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Theoretical Approach to the Thermochemistry and Barrier Heights of the First Steps of the Radical and Anionic Polymerization of Ethene and Formaldehyde

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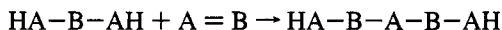
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The gas phase enthalpies of reaction and activation for the initiation and the first propagation steps of the radical and anionic polymerizations of ethene and formaldehyde were theoretically determined by high-level *ab initio* calculations, using respectively H^\bullet and H^- as model initiators. To correctly describe the behavior of the anionic reactions, the hydride anion must be described by a larger basis set than the hydrogen atom. It is found that the initiation step of the radical polymerization of ethene is favored, but, conversely, the anionic initiation step is favored in the case of formaldehyde. These results agree with the experimental evidence. They also demonstrate the capacity of theoretical chemistry to describe the behavior of these reactions when a high-level methodology is used.

I. Introduction

The discovery of new polymeric materials is very important from the industrial point of view. It can be greatly facilitated by *a priori* knowledge of the thermochemistry of the corresponding polymerization reactions.

One of us has proposed a very simple model for calculating the heat of polymerization of any monomer $A = B$. It is equal to the enthalpy change of the reaction¹



This simple model has been used in the study of the propagation enthalpies for the radical and anionic polymerization of formaldehyde and methanimine using *ab initio* calculations.²

In the present work, we try to discover which energy factors are responsible for the preferred modes of polymerization of two particular monomers, ethene and formaldehyde. Indeed, it is well-known that ethene is readily polymerized by a radical mechanism but not by an anionic one, while formaldehyde presents the opposite behavior.³

To rationalize these observations, we set out to determine theoretically the enthalpies of reaction and activation for the initiation and the first propagation steps of the radical and anionic polymerizations of these two monomers using high-level *ab initio* calculations and choosing respectively H^\bullet and H^- as model initiators.

With respect to the initiation step, the addition of hydrogen or hydride to the double bonds of ethene^{4–11} and formaldehyde^{11–14} have received considerable attention from the theoretical point of view, but to the best of our knowledge, a study of the propagation steps has not been made.

II. Methods and Calculation Details

Geometries and energies were calculated using the GAUSS-92 system of programs.¹⁵ The stationary point geometry (reactants, products, and saddle points) is optimized in restricted

(R) or unrestricted (U) second-order Møller–Plesset perturbation theory,¹⁶ MP2, with full electron correlation, using the 6-31G-(d,p) basis set of Pople¹⁷ for the ethene compounds and the 6-31+G(d,p) for the formaldehyde compounds, because the *sp* diffuse functions (+) are of great importance for compounds with free electron pairs.¹⁸ Analytical first and second derivatives of the energies were used for optimization, as implemented in GAUSSIAN 92. Then we made a single-point calculation at the fourth-order Møller–Plesset perturbation theory, with a frozen core approximation and single, double, triple, and quadruple replacements (MP4sdq), with larger basis sets [6-311+G(d,p), and 6-311++G(d,3pd)]. This approach presents two problems. First, it is well-known that, in the case of free radicals, the unrestricted Møller–Plesset perturbation theory converges slowly,^{19,20} and in the present work we used the fourth-order invariant quantity of Feenberg^{21,22} with the aim of taking the post-MP4 energy into account. Second, as the UHF wavefunction is not necessarily an eigenfunction of the S^2 operator, we find spin contamination in the radicals. This contamination was corrected by use of projection operators as implemented in GAUSSIAN 92 (PMP4 level: projected MP4).

In earlier thermochemistry and kinetics work^{23–27} we verified that the results at the post-PMP4 level of calculation are equivalent to more sophisticated methods, such as the quadratic configuration interaction (QCI) or the coupled-cluster (CC), with differences of about 1 kcal mol^{–1}.

With respect to the basis set, due to the size of the systems, we needed to strike a balance between the accuracy of the results and the computational possibilities. We used two basis sets: 6-311+G(d,p) (b2 basis), and the larger 6-311++G(d,3pd) (b4 basis). We tested these bases on a difficult system, the hydride anion, H^- (Table 1). Firstly, the diffuse function (+) is more important than the 3p polarization orbital (bases 2 and 3). Secondly, basis 4 yields good agreement with the more sophisticated basis 5, but the number of basis functions is noticeably less. Hence, the b4 basis was used for the initiation step and the b2 basis, for computational economy, for the first propagation step. As an independent test of the basis set selection, we also checked for agreement with the experimentally

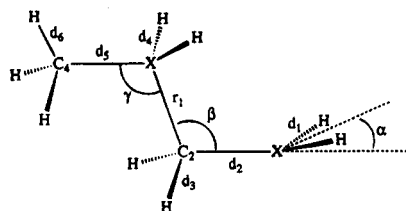
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TABLE 1: MP4 Energy (hartrees) with Different Basis Sets for the Hydride Anion

no.	basis	basis function	energy
1	CC-PVTZ ^a	14	-0.49560
2	6-311+G(d,3pd)	17	-0.50039
3	6-311++G(d,2pd)	15	-0.51859
4	6-311++G(d,3pd)	18	-0.52250 ^b
5	AUG-CC-PVTZ ^c	23	-0.52508

^a Correlation-consistent polarized valence triple- ζ sets.²⁸⁻³⁰ ^b Post-MP4 Freenberg correction: -0.52430 hartree. ^c Augmented CC-PVTZ.²⁸⁻³⁰

**Figure 1.** Internal coordinates definition in the molecules and in the transition structures. For ethene compounds, X is C, and for formaldehyde compounds, X is O.

known enthalpies of reaction, $\Delta H^\circ_R = \sum \Delta H^\circ_{fi}$, where ΔH°_{fi} are the standard enthalpies of formation of the related compounds.

III. Results and Discussion

The geometric parameters of all the stationary points are listed in Tables 2 and 3 for the ethene and formaldehyde compounds, respectively, using the internal coordinate system defined in Figure 1. The total energies are listed in Table 4.

In the only cases where comparison is possible, CH_2CH_2 , and CH_2O , the MP2/6-31G(d,p) or /6-31+G(d,p) geometries are in excellent agreement with the experimental values. In the transition structures, the geometries more closely resemble the reactants than the intermediate radicals or anions, as expected for very exothermic reactions (Table 5). Thus, the transition states are early, reactant-like. Moreover, this is the behavior that would be expected from Hammond's postulate. Our geometrical results are in excellent agreement with earlier

theoretical calculations, both for the $[\text{H}\cdot\cdot\text{CH}_2=\text{CH}_2]^{9,11}$ and for the $[\text{H}\cdot\cdot\text{CH}_2=\text{O}]^{11-14}$ transition states.

The energies and enthalpies of reaction are presented in Table 5 at the Feenberg level, using the required data given in Table 6. To avoid errors, we used experimental thermal corrections (TC) and heats of formation whenever possible. We can calculate the thermal corrections to the total energy using the classical formalism of statistical thermodynamics:

$$\text{TC} = H^\circ(T) - H^\circ(0) = \text{ZPE} + \int_0^T C_p dT$$

where C_p is the calorific capacity and ZPE the zero-point energy.

For the enthalpies of the radical reactions involving both small and large systems, we obtained an excellent agreement with experimental and theoretical values using the smaller b2 basis. The larger b4 basis did not improve on these results, except for the $\text{H}\cdot + \text{CH}_2\text{O}$ reaction. This agreement lent confidence to the values for the radical reactions using the b2 basis. For the anionic reactions the situation was completely different, with a difference between small and large systems. For the small systems, the b2 basis gave enthalpies of reaction very far from the experimental values: $\Delta = 16.43$, and $13.87 \text{ kcal mol}^{-1}$ for the ethene and formaldehyde, respectively. These discrepancies were due to the poor description of the hydride anion with this basis set, as we have already seen in the basis set selection (section II). When the best b4 basis was used, the agreement with experimental values was excellent, with errors of about $\pm 1 \text{ kcal mol}^{-1}$. For the large systems, fortunately, this effect of poor description was minimized and/or compensated, and the smaller b2 basis presented an acceptable behavior.

The energies and enthalpies of activation are listed in Table 7 at the Feenberg level. In earlier work,²³⁻²⁵ we have shown that the quality of the theoretical barrier height depends, fundamentally, on the amount of correlation energy taken into account, on the post-MP4 corrections, and on the spin decontamination when radicals are involved. Moreover, the QCI method gives similar values to the Feenberg ones. Unlike the enthalpies of reaction seen above, here there is less experimental or theoretical information available and, to the best of our knowledge, only for the radical initiation step ($\text{CH}_2=\text{CH}_2$ and $\text{CH}_2=\text{O}$).

TABLE 2: Geometrical Parameters^a of the Radical and Anionic Combinations with Ethene

param	C_2H_4	$\text{C}_2\text{H}_5^\cdot$	C_2H_5^-	$\text{C}_4\text{H}_9^\cdot$	C_4H_9^-	$\text{TSC}_2\text{H}_5^\cdot$	TSC_2H_5^-	$\text{TSC}_4\text{H}_9^\cdot$	TSC_4H_9^-
d_1	1.079	1.077	1.077	1.078	1.103	1.078	1.082	1.079	1.082
d_2	1.334	1.487	1.487	1.488	1.535	1.333	1.357	1.341	1.353
d_3	1.079	1.090	1.090	1.090	1.098	1.079	1.075	1.079	1.075
r_1				1.530	1.530	1.862	2.281	2.253	2.719
d_4				1.090	1.092			1.080	1.101
d_5				1.530	1.530			1.495	1.523
d_6				1.090	1.098			1.090	1.104
α		+7.5	-35.7	+8.3	-34.5	-5.5	+6.7	+2.5	+5.8
β		111.9	114.4	112.7	114.0	107.2	128.8	111.2	126.3
γ				112.7	114.0			104.5	119.0

^a Bonds in angstroms and angles in degrees. Experimental values:³¹ $\text{CH}_2=\text{CH}_2$ (D_{2h}): 1.086, 1.337 Å.

TABLE 3: Geometrical Parameters^a of the Radical and Anionic Combinations with Formaldehyde

param	CH_2O	$\text{CH}_3\text{O}^\cdot$	CH_3O^-	$\text{C}_2\text{O}_2\text{H}_5^\cdot$	$\text{C}_2\text{O}_2\text{H}_5^-$	$\text{TSCH}_3\text{O}^\cdot$	$\text{TSC}_2\text{O}_2\text{H}_5^\cdot$
d_2	1.223	1.389	1.359	1.353	1.293	1.215	1.241
d_3	1.097	1.092	1.124	1.103	1.124	1.100	1.095
r_1		1.092	1.124	1.409	1.565	1.663	1.813
d_5				1.423	1.397		1.415
d_6				1.090	1.100		1.090
β		112.5	115.0	112.1	113.5	101.7	103.6
γ				111.3	109.9		106.9

^a Bonds in angstroms and angles in degrees. Experimental values:³¹ CH_2O (C_{2v}): 1.12, 1.21 Å.

TABLE 4: Total Energies (hartrees) of the Stationary Points

compounds	MP4	PMP4	Feenberg
6-311+G(d,p) Basis Set			
H			-0.499 81
H ⁻	-0.487 83		-0.488 52
CH ₂ CH ₂	-78.384 06		-78.387 89
CH ₃ CH ₂ [•]		-78.947 20	-78.950 94
CH ₃ CH ₂ ⁻	-78.921 87		-78.925 96
C ₄ H ₉ [•]		-157.372 67	-157.379 76
C ₄ H ₉ ⁻	-157.358 41		-157.365 70
TSCH ₃ CH ₂ [•]		-78.879 33	-78.883 49
TSCH ₃ CH ₂ ⁻	-78.882 71		-78.887 65
TSC ₄ H ₉ [•]		-157.322 28	-157.330 25
TSC ₄ H ₉ ⁻	-157.308 86		-157.316 83
CH ₂ O	-114.269 11		-114.269 79
CH ₃ O [•]		-114.804 24	-114.804 93
CH ₃ O ⁻	-114.850 24		-114.851 37
C ₂ O ₂ H ₅ [•]		-229.091 28	-229.095 87
C ₂ O ₂ H ₅ ⁻	-229.163 58		-229.164 40
TSCH ₃ O [•]		-144.759 34	-114.761 39
TSC ₂ O ₂ H ₅ [•]		-229.038 83	-229.043 03
6-311++G(d,3pd) Basis Set			
H			-0.499 81
H ⁻	-0.522 50		-0.524 30
CH ₂ CH ₂	-78.406 74		-78.410 29
CH ₃ CH ₂ [•]		-78.974 17	-78.977 70
CH ₃ CH ₂ ⁻	-78.955 80		-78.959 59
TSCH ₃ CH ₂ [•]		-78.904 83	-78.908 77
TSCH ₃ CH ₂ ⁻	-78.924 00		-78.928 90
CH ₂ O	-114.280 84		-114.281 45
CH ₃ O [•]		-114.821 99	-114.824 97
CH ₃ O ⁻	-114.872 05		-114.874 31
TSCH ₃ O [•]		-114.774 65	-114.776 74

TABLE 5: Energies and Enthalpies of Reaction (kcal mol⁻¹) at Room Temperature

reaction	ΔE_R	ΔH_R^a	exptl ^b
6-311+G(d,p) Basis Set			
H [•] + CH ₂ CH ₂	-39.68	-35.93	-36.65
H ⁻ + CH ₂ CH ₂	-31.10	-28.62	-12.19
CH ₃ CH ₂ [•] + CH ₂ CH ₂	-25.68	-22.97	-22.45
CH ₃ CH ₂ ⁻ + CH ₂ CH ₂	-32.53	-26.65	-22.94
H [•] + CH ₂ O	-22.17	-17.13	-22.02 ± 1.0
H ⁻ + CH ₂ O	-58.40	-54.42	-40.55 ± 2.5
CH ₃ O [•] + CH ₂ O	-13.27	-9.56	-12.63 ± 1.0
CH ₃ O ⁻ + CH ₂ O	-27.76	-24.11	-28.36 ± 2.5
6-311++G(d,3pd) Basis Set			
H [•] + CH ₂ CH ₂	-42.42	-38.67	-36.65
H ⁻ + CH ₂ CH ₂	-15.70	-13.22	-12.19
H [•] + CH ₂ O	-27.42	-22.38	-22.02 ± 1.0
H ⁻ + CH ₂ O	-43.02	-39.04	-40.55 ± 2.5

^a $\Delta H_R = \Delta E_R + \Delta TC$. ^b $\Delta H_R = \sum \Delta H_{fi}$ (Table 6).

Firstly, for the radical reaction initiation steps, H[•] + CH₂=CH₂ and H[•] + CH₂=O, we analyzed the influence of the basis set. The only available experimental information is the enthalpy of reaction, ΔH_R , and in accordance with the good behavior of the b4 basis set in the description of this enthalpy, we obtain for the enthalpies of activation the values $\Delta H^\ddagger = 1.03$ and 3.73 kcal mol⁻¹, respectively. The first value is in good agreement with other theoretical results,^{11,40} taking into account that the value 1.8 kcal mol⁻¹ of Sosa and Schlegel¹¹ was obtained with the smaller 6-31G(d) basis. The second is in the range of $3-8$ kcal mol⁻¹.^{11,13,14,42} To establish this range, the MP3 result without the spin projection of Saebø et al.¹² ($\Delta H^\ddagger = 12.4$ kcal mol⁻¹) was not considered because Sosa and Schlegel¹¹ showed that spin projection is crucial to the quality of the barrier height. Therefore, the b2 basis seems to overestimate the barrier height at this level. The barrier heights of the large radical systems, CH₃CH₂[•] + CH₂=CH₂, and

TABLE 6: Enthalpies of Formation (kcal mol⁻¹) and Thermal Corrections^a (kcal mol⁻¹) at Room Temperature

	ΔH_f°	ref	TC	ref.
H	52.10	31	1.48	31
H ⁻	33.23	31	1.48	31
CH ₂ CH ₂	12.55	31	33.38	31
CH ₃ CH ₂ [•]	28.00	32	38.61	33
CH ₃ CH ₂ ⁻	33.59	34	37.34	35
C ₄ H ₉ [•]	18.1	36	74.7	37
C ₄ H ₉ ⁻	23.2	37	73.6	37
CH ₂ O	-25.98 ± 0.12	41	18.50	31
CH ₃ O [•]	4.1 ± 0.9	38	25.02	2
CH ₃ O ⁻	-33.3 ± 2.4	39	23.96	2
C ₂ O ₂ H ₅ [•]	-34.51	2	47.23	2
C ₂ O ₂ H ₅ ⁻	-87.64	2	46.11	2

^a $TC = H^\circ(T) - H^\circ(0) = ZPE + \int C_p dT$.

TABLE 7: Energies and Enthalpies of Activation (kcal mol⁻¹) at Room Temperature

reaction	ΔE^\ddagger	ΔH^\ddagger^a	other values
6-311+G(d,p) Basis Set			
H [•] + CH ₂ CH ₂	2.64	2.84	1.8 ^b , 2.04 ^c
H ⁻ + CH ₂ CH ₂	-7.05		
CH ₃ CH ₂ [•] + CH ₂ CH ₂	5.38		
CH ₃ CH ₂ ⁻ + CH ₂ CH ₂	-1.87		
H [•] + CH ₂ O	5.15	5.95	12.4 ^d , 4.6 ^b 8 ^e , 5.6 ^f
CH ₃ O [•] + CH ₂ O	19.88		
6-311++G(d,3pd) Basis Set			
H [•] + CH ₂ CH ₂	0.83	1.03	
H ⁻ + CH ₂ CH ₂	3.57		
H [•] + CH ₂ O	2.83	3.73	

^a $\Delta H^\ddagger = \Delta E^\ddagger + \Delta ZPE$ (with the harmonic frequencies of ref 11).

^b Reference 11. ^c Reference 40. ^d Reference 12. ^e Reference 13. ^f Reference 14.

CH₃O[•] + CH₂=O using the small b2 basis, would therefore be overestimated, and values of about $\Delta H^\ddagger \approx 4$ and 17 kcal mol⁻¹, respectively, should be more recommendable.

Secondly, we analyzed the anionic reactions. Using CH₂=O as monomer, we did not find any transition structure, possibly due to the large exothermicity of these anionic reactions (Table 5). These reactions thus evolve presumably without a barrier on the electronic potential energy surface. With respect to the CH₂=CH₂ monomer, and with use of the small b2 basis set, we found surprisingly that the transition structure was more stable than the reactants. The anomalous behavior of this basis in anionic reactions has already been seen in the enthalpy of reaction analysis. When we used the b4 basis, the barrier height of the H⁻ + CH₂=CH₂ reaction changed to $+3.57$ kcal mol⁻¹. With this criterion, and taking into account that this basis set effect is minimized and/or compensated by other effects in large systems (as we have already seen in the enthalpy of reaction analysis), we concluded that the CH₃CH₂⁻ + CH₂=CH₂ reaction also evolves without a barrier on the electronic potential energy surface.

With this thermochemical and barrier height information, we could analyze the competition between radical and anionic polymerization. Using CH₂=CH₂ as monomer, the radical reaction is favored (Tables 5 and 7). Using CH₂=O as monomer, we obtained the opposite behavior. These results are in agreement with the available experimental information on the polymerization reactions. They also demonstrate the capacity of theoretical chemistry to predict the behavior of such reactions.

IV. Conclusions

This paper reported theoretical calculations of the thermochemical and barrier height data of the first steps of polymer-

ization using $\text{CH}_2=\text{CH}_2$ and $\text{CH}_2=\text{O}$ as monomers. Firstly, we have shown that the initiation step of the anionic reactions, when the hydride anion is a reactant, needs a more complete basis set than the radical reactions due to the difficulty of correctly describing this anion. Secondly, using high-level ab initio calculations, and testing the theoretical results against the available experimental information, we concluded that the initiation step of the radical polymerization is favored for the $\text{CH}_2=\text{CH}_2$ monomer, and the anionic polymerization is favored for the $\text{CH}_2=\text{O}$ monomer.

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