Figure 1. Relative energies for the transition-state structures (upper curve) and the product complexes (lower curve), calculated relative to the ground state of the metal atom and free methane. The upper curve corresponds to the addition barrier and a large positive value for ΔE corresponds to a high activation barrier. The lower curve corresponds to the binding energy of the product complex and a large positive value for ΔE corresponds to a strongly endothermic addition reaction, while a negative value for ΔE corresponds to an exothermic addition reaction.

3. For each metal at least two different spin cases have been considered, the atomic ground-state spin and the product ground-state spin (referred to as the low-spin state). The basis sets and methods used are the same as in ref 5. The basis sets are of double-ζ to triple-ζ quality, including f functions on the metal and d functions on carbon. The correlation energy for all the valence electrons was calculated with use of size consistent methods.

The first conclusion about the second-row metals to be drawn from the results in Figure 1 is that the most efficient catalyst for C–H activation should be rhodium, since it has the lowest barrier for the addition reaction and a relatively strongly bound product complex. This conclusion is in agreement with available experimental information for metal complexes.[4] The main reason for the low barrier for rhodium is that both the s^0 ($4d^9$) and s^1 ($4d^8 5s^1$) states are low in energy. A low-lying s^0 state is also important for the occurrence of the precursor complex 1. Palladium is the only metal having a bound precursor complex on the atomic ground-state potential surface. Rhodium and ruthenium have bound precursor complexes on the low spin surfaces.

The barrier for the reaction between methane and the transition-metal atoms is a result of a crossing between two surfaces. Before the barrier the C–H bond starts to break and methane prepares for the bonding toward the metal. In this region the interaction between methane and the metal atom is essentially repulsive and the metal adopts the state that is least repulsive. For the atoms to the right with more or equal to five (s + d) electrons the least repulsive state is s^0 whereas for the atoms to the left it is the s^1 state, since for these atoms the lowest s^0 state has the wrong spin. After the barrier the two bonds are formed and for most of the atoms the s^1 state dominates in this region. For the atoms to the left there are significant contributions to the bonding from $s^1 p^1$ states and to the right s^0 states contribute. The barrier height for the addition reaction is thus reduced both by strong bond formation to the s^1 state in the product region and by a low repulsion to the s^0 state in the entrance region. Both these factors influence the position of the crossing point between the two surfaces.

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Two effects dominate the variation of the binding energies, the promotion energy to the bonding s^1 state and the loss of exchange energy upon bond formation.[6] If the promotion energy and the loss of exchange energy are subtracted from the ΔE values given in Figure 1, similar values are obtained for all the metals. The lowest elimination barrier is found for palladium, which is a consequence of the unstable product complex in combination with a rather low energy of the transition state.

More details will be published in a separate paper where also the reactions of the second-row transition-metal cations will be discussed.

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Reaction of O(^{3}P) with Cyclohexane Clusters. Hint for the Mechanism in the Liquid Phase

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Investigations of gas-phase processes are commonly used to gain microscopic insight on the corresponding liquid-phase reactions.[1] However, there are reactions for which it is known that the products of the gas-phase reaction differ from those in the condensed medium. One such case is the reaction of O(^{3}P) with saturated hydrocarbons. In the gas phase, a rotationally cold OH[2,3] and a free radical are obtained (RH + O(^{3}P) → R + OH), indicating a collinear abstraction mechanism.[4] In the condensed phase, alcohols are formed (RH + O(^{3}P) → ROH), suggesting biradical recombination in a solvent cage.[5] However, this is not generally compatible with the high retention of configuration observed in chiral carbons.

In the present crossed molecular beam study of the reaction of cyclohexane with O(^{3}P), clusters as small as dimers yield the same product as the liquid, namely cyclohexanol. This suggests that the alcohol is formed through insertion rather than biradical recombination.

An O(^{3}P) atomic beam is produced by microwave discharge in a continuous flow of O$_2$. It collides with a beam of cyclohexane seeded in various inert gases, which is expanded through a 0.5 mm diameter pulsed nozzle. The molecules cool by the adiabatic expansion and form dimers and larger clusters, depending on the expansion conditions. At the beginning and at the end of the pulse, the molecules expand through an effectively smaller nozzle, and therefore fewer clusters are formed.

The production of OH radicals from monomers and clusters is monitored by laser-induced fluorescence (LIF). The density of the OH (K = 1) is shown in Figure 1 as a function of the time delay between the nozzle and laser pulses, for (A) 100 Torr of cyclohexane seeded in 2.4 atm He and (B) 100 Torr of neat cyclohexane, where cooling is low and clusters are not formed. The dip in the center of Figure 1A indicates that clusters reduce the formation of OH.

The other components of the seeded molecular beam were monitored by a quadrupole mass spectrometer collinear with the

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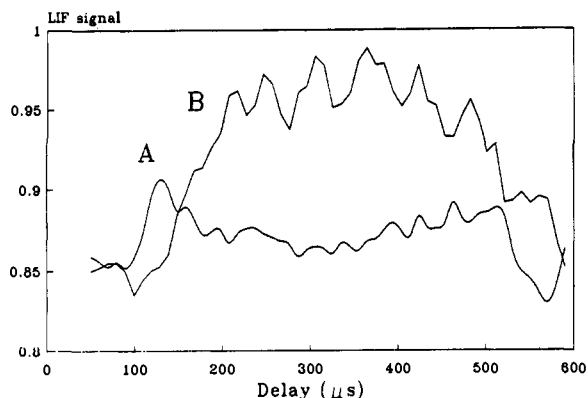(5) Zadok, E.; Mazur, Y. J. Org. Chem. 1982, 47, 2223.

Figure 1. The LIF signal from the OH product at two expansion conditions: 100 Torr of cyclohexane seeded with 2.4 atm of He (A) and 100 Torr neat cyclohexane (B).
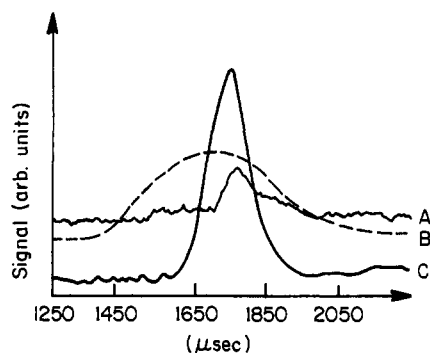

Figure 2. The time of arrival signal at the mass spectrometer when it is set to probe the cyclohexanol (A), the cyclohexane monomers (B), and the dimers (C). Curves A and C were taken with a sensitivity one-hundred times larger than that used for curve B.

molecular beam. Figure 2A shows the signal for mass 82, the strongest peak in the $C_6H_{11}OH$ mass spectrum. It was obtained by averaging over 200 nozzle pulses, with and without the oxygen beam, and taking the difference. For comparison we present the signal of the cyclohexane monomers (curve B) and dimers (curve C). Neither $(C_6H_{12})_2$ nor $C_6H_{11}OH$ was observed in the neat cyclohexane beam. The data indicate that the alcohol is produced from dimers and larger clusters but not from the monomers. The following considerations suggest that this reaction does not occur on the triplet potential energy surface, but proceeds via the singlet surface due to intersystem crossing in the entrance channel.

The reaction of $O(^3P)$ with the monomer has a barrier of 4.5 kcal/mol,[2] while the mean collision energy in our experiment did not exceed 2 kcal/mol. Therefore, the reaction was fed only by the upper edge of the collision energy distribution. When a saturated hydrocarbon looses a hydrogen to become a radical, its three remaining orbitals tend to be coplanar. This is accomplished by a conformational change of the molecule and a corresponding increase, ΔE, in the conformational energy. ΔE is larger in dimers than in monomers because the equilibrium of the intermolecular van der Waals interaction is disturbed. We calculated ΔE, using the empirical force field method with the MM2 program,[6] and obtained 0.7 and 3.2 kcal/mol for monomers and dimers, respectively. This implies a 2.5 kcal/mol increase of the barrier from 4.5 to about 7 kcal/mol, sufficient to block the reaction in the dimers. Due to the high density of states in the dimer and since the direct reaction channel is closed, the collision complex oxygen–cyclohexane dimer can have a long lifetime.

In gas-phase reactions of $O(^1D)$ with hydrocarbons, an efficient intersystem crossing between the singlet and the low-lying triplet potential energy surfaces was suggested.[7] The crossing region

lies farther out in the entrance channel than in the case of $O + H_2$.[8] For low-energy collisions and when a long-lived collision complex is formed, intersystem crossing can take place with probability close to unity.[9,10] The mechanism of low-energy collision-complex formation followed by intersystem crossing is well suited for explaining the reaction of the cyclohexane clusters with $O(^3P)$. Crossing from the triplet to the singlet surface, an insertion instead of abstraction reaction takes place and cyclohexanol is formed. This mechanism is also consistent with the results of liquid cyclohexane studies.

Registry No. H_2, 1333-74-0; O, 17778-80-2; OH, 3352-57-6; cyclohexane, 110-82-7; cyclohexanol, 108-93-0; cyclohexyl radical, 3170-58-9.

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Synthesis and Characterization of the $[Ni_4Se_4(Se_3)_5(Se_4)]^{4-}$ Anion, a Ni^{IV} Cubane Species

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The chemistry of soluble metal chalcogenides has afforded some diverse and unusual species, such as $Mo_3S_{13}^{2-}$,[1] $Na_2Fe_{18}S_{30}^{8-}$,[2] $V_2Se_{13}^{2-}$,[3] $In_2(Se_4)_4(Se)_5^{4-}$,[4] and $NbTe_{10}^{3-}$.[5] The chemistry of the selenides and tellurides frequently differs markedly from that of the sulfides,[6] but the anions $M(Q_4)_2^{2-}$ are now known for all three chalcogens (M = Pd and Hg; Q = S, Se, and Te).[7-9] We recently reported the synthesis, characterization, and some reaction chemistry of the soluble transition-metal selenide ions $M(Se_4)_2^{2-}$, M = Ni, Pd, Pt, Zn, Cd, Hg, and Mn.[8a] Further investigation into the chemistry of the soluble chalcogenides of the nickel triad has uncovered a remarkable Ni^{IV} cubane complex: $[NEt_4]_4$-$[Ni_4Se_4(Se_3)_5(Se_4)] \cdot NEt_4Cl$. The anion (Figure 1) possesses a Ni_4Se_4 cubane core and has five Se_3^{2-} chains and one Se_4^{2-} chain bridging the cubane faces between the Ni^{IV} atoms.

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