Dynamics of Y+H_2CO reactions

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The reactions of ground state yttrium atoms (Y) with formaldehyde (H_2CO) have been studied in crossed molecular beams as a function of collision energy (E_{coll}). The potential energy barrier for C–H insertion is found to lie below 12 kcal/mol. It is proposed that the reaction is initiated by C–H insertion, producing HYCHO followed by H atom migration forming H_2YCO. Although Y–CO bond fission leading to YH_2+CO is dominant, a secondary minor channel also leads to the production of YCO+H_2. Formation of YCHO+H is not observed at 16 kcal/mol, but is clearly seen at 31 kcal/mol, indicating that D_0(Y–CHO) lies between 58 and 73 kcal/mol. © *1999 American Institute of Physics.* [S0021-9606(99)01748-1]

I. INTRODUCTION

Because of its importance to homogeneous catalysis, there is considerable interest in better understanding the factors controlling the insertion of unsaturated transition metal centers into the C–H and C–C bonds of hydrocarbons.[1] An important long-term goal is to better design catalysts able to more selectively convert simple saturated hydrocarbons into more useful forms. This goal requires applied and basic research, using both experiment and theory. One approach that has been taken in recent *ab initio* quantum chemistry calculations has been to study reactions of many second row neutral *d*-electron species with closely related small molecules.[2–6] Over the past several years, reactions of bare transition metal atoms (M) and covalently-substituted species such as MH_x ($x=1-4$) (Ref. 5) and MCO (Ref. 6) have been systematically studied using a variety of theoretical methods. One conclusion to emerge from this work is that the general trends in reactivity are closely correlated to the electronic structure of the transition metal center.[2–6] Furthermore, the addition of covalent ligands to the metal atom shifts the electronic structure of the metal in a well-defined manner, leading to a systematic increase or decrease in barrier heights for insertion and reaction.[5,6] A number of the theoretical studies have led to quantitative predictions thought to approach chemical accuracies. However, because relatively few experimental studies have been carried out on the neutral systems,[3,4] it is difficult to critically evaluate the quantitative aspects of the theoretical predictions.

Using the crossed molecular beams method, we have recently studied the dynamics of several second row neutral transition metal atom reactions with alkanes, alkenes, and alkynes.[7–11] We now turn to the reaction involving the simplest carbonyl-containing molecule, formaldehyde, with the simplest second row transition metal atom, yttrium. The presence of the carbonyl group introduces several new and interesting features not seen in the previous studies. For example, the C–H bond dissociation energy in formaldehyde is 89 kcal/mol, substantially smaller than that in saturated hydrocarbons like ethane (105 kcal/mol) or unsaturated hydrocarbons like ethylene (111 kcal/mol) and acetylene (133 kcal/mol).[12] However, as in the reactions of transition metal atoms with ethylene[4,9] and acetylene,[10] the π-electron system of the carbonyl group may facilitate initial formation of an association complex prior to insertion (Fig. 1). Possible chemical products following C–H insertion include the transition metal dihydride[13,14] (YH_2), the monocarbonyl[15] (YCO), as well as the metal-formyl complex YCHO.[15] Although all are important benchmark systems, the dynamics of reactions leading to these products have not been studied previously.

II. EXPERIMENT

The rotatable source crossed molecular beams apparatus consists of a source assembly facilitating production of two supersonic molecular beams crossing at right angles in a separately-pumped vacuum chamber held below 1×10^{-6} Torr with the beams running.[8] The transition metal atomic beam, produced by laser vaporization and entrained in a carrier gas, was crossed at 90° with a beam containing 8% H_2CO in He or H_2. In a previous paper, fluorescence excitation spectroscopy indicated that the Y beam produced in our apparatus contains only ground state Y($a\,^2D_{3/2}$) and spin–orbit excited Y($a\,^2D_{5/2}$) lying at $E=1.5$ kcal/mol.[10] No evidence for higher-lying electronically excited state atoms was observed.[10] The H_2CO beam was produced by heating paraformaldehyde powder (Aldrich) to 98 °C in a glass reservoir pressurized to 1 atm with a carrier gas. The resulting mixture was sent directly to the piezoelectrically actuated pulsed valve. The velocity distributions of both beams were measured using the time-of-flight method.

Bimolecular collisions occur during a time window determined by the opening of a slotted chopper wheel inserted into the metal beam. Both beams may be rotated together with respect to a triply differentially pumped mass spectrometric detector located ≈25 cm from the interaction region. Chemical products or nonreactively scattered metallic reac-

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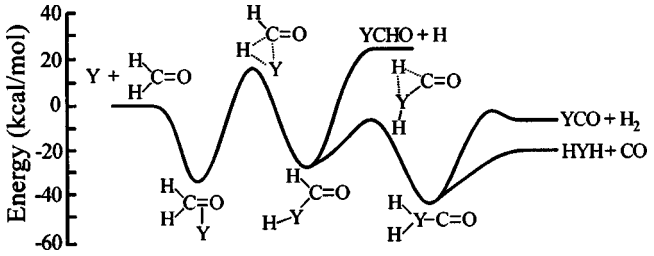

FIG. 1. Schematic energy level diagram for the Y+formaldehyde reaction. Energetics for products are taken from *ab initio* calculations. Depths of local minima are estimated by comparison with other Y+hydrocarbon systems.

tants are ionized at the detector by 157 or 193 nm photoionization using an excimer laser (LPX220i).[8] The single photon ionization potentials of Y atoms and many simple molecules containing Y are believed to lie below the photon energies at 157 nm (7.9 eV) and 193 nm (6.4 eV).[8] By scanning the delay time of the excimer laser relative to time zero for reaction, product time-of-flight (TOF) spectra are measured at various beam-detector laboratory angles. Product laboratory angular distributions are determined by integrating the total (TOF) signal at each laboratory angle. The center-of-mass translational energy distributions $P(E)$, and angular distributions $T(\Theta)$, are determined using an iterative forward convolution method described in detail elsewhere.[7]

III. RESULTS AND DISCUSSION

The Y+H_2CO reaction was studied at collision energies of 12, 16, 21, and 31 kcal/mol. In Fig. 2, the angular distributions for the YH_2 and YCO products at E_{coll} = 21 kcal/mol are shown. The product TOF spectra for the YH_2 channel are illustrated in Fig. 3. Little difference is seen between YH_2 data recorded using 157 and 193 nm photoionization. However, the signal to noise ratio for YCO is found to be improved by approximately a factor of 2 at the lower photon energy. The solid curves (in Figs. 2 and 3) represent the best-fit simulations calculated using the known apparatus

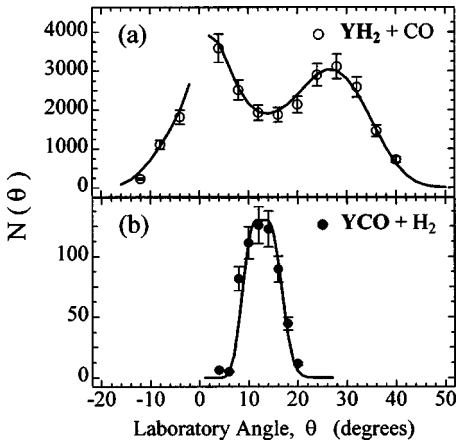

FIG. 2. Laboratory angular distributions for (a) YH_2 and (b) YCO products at E_{coll}=21 kcal/mol. YH_2 angular distribution was recorded using 157 nm photoionization; YCO detection employed using 193 nm photoionization. Solid curves represent simulations using the c.m. distributions in Fig. 4.

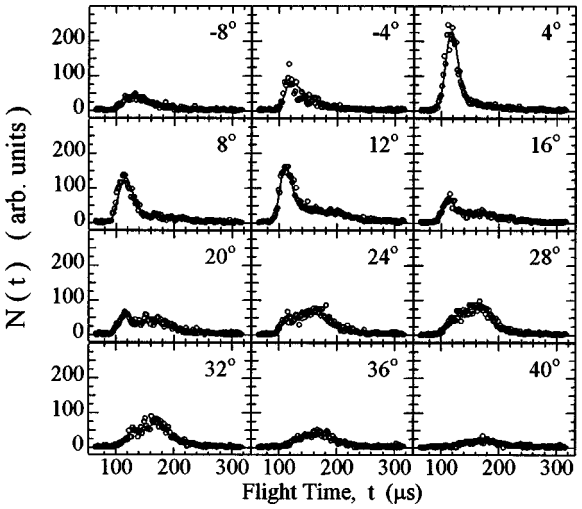

FIG. 3. TOF spectra at indicated laboratory angles for YH_2 products at E_{coll}=21 kcal/mol. The solid line is theoretical simulation using $P(E)$ and $T(\Theta)$ from Fig. 4(a).

functions,[8] as well as the optimized translational energy $P(E)$ and angular distributions $T(\Theta)$, shown in Fig. 4.

Due to linear momentum conservation, the YCO products recoiling from H_2 are constrained to appear over a much smaller angular range than YH_2, enhancing the detection sensitivity for YCO relative to YH_2. Yet, the YH_2 signal is far stronger than that for YCO using both 193 and 157 nm photoionization. By analogy with the M+hydrocarbon systems studied previously in our laboratory,[9,10] both channels result from initial C–H insertion to form HYCHO followed by unimolecular rearrangement, which in this case likely involves a tricoordinate H_2YCO intermediate (Fig. 1). Based on *ab initio* calculations by Siegbahn of the stabilities of YH_2 and YCO,[14,15] formation of YH_2+CO from Y+H_2CO is predicted to be exoergic by 21 kcal/mol, whereas formation of YCO+H_2 should be exoergic by 12 kcal/mol.[16] Simple Y–CO bond fission forming YH_2+CO is likely to proceed with no potential energy barrier in excess of the reaction endoergicity from the H_2YCO intermediate. In contrast, production of YCO+H_2 is not only the less thermodynamically favored process but is expected to involve a potential energy

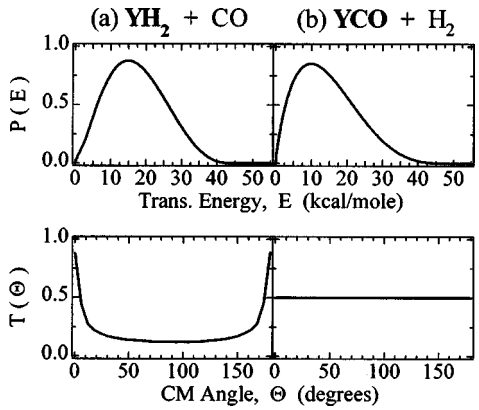

FIG. 4. Translational energy distributions [$P(E)$] and center of mass angular distributions [$T(\Theta)$] for (a) YH_2+CO and (b) YCO+H_2 channels from the Y+H_2CO reaction at E_{coll}=21 kcal/mol.

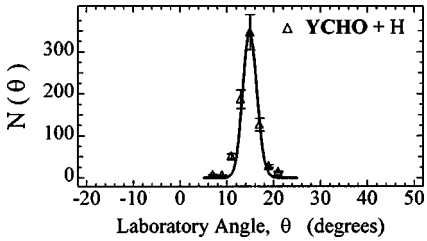

FIG. 5. Laboratory angular distribution for YCHO from the H atom elimination channel at $E_{coll}=31$ kcal/mol.

barrier of at least several kcal/mol (Fig. 1) above the energy of the product asymptote. The origin of the potential energy barrier for H_2 elimination from H_2YCO is best understood by considering the reverse process, insertion of ground state YCO into H_2 (Fig. 1). The ground state electronic configuration of Y is s^2d^1 and the bonding in the ground state YCO molecule primarily involves the *d* electron in Y.[6] Consequently, the ground state of YCO has appreciable ''closed shell'' s^2 character, which leads to a barrier for insertion into H_2. Note that such a barrier would be much smaller or absent for NbCO or ZrCO, both of which have a ground state s^1 character at the metal center.[6]

The broad forward–backward symmetric CM angular distribution $[T(\Theta)]$ for the YH_2+CO channel (Fig. 4) strongly suggests that reaction involves participation of complex intermediates having lifetimes exceeding their picosecond rotational time scales. The CM angular distribution for the YH_2+CO channel peaks very sharply at $\Theta=0°$ and 180°. This is characteristic of a reaction involving a prolate collision complex in which only a small fraction of the total angular momentum, **J**, of the complex is channeled into product rotational excitation. In the case of the $YCO+H_2$ channel, the relatively small reduced mass of the products severely constrains the maximum possible product orbital angular momentum, $\mathbf{L}'$. This results in a larger fraction of total angular momentum appearing in product rotation, leading to an essentially isotropic $T(\Theta)$.

As illustrated in Fig. 5, at a collision energy of 31 kcal/mol, an additional chemical channel, formation of YCHO+H is observed. This signal at $m/e=118$ appears over a very narrow range of laboratory angles near the center of mass of the system (15°). Note that at this collision energy, the $YCO+H_2$ channel is also seen, but the angular distribution for that channel is broader and the signal is considerably weaker. Since the YCO products appear at $m/e=117$, the two channels may be easily distinguished from one another with the mass spectrometer set to a relatively high mass resolution. Fragmentation of YCHO to YCO^+ is found to be minimal at both 157 and 193 nm.

The YCHO+H channel is somewhat analogous to the YCCH+H channel recently observed[10] from $Y+C_2H_2$ collisions, and likely involves simple M–H bond fission in the initially formed C–H insertion intermediate HYCHO. Since the M–H bond fission channel is expected to proceed with essentially no potential energy barrier in excess of the reaction endoergicity, using $D_0(\text{H–HCO})=89$ kcal/mol,[12] the observation of YCHO+H at $E_{coll}=31$ kcal/mol (but not at 16 kcal/mol) indicates that $D_0(\text{Y–CHO})$ likely lies in the range 58–73 kcal/mol.

According to *ab initio* calculations, the formyl isomer, YCHO, is bound by 68 kcal/mol relative to Y+HCO.[15] This isomer has been calculated[15] to be more stable than the ''insertion isomer'' HYCO by 13 kcal/mol, suggesting that the isomer seen in our experiment is YCHO. It is interesting to note that in the case of Nb, the calculated relative stabilities for the two isomers are reversed, with formation of HNbCO from Nb+HCO exoergic by 70.4 kcal/mol, and production of NbCHO exoergic by only 60.0 kcal/mol.[15] In recent experiments on $Nb+H_2CO$ carried out in our laboratory, very strong product signal at $m/e=122$, corresponding to an H atom elimination channel, has been observed at a collision energy of 21 kcal/mol. According to the above thermodynamic quantities, the collision energy threshold for formation of HNbCO+H from $Nb+H_2CO$ should be 18.6 kcal/mol, whereas that for NbCHO+H should lie substantially higher, near 29 kcal/mol. Based on these energetics, the species observed in our Nb experiment must be the ''inserted'' complex, HNbCO.

Formation of both YH_2+CO and $YCO+H_2$ requires initial insertion of Y into the C–H bond of H_2CO. The maximum translational energy release at $E_{coll}=21$ kcal/mol (Fig. 4) indicates that both channels are substantially exoergic, in agreement with the theoretical calculations. Our finding that both channels are competitive at 12 kcal/mol indicates that the largest potential energy barrier along the reaction coordinate is smaller than 12 kcal/mol. This largest barrier may be associated with either C–H insertion forming HYCHO or intramolecular H atom migration producing H_2YCO (Fig. 1). Although neither of these barrier heights have been calculated to date, several considerations strongly suggest that the largest barrier is associated with the C–H insertion step, as indicated in Fig. 1. The C–H bond in HCO (formyl) is extremely weak [15 kcal/mol (Ref. 12)], and is likely to be further weakened by donation of σ-electron density into unfilled *d*-orbitals in the metal. Furthermore, recent calculations on barrier heights for C–H insertion and secondary H atom migration reactions for early second row transition metal atoms indicate that the largest barriers are associated with initial C–H insertion.[4] Further experiments are in progress to more precisely determine fundamental quantities such as barrier heights and $D_0(\text{Y–CHO})$. Because of the relative simplicity of $Y+H_2CO$, calculations at high levels of accuracy are feasible and would be interesting to compare with our experimental results.

The bond dissociation energy of YO is 171.6 kcal/mol.[12] Since $D_0(CH_2\text{–}O)=178.8$ kcal/mol,[12] production of $YO+CH_2$ is endoergic by 7.2 kcal/mol. Indeed, we clearly observe this channel at all collision energies studied, including $E_{coll}=12$ kcal/mol. We note that unlike the YH_2+CO and $YCO+H_2$ channels, the formation of $YO+CH_2$ does *not* require C–H bond insertion. Instead, YO production may involve electronic rearrangement within an initially-formed association complex. Unfortunately, interference from nonreactive inelastic scattering of YO present in the metal beam itself has made it difficult to obtain reliable YO angular distributions so far. However, we expect that this impurity can

be substantially reduced, facilitating a more thorough study of the competing $YO+CH_2$ channel in the near future.

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