Chapter 5. OH Hydrogen-Abstraction from FCHO and ClCHO

5.1. Introduction

Earlier experimental and theoretical studies on reactions between OH radicals and aldehydes have been performed.[1,2] In an earlier study[3] described in Chapter 4, the OH hydrogen-abstraction reaction from formaldehyde and acetaldehyde was examined. A complex mechanism in which 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 was considered. TST was applied for the calculation of the rate constants with successful results. Tunneling corrections were incorporated assuming an unsymmetrical Eckart barrier.

Consideration of the reactant complex formation has two important consequences in the kinetics calculations of these systems. It explains the negative activation barriers observed (especially for acetaldehyde) 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. In view of the previous successful results, it was 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 for which activation energy values are unknown.[1a,4,5]

Formyl fluoride (FCHO), one of the halogenated molecules in the upper stratosphere, is a major product of the degradation in the troposphere of CH_3CFH_2 (HFC-134a).[6] 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_3Cl, CH_2Cl_2, $CHCl_3$, and hydrochlorofluorocarbons (HCFCs),[7] as well as from the tropospheric reaction of Cl atoms with volatile organic compounds such as isoprene.[8] The

reaction of FCHO and ClCHO with OH radicals is thought to be a tropospheric removal route for these compounds.

The OH reaction with the substituted aldehydes of interest was first examined theoretically by Francisco[9] 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. 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 the new data reported here, for comparison.

A DFT study on the FCHO + OH reaction was performed by Jursic,[10] who used hybrid functionals (B3LYP, B3P86 and B3PW91) 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, TST is applied to the calculation of the rate constants and tunneling corrections are considered. The aim of this study is to show that the same complex mechanism can be applied to these reactions and to provide better theoretically-determined kinetics parameters.

5.2. Computational details

Geometries were optimized at the MP2(FC)/6-311++G(d,p) 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 HCHO and CH_3CHO with OH radicals were characterized. The same two mechanisms previously considered in Chapter 4 will be taken into account in this study. TST with Eckart tunneling corrections will be applied for the calculation of the rate constants.

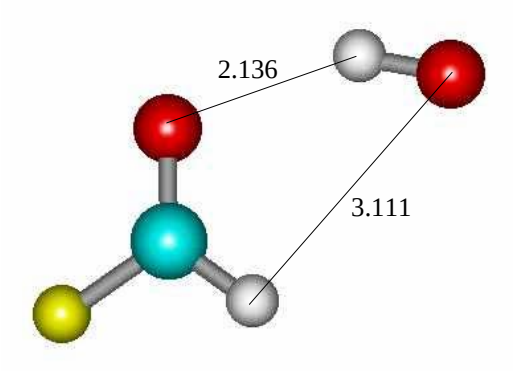
For the reactions under study the tunneling correction (κ) is the only factor that allows the quantitative differentiation between the two proposed mechanisms. It has been shown previously that for the HCHO and CH_3CHO reactions with OH the present combination of methods (with all the approximations they imply) reproduce correctly the experimental kinetic parameters of these reactions. This fact demonstrates that the approximations are reasonable 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.

5.3. Results and discussion

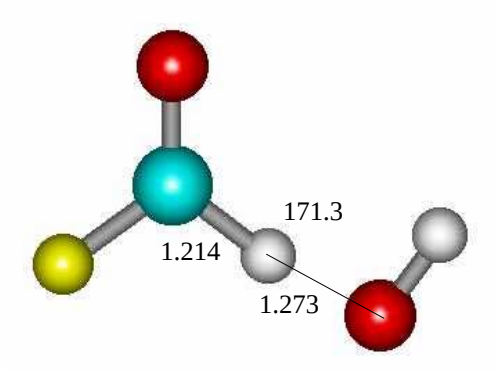
The OH radical attack on FCHO and ClCHO seems to occur in a very similar way as described previously for HCHO and CH_3CHO. The MP2 optimized geometries of the intermediate structures along the hydrogen-abstraction pathway are shown in Fig. 5.1 (FCHO + OH) and 5.2 (ClCHO + OH), where relevant geometrical parameters have been indicated. The reaction profiles for these four reactions (the results for the reactions with HCHO and CH_3CHO are included for comparison) using CCSD(T)/6-311++G(d,p) energies are shown in Fig. 5.3.

The reactant complexes for the FCHO + OH and ClCHO + OH reactions are calculated 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 (Fig. 5.1a and 5.2a) are very similar to those calculated for the reactions with HCHO and CH_3CHO (Fig. 4.1), 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_3, 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 $CH_3CHO^{\cdots}OH$ to 2.136 Å in $FCHO^{\cdots}OH$, and its stabilization energy is reduced. Consequently, the reactant complex of the FCHO + OH reaction is the least stable.

(a) FCHO···HO



(b) FCO···H···OH



(c) FCO···H_2O

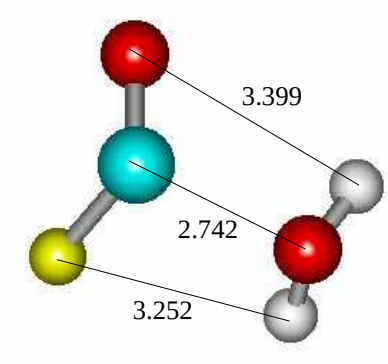
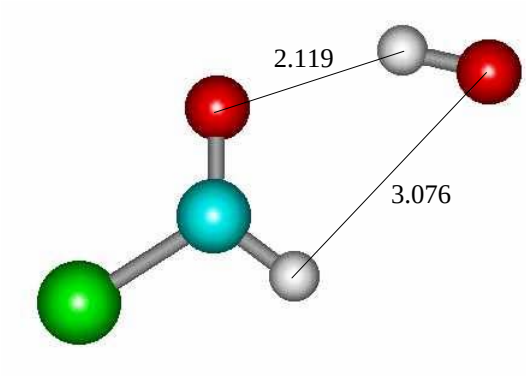
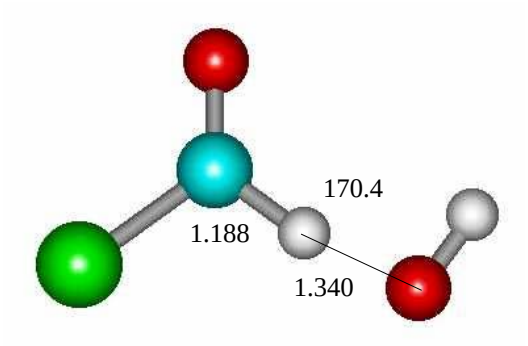


Figure 5.1. Optimized structures of the FCHO + OH hydrogen-abstraction reaction (a) Reactant complex, (b) TS and (c) Product complex. (Bond distances are given in Å and angles in degrees)

(a) ClCHO···HO



(b) ClCO···H···OH



(c) ClCO···H_2O

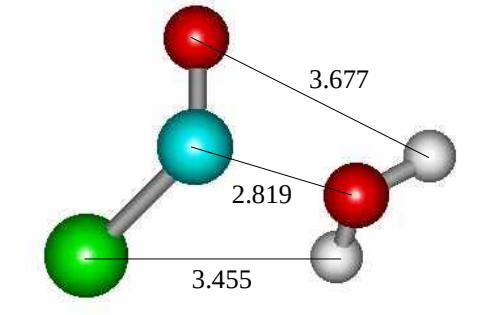


Figure 5.2. Optimized structures of the ClCHO + OH hydrogen-abstraction reaction (a) Reactant complex, (b) TS and (c) Product complex. (Bond distances are given in Å and angles in degrees)

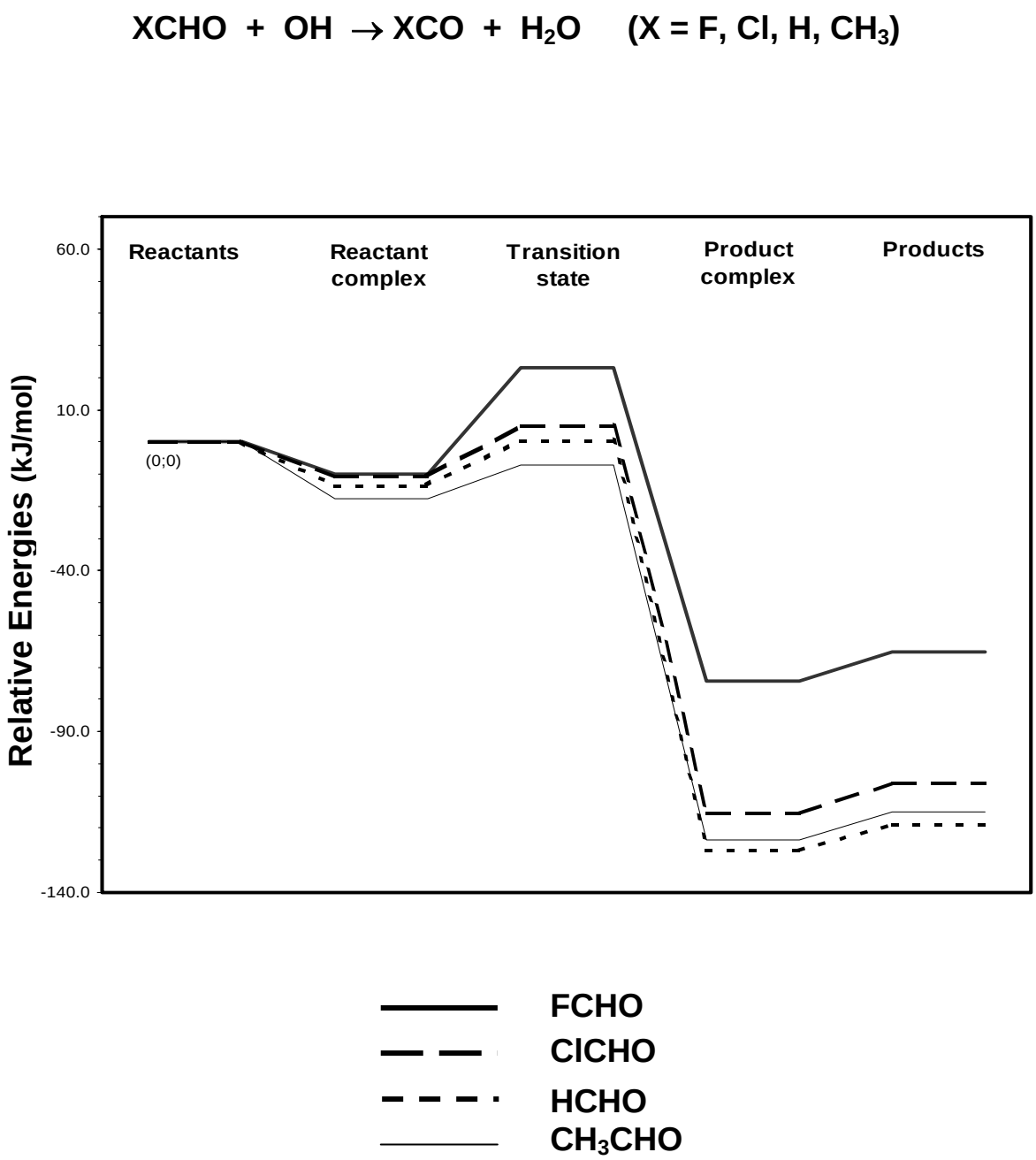


Figure 5.3. Schematic reaction profiles for the XCHO + OH (X = F, Cl, H, CH_3) hydrogen-abstraction reactions using the calculated CCSD(T)/6-311++G(d,p) energy values, including the MP2(FC)/6-311++G(d,p) zero-point energy corrections.

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

The C···H and H···O distances in the TS (Fig. 5.1b and 5.2b) can be used 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···H distance is smaller (and the O···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 in ClCHO is more favoured since the TS is more stable and a smaller activation energy barrier is found (Fig. 5.3). The same reasoning explains why the radical product generated in the ClCHO reaction is more stable, and also explains the greater endothermicity of this reaction in comparison to that of the FCHO reaction.

In the series of substituents, CH_3, H, Cl and F, the TS is achieved later (the C···H distances in the case of CH_3CHO and HCHO are 1.171 and 1.177 Å, respectively, see Fig. 4.2) and a larger activation energy must 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 towards the OH hydrogen-abstraction reaction.

As the electron-withdrawing effect of the substituent (when going from CH_3 to F) increases, the activation energy of these reactions increases while the enthalpy of reaction and the stabilization energy of the reactant complex decreases.

A full discussion and tabulation of the geometrical information regarding the reactants and products of the reactions studied is not included because at the levels of theory used no significant differences were found with respect to the calculations reported by Francisco.

The Cartesian coordinates of the optimized structures along the reaction pathway for the systems under study, as well as the calculated PMP2 and CCSD(T) total energies, 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 available.[11]

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, reliable results are expected 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^{eff}), calculated according to equation (4.4), are given in Table 5.1 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 MP2 vibrational corrections were used to obtain the CCSD(T) energy differences.

The stabilization energies of the reactant complexes agree to within 0.5 kJ/mol in both cases with the two methods used. Based on the results obtained for the HCHO and CH_3CHO reactions, 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 fall between the PMP2 and CCSD(T) results. His values at 298 K are between 4.7 and 7.0 kJ/mol larger than the CCSD(T) effective energy barriers calculated.

Table 5.1. Relevant barriers (E_a) and reaction enthalpies (ΔH), 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^{eff}	E_a^{eff} [(b)]	ΔH	ΔH [(b)]
FCHO + OH							
PMP2	9.5	7.6	39.5	30.0	29.8	-83.9	-82.7
CCSD(T)	10.0	8.0	33.1	23.1	23.0	-65.2	-64.0
Previous calculations [(a)]				25.1	27.7	-72.8	
[(c)]						-69.0, -71.1, -73.6	
Experiment [(d)]							-60.1
ClCHO + OH							
PMP2	10.1	8.2	25.5	15.4	15.2	-125.3	-123.8
CCSD(T)	10.6	8.7	15.6	5.0	4.8	-105.9	-104.4
Previous calculations [(a)]				9.6	11.8	-115.9	

[(a)] Ref. 9 (1992); [(b)] Including thermal correction (TCE) at 298.15 K; [(c)] Ref. 10 (1998); [(d)] Ref. 1a (1997)

The DFT barriers calculated by Jursic for the FCHO + OH reaction are zero or negative, which shows the inability 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 the new calculations.

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 5.2, 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 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···OH and XCO···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}).[12,13]

The harmonic contributions of these two 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 FCHO, Q_{corr}^{TS} is calculated as:

$$Q_{corr}^{TS} = \frac{Q^{TS}\ Q_{IR}^{TS}}{Q_{v=1}\ Q_{v=3}} \tag{5.1}$$

For the reaction with ClCHO, Q_{corr}^{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-rotational partition function of the TS for the OH hydrogen-abstraction reaction from HCHO and CH_3CHO.

Inspection of the vibrational mode corresponding to the imaginary frequency of the TS of these reactions shows 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.

Table 5.2. 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 FCHO and ClCHO, calculated at the MP2(FC)/6-311++G(d,p) level.

System	**FCHO + OH**	**ClCHO + OH**
Q^{OH}	$6.02509 \cdot 10^{7}$	$6.02509 \cdot 10^{7}$
Q^{XCHO}	$1.14742 \cdot 10^{11}$	$3.87097 \cdot 10^{11}$
Q^{TS}	$3.64161 \cdot 10^{13}$	$8.57899 \cdot 10^{13}$
$\prod Q_{v=i}$ [(a)]	4.827 [(e)]	3.828 [(f)]
Q_{IR}^{TS} [(b)]	50.449	54.772
Q_{corr}^{TS} [(c)]	$3.80628 \cdot 10^{14}$	$1.22747 \cdot 10^{15}$
$\nu^{\neq}$	2455	1939
$\nu^{\neq}$ [(d)]	3482	3535

[(a)] Vibrational components that were eliminated from the calculation of Q_{corr}^{TS}; [(b)] Total internal-rotational partition function of the TS; [(c)] Corrected total partition function of the TS; [(d)] Ref. 9 (HF/6-31G(d)); [(e)] i=1, 3; [(f)] i=2, 3

The best values for the activation energies and the rate constants for the reactions of HCHO and CH_3CHO with OH radicals were obtained with the CCSD(T) method using MP2 geometries. Therefore, the same level of theory has been used in the present study. The results of the rate constant calculations for the reactions of FCHO and ClCHO with OH radicals, at 298 K using the CCSD(T)/6-311++G(d,p) energy values are given in Table 5.3, for both the direct (k_D) and complex (k_{eff}) reaction mechanisms. Experimental upper bounds and the results calculated by Francisco have been included for comparison. The tunneling corrections (κ) and the full width of each barrier at half its height ($\Delta s_{½}$) have also been reported in Table 5.3.

Table 5.3. 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.

	FCHO + OH	**ClCHO + OH**
Direct Mechanism		
κ	70.12	2.60
$\Delta s_{½}$ (Å)	0.24	0.15
k_D (L/mol·s)	$2.10 \cdot 10^6$	$1.12 \cdot 10^8$
Complex Mechanism		
κ	244.30	12.10
$\Delta s_{½}$ (Å)	0.29	0.26
k_{eff} (L/mol·s)	$7.33 \cdot 10^6$	$5.21 \cdot 10^8$
Experiment		
k (L/mol·s)	$< 6.03 \cdot 10^6$ [(a)]	$< 3.01 \cdot 10^8$ [(a)]
	$< 2.41 \cdot 10^6$ [(b)]	$< 1.93 \cdot 10^8$ [(c)]
Previous Calculation [(d)]		
κ	13.83	16.26
k (L/mol·s)	$4.03 \cdot 10^5$	$1.89 \cdot 10^8$

[(a)] Ref. 1a (1997); [(b)] Ref. 4 (1993); [(c)] Ref. 5 (1990); [(d)] Ref. 9 (1992)

If the rate constant (all the rate constant values reported henceforth are expressed in units of $Lmol^{-1}s^{-1}$) is calculated according to the complex mechanism, tunneling factors (κ) of 244.30 (FCHO) and 12.10 (ClCHO) are obtained, and the effective rate constants are $7.33 \cdot 10^6$ (FCHO) and $5.21 \cdot 10^8$ (ClCHO), in very good agreement (just slightly greater) with the most recent upper-bound limits of $6.03 \cdot 10^6$ (FCHO) and $3.01 \cdot 10^8$ (ClCHO) reported by Atkinson *et al.*[1a] 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 ($2.10 \cdot 10^6$ for FCHO and $1.12 \cdot 10^8$ for ClCHO) than the effective rate constants. These values are in very good agreement (just slightly smaller) with the first reported upper-bound limits ($2.41 \cdot 10^6$ for FCHO and $1.93 \cdot 10^8$ for ClCHO). From the first experimental measurements[4,5] on these systems in 1990 and 1992, to the latest experimental results in 1997,[1b] the upper-bound limit reported for the rate constants has increased. Moreover, 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 for the ClCHO + OH reaction ($1.89 \cdot 10^8$) is in very good agreement with the first upper-bound value reported for this reaction, but the author's result for the FCHO + OH system is an order of magnitude smaller ($4.03 \cdot 10^5$). This discrepancy may be a consequence of the calculation of the tunneling factor. The energy barriers calculated by Francisco as well as the imaginary frequency of the TS (see Table 5.2) are greater than the new values reported in the present study, in accordance with the methods employed by the author. Hence, Francisco's tunneling factors (13.83 for FCHO and 16.26 for ClCHO) should be greater than the values reported for the direct mechanism, but that is not the case. Tunneling factors of 397.40 and 11.88 for the FCHO + OH and ClCHO + OH reactions, respectively, were calculated using the previously-mentioned program. An unsymmetrical Eckart barrier was assumed, with the forward and reverse potential energy barriers and the imaginary frequency of the TS reported by Francisco. Furthermore, the tunneling corrections reported by the author decrease as the activation barriers increase (for the reactions of HCHO, ClCHO and FCHO with OH radicals) but the opposite is expected.[14]

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. The data in Table 5.4 shows

that the greater the effective activation energy (when going from HCHO to FCHO) the smaller the difference between the calculated rate constants. This shows that even for FCHO the discrepancy between considering an elementary or complex mechanism to describe the kinetics of its reaction with OH radicals is still significant. This difference tends to be reduced as the activation energy increases and the stabilization energy of the reactant complex decreases.

Table 5.4. Estimate of the difference between the effective and direct rate constants for the aldehyde + OH reactions studied with positive effective activation energies.

Adehyde + OH	$\left(\frac{k_{eff} - k_D}{k_{eff}}\right)\cdot 100\%$
HCHO	82.4
ClCHO	78.5
FCHO	71.3

5.4. Conclusions

The significance of considering the complex character of the kinetics of a radical-molecule reaction was shown in Chapter 4. This chapter has focused on 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 it has been shown that the same complex mechanism considered for the reactions from HCHO and CH_3CHO 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. The rate constants calculated in this study are in better agreement with experiment than previous

calculations performed on these reactions. Hence better activation energies and reaction enthalpies have been reported for which there is 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 behaviour resembles an elementary reaction. In other words, if the mechanism and the rate constant of another aldehyde much less reactive than FCHO, such as, perhaps, CF_3CHO, were to be calculated, the formation of the reactant complex could probably be ignored, since its consideration would provide no new qualitative or quantitative information about the mechanism. Hence, the assumption of an elementary mechanism should give similar results to those obtained by considering a complex mechanism.

Two extreme behaviours 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 is a satisfactory approximation.

5.5. References

1. (a) Atkinson, R.; Baulch, D.L.; Cox, R.A.; Hampson, R.F., Jr.; Kerr, J.A.; Rossi, M.J.; Troe, J. *J. Phys. Chem. Ref. Data* **1997**, *26*, 521. (b) DeMore, W.B.; Sander, S.P.; Golden, D.M.; Hampson, R.F.; Kurylo, M.J.; Howard, C.J.; Ravishankara, A.R.; Kolb, C.E.; Molina, M.J. *JPL Publication* 97-4 **1997**. (c) Taylor, P.H.; Rahman, M.S.; Arif, M.; Dellinger, B.; Marshall, P. *Symp. Int. Combust. Proc.* **1996**, *26*, 497, and references therein.

2. The NIST Chemical Kinetics Database, NIST Standard Reference Database, U.S. Dept. of Commerce, Technology Administration, National Institute of Standards and Technology: Gaithersburg, MD, 17-2Q98.

3. Alvarez-Idaboy, J.R.; Mora-Diez, N.; Boyd, R.J.; Vivier-Bunge, A. *J. Am. Chem. Soc.* **2001**, *123*, 2018.

4. Wallington, T.J.; Hurley, M.D. *Environ. Sci. Technol.* **1993**, *27*, 1448.

5. Libuda, H.G.; Zabel, F.; Fink, E.H.; Becker, K.H. *J. Phys. Chem.* **1990**, *94*, 5860.

6. (a) Wallington, T.J.; Hurley, M.D.; Ball, J.C.; Kaiser, E.W. *Environ. Sci. Technol.* **1992**, *26*, 1318. (b) Hasson, A.S.; Moore, C.M.; Smith, I.W.M. *Int. J. Chem. Kinet.* **1998**, *30*, 541.

7. (a) Sanhueza, E.C.; Heicklen, J. *J. Phys. Chem.* **1975**, *79*, 7. (b) Gay, B.W.; Hanst, P.L.; Bufalini, J.J.; Noonan, R.C. *Environ. Sci. Technol.* **1976**, *10*, 58. (c) Niki, H.; Maker, P.D.; Savage, C.M.; Breitenbach, L.P. *Int. J. Chem. Kinet.* **1980**, *12*, 1001. (d) Niki, H.; Maker, P.D.; Savage, C.M.; Breitenbach, L.P.; Martinez, R.I.; Herron J.T. *J. Phys. Chem.* **1982**, *86*, 1858. (e) Tuazon, E.C.; Atkinson R.; Aschmann, S.M.; Goodman, M.A.; Winer, A.M. *Int. J. Chem. Kinet.* **1988**, *20*, 241.

8. Fantechi, G.; Jensen, N.R.; Saastad, O.; Hjorth, J.; Peeters, J. *J. Atmos. Chem.* **1998**, *31*, 247.

9. Francisco, J.S. *J. Chem. Phys.* **1992**, *96*, 7597.

10. Jursic, B.S. *J. Mol. Struct. (Theochem)* **1998**, *434*, 53.

11. Mora-Diez, N.; Alvarez-Idaboy, J.R.; Boyd, R.J. *J. Phys. Chem.*, **2001**, in press.

12. Benson, S.W. *Thermochemical Kinetics*, 2nd Ed., Wiley & Sons, New York, p. 43, 1976.

13. Chuang, Y-Y; Truhlar, D.G. *J. Chem. Phys.* **2000**, *112*, 1221.

14. Johnston, H.S. *Gas Phase Reaction Rate Theory*, Ronald Press Company, New York, 1966.