Ab initio calculations on the barrier height for the hydrogen addition to ethylene and formaldehyde. The importance of spin projection

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Ab Initio Calculations on the Barrier Height for the Hydrogen Addition to Ethylene and Formaldehyde. The Importance of Spin Projection

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Abstract

Heats of reaction and barrier heights have been computed for $H + CH_2CH_2 \rightarrow \dot{C}_2H_5$, $H + CH_2O \rightarrow CH_3\dot{O}$, and $H + CH_2O \rightarrow \dot{C}H_2OH$ using unrestricted Hartree–Fock and Møller–Plesset perturbation theory up to fourth order (with and without spin annihilation), using single-reference configuration interaction, and using multiconfiguration self-consistent field methods with 3-21G, 6-31G(d), 6-31G(d, p), and 6-311G(d, p) basis sets. The barrier height in all three reactions appears to be relatively insensitive to the basis sets, but the heats of reaction are affected by p-type polarization functions on hydrogen. Computation of the harmonic vibrational frequencies and infrared intensities with two sets of polarization functions on heavy atoms [6-31G(2d)] improves the agreement with experiment. The experimental barrier height for $H + C_2H_4$ (2.04 ± 0.08 kcal/mol) is overestimated by 7–9 kcal/mol at the MP2, MP3, and MP4 levels. MCSCF and CISD calculations lower the barrier height by approximately 4 kcal/mol relative to the MP4 calculations but are still almost 4 kcal/mol too high compared to experiment. Annihilation of the largest spin contaminant lowers the MP4SDTQ computed barrier height by 8–9 kcal/mol. For the hydrogen addition to formaldehyde, the same trends are observed. The overestimation of the barrier height with Møller–Plesset perturbation theory appears to be due to a large spin contamination in the unrestricted wave function. The predicted barrier heights for $H + C_2H_4 \rightarrow \dot{C}_2H_5$, $H + CH_2O \rightarrow CH_3\dot{O}$, and $H + CH_2O \rightarrow \dot{C}H_2OH$ at the MP4SDTQ/6-31G(d) after spin annihilation are respectively 1.8, 4.6, and 10.5 kcal/mol.

Introduction

Although the addition of hydrogen to the double bonds of C_2H_4 or CH_2O appears to be a simple reaction, accurate barrier heights seem to be rather difficult to calculate. Even extensive calculations with large basis sets and reliable estimates of correlation energy predict barriers that are 3–8 kcal/mol too high. Experimentally the barrier for the addition of atomic hydrogen to ethylene is 2.04 ± 0.08 kcal/mol [1]. In theoretical studies, Schlegel, Bhalla, and Hase [2] have found good agreement with experiment at the UHF level, but an overestimation of the barrier by 8–9 kcal/mol by using Møller–Plesset theory up to fourth order. Similar results at the UHF level have been calculated by Nagase and Kern [3] and Nagase, Fueno, and Morokuma [4]. The same trend has also been found for hydrogen addition to substituted olefins, $H + C_2H_3X$, $X = F$, Cl, OH [2, 5, 6]. Harding [7] has carried out calculations on the $H + C_2H_4$ systems with the POL-CI method, using double-ζ basis sets

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with one set of polarization functions and including extensive configuration interaction based on a GVB wave function, and has obtained a barrier height of 3.7 kcal/mol. There is no direct experimental information on the addition of hydrogen to formaldehyde. Saebø, Radom, and Schaefer [8] have calculated a barrier height of 12.4 kcal/mol for the addition of atomic hydrogen to the carbon in formaldehyde and 20.1 kcal/mol for addition to the oxygen using a 6-31G(d, p) basis set and third-order Møller–Plesset perturbation theory. This appears to be in qualitative agreement with Harding's results [9], in which the barrier for hydrogen to the oxygen is 15 kcal/mol and 8 kcal/mol for the carbon in formaldehyde addition. Harding and Schatz [10] have reported a barrier height of 7.8 kcal/mol at the POL-CI level for the $H + CH_2O \rightarrow CH_3\dot{O}$.

The present study addresses questions concerning the accuracy of the different theoretical methods in predicting the barrier height for hydrogen adding to ethylene and formaldehyde to form ethyl radical, hydroxymethyl radical, and methoxy radical. In addition, vibrational frequencies and infrared intensities have been calculated to help characterize the radicals and transition states.

Computational Method

Calculations were performed with the GAUSSIAN 82 system of programs [11]. Optimized geometries at the HF/3-21G and HF/6-31G(d) levels were taken from the literature [2, 8, 12]. Single-point computations at the HF/6-31G(d) optimized geometries were also performed with a 6-31G(d, p) [13] basis set (i.e., 6-31G** split-valence plus a set of polarization functions on heavy atoms and hydrogen), and with 6-311G(d, p) [14] (i.e., 6-311G**, triple split-valence basis set plus a set of polarization functions on heavy atoms and hydrogen).

Electron correlation corrections to the energy were computed using fourth-order Møller–Plesset perturbation theory [15] in the space of single, double, triple, and quadruple excitations (MP4SDTQ, frozen core). Configuration interaction calculations were based on the UHF single determinant and included all double excitations (CID, frozen core) and all single and double excitations (CISD, frozen core). Size consistency corrections (SCC) were computed with a modified form of the Davidson correction [16, 17]. The MCSCF computations were performed with the 3-21G and 6-31G(d) basis sets, using the unitary group method described by Hegarty and Robb [18] and the programs outlined in Ref. 19 in conjunction with the GAUSSIAN 82 system. The MCSCF calculations involved a complete CI in the valence space consisting of the π and π^* orbitals of the double bond and the 1s orbital of hydrogen (total of eight configurations).

The effects of spin contamination were examined by annihilation of the next highest spin component in the UHF wave function, Φ_0,

$$\hat{A}_{s+1}\Phi_0 = \frac{\hat{S}^2 - (s + 1)(s + 2)}{\langle \hat{S}^2 \rangle_0 - (s + 1)(s + 2)} \Phi_0$$

$$= \Phi_0 + \sum_i \frac{\psi_i \langle \psi_i | \hat{S}^2 | \Phi_0 \rangle}{\langle \Phi_0 | \hat{S}^2 | \Phi_0 \rangle - (s + 1)(s + 2)}$$

$$= \Phi_0 + \tilde{\Phi}_1$$

where s is the desired spin of Φ_0, and ψ_i includes all single and double excitations from Φ_0. The projected HF energy after single annihilation is computed to be

$$\langle \Phi_0 | \hat{H} | \hat{A}_{s+1} \Phi_0 \rangle = E_{\text{UHF}} + \sum_i \frac{\langle \Phi_0 | \hat{H} | \psi_i \rangle \langle \psi_i | \hat{S}^2 | \Phi_0 \rangle}{\langle \Phi_0 | \hat{S}^2 | \Phi_0 \rangle - (s + 1)(s + 2)}$$

$$= E_{\text{UHF}} + \Delta E_{\text{PUHF}} = E_{\text{PUHF}}$$

For the projected MP2, MP3, and MP4 energies, the following approximate formulae are used:

$$E_{\text{PMP2}} \simeq E_{\text{MP2}} + \Delta E_{\text{PUHF}} \{1 - \langle \tilde{\Phi}_1 | \Phi_1 \rangle [\langle \Phi_0 | \hat{S}^2 | \Phi_0 \rangle - (s + 1)(s + 2)]/\langle \tilde{\Phi}_1 | \tilde{\Phi}_1 \rangle \}$$

$$E_{\text{PMP3}} \simeq E_{\text{MP3}} + \Delta E_{\text{PUHF}} \{1 - \langle \tilde{\Phi}_1 | \Phi_1 + \Phi_2 \rangle [\langle \Phi_0 | \hat{S}^2 | \Phi_0 \rangle - (s + 1)(s + 2)]/\langle \tilde{\Phi}_1 | \tilde{\Phi}_1 \rangle \}$$

$$E_{\text{PMP4}} \simeq E_{\text{MP4}} + \Delta E_{\text{PUHF}} \{1 - \langle \tilde{\Phi}_1 | \Phi_1 + \Phi_2 \rangle [\langle \Phi_0 | \hat{S}^2 | \Phi_0 \rangle - (s + 1)(s + 2)]/\langle \tilde{\Phi}_1 | \tilde{\Phi}_1 \rangle \}$$

where Φ_1 and Φ_2 are the first- and second-order corrections to the wave function by Møller–Plesset perturbational theory. The energies correspond to the spin-projection correction $\tilde{\Phi}_1$ reduced by the amount already contained in Φ_1 and Φ_2. Details are reported elsewhere [20].

Vibrational frequencies and zero-point energies were obtained from analytical second derivatives [21] calculated at the HF level with the split-valence basis set including a second set of polarization functions on heavy atoms 6-31G(2d) (d exponents of 1.6 and 0.4 on both carbon and oxygen). The derivatives of the dipole moment with respect to the Cartesian coordinates, i.e., the atomic polar tensors have been calculated analytically with the same basis sets, according to the equation

$$\frac{\partial \mu_\alpha}{\partial \beta_A} = -\sum_{\mu\nu} \left[\frac{\partial P_{\mu\nu}}{\partial \beta_A} \langle \nu | \alpha | \mu \rangle + P_{\mu\nu} \frac{\partial \langle \nu | \alpha | \mu \rangle}{\partial \beta_A} \right] + \sum_A \alpha_A \delta_{\alpha\beta}$$

where $\alpha, \beta = x, y, z$ (the subscript A indicates that the Cartesian coordinates refer to the center A). After transforming the atomic polar tensor to normal mode coordinates [22], we computed the absolute infrared intensities in the double-harmonic approximation [23]:

$$A_i = (N\pi d_i / 3c^2)[\partial \boldsymbol{\mu} / \partial Q_i]^2$$

where N is Avogadro's number, d_i, is the degeneracy of the normal mode, and c is the velocity of light.

Results and Discussion

Structures

The geometries for the reactants, transition structures, and products for the addition of hydrogen to ethylene and formaldehyde have been discussed previously [2–10, 24–40]. To facilitate comparisons, the structures of the saddle points have been reproduced in Figure 1. The shortening of the C—O distance in the two transition states for hydrogen adding to formaldehyde with the improvement in the basis sets is consistent with changes in the equilibrium structures. The bond length for the attacking hydrogen is more sensitive to basis set quality in the addition to formaldehyde than to ethylene.
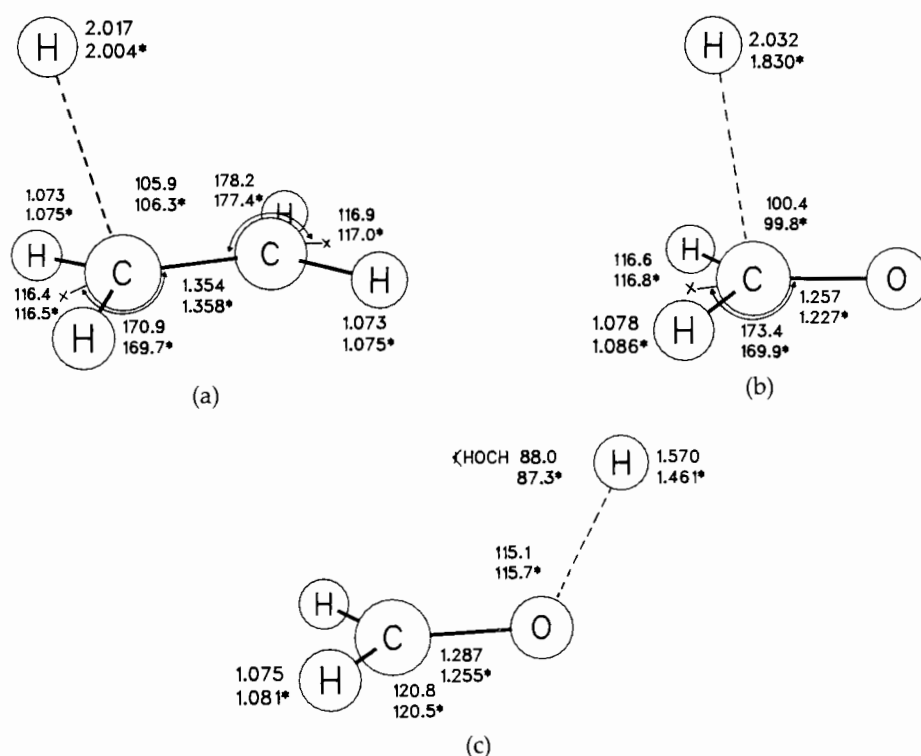
Figure 1. Comparison of the theoretical optimized geometries for the transition states:
HF/3-21G (no superscript), HF/6-31G(d) (asterisk).

Barrier Heights

The total energies with the 6-31G(d) basis set for the addition of atomic hydrogen to ethylene and formaldehyde are collected in Table I. The barrier heights for the three additions are in Table II grouped according to the basis sets. For the 6-31G(d) basis set the barrier heights are also presented in Figure 2 to illustrate the effect of different levels of theory. For comparison the experimental barrier height for H + C_2H_4 is 2.04 ± 0.08 kcal/mol and in the range of 3–8 [41] kcal/mol for H + $CH_2O \rightarrow CH_3\dot{O}$.

Improvement of the basis sets by adding d functions on heavy atoms has a larger effect on H + CH_2O than on H + C_2H_4, especially at the UHF and ROHF levels. However, adding a second set of d functions for the heavy atoms has very little effect [42]. Polarization functions on hydrogen [6-31G(d)$\rightarrow$ 6-31G(d, p)] are more important for H addition to oxygen than carbon. Increasing the number of valence basis functions from double-ζ to triple-ζ [6-31G(d, p) to 6-311G(d, p)] has a relatively small effect on the barriers at the MP2 and MP3 levels.

Inspection of the unrestricted Møller–Plesset theory results reveals that the MP3 and MP4SDTQ barrier heights are very similar, suggesting that the perturbation series

TABLE I. Total energies[a] for the hydrogen addition to ethylene and formaldehyde.

Level	H + C$_2$H$_4$[b]	H + C$_2$H$_4$(t.s.)	Ċ$_2$H$_5$	H + CH$_2$O[b]	H + CH$_2$O(t.s.)	CH$_2$O + H(t.s.)	ĊH$_3$O	ĊH$_2$OH
UHF/6-31G(d)[c]	-78.52995	-78.52532	-78.59715	-114.36456	-114.35490	-114.33886	-114.42075	-114.40876
ROHF/6-31G(d)	-78.52995	-78.51497	-78.59275	-114.36456	-114.34278	-114.31953	-114.41623	-114.40498
PUHF/6-31G(d)	-78.52995	-78.53951	-78.60037	-114.36456	-114.37088	-114.35780	-114.42392	-114.41148
MP2/6-31G(d)	-78.78258	-78.76377	-78.83537	-114.66348	-114.63570	-114.62119	-114.68570	-114.69543
PMP2/6-31G(d)	-78.78258	-78.78551	-78.84651	-114.66348	-114.65669	-114.64488	-114.69461	-114.70417
MP3/6-31G(d)	-78.80358	-78.78718	-78.86156	-114.66993	-114.64890	-114.63518	-114.70753	-114.70975
PMP3/6-31G(d)	-78.80359	-78.80069	-78.86354	-114.66993	-114.66437	-114.65359	-114.70933	-114.71145
MP4DQ/6-31G(d)	-78.80622	-78.79042	-78.86500	-114.67354	-114.65244	-114.63901	-114.71034	-114.71297
MP4SDQ/6-31G(d)	-78.80878	-78.79406	-78.86670	-114.67772	-114.65815	-114.64474	-114.71302	-114.71557
MP4SDTQ/6-31G(d)	-78.81693	-78.80091	-78.87202	-114.68727	-114.66590	-114.65211	-114.71842	-114.72142
PMP4/6-31G(d)	-78.81693	-78.81442	-78.87400	-114.68727	-114.68137	-114.67052	-114.72022	-114.72312
CID/6-31G(d)	-78.78701	-78.77313	-78.84737	-114.65267	-114.63323	-114.61949	-114.69231	-114.69321
CID/6-31G(d) + SCC	-78.80917	-78.79394	-78.86734	-114.67490	-114.65482	-114.64169	-114.71227	-114.71411
CISD/6-31G(d)	-78.78919	-78.77774	-78.84898	-114.65550	-114.63977	-114.62638	-114.69479	-114.69539
CISD/6-31G(d) + SCC	-78.81241	-78.80289	-78.86967	-114.67940	-114.66742	-114.65498	-114.71615	-114.71762
MCSCF/6-31G(d)	-78.55795	-78.54768	-78.60862	-114.39898	-114.38301	-114.36539	-114.41750	-114.42573

[a] Total energies in a.u. (1 a.u. = 627.51 kcal/mol).

[b] Total energies for hydrogen atom HF/3-21G = -0.49620, HF/6-31G(d) = -0.49823, HF/6-311G(d, p) = -0.49981 a.u.

[c] All the geometries were optimized at the UHF/6-31G(d) level.

TABLE II. Comparison of barrier heights.[a]

Level	H + $C_2H_4 \rightarrow \dot{C}_2H_5$				H + $CH_2O \rightarrow CH_3\dot{O}$				H + $CH_2O \rightarrow \dot{C}H_2OH$			
	3-21G	6-31G(d)	6-31G(d,p)	6-311G(d,p)	3-21G	6-31G(d)	6-31G(d,p)	6-311G(d,p)	3-21G	6-31G(d)	6-31G(d,p)	6-311G(d)
UHF	2.27	2.90	2.82	3.70	1.38	6.06	5.85	6.52	7.00	16.13	15.35	16.21
ROHF	8.33	9.40			8.90	13.67			20.46	28.26		
MP2	10.88	11.80	11.02	10.49	18.08	17.43	16.37	16.34	25.08	26.54	24.27	24.77
MP3	9.88	10.30	9.48	8.63	13.41	13.20	12.10	11.56	19.84	21.81	19.53	19.49
MP4DQ	9.81	9.91	9.11	(8.26)	13.86	13.24	12.20	(11.66)	20.24	21.67	19.44	(19.40)
MP4SDQ	9.09	9.24	8.40	(7.55)	12.67	12.28	11.28	(10.68)	19.27	20.70	18.47	(18.43)
MP4SDTQ	9.54	10.05	(9.21)[c]	(8.36)	13.94	13.41	(12.35)	(11.81)	20.74	22.06	(19.83)	(19.79)
CID	8.47	8.71			11.91	12.20			17.96	20.82		
CID + SCC	9.33	9.56			12.99	12.60			18.95	20.84		
CISD	6.37	7.18		6.05	7.57	9.87		9.07	13.84	18.27		16.80
CISD + SCC	5.11	5.97		4.59	3.92	7.52		6.68	10.40	15.32		13.64
MCSCF	5.73	6.44			5.61	10.02			14.04	21.08		
PUHF	-6.40	-6.00			-9.75	-3.97			-6.12	4.24		
PMP2	1.24	-1.84			6.09	4.26			11.26	11.67		
PMP3	1.69	1.82			2.38	3.49			7.04	10.25		
PMP4	1.35	1.58			2.92	3.70			7.94	10.51		
ΔZPE[d]	0.20				0.90				0.70			
EXP	2.04 ± 0.08[b]											

[a] In kcal/mol.

[b] See Ref. 1.

[c] The values in parentheses have been estimated according to the formula defined in the computational method section.

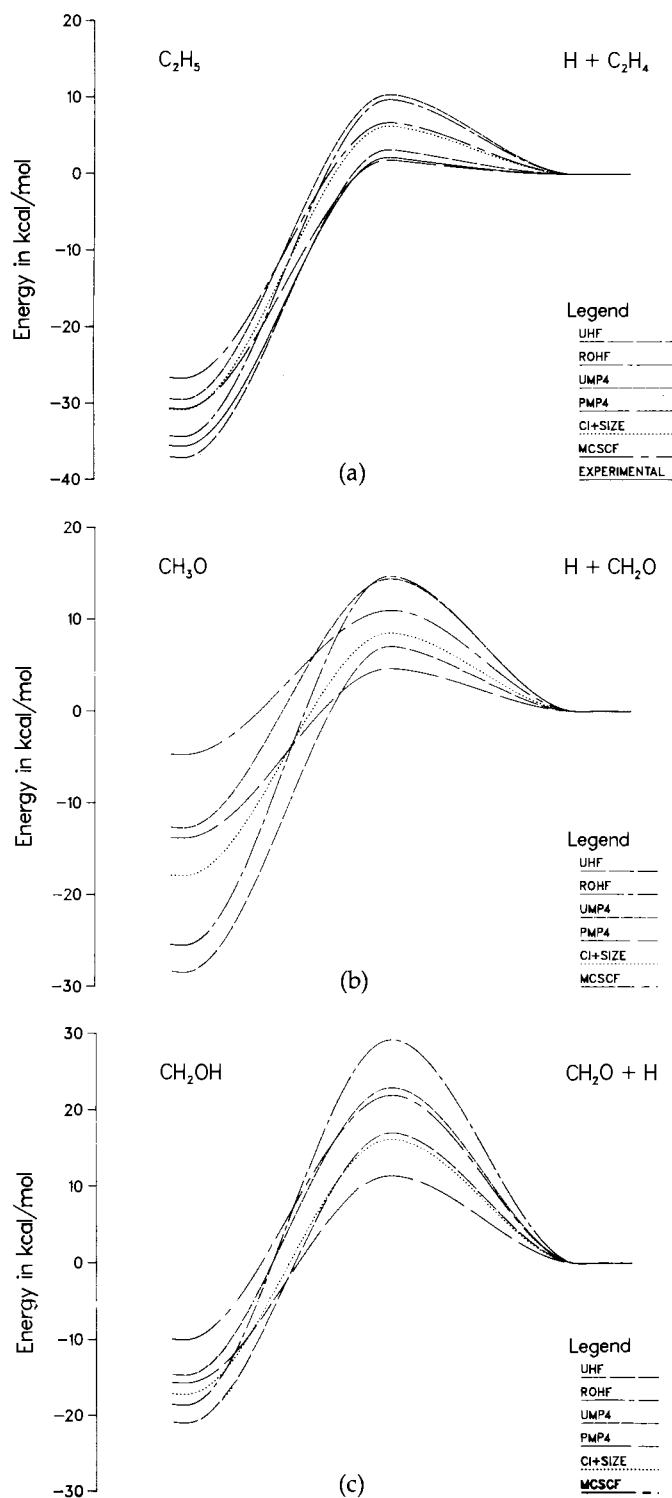[d] The ΔZPE have been computed at the HF/6-31G(2d) level.

Figure 2. Barrier heights and heats of reaction for (a) H + C$_2$H$_4$ → Ċ$_2$H$_5$, (b) H + CH$_2$O → CH$_3$Ȯ, and (c) CH$_2$O + H → ĊH$_2$OH computed at various levels of theory with the 6-31G(d) basis sets.

might be reasonably well converged at the MP4 level (but see below). With the larger basis sets, full MP4SDTQ calculations were not practical, but they have been estimated according to

$$E(\text{MP4SDTQ}/6\text{-}31G(d,p)) \simeq E(\text{MP4SDQ}/6\text{-}31G(d,p)) + E_{4T}(6\text{-}31G(d))$$

$$E(\text{MP4}/6\text{-}311G(d,p)) \simeq E(\text{MP3}/6\text{-}311G(d,p)) + E_{4SDQ}(6\text{-}31G(d,p)) + E_{4T}(6\text{-}31G(d))$$

where E_{4SDQ} and E_{4T} are the fourth-order Møller–Plesset contributions to the energy arising from single, double, and quadruple excitations and from triple excitations, respectively, computed with the basis sets indicated. Compared to experiment, the barrier heights at the MP2, MP3, and MP4 levels are consistently 6–12 kcal/mol too high. The trends suggest that the next order of perturbation theory would not change the results drastically. It is also apparent that further increases in the basis set size will not correct the errors in the barrier heights.

The configuration interaction calculations, including all double excitation from the UHF determinant (CID and CID + SCC) are very similar to the MP3 and MP4 results. However, when single excitations are included (CISD and CISD + SCC), the barriers are lowered significantly. The contribution from the single excitations is estimated rather poorly by the MP4 calculations (MP4DQ vs. MP4SDQ and MP4SDTQ), since single excitations enter the perturbation series for the first time at fourth order. The perturbation series is apparently slow to converge for the energies of the transition structures, paralleling the slow convergence observed in the iterative solution of the CI equations. Even though the CISD + SCC results are considerably better than the MP4 values, the computed barriers are still at least 3 kcal/mol higher than experiment for H + C_2H_4.

Closely related to the overestimation of the barrier heights is the problem of spin contamination in the UHF wave function. Usually this is not a serious difficulty, since the spin contamination is often relatively small. For example, $\langle S^2 \rangle = 0.7623$, 0.7575, and 0.7591 for $\dot{C}_2H_5$, $CH_3\dot{O}$, and $\dot{C}H_2OH$, respectively, at the UHF/6-31G(d) level compared to 0.75 for a pure doublet. However, the transition states for H addition show a large contamination: $\langle S^2 \rangle = 0.9883$, 0.9496, and 0.9916 for H + $C_2H_4 \rightarrow \dot{C}_2H_5$, H + $CH_2O \rightarrow CH_3\dot{O}$, and H + $CH_2O \rightarrow \dot{C}H_2OH$, respectively, at UHF/6-31G(d). Such a large spin contamination corresponds to a sizable admixture of quartet spin states into the doublet state (0.7539, 0.7519, and 0.7539 after annihilation of the quartet). Since the quartets are higher in energy, the net effect is to elevate the energy of the transition state. This is most noticeable when correlation energy is included. At the UHF level, mixing in the higher spin state also allows for some electron correlation, hence lowering the barrier. At the MPn level, electron correlation is treated roughly equally in the (spin-uncontaminated) reactants and the (spin-contaminated) transition structure; hence, the barrier is high due to the contribution from the higher-lying quartet.

Two approaches can be used to solve the UHF spin-contamination problem. One can start with a pure spin state such as an ROHF wave function, or one can annihilate the spin contamination in the UHF function. The ROHF barriers are too high by 5–15 kcal/mol, but a small CI or MCSCF calculation improves the barriers consider-

ably. If the valence space is chosen to be the three orbitals involved in breaking the π bond and forming the σ bond to H (π, π^*, and hydrogen 1s), about one-third to one-half of the error in the ROHF barrier is recovered at the MCSCF level. In the case of hydrogen addition to ethylene, enlarging the valence space to 75 configurations further improves the barrier only by about 0.5 kcal/mol. A large POL-CI calculation by Harding [7], based on a spin-restricted GVB reference wave function, gives a barrier of 3.7 kcal/mol. Apparently a larger multireference CISD would be needed to obtain a lower barrier.

An alternative approach is to use projection or annihilation operators to eliminate the higher spin configurations from the UHF and unrestricted Møller–Plesset wave functions. As can be seen from Table II, the projected UHF barriers are clearly unacceptable. This is similar to the problem encountered in computing bond dissociation potentials, where the PUHF curve has a spurious minimum in a region where the bond is partially broken [20]. Both difficulties can be traced to the fact that a UHF wave function does contain some correction for electron correlation associated with the incorporation of the higher spin state. However, if correlation corrections are added, the bond dissociation potentials computed at the PMP4 level are in very good agreement with accurate calculations [20]. Likewise, acceptable barrier heights are obtained at the PMP2, PMP3, and PMP4 levels. Except for H + C_2H_4 with the 6-31G(d) basis set, the PMP2 computed barriers are quite reasonable. The PMP4/6-31G(d) barrier height for H + C_2H_4 is in good agreement with experiment (but perhaps a little too low). Similar agreement can be expected for the other barriers.

Heats of Reaction

Table III summarizes the heats of reaction for H + C_2H_4 and H + CH_2O. Inspection of the data reveals that p-polarization functions on hydrogen [6-31G(d) → 6-31G(d, p)] are needed for the MP calculations. Adding a second set of d functions (not shown) has a small effect on the UHF and MP2 energies. Increasing the basis set to triple split-valence [6-311G(d, p)] changes the heats of reaction by 1–2 kcal/mol. The CISD + SCC values are very similar to the MP4SDTQ results, but examination of the energy difference at MP4SDTQ reveals that triple excitations contribute about 2 kcal/mol. The spin contamination in the products is small, but spin projection nevertheless changes the energies by about 1 kcal/mol (PMP4 vs. MP4). The final theoretical estimates at the PMP4/6-311G(d, p) level plus change in zero-point energy are -35.5, -17.6, and -24.1 kcal/mol (-40.7, -24.5, -31.0 kcal/mol without zeropoint energy correction) for H + $C_2H_4 \rightarrow \dot{C}_2H_5$, H + $CH_2O \rightarrow CH_3\dot{O}$, and H + $CH_2O \rightarrow \dot{C}H_2OH$, respectively. The H + $C_2H_4 \rightarrow \dot{C}_2H_5$ results are in very good agreement with experiment. The calculated ΔH^0 for H + $CH_2O \rightarrow CH_3\dot{O}$ disagrees with two recent experimental values: -22.6 kcal/mol (based on ΔH_f^0 (0 K) = 5.7 [43] kcal/mol for $CH_3\dot{O}$, obtained by Batt and McCulloch [44]) and -24.5 [43] kcal/mol (based on ΔH_f^0 (0 K) = 2.4 [43] kcal/mol for $CH_3\dot{O}$, obtained by Engelking, Ellison, and Lineberger [45]). However, the present computations agree well with the ΔH^0 (0 K) = -16.7 kcal/mol calculated by Melius, Binkley, and Koszykowski [46] with the BAC-MP4 approach (MP4 with bond additivity correc-

TABLE III. Calculated and experimental heats of reaction.[a]

Level	H + C₂H₄ → Ċ₂H₅				H + CH₂O → CH₃Ȯ				H + CH₂O → CH₂OH			
	3-21G	6-31G(d)	6-31G(d,p)	6-311G(d,p)	3-21G	6-31G(d)	6-31G(d,p)	6-311G(d,p)	3-21G	6-31G(d)	6-31G(d,p)	6-311G(d,p)
UHF	−41.70	−42.17	−42.95	−40.92	−46.39	−35.26	−36.15	−34.17	−35.03	−27.74	−32.08	−31.33
ROHF	−39.47	−39.41			−45.33	−32.42			−33.15	−25.36		
MP2	−32.30	−33.13	−38.12	−37.24	−20.63	−13.94	−18.97	−16.75	−20.24	−20.05	−27.77	−28.21
MP3	−34.87	−36.38	−41.72	−41.36	−29.81	−23.59	−28.97	−27.69	−25.73	−24.99	−32.84	−33.64
MP4DQ	−34.86	−36.89	−42.16	(−41.80)	−28.53	−23.09	−28.34	(−24.06)	−24.74	−24.74	−32.44	(−33.24)
MP4SDQ	−34.39	−36.35	−41.55	(−41.19)	−26.97	−22.15	−27.24	(−25.96)	−23.85	−23.75	−31.40	(−32.20)
MP4SDTQ	−33.30	−34.57	(−39.77)[e]	(−39.41)	−24.42	−19.55	(−24.64)	(−23.36)	−21.81	−21.43	(29.08)	(−29.88)
CID	−36.14	−37.88			−31.21	−24.87			−26.70	−25.44		
CID + SCC	−34.58	−36.50			−29.07	−23.45			−24.94	−24.60		
CISD	−35.76	−37.52		−41.80	−30.40	−24.65		−27.57	−26.26	−25.03		−32.82
CISD + SCC	−34.00	−35.93		−41.13	−27.88	−23.06		−26.41	−24.33	−23.98		−32.35
MCSCF	−30.83	−31.80			−20.91	−11.62			−21.15	−16.79		
PUHF	−43.49	−44.19			−47.30	−37.25			−36.43	−29.44		
PMP2	−35.53	−40.12			−23.39	−19.53			−23.31	−25.53		
PMP3	−35.96	−37.62			−30.43	−24.72			−26.61	−26.05		
PMP4	−34.38	−35.81	(−41.01)	(−40.65)	−25.04	−20.68	(−25.77)	(−24.49)	−22.68	−22.50	(−30.15)	(−30.95)
ΔZPE[g]	5.20					6.90				6.90		
EXP				−35.5±[b]				−22.6[c] −24.4[d]			−29.0[f]	

[a] In kcal/mol.

[b] The heat of reaction has been estimated in Ref. 2 based on the $\Delta H_{f,300}$ (C₂H₅) = 28.0 kcal/mol from Ref. 64.

[c] Based on the ΔH_f^0 obtained from Ref. 44.

[d] Based on the ΔH_f^0 obtained from Ref. 45.

[e] The values in parentheses have been estimated according to the formula given in the computational method section.

[f] See Ref. 47.

[g] The ΔZPE have been computed at the HF/6-31G(2d) level.

tions). The computed ΔH^0 (0 K) for H + $CH_2O \rightarrow CH_2OH$ is less exothermic than experiment (-29 kcal/mol) [47]. Previous calculations have found -20.7 [8], -29 [46], and -24 [9] kcal/mol.

The difference between ΔH^0 (298 K) for H + $CH_2O \rightarrow CH_3\dot{O}$ and H + $CH_2O \rightarrow \dot{C}H_2OH$ is the heat of reaction for the isomerization $CH_3\dot{O} \rightarrow \dot{C}H_2OH$. The ΔH^0 obtained here, -6.5 kcal/mol, agrees with experimental estimates (-4 ± 1 [45] and $-7.5 \pm .5$ [49] kcal/mol) and the calculations of Saebø, Radom, and Schaefer [8] (-5.0 kcal/mol) but not others (-2 [9], ca. 9 [27, 48], and -11.8 [46] kcal/mol). The estimated MP4/6-311G(d, p) values for $CH_3\dot{O} \rightarrow \dot{C}H_2OH$ can be compared to the isomerization $CH_2O \rightarrow HCOH$, which should display a similar sensitivity to basis sets and level of theory. Extensive calculations by Frisch, Binkley, and Schaefer [50] show that increasing the basis sets beyond 6-311G(d, p) changes the $CH_2O \rightarrow$ HCOH isomerization energy by less than ± 1 kcal/mol. This suggests that -6.5 kcal/mol is probably a reliable estimate for the ΔH^0 of $CH_3\dot{O} \rightarrow \dot{C}H_2OH$.

Vibrational Frequencies and IR Intensities

Calculated and experimental vibrational frequencies and infrared intensities for reactants, products, and transition structures (6-31G(2d) SCF level) are summarized in Table IV. In previous studies harmonic vibrational frequencies computed at HF/3-21G and HF/6-31G(d) levels have been compared extensively with experimental anharmonic frequencies [21]. On average, the harmonic frequencies calculated at the HF/3-21G level are 11% higher than experimental values, due to a combination of electron correlation and vibrational anharmonicity effects [21, 51]. The errors with 6-31G(2d) basis sets appear to be somewhat lower. In a recent study we have found that a second set of polarization functions on the heavy atoms improves the infrared intensities [52]. The infrared intensities of the fundamental bands for ethylene and formaldehyde have already been studied by several authors [53–62]. For ethylene, very good agreement is found with the experimental infrared intensities reported by Nakanda, Kondo, and Saëki [62] as well as the theoretical values of Amos [60]. The largest discrepancy appears to be with the calculated intensity for ν_1. Good agreement is also found for the IR intensities of formaldehyde, except for the C—H stretch and the carbonyl stretch, where correlation corrections may be important.

Conclusions

In the present study we have shown that for spin-unrestricted calculations, spin contamination plays an important role in the computation of the barrier height of hydrogen adding to double bonds. Inclusion of electron correlation at the fourth-order Møller–Plesset level does not reduce the spin contamination nor does it lower the barrier. Only when single excitations are included in a configuration interaction calculation (CISD) is the barrier somewhat lower (but still ca. 3 kcal/mol higher than experiment for H + C_2H_4). Spin-restricted open-shell Hartree–Fock calculations also yield high barriers, and a small MCSCF (spin restricted) recovers only about one-third of the error. Annihilation of the largest spin contaminant in unrestricted MP4 calculations results in good estimates of barrier heights.

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TABLE IV. Vibrational frequencies and infrared intensities.[f]

Structure	Symmetry	Calculated		Experimental	
		w (cm^{-1})	A (km/mol)	ν (cm^{-1})[a]	A (km/mol)[b]
C_2H_4	a_g	3296		3026	
		1834		1623	
		1483		1342	
	a_u	1145		1023	
	b_{3g}	3353		3103	
		1342		1236	
	b_{3u}	1069	80.5	949	84.4
	b_{2g}	1065		943	
	b_{2u}	3381	26.8	3106	26.0
		879	0.01	826	0.03
	b_{1u}	3271	18.8	2989	14.3
		1592	7.4	1444	10.4
CH_2O	a_1	3111	47.0	2783[a]	75.5[c]
		1980	144.3	1746	74.0
		1649	12.2	1500	11.15
	b_2	3192	108.5	2843	87.6
		1363	22.7	1249	9.9
	b_1	1313	0.75	1167	6.5
H + C_2H_4(t.s.)	a'	3291	15.6		
		3278	456.1		
		1672	49.9		
		1583	54.2		
		1305	133.6		
		996	19.6		
		895	126.1		
		409	0.9		
		680i			
	a''	3392	360.5		
		3365	8.4		
		1328	0.1		
		1026	0.02		
		863	17.7		
		432	0.4		
H + CH_2O(t.s.)	a'	3154	49.1		
		1669	0.2		
		1484	192.5		
		1181	15.9		
		514	10.9		
		994i			
	a''	3256	83.2		
		1328	0.3		
		662	0.1		
CH_2O + H(t.s.)	a'	3197	250.5		
		1656	70.7		
		1408	63.3		
		978	75.8		
		757	24.2		
		1761i			

TABLE IV. *(Continued.)*

	a''	3314	155.8		
		1304	0.02 ·		
		480	4.4		
$C_2H_5\cdot$	a'	3268	272.5	3033^d	m^d
		3193	105.3	2920	m
		3123	71.6	2842	s
		1618	15.6		
		1589	8.6		
		1527	24.2	1366	m
		1099	6.4	1138	w
		1067	1.8		
		409	180.6	540	vs
	a''	3373	251.5	3112	s
		3229	80.1	2987	s
		1625	10.4	1440	m
		1295	3.1	1175	m
		851	16.7		
		111	3.5		
$CH_3O\cdot$	a'	3214	72.5		
		3141	85.0		
		1644	17.9		
		1557	14.0	1325^e	
		1192	17.9		
		1087	32.1	1015	
	a''	3230	90.4		
		1575	6.5		
		785	0.0		
$\dot{C}H_2OH$		3999	622.9	3650^e	
		3385	176.6		
		3243	39.6		
		1600	6.2	1459	
		1502	84.9	1334	
		1261	14.5	1183	
		1159	53.4	1048	
		824	116.7	569	
		452	142.8	420	

[a]See Ref. 24.

[b]See Ref. 62.

[c]See Ref. 58.

[d]See Ref. 63.

[e]See Ref. 8.

[f]The zero-point energy in kcal/mol for each of the structures at the HF/6-31G(2d) is C_2H_4 (33.9), CH_2O (18.0), $\dot{C}_2H_5$ (39.1), $CH_3\dot{O}$ (24.9), $\dot{C}H_2OH$ (24.9), H + C_2H_4 t.s. (34.1), H + CH_2O t.s. (18.9), and CH_2O + H t.s. (18.7).

Acknowledgments

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