The efficiency of the present system in terms of the yield in the halogen exchange reaction was comparable to that of the phase-transfer reactions using low molecular weight catalysts[10] and generally higher than that of triphase reactions using insoluble polymer catalysts.[14] The present system has some similarity in appearance with triphase systems but showed much higher efficiency. Most of the triphase reactions required vigorous agitation and reaction temperatures 20–40 °C higher than the present case to produce similar yields,[14] because of the slow diffusion involved with insoluble polymer catalysts.

As shown above, the present system has advantages that it needs neither a catalyst nor stirring during the reaction, in addition to the features found with triphase catalyzed reactions. The results suggest the possibility of synthetic use of the interfacial reactions which have been believed to be very slow. In addition to this, it may become possible to measure the reactivity of water-insoluble substrates in contact with aqueous reagent solutions without diffusion problems. This is in clear contrast with other reaction systems under homogeneous, phase-transfer-catalyzed, and triphase catalyzed conditions, where the actual reacting species do not react across the phase boundary between the aqueous phase and the organic phase. Although there are very few data available for comparative purposes in this respect,[15] the rate constants in Table I indicate the unexpectedly high reactivity of the molecules placed at the phase boundaries.

Further studies are currently in progress on the mechanism of the reactions along with the synthetic applications of the present reaction system.

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[15] There were very few cases that measured the rates of truly interfacial reactions without diffusion problems.[4d]

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# Encapsulation and Electronic Effects in a Thin-Film Model of a Rhodium–Titania Strong Metal-Support Interaction Catalyst[†]

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Active debate has recently centered on systems that exhibit strong metal–support interactions (SMSI).[1-7] These interactions are generally diagnosed by supressed $H_2$ chemisorption. The proposed explanations inlcude encapsulation of the metal by the support[6,7] and charge transfer from the support to the metal.[8-10] We have constructed thin-film model catalysts under controlled conditions in order to study the interactions between the support and the metal. Here we present preliminary results for the $Rh/TiO_2$ system studied using static secondary ion mass spectroscopy (SSIMS), thermal desorption spectroscopy (TDS), and Auger electron spectroscopy (AES).

The model consists of an oxidized Ti(0001) single crystal onto which controlled amounts of Rh were vapor deposited. The Ti(0001) was oxidized in vacuum at 775 K in $5 \times 10^{-7}$ torr of $O_2$ for 20 min. This produced a $TiO_2$ film approximately 20 Å thick. Underlying the $TiO_2$ is another region of about 30 Å of oxygen-rich Ti ($TiO_x$, $x < 2$). The characterization of the oxide film is based on the AES line shapes of the Ti transitions, which are correlated with previous X-ray photoelectron spectroscopy (XPS) work.[5,11] The Rh overlayer was deposited with the oxide layer at room temperature, and its thickness was estimated from the attenuation of the substrate Ti and O AES signals. Assuming layered growth of the overlayer, we calculate the Rh thickness to be 30 ± 10 Å.[12] The quoted uncertainty accounts for the possibility of some nonuniform growth and for the very small substrate signals detectable at this thickness of Rh. To obtain a more uniform overlayer, the deposited Rh was annealed in vacuum to 625 K for 1 min during which small Ti and O AES signals appeared. These were sputtered away with a 1-KV and 100-nA $Ar^+$ beam. The sample was then annealed again at 625 K for 1 min. Neither the Ti nor the O signal reappeared; this is referred to as the clean surface.

The clean surface was dosed with 10 L of $H_2$ at 130 K and TDS (10 K/s to 450 K) performed to obtain the hydrogen uptake. The desorption maximum was at 280 K with a half-width of 100 K. The clean surface was further characterized with AES and SSIMS. Before TDS, AES showed no detectable Ti or O, while SSIMS detected a Ti/Rh ratio of 7.6. This result reveals the excellent sensitivity of SSIMS are compared, under these conditions, to AES. This ability to detect very small concentrations coupled with its excellent surface sensitivity makes SSIMS an excellent technique for this type of study.

Following characterization of the clean surface, the sample was heated at 1 K/s to 775 K and maintained at that temperature for 8 min. Depth profiling experiments show that the $TiO_2$ layer remains intact throughout the annealing process. Subsequent TDS of 10 L of $H_2$ adsorbed at 130 K was 75% lower than for the clean surface (see Figure 1). In addition to the decrease in $H_2$ uptake, an increase in the Ti/Rh ratio, as measured by SSIMS and AES, was observed. There was a concurrent increase in the O/Rh AES ratio; however, the O/Ti ratio was about one-half that of $TiO_2$. Moreover, the line shapes of the Ti AES peaks were indicative of reduced titanium oxide.

Figure 1 shows SSIMS, AES, and TDS signals as a function of the integrated sputtering current during a depth profile of the sample that was annealed to 775 K. It was sputtered with a 1-KV and 100-nA $Ar^+$ beam. After each sputtering interval and before taking the SSIMS, AES, and TDS data, the sample was reannealed to 525 K to facilitate removal of surface roughness caused by the sputtering. Great care was taken to assure that changes in effective Rh surface area were not responsible for the increases in $H_2$ uptake observed during the depth profile.

To demonstrate convincingly that surface-area changes induced by sputtering were an unimportant effect, we performed a second experiment on a Rh surface prepared as above. After characterization of the *clean* surface by SSIMS, AES, and TDS, it was sputtered (1 KV, 100 nA) and annealed to 525 K. The $H_2$ TDS peak area increased by no more than 5% compared to the clean surface. This shows that the changes in peak area observed in the depth profile experiment cannot be accounted for by changes in surface area of the Rh.

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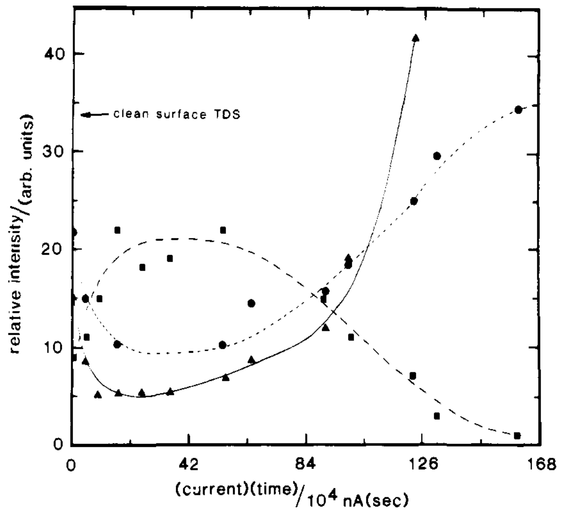

**Figure 1.** Relative intensities as a function of $Ar^+$ dose onto a $Rh/TiO_2$ thin-film system preheated to 775 K for 8 min in vacuum. The solid squares denote the $H_2$ TDS peak area after a 10 L exposure at 130 K, the solid triangles, the Ti/Rh AES ratio, and the solid circles, the $Ti^+/Rh^+$ SSIMS ratio. The arrow marks the $H_2$ TDS area measured for the clean sample before heating to 775 K.

With increasing $Ar^+$ dose, Figure 1 is characterized by a sharply declining Ti/Rh ratio and an increasing $H_2$ TDS peak area. For intermediate doses, these parameters remain relatively constant. As expected, the Ti/Rh ratio increases and the $H_2$ TDS area decreases for larger sputtering doses because the Rh layer is removed. Not shown in Figure 1 are the data for the O/Rh AES ratio, which follow the same trend as the Ti/Rh AES data. Clearly the ability to adsorb $H_2$ correlates with the amount of Ti and O present at the surface.

To explain these results, we proposed the following model. When the sample is heated, the surface of the Rh becomes more uniform and is partially encapsulated with a $TiO_x$ species. This species, which segregates to the Rh surface, probably migrates through defects in the Rh overlayer. It is a reduced oxide, as evidenced by the O/Ti AES ratio and Ti AES line shape. Further characterization of this Ti–O–Rh interface awaits XPS analysis. As the sample is depth profiled about 60% of the clean surface uptake capacity of $H_2$ is restored as the surface Ti is decreased. Since it is unlikely that implantation of Ti during the sputtering process could be responsible for the amounts of Ti present throughout the Rh overlayer, we suggest that some Ti diffuses into the Rh during annealing. Whether the Ti forms an alloy or is present in some other form is unclear from this work. The presence of Ti throughout the Rh layer coupled with the decrease in surface area expected from annealing the sample at 775 K for 8 min accounts for the inability of the sample to recover completely the original clean surface $H_2$ uptake.

Previously we reported that reduced titanium oxide interacts electronically with Pt to shift $H_2$ desorption to lower temperatures by 70 K.[5] This work was repeated for Rh under very carefully controlled conditions where neither Ti or O were present on the Rh surface (i.e., no encapsulation). As for Pt there was a significant shift of $H_2$ desorption peak to lower temperatures. Evidence of electronic interactions between metal and support has also been obtained using extended X-ray absorption fine structure (EXAFS).[4]

To summarize, the present work demonstrates that during heating to 775 K, Ti and O migrate through and segregate at the surface of thin Rh overlayers. As a result, sites for $H_2$ chemisorption are blocked. Previous work from this laboratory suggesting an electronic effect of $TiO_x$ on the ability of metals to chemisorb $H_2$ was verified for Rh. Taken together these results illustrate that SMSI effects can arise from a number of sources and that both encapsulation and electronic effects must be considered for the $Rh/TiO_2$ system.

**Registry No.** Rh, 7440-16-6; $TiO_2$, 13463-67-7.

# Electron-Transfer Photochemistry of Allene–Iminium Salt Systems. Probes of Allene Cation Radical Structure by Theoretical and Chemical Techniques

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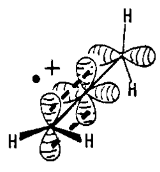
During the past several years the area of electron-transfer photochemistry has received increasingly intense attention owing to the intriguing mechanistic and synthetic features of excited-state reactions initiated by single electron transfer (SET) between donor–acceptor pairs.[2] The reaction pathways promoted by this process are, for the most part, governed by secondary transformations of the initially formed radical ion species which compete with back electron transfer generating donors and acceptors in the ground state. Importantly, the results of photochemical processes initiated in this fashion contain an abundance of useful information about the solution-phase chemistry of ion radical species. Reaction processes promoted in this fashion have the potential for providing knowledge about regiochemical selectivities for nucleophilic and radical attack on delocalized radical cation systems.

Our previous studies with iminium salt systems[2c,3] have taken advantage of this unique feature of electron-transfer photochemistry to explore the solution-phase chemistry of radical cations generated from a variety of n-electron (alcohols, ethers) and $\pi$-electron (olefins, arenes, allylsilanes) donors. Recent efforts have focused on iminium salt–allene photoaddition reactions and have uncovered fundamentally important information about the structure and chemistry of allene-derived, cation radicals.[4]

A simple valence bond analysis of allene cation radicals suggests that several structures are possible for these systems, each having characteristic odd-electron and charge density profiles. The limiting structures are represented by what we shall designate as the linear-0°-twisted, linear-90°-twisted and bent-90°-twisted allene cation radicals, **1**, **2**, and **3**. Estimates of structure vs. energy, charge density, and odd-electron density relationships for these systems were made by using ab initio MO calculations on the parent species, $[C_3H_4]^{+\cdot}$. The results of SCF level (UHF) calculations, employing minimal (STO-3G) and higher level (4-31G) basis sets[5] and the GAMESS program,[6] show that a linear-45°-twisted structure **4** represents the energy minimized geometry of $[C_3H_4]^{+\cdot}$ and that this species has high positive charge density at the central carbon atom and large odd-electron density at the terminal carbons. Importantly, the energy vs. structure results are in accord with those obtained by MINDO/2[7] and MNDO-



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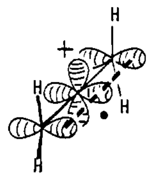

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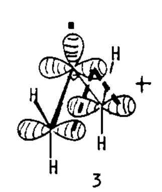

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