of the double bond to give 11, no cyclization of any type was observed, the only product being 23.

In the case of aldehyde 12, only 24 was detected, there being no evidence of the desired cycloheptanol.

Further studies to determine the full scope of these cyclizations are under way and will be described in due course.

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Absence of the Metal–Support Interaction for Ni/TiO₂ Composites Prepared by Ion-Exchange Techniques

Hans-Conrad zur Loye, Tanya A. Faltens, and Angelica M. Stacy*

Department of Chemistry, University of California Berkeley, California 94720

Many recent reports on the surface properties of transition-metal catalysts dispersed on high surface area oxide supports have shown that the support can alter markedly the intrinsic activity of the metal.[1] In particular, when group 8–10 metals are supported on reducible metal oxides, the surface chemistry and the electronic properties of the composite depend on the reduction temperature used for pretreatment. For example, the chemisorption of H_2 at room temperature on metal–TiO₂ composites decreases sharply as the reduction temperature used to prepare the catalyst is increased from 573 to 773 K. This change in surface chemistry has been attributed to a strong interaction between the metal and the TiO_x ($x < 2$). By understanding the conditions required to induce this interaction, the acitivity and selectivity of supported metal catalysts can be tailored for specific applications. In this paper, we show that the extent of the interaction can be controlled if the composition at the interface between the nickel and TiO₂ is manipulated by varying the method used to disperse the nickel.

In typical preparations of heterogeneous catalysts, group 8–10 metals are dispersed on metal oxides either by incipient wetness or ion-exchange techniques. The initial composition of the interface is quite different in the two cases. If incipient wetness techniques are used, the metal is deposited as a salt; a counterion is codeposited with the metal and the number of hydroxyl groups on the TiO₂ surface remains unchanged. By ion-exchange methods, the transition-metal cation is exchanged for H^+ from surface hydroxyl groups; no counterion remains behind and surface hydroxyl groups are replaced by metal cations bound directly to surface oxygen. We have prepared samples of nickel dispersed on a low surface area TiO₂ (5.1 m²/g) by both methods and studied their chemisorption properties and magnetism as a function of the pretreatment temperature used to reduce the Ni^{+2} to Ni^0. In agreement with previous studies,[1,2] we find a strong metal–support interaction for the Ni/TiO₂ composite prepared by incipient wetness. However, the properties of the sample prepared

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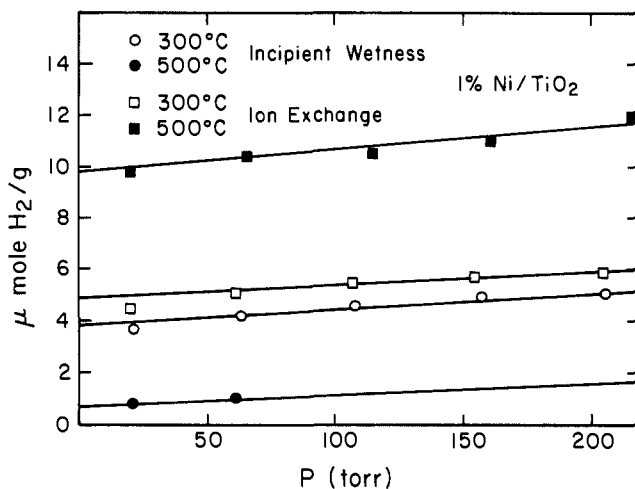

Figure 1. Hydrogen uptake in moles of H per mole of Ni vs. hydrogen pressure for (A) 1.0% Ni/TiO₂ prepared by incipient wetness (circles) and (B) 1.0% Ni/TiO₂ prepared by ion exchange (squares). Open circles and squares are for samples reduced at 573 K for 4 h. Closed circles and squares indicate samples reduced at 773 K for 4 h.

by ion exchange are strikingly different; the intrinsic activity of the nickel in this sample is not modified by the TiO₂. Instead, the properties of this composite are similar to those observed for nickel supported on a more inert support, such as SiO₂.

Two samples of 1.0% Ni/TiO₂ were prepared from TiO₂ (Cerac, 99.9% pure) which was 10–15% rutile and 85–90% anatase with a surface area of 5.1 m²/g. Sample A was prepared by incipient wetness techniques using reagent grade $Ni(NO_3)_2$·6H₂O (99.95% pure) dissolved in distilled, deionized water. Approximately 4 g of TiO₂ were slurried with 1 mL of a nickel solution containing the amount of nickel needed to give a 1.0% loading of nickel by weight. After adding 3–4 mL of acetone, the slurry was ground until dry and then further dried for 1 h under vacuum. The unreduced composite consisted of $Ni(NO_3)_2$·6H₂O deposited on TiO₂. To prepare sample B by ion-exchange methods, approximately 4 g of TiO₂ was refluxed at 373 K for 20 h in 67 mL of a solution of $Ni(NO_3)_2$·6H₂O dissolved in an aqueous solution of NH₄OH with a pH of 11. The concentration of the nickel solution was adjusted to give a loading of 1.0% nickel by weight. After 20 h the blue solution had turned clear and the pH was 8–9 due to the release of H^+ from the TiO₂ surface. Although 1.2×10^{-3} mol of protons are released, the pH remains basic due to the buffering of the NH₃ solution. The mixture was filtered hot and analyzed for the Ni^{+2} concentration with a Perkin-Elmer Lambda-9 spectrometer with a detection limit for absorbance of 0.001. Since no absorbance due to Ni^{+2} was detected, nearly all the Ni^{+2} ion-exchanged onto the support. The solid was dried at 368 K. Both samples were reduced initially in flowing hydrogen at 573 K for 4 h and then at 773 K for 4 h.

Changes in the surface chemistry of the nickel were monitored by the chemisorption of hydrogen at room temperature. The amount of H_2 that chemisorbed on both composites after reduction at 573 K, as shown in Figure 1, was similar; sample A chemisorbed 0.042 mol of H per mol of Ni added to the support and sample B chemisorbed 0.054 mol of H per mol of Ni. After sample A was reduced at 773 K for 4 h, the hydrogen uptake decreased to 0.005 mol of H per mol of Ni. This suppression of hydrogen chemisorption is observed typically for group 8–10 metals supported on TiO₂ and is accepted as the signature that there is a strong interaction between the metal and the support.[1] In sharp contrast, the chemisorption on the ion-exchanged sample increased to 0.110 mol of H per mol of Ni after reduction at 773 K for 4 h. This is a value similar to that which we have observed for 1.0% Ni/SiO₂. Since no drop in chemisorption is observed for the ion-exchanged sample after reduction at 773 K, we conclude that the reaction of the metal with the support is suppressed.

In order to determine the amount of nickel present as the pure metal,[2] the saturation magnetization M_s was measured at 5 K on