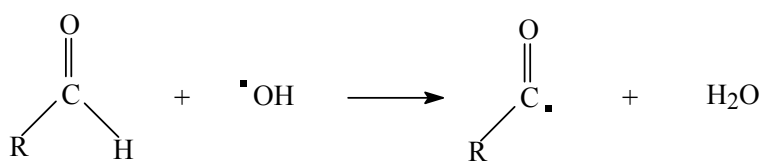
Chapter 4. OH Hydrogen-Abstraction from HCHO and CH_3CHO

4.1. Introduction

The atmosphere is a very complex chemical system that is of crucial importance to life on Earth. Aldehydes, known to play an important role in the chemistry of the polluted troposphere,[1] are directly emitted as primary pollutants from biogenic and anthropogenic sources.[2] They are also formed in large concentrations as end products of the partial oxidation of hydrocarbon fuels and arise as secondary pollutants from the oxidation of volatile organic compounds. Once in the atmosphere, aldehydes either photolyse or react further with OH radicals, the most important tropospheric daytime oxidant, or with NO_3 radicals during the night.

Since a likely route for the tropospheric removal of aldehydes in the atmosphere is by reaction with OH radicals, attention will be given to this reaction described by the following overall equation:



(4.1)

Bimolecular rate constants for the OH reaction with a variety of aldehydes have been measured and their Arrhenius parameters have been reported[1,3] but there are uncertainties as to the reaction mechanism. The negative temperature dependence of the rate constant is well established, except in HCHO, for which the activation energy is known to be almost zero, most experimental results varying between +0.7 and –1.9 kJ/mol. This 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.*[6] ruled out the formation of HCOOH + H but not the reaction:

$$HCHO + {}^{\bullet}OH \rightarrow [HCHO^{\cdots}OH]^{\bullet} \rightarrow HCO^{\bullet} + H_2O \qquad (4.2)$$

However, for HCHO it is believed that only hydrogen abstraction occurs. Recent experimental work by Butkovskaya and Setser[7] using infrared chemiluminescence confirms that the results are consistent with many polyatomic reactions in which the H atom is directly abstracted.

Michael *et al.*[4c] have presented a very complete mechanistic discussion of their experimental data for the CH_3CHO + OH reaction in the temperature range 244-528 K. They suggested two alternative mechanisms for this reaction, one of them being the addition-elimination mode in which CH_3COOH and H are formed. The authors suggest that this reaction proceeds through a vibrationally excited adduct radical that would be expected to undergo collisional stabilization. The other mechanistic alternative suggested by these authors is the direct aldehydic hydrogen-abstraction process. Taylor *et al.* favour an addition-elimination mechanism at low temperatures. Atkinson[8] postulated that the reaction proceeds via overall H-atom abstraction, although the initial reaction possibly involves the OH radical addition to the C=O double bond. However, it is not clear why this hydrogen abstraction reaction presents a negative activation energy, and why the overall OH addition to the double bond does not occur.

The behaviour of reactions having a negative temperature dependence has been successfully described, for systems at low pressures, by Mozurkewich and Benson,[9] and for systems at high pressures, by Singleton and Cvetanović.[10] For this phenomenon several explanations have been proposed which are summarized in Section 3.5.1. Some of them maintain the idea of an elementary reaction but suggest a modification of the pre-exponential factor in the Arrhenius equation to allow for a term T^n. Singleton and Cvetanović proposed a complex mechanism, and explained the occurrence of these negative activation energies as being due to the reversible formation of a loosely bound

reactant complex which is formed without activation energy. A second (irreversible) step follows whose TS energy is lower than the energy of the isolated reactants.

A reactant complex has, in fact, been identified in several OH-addition reactions to alkenes,[11] haloethanes[12] and aromatic hydrocarbons (toluene and xylenes).[13] In a recent study on the OH addition to substituted alkenes,[11e] by calculating the rate constants for the individual steps, it was shown that the mechanism proposed by Singleton and Cvetanović provides a clear explanation of the experimental data.

Reactant complexes seem to be common in all radical-molecule reactions, and are due mainly to long-range Coulombic interactions between the reactants. In fact, in the reactant complex formed between the OH radical and an unsaturated hydrocarbon, it is the H atom of the OH radical which points towards 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.[11,13] If the reaction occurs at sufficiently high pressures, the complexes are collisionally stabilized, and if the energy barriers are small, these complexes 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.

If reaction (4.1) were elementary with a negligible energy barrier, the rate constant of the aldehyde reactions with OH should depend essentially on the pre-exponential factor. Thus, because HCHO has two abstractable hydrogen atoms, one would expect its reaction with OH to be about twice as fast as the one of CH_3CHO, contrary to the observed experimental results at 298 K:[14a] $5.54 \cdot 10^9$ (HCHO) and $9.55 \cdot 10^9$ (CH_3CHO) L/mol·s. However, the experimentally determined Arrhenius parameters indicate a very small negative activation energy and a pre-exponential factor which is larger for HCHO than for CH_3CHO. Selected experimental data for these reactions are shown in Tables 4.1 and 4.2.[3,14,15] On the other hand, the greater reactivity of CH_3CHO is in line with the fact that the inductive effect of the methyl group should help stabilize the corresponding TS.

Table 4.1. Selected experimental data for the reaction HCHO + OH = HCO + H_2O.

Ref. (Year)	E_a [(a)]	A [(b)]	k [(c)]	T (K)	P (atm)
14a, b (1999, 1997)	-0.2	$5.18 \cdot 10^9$	$5.54 \cdot 10^9$	240 – 230	[(d)]
14c (1997)	-	-	$6.03 \cdot 10^9$	200 – 300	[(d)]
14d (1992) [(e)]	-1.9	$3.43 \cdot 10^6$	$6.07 \cdot 10^9$	300 – 3000	[(d)]
14e (1989)	-	-	$4.67 \cdot 10^9$	298	0.00395
14f (1988)	0.7	$1.00 \cdot 10^{10}$	$7.49 \cdot 10^9$	296 – 576	0.132
14g (1986) [(e)]	-1.9	$3.44 \cdot 10^6$	$6.08 \cdot 10^9$	200 – 1600	[(d)]
14h (1986)	-	-	$5.42 \cdot 10^9$	228 – 426	[(d)]
6 (1984)	-	-	$5.06 \cdot 10^9$	299	0.921
14i (1980)	-	-	$6.32 \cdot 10^9$	228 – 362	[(f)]
14j (1978)	-	-	$9.04 \cdot 10^9$	298	0.921
14k (1978)	0.7	$7.53 \cdot 10^9$	$5.61 \cdot 10^9$	299 – 426	0.0658
14m (1971)	-	-	$8.43 \cdot 10^9$	298	0.00132

[(a)] kJ/mol; [(b)] L/mol·s; [(c)] At 298 K, in L/mol·s; [(d)] Literature review; [(e)] $k = AT^{1.18} \exp(-E_a/RT)$; [(f)] 0.0263 – 0.0526 atm

Table 4.2. Selected experimental data for the reaction $CH_3CHO + OH = CH_3CO + H_2O$.

Ref. (Year)	E_a [(a)]	A [(b)]	k [(c)]	T (K)	P (atm)
14a, b (1999, 1997)	-2.6	$3.37 \cdot 10^9$	$9.55 \cdot 10^9$	240 – 530	[(d)]
14c (1997)	-2.2	$3.37 \cdot 10^9$	$8.35 \cdot 10^9$	200 – 300	[(d)]
15a (1995)	-	-	$8.73 \cdot 10^9$	298	[(e)]
15f (1984)	-	-	$1.00 \cdot 10^{10}$	300 – 2000	[(d)]

Selected experimental data for the reaction $CH_3CHO + OH$ = Products.

Ref. (Year)	E_a [(a)]	A [(b)]	k [(c)]	T (K)	P (atm)
5 (1996)	-2.6	$2.59 \cdot 10^9$	$7.32 \cdot 10^9$	295 – 550	0.974
15b (1993)	-	-	$9.75 \cdot 10^9$	298	[(f)]
14d (1992) [(g)]	-4.7	$2.35 \cdot 10^7$	$9.84 \cdot 10^9$	250 – 1200	[(d)]
15c (1992)	-	-	$1.02 \cdot 10^{10}$	298	0.0355
15d (1989)	-1.7	$5.20 \cdot 10^9$	$1.03 \cdot 10^{10}$	296 – 520	[(h)]
14h (1986)	-2.1	$4.14 \cdot 10^9$	$7.77 \cdot 10^9$	298 – 426	[(d)]
4c (1985)	-2.6	$3.33 \cdot 10^9$	$9.32 \cdot 10^9$	244 – 528	[(i)]
15e (1985)	-1.4	$4.28 \cdot 10^9$	$7.44 \cdot 10^9$	253 – 424	0.132
15g (1981)	-	-	$7.23 \cdot 10^9$	298	1
14j (1978)	-	-	$9.64 \cdot 10^9$	298	0.921
14k (1978)	-2.1	$4.14 \cdot 10^9$	$9.81 \cdot 10^9$	299 – 426	0.0658
15h (1971)	-	-	$9.04 \cdot 10^9$	300	0.00132

[(a)] kJ/mol; [(b)] L/mol·s; [(c)] At 298 K, in L/mol·s; [(d)] Literature review; [(e)] 0.00263 – 0.00395 atm; [(f)] 0.0961 – 0.987 atm; [(g)] $k = AT^{0.73} \exp(-E_a/RT)$; [(h)] 0.00138-0.00326; [(i)] 0.00132-0.00421

Using quantum chemical methods, it is possible to calculate energies of intermediate structures and TSs with a reasonable degree of accuracy, and thus to model the reaction path of a reaction. Indeed, a 0.996 correlation factor was recently obtained[11e] after plotting the logarithm of the experimental rate constants *versus* the *ab initio* calculated effective activation energies for the OH radical addition to a series of substituted alkenes.

Previous theoretical work on the HCHO + OH reaction has been reported by Dupuis and Lester[16] using HF, multiconfiguration HF and CI wavefunctions. They predicted a positive activation barrier of 23.0 kJ/mol for the OH hydrogen-abstraction reaction. Francisco[17] performed optimizations at the PMP4SDTQ(FC)/6-311++G(d,p)//MP2/ 6-311G(d,p) level with vibrational frequencies calculated at the HF/6-31G(d) level; a barrier of 6.7 kJ/mol was calculated. Francisco also calculated the rate constant, in good agreement with experiment, by means of TST; tunneling corrections were considered assuming an unsymmetrical Eckart barrier. The formation of a reactant complex was not considered in the above papers. In the present work, the results of the previous studies are included for comparison and discussion. In addition to these studies, the weakly bound complexes of the OH radical with HCHO and CH_3CHO were recently calculated by Aloisio and Francisco[18] using DFT.

In the more recent study of Takahashi *et al.*,[19] a real space *ab initio* molecular dynamic simulation of the HCHO + OH reaction was performed. Their simulation revealed that the hydrogen-abstraction reaction takes place without potential energy barrier according to gradient-corrected DFT calculations. They calculated the enthalpy of reaction to be -164.1 kJ/mol, based on LDA calculations, and -139.4 kJ/mol by means of BLYP computations.

Taylor *et al.* have investigated the reaction of OH radicals with CH_3CHO in a wide temperature range with the laser photolysis/laser-induced fluorescence technique. Possible reaction pathways (OH-addition and H-atom abstraction) were evaluated with a quantum RRK model. They concluded that different reaction mechanisms occur depending on the temperature, and that OH addition followed by CH_3 elimination is the

dominant pathway for reactions occurring between 295 and 600 K. Moreover, they found that the H-atom abstraction from the CH_3 group is dominant at high temperatures. They also concluded that the aldehydic hydrogen-abstraction pathway is largely insignificant, except possibly at the lowest temperatures. However, their calculated rate constant at 298 K is about a factor of 10 too low.

HCHO and CH_3CHO are the most abundant aldehydes in the atmosphere and furthermore, have been regulated as hazardous air pollutants. As a consequence of the chain of reactions that follow after OH and CH_3CHO react in the troposphere, a very problematic compound is formed: $CH_3C(O)OONO_2$, also known as PAN, the smallest member of the family of peroxyacyl nitrates. PAN is a strong eye irritant, with phytotoxic properties and mutagenic and carcinogenic activity.[20] Moreover, in the 1950's PAN was identified as a component of photochemical smog.[1,21]

In this study, the HCHO + OH and CH_3CHO + OH reactions are characterized using several methods and large basis sets, in order to obtain an accurate reaction profile and to reproduce the experimentally observed values of the activation energy (approximately –0.2 and –2.6 kJ/mol for HCHO and CH_3CHO,[14a] respectively). With the corresponding partition functions, the effective rate constants are calculated, using TST and the proposed hydrogen-abstraction complex mechanism. The results are compared with the experimental data and with the results of previous calculations. The purpose of this study is:

(i) To show that the complex mechanism proposed by Singleton and Cvetanović can be applied to both the formaldehyde and the acetaldehyde reactions.

(ii) To show that consideration of the reactant 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.

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

4.2. Computational details

All geometries were fully optimized at the MP2(FC)/6-311++G(d,p) level and energies were further calculated at the CCSD(T)/6-311++G(d,p) level.

For the reactions under study two reaction mechanisms will be taken into account, a complex and a direct mechanism. For the complex mechanism the following steps are considered:

Step 1: $$\mathrm{RCHO} + \mathrm{OH} \underset{k_{-1}}{\overset{k_1}{\leftrightarrows}} [\mathrm{RCHO}^{\cdots}\mathrm{HO}]$$

Step 2: $$[\mathrm{RCHO}^{\cdots}\mathrm{HO}] \xrightarrow{k_2} [\mathrm{RCO}^{\cdots}\mathrm{H_2O}] \rightarrow \mathrm{RCO} + \mathrm{H_2O}$$

Step 1 involves a fast pre-equilibrium between the reactants and the reactant complex, followed by an internal rearrangement leading to the elimination of a water molecule in the second step.

If k_1 and k_{-1} are the forward and reverse rate constants, respectively, for the first step, and k_2 is the rate coefficient of the second step, the overall rate constant can be written as:

$$k_{eff} = \frac{k_1\ k_2}{k_{-1}} = \left(\frac{A_1\ A_2}{A_{-1}}\right) \exp\left(-\frac{E_{a(1)} + E_{a(2)} - E_{a(-1)}}{RT}\right) \tag{4.3}$$

Since $E_{a\,(1)}$ is zero, the net activation energy for the overall reaction is:

$$E_a^{eff} = E_{a\,(2)} - E_{a\,(-1)} = E^{TS} - E^{React} \tag{4.4}$$

Thus, the activation energy at high pressures can be calculated as the difference between the total energy of the TS (E^{TS}) and that of the reactants (E^{React}), without having to obtain the reactant complex.

Applying basic statistical thermodynamic principles (see Section 3.1), the equilibrium constant of the fast pre-equilibrium between the reactants and the reactant complex (RC) may be obtained as:

$$K_{eq} = \frac{Q^{RC}}{Q^{React}} \exp\left(-\frac{E^{RC} - E^{React}}{RT}\right) \tag{4.5}$$

Under high-pressure conditions, an equilibrium distribution of the reactants (the reactant complex, for the second step of the complex mechanism) is maintained in a unimolecular process, and the TST formula can be applied to calculate k_2:

$$k_2 = \kappa \frac{k_B T}{h} \frac{Q^{TS}}{Q^{RC}} \exp\left(-\frac{E^{TS} - E^{RC}}{RT}\right) \tag{4.6}$$

The effective rate constant for the above mechanism may be written as:

$$k_{eff} = \frac{k_1 k_2}{k_{-1}} = K_{eq} k_2 \tag{4.7}$$

$$k_{eff} = \kappa \frac{k_B T}{h} \frac{Q^{TS}}{Q^{React}} \exp\left(-\frac{E^{TS} - E^{React}}{RT}\right) \tag{4.8}$$

In the second mechanism considered the reaction is assumed to be elementary:

$$RCHO + OH \xrightarrow{k_D} RCO + H_2O$$

The formation of the reactant and product complexes is ignored, and the rate constant is calculated as:

$$k_D = \kappa_D \frac{k_B T}{h} \frac{Q^{TS}}{Q^{React}} \exp\left(-\frac{E^{TS} - E^{React}}{RT}\right) \tag{4.9}$$

It is important to notice that expressions (4.8) and (4.9) are identical except for the tunneling factor κ, which depends on the forward and reverse potential energy barriers of the elementary process in which the hydrogen atom is abstracted. For the complex mechanism these energy barriers are calculated from the energies (including ZPE) of the reactant complex, TS and product complex, while for the direct mechanism the energies of the isolated reactants and products as well as the energy of the TS are considered. The tunneling factor and $\Delta s_{1/2}$ were calculated by assuming an unsymmetrical Eckart barrier.[22]

4.3. Results and discussion

The OH radical attack on aldehydes appears to occur in the following way. At first, the electron-deficient hydrogen atom of the OH radical approaches a lone pair of the carbonylic oxygen atom to form a stable reactant complex, whose energy is more than 13 kJ/mol lower than the energy of the reactants (Fig. 4.1). Several such reactant complexes were identified in the case of the HCHO + OH reaction, but, in the most stable one, the OH radical lies in the plane of the CHO group. From this structure, the oxygen of the OH may flip, in the plane, towards the hydrogen to be abstracted as the energy increases to a maximum at the TS.

The geometries of the reactant complexes obtained for the HCHO + OH and CH_3CHO + OH reactions are very similar to those obtained by Aloisio and Francisco using a DFT method.

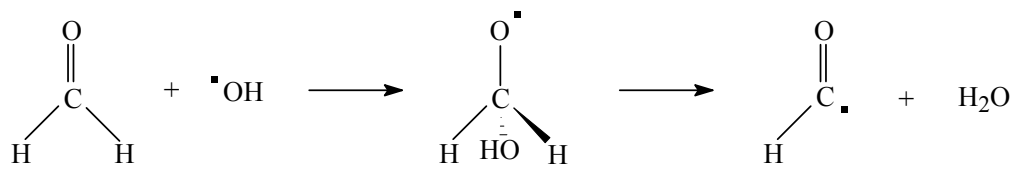
Besides the aldehydic hydrogen-abstraction, another process (4.10) may also occur which leads to the OH addition to the carbonylic double bond. Starting from the same reactant complex, the OH group may flip in a plane perpendicular to the CHO plane, such that the oxygen atom may approach the carbon atom of the aldehyde from above. It will be shown below that the corresponding TS has a considerably higher energy than that for the abstraction channel.

The following complex mechanism can be considered for the OH addition reaction to HCHO:

Step 1: $RCHO + OH \leftrightarrows [RCHO^{\cdots}HO]$

Step 2: $[RCHO^{\cdots}HO] \rightarrow [RCHO(OH)]$

Step 3: $[RCHO(OH)] \rightarrow [RCO^{\cdots}H_2O] \rightarrow RCO + H_2O$



(4.10)

A third process could also be considered, in which the OH radical attacks CH_3CHO at the methyl group and produces the CH_2CHO radical. Indeed, this hydrogen-abstraction is about 105 kJ/mol exothermic. The energy of the methyl C-H bond is about 30 kJ/mol larger than that of the carbonyl C-H bond:

$CH_3CHO + OH \rightarrow CH_3CO + H_2O$ $\Delta H_{298} = (-134.4 \pm 9.4)$ kJ/mol

$CH_3CHO + OH \rightarrow CH_2CHO + H_2O$ $\Delta H_{298} = (-104.7 \pm 9.0)$ kJ/mol

The above ΔH_{298} values were calculated from the following bond enthalpies (DH_{298} in kJ/mol) taken from Ref. 23:

DH_{298} (H-OH) = 499.5 ± 0.2

DH_{298} (CH_3CO-H) = 365.1 ± 9.6

DH_{298} (H-CH_2CHO) = 394.8 ± 9.2

Since the aldehydic hydrogen-abstraction is more exothermic, according to Hammond's postulate its TS should resemble more closely the reactants, *i.e.*, this TS should be earlier than the methyl hydrogen-abstraction TS and thus easier to achieve. Following these

ideas the former reaction should be faster than the latter. In addition, the position of the OH hydrogen atom in the reactant complex is very far from the methyl hydrogen atoms. Indeed, it has been shown that the calculated rate constant for the methyl hydrogen-abstraction process, applying TST, is ten times smaller than the aldehydic hydrogen-abstraction reaction. Moreover, in the Cl + CH_3CHO reaction the CH_3CO radicals are the only ones observed.[24] Hence, even though the methyl hydrogen-abstraction is entropically more favoured (there are three H atoms available instead of just one), other factors (energetic and dynamic) determine the lower reactivity of the methyl site in CH_3CHO.

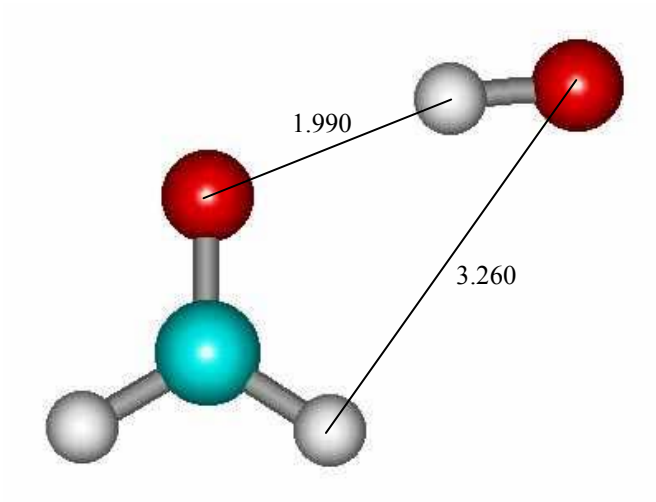
The proposed abstraction mechanism resembles closely that described by Sekušak and Sabljić for the hydrogen-abstraction reaction from haloethanes. These authors have stressed the importance of the reactant complex and the role of a strongly electronegative atom in guiding the reaction from the very beginning and in lowering the energy of the TS.

The MP2 optimized geometries of the TSs and product complexes of the hydrogen-abstraction reactions under study are shown in Figs. 4.2 and 4.3, respectively. Relevant geometric parameters have been indicated on the figures (bond distances are given in Angströms and angles in degrees). Both the hydrogen abstraction and the OH addition channels have been investigated in the case of the HCHO reaction. For CH_3CHO, however, only the abstraction channel was studied. The TS and addition product of the OH addition reaction to HCHO are shown in Figs. 4.4 and 4.5, respectively.

The C···H and O···H distances for the abstraction TS (Fig. 4.2) indicate that the TS for CH_3CHO is formed earlier than that for HCHO. This situation is a consequence of the positive inductive effect of the CH_3 group that increases the electronic density at the carbonyl carbon, favouring the abstraction of the hydrogen atom.

The symmetry of the TS for the HCHO and CH_3CHO reaction with OH is $^2A'$, implying that the unpaired electron is in the plane where the OH attack takes place. $^2A'$ is also the symmetry of the RCO radical generated. The Cartesian coordinates of the optimized species along the reaction paths of the reactions studied are available.[25]

(a)



(b)

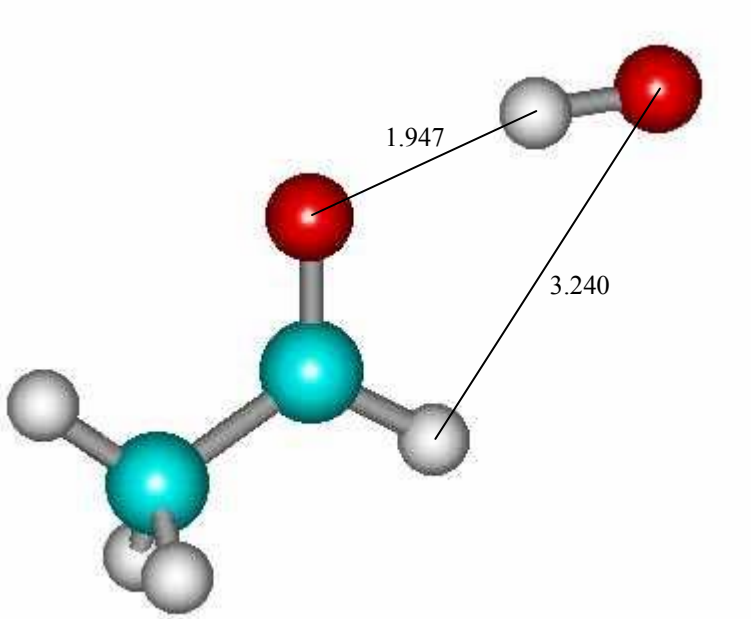
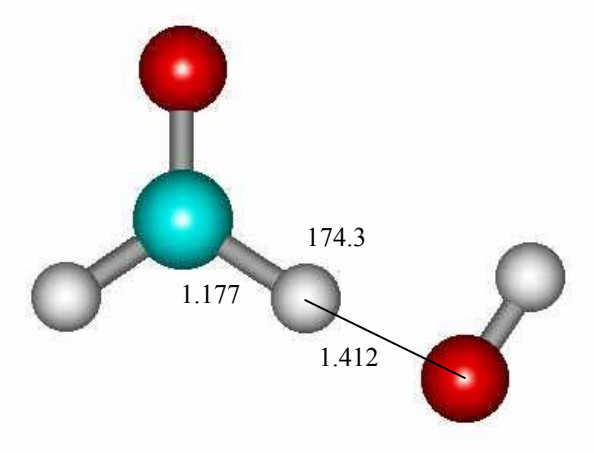


Figure 4.1. Optimized structures of the reactant complex of the (a) HCHO + OH and (b) CH_3CHO + OH hydrogen-abstraction reactions.
(Bond distances are given in Å)

(a)



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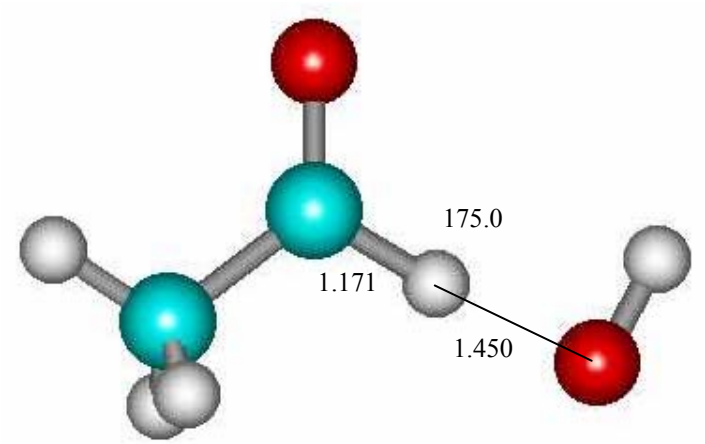
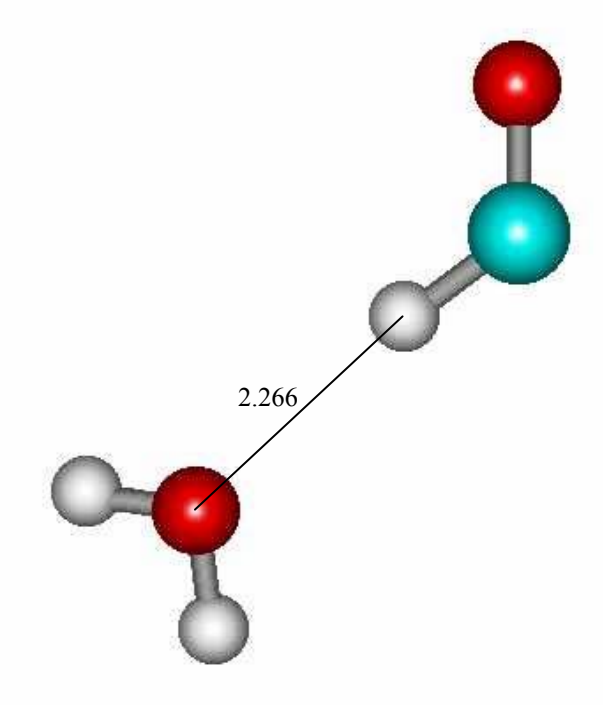


Figure 4.2. Optimized structures of the TS of the (a) HCHO + OH and (b) CH_3CHO + OH hydrogen-abstraction reactions. (Bond distances are given in Å and angles in degrees)

(a)



(b)

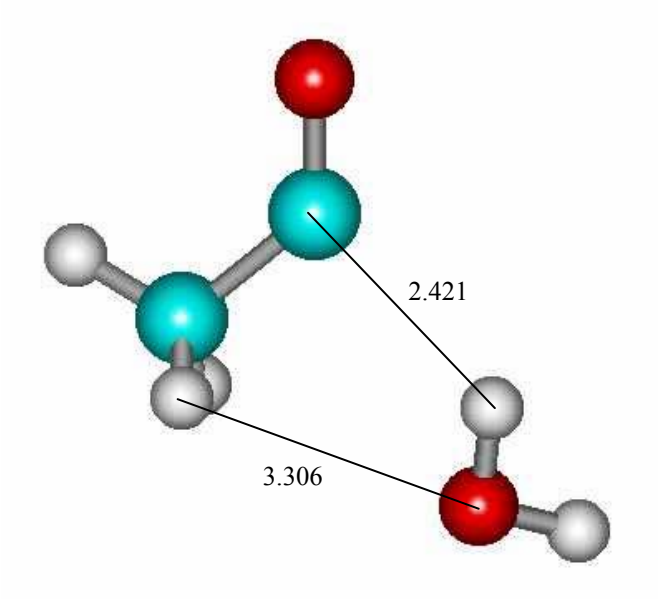


Figure 4.3. Optimized structures of the product complex of the (a) HCHO + OH and (b) CH_3CHO + OH hydrogen-abstraction reactions.
(Bond distances are given in Å)

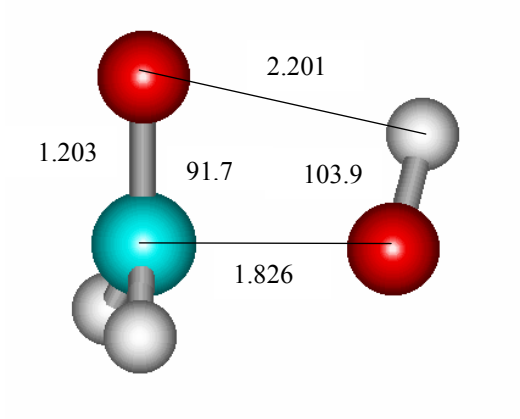


Figure 4.4. Optimized structure of the TS of the HCHO + OH addition reaction. (Bond distances are given in Å and angles in degrees)

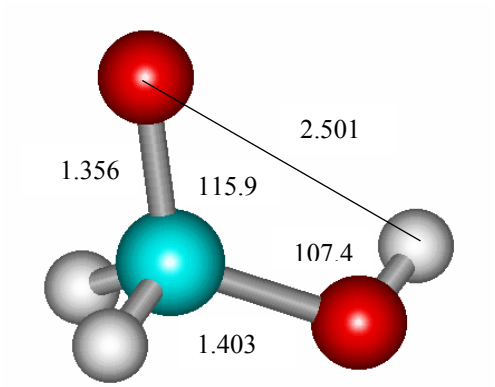


Figure 4.5. Optimized structure of the addition product of the HCHO + OH reaction. (Bond distances are given in Å and angles in degrees)

For the abstraction reactions, spin contamination is only significant (but small) at the TS: the expectation value of S^2 is 0.779 for the HCHO abstraction reaction and 0.774 for CH_3CHO, 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 completely eliminated by projection, a situation that is not unusual. In fact, Sekušak *et al.*[11c] also observed, in the alkene + OH reactions, that single point CC calculations do not give satisfactory results, probably due to the fact that the geometry is not optimized at this level and because spin contamination is not eliminated. Thus, for the addition channel, the PMP2 results are expected to be more reliable.

The calculated total energies (PMP2, CCSD(T)), zero-point and thermal (at 298.15 K) vibrational energy corrections (calculated at the MP2 level) of the species involved in the reactions of OH with the aldehydes studied, are available.

The stabilization energy of the reactant complexes ($E_{a\ (-1)}$), the activation barriers of the second step of the complex mechanisms ($E_{a\ (2)}$) and the effective activation energies (E_a^{eff}), calculated as described in equation (4.4), are given in Table 4.3 at 0 K. This table also includes reaction enthalpies (ΔH) for the addition and hydrogen-abstraction reactions for the methods employed, as well as effective activation energies, stabilization energies of the reactant complexes and reaction enthalpies at 298.15 K. Other calculated or measured values are shown for comparison. The ZPE and TCE values calculated at the MP2 level are used to obtain the CCSD(T) energy differences.

The reaction energy profiles for the OH addition and hydrogen-abstraction reactions with HCHO are shown in Fig. 4.6. The best energies were used for each reaction, *i.e.*, PMP2 energies for the addition and CCSD(T) energies for the hydrogen-abstraction reaction (with MP2 ZPE included). The PMP2 effective activation energy of the addition reaction (32.2 kJ/mol) is considerably greater that the energy barrier calculated for the hydrogen-abstraction process (13.0 at the PMP2 level and 0.5 at the CCSD(T) level). Based on this

situation it is clear why the addition pathway is not favoured in these reactions. The difference between the CCSD(T) energies of the TSs for these two channels is more than 35 kJ/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 TS for the addition is expected to be much tighter than the one for the 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 TSs for addition and abstraction is also large enough (about 20 kJ/mol) at the PMP2 level to guarantee that only the abstraction channel occurs.

The energy profiles obtained using the CCSD(T) energies (including the MP2 ZPEs) for the HCHO + OH and CH_3CHO + OH hydrogen-abstraction reactions are shown in Fig. 4.7. The formation of a stable reactant complex followed by a transition state whose energy is lower (CH_3CHO) or slightly higher (HCHO) than the energy of the reactants is clearly observed.

The calculated stabilization energies of the reactant complexes (Fig. 4.1) obtained at the PMP2 and the CCSD(T) levels agree to within 0.1 kJ/mol. The predicted stabilization energies at 0 K are 13.6 kJ/mol and 17.5 kJ/mol for the HCHO$^{\cdots}$OH and $CH_3CHO^{\cdots}$OH reactant complexes, respectively. Aloisio and Francisco estimated binding energies at 0 K of 12.6 (HCHO$^{\cdots}$OH) and 16.7 kJ/mol ($CH_3CHO^{\cdots}$OH) at the B3LYP/6-311++(2d,2p) level, in very good agreement with the new calculations.

The PMP2 effective activation energies are overestimated; for these reactions, CCSD(T) seems to be the most appropriate method for obtaining activation energies and rate constants. Indeed, the CCSD(T) results agree remarkably well with the experimental values. For the OH hydrogen-abstraction reactions, the best value of the effective activation barrier at 298 K is calculated to be 0.1 for HCHO and –7.2 kJ/mol for CH_3CHO, in very good agreement with the experimental results (see

Table 4.3. Relevant barriers (E_a) and reaction enthalpies (ΔH), in kJ/mol, including zero-point vibrational corrections (ZPE), unless otherwise specified, for the OH addition to HCHO and the OH hydrogen-abstraction reaction from HCHO and CH_3CHO.

Basis set: 6-311++G(d,p)	$E_{a\,(2)}$	E_a^{eff}	$E_a^{eff\,(a)}$	ΔH	$\Delta H^{(a)}$
Addition: HCHO + OH					
PMP2	47.2	33.6	32.2	-67.9	-69.7
CCSD(T)	52.6	38.9	37.6	-71.8	-73.6

Basis set: 6-311++G(d,p)	$E_{a\,(-1)}$	$E_{a\,(-1)}^{(a)}$	$E_{a\,(2)}$	E_a^{eff}	$E_a^{eff\,(a)}$	ΔH	$\Delta H^{(a)}$
HCHO + OH							
PMP2	13.6	13.0	26.6	13.0	12.6	-142.0	-140.8
CCSD(T)	13.6	13.0	14.1	0.5	0.1	-118.9	-117.7
Previous calculations	12.6 [(b)]			5.0 [(c)] 23.0 [(d)]	6.7 [(c)]	-126.9 [(c)] -139.4 [(e)] -129.4 [(f)]	
Experiment					-0.2 [(g)] -1.9 [(h)] 0.7 [(i)]		-129.4 [(j)] -130.7 [(k)] -135.3 [(l)]
CH_3CHO + OH							
PMP2	17.4	16.4	23.4	6.0	6.0	-134.7	-133.2
CCSD(T)	17.5	16.5	10.3	-7.2	-7.2	-115.0	-113.5
Previous calculations	16.7 [(b)]			-5.4 [(m)]			
Experiment					-2.6 [(n)] -2.2 [(o)] -4.7 [(p)]		-125.3 [(j)] -139.6 [(k, l)]

[(a)] Including thermal correction (TCE) at 298.15 K; [(b)] Ref. 18 (2000); [(c)] Ref. 17 (1992); [(d)] Ref. 16 (1984); [(e)] Ref. 19 (2001); [(f)] Ref. 26 (1998); [(g)] Ref. 14a, b (1999, 1997); [(h)] Ref. 14d, g (1992, 1986); [(i)] Ref. 14f, k (1988, 1978); [(j)] Ref. 14a (1999); [(k)] Ref. 14b (1997); [(l)] Ref. 27 (1992); [(m)] Ref. 5 (1996); [(n)] Ref. 14a, b (1999, 1997), 5 (1996), 4c (1985); [(o)] Ref. 14c (1997); [(p)] Ref. 14d (1992)

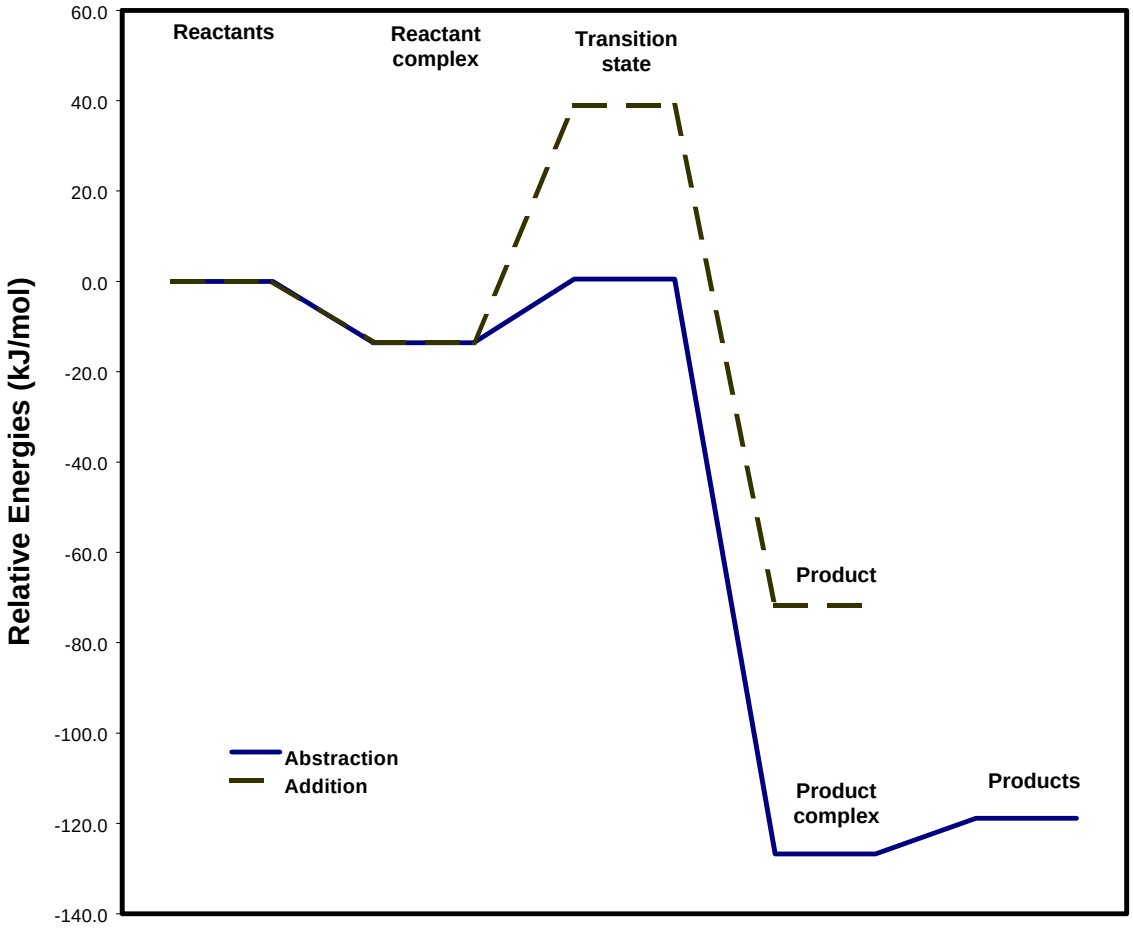


Figure 4.6. Schematic reaction profiles for the addition (PMP2 energies) and hydrogen-abstraction (CCSD(T) energies) in the HCHO + OH reaction, with the 6-311++G(d,p) basis set. ZPEs calculated at the MP2 level have been included.

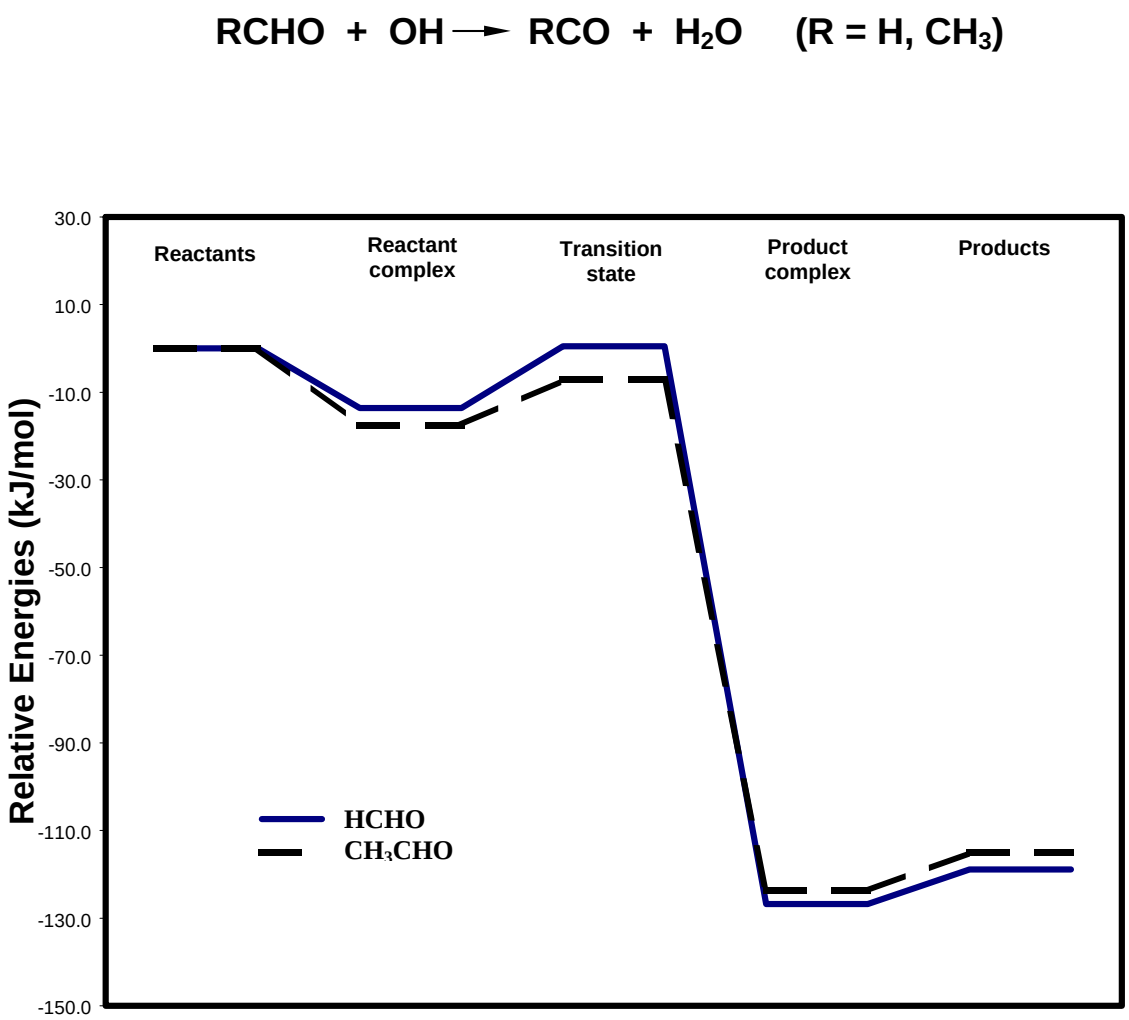


Figure 4.7. Schematic reaction profiles for the RCHO + OH (R = H, CH_3) using the calculated CCSD(T)/6-311++G(d,p) energy values, including the MP2(FC)/ 6-311++G(d,p) ZPEs.

Tables 4.1 and 4.2). At the same level, considering the formation of the reactant complex, the activation energy of the second step in the complex mechanism ($E_{a\,(2)}$ at 0 K) is 14.1 for HCHO and 10.3 kJ/mol for CH_3CHO.

Product complexes (Fig. 4.3), which present hydrogen bonds between the water molecule and the aldehydic radicals, are about 8 kJ/mol more stable than the corresponding separated products at 0 K. The most recently reported heats of reaction for the hydrogen-abstraction processes[14a] lie between those obtained with the PMP2 and CCSD(T) calculations at 298 K. However, the theoretical methods employed reproduce correctly the observed trends.

The values of the partition functions needed for the calculation of the rate constants of the reactions studied at the MP2 level are given in Table 4.4, as well as the imaginary frequency of the TS. Three low frequencies (below 210 cm^{-1}) in addition to the imaginary frequency were calculated for the hydrogen-abstraction TSs. Of these, two were identified as internal rotations (or torsional vibrations) by visualization of the normal modes: frequencies 1 and 3 for both TSs. These harmonic modes correspond most closely to the two new internal rotors created in the TS ($RCOH^{\cdots}OH$ and $RCO^{\cdots}HOH$), where the common axes for internal rotation are the ones linking the reactants and products, respectively, and were the axes considered in the calculation of the reduced moments of inertia. These harmonic modes were treated as free rotors in the calculation of the internal-rotation partition function of the TS (Q_{IR}^{TS}).[28,29] For CH_3CHO and its TS, the internal rotation around the C-C single bond was also considered and treated as a free rotor.

The harmonic contributions of these low frequencies were eliminated from the vibrational partition function in order to correct the total partition function of the TS (Q_{corr}^{TS}). For the OH reaction with CH_3CHO, Q_{corr}^{TS} is calculated as:

$$Q_{corr}^{TS} = \frac{Q^{TS}\, Q_{IR}^{TS}}{Q_{v=1}\, Q_{v=3}\, Q_{v=4}} \tag{4.12}$$

Table 4.4. Total partition functions (Q) of the reactants and the TS, and imaginary frequency ($\nu^{\neq}$ in cm^{-1}) of the TS of the OH hydrogen-abstraction reaction from HCHO and CH_3CHO, calculated at the MP2(FC)/6-311++G(d,p) level.

System	**HCHO + OH**	**CH_3CHO + OH**
Q^{OH}	$6.02509 \cdot 10^{7}$	$6.02509 \cdot 10^{7}$
Q^{RCHO}	$4.63150 \cdot 10^{9}$	$3.11890 \cdot 10^{11}$ [(a)]
Q^{TS}	$7.94138 \cdot 10^{12}$	$1.44177 \cdot 10^{14}$
$\prod Q_{v=i}$ [(d)]	5.439 [(b)]	12.413 [(c)]
Q_{IR}^{TS} [(e)]	43.660	162.362
Q_{corr}^{TS} [(f)]	$6.37514 \cdot 10^{13}$	$1.88582 \cdot 10^{15}$
$\nu^{\neq}$	1522	1066
$\nu^{\neq}$ [(g)]	3325	

[(a)] $Q_{corr}^{CH_3CHO} = 5.40018 \cdot 10^{11}$; [(b)] i=1, 3; [(c)] i=1, 3, 4;
[(d)] Vibrational components that were eliminated from the calculation of Q_{corr}^{TS}; [(e)] Total internal-rotational partition function of the TS; [(f)] Corrected total partition function of the TS; [(g)] Ref. 17 (HF/6-31G(d))

Details of the calculation of the rate constants using the CCSD(T)/6-311++G(d,p)//MP2/6-311++G(d,p) energy values and the MP2/6-311++G(d,p) frequency calculation, are given in Table 4.5.

Thus, if the rate constant for the HCHO + OH reaction is calculated according to the complex mechanism, a tunneling factor $\kappa = 5.69$ is obtained, and the rate constant is calculated to be $6.65 \cdot 10^{9}$ L/mol·s, in excellent agreement with the experimental values (see Table 4.1). If an elementary mechanism is assumed, κ is 0.724, so tunneling can be neglected and the calculated rate constant is only $1.17 \cdot 10^{9}$ L/mol·s. The excellent

agreement obtained by Francisco for the rate constant of this reaction ($5.64 \cdot 10^9$ L/mol·s) using the direct mechanism, is probably due to a cancellation of errors. The activation energy calculated by the author at 0 K is 5.0 kJ/mol and the tunneling correction is estimated to be 17.85. The direct barriers at 0 K used in the present study to calculate the Eckart tunneling corrections are 0.5 (κ = 0.724) and 14.1 (κ = 5.69) kJ/mol. Francisco's value of the Eckart tunneling correction should be intermediate between the two values reported above.

Table 4.5. Rate constants and tunneling parameters for the OH hydrogen-abstraction reaction from HCHO and CH_3CHO, calculated using CCSD(T)/6-311++G(d,p)//MP2(FC)/6-311++G(d,p) energies that include zero point corrections, for both the direct and complex mechanisms at 298.15 K. The frequency calculations were performed at the MP2(FC)/6-311++G(d,p) level.

	HCHO + OH	**CH_3CHO + OH**
Direct Mechanism		
κ	[(a)]	[(a)]
$\Delta s_{½}$ (Å)	[(a)]	[(a)]
k_D (L/mol·s)	$1.17 \cdot 10^9$	$6.46 \cdot 10^9$
Complex Mechanism		
κ	5.69	2.47
$\Delta s_{½}$ (Å)	0.30	0.38
k_{eff} (L/mol·s)	$6.65 \cdot 10^9$	$1.59 \cdot 10^{10}$
Experiment		
k (L/mol·s)	$5.54 \cdot 10^9$ [(b)]	$9.55 \cdot 10^9$ [(b)]
	$6.03 \cdot 10^9$ [(c)]	$8.35 \cdot 10^9$ [(c)]
Previous Calculation		
κ	17.85 [(d)]	
k (L/mol·s)	$5.64 \cdot 10^9$ [(d)]	$5.11 \cdot 10^8$ [(e)]

[(a)] $\kappa < 1.0$, so tunneling is ignored; [(b)] Ref. 14a, b (1999, 1997); [(c)] Ref. 14c (1997); [(d)] Ref. 17 (1992); [(e)] Ref. 5 (1996)

The tunneling correction for the CH_3CHO + OH reaction assuming a complex mechanism is 2.47 and the rate constant is $1.59 \cdot 10^{10}$ L/mol·s, in good agreement with experiment (see Table 4.2). If the reaction were considered elementary, the forward barrier would be negative and the tunneling calculation meaningless.

The importance of considering the reactant complex formation when calculating the tunneling correction has been discussed by Sekušak and Sabljić 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.

4.4. Conclusions

From the above discussion it is concluded that, when the RCHO + OH (R = H, CH_3) reaction occurs at atmospheric pressure, the following observations hold:

(i) The addition of the OH radical to the carbonylic double bond is excluded because its activation energy is much higher than that for OH hydrogen-abstraction. The methyl H-atoms in CH_3CHO should be less reactive towards OH attack than the aldehydic H-atom. Hence, the reaction basically only involves the aldehydic hydrogen-abstraction.

(ii) The OH hydrogen-abstraction reaction from aldehydes is not elementary.

(iii) The overall rate depends on the rates of two competitive reactions: a reversible step where a reactant complex is formed, followed by the irreversible hydrogen-abstraction to form the products.

The proposed mechanism provides a clear explanation of the experimental behaviour. If $E_{a\ (-1)}$ is larger than $E_{a\ (2)}$, *i.e.*, the effective activation energy is negative, the decomposition of the reactant complex (step –1) will be relatively more favoured by an

increase in temperature than the hydrogen-abstraction process (step 2) 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[30] for similar radical-molecule reactions.

The consideration of the reactant complex formation in the kinetic calculations has two important consequences: it explains the negative activation energies observed, and it also affects the rate constant calculations, as it determines the barrier height of the hydrogen-abstraction process and hence the value of the tunneling correction.

It is claimed in this study that the present results, together with those of Sekušak and Sabljić and previous studies[11,13] 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, previous to the TS, which is commonly called the reactant complex, van der Waals complex or pre-reactive complex. This implies that, strictly speaking, in the gas phase there are no elementary bimolecular reactions, even though, in most cases, the possible formation of the complex is irrelevant. Nevertheless, the point corresponding to the reactant 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 (or any other light particle for which tunneling must be considered), if the reactant 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 both effects are present: a negative activation barrier and hydrogen atom migration.

4.5. References

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