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# Theoretical Study of the Reaction of Yttrium with Formaldehyde

**Craig A. Bayse***

*Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, Virginia 23529*

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This work describes single-(DFT, CCSD(T)) and multireference (CASSCF, CASPT2) theoretical calculations on the reaction of yttrium atoms with formaldehyde studied recently in crossed molecular beam experiments. The reaction is shown to proceed through the exothermic formation of a side-bound $\pi$-complex followed by C−H insertions which branch out to competing pathways to products. Dihydridoyttrium(II) is formed through the decomposition of the double insertion product, whereas carbonylyttrium(0) and high-energy formylyttrium(I) result from the single insertion intermediate. The product and transition state energetics are consistent with experimental results and allow one to rule out the direct reductive elimination pathway for the formation of carbonylyttrium(0).

## 1. Introduction

Recent studies of the reaction of metal atoms with organic molecules in crossed molecular beams (CMBs) have given an increased understanding of how transition metals insert into C−H and C−C bonds and have the potential to shed new light on catalytic mechanisms.,[1−3] Within these studies, reaction pathways can be opened or closed by varying the collision energy ($E_{\mathrm{coll}}$), thus allowing examination of the finer details of competing mechanisms. Stauffer, et al. examined the reaction of bare yttrium atoms with formaldehyde in CMBs at varying collision energies; their products were indicative of several competing pathways following initial C−H insertion.[1] At low $E_{\mathrm{coll}}$ ($\leq$21 kcal/mol), only carbonylyttrium(0) **J** and dihydridoyttrium(II) **K** were observed, whereas higher $E_{\mathrm{coll}}$ ($>$ 31 kcal/mol) also produced a formylyttrium(I) complex. The suggested mechanism for the reaction involves initial formation of a $Y-H_2CO$ complex **B** followed by two C−H insertions to carbonyldihydridoyttrium(II) **F**. The two major products are produced through the decomposition of **F** by two competing pathways: loss of carbonyl (to **K**) and loss of dihydrogen (to **J**). Although the former is expected to be barrierless, the latter should have some barrier to reductive elimination. Formation of formylyttrium(I) **L** is expected to occur through loss of hydrogen from HYHCO.

Through consideration of the electron deficiency of the metal and the character of its lone pairs, we can expect that symmetric reductive elimination of $H_2$ from **F** would have a significantly higher barrier than for other similar metal complexes. The ground state of Y is $s^2d^1$, likewise, the product YCO has $\sigma^2\pi^1$ character. However, direct symmetric reductive elimination of hydrogen from $Y(H)_2CO$ **F** would be expected to produce YCO with $\pi^3$ character due to the correlation of the asymmetric Y−H bonding orbital in the reactant and a $d_\pi$ orbital in YCO. Therefore, the reaction is "forbidden" by symmetry and should have a high barrier.[5] However, this result is inconsistent with the experimental results as no YCO would be observed. Fortunately, work on various metal and metal ion reactions with organic molecules provides an answer to this problem.[3,5,6] For example, calculations on Y reacting with ethene[6b] show a lower-lying asymmetric transition state consistent with concerted C−H insertion and H−H bond formation from the metal vinyl hydride to produce a weakly bound $\eta^2$-dihydrogen complex. This transition state lies ∼22 kcal/mol below the "forbidden" symmetric one and gives much more reasonable RRKM rates.

Supplemental theoretical studies can provide valuable structural information for intermediate steps in the reaction to further elucidate the similarities between the "model" CMB studies and true catalytic systems. Various studies at the HF, MCPF and PCI-80 levels have provided much detail of the reactions of metal atoms with various small organic compounds.[5a−g] More recent studies have shown the success of DFT as a method for modeling these simple reactions.[5h,6] In this study, we map out the reaction pathway of yttrium and formaldehyde using the B3LYP hybrid density functional method. As the energetics of this method can be unreliable, coupled cluster (CCSD(T)) energies have been calculated to provide an accurate picture of the transition barriers. We also examine the question of the elimination of $H_2$. Multireference calculations place the symmetric transition state too high in energy, but an asymmetric transition state is found with more reasonable energetics.

## 2. Theoretical Section

Most calculations were performed in two basis sets using the Gaussian 98 software package.[7] BSI uses the Dunning cc-pVDZ basis sets[8] on carbon, hydrogen and oxygen and the relativistic ECP (EC−RECP) basis[9] of Lajohn, et al. on yttrium (5s5p4d)/[3s3p3d]. The metal basis set includes the improved (n+1)p coefficients due to Couty and Hall.[10] BSII uses the Dunning cc-pVTZ basis[11] on carbon, hydrogen and oxygen minus the f polarization functions on the heavy atoms and the d polarization functions on hydrogen. The metal is represented in BSII by the EC−RECP basis set uncontracted slightly for additional flexibility. Even-tempered diffuse s, p, and d functions and a set of STO-3G f-type polarization functions[12] contracted 21 are also added to the metal for a final representation of (6s6p5d3f)/[5s5p5d2f]. Geometries were optimized using unrestricted B3LYP[13] Kohn−Sham[14] orbitals. Vibrational frequencies and zero point energy (ZPE) corrections were calculated in BSI. Energies were recalculated from the B3LYP/BSII level at the couple cluster level (CCSD(T)).[15] Complete active space

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* To whom correspondence should be addressed. E-mail: cbayse@odu.edu

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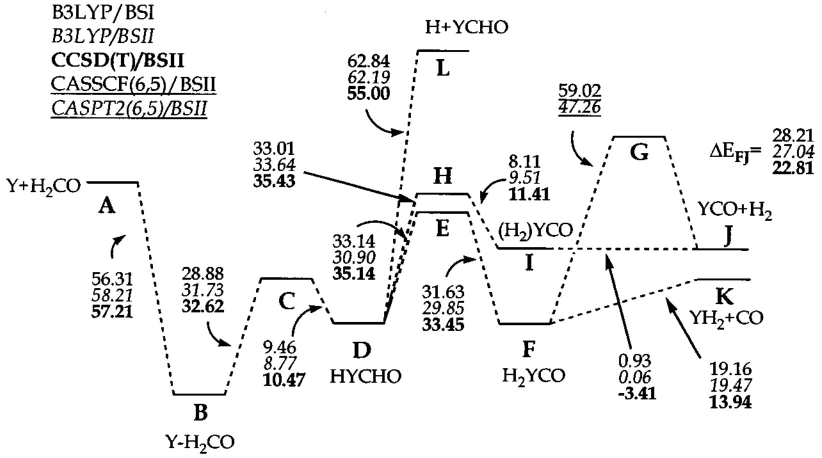

**Figure 1.** Reaction pathway for yttrium and formaldehyde calculated at various levels of theory. All energies are corrected for ZPE.

**TABLE 1: Energies of B through L Relative to Reactants Y + Formaldehyde**

| | B3LYP/BSI | B3LYP/BSII | CCSD(T)/BSII |
|---|---|---|---|
| B | −56.31 | −58.21 | −57.21 |
| C | −31.16 | −30.21 | −28.33 |
| D | −41.10 | −39.46 | −39.29 |
| E | −10.55 | −11.15 | −6.74 |
| F | −43.49 | −42.31 | −41.50 |
| G | 16.71[a] | 5.76[b] | |
| H | −8.09 | −5.82 | −3.86 |
| I | −16.20 | −15.34 | −15.27 |
| J | −15.27 | −15.27 | −18.69 |
| K | −24.33 | −22.85 | −27.56 |
| L | 24.74 | 22.73 | 15.71 |

[a] CASSCF(6,5)/BSII [b] CASPT2(6,5)/BSII//CASSCF(6,5)/BSII

(CASSCF[16] and CASPT2[17]) calculations were performed using the GAMESS−UK package.[18]

## 3. Results and Discussion

The reaction pathway labeled with relative energies is shown in Figure 1. The energies relative to the reaction asymptote are listed in Table 1. Energetic data within the text are generally CCSD(T)/BSII//B3LYP/BSII values with ZPE correction. In most cases, the unprojected spin contamination is minimal; the majority of species are well-described by doublet Kohn−Sham orbitals, although the yttrium atom and YCO have slight spin contamination ($S^2 \approx 0.8$). Selected structural features of minima and transition states are located in Figure 2. Geometric data within the text refers to the results of B3LYP/BSII calculations unless otherwise specified.

The initial association of yttrium and formaldehyde is very exothermic at all levels of theory (57−59 kcal/mol, Figure 1). The product is the expected $\pi$-complex **B** with the aldehyde bound side-on to the metal. The structural and charge data is such that the species could be considered a "metallepoxide" where the metal replaces one carbon of an epoxide. The C−O bond distance is stretched by ~0.24 Å over free formaldehyde suggesting a single C−O bond, and the Y−C bond is shorter than the Y−O bond. The hydrogens bend back away from the metal and are almost coplanar with the metal and carbon. Mulliken population analysis (Table 2) shows that charge is transferred from the yttrium atom (BSI: 0.55e; BSII: 0.63e) to the oxygen (BSI: −0.48e; BSII: −0.53e). The $^2A''$ state of this complex lies 28.3 kcal/mol (B3LYP/BSI) above this $^2A'$ state. This higher energy complex may correlate better with the Y ground state.

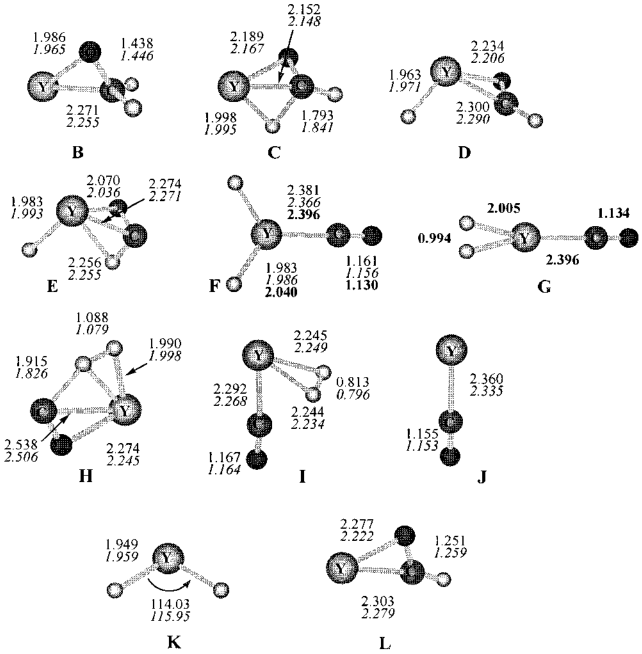

**Figure 2.** Selected geometric parameters for intermediates and transition states for the reaction of yttrium and formaldehyde. Bond lengths are given in Ångstroms.

**TABLE 2: Mulliken Charges and Populations for Y + Formaldehyde Intermediates and Products**

| | $q_Y$ | $q_C$ | $q_O$ | $q_H$ | $q_{H'}$ | (n+1)s | nd | (n+1)p |
|---|---|---|---|---|---|---|---|---|
| B | 0.55 | −0.13 | −0.48 | 0.03 | 0.03 | 0.980 | 1.211 | 0.254 |
| | 0.63 | −0.35 | −0.53 | 0.12 | 0.12 | 0.955 | 1.162 | 0.212 |
| C | 0.51 | −0.05 | −0.33 | −0.16 | 0.04 | 0.849 | 1.353 | 0.291 |
| | 0.67 | −0.10 | −0.45 | −0.25 | 0.13 | 0.810 | 1.279 | 0.219 |
| D | 0.55 | −0.09 | −0.27 | −0.23 | 0.04 | 0.829 | 1.237 | 0.383 |
| | 0.72 | −0.14 | −0.38 | −0.32 | 0.13 | 0.822 | 1.055 | 0.370 |
| E | 0.72 | −0.19 | −0.40 | −0.21 | 0.07 | 0.522 | 1.445 | 0.311 |
| | 0.96 | −0.25 | −0.48 | −0.32 | 0.08 | 0.443 | 1.334 | 0.209 |
| F | 0.71 | −0.21 | −0.03 | −0.24 | −0.24 | 0.508 | 1.338 | 0.444 |
| | 0.99 | −0.18 | −0.15 | −0.33 | −0.33 | 0.452 | 1.203 | 0.287 |
| H | 0.41 | −0.11 | −0.19 | −0.13 | 0.02 | 0.797 | 1.470 | 0.322 |
| | 0.59 | −0.05 | −0.34 | −0.21 | 0.08 | 0.796 | 1.349 | 0.251 |
| I | 0.18 | −0.16 | −0.06 | −0.01 | 0.08 | 1.228 | 1.347 | 0.245 |
| | 0.36 | −0.16 | −0.20 | −0.07 | 0.07 | 1.146 | 1.308 | 0.163 |
| J | 0.17 | −0.16 | −0.01 | | | 1.654 | 1.030 | 0.145 |

Following initial complexation, the metal of the $\pi$-complex **B** inserts into one of the C−H bonds with a barrier of 32.62 kcal/mol. To form the C−H insertion transition state **C**, the complexed formaldehyde must twist by 90°, while retaining its side-on coordination. The C−H bond distance is stretched to 1.841 Å (BSI: 1.793 Å) at the transition state, whereas the Y−H distance decreases to 1.99 Å. The Y−C distance decreases slightly due to the formation of a covalent bond, but the increased number of bonds to the metal decreases the interaction between yttrium and oxygen (d(Y−O) increases by 0.2 Å). The Mulliken charge on the newly forming hydride ligand increases from 0.03 in **B** to −0.16 in the transition state **C**. The geometry of **C** shows many similarities to its counterpart in the Y-ethene pathway. In the first C−H insertion of Y into ethene, the Y−C bond of the α-carbon shortens by 0.1 Å, whereas the $\beta$-carbon Y−C bond lengthens by 0.15 Å. Similarly, here the Y−C bond shortens, whereas the Y−O bond lengthens. The Y−H distances are also similar at the transition state: 2.0 Å (Y−$H_2$CO) versus 1.95 Å (Y-ethene). However, the C−H distance in the ethene insertion is shorter by ~0.3 Å indicating a later transition state for the aldehyde insertion. The resulting yttrium formyl hydride intermediate **D** lies roughly 11 kcal/mol below transition state **C**. The side-bound formyl complex is similar to the formyl and acyl complexes of zirconium,[19] ruthenium,[20] and thorium.[21] The hydride ligand in the structure **D** shown in Figure 2 makes a 101.6 angle (BSII) with the carbon atom, but the hydride can swing around the metal for similar energy conformations.

From intermediate **D**, the metal can insert either into the other C−H bond to form the yttrium carbonyl dihydride **F** ($\Delta E_{\mathbf{DF}}$ = −1.80 kcal/mol) or the complex can lose an H atom to form formylyttrium(I) **L** ($\Delta E_{\mathbf{DL}}$ = 55.00 kcal/mol). Due to the large endothermicity of H loss, the metal formyl complex is only observed at high collision energies. The singlet formylyttrium(I) complex **L** contains a side-bound ligand with similar bond lengths to the parent. These bond lengths are also similar to those reported at the SCF level,[5c] though the current study shows a slightly shorter Y−C distance.

The transition state for the second C−H insertion **E** is slightly higher in energy than the first (35.14 kcal/mol). The structure of the transition state is similar to the geometry of reactant **D** with a much shorter C−H distance (1.166 Å) than transition state **C** indicating an early transition state; however, the nature of this C−H insertion is different from the first insertion. The reaction is presumed to be a hydride shift because the metal in **D** is too electron-deficient ($d^1$) to undego oxidative addition. Several transition states are possible for this reaction step, but all are essentially equal in energy due to the fluxional nature of the hydride. Carbonyldihydridoyttrium(II) **F** lies 33.45 kcal/mol below the second insertion barrier. This $^2A_1$ complex has an carbon-bound carbonyl and an unpaired electron localized in a metal sd orbital. The hydrides are very hydridic and are bound through a mixture of s, p, and d orbitals (Table 2).[22] The Y−H bond distances are slightly longer than those found in $YH_2$ due to the $\pi$-accepting quality of the carbonyl. A side-bound isomer also exists, but is 24.5 kcal/mol higher than the carbon-bound species.

The decomposition of the dihydride **F** proceeds by two different mechanisms: reductive elimination of $H_2$ (to YCO **J**) and loss of the carbonyl (to $YH_2$ **K**). Each of these reactions are endothermic from **F** by 22.81 and 13.94 kcal/mol, respectively. The exothermicities of these products relative to the original reactants **A** (B3LYP/BSII −15.27 and −22.85 kcal/mol, respectively) are consistent in ordering with previous results (−12 and −21 kcal/mol, respectively).[2,5c,5d] The loss of carbonyl is expected to be barrierless, whereas the elimination of $H_2$ should have some barrier.

Modeling the reductive elimination of $H_2$ poses a more complicated theoretical problem than the typical DFT calculation. The metal-hydride bonding in **F** occurs through an a′ and an a″ orbital (reduced from $a_1$ and $b_2$ in $C_{2v}$); the unpaired electron is located in a $\pi$-type orbital. In a direct reductive elimination, the a′ orbital correlates to a purely $H_2$ $\sigma$ orbital and the a” orbital to a metal $d_\pi$ orbital. However, as the ground state of YCO is $\sigma^2\pi^1$, a pair of electrons must move from the a″ orbital to a $\sigma$-type orbital on Y. As a result, we would expect the reaction to be thermally “forbidden” and have a high transition state (Figure 3).[4] Multireference methods are required to model this process. The potential energy surface for reductive elimination was mapped in $C_s$ symmetry by plotting H−H distance versus Y−H distance using a five-electron in six orbital CASSCF wave function (CASSCF(6,5)/BSII) using GAMESS−UK. A recent study by Minaev discusses forbidden reaction in terms of the coupling of singlet-coupled excited-state triplets to the ground-state singlet.[23] This simplified VB approach is included in the CASSCF calculations presented here. The active space included the two Y−H bonding orbitals, the singly occupied $\pi$-type orbital, the Y−H antibonding orbitals and the empty Y $d_\sigma$ orbital. The resulting approximate transition state was refined using the partitioned Rational Function Optimization (P−RFO) method.[25] As the H−H distance becomes smaller, the occupation of the a′ $d_\sigma$ orbital increases while the occupation of the a″ Y−H bonding orbital decreases. Post-transition state the Y $d_\sigma$ orbital becomes essentially doubly occupied corresponding to the ground state of YCO. Due to the change in electronic state, the barrier to reductive elimination is very high (59.02 kcal/mol CASSCF(6,5)/BSII, 47.26 kcal/mol CASPT2-(6,5)/CASSCF(6,5)), but similar to the barrier calculated for the reduction elimination of methane from hydridomethylyttrium(II) at the MCPF level (45.6 kcal/mol).[5a] Even though the CASPT2 calculation significantly reduces the barrier, the transition state **G** lies above the reactant asymptote. Unfortunately, although intuition may indicate reductive elimination of $H_2$ from the dihydride carbonyl complex, this is not consistent with the observed products. If the theoretical barrier is correct, no YCO should be observed in the experiment at low $E_{\text{coll}}$. A possible solution is the asymmetric transition state shown by many other researchers.[3,5h,6]

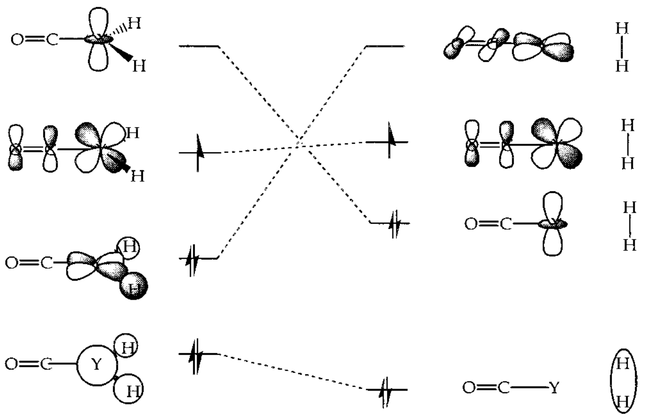

**Figure 3.** Orbital correlation diagram for the symmetric reductive elimination of hydrogen from $H_2$YCO.

If, during the second C−H insertion, the hydride ligand is close enough to interact with the formyl hydrogen, the proton is transferred to the hydride rather than to the metal to form the weakly bound carbonyl($\eta^2$-dihydrogen)yttrium(0) **I**. The transition state was found using the P−RFO method found in GAMESS−UK and is very similar to Poremski and Weisshaar’s multicenter transition state in the reaction pathway for yttrium and ethene.[6] The transition state **H** lies at a point where the C−H distance has been extended to 1.83 Å compared to 1.68

Å in the ethene system. The Y−C bond in **H** appears to have broken slightly with a 2.5 Å bond length, but this may not be significant considering the increased distance in the equivalent Y-ethene transition state. The H−H distance is 0.1 Å larger in the aldehyde system compared to that of the ethene. The dihydrogen complex **I** is also similar to its counterpart in the Y-ethene pathway. Unlike the ethene complex, the carbonyl reverts to the $\eta^1$ carbon-bound conformation; but, both complexes have dihydrogen ligands which are only slightly stretched over free $H_2$ (Figure 2). This result is not surprising considering that the $\pi$-type electron is located an orbital perpendicular to the dihydrogen. As a result, no $d \rightarrow \sigma^*$ back-donation can occur.

Not surprisingly, as the bonding of the $H_2$ occurs only through the primary $M \leftarrow \sigma$ interaction, the $H_2$ is weakly bound is these systems. By comparison, the loss of $H_2$ in cationic complexes of first row metal ions is much more endothermic, due to the ionic character of the system. As a result, loss of $H_2$ and organic fragments can compete from the ($\eta^2$-alkene)($\eta^2$-dihydrogen)-metal cation. This competition is not possible in the neutral yttrium reactions with ethene and formaldehyde where the weakly bound dihydrogen complex has a very short lifetime and, thus, these species produce only YCO/Y-ethyne and $H_2$ by this pathway. Therefore, the second C−H insertion pathway (**D**→**F**) must be the origin of the dihydridoyttium(II) **K** and carbon monoxide products.

## 4. Conclusions

The above theoretical calculations provide mechanistic details of the reaction of yttrium and formaldehyde. After initial formation of the $\eta^2$-aldehyde complex, the metal inserts into the first C−H bond. From this formylhydridoyttrium(II) intermediate, the reaction pathway forks in three directions each of which provides one of the observed products. Of these three pathways, two lie below the reactant asymptote. The lowest of these pathways is the second C−H insertion. This pathway provides the $YH_2$, the apparent major product in the CMB study. Loss of dihydrogen is theoretically possible through this pathway; but, in practice, as the barrier for reductive elimination lies many kcal/mol above the reactant asymptote, YCO is not obtained by this pathway except at high $E_{coll}$. Carbonylyttrium(0) is produced by the second pathway which is nearly equal in energy to the first path. Its weakly bound carbonyl($\eta^2$-hydrogen)yttrium(0) **I** precursor results from an asymmetric multicenter transition state similar to those seen for many other reactions of hydrocarbons with metals and metal ions.[3,5h,6] The last product, formylyttrium(I) **L** results from the high-energy pathway corresponding to the homolytic cleavage of an Y−H bond. The results of these calculations are in agreement with RRKM studies.[25]

At present, theoretical studies are also being performed on similar pathways for other metals and organic carbonyl complexes. These studies will shed light on the mechanisms of these more complicated systems. For example, the addition of a methyl group in the reaction of yttrium and acetaldehyde opens several new pathways corresponding to C−H insertion to the methyl group and C−C bond cleavage.

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