Ab Initio Mechanistic Study of Radical Reactions. Relative Reactivity of Olefinic and Acetylenic Bonds in Addition Reactions

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Abstract: Ab initio molecular orbital calculations on the transition state and barrier height for the addition of atomic hydrogen to ethylene are carried out. The higher reactivity of olefinic compared to acetylenic bonds toward free radicals is examined in terms of chemically interpretable contributions.

Radical additions to molecules containing multiple bonds are among the most important processes in a variety of free-radical chain reactions. Although these reactions have been receiving attention for many years,[1] it is only recently that experiments have provided reliable, quantitative kinetic data of the addition processes[2]

$$X\cdot + CH_2{=}CH_2 \xrightarrow{k_1} CXH_2\dot{C}H_2$$

and

$$X\cdot + CH{\equiv}CH \xrightarrow{k_2} CXH{=}\dot{C}H$$

An important generalization is that olefinic bonds are usually more reactive than acetylenic bonds toward free radicals.[3] In the case of X = H, for example, the absolute rate constants, k_1 and k_2, are $\sim 10^{11}$ and $\sim 10^{10}$ cm^3 mol^{-1} s^{-1} at room temperature,[2,4] respectively, while the ratios, k_1/k_2, are found to be 8.6 at room temperature[5] and 6×10^3 at 77 K.[6] By contrast, it is known that anionic additions give rise to the reverse trends, while cationic additions are the same as radical additions.[7] Relatively little effort has been given to factors influencing the differential reactivities of unsaturated bonds.

We report here ab initio calculations on the transition state and barrier height for the H-atom addition to ethylene. From a mechanistic point of view, we compare these results with our recent study of H-atom addition to acetylene.[8] For this purpose, the reaction barrier, ΔE, is expressed as a sum of the intramolecular deformation (DEF) energy and intermolecular interaction energy which consists of electrostatic (ES), exchange repulsion (EX), polarization (PL), charge transfer (CT), and mixing (MIX) energies.[9,10] All computations reported here are carried out within the framework of unrestricted Hartree–Fock SCF theory, using the split valence 4-31G basis set.[11]

Geometrical parameters necessary for describing the addition reaction of H with C_2H_4 are defined in Figure 1. The calculated molecular geometries and relative energies for the reactant, transition state, and product are summarized in Table I. We see that the transition state is at a fairly early stage, though there are some significant geometrical changes in the ethylene fragment. The approach distance, R = 2.015 Å, is somewhat longer than is the corresponding one (1.930 Å)[8] for the transition state of the H + C_2H_2 reaction. The calculated barrier height of 2.2 kcal/mol is in reasonable agreement with recent experimental Arrhenius activation energies:[12] 1.6 kcal/mol over temperature ranges 293–600 K,[13] 1.5 kcal/mol over 303–478 K,[14] and 2.1 kcal/mol over 198–320 K.[15] The barrier height for the H-atom addition to C_2H_4 is lower by 4.0 kcal/mol than is that of its addition to C_2H_2.[8]

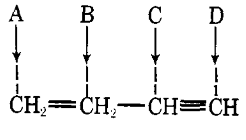
One might expect, simply from the smaller ionization potentials of olefins,[16] that the higher reactivity of olefinic bonds toward free radicals is due to the charge-transfer interaction. To examine this quantitatively, we consider in Table II energy components for the transition states and products in the H + C_2H_4 as well as H + C_2H_2 reactions. [A negative (positive) value corresponds to stabilization (destabilization).] Although the energy component decomposition scheme is not unique and somewhat dependent on basis set size, it provides a convenient framework to discuss the properties of unsaturated bonds toward free radicals along reaction pathways.

Let us examine first the situation at the transition state where we notice that the electrostatic (ES), exchange (EX), polarization (PL), and charge transfer (CT) for C_2H_4 are each somewhat larger than for C_2H_2. The individual differences are rather small but their collective effects amount to +5.3 kcal/mol for C_2H_4 and +1.8 kcal/mol for C_2H_2. The resultant destabilization, which arises from the EX term, is offset almost completely for C_2H_4 by the mixing (MIX) term, whereas for C_2H_2 MIX has virtually no effect at all. These trends are also found in cationic and anionic additions.[17] Thus, the reaction course up to the transition state is dominated mainly by the EX term, as has already been pointed out.[8]

At the product end of the reaction channel, all of the energy components are larger in magnitude as expected from the more compact and stable nature of the system. We find in this case that the EX term is not large enough to outweigh the combined effects of ES, PL, and CT, that the MIX terms for C_2H_4 and C_2H_2 are again of opposite signs, and that the sum of all components including DEF produces nearly equal ΔE's for both the olefinic and acetylenic reaction products.

The changing nature of the energy components along the reaction coordinate is subject to various interpretations. One view is that the MIX term distinguishes the reactivities of olefinic and acetylenic bonds toward free radicals. The MIX contribution can be partitioned further into several chemically interpretable coupling terms.[17] The actual calculations reveal that the MIX term at the transition state for the H + C_2H_4 reaction is dominated by an attraction of −3.5 kcal/mol arising from the coupling interaction between charge transfer from C_2H_4 to H and polarization of C_2H_4. This suggests that a coupled interaction, although it originates from third and higher orders in terms of perturbation theory,[18] plays an important role in weakly as well as strongly interacting systems.

In order to examine further the role of the MIX term, we have considered competition additions of atomic hydrogen to vinylacetylene in which *both* olefinic and acetylenic bonds are available. For this purpose, we carried out the following model calculations employing a standard geometry[19] and intermolecular distance of 2.0 Å at four attacking points, A–D:



$$CH_2{=}CH_2{-}CH{\equiv}CH$$

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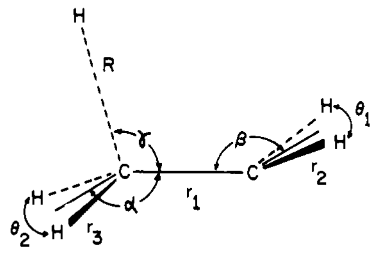

Figure 1. Geometrical parameters for the reaction of atomic hydrogen with ethylene.

Table I. Computed Optimized Geometries and Relative Energies for Reactant, Transition State, and Product in the Addition Reaction of H with C_2H_4

parameters[a]	reactant[c]	transition state	product
R	∞	2.015	1.089
r_1	1.316 (1.330)	1.357	1.496
r_2	1.073 (1.076)	1.072	1.073
r_3	1.073 (1.076)	1.072	1.084
α	180.0 (180.0)	170.5	128.4
β	180.0 (180.0)	178.1	171.6
γ	—	106.2	111.7
θ_1	116.0 (116.6)	116.7	117.8
θ_2	116.0 (116.6)	116.2	107.9
ΔE[b]	0.0	2.2	−41.3

[a] Bond lengths in ångstroms and bond angles in degrees. [b] Energies in kcal/mol. [c] Values in parentheses are experimental results: K. Kuchitsu, *J. Chem. Phys.*, **44**, 906 (1966).

Table II. Energy Component Analyses for Transition States and Products in the Atomic H Additions to C_2H_4 and C_2H_2[a]

	transition state		product	
	$CH_2{=}CH_2$	$CH{\equiv}CH$[b]	$CH_2{=}CH_2$	$CH{\equiv}CH$[b]
ES	−7.5	−9.0	−73.6	−64.7
EX	19.2	18.9	217.2	98.8
PL	−0.4	−0.6	−23.5	−10.8
CT	−6.0	−7.5	−173.1	−135.7
MIX	−5.1	0.1	−26.3	42.3
DEF	2.0	4.3	38.0	30.0
ΔE	2.2	6.2	−41.3	−40.1

[a] Energies in kcal/mol. [b] Reference 8.

Table III. Energy Components Analysis for Model Calculations in the Atomic Hydrogen Additions to Vinylacetylene, Ethylene, and Acetylene[a,b]

	reaction points for vinylacetylene				C_2H_4	C_2H_2
	A	B	C	D	A	D
ES	−9.2	−9.7	−9.5	−9.0	−9.4	−8.9
EX	24.0	25.6	24.8	23.4	24.7	23.9
PL	−0.6	−0.6	−0.5	−0.5	−0.6	−0.5
CT	−7.1	−6.6	−5.9	−6.6	−7.3	−6.4
MIX	−5.7	−3.8	−1.6	−3.4	−3.0	0.2
ΔE	1.4	4.9	7.3	3.9	4.4	8.3

[a] Energies in kcal/mol. [b] DEF = 0.0.

Table III shows that the stability of the attacking points decreases in the order of A > D > B > C. This order is consistent with the experimental results;[20] attack of *tert*-butoxy radical at the olefinic terminus is favored over attack at the acetylenic terminus by a factor of ~4. We see again that the MIX term plays an important role for the relative reactivity and direction of addition to unsaturated bonds. In the last two columns of Table III we also give the corresponding model results for C_2H_4 and C_2H_2, in order to buttress the conclusion drawn from Table II regarding the role of the MIX term and to show quantitatively how a double (triple) bond in vinylacetylene is influenced by the adjacent triple (double) bond.

We see that an understanding of chemical reactivity is aided by decomposing the energy difference into terms whose interpretation can possibly be extended to other systems. Recent theoretical work on reactivity differences between alkenes and alkynes in anionic additions is relevant in this regard. It is argued by Strozier, Caramella, and Houk[21] that, although the LUMO energy of C_2H_2 is higher than that of C_2H_4, bending distortions of C_2H_2, which occur upon interaction with H^-, dramatically lower the LUMO energy (facilitate the CT interaction), and lead to the greater reactivity of alkynes.[22] Thus, at the transition state where reactant molecules are distorted, the LUMO of acetylene has a more stabilizing interaction with a nucleophilic HOMO than is the case of ethylene.

Our energy component analyses at the transition states show that the CT (as well as ES, PL, and MIX) interaction is less favorable for the H + C_2H_2 reaction, while the EX repulsion is considerably smaller, as compared with the H^- + C_2H_4 reaction. The LUMO energy of C_2H_2 is rather higher even at the transition state than that of C_2H_4. Clearly, more extensive studies[23] together with kinetic treatments[24] are needed to understand reactivity differences between alkenes and alkynes toward nucleophiles, electrophiles, and free radicals from a unified point of view.

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(23) We have also performed calculations on the anionic additive reactions. In contrast to ref 21, we use diffuse functions on hydrogen and carbon and find, in the Hartree–Fock (HF) approximation, barrier heights of 17.4 and 20.0 kcal/mol for the addition of H^- to C_2H_2 and C_2H_4, respectively. These results are much larger than the HF values of 3.2 and 1.9 kcal/mol reported in ref 21, but rather close to their 3 × 3 CI values of 16.7 and 16.6 kcal/mol. For a more complete study of the $H^- + C_2H_2$ reaction, cf. C. E. Dykstra, A. J. Arduengo, and T. Fukumaga, *J. Am. Chem. Soc.*, **100**, 6007 (1979).

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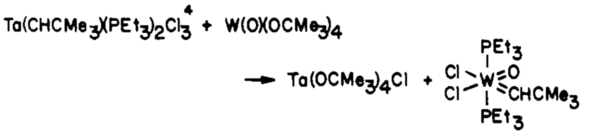
Communications to the Editor

Tungsten–Oxo Alkylidene Complexes as Olefin Metathesis Catalysts and the Crystal Structure of W(O)(CHCMe$_3$)(PEt$_3$)Cl$_2$[1]

Sir:

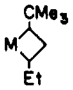
For some time we have been trying to prepare molybdenum- or tungsten-alkylidene complexes which are isoelectronic with known niobium or tantalum alkylidene complexes.[2a] Since a direct approach so far has yielded only one, rather esoteric type,[2b] we turned to indirect routes. The first successful reaction of this type is shown in eq 1.[3] Analogous benzylidene (**1b**), ethylidene (**1c**), propylidene (**1d**), and methylene (**1e**) complexes were prepared by treating **1a** with RCH=CH$_2$ (R = Ph, Me, Et, H) in the presence of a trace of AlCl$_3$.[5] We report here that these oxo alkylidene complexes are catalysts for the metathesis of terminal and internal olefins and describe the isolation and crystal structure of a *five*-coordinate, active metathesis catalyst, W(O)(CHCMe$_3$)(PEt$_3$)Cl$_2$.



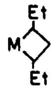
$$\mathrm{Ta(CHCMe_3)(PEt_3)_2Cl_3}^{4} + \mathrm{W(O)(OCMe_3)_4} \rightarrow \mathrm{Ta(OCMe_3)_4Cl} + \mathrm{WCl_2(O)(CHCMe_3)(PEt_3)_2} \quad (1)$$

1a

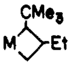
W(O)(CHCMe$_3$)(PEt$_3$)$_2$Cl$_2$ in benzene in the presence of ~0.5 equiv of AlCl$_3$[6] in 1–2 h reacts with 1-butene to give 3,3-dimethyl-1-butene (0.95+ equiv), but no 2,2-dimethyl-3-hexenes (the other possible type of metathesis product) or olefin products of β elimination from a metallacyclobutane intermediate.[7] The solution also contains 1-2 equiv of 3-hexene(s) (geometry undetermined) and some ethylene (most is in the gas phase). The solution was filtered at this point and the contents were examined by ^{1}H, ^{13}C, and ^{31}P NMR in C$_6$D$_6$. We showed an organometallic product of type **1** to be present in ~55% yield (by ^{1}H NMR integration vs a toluene standard); it was a mixture of **1d** (~80%) *and* **1e** (~20%).[8] Since 3,3-dimethyl-1-butene is the only product of the initial reaction between **1a** and 1-butene, **1e** must form in a subsequent reaction of **1d** with 1-butene. This suggests that formation and metathesis of **2a** is faster than formation and metathesis of **3a**. Presumably, the same is true of **2b** vs. **3b**.[9]



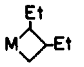
2a



2b



3a



3b

A reaction identical with the above continues to produce ethylene (which is vented every few hours) and 3-hexenes. After 24 h ~17 equiv of 3-hexenes are found.

W(O)(CHCMe$_3$)(PEt$_3$)$_2$Cl$_2$ in chlorobenzene in the presence of ~0.5 equiv of AlCl$_3$ reacts with *cis*-2-pentene to give the two initial metathesis products shown in eq 2 in 2 h, **1c** and **1d** in a ratio of ~1:1, and 2-butenes (~70% trans) and 3-hexenes steadily over the next 24 h. The total number of turnovers in 24 h is ~50.

$$\mathbf{1a} + cis\text{-}\mathrm{MeCH{=}CHEt} \xrightarrow{2\ \mathrm{h}} (0.22)\,trans\text{-}\mathrm{Me_3CCH{=}CHMe_3} + (0.13)\ trans\text{-}\mathrm{MeCCH{=}CHEt} + \mathbf{1c} + \mathbf{1d} \quad (2)$$

The metathesis reactions (especially of 2-pentene) proceed more slowly in benzene than they do in chlorobenzene. If AlEtCl$_2$ is used instead of AlCl$_3$, 1-hexene is metathesized at about the same rate for the first 12 h (as is observed with AlCl$_3$), but then 2-butene forms (probably via a nonmetathesis related isomerization pathway) and all possible metathesis products are produced. Other Lewis acids such as TaCl$_5$, SnCl$_2$, ZrCl$_4$, or SbCl$_5$ also are successful cocatalysts. In all reactions the catalytic activity slows considerably with time and eventually no oxo alkylidene complexes of type **1** can be recovered from or observed in the mixture.

In other studies[10] we postulate that an octahedral coordination site must be present on tantalum for an olefin to react with the alkylidene ligand. The following results suggest that this is true here as well. Halides exchange readily between W and Al; when 1 equiv of AlBr$_3$ is added to **1a** in benzene, W(O)(CHCMe$_3$)(PEt$_3$)$_2$Br$_2$ is formed essentially quantitatively in a few minutes, according to the ^{31}P NMR spectrum of the filtered mixture.[11] We also know that, in the absence of a Lewis acid, complexes of type **1** react very slowly with olefins and not at all in the presence of added PEt$_3$. Unfortunately, these results do not tell us whether loss of halide, loss of PEt$_3$, or loss of both yields a metathesis catalyst.

We can remove one PEt$_3$ ligand by adding transition metal complexes which will scavenge phosphine. One of the most successful experiments is shown in eq 3. Interestingly, **4** will metathesize terminal and internal olefins in chlorobenzene *in the absence of AlCl$_3$* at an initial rate which is at least equal to that of **1** plus AlCl$_3$, but the system is shorter lived. Therefore **4** is at least a plausible active intermediate in the system **1** plus AlCl$_3$.

$$\mathbf{1a} + 0.5\mathrm{Pd(PhCN)_2Cl_2} \xrightarrow[\text{toluene}]{3\ \mathrm{h}} 0.5\mathrm{Pd(PEt_3)_2Cl_2} + \underset{\mathbf{4}}{\mathrm{W(O)(CHCMe_3)(PEt_3)Cl_2}}{}^{12} \quad (3)$$

W(O)(CHCMe$_3$)(PEt$_3$)Cl$_2$ crystallizes in the centrosymmetric orthorhombic space group *Pbca* with $a = 9.111$ (2), $b = 15.709$ (4), $c = 24.207$ (6) Å; $V = 3465$ (1) Å^3 and ρ(calcd) = 1.76 g cm^{-3} for mol wt 459.0; and $Z = 8$. Diffraction data were collected with a Syntex P2$_1$ automated four-circle diffractometer using a coupled θ(crystal)–2θ(counter) scan technique[13] and graphite-monochromatized Mo Kα radiation. Data were corrected for absorption ($\mu = 74.3$ cm^{-1}) and the structure was solved by a combination of Patterson, difference-Fourier, and full-matrix least-squares refinement techniques. All nonhydrogen atoms were located. The tungsten atom lies in a pseudo special position (~1/2, ~1/2, ~1/8) and

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