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Competition between C−C and C−H Activation in Reactions of Neutral Yttrium Atoms with Four Butene Isomers

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The reactions of neutral, ground-state Y (a^2D, s^2d^1) with 1-butene, *cis*-2-butene, *trans*-2-butene, and isobutene were studied using crossed molecular beams. At a collision energy of 26.6 kcal/mol, four processes were observed for reactions with *cis*- and *trans*-2-butene and 1-butene, corresponding to nonreactive scattering of yttrium atoms and formation of $YC_4H_6 + H_2$, $YH_2 + C_4H_6$, and $YCH_2 + C_3H_6$. For the isobutene reaction, all channels but the YH_2 product channel were observed. Experimentally measured product branching ratios indicate that YC_4H_6 formation is always the dominant process. However, for *cis*- and *trans*-2-butene and 1-butene, YH_2 formation is significant. Formation of YCH_2 was minor for all four isomers. At a collision energy of 11.0 kcal/mol, only $YC_4H_6 + H_2$ and nonreactive scattering were observed for all four butene isomers. A common mechanism is proposed for reactions of Y with all four isomers, involving formation of a π-complex, followed by insertion of Y into a methyl C−H bond producing a methyl-substituted H−Y−allyl intermediate, followed by competition among three hydrogen migration processes each leading to a distinct product channel.

I. Introduction

The reactions of neutral ground-state yttrium atoms, Y (a^2D, s^2d^1), with small molecules have been studied fairly extensively, both experimentally and theoretically. These reactions are important because Y is the simplest second-row transition metal atom, possessing only one d electron. Some of the earliest studies focused on reactions with acetylene,[1,2] ethene,[3−6] and ethane,[5,7−9] for which the comparison between experiment and theory led to a good understanding of the potential energy surfaces for the reactions. Subsequently, reactions with larger molecules have been examined. In particular, we have recently reported on the reaction of yttrium atoms with cyclopropane[10,11] and propene,[11] as well as with propyne and 2-butyne.[12] Of these larger molecules, only the reaction of Y with cyclopropane has been studied theoretically.[5,9]

While reactions of Y with acetylene, ethene, and ethane are quite interesting from a dynamics viewpoint, they are mechanistically very simple. In each case, only products resulting from C−H activation were observed. The proposed mechanism involved formation of a π-complex between Y and C_2H_2 or C_2H_4, followed by C−H bond insertion (or direct C−H bond insertion in the case of C_2H_6).[2,4,5] In each case, H migration led to elimination of H_2 (or additionally, $YH_2 + C_2H_4$ in the case of ethane[7]). As described in the previous paper, for the Y + propene reaction, a slightly more complicated mechanism was proposed to explain the experimental observation that C−C activation, producing $YCH_2 + C_2H_4$, was competitive with C−H activation producing $YC_3H_4 + H_2$ and $YH_2 + C_3H_4$.[11] In this study, we expand upon that work by examining the reactions with four isomeric butenes, which are essentially propene molecules with one additional methyl group (Figure 1). On the basis of estimated potential energy barrier heights[5] and thermodynamics (Figure 2),[5,13−16] it is expected that analogous product channels to those observed for propene should be seen for the butenes. Therefore, a comparison between reactions with butene isomers to reactions with propene should allow us to further test the validity of the proposed mechanisms.

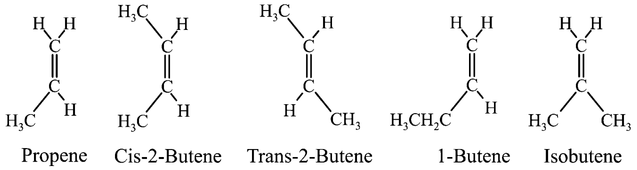

Figure 1. Structures of propene and four butene isomers.

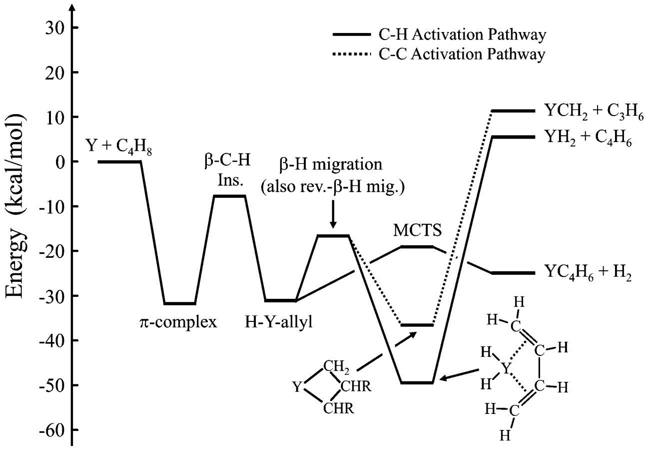

Figure 2. Schematic potential energy diagram for the reaction of ground-state Y (a^2D) with *cis*-2-butene. Energies of stationary points were estimated from calculations on $Y + C_2H_4$.[5] Energies of product asymptotes were calculated from known thermodynamic values and calculated bond dissociation energies.[5,13−16]

II. Experimental Section

The reactions of Y (a^2D) and 1-butene, *cis*- and *trans*-2-butene, and isobutene were studied using a crossed molecular

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TABLE 1: Experimental Conditions for Y + Butene Reactions

Y + Butenes						
E_{coll}[a]	Y carrier gas	Y beam velocity[b]	Y beam fwhm[b]	butene mixture	butene beam velocity[b]	butene beam fwhm[b]
11.0	Ne	1100	150	8% in He	1275	116
26.6	He	2200	370	8% in He	1275	116

[a] Values in kcal/mol. [b] Values in m/s.

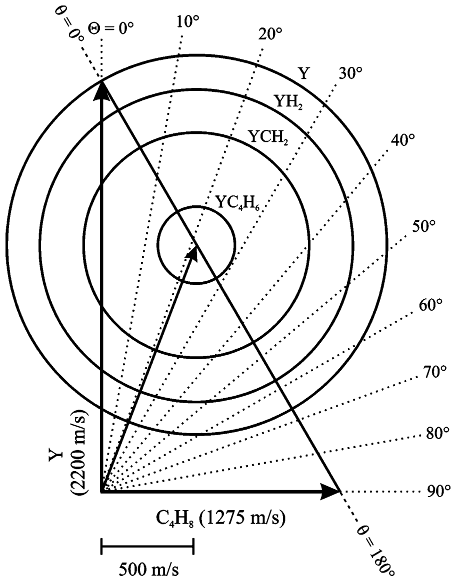

Figure 3. Newton diagram in velocity space for the reaction Y + *cis*-2-butene at E_{coll} = 26.6 kcal/mol. Circles represent the maximum CM velocity constraints on the indicated metal-containing fragment from the various product channels based on reaction thermodynamics as shown in Figure 2 and momentum conservation.

beams apparatus.[17] The atomic Y beam and the molecular C_4H_8 beams were produced using the same methods as described in the previous paper. Relevant parameters for these beams are given in Table 1. All other conditions for the reactions described here, along with the procedures for gathering and fitting the data, were the same as those described previously.[11,17]

III. Results

A. E_{coll} = 26.6 kcal/mol. The reactions of Y with four butene isomers, namely, 1-butene, *cis*-2-butene, *trans*-2-butene, and isobutene, were studied at a collision energy (E_{coll}) of 26.6 kcal/mol. In reactions with 1-butene and *cis*- and *trans*-2-butene, four processes were observed:

$$Y\ (a^2D_J;\ 5s^24d^1) + C_4H_8 \rightarrow YC_4H_6 + H_2 \qquad (1)$$

$$\rightarrow YH_2 + C_4H_6 \qquad (2)$$

$$\rightarrow YCH_2 + C_3H_6 \qquad (3)$$

$$\rightarrow Y + C_4H_8 \qquad (4)$$

Reactions with isobutene led to channels 1, 3, and 4. Time-of-flight (TOF) spectra for all four isomers were similar in appearance, so only data for the Y + *cis*-2-butene reaction will be shown. A Newton diagram for this reaction is shown in Figure 3.[18]

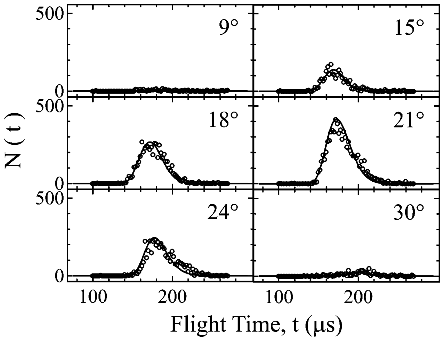

Figure 4. Sample TOF spectra for YC_4H_6 products at indicated lab angles for the Y + *cis*-2-butene reaction at E_{coll} = 26.6 kcal/mol (○). Solid-line fits were generated using CM distributions shown in Figure 8.

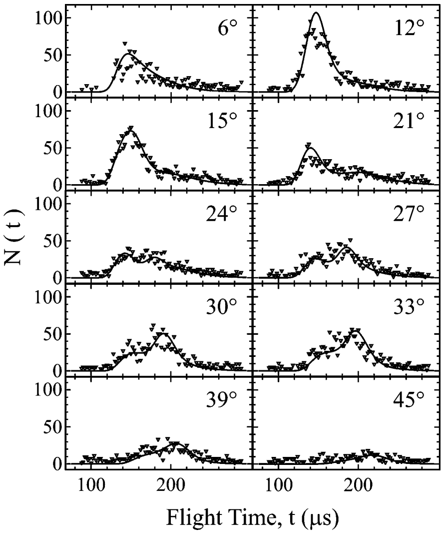

Figure 5. Sample TOF spectra for YH_2 products at indicated lab angles for the Y + *cis*-2-butene reaction at E_{coll} = 26.6 kcal/mol (▼). Solid-line fits were generated using CM distributions shown in Figure 8.

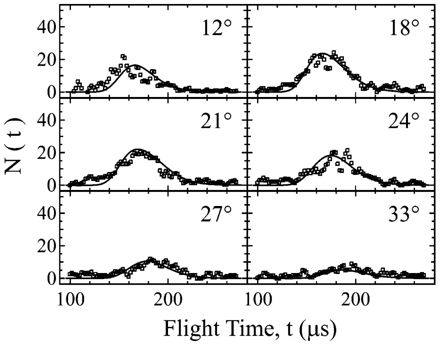

Figure 6. Sample TOF spectra for YCH_2 products at indicated lab angles for the Y + *cis*-2-butene reaction at E_{coll} = 26.6 kcal/mol (□). Solid-line fits were generated using CM distributions shown in Figure 8.

Time-of-flight spectra for formation of YC_4H_6, YH_2, and YCH_2 are shown as open points for indicated lab angles in Figures 4, 5, and 6, respectively. The TOF spectra for YC_4H_6 and YCH_2 exhibited only one peak, while those for YH_2 showed two peaks at some angles. This is expected on the basis of the Newton diagram (Figure 3). The Newton circle for YH_2 is larger than that for YC_4H_6 because of a heavier recoiling partner (C_4H_6 versus H_2) and is larger than that for YCH_2 because YH_2 formation is less endoergic. This can also be seen in the corresponding lab angular distributions, which are shown in the second panel of Figure 7, along with the lab angular distributions for the other three butene isomers. The angular distributions for YH_2 span a much larger range of lab angles than those for YC_4H_6 or YCH_2. Solid-line fits to the data were generated using

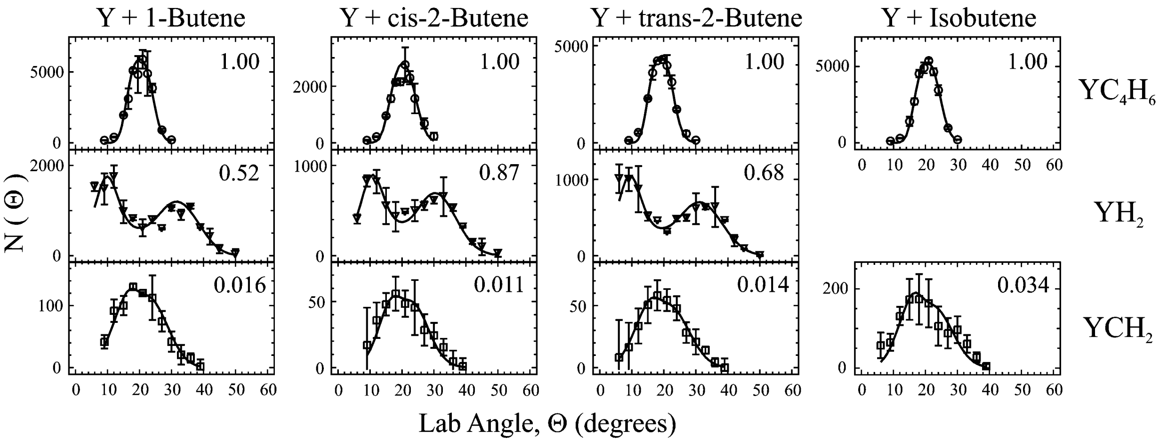

Figure 7. Lab angular distributions for all reactive product channels from the reaction of Y with all four butene isomers at $E_{coll} = 26.6$ kcal/mol. Products are, from top to bottom, YC_4H_6 (○), YH_2 (▽), and YCH_2 (□). Solid-line fits were generated using CM distributions shown in Figure 8. Corresponding product yields are given in upper right corner of each graph. Each distribution is scaled to the same number of scans (two).

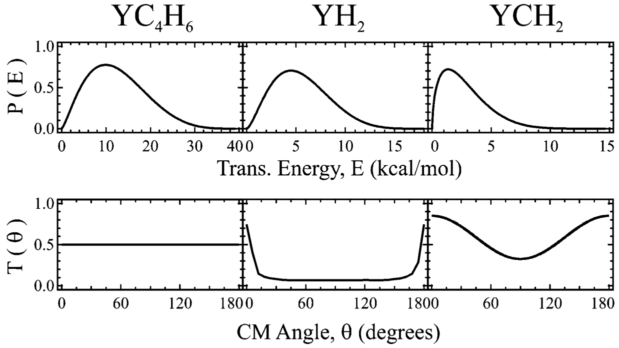

Figure 8. Center-of-mass distributions used to fit the YC_4H_6, YH_2, and YCH_2 data shown in Figures 4, 5, 6, and 7 at $E_{coll} = 26.6$ kcal/mol.

the center-of-mass (CM) distributions shown in Figure 8. Interestingly, the same CM distributions could be used to fit the data for each of the butene isomers. The translational energy distributions for YC_4H_6 and YH_2 were peaked well away from the zero of kinetic energy with $\langle P(E)\rangle = 12.6$ and 5.6 kcal/mol, respectively, while for YCH_2, $\langle P(E)\rangle = 2.8$ kcal/mol. Using the thermodynamics shown in Figure 2 for *cis*-2-butene, one can calculate the average fraction of energy appearing in translation (f_T) for each channel. For YC_4H_6, $f_T = 0.24$, which is typical for reactions of Y involving elimination of H_2. For YCH_2 and YH_2, $f_T = 0.18$ and 0.27, respectively. Similar values were obtained for the other butene isomers. The CM angular distributions were symmetric about $\theta = 90°$ for each product, indicating the presence of at least one long-lived intermediate along the reaction pathway. For YC_4H_6, the CM angular distribution was isotropic, as expected on the basis of angular momentum considerations.[19] The CM angular distributions for YCH_2 and YH_2 were forward−backward peaking with $T(0°)/T(90°) = 2.8$ and 11.0, respectively.

The product branching ratios between formation of YC_4H_6, YCH_2, and YH_2 were measured for each butene isomer. The values obtained were as follows: for 1-butene, $\phi_{YC_4H_6}/\phi_{YH_2}/\phi_{YCH_2} = 1.00{:}0.52{:}0.016$; for *cis*-2-butene, $\phi_{YC_4H_6}/\phi_{YH_2}/\phi_{YCH_2} = 1.00{:}0.87{:}0.011$; for *trans*-2-butene, $\phi_{YC_4H_6}/\phi_{YH_2}/\phi_{YCH_2} = 1.00{:}0.68{:}0.014$; for isobutene, $\phi_{YC_4H_6}/\phi_{YH_2}/\phi_{YCH_2} = 1.00{:}0.00{:}0.034$ (upper right corners of Figure 7 graphs). In determination of these values, Jacobian factors related to the transformations from the lab to the CM reference frame and product fragmentation patterns were explicitly considered. It was assumed, on the basis of experiments in the previous paper, that the 157 nm photoionization cross-sections were the same for each product.

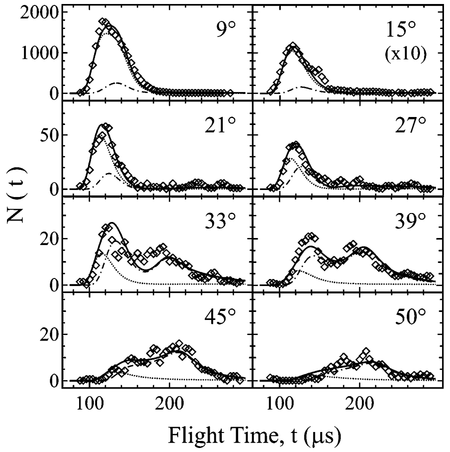

Figure 9. Sample TOF spectra for nonreactively scattered Y atoms at indicated lab angles for the Y + *cis*-2-butene reaction at $E_{coll} = 26.6$ kcal/mol (◇). Solid-line fits are the sum of the dashed-line and dash−dot line contributions generated using CM distributions shown in Figure 10. See text for details.

Time-of-flight spectra for nonreactively scattered Y atoms are shown in Figure 9 for indicated lab angles. The solid-line fits were generated as the sum of two contributions, one corresponding to a direct inelastic scattering process (dashed lines) and one corresponding to decay of long-lived complexes (dash−dot lines). The CM distributions used for each process are shown in Figure 10. The $P(E)$ for inelastic scattering extended to the maximum of the collision energy distribution with $\langle P(E)\rangle = 20.4$ kcal/mol, while that for complex decay peaked at lower kinetic energy with $\langle P(E)\rangle = 11.6$ kcal/mol. Thus the process of complex decay led to greater conversion of incident kinetic energy into internal excitation of the molecular reactant (56%) than did direct inelastic scattering (23%). The CM angular distribution for inelastic scattering was peaked in the forward direction (near $\theta = 0°$), whereas that for complex decay was symmetric about $\theta = 90°$ and forward−backward peaked.

B. $E_{coll} = 11.0$ kcal/mol. Data were also recorded for the reaction of Y with all four butene isomers at a lower collision energy of 11.0 kcal/mol. Time-of-flight spectra were taken at the CM angle for each isomer. For Y + *cis*-2-butene, only YC_4H_6 products were observed. This collision energy corresponded to the thermodynamic threshold for YCH_2 formation and was only slightly above the threshold for the YH_2 channel (Figure 2).

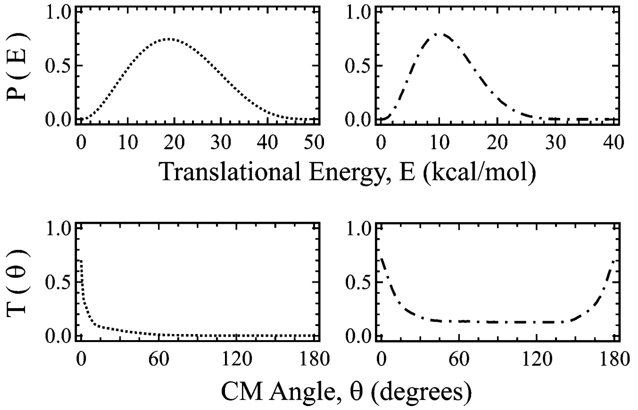

Figure 10. Center-of-mass distributions used to generate the corresponding dashed-line and dash−dot line contributions to the solid-line fits shown in Figure 9 for E_{coll} = 26.6 kcal/mol.

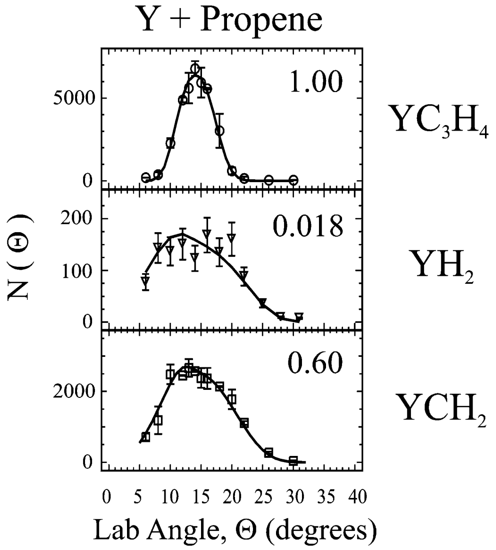

Figure 11. Lab angular distributions for YC_3H_4, YH_2, and YCH_2 products from the Y + propene reaction at E_{coll} = 28.8 kcal/mol.[11] Corresponding product yields are given in upper right corner of each graph. Note that each distribution is scaled to the same number of scans (two).

IV. Discussion

When one looks at the data for the reactions of all four butene isomers (Figure 7), several observations are immediately evident. The first is that the data for all four isomers are quite similar, except that there is no YH_2 from isobutene. Second, the branching ratios for each isomer are similar, except that $\phi_{YCH_2}/\phi_{YC_4H_6}$ is approximately a factor of 2 greater for isobutene than for the other isomers. Finally, for propene, YCH_2 is a much more important channel than is YH_2 (Figure 11), a situation that is exactly the opposite to that for the butene reactions (Figure 7).

In our previous paper on the reactions with cyclopropane and propene, a mechanism was proposed for propene involving initial π-complex formation, followed by β-C−H bond insertion to form an H−Y−allyl intermediate.[11] From this intermediate, there was a competition among three processes (top to bottom in Figure 12a): (1) elimination of molecular hydrogen over a multicentered transition state (MCTS) forming YC_3H_4, (2) β-H migration to form a dihydride intermediate, which subsequently decayed to $YH_2 + C_3H_4$, and (3) reverse β-H migration to form the metallacyclobutane intermediate, which subsequently decayed to give $YCH_2 + C_2H_4$.

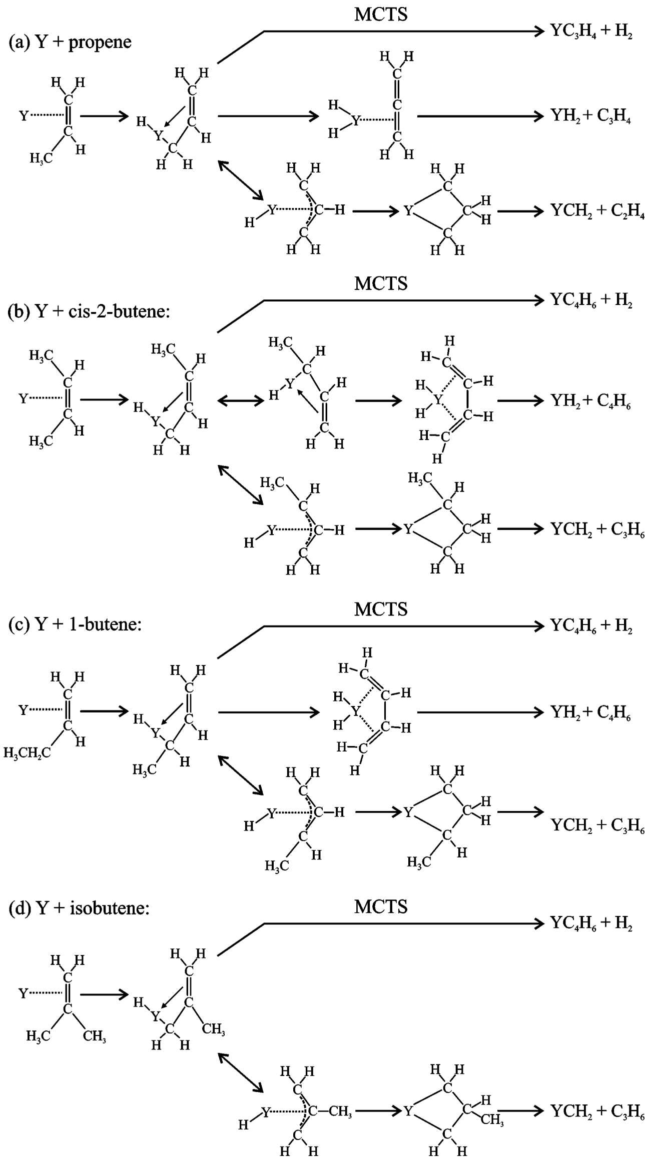

Figure 12. Proposed mechanisms for the reactions: (a) Y + propene; (b) Y + *cis*-2-butene; (c) Y + 1-butene; and (d) Y + isobutene. Note that the mechanism for Y + *trans*-2-butene is similar to that for Y + *cis*-2-butene so is not shown. Double-sided arrows indicate resonance structures. See text for details.

It was noted that the branching ratio for decay of π-complexes to products relative to that for decay back to reactants ($\phi_{reactive}/\phi_{nonreactive}$) was an order of magnitude greater for propene compared to ethene, indicating that insertion of Y into the β-C−H bonds of the methyl group in propene (forming H−Y−allyl) was an important reaction channel that was not available for ethene.[11] The presence of a MCTS along the pathway to YC_3H_4 formation was postulated by analogy to calculations on H_2 elimination from C_2H_4[4] and H_2CO.[20] The step following H−Y−allyl formation on the pathway to formation of YH_2 is an example of intramolecular β-H migration. Such a mechanism is well-known in solution-phase organometallic chemistry, where transition metal alkyl complexes containing β-H atoms have been observed to be kinetically much less stable than those complexes lacking β-H atoms.[21,22] The mechanism for YCH_2 formation involving decomposition of a metallacyclobutane intermediate[23] allowed for C−C activation to occur without direct insertion of the metal atom into a C−C bond. For propene, the availability of a low-energy pathway involving H atom migration for YCH_2 production facilitated effective competition with YC_3H_4 production. The YCH_2 product channel would be expected to be very minor if C−C bond insertion was required because the barrier for that process should be significantly larger than that for C−H insertion.[11]

Owing to the similarity in structures (Figure 1) and the magnitude of $\phi_{reactive}/\phi_{nonreactive}$ for propene and the four butene isomers, we propose mechanisms for the butenes similar to that postulated previously for propene, as shown in Figure 12. The first step is again formation of a π-complex, which should be bound by approximately 30 kcal/mol relative to reactants (Figure 2). Because of this deep well, this complex should be long-lived with respect to its picosecond rotational period, consistent with the observation of wide-angle nonreactive scattering for all four butene isomers (Figures 9 and 10). The next step is β-C−H bond insertion, forming a methyl-substituted H−Y−allyl intermediate that can subsequently decay by the three competing processes described above for propene.

Formation of $YC_4H_6 + H_2$ and $YCH_2 + C_3H_6$ in the butene reactions are similar to those for the analogous products from propene. However, there exists a significant difference between the reaction mechanisms for butene and propene for the β-H migration step on the pathway leading to $YH_2 + C_3H_4$ and $YC_3H_4 + H_2$. For propene, there is only one β-H atom in the H−Y−allyl intermediate available to undergo migration, residing on the central sp^2-hybridized C atom (Figure 12a). For *cis*- and *trans*-2-butene (Figure 12b) and 1-butene (Figure 12c), the extra methyl group presents three β-H atoms attached to an sp^3-hybridized carbon atom. Because $C(sp^3)$−H bond strengths are smaller than those for $C(sp^2)$−H bonds (86.7 kcal/mol for propene versus 109.7 kcal/mol for ethene, respectively[24]), β-H migration for the butenes should be more thermodynamically favorable than that for propene. There is also a statistical advantage for the butenes because there are three β-H atoms available for migration, rather than one. Both of these factors should greatly enhance the rate of β-H migration leading to $YH_2 + C_3H_4$ and $YC_3H_4 + H_2$. These factors, combined with more favorable thermodynamics for YH_2 formation from butene reactions than from propene, should cause YH_2 formation to be very important for the butene reactions. Indeed, the branching ratios for Y + *cis*- and *trans*-2-butene and 1-butene (Figure 7) indicate that the YH_2 yield is much greater than that for YCH_2, exactly opposite to that observed for propene (Figure 11).[25] Further evidence for the importance of β-H migration comes from the Y + isobutene reaction (Figure 12d). In this case, the extra methyl group resides on the central carbon atom, so the methyl-substituted H−Y−allyl intermediate contains no β-H atoms. This is consistent with the lack of YH_2 products from the isobutene reaction (Figure 7).

On the basis of the proposed mechanisms, it is not surprising that formation of YC_4H_6 and YCH_2 from all four butene isomers and formation of YH_2 from *cis*- and *trans*-2-butene and 1-butene look similar because each product channel is the result of competition from similar methyl-substituted H−Y−allyl intermediates. However, the fact that the branching ratio between YC_4H_6 and YCH_2 formation from isobutene was approximately twice that from the other three butene isomers is interesting. This behavior can be understood by examining the final intermediate along the $YCH_2 + C_3H_6$ reaction coordinate, that is, the metallacyclobutane (Figure 12). For propene, there is a 2-fold symmetry in this intermediate, allowing two ways for both a Y−C and a C−C bond to be broken to yield $YCH_2 + C_2H_4$. For Y + isobutene, because the methyl group is on the central carbon, 2-fold symmetry is also present, so there are again two ways to break bonds to form $YCH_2 + C_3H_6$. However, for Y + *cis*- and *trans*-2-butene and 1-butene, the position of the methyl group in the metallacyclobutane intermediate allows for only one way to break bonds to form $YCH_2 + C_3H_6$.[26] The alternative bond fission process leads to formation of a thermodynamically unfavorable radical species rather than a stable alkene. This difference in the position of the methyl group on the metallacyclobutane should inherently decrease the yield of YCH_2 from *cis*- and *trans*-2-butene and 1-butene relative to that from isobutene by a factor of 2, in good accord with experimental observations (Figure 7).

V. Conclusion

The reactions of neutral, ground-state Y atoms with 1-butene, *cis*- and *trans*-2-butene, and isobutene have been studied at two different collision energies. At $E_{coll} = 26.6$ kcal/mol, three product channels were observed in addition to nonreactive scattering for 1-butene and *cis*- and *trans*-2-butene: $YC_4H_6 + H_2$, $YH_2 + C_4H_6$, and $YCH_2 + C_3H_6$. For isobutene, all channels but the YH_2 product channel were observed. Analogous product channels were observed previously for Y + propene at high collision energies. At $E_{coll} = 11.0$ kcal/mol, only $YC_4H_6 + H_2$ was observed, consistent with this collision energy being near threshold for YCH_2 formation and very near threshold for YH_2 formation. A mechanism involving formation of a methyl-substituted H−Y−allyl intermediate, followed by competition among three H atom migration processes each leading to a distinct chemical channel, was proposed. This mechanism is consistent with similarities and differences among reactions of each butene isomer and also with comparisons to the propene reaction studied previously.

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(25) Note that the total product intensity for H_2 elimination was similar for the Y + propene and Y + butene reactions.

(26) Note that formation of $YC_2H_4 + C_2H_4$ from the reactions of Y with *cis*- and *trans*-2-butene and 1-butene was not observed experimentally.