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On the Importance of Prereactive Complexes in Molecule−Radical Reactions: Hydrogen Abstraction from Aldehydes by OH

J. Raúl Alvarez-Idaboy,[†,‡] Nelaine Mora-Diez,[†,§] Russell J. Boyd,[§] and Annik Vivier-Bunge*,[||]

Contribution from the Laboratorio de Química Computacional y Teórica, Facultad de Química, Universidad de La Habana, Habana 10400, Cuba, Instituto Mexicano del Petróleo, 07730 México, D.F., México, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3, and Departamento de Química, Universidad Autónoma Metropolitana, Iztapalapa, 09340 México, D.F., México

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Abstract: In this work, the OH + formaldehyde and OH + acetaldehyde reactions have been characterized using accurate ab initio methods with large basis sets. The results clearly indicate that the reaction occurs by hydrogen abstraction, and that the OH addition channel is unfavorable. Close to zero (for formaldehyde) and negative (for acetaldehyde) activation energy values are obtained, which are in excellent agreement with the experimentally observed values. The reaction rate constants, calculated using the classical transition-state theory as applied to a complex mechanism involving the formation of a prereactive complex, reproduce very well the reported experimental results. Consideration of the prereactive complex is shown to be essential for the determination of the height of the energy barrier and thus for the correct calculation of the tunneling factor.

1. Introduction

Carbonyl compounds are directly emitted into the troposphere from biogenic and anthropogenic sources,[1] and they are also formed in large concentrations as end products in the oxidation reactions of hydrocarbons. They are known to enter the tropospheric reactants pool mainly through one reaction,[2] that is, the reaction with the OH radical, according to the following overall equation:

$$\mathrm{RHC=O + OH^{\bullet} \rightarrow [RC=O]^{\bullet} + H_2O} \qquad (1)$$

Bimolecular rate constants for the OH reaction with a variety of aldehydes have been measured, and their Arrhenius parameters have been reported,[2,3] but there are serious uncertainties as to the reaction mechanism. The negative temperature dependence of the rate constant is well established, except in formaldehyde, for which the activation energy is known to be almost zero, most experimental results varying between +0.4 and −0.4 kcal/mol.[3] It suggests the possibility that the reactions of aldehydes with the hydroxyl radical, in general, occur by an addition−elimination mode,[4,5] since many addition reactions of OH show overall negative temperature dependence. Niki et al.[7] ruled out the formation of HC(O)OH + H but not the reaction

$$\mathrm{H_2C=O + OH^{\bullet} \rightarrow [H_2C=O(OH)]^{\bullet} \rightarrow [HC=O]^{\bullet} + H_2O} \qquad (2)$$

However, for formaldehyde it is believed that only hydrogen abstraction occurs. Recent experimental work by Butkovskaya and Setser[8] using infrared chemiluminescence confirms that the results are consistent with many polyatomic reactions in which a H atom is directly abstracted. For acetaldehyde, Michael et al.[4] have presented a very complete mechanistic discussion of their experimental data of the OH-acetaldehyde reaction in the range 244−528 K. They conclude that the preferred process appears to be the abstraction of the aldehydic hydrogen atom. Taylor et al.[5] favor an addition−elimination mechanism at low temperatures. Atkinson[9] postulated that the reaction proceeds via overall H-atom abstraction, although the initial reaction possibly involves the OH radical addition to the >C═O bond system However, it is not clear why a hydrogen abstraction reaction presents a negative activation energy and why the overall OH addition to the double bond does not occur.

It is interesting to know the energetics of the target reactions. These can be calculated using the values of the bond energies given by Berkowitz et al.,[6] wherein all original references can be found. The bond enthalpies (in kcal/mol) are ΔH_{298} (HO−H) = 119.30 ± 0.05, ΔH_{298} (H−CHO) = 88.04 ± 0.16, ΔH_{298} (H−CH$_2$ CHO) = 94.3 ± 2.2, and ΔH_{298} (CH$_3$ CO−H) = 89.4 ± 0.3. Consequently, the heats of reaction at 298 K in kcal/mol are estimated to be:

$$\mathrm{H_2C=O + OH^{\bullet} \rightarrow [HC=O]^{\bullet} + H_2O} \qquad \Delta H_{298}\ -31.3 \pm 0.2 \quad (3)$$

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[*] Corresponding author. E-mail: annik@xanum.uam.mx.

[†] Universidad de La Habana.

[‡] Instituto Mexicano del Petróleo, 07730 México, D.F., México.

[§] Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3.

[||] Departamento de Química, Universidad Autónoma Metropolitana, Iztapalapa, 09340 México, D.F., México.

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$$CH_3CH{=}O + OH^\bullet \rightarrow [CH_3C{=}O]^\bullet + H_2O \qquad \Delta H_{298}\ -29.90 \pm 0.23 \quad (4)$$

$$CH_3CH{=}O + OH^\bullet \rightarrow [CH_2CH{=}O]^\bullet + H_2O \qquad \Delta H_{298}\ -25 \pm 2 \quad (5)$$

The behavior of reactions having a negative temperature dependence has been successfully described, for systems at low pressures, by Mozurkewich and Benson,[10] and for systems at high pressures, by Singleton and Cvetanovic.[11] In this case, several explanations have been proposed, which are summarized in ref 2. Three of them maintain the idea of an elementary reaction but suggest a modification of the preexponential factor in the Arrhenius equation to allow for a term $T^{-1.5}$. Singleton and Cvetanovic[11] propose a complex mechanism and explain the occurrence of these negative activation energies as being due to the reversible formation of a loosely bound prereactive complex which is formed without activation energy, followed by a second reaction, which is irreversible, and whose transition-state energy is lower than the energy of the separated reactants.

A prereactive complex has, in fact, been identified in several OH-addition reactions to alkenes,[12−15,19] haloethanes[16] and aromatic hydrocarbons (toluene and xylenes).[17,18] In a recent study on the OH addition to substituted alkenes,[19] we have shown, by calculating the rate constants for the individual steps, that the mechanism proposed by Singleton and Cvetanovic[11] provides a clear explanation of the experimental data.

Prereactive complexes seem to be common in all radical−molecule reactions, and they are due mainly to the long-range Coulombic interactions between the reactant molecules. In fact, in the prereactive complex formed between the OH radical and an unsaturated hydrocarbon, it is the H atom of the OH radical which points toward the π electrons of the double bond, even though the OH group has to flip over in order to form the C−O bond in the adduct.[12−15,17−19] If the reaction occurs at pressures high enough for these complexes to be collisionally stabilized, and if the energy barriers are small, they are likely to play an important role. Sekušak and Sabljić have also found that such intermediate complexes play a key role in hydrogen abstraction reactions from haloethanes.[16]

Considering the OH + aldehyde reactions, if reaction 1 were elemental with a negligible energy barrier, the rate constant should depend essentially on the preexponential factor. Thus, because formaldehyde has two abstractable hydrogen atoms, one would expect its reaction to be about twice as fast as the one of acetaldehyde. This disagrees with the observed experimental results, the reported rate constants at 298 K for OH-aldehyde reactions being 5.54 × 10^9 L mol^{-1} s^{-1} [20] and 6.03 × 10^9 L mol^{-1} s^{-1} [21] for formaldehyde, and 9.55 × 10^9 L mol^{-1} s^{-1} [20] for acetaldehyde. The experimentally determined Arrhenius parameters,[20,21] however, do indicate a very small negative activation energy and a preexponential factor which is larger for formaldehyde than for acetaldehyde (see Table 1). On the other hand, a higher reactivity of acetaldehyde is in line with the fact that the inductive effect of the methyl group should help stabilize the corresponding transition state.

Table 1. Selected Experimental Data for the Reactions: XCHO + OH = H_2 O + XCO[a]

X	T(K)	A	E_a (kcal/mol)	k (L/mol s)	ref
H	200−300			6.03 × 10^9	21
	240−300	5.18 × 10^9	−0.04	5.54 × 10^9	20
	298			4.67 × 10^9	32
	200−1600	2.86 × 10^9	−0.45	6.08 × 10^9	33
CH_3	200−300	3.37 × 10^9	−0.54	8.35 × 10^9	21
	240−530	3.37 × 10^9	−0.62	9.55 × 10^9	20
	298			8.73 × 10^9	34

[a] Rate constants in column 5 are at 298 K.

Using quantum chemical methods, it is possible to calculate energies of intermediate structures and transitions states with a reasonable degree of precision, and thus to model the reaction path of a reaction. Indeed, a 0.996 correlation factor was recently obtained[19] between our ab initio calculated effective activation energies and the experimental rate constants, for the OH radical addition to a series of substituted ethenes.

Previous theoretical work on the formaldehyde + OH reaction has been reported by Dupuis and Lester[22] using multiconfiguration self-consistent-field Hartree−Fock (MCSCF) and configuration interaction (CI) wave functions. They predicted a positive activation barrier for the aldehydic hydrogen OH abstraction reaction, of 5.5 kcal/mol. Francisco[23] used the ab initio Møller−Plesset method up to fourth order (MP4) to determine the barriers and energetics. He obtained a small positive barrier of 1.2 kcal/mol and a rate constant in very good agreement with experiment. The formation of a prereactive complex was not considered in this paper. In the present work, his results will be discussed and compared with ours. The weakly bound complexes of the hydroxyl radical with formaldehyde and acetaldehyde were calculated recently by Aloisio and Francisco[24] using a density functional approach.

Taylor et al.[5] have investigated the reaction of hydroxyl radicals with acetaldehyde in a wide temperature range using a quantum RRK model to describe the competition between addition and abstraction. They conclude that different reaction mechanisms occur, depending on the temperature, and that OH addition followed by CH_3 elimination is the dominant reaction pathway between 295 and 600 K. Moreover, they claim that the H-atom elimination pathway is largely insignificant, except possibly at the lowest temperatures. Their calculated rate constant, at 298 K, however, is about a factor of 10 too low.

In this work, the OH + formaldehyde and the OH + acetaldehyde reactions shall be characterized using several methods and large basis sets to obtain an accurate reaction profile and to reproduce the experimentally observed values of the activation energy (approximately zero[8,20] for formaldehyde,

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−0.5 kcal/mol for acetaldehyde.[5,20] With the corresponding partition functions, the effective rate constants will then be calculated, using classical transition-state theory and the proposed hydrogen abstraction mechanism. The results will be compared with the experimental data and with the results of previous calculations. Our aim is the following:

(i) to show that the same complex mechanism can be applied to both the formaldehyde and the acetaldehyde reactions,

(ii) to show that consideration of the prereactive complex is essential for the correct calculation of the rate constant, when the tunneling factor is significant, as is the case in hydrogen abstraction reactions, and

(iii) to define a theoretical methodology which is able to reproduce theoretically the rate constants of the two reactions.

2. Computational Methodology

Electronic structure calculations have been performed with the system of programs Gaussian98.[25] Unrestricted ab initio methods were used to calculate the energies of the radicals. The correlation energy corrections were introduced with Møller−Plesset perturbation theory and with the coupled cluster method at the CCSD(T) level.

All geometries were fully optimized at the MP2(FC)/6-311++G(d,p) level, and the character of the transition states was confirmed by a frequency calculation, performed at the same level, and presenting only one imaginary frequency corresponding to the expected transition vector.

We assume that the reaction occurs according to the following two-step mechanism:

$$\text{Step 1:}\;\; \mathrm{RHC{=}O + OH^{\bullet} \rightleftharpoons [RHC{=}O\cdots HO^{\bullet}]} \qquad (6)$$

$$\text{Step 2:}\;\; \mathrm{[RHC{=}O\cdots HO^{\bullet}] \rightarrow RC{=}O^{\bullet} + H_2O} \qquad (7)$$

involving a fast preequilibrium between the reactants and the prereactive complex followed by an internal rearrangement leading to the elimination of a water molecule. If k_1 and k_{-1} are the rate constants for the first step and k_2 corresponds to the second step, a steady-state analysis leads to a rate constant for the overall reaction which can be written as:

$$k = \frac{k_1 k_2}{k_{-1}} = \left(\frac{\mathrm{A}_1 A_2}{A_{-1}}\right) \exp[-(E_1 + E_2 - E_{-1})/RT] \qquad (8)$$

Since E_1 is zero, the net activation energy for the overall reaction is:

$$E_a = E_2 - E_{-1} = (E_{TS} - E_{P-R}) - (E_R - E_{P-R}) = E_{TS} - E_R \qquad (9)$$

where $\mathrm{E_R}$, E_{P-R}, and E_{TS} are the total enegies of the reactants, the prereactive complex, and the transition state, respectively. Thus, the activation energy at high pressures can be calculated as the difference between the energy of the TS and that of the reactants, without having to obtain the prereactive complex.

Applying basic statistical thermodynamic principles, the equilibrium constant of the fast preequilibrium between the reactants and the prereactive complex may be obtained as:

$$K_{\mathrm{eq}} = \frac{Q_{\mathrm{P-R}}}{Q_{\mathrm{R}}} \exp[(E_{\mathrm{R}} - E_{\mathrm{P-R}})/RT] \qquad (10)$$

Under high-pressure conditions, an equilibrium distribution of reactants is mantained in a unimolecular process, and the classical TST formula can be applied[26] to calculate k_2:

$$k_2 = \kappa \frac{k_{\mathrm{B}}T}{h} \frac{Q_{\mathrm{TS}}}{Q_{\mathrm{P-R}}} \exp[(E_{\mathrm{P-R}} - E_{\mathrm{TS}})/RT] \qquad (11)$$

where κ is the tunneling factor. The reaction path degeneracy is not included in this expression since the rotational symmetry numbers are already introduced in the calculation of the partition functions. The partition functions are obtained from the rotational constants and the vibrational frequencies of the ab initio calculations. The energy differences include the zero-point corrections.

The rate constants of the hydrogen abstraction reactions have been calculated in two different ways, for comparison. In the first one, the two-step mechanism described above is assumed to hold, and the effective rate constant is obtained according to the following equation:

$$k = K_{\mathrm{eq}} k_2 \qquad (12)$$

In the second one, it is assumed that the reaction is elemental, the formation of the prereactive complex is ignored, and the rate constant is calculated as:

$$k = \kappa \frac{k_{\mathrm{B}}T}{h} \frac{Q_{\mathrm{TS}}}{Q_{\mathrm{R}}} \exp[(E_{\mathrm{R}} - E_{\mathrm{TS}})/RT] \qquad (13)$$

It is important to note that these two expressions turn out to be identical *except* for the value of the tunneling factor κ, which depends on the activation barrier of the elemental process in which the hydrogen atom is abstracted.

The tunneling correction is defined as the ratio of the quantum-mechanical to the classical barrier crossing rate, and it is calculated assuming an unsymmetrical, one-dimensional Eckart function barrier.[27] For this, we have used the numerical integration program of Brown.[28] The Gaussian quadrature was performed at 40 points, for increased accuracy. A useful measure of the barrier width is the full width of the barrier at half its height in the forward direction, $\Delta s_{1/2}$. Its value will also be reported.

3. Results and Discussion

The OH radical attack on aldehydes appears to occur in the following way. At first, the positively charged hydrogen atom of the OH radical approaches a lone pair of the oxygen atom to form a very stable prereactive complex, whose energy is found to be more than 3 kcal/mol lower than the energy of the reactants. Several such prereactive complexes were identified in the case of the formaldehyde OH reaction, but in the most stable one, the OH radical lies in the plane of the CHO group (Figures 1 and 2). From this structure, the oxygen of OH may flip, in the plane, toward the hydrogen to be abstracted as the energy increases to a maximum at the transition state. Another process may also occur, which leads to OH addition. Starting from the same prereactive complex, the OH group may flip in a plane perpendicular to the CHO plane, in such a way as to let the oxygen atom approach the carbon atom of the aldehyde from above. It will be shown that the corresponding transition state has a considerably larger energy than in the abstraction channel.

A third process could be considered, in which the OH radical would attack acetaldehyde at the methyl group and produce the formylmethyl radical, $\mathrm{CH_2\,CHO}$. Indeed, this hydrogen abstrac-

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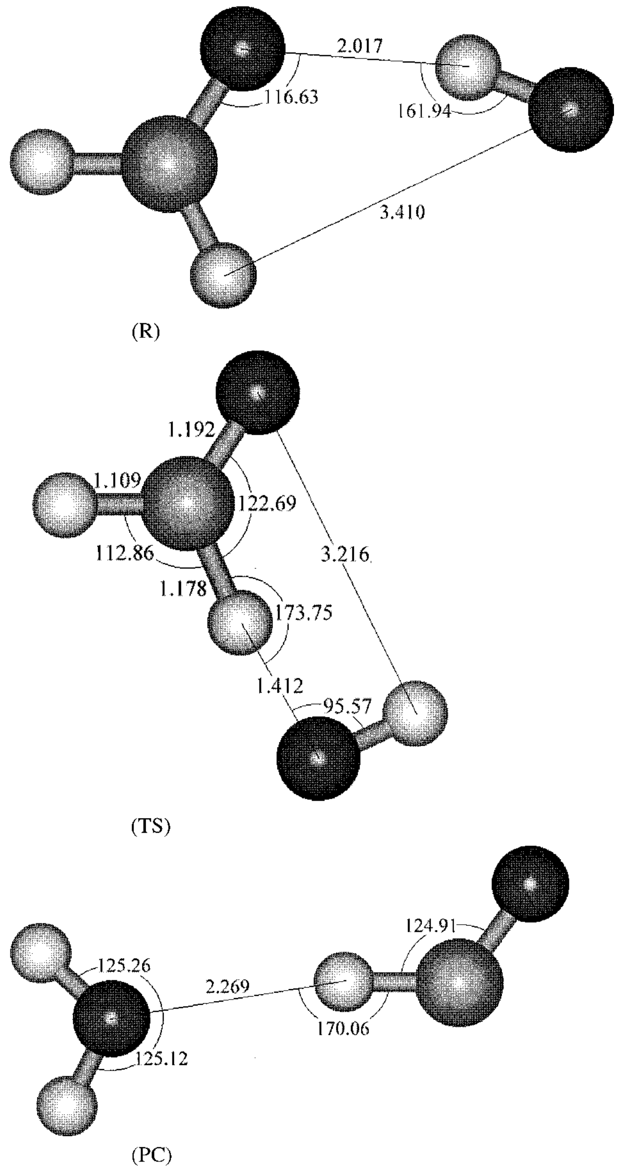

Figure 1. Optimized structures in the OH + formaldehyde hydrogen abstraction reaction, as obtained at the MP2(FC)/6-311++G(d,p) level.

tion is 25 kcal/mol exothermic. However, the position of the OH hydrogen atom in the prereactive complex is very far from the methyl hydrogens. In addition, the energy of the methyl C−H bond is about 5 kcal/mol larger than that of the carbonyl C−H bond (eqs 4 and 5).

The proposed abstraction mechanism resembles closely the one described by Sekušak and Sabljić[16] in the case of the hydrogen abstraction reaction from haloethanes. These authors have stressed the importance of the prereactive complex and the role of a strongly electronegative atom in guiding the reaction from the very beginning and in lowering the transition-state energy.

The MP2 optimum geometries of the intermediate structures along the hydrogen abstraction reaction paths are shown in Figures 1 and 2, and the relevant parameters have been indicated on the figures. The geometries of the prereactive complexes obtained for OH + formaldehyde and OH + acetaldehyde are very similar to those obtained by Aloisio and Francisco[24] using a density functional method.

Both the hydrogen abstraction and the OH addition channels have been investigated in the case of the formaldehyde reaction. For acetaldehyde, however, we have studied only the abstraction channel.

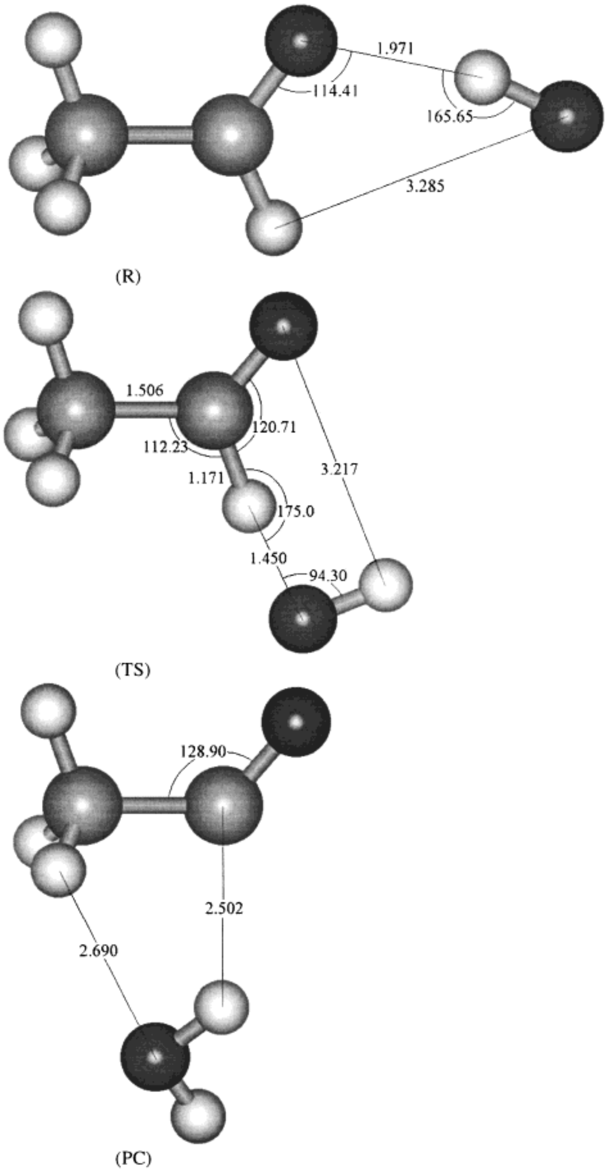

Figure 2. Optimized structures in the OH + acetaldehyde hydrogen abstraction reaction, as obtained at the MP2(FC)/6-311++G(d,p) level.

The transition states corresponding to the addition and abstraction channels in formaldehyde + OH are shown in Figure 3. Comparing their structures with the ones for similar reactions, it is possible to explain why the abstraction transition state is the one with the lowest energy. The transition state for hydrogen abstraction from ethane[29] calculated at the same level, occurs considerably later, when the O$\cdots$H distance between the oxygen atom of the OH radical and the hydrogen atom which is abstracted is 1.33 Å, as compared to 1.41 Å for formaldehyde, indicating that the hydrogen atom in formaldehyde is less tightly bound. On the contrary, the transition state for addition to formaldehyde occurs much later than, for example, the one in the ethene + OH reaction[13] (the C$\cdots$O distance in this reaction is 2.06 Å, as compared to 1.83 Å).

It can also be observed that, in the abstraction transition-state structures, the C$\cdots$H and O$\cdots$H distances in the case of

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Table 2. Relevant Barriers (including the ZPE) and Heat of Reaction Energies (ΔH), (including the thermal energy corrections, TCE), in kcal/mol, for the OH Hydrogen Abstraction Reaction in Formaldehyde and Acetaldehyde and for the OH Addition to Formaldehyde

	E_{-1}	E_2 (abstraction)	E_a^{eff} (abstraction)	ΔH (abstraction)	E_2 (addition)	E_a^{eff} (addition)	ΔH (addition)
			Formaldehyde				
PMP2	3.24	6.33	3.09	−35.79	11.05	7.81	−16.07
PMP4	2.96	4.94	1.98	−32.01	10.81	7.86	−15.60
CCSD(T)	3.03	3.19	0.03	−28.13	12.34	9.31	−17.00
experimental			−0.04[a]	−33.62[b]			
			−0.05 ± 0.3[c]				
			Acetaldehyde				
PMP2	4.17	5.60	1.43	−31.84			
CCSD(T)	4.18	2.47	−1.71	−27.14			
experimental			−0.62[a]				
			−0.54[d]				
			−1.3[e]				

[a] Reference 20. [b] Calculated from data in ref 20. [c] Reference 8. [d] Reference 21. [e] Reference 5.

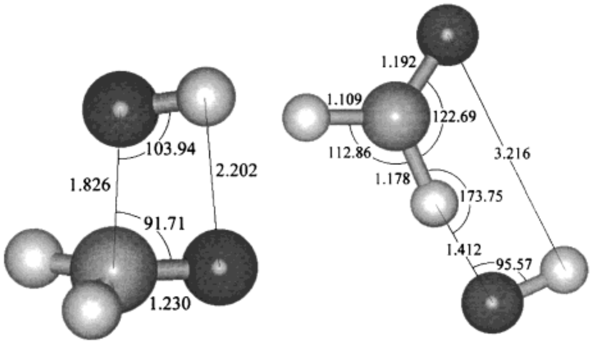

Figure 3. OH addition and hydrogen abstraction and transition-state structures of the OH + formaldehyde reaction, optimized at the MP2-(FC)/6-311++G(d,p) level.

acetaldehyde indicate that it is formed earlier than for formaldehyde. The effect is probably due to the electronic effect of the methyl group, which increases the electronic density at the carbonyl carbon, favoring the abstraction of the hydrogen atom.

The symmetries of the prereactive complexes and of the transition states are $^2A'$, implying that the radical electron is in the plane, where it can attack the aldehyde.

In Table 1, selected experimental data for the rate constants and the Arrhenius parameters of the OH + aldehyde reactions are reported. Considerable differences are observed among the experimental parameters reported for the formaldehyde reaction.

The calculated total energies, the zero-point vibrational energy corrections (ZPE) of the reactants, the prereactive complex, the transition state, the product complex, and the separated products along the reaction paths for the OH reaction with formaldehyde and acetaldehyde are given as Supporting Information for the methods employed in this work. The thermal corrections (TCE) are also included for the main stationary points. In these tables, both corrections are given at the MP2 level, and these values are used to obtain the CCSD(T) energy differences. For the abstraction reactions, spin contamination is only significant (but small) at the transition states: it is 0.779 for the formaldehyde reaction and 0.774 for acetaldehyde, and in the MP2 calculations it is completely eliminated by projection. Thus, for these particular reactions, the CCSD(T) method applied to an MP2 optimized geometry can be expected to yield reliable energies. In contrast, results obtained in the OH addition channel indicate that spin contamination is much more important, 0.919, and it is not eliminated completely by projection. This is not unusual. In fact, Sekušak et al.[15] also observed, in the case of the OH-alkene reactions, that the single-point coupled cluster method does not give satisfactory results, probably due to the fact that the geometry is not optimized at this level and that spin contamination is not eliminated. Thus, for the addition channel, the PMP2 results are expected to be more reliable.

The stabilization energy of the prereactive complexes (which is equal to E_{-1}), the effective activation energies ($E_a^{eff} = E_2 - E_{-1}$) at 0 K, and the heat of reaction ($E_P - E_R$), at 298 K, of the formaldehyde + OH and acetaldehyde + OH reactions are given in Table 2 for the methods employed. The ZPE corrections have been included in all the energy differences, except in the case of the heats of reaction, which include the TCE.

Concerning the stabilization energies of the prereactive complexes, the sets of results obtained with the three different methods agree to within 3 kcal/mol for the formaldehyde reaction and about 4 kcal/mol for the acetaldehyde reaction. Aloisio and Francisco[24] obtained 8.9 kcal/mol for the former one, which is not surprising since density functional methods in general are known to emphasize positive interactions in weakly bound systems.

It can be seen that the PMP2 effective activation energies are overestimated and that, in these reactions, the CCSD(T) seems to be the most appropriate method to use to obtain good activation energies. Indeed, the CCSD(T) results agree remarkably well with the experimental values.

On the basis of the energy barriers for addition and abstraction in the case of formaldehyde, it is clear why the addition pathway is not favored in these reactions. The difference between the CCSD(T) energies of the transition states for these two channels is more than 8 kcal/mol. It is interesting to note that almost half of this energy difference arises from the zero-point correction energies. This is clearly due to the fact that the transition state for addition is expected to be much tighter than the one for abstraction, and thus its vibrational zero-point correction is larger. Even considering that the CCSD(T) method is not adequate for the addition channel, the difference in energy between the transition states for addition and abstraction is also large enough at the PMP2 and PMP4 levels to guarantee that only the abstraction channel occurs.

The energy profiles obtained using the CCSD(T) energies are shown in Figures 4 and 5. The formation of a stable prereactive complex followed by a transition state whose energy is lower (or very slightly higher, in the case of formaldehyde) than the energy of the reactants is clearly observed.

Product complexes are formed, which present hydrogen bonds between the water molecule and the aldehydic radicals and which are about 2 kcal/mol more stable than the corresponding separated products. The best values for the heats of reaction are the ones obtained from the PMP2 energies with TCE

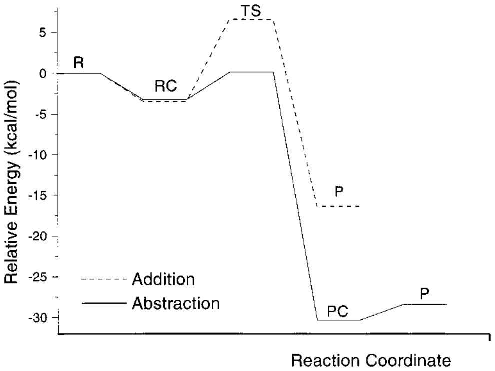

Figure 4. Reaction profile for OH addition and hydrogen abstraction in the OH + formaldehyde reaction. In this graph, the best energies were used in each case: CCSD(T), for abstraction, and PMP2, for addition.

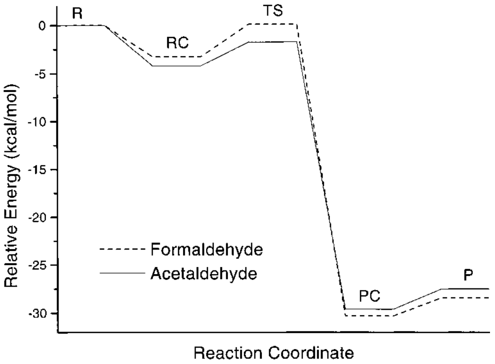

Figure 5. Reaction profile for OH hydrogen abstraction in formaldehyde and acetaldehyde using the calculated CCSD(T) energy values.

Table 3. Partition Functions (*Q*), Preexponential Factors (*A*) (Not Including Tunneling Correction), and Imaginary Frequencies ($\bar{\nu}_i$ in cm^{-1}) of the TS of the OH + Formaldehyde and OH + Acetaldehyde Hydrogen Abstraction Reactions, Calculated at the MP2(FC)/6-311++G(d,p) Level[a]

reaction	HCHO + OH	CH_3CHO + OH
Q_{OH}	6.02509×10^7	6.02509×10^7
Q_{RCOH}	4.63150×10^9	3.11890×10^{11}
Q_{RCOH} corr (*)		9.88349×10^{11}
Q_{P-R}	1.45889×10^{12}	3.14575×10^{14}
Q_{TS}	7.94138×10^{13}	1.44177×10^{14}
Q_{TS} corr (*)	6.37514×10^9	1.88582×10^{15}
A	1.42×10^9	1.97×10^8
$\bar{\nu}_i$	1522	1066

[a] The indicated partition functions (*) have been corrected for internal rotations (see text), the other values are those calculated by Gaussian98.

corrections. The CCSD(T) energies yield poorer results, as compared with the experimental results, but all of the theoretical methods employed reproduce correctly the observed trends.

All quantities necessary for the calculation of the rate constants of the abstraction reactions are given in Table 3. Three (for formaldehyde) and four (for acetaldehyde) low frequencies are present in the hydrogen abstraction transition states, in addition to the imaginary frequency. Of these, two (for formaldehyde) and three (for acetaldehyde) can be viewed as internal rotations. Thus, in the partition function of the transition state, their harmonic contributions have been replaced by those of free rotors.[30] The vibration corresponding to the free rotor motion of the methyl group in acetaldehyde was also replaced in the partition function.

Table 4. Tunneling Parameters and Rate Constants of the OH + Formaldehyde and OH + Acetaldehyde Hydrogen Abstraction Reactions Calculated Using CCSD(T)/6-311++G(d,p)//MP2(FC)/6-311++G(d,p) and Both the Direct and the Complex Mechanisms[a]

direct mechanism	HCHO + OH	CH_3CHO + OH
κ	*b*	*b*
$\Delta s_{1/2}$ (Å)	*b*	*b*
k (L/mol·s)	1.17×10^9	3.53×10^9
complex mechanism	HCHO + OH	CH_3CHO + OH
κ	5.69	2.47
$\Delta s_{1/2}$ (Å)	0.30	0.38
K_{eq} (L/mol)	1.27×10^{-2}	1.94×10^{-2}
k_2 (s^{-1})	6.52×10^{10}	1.09×10^{11}
k^{eff} (L/mol·s)	6.65×10^9	8.72×10^9

[a] Energies include the zero point corrections at the MP2(FC)/6-311++G(d,p) level. κ is the tunneling correction and $\Delta s_{1/2}$ is the full width of the barrier at half its height. [b] $\kappa < 1.0$; therefore, tunneling is ignored.

The details of the calculation of the rate constants are given in Table 4. In the case of the formaldehyde hydrogen abstraction, the best value of the effective activation barrier, which is obtained with the CCSD(T) method using the MP2 optimized geometry, is calculated to be 0.03 kcal/mol. At the same level, considering the formation of the prereactive complex, the actual activation energy of the second step in the complex mechanism of eq 2 is 3.19 kcal/mol. Thus, if the rate constant is calculated according to the complex mechanism, a tunneling factor $\kappa = 5.69$ is obtained, and the rate constant is 6.65×10^9 L mol^{-1} s^{-1}, in excellent agreement with the experimental values. If an elementary mechanism is assumed, κ is 0.724, and thus tunneling can be neglected and the calculated rate constant is only 1.17×10^9 L mol^{-1} s^{-1}. In this context, we would like to suggest that the excellent agreement obtained by Francisco[23] for the rate constant of the OH-formaldehyde reaction, using the direct mechanism, is probably due to a cancellation of errors. His best calculated value for the activation energy was found to be 1.2 kcal/mol, and his tunneling factor should have been intermediate between the two κ values calculated above.

The importance of considering the prereactive complex when calculating the tunneling correction was already mentioned by Sekušak and Sabljić[16] in the case of the hydrogen abstraction reaction from haloethanes. However, these authors calculated the rate constants, assuming a direct reaction mechanism, and hence they found significant discrepancies with the experimental results.

4. Conclusions

From the above discussion we conclude that, when the OH-aldehyde reaction occurs at atmospheric pressure, the following hold:

(i) The addition of the OH radical to the double bond is excluded because its activation energy is much higher than the one for hydrogen abstraction. The aldehydic hydrogen atom has a relatively small bonding energy (as compared with that of alkanes), while the addition of OH to the carbon atom is unfavorable. This process resembles the OH hydrogen abstraction from haloethanes, already described by Sekušak and Sabljić.[16]

(ii) The reaction is not elemental.

(iii) The overall addition of OH is irreversible, due to the large thermal effect of reaction 1 (ΔH is about −30 kcal/mol).

(iv) The overall rate depends on the rates of two competitive reactions (the reverse of the first step and the second step in reaction 1). If the activation energy is negative, the former is more affected by temperature than the latter.

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(30) Benson, S. W. *Thermochemical Kinetics*; Wiley & Sons: New York, 1976; p 43.

The proposed mechanism provides a clear explanation of the experimental behavior. If E_{-1} is larger than E_2, the former will be relatively more favored by an increase in temperature, and the overall rate will decrease. In the OH + aldehyde reactions, the effective negative activation energy is well founded and cannot be an artifact of the experimental method, as claimed by Benson and Dobis[31] for similar radical−molecule reactions.

We claim that the results of the present work, together with those of Sekušak and Sabljić[16] and previous results obtained in our group[13,14,17−19] have significant implications on the theory of transition states in general. In fact, it is well-known that the reaction profile of any bimolecular reaction presents a minimum along the reaction coordinate, previouis to the transition state, which is commonly called reactants complex, van der Waals complex, or prereactive complex. This implies that, strictly speaking, in the gas phase there are no elemental bimolecular reactions, even though, in most cases, the possible formation of the complex is irrelevant. Nevertheless, the point corresponding to the prereactive complex on the potential energy surface is especially important in radical−molecule reactions, many of which are known to occur with an apparent negative activation energy.

In the particular case of a reaction involving the migration of a hydrogen atom, if the prereactive complex is not considered, the height of the actual energy barrier is too small, and the tunneling factor is underestimated, affecting the calculation of the rate constant. In the reactions studied in this work, both effects are present: a negative activation barrier and a hydrogen atom migration.

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Supporting Information Available: Tables of total energies, zero-point and thermal energy corrections, in hartrees, tables of optimized geometries in Cartesian coordinates (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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