

## A Quantum Chemical and TST Study of the OH Hydrogen-Abstraction Reaction from Substituted Aldehydes: FCHO and ClCHO

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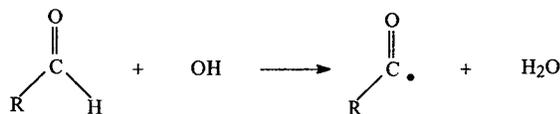
In the present study, ab initio methods have been used to study the OH hydrogen-abstraction reaction from two substituted aldehydes: FCHO and ClCHO. A complex mechanism in which the overall rate depends on the rates of two competitive reactions, a reversible step where a reactant (or prereactive) complex is formed, followed by the irreversible hydrogen abstraction to form the products, is corroborated. This mechanism was previously shown to describe accurately the kinetics of the OH hydrogen-abstraction reaction from formaldehyde and acetaldehyde. Classical transition state theory (TST) rate constants calculated with tunneling corrections, assuming an unsymmetrical Eckart barrier, agree very well with experimental upper bound values. Activation energy barriers and enthalpies of reaction have been estimated through CCSD(T) single point calculations using MP2 geometries and frequencies and the 6-311++G(d,p) basis set.

### Introduction

The atmosphere is a very complex chemical system and of crucial importance to life on Earth. Aldehydes, known to play an important role in the chemistry of the polluted troposphere,<sup>1</sup> are emitted as primary pollutants from partial oxidation of hydrocarbon fuels and arise as secondary pollutants from the oxidation of volatile organic compounds. Once in the atmosphere, aldehydes may either photolyze or react further with OH radicals, the most important tropospheric daytime oxidant, or with NO<sub>3</sub> radicals during the nighttime.

The chemistry of the atmosphere is quite complex.<sup>2</sup> The life cycles of the atmospheric species (including traces) are strongly coupled, and the results of this are often unexpected. Depending on their atmospheric lifetimes these species can exhibit an enormous range of spatial and temporal variability, but every substance emitted into the atmosphere is eventually removed so that a biogeochemical cycle is established. To estimate the lifetimes of pollutants in the atmosphere different removal options have to be considered, and for this, the development of a reliable database of atmospheric reactions is extremely important. However, such reactions are often difficult to study experimentally.

Since a likely tropospheric removal route for aldehydes in the atmosphere is by the reaction with OH radicals, we focus on this reaction that occurs according to the following overall equation:



Previous calculations on the reaction of formaldehyde with OH radicals<sup>3</sup> showed why the addition reaction of OH radicals

to the carbonylic double bond does not occur. A discussion based on activation energy values and also on a comparison of structural parameters of the TS of this reaction with those of similar reactions clarified this topic.

Earlier experimental and theoretical studies on reactions between OH radicals and aldehydes have been performed.<sup>4,5</sup> In a former study<sup>3</sup> the OH hydrogen-abstraction reaction from formaldehyde and acetaldehyde was examined by considering a complex mechanism in which the overall rate depends on the rates of two competitive reactions: a reversible step where a reactant (or prereactive) complex is formed, followed by the irreversible hydrogen abstraction to form the products. TST<sup>6</sup> was applied for the calculation of the rate constants with successful results. Tunneling corrections were incorporated assuming an unsymmetrical Eckart barrier.

The consideration of the reactant complex formation has two important consequences in the kinetics calculations of these systems since it explains the negative activation barriers observed (especially for acetaldehyde) and 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. In view of the previous successful results, we decided to extend these ideas to the OH hydrogen-abstraction reaction from FCHO and ClCHO, for which only experimental upper bound rate constants have been reported and activation energy values are unknown.<sup>4a,7,8</sup>

Formyl fluoride (FCHO) is one of the halogenated molecules in the upper stratosphere and a major product of the degradation in the troposphere of CH<sub>3</sub>CFH<sub>2</sub> (HFC-134a).<sup>9</sup> It is also a product of the subsequent dissociation of fluorinated radicals that originate in the atmosphere. Formyl chloride (ClCHO) is a reactive molecule that forms as an atmospheric degradation intermediate of several chlorinated hydrocarbons such as CH<sub>3</sub>Cl, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and hydrochlorofluorocarbons (HCFCs),<sup>10</sup> as well as from the tropospheric reaction of Cl atoms with volatile organic compounds such as isoprene.<sup>11</sup> The reaction of FCHO and ClCHO with OH radicals is supposed to be a tropospheric removal route for these compounds.

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The OH reaction with the substituted aldehydes of interest was first examined theoretically by Francisco<sup>12</sup> in 1992. Activation energies and heats of reaction were estimated at the PMP4SDTQ(FC)/6-311++G(d,p)//MP2/6-311G(d,p) level. Vibrational frequencies were calculated at the HF/6-31G(d) level. Classical TST was also employed for the rate constant calculation, and tunneling corrections were considered, assuming an unsymmetrical Eckart barrier. These reactions were considered to be elementary. The results obtained in the previous work will be shown together with our new data, for comparison.

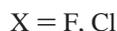
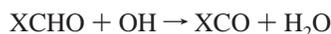
A DFT study on the FCHO + OH reaction was performed by Jursic,<sup>13</sup> where hybrid functionals (B3LYP, B3P86, and B3PW91) were applied to estimate the heat of reaction and the activation energy.

In the present study high-level ab initio calculations are performed to investigate the OH hydrogen-abstraction reaction from FCHO and ClCHO. In addition, classical transition state theory (TST) is applied to the calculation of the rate constants and tunneling corrections are considered. Our aim is to show that the same complex mechanism can be applied to these reactions and to provide better theoretically determined kinetic parameters. This work is a continuation of the previous study performed on the OH hydrogen-abstraction reaction from HCHO and CH<sub>3</sub>CHO.<sup>3</sup>

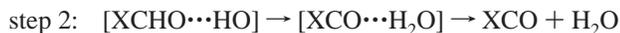
### Computational Details

Electronic structure calculations have been performed using the Gaussian98 set of programs.<sup>14</sup> All geometries of the reactants, products, and stationary points were fully optimized. Unrestricted ab initio methods were used to calculate the energy of the radical species. Geometries were optimized at the MP2-(FC)/6-311++G(d,p) level, and the character of all species was confirmed by a frequency calculation at the same level. Energies at the CCSD(T)/6-311++G(d,p) level were calculated using the MP2 geometries. This is the same level of theory at which the reactions of formaldehyde and acetaldehyde with OH radicals were recently characterized.

Two possible mechanisms were considered: a direct mechanism, in which the hydrogen-abstraction takes place in an elementary step,



and a two-step mechanism that involves a fast preequilibrium between the reactants and the reactant complex, followed by the irreversible hydrogen-abstraction that takes place in the reactant complex to form the products (product complex),



The overall rate constant for the complex mechanism ( $k_{\text{eff}}$ ) can be written as

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

where  $k_1$  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.

With application of the basic statistical thermodynamics principles<sup>15</sup> for the calculation of the equilibrium constant of

the first step ( $K_{\text{eq}}$ ) and the classical TST formula to calculate  $k_2$ ,  $k_{\text{eff}}$  can be written as

$$k_{\text{eff}} = \kappa \frac{k_{\text{B}} T}{h} \frac{Q^{\text{TS}}}{Q^{\text{React}}} \exp\left(-\frac{E^{\text{TS}} - E^{\text{React}}}{RT}\right) \quad (1)$$

where  $\kappa$  is the tunneling factor,  $k_{\text{B}}$  is Boltzmann's constant,  $h$  is Planck's constant,  $R$  is the ideal gas constant, and  $E^{\text{X}}$  and  $Q^{\text{X}}$  are total energies (at 0 K) and standard molar partition functions (divided by Avogadro's number) of the transition structure (TS) and the reactants (React), respectively. These partition functions are approximated as products of electronic, vibration, internal rotation (where applicable), rotation, and translation partition functions. We should mention that this expression is valid when the reaction takes place at pressures sufficiently high to collisionally stabilize the reactant complex, as in our case.

Standard molar partition functions were calculated by using the molar volume of an ideal gas at the standard pressure (we have used  $p^\circ = 1$  atm) in the calculation of the translation partition function. Rotational constants and harmonic vibrational frequencies obtained from the ab initio calculations were used to calculate the rotational and vibrational components of the total partition function. For the TS, the contribution of the imaginary frequency to the vibrational partition function was excluded. This is the procedure followed by Gaussian98.

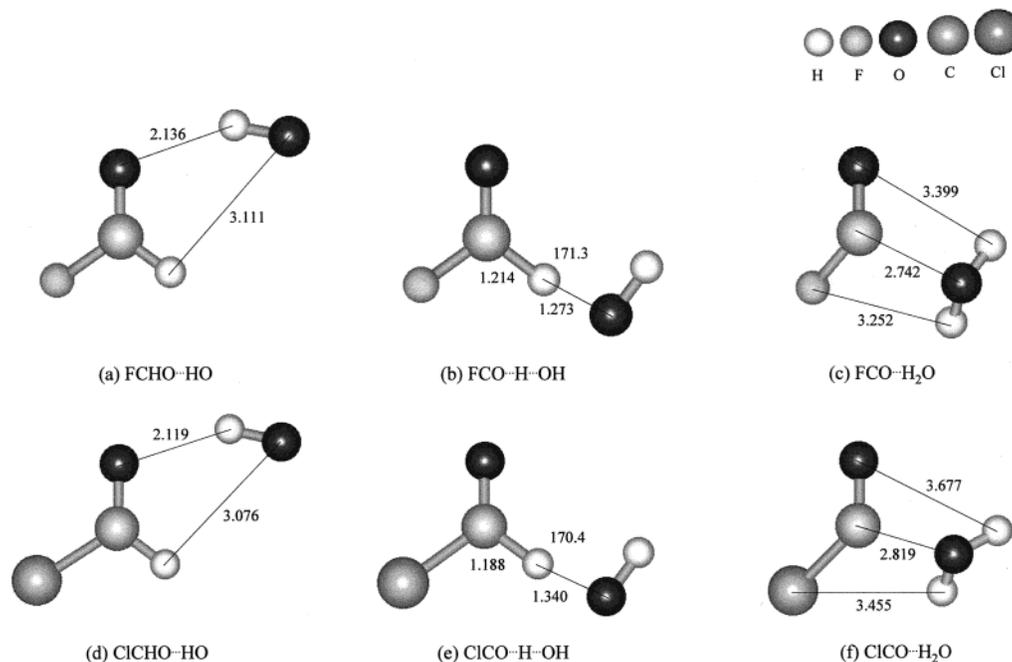
In a similar way, the rate constant for the direct mechanism ( $k_{\text{D}}$ ) can be derived:

$$k_{\text{D}} = \kappa_{\text{D}} \frac{k_{\text{B}} T}{h} \frac{Q^{\text{TS}}}{Q^{\text{React}}} \exp\left(-\frac{E^{\text{TS}} - E^{\text{React}}}{RT}\right) \quad (2)$$

The only difference between expressions 1 and 2 lies in the value of the tunneling factor, 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 the ones to be considered.

The tunneling factor and the full width of the barrier at half its height ( $\Delta S_{1/2}$ ) were calculated by assuming an unsymmetrical Eckart barrier.<sup>16</sup> The values of these two magnitudes also depend on the value of the imaginary frequency of the TS. A modified version of the numerical integration program of Brown<sup>17</sup> was used for the calculation of the tunneling factor. The output of the program with different input parameters was compared with the results reported by Johnston<sup>18</sup> for this kind of barrier, with excellent agreement.

Tunneling calculations considering an Eckart-type barrier are a simple (but not as simple as Wigner<sup>19</sup> or parabolic-type barrier<sup>20</sup> tunneling corrections), still practical way of accounting for tunneling that has been and still is widely used in the literature, even though more sophisticated methods to account for this phenomenon have been created, such as the multidimensional semiclassical zero- (ZCT) and small-curvature (SCT) tunneling methods.<sup>21</sup> A few years ago a study on the importance of quantum mechanical tunneling effects on the kinetics of the hydrogen exchange reaction of methane in a zeolite was published.<sup>22</sup> In Truong's paper,<sup>22</sup> the accuracy of Eckart tunneling calculations was demonstrated, in agreement with his previous work.<sup>23</sup> Not only different tunneling corrections were considered, but also variational TST (VTST) results were



**Figure 1.** Optimized structures in the OH hydrogen-abstraction reaction from FCHO and ClCHO, as obtained at the MP2(FC)/6-311++G(d,p) level: (a) FCHO...HO; (b) FCO...H...OH; (c) FCO...H<sub>2</sub>O; (d) ClCHO...HO; (e) ClCO...H...OH; (f) ClCO...H<sub>2</sub>O. Key: reactant complexes (a, d); transition states (b, e); product complexes (c, f).

compared with classical TST calculations. The success of the TST/Eckart combination has been clearly shown.

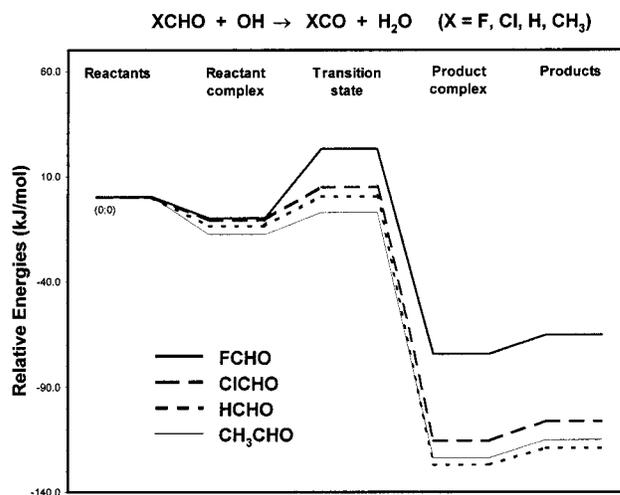
It is well-known that the Eckart method tends to overestimate the tunneling contributions especially at very low temperatures. In the previously mentioned papers,<sup>22,23</sup> where there is approximately the same degree of heavy-atom motion as the system moves along the reaction path, in comparison with the reactions under study, the Eckart corrections do not overestimate the rate constant at room temperature, as happens at much lower temperatures.

In our case the tunneling correction ( $\kappa$ ) is the only factor that allows us to differentiate quantitatively between the two proposed mechanisms for the reactions studied. We have previously shown<sup>3</sup> for the OH reaction with HCHO and CH<sub>3</sub>CHO that the present combination of methods (with all the approximations they imply) allows us to reproduce correctly the experimental kinetic parameters of these reactions. This fact proves that the approximations are valid and that they can be used to predict similar kinetic parameters in reactions between the same kinds of compounds. The validity of this statement will be shown in the present study.

## Results and Discussion

The OH radical attack on FCHO and ClCHO seems to occur in a very similar way as described previously<sup>3</sup> for HCHO and CH<sub>3</sub>CHO. The MP2-optimized geometries of the intermediate structures along the hydrogen-abstraction pathway are shown in Figure 1, where relevant geometrical parameters have been indicated. The reaction profiles for these four reactions (the results for the reactions with HCHO and CH<sub>3</sub>CHO are included for comparison) using CCSD(T)/6-311++G(d,p) energies are shown in Figure 2.

The reactant complexes for the FCHO + OH and ClCHO + OH reactions were found to be between 10 and 11 kJ/mol lower in energy than the isolated reactants, at 0 K. At 298 K their stabilization energies decrease by 2 kJ/mol. The structures of these complexes (Figure 1a,d) are very similar to those



**Figure 2.** Reaction profiles for the XCHO + OH (X = F, Cl, H, CH<sub>3</sub>) hydrogen-abstraction reactions using the calculated CCSD(T)/6-311++G(d,p) energy values, including the MP2(FC)/6-311++G(d,p) zero-point energy corrections.

calculated for the reactions with HCHO and CH<sub>3</sub>CHO and are determined by dipole-dipole interactions, or, more specifically, by hydrogen bonding. The interaction established between the carbonylic oxygen atom and the hydrogen atom of the OH radical becomes weaker as the electron-withdrawing effect of the substituent increases (in the series CH<sub>3</sub>, H, Cl, and F) because this effect reduces the electronic density on the oxygen atom of the aldehyde. As a result, the distance between the carbonylic oxygen and the hydroxyl hydrogen in the complex increases from 1.947 Å in CH<sub>3</sub>CHO...OH to 2.136 Å in FCHO...OH, and its stabilization energy is reduced. Consequently, the reactant complex of the FCHO + OH reaction is the least stable of all.

The symmetry of the TS for the OH reaction with FCHO and ClCHO is <sup>2</sup>A', implying that the unpaired electron is in the plane where the OH attack takes place. <sup>2</sup>A' is also the symmetry of the XCO radical generated.

The C $\cdots$ H and H $\cdots$ O distances in the TS (Figure 1b,e) allow us to rationalize the electronic effects of these substituents (F and Cl) on the kinetics. The TS in the case of ClCHO is formed earlier since the C $\cdots$ H distance is smaller (and the O $\cdots$ H distance is larger). It resembles more closely the reactants and is consistent with the fact that Cl is less electron-withdrawing than F and the electronic density at the carbonylic carbon is less reduced in ClCHO than in FCHO. Consequently, the abstraction of the hydrogen atom is more favored since the TS is more stable in ClCHO and a smaller activation energy barrier is found (Figure 2). The same reasoning explains the radical product generated in the ClCHO reaction is more stable and the greater endothermicity of this reaction in comparison to the FCHO reaction.

In the series of substituents CH<sub>3</sub>, H, Cl, and F, the TS is achieved later (the C $\cdots$ H distances in the case of CH<sub>3</sub>CHO and HCHO are 1.171 and 1.177 Å, respectively)<sup>3</sup> and a larger activation energy has to be overcome. This trend is consistent with the decreasing electron-donating effect of these substituents that is also the cause for the decreasing reactivity of these aldehydes toward the OH hydrogen-abstraction reaction.

As the electron-withdrawing effect of the substituent (when going from CH<sub>3</sub> to F) increases, the activation energy of these reactions increases while the enthalpy of reaction and the stabilization energy of the reactant complex decreases.

We have not included any discussion or tables with geometrical information regarding the reactants and products of the reactions studied because at the levels of theory used no significant differences are found with respect to the calculations reported by Francisco.<sup>12</sup>

The calculated PMP2 and CCSD(T) total energies, as well as the zero-point and thermal (at 298.15 K) vibrational energy corrections (calculated at the MP2 level) of the species involved in the reaction of OH with FCHO and ClCHO, are given as Supporting Information. The MP2 vibrational corrections were used to obtain the CCSD(T) energy differences. For these reactions spin contamination is only significant (but small) at the TS: the expectation value of  $S^2$  is 0.785 for the FCHO reaction and 0.780 for ClCHO, and in the MP2 calculation it is completely eliminated by projection. Hence, we should expect reliable results when applying the CCSD(T) method to an MP2-optimized geometry.

The stabilization energy of the reactant complexes ( $E_{a(-1)}$ ), the activation barriers of the second step of the complex mechanism ( $E_{a(2)}$ ), and the effective activation energies ( $E_a^{\text{eff}}$ ), calculated as

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

are given in Table 1 at 0 K together with the reaction enthalpies, for the methods employed. Effective activation energies and stabilization energies of the reactant complexes at 298.15 K have also been included. Values previously calculated or measured are shown for comparison.

The stabilization energies of the reactant complexes agree to within 0.5 kJ/mol in both cases with the two methods used. On the basis of the results obtained for the HCHO and CH<sub>3</sub>CHO reactions,<sup>3</sup> the PMP2 effective activation energies should be overestimated and the best values should be the ones given by the CCSD(T) method. The effective activation energies calculated are 23.1 and 5.0 kJ/mol for the FCHO + OH and ClCHO + OH reactions, respectively. The MP4 energy parameters (activation energies and enthalpies of reaction) reported by Francisco<sup>12</sup> fall between our PMP2 and CCSD(T) results. His

**TABLE 1: Relevant Barriers ( $E_a$ ) and Reaction Enthalpies ( $\Delta H$ ), in kJ/mol, Including Zero-Point Vibrational Corrections (ZPE), Unless Otherwise Specified, for the OH Hydrogen-Abstraction Reaction from FCHO and ClCHO**

basis set:							
6-311++G(d,p)	$E_{a(-1)}$	$E_{a(-1)}^b$	$E_{a(2)}$	$E_a^{\text{eff}}$	$E_a^{\text{eff} b}$	$\Delta H$	
FCHO + OH							
PMP2	9.5	7.6	39.5	30.0	29.8	-83.9	
CCSD(T)	10.0	8.0	33.1	23.1	23.0	-65.2	
previous calcs <sup>a</sup>				25.1	27.7	-72.8	
						-69.0, -71.1, 73.6 <sup>c</sup>	
expt						60.1 <sup>d</sup>	
ClCHO + OH							
PMP2	10.1	8.2	25.5	15.4	15.2	-125.3	
CCSD(T)	10.6	8.7	15.6	5.0	4.8	-105.9	
previous calcs <sup>a</sup>				9.6	11.8	-115.9	

<sup>a</sup> Reference 12. <sup>b</sup> Including thermal correction (TCE) at 298.15 K. <sup>c</sup> Reference 13 (DFT). <sup>d</sup> Reference 4a.

**TABLE 2: Total Partition Functions ( $Q$ ) of the Reactants and the TS and Imaginary Frequency ( $\nu^\ddagger$  in cm<sup>-1</sup>) of the TS of the OH Hydrogen-Abstraction Reaction from FCHO and ClCHO, Calculated at the MP2(FC)/6-311++G(d,p) Level<sup>a</sup>**

param	system	
	FCHO + OH	ClCHO + OH
$Q^{\text{OH}}$	$6.025\ 09 \times 10^7$	$6.025\ 09 \times 10^7$
$Q^{\text{FCHO/ClCHO}}$	$1.147\ 42 \times 10^{11}$	$3.870\ 97 \times 10^{11}$
$Q^{\text{TS}}$	$3.641\ 61 \times 10^{13}$	$8.578\ 99 \times 10^{13}$
$Q_{i=i} Q_{j=j}$	$4.826\ 67^b$	$3.828\ 09^c$
$Q_{\text{IR}}^{\text{TS}}$	50,449 19	54,771 79
$Q_{\text{corr}}^{\text{TS}}$	$3.806\ 28 \times 10^{14}$	$1.227\ 47 \times 10^{15}$
$\nu^\ddagger$	2455	1939
$\nu^\ddagger_{\text{ThinSpace}d}$	3482	3535

<sup>a</sup> Total internal rotation partition functions ( $Q_{\text{IR}}^{\text{TS}}$ ) for the TS are also reported, as well as the vibrational components ( $Q_{i=i} Q_{j=j}$ ) that were eliminated from the calculation of the corrected total partition function ( $Q_{\text{corr}}^{\text{TS}}$ ). All partition functions, except  $Q_{\text{IR}}^{\text{TS}}$  and  $Q_{\text{corr}}^{\text{TS}}$ , were calculated by Gaussian98. <sup>b</sup>  $i = 1$  and  $j = 3$ . <sup>c</sup>  $i = 2$  and  $j = 3$ . <sup>d</sup> Reference 12 (HF/6-31G(d)).

values at 298 K are between 4.7 and 7.0 kJ/mol larger than our CCSD(T) effective energy barriers.

The DFT barriers calculated by Jursic<sup>13</sup> for the FCHO + OH reaction are zero or negative, which shows the failure of DFT methods to predict the activation energy for this reaction. However, on the basis of calculations performed for a similar reaction with DFT and CCSD(T) methods, he estimated an activation energy of about 21 kJ/mol, in good agreement with our calculation.

The best value for the heat of reaction of the FCHO + OH system is the one obtained from the CCSD(T) energies. It is -65.2 kJ/mol at 0 K and -64.1 at 298 K, in very good agreement with the experimental value of -60.1 kJ/mol. The heat of reaction calculated for the ClCHO reaction is -105.9 kJ/mol at 0 K and -104.5 at 298 K.

The values of the partition functions needed for the calculation of the rate constants of the reactions studied are given in Table 2, as well as the imaginary frequency of the TS. Three low frequencies (below 210 cm<sup>-1</sup>) in addition to the imaginary frequency were calculated for the hydrogen-abstraction TS. Of these, two were identified as internal rotations (or torsional vibrations) by visualization of the normal modes: frequencies 1 and 3 for the FCHO-TS and frequencies 2 and 3 for the ClCHO-TS. These harmonic modes correspond most closely to the two new internal rotors created in the TS (XCOH $\cdots$ OH and XCO $\cdots$ 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

**TABLE 3: Rate Constants and Tunneling Parameters for the OH Hydrogen-Abstraction Reaction from FCHO and ClCHO, 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<sup>a</sup>**

	FCHO + OH	ClCHO + OH
Direct Mechanism		
$\kappa$	70.12	2.60
$\Delta s_{1/2}$ (Å)	0.24	0.15
$k_D$ (L/(mol·s))	$2.10 \times 10^6$	$1.12 \times 10^8$
Complex Mechanism		
$\kappa$	244.30	12.10
$\Delta s_{1/2}$ (Å)	0.29	0.26
$k_{\text{eff}}$ (L/(mol·s))	$7.33 \times 10^6$	$5.21 \times 10^8$
Experiment		
$k$ (L/(mol·s))	$<6.03 \times 10^6$ <sup>b</sup>	$<3.01 \times 10^8$ <sup>b</sup>
	$<2.41 \times 10^6$ <sup>c</sup>	$<1.93 \times 10^8$ <sup>d</sup>
Previous Calculation <sup>e</sup>		
$\kappa$	13.83	16.26
$k$ (L/(mol·s))	$4.03 \times 10^5$	$1.89 \times 10^8$

<sup>a</sup> The frequency calculations were performed at the MP2(FC)/6-311++G(d,p) level.  $\kappa$  is the tunneling correction and  $\Delta s_{1/2}$  is the full width of the barrier at half its height. <sup>b</sup> Reference 4a (1997). <sup>c</sup> Reference 7 (1993). <sup>d</sup> Reference 8 (1990). <sup>e</sup> Reference 12 (1992).

moments of inertia. These harmonic modes were treated as free rotors in the calculation of the internal rotation partition function of the TS ( $Q_{\text{IR}}^{\text{TS}}$ ).<sup>24,25</sup>

The harmonic contributions of these two low frequencies were eliminated from the vibrational partition function to correct the total partition function of the TS ( $Q_{\text{corr}}^{\text{TS}}$ ). For the OH reaction with FCHO,  $Q_{\text{corr}}^{\text{TS}}$  is calculated as

$$Q_{\text{corr}}^{\text{TS}} = \frac{Q^{\text{TS}} Q_{\text{IR}}^{\text{TS}}}{Q_{\nu=1} Q_{\nu=3}}$$

For the reaction with ClCHO,  $Q_{\text{corr}}^{\text{TS}}$  is calculated in a very similar way except that the vibrational components of frequencies 2 and 3 are the ones considered. This was also the procedure followed in the calculation of the internal-rotation partition function of the TS for the OH hydrogen-abstraction reaction from HCHO and CH<sub>3</sub>CHO.

We would also like to mention that the inspection of the vibrational mode corresponding to the imaginary frequency of the TS of these reactions shows us that this vibration can be approximated by the simple movement of a light atom (H) between two fixed heavier atoms (C and O). There is little heavy atom motion as the system moves along the reaction path.

The best values for the activation energies and the rate constants for the reactions of HCHO and CH<sub>3</sub>CHO with OH radicals were obtained with the CCSD(T) method using MP2 geometries, and therefore, we have used the same level of theory in the present study. The results of the rate constant calculations for the reactions of FCHO and ClCHO with OH radicals using the CCSD(T)/6-311++G(d,p) energy values are given in Table 3, for both the direct ( $k_D$ ) and complex ( $k_{\text{eff}}$ ) reaction mechanisms at 298.15 K. Experimental upper bounds and the results previously calculated by Francisco<sup>12</sup> have been included for comparison. The tunneling corrections ( $\kappa$ ) and the full width of each barrier at half its height ( $\Delta s_{1/2}$ ) have also been reported in Table 3.

If the rate constant (all the rate constant values reported henceforth are expressed in units of L mol<sup>-1</sup> s<sup>-1</sup>) is calculated according to the complex mechanism, tunneling factors ( $\kappa$ ) of 244.30 (FCHO) and 12.10 (ClCHO) are obtained, and the

**TABLE 4: Estimate of the Difference between the Effective and Direct Rate Constants for the Aldehyde + OH Reactions Studied with Positive Effective Activation Energies**

aldehyde + OH	$((k_{\text{eff}} - k_D)/k_{\text{eff}}) \times 100\%$
HCHO	82.4
ClCHO	78.5
FCHO	71.3

effective rate constants are  $7.33 \times 10^6$  (FCHO) and  $5.21 \times 10^8$  (ClCHO), in very good agreement (just slightly greater) with the most recent upper bound limits of  $6.03 \times 10^6$  (FCHO) and  $3.01 \times 10^8$  (ClCHO) reported by Atkinson et al.<sup>4a</sup> If an elementary mechanism is assumed, smaller tunneling factors are calculated (70.12 for FCHO and 2.60 for ClCHO) as expected, since the forward and reverse potential energy barriers of the elementary process in which the hydrogen atom is abstracted are both reduced. But the forward barrier is reduced to a greater extent, and as a consequence, the direct rate constants are smaller ( $2.10 \times 10^6$  for FCHO and  $1.12 \times 10^8$  for ClCHO) than the effective rate constants. These values are in very good agreement (just slightly smaller) with the first reported upper bound limits ( $2.41 \times 10^6$  for FCHO<sup>7</sup> and  $1.93 \times 10^8$  for ClCHO<sup>8</sup>). We note that from the first experimental measurements<sup>7,8</sup> on these systems in 1990 and 1992 to the latest experimental results in 1997,<sup>4a</sup> the upper bound limit reported for the rate constants has increased. Moreover, we observe that the values in best agreement with the latest experimental results are the ones obtained by considering a complex mechanism.

The rate constant reported by Francisco<sup>12</sup> for the ClCHO + OH reaction ( $1.89 \times 10^8$ ) is in very good agreement with the first upper bound value reported for this reaction, but his result for the FCHO + OH system is 1 order below ( $4.03 \times 10^5$ ). We think the cause for this discrepancy lies in the calculation of the tunneling factor. The energy barriers calculated by Francisco as well as the imaginary frequency of the TS (see Table 2) are bigger than ours, in accordance with the methods employed by him. Hence, his tunneling factors (13.83 for FCHO and 16.26 for ClCHO) should be greater than the values reported by us for the direct mechanism, but that is not the case. Using our program for the calculation of the tunneling factors assuming an unsymmetrical Eckart barrier, and using as input data the forward and reverse potential energy barriers calculated by Francisco, as well as the imaginary frequency of the TS reported by him, tunneling factors of 397.40 and 11.88 are obtained for the FCHO + OH and ClCHO + OH reactions, respectively.

Consideration of the results obtained for the direct and effective rate constants of the reactions with positive effective activation energies among the four reactions studied indicates that it is possible to estimate the percentage by which these two rate constants differ due to an increase of the effective activation energy. It can be seen from Table 4 that the bigger the effective activation energy (when going from HCHO to FCHO), the smaller the difference between the rate constants calculated, showing that even for the FCHO case the discrepancy between considering an elementary or complex mechanism to describe the kinetics of its reaction with OH radicals is still significant, and this difference tends to be reduced as the activation energy increases and the stabilization energy of the reactant complex decreases.

## Conclusions

The significance of considering the complex character of the kinetics of a radical–molecule reaction was one of the main conclusions of a recent publication.<sup>3</sup> The importance of taking into account the formation of the reactant complex for the OH

hydrogen-abstraction reaction from HCHO and CH<sub>3</sub>CHO was demonstrated. For these systems very small or negative activation energies have been experimentally measured. This paper has focused on a similar study for the reaction of OH with FCHO and ClCHO, systems for which there is very little experimental information available (only upper bound limit rate constants).

By applying the same methodology, we have shown that the same complex mechanism considered for the reactions from HCHO and CH<sub>3</sub>CHO can be applied to the OH hydrogen-abstraction reaction from FCHO and ClCHO, and furthermore (effective) activation energies and rate constants have been calculated successfully. Our rate constant calculations are in better agreement with experiment than previous calculations performed on these reactions, and this allows us to report better activation energies and reaction enthalpies for which there are no experimental data.

It can also be rationalized from these results that the bigger the effective energy barrier for radical–molecule reactions and the smaller the stabilization energy of the reactant complex, the more closely its behavior resembles an elementary reaction. In other words, if we were able to calculate the mechanism and the rate constant of another aldehyde much less reactive than FCHO, very probably it would be the case that the formation of the reactant complex could be ignored, because no new qualitative or quantitative information about the mechanism will be provided by considering its formation, and the assumption of an elementary mechanism will give similar results to those obtained by considering a complex mechanism.

Two extreme behaviors can be considered for a radical–molecule reaction: for systems with very low or negative activation energies the consideration of a complex mechanism is essential, but if the activation energy is significantly higher and the stabilization energy of the reactant complex is negligible, then the consideration of an elementary process will be a satisfactory approximation.

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**Supporting Information Available:** The MP2(FC)/6-311++G(d,p) optimized geometries in Cartesian coordinates (Table S1) and total energies, zero-point, and thermal (at 298.15 K) vibrational corrections in atomic units (Table S2) of the species involved in the reactions studied. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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