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1 **Temperature dependence of rate coefficients for the gas phase reaction of**
2 **OH with 3-chloropropene. A theoretical and experimental study.**

3
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12
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18
19
20 **Credit Author Statement**

21 **Mariela Aguilera Sammaritano:** investigation, formal analysis, visualization, writing (review).

22 **Mauro González Vera:** investigation, formal analysis. **Pablo Cometto:** conceptualization,
23 investigation, formal analysis, writing (original draft, review & editing), resources, funding
24 acquisition and supervision. **Tatiane Nicola Tejero:** investigation. **Glauco Bauerfeldt:**
25 software, resources, formal analysis, writing (review), supervision. **Abdelwahid Mellouki:**
26 resources, formal analysis, funding acquisition, writing (review), supervision.

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Abstract

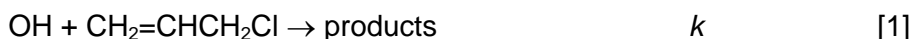
This work studies the mechanism steps of the OH radical + 3-chloropropene gas phase reaction that could explain the apparent negative activation energy experimentally observed. A reinvestigation of the rate coefficients (k) temperature dependence, using a PLP-LIF technique, between 253 and 371 K, was performed to provide new data for kinetic parameters critical revisions. A canonical Variational Transition State Theory study was performed to obtain the k temperature dependence considering four additions and one H atom abstraction pathways. The theoretical results can explain the experimental Arrhenius behavior, being an OH addition channel not described in previous literature the main reaction pathway.

1. Introduction.

3-Chloropropene is an important intermediate in the petrochemical industry that is used to synthesize epichlorohydrin and glycerin, allyl compounds such as allyl alcohol, allyl amines, allyl esters, and polyesters¹. Its derivatives are found in varnishes, plastics, adhesives, perfumes, pharmaceuticals, and insecticides². U.S. Environmental Protection Agency (EPA) considers 3-Chloropropene to be a possible human carcinogen³ and that individuals may be exposed through breathing contaminated air².

Its atmospheric chemistry has been investigated by various groups, Albaladejo et al.⁴ have concluded that the gas phase reaction with OH radical constitutes its main atmospheric removal process in the troposphere. Grosjean⁵ has proposed that the reaction releases Cl atoms and leads to carbonyl compounds as reported by Zhang et al.⁶ and Tuazon et al.⁷

To the best of our knowledge, the reaction of OH with 3-chloropropene has been investigated by a limited number of groups. Edney et al.^{8,9} and Tuazon et al.⁷ used the relative rate method to determine the rate coefficient value at room temperature in N₂ as bath gas. Martinez et al.¹⁰ have estimated k_{298K} by the relationship between the rate coefficients of the reactions of the OH and NO₃ radical with a haloprenes series. The only absolute measurement was performed by Albaladejo et al.⁴ in the temperature range 228 - 388 K, using the pulsed laser photolysis-laser induced fluorescence technique (PLP-LIF) with He as carrier gas.



k refers to the second order rate coefficient for the global reaction (that will be under scripted as $k_{\text{-CVTST}}$, when is theoretically calculated in this work). The temperature dependence of k shows slight negative activation energy. This behavior is widely observed in the gas phase reaction of OH radical with unsaturated volatile organic compounds (UVOCs)¹¹⁻¹³. In general, the negative dependence of the rate coefficients with the temperature has been justified by a mechanism in which the reversible formation of a pre-barrier complex takes place in the OH radical electrophilic addition to the double bond, followed by an irreversible reaction step through a saddle point, to products.¹⁴⁻¹⁶ In particular, Zhang et al.⁶ have computationally investigated the gas phase reaction of OH radical with 3-Chloropropene to products at 100 Torr and between 200–600 K temperature range. They have considered two addition and four hydrogen abstraction pathways. They have employed a variational transition state model and multichannel RRKM theory to calculate the temperature and pressure dependence of the rate constants.

83 In the present work we have reinvestigated the temperature dependence of k
84 using a PLP-LIF apparatus, in order to provide new data for critical revisions of kinetic
85 parameters. In addition, we have conducted a computational study paying special
86 attention to the OH addition channels. To the best of our knowledge, this is the first
87 study that uses a canonical Variational Transition State Theory (cVTST) over four
88 addition and one H atom abstraction pathways to calculate the temperature
89 dependence of k .

90

91 **2. Methodology**

92 **2.1. Experimental**

93 The experiments were conducted using the absolute method of PLP-LIF to
94 determine the rate coefficients for the reaction [1] in the temperature range 253-371 K
95 at around 100 Torr.

96 The PLP-LIF experimental system used is located at the CNRS (Orléans,
97 France). The details of the experimental setup and methodology used have been
98 presented previously¹⁷. Therefore, the description below is limited to the necessary
99 features to understand the current experiments.

100 OH radicals were generated by photolysis of H_2O_2 at $\lambda = 248$ nm (KrF excimer
101 laser). The concentration of OH radicals was monitored at various reaction times
102 ranging from 10 μs to 10 ms, by pulsed laser induced fluorescence (LIF). A frequency-
103 doubled dye laser pumped by a Nd:YAG laser was used to excite the OH radicals at $\lambda =$
104 282 nm, and fluorescence from OH radicals was detected by a photomultiplier tube
105 fitted with a 309 nm narrow bandpass filter. The output pulse from the photomultiplier
106 was integrated for a preset period by a gated charge integrator. Typically, the
107 fluorescence signal resulting from 100 probe laser shots was measured for 10 to 15
108 different delay times and averaged to generate OH concentration-time profiles over 2.5
109 - 3 lifetimes. H_2O_2 was introduced into the reaction cell by passing a small flow of
110 helium through a glass bubbler containing a solution of H_2O_2 . 3-chloropropene was
111 premixed with helium in a 10 L glass bulb to form a 0.2-0.4% mixture at total pressure
112 of about 1000 Torr. The gas mixture, the photolytic precursor (H_2O_2), and the bath gas
113 (He) were flowed through the cell with a linear velocity in the range 3-10 cm s^{-1} and the
114 residence time in the cell reaction zone is estimated less than 0.1 s. Each
115 photolysis/probe sequence interrogated a fresh gas mixture, and reaction products did
116 not build up in the cell. The 3-chloropropene concentrations were calculated from their
117 mass flow rates, the temperature and the pressure in the reaction cell. All flow rates
118 were measured with mass flow meters calibrated by measuring the rate of pressure

119 increase in a known volume. The pressure in the cell was measured with a capacitance
120 manometer connected at the entrance of the cell.

121 Rate coefficients were determined under pseudo-first-order conditions with the
122 concentration of 3-Chloropropene in excess over that of OH radicals
123 ($[\text{CH}_2=\text{CHCH}_2\text{Cl}]_0 > 10 [\text{OH}]_0$). The rate of disappearance of OH radical followed a
124 simple exponential rate law:

$$125 \quad [\text{OH}]_t = [\text{OH}]_0 e^{-k't} \quad \text{where} \quad k' = k [\text{CH}_2=\text{CHCH}_2\text{Cl}] + k'_0$$

126 Where k represents the second order rate coefficient for the global reaction [1]
127 and k'_0 is the first-order rate coefficient for OH removal in the absence of 3-
128 chloropropene due to the diffusion of OH radicals out of the detection zone (which have
129 a rate coefficient of 30 s^{-1} in the set up) and the reaction between OH radicals and their
130 precursor (H_2O_2).

131 Experiments were carried out in the temperature range 253-371 K and at total
132 pressure between 101 and 107 Torr of helium. The experimental conditions are
133 summarized in Table 1.

134

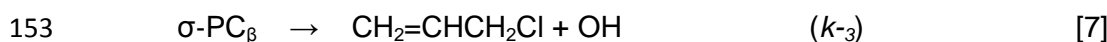
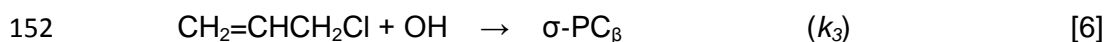
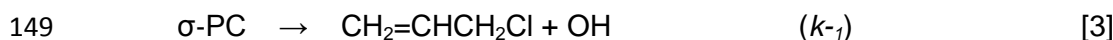
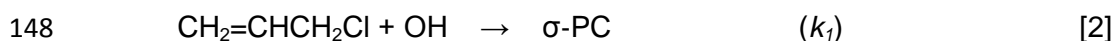
135 **2.3. Materials.**

136 The helium carrier gas (Alpha Gas UHP certified to $> 99.9995\%$). The 50 wt%
137 H_2O_2 solution, from Prolabo, was concentrated by bubbling helium through the solution
138 to remove water for several days prior to use and constantly during the experiment. 3-
139 Chloropropene Aldrich (99%), was degassed by repeated freeze-pump-thaw cycles
140 and purified by vacuum distillation before use.

141

142 **2.4. Theoretical Calculations**

143 Taking into account the experimental and theoretical results of Tuazon et al.⁷ and
144 Zhang et al.⁶, we have considered in this work that at temperatures lower than 600 K
145 the rate limiting step of the reaction [1] is determined by a mechanism composed by
146 OH addition to double bond and the β -H atom abstraction parallel reactions, according
147 to the following general scheme:



155 where, σ -PC is the pre-barrier complex, I_c and I_t are the products of the OH addition to
156 the central and terminal carbon atoms, σ -PC $_{\beta}$ is the pre-barrier complex and I_d is the
157 product of the β -H atom abstraction, and, in parentheses, the k_i (being $i = 1, 2, 3, 4, -1$
158 and -3) are the rate coefficients corresponding to each reaction step. k_4 is the rate
159 coefficient for the H abstraction channel.

160 Reaction [1] (involving the elementary reactions [2-8] and the further splitting
161 explained in the discussion section) has been described at Density Functional Theory
162 (DFT) level,¹⁸ adopting the M06-2X functional¹⁹ along with the aug-cc-pVTZ basis sets
163 ²⁰. Geometry optimizations aiming to the location of all minima and saddle points have
164 been performed and the characterization of these stationary points, after the converged
165 geometry optimization calculations, has been done by analysis of the vibrational
166 frequencies, calculated at the same level. Also, in order to guarantee that the optimized
167 structure corresponds to a global or local minimum, relaxed scans along one or more
168 dihedral angles have been calculated. This procedure has been adopted because the
169 potential energy surface is expected to show a high density of minima, due to the
170 combination of some internal rotations, differing one from the other by a few kcal mol⁻¹.
171 Theoretical calculations have been performed with the GAUSSIAN09 program
172 packages²¹. The stationary points can be summarized as reactants, pre-barrier
173 complex, saddle point and products. The minimum energy paths connecting the pre-
174 barrier complex and product and passing through the saddle point have been
175 calculated using the intrinsic reaction path (IRC) method²². For the description of the
176 minimum energy path connecting the pre-barrier complex and the reactants, scan
177 calculations have been performed by partially optimizing the geometries along a path of
178 increasing C–OH interatomic distances. Thermochemical quantities have been
179 calculated using conventional statistical thermodynamics relations, assuming the
180 harmonic oscillator, rigid rotor and ideal gas models²³. In this work, we have also
181 carried out single point calculations at the CCSD(T)/aug-cc-PVTZ level based on the
182 M06-2X/ aug-cc-PVTZ optimized geometries, in order to improve the electronic
183 energies. The Zero Point Energy (ZPE) corrections at the CCSD(T)/cc-aug-PVTZ were
184 assumed the same corrections obtained from the vibrational frequencies calculated at
185 the M06-2X/cc-aug-PVTZ level, then, unless otherwise specified, the geometric
186 parameters and energies used in the following discussion is CCSD(T)/cc-aug-PVTZ//
187 M06-2X/aug-cc-PVTZ + ZPE level. All open-shell stationary points showed T1
188 diagnosis values lower than 0.04 and no multiconfigurational character should be
189 expected.

190

191 Canonical Variational Transition State rate coefficients have been calculated
192 using the model described elsewhere²⁴. Briefly, the minimum energy path, described by
193 the total energy as a function of the reaction coordinate (s) and suggested from IRC or
194 scan calculations, is transformed into a vibrationally adiabatic potential energy curve by
195 including the zero-point energy corrections of the non-stationary points that define the
196 reaction path. A further transformation into a Gibbs free energy curve, $G(s,T)$, at each
197 temperature, is possible with the inclusion of the enthalpy and entropic correction terms
198 provided from the thermodynamics formulations mentioned above. A polynomial of
199 third or fifth order is fitted to the Gibbs free energy curves and the resulting $G(s,T)$
200 functions are analytically maximized to obtain the s values that correspond to the
201 location of the generalized transition state at each temperature. Molecular properties
202 (vibrational frequencies, moments of inertia and critical energy) of the generalized
203 transition states are interpolated and applied as the input quantities for the
204 conventional Eyring equation²⁵ over the temperature range 200–400 K. Tunneling
205 coefficients were calculated using the Wigner's expression²⁶.

206 Since formation of the prebarrier complexes are barrierless reaction paths,
207 conventional transition state method does not apply for the prediction of the rate
208 coefficients. Moreover, entropy effects are important for the best evaluation of rate
209 coefficients of reaction that proceed through relatively small barrier heights. For these
210 reasons, the adoption of the canonical variational method for predicting rate
211 coefficients is crucial.

212

213 **3. Results and discussion**

214 **3.1. Experimental**

215 The absolute rate coefficients were measured in the temperature and pressure
216 ranges 253 - 371 K and 101-104 Torr (of helium) under pseudo-first-order conditions in
217 which the concentration of the 3-Chloropropene was at least 10 times than OH radicals'
218 concentration. The OH decays were found to be exponential over at between 2.5 and 3
219 lifetimes while k'_0 and k' were in the ranges 212-617 s⁻¹ and 552-2875 s⁻¹, respectively.
220 The variation of the photolysis fluence (7.7-21 mJ cm⁻²) had no effect on the
221 determined rate coefficient indicating that there was no noticeable contribution of
222 photofragments to the OH consumption. The CH₂=CHCH₂Cl samples were purified to
223 better than 99% and hence loss of OH radicals by reaction with impurities is expected
224 to be insignificant.

225 Figure 1.a. shows an example of pseudo-first-order plots for the OH radical signal
226 decay and in Fig 2.b., as an example, a plot of $(k'-k'_0)$ as a function of CH₂=CHCH₂Cl
227 concentration at different temperatures, is presented. The k values obtained in this

228 work at different temperatures are shown in Table 1, related to experimental conditions.
229 The rate coefficient, taken as the average of all values obtained at 298 ± 2 K was

$$230 \quad k = (1.69 \pm 0.12) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

231 The errors quoted for k is 2σ from the linear least-squares fit to the data points
232 and do not include systematic errors. This value is in good agreement with those
233 obtained by other authors^{4, 6, 7-9} using different techniques, which are presented in
234 Table 2. There is no significant difference between the k value, obtained in this work at
235 298 K and a pressure of 100 Torr, and the value of $(1.64 \pm 0.18) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
236 obtained in similar experimental conditions by Albaladejo et al.⁴, and the values of
237 $(1.66 \pm 0.23) \times 10^{-11}$, $(1.70 \pm 0.70) \times 10^{-11}$, $(1.96 \pm 0.32) \times 10^{-11}$ and $(1.69 \pm 0.07) \times 10^{-11}$, (in units of
238 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), obtained by Albaladejo et al.⁴, Edney et al.^{8, 9} and Tuazon et al.⁷,
239 respectively, at 298 K and 1 atm. Thus, our results confirm that at 100 Torr k is in its
240 high-pressure limit. All these values are presented in the inset of the Figure 2.

241 Figure 2 show the measured rate coefficients for the studied reaction plotted as a
242 function of the reciprocal of temperature along with k obtained in this work. A least-
243 squares analysis of the $\ln k$ versus $1/T$ plot leads to the following expression for the
244 temperature dependence of k , in the temperature range 253-371 K (in units of cm^3
245 $\text{molecule}^{-1} \text{ s}^{-1}$):

$$246 \quad k = (2.82 \pm 0.38) \times 10^{-12} \exp \{ (540 \pm 42) / T \}$$

247 Uncertainties are $2 \sigma_{\ln A}$ and $2 \sigma_{E/R}$ for A and E/R, respectively.

248 Table 2 presents theoretical and experimental rate coefficients temperature
249 dependence for the global reaction [1] determined previously by other authors^{4, 6}. The
250 results show negative temperature dependence for k in agreement with the Albaladejo
251 et al.⁴ work. This fact is consistent with the hypothesis that the addition mechanism is
252 the main reaction pathway in the considered temperature range.

253

254 **3.2. Theoretical Calculations**

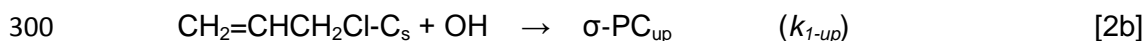
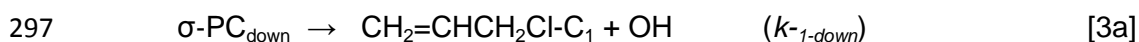
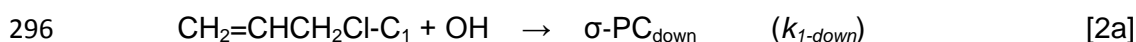
255 We begin our discussion by investigating the $\text{CH}_2=\text{CHCH}_2\text{Cl}$ potential energy
256 surface aiming to explore the possible rotamers of the reactant and the location of the
257 minimum energy geometry. Therefore, scan calculations over the dihedral angles were
258 performed at the M06-2X/aug-cc-pVTZ level. Possible rotamers can arise from the
259 rotation of the $-\text{CH}_2\text{Cl}$ group. Three minima were found, one of them correspond to the
260 structure $\text{CH}_2=\text{CHCH}_2\text{Cl}-C_s$ (rotamer belonging to the C_s symmetry group), shown in
261 the Figure 3, the other minima are mirror images belonging to the C_1 symmetry group,
262 and have the structure shown in the same Figure labeled as $\text{CH}_2=\text{CHCH}_2\text{Cl}-C_1$.
263 $\text{CH}_2=\text{CHCH}_2\text{Cl}-C_s$ lies $0.49 \text{ kcal mol}^{-1}$ above the $\text{CH}_2=\text{CHCH}_2\text{Cl}-C_1$ rotamer and the

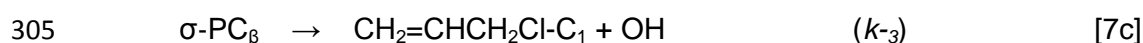
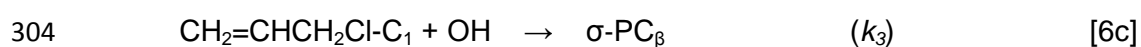
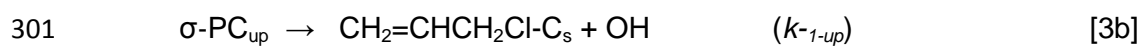
264 barrier height separating them is 2.47 kcal mol⁻¹, as predicted at the M06-2X/aug-cc-
 265 pVTZ level. Reactions of each rotamer were treated individually. After the location of
 266 the possible rotamers, from the scan calculations, the energy was corrected at the
 267 CCSD(T)/aug-cc-pVTZ level.

268 The finding of the CH₂=CHCH₂Cl-C_s and CH₂=CHCH₂Cl-C₁ rotamers suggests
 269 that the OH radical can attack in two different ways. The first one is from the upside of
 270 the plane defined by the three C atoms, *i.e.*, from the same side where the Cl atom is
 271 located, hereafter referred as the upward attack. The second way is given if the OH
 272 attack is from the opposite side of that plane, thus, a downward attack is proposed. For
 273 the CH₂=CHCH₂Cl-C₁ rotamers only the downward attack leads to a sigma pre-barrier
 274 complex (σ -PC_{down}) connected by TS_{c-down} and TS_{t-down} to I_{c-down} and I_{t-down}, whose
 275 geometries are also shown in Figure 3. The subscripted c-down and t-down denote the
 276 downward addition pathways to the central and the terminal carbon atoms of the
 277 double bond of the CH₂=CHCH₂Cl-C₁, respectively. In the Figure 4a-b, the
 278 geometries of 2 stereoisomers of the σ -PC_{down} (energetically degenerated) are shown.
 279 As far as we know, this work provides the first description of these OH addition
 280 pathways for the reaction [1].

281 On the other hand, in the CH₂=CHCH₂Cl-C_s rotamer the chlorine atom lies in the
 282 same plane defined by the three C atoms, as can be observed in Figure 3. During the
 283 OH radical attack, the Cl atom takes place over the plane at the same side of the OH
 284 (forming an 8° dihedral angle between the plane and the C-Cl bond), to form the
 285 σ -PC_{up} connected by TS_{c-up} and TS_{t-up} to I_{c-up} and I_{t-up}. Accordingly, the subscripted c-up
 286 and t-up denote the upward addition pathways to the central and the terminal carbon of
 287 the double bond of the CH₂ClCH=CH₂ -C_s, respectively. All these structures are
 288 shown in Figure 3. In the upward OH attack 2 σ -PC_{up} stereo-isomers can be formed,
 289 which are energetically degenerated. The geometries for those isomers are shown in
 290 Figure 4c-d. Then, two parallel reaction pathways (one for each stereo-isomer) for the
 291 upward OH addition have been considered. Along the upward reaction channel, we
 292 have found molecular structures similar to the CR1, TS1, TS2, IM1 and IM2 proposed
 293 by Zhang et al.⁶ for the OH addition to CH₂ClCH=CH₂.

294 Summarizing, as a consequence of the presence of the σ -PC_{down} and the σ -PC_{up},
 295 the reactions [2]-[5] are splitted, and the reactions 6-8 are reformulated as follows:





307 Regarding on the β -H atom abstraction channel, in this work only the
 308 $\text{CH}_2=\text{CHCH}_2\text{Cl-C}_1$ rotamer was considered because it is the most stable one and
 309 presents two specular structures. A $\sigma\text{-PC}_{\beta}$ connecting reagents to the I_{d} via the $\text{TS}_{\beta\text{-H}}$
 310 was found, which presents two energetically degenerated stereoisomers. The
 311 molecular structures are, also, shown in the Figures 4e-f. The $\text{CH}_2\text{ClCH}=\text{CH}_2 -\text{C}_1$
 312 rotamer belongs to the C_1 symmetry group, thus in the β position the two H atoms are
 313 not equivalent. The $\text{TS}_{\beta\text{-H}}$ was found only when the OH attack was on the H atom
 314 located below the plane of the three carbon atoms. At the considered temperature the
 315 abstraction pathways are expected to be minority⁶. Then, in order to study alternative
 316 reactions channels to those presented by Zhang et al.⁶ in this paper we have just
 317 focused beta H abstraction.

318 The molecular properties (including optimized geometries and frequencies) for all
 319 the stationary points, shown in Figure 3, obtained at the CCSD(T)/ aug-cc-PVTZ// M06-
 320 2X/ aug-cc-PVTZ level, are given as Supporting Information.

321 The Table 3 summarizes the relative energy (with respect to the isolated
 322 Reactants), expressed in kcal mol⁻¹, for the stationary points along the described
 323 reaction pathways. At the M06-2X/aug-cc-PVTZ level the S^2 values were lower than
 324 0.78, then, regarding to the spin contamination, the wave function and electronic
 325 energies are not affected by states of higher multiplicity. No calculations with different
 326 basis set were carried out because Zhang et al.⁶ have obtained ΔE values comparable
 327 to the obtained in this work for the species $\sigma\text{-PC}_{\text{up}}$, $\text{TS}_{\text{c-up}}$, $\text{TS}_{\text{t-up}}$, $\text{I}_{\text{c-up}}$ and $\text{I}_{\text{t-up}}$, at the
 328 CCSD(T)/cc-PVTZ//M06-2x/6-311++G(d,p)) level. Also, they have not found
 329 dependency of the basis sets in the results.

330 A description of the potential energy surface for the four addition reactions
 331 channels and the β - H atom abstraction pathway is provided in the Figure 5 (and Table
 332 3) and as can be observed, the pre-complexes present ΔE ranging between -3.30 and -
 333 4.09 kcal mol⁻¹. The $\text{TS}_{\text{c-down}}$, $\text{TS}_{\text{t-down}}$, $\text{TS}_{\text{c-up}}$ and $\text{TS}_{\text{t-up}}$ present negative ΔE ranging
 334 between -1.07 and -1.80 kcal mol⁻¹, *i.e.*, below reactants. $\text{TS}_{\beta\text{-H}}$ has a ΔE of 0.19 kcal
 335 mol⁻¹, over the reactants.

336 Starting from each saddle point, IRC calculations were performed for the
 337 description of the reaction profiles leading to the formation of the chlorinated hydroxy

338 radicals resulting from the addition of the hydroxyl radical to either the central or the
 339 terminal carbon atoms, from upward and downward attacks: I_{c-down} , I_{t-down} , I_{c-up} and I_{t-up} .
 340 On the side, in the β -H atom abstraction channel, the IRC confirmed the reaction path
 341 from σ -PC $_{\beta}$ to the I_d radical.

342 For the OH addition to the double bond reactions, π pre-barrier complexes have
 343 been proposed in previous studies^{14-16, 25}, in which the OH radical moiety lies nearly
 344 perpendicular to the C=C plane. Such pre complexes were not found in the present
 345 work at the level of theory used.

346 Regarding the reactions pathways, the rate coefficients were calculated for the
 347 association step and dissociation and addition reactions of the PC, represented in the
 348 reactions 2a-5a, 2b-5b and 6c-8c.

349 The canonical variational transition state method was adopted using the
 350 theoretical molecular properties calculated at M062X level with both and aug-cc-pVTZ
 351 basis sets. For the prediction of the global rate coefficients, the mechanism described
 352 by the chemical steps 2a-5a, 2b-5b (addition channels) and $CH_2=CHCH_2Cl-C_1 + OH \rightarrow$
 353 σ -PC $_{\beta}$ (6c); σ -PC $_{\beta} \rightarrow CH_2=CHCH_2Cl-C_1 + OH$ (7c); σ -PC $_{\beta} \rightarrow I_{\beta}$ (8c) was assumed. The
 354 steady state is assumed for each PC in this mechanism (ie. $d[\sigma$ -PC $_{down}]/dt = d[\sigma$ -
 355 PC $_{up}]/dt = d[\sigma$ -PC $_{\beta}]/dt = 0$), and following expressions are obtained for k_{down} , k_{up} and
 356 k_{abs} and k_{cVTST} (which is equal to the sum $k_{down} + k_{up} + k_{abs}$):

357

$$358 \quad k_{down} = 2 \frac{k_{1-down} \times (k_{2c-down} + k_{2t-down})}{k_{-1-down} + k_{2c-down} + k_{2t-down}} \quad \text{Eq. 1}$$

359

$$360 \quad k_{up} = 2 \frac{k_{1-up} \times (k_{2c-up} + k_{2t-up})}{k_{-1-up} + k_{2c-up} + k_{2t-up}} \quad \text{Eq. 2}$$

361

$$362 \quad k_{abs} = 2 \frac{k_{1-abs} \times (k_{2-abs} + k_{2-abs})}{k_{-1-abs} + k_{2-abs} + k_{2-abs}} \quad \text{Eq. 3}$$

363

$$364 \quad k_{cVTST} = (k_{down} + k_{up} + k_{abs}) \quad \text{Eq. 4}$$

365

366 The factor 2 in the Eq. 1-3 accounts for the degeneracy of the 3 reaction paths
 367 (addition -up and down- and abstraction) due to stereochemistry. Tunneling corrections
 368 do not apply for the barrierless addition but can slightly increase $k_{2c-down}$, $k_{2t-down}$, k_{2c-up} ,

369 k_{2t-up} and k_4 values. For the hydrogen abstraction channel, the tunneling coefficients
370 ranged from 2.46 to 1.36, as the temperature increases from 200 to 400 K, whereas a
371 range from 1.41 to 1.06 was observed for the Wigner coefficients related to the addition
372 channels. The Table 4 summarizes the results for k_{down} , k_{up} , k_{abs} and k_{cVTST} (in this
373 work, predicted using the cVTST method) between 200 and 400 K. These values were
374 plotted in the Figure 2 along with the Arrhenius plot obtained in this work and
375 experimental and theoretical rate coefficient values in previous literature.

376 The obtained Arrhenius equation is:

$$377 k_{cVTST} = (1.54 \pm 0.08) \times 10^{-12} \exp [(532 \pm 18) / T], 275 - 400 \text{ K}$$

378 where k_{cVTST} is the expression obtained by fitting the rate coefficients between 275 –
379 400 K. Linearity of the classical Arrhenius expression is lost with the extension of the
380 temperature range from 200 – 400 K and the rate coefficients are better fitted by:

$$381 k_{cVTST} = (3.01 \pm 1.21) \times 10^{-19} [T^{(2.27 \pm 0.06)}] \exp [(1284 \pm 16) / T], 200 - 400 \text{ K}$$

382 The quoted uncertainties in the equations above were obtained by evaluation the
383 standard errors of regression, at 95% of confidence level.

384 In agreement with the previous literature concerning the OH addition to
385 unsaturated compounds, addition is the dominant channel at this range of
386 temperatures and shows negative temperature dependence. As is shown in the Table
387 4 and Figure 2, the H abstraction pathway present positive activation energy and the
388 k_{abs} values are, at least, one order of magnitude lower than the values of k_{down} and k_{up} ,
389 at the same temperature. Then, other less important abstraction channels studied by
390 Zhang et al.⁶ can be neglected in the k_{cVTST} calculation.

391 The k_{cVTST} value at 298 K of $9.13 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ reach the 54% and the
392 59% of the values $(1.69 \pm 0.12) \times 10^{-11}$ and 1.56×10^{-11} (in unit of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$),
393 experimentally obtained in this work and calculated by Zhang et al.⁶, respectively.

394 The rate coefficients predicted from the canonical variational transition state
395 method, employed in this work, are underestimated by factors ranging from 1.4 – 2.0
396 (200 – 400 K). In particular, the room temperature rate coefficient is underestimated by
397 a factor of 1.9. Calculated rate coefficients are also lower than those predicted by
398 Zhang and coworkers, who adopted a microcanonical method, based on the RRKM
399 model, for the calculation of the rate expression. A comparison among canonical and
400 microcanonical rate coefficients for OH reactions with unsaturated compounds can be
401 found elsewhere^{15, 16}.

402 Although the rate coefficients have been underestimated with respect the
403 experimental and literature values, the predicted global activation energy agrees very
404 well with the experimental value ($-1.06 \text{ kcal mol}^{-1}$, in comparison with $-1.07 \text{ kcal mol}^{-1}$,

405 respectively, calculated from 275 – 400 K). The ratio between the calculated and the
406 experimental activation energies between 275 and 400 K is 0.99, which represent a
407 good agreement taking into account the two different employed methods. Our
408 calculations show negative temperature dependence for k_i in accordance with the
409 experimental results of Albaladejo et al.⁴ This behavior is also predicted by theoretical
410 calculations by Zhang et al.⁶ At the same range, the activation energy calculated for the
411 rate coefficients reported by Zhang and coworkers is $-1.48 \text{ kcal mol}^{-1}$.

412 The deviation of the cVTST rate coefficients from the experimental values mostly
413 arise from the entropic term in the Eyring expression, which is governed by the values
414 of the lowest vibrational frequencies. Considering the errors in the theoretical prediction
415 of all these parameters, the agreement between predicted and experimental rate
416 coefficients must be considered very good.

417

418 **Conclusions**

419 There is only one previous study of the rate coefficient temperature dependence
420 which is not enough for recommendation in critical revisions, then, this work provides
421 new valuable experimental data of kinetic parameters of the title reaction.

422 As far as we know, this is the first study that uses a cVTST to obtain the
423 temperature dependence of the k of the reaction [1] considering four additions and one
424 H atom abstraction pathways.

425 The ratio between the calculated and the experimental activation energies
426 indicates a good agreement between experimental and theoretical results, then,
427 although the calculation of cVTST may underestimate the values of rate coefficients,
428 considering its simplicity, it could be used as an alternative method to describe the
429 temperature dependence for the reactions of haloalkenes with the OH radical.

430 The negative temperature dependence of k_{exp} and k_{cVTST} (the last one obtained
431 considering the proposed global mechanism described in the reactions 2a-5b and 6c-
432 8c) could explain the experimental results, and supports the hypothesis that the OH
433 radical addition is the main reaction mechanism for the studied global reaction, being
434 the downward addition the most important reaction channel in the considered
435 temperature range. To the best of our knowledge these not negligible reaction
436 channels have been considered for the first time in this work in order to calculate the
437 temperature rate constant dependence for the global reaction.

438 As a perspective of the ongoing research, a future study on the effects of the DFT
439 method and basis sets over the computational capability to found the π or σ pre-

440 complexes could be studied. Also, a further study on the impact of the kind of pre-
441 complexes on the cVTST rate coefficient calculations is previewed to be carried out.

442

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444

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448

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506

507 **Table 1:** Summary of experimental conditions and results for measurements of the rate

T (K)	P (torr)	f *	[OH] / (10 ¹¹) ^a	[H ₂ O ₂] / (10 ¹⁴) ^a	[CH ₂ CICH=CCH ₂] / (10 ¹³) ^a	k' _o (s ⁻¹)	k' (s ⁻¹)	k ± 2σ / (10 ⁻¹¹) ^b
253	102-103	8.4	6.3	3.4	2.00-9.15	525-617	1028-2782	2.49±0.16
273	102-103	8.4	6.2	3.3	2.33-9.40	532-592	1053-2523	2.16±0.10
273	102-103	7.7	5.9	3.4	1.61-6.29	550-610	973-1949	2.15±0.15
298	101-103	21.0	13.2	2.9	1.42-14.67	473-517	713-2875	1.63±0.05
298	102-104	9.1	6.3	3.1	2.23-10.66	497-565	965-2471	1.78±0.12
298	102-104	7.7	7.7	4.3	1.87-8.29	861-601	886-1954	1.67±0.08
323	101-103	11.2	4.9	2.2	2.08-16.19	337-405	680-2828	1.54±0.07
347	102-104	11.2	5.2	2.3	2.72-18.48	356-416	800-2741	1.33±0.06
370	101-103	9.8	2.6	1.5	2.52-19.60	212-308	552-2620	1.21±0.08
371	101-104	9.8	4.0	2.1	2.33-18.18	326-378	651-2649	1.26±0.05

508 coefficient of the gas phase reaction between OH and CH₂CICH=CCH₂.

509 ^a molecule cm⁻³

510 ^b cm³ molecule⁻¹ s⁻¹

511 *Laser Pulse Fluency. mJ cm⁻²

512

513 **Table 2:** Summary of previous experimental and theoretical values obtained for k_{global} in
 514 the high-pressure limit between 253 K and 371 K.

515

Temperature (K)	k^* Ref. 4	k^* Ref. 8	k^* Ref. 9	k^* Ref. 7	k^* Ref.10	k^{*a} Ref.6
228	2.64±0.40					3.51
253	2.41±0.32					2.49
273	2.05±0.28					1.98
296	1.66±0.23					1.59
298	1.64±0.18	1.70±0.70	1.96±0.32	1.69±0.07	1.53±0.40	1.56
323						1.28
328	1.48±0.25					1.24
347						1.10
370						0.960
371						0.955
388	1.18±0.20					0.877

516 * All the values are in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and were multiplied by 1×10^{11} .

517 ^a The values were calculated using the expression $k = 2.64 \times 10^{-14} \times T^{0.57} \times \exp$
 518 $(934.47/T)$ for the high-pressure limit and the 200-500K temperature range. Ref. 6 the k
 519 values were theoretically calculated.

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522 **Table 3:** Summary of the relative energy (with respect to the isolated Reactants),
 523 expressed in kcal mol⁻¹, obtained in this work along with comparable values from Ref.
 524 6.

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Species	$\Delta E + ZPE$ (M06-2X/aug- cc-PVTZ)	$\Delta E + ZPE^*$ (CCSD(T)/aug-cc- PVTZ)	$\Delta E +$ ZPE ^a Ref. 6.
Addition			
CH ₂ ClCH=CH ₂ - C _t + OH	0.00	0.00	
σ -PC _{down}	-3,30	-1,90	
TS _{c-down}	-1,28	-1,58	
TS _{t-down}	-1,07	-1,13	
I _{c-down}	-30,44	-27,44	
I _{t-down}	-31,16	-27,51	
CH ₂ ClCH=CH ₂ - C _c +OH	0.00	0.00	0.00
σ -PC _{up}	-4,09	-2,49	-3.56
TS _{c-up}	-1,80	-2,05	-1.96
TS _{t-up}	-1,15	-1,28	-1.03
I _{c-up}	-31,84	-28,76	-29.91
I _{t-up}	-31,86	-27,43	-29.86
β -H atom abstraction			
CH ₂ ClCH=CH ₂ + OH	0.00	0.00	
σ - PC _{β}	-3,48	-2,41	
TS _{β-H}	0,189	0,64	
I _d + H ₂ O	-33,38	-31,61	

526 * Zero Point Energy corrections were calculated from the vibrational frequencies obtained at
 527 the M06-2X/cc-aug-PVTZ level.

528 ^a(CCSD(T)/cc-PVTZ//M06-2x/6-311++G(d,p))

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530

531 **Table 4:** Summary of conditions and results for cVTST calculations of the rate
532 coefficients for the pathways down, up and abstraction and the global reaction.

Temperature (K)	k_{down}	k_{up}	k_{abs}	k_{-cVTST}
200	1.01×10^{-11}	1.98×10^{-11}	6.87×10^{-13}	3.06×10^{-11}
225	7.28×10^{-12}	1.17×10^{-11}	7.36×10^{-13}	1.97×10^{-11}
250	5.65×10^{-12}	7.67×10^{-12}	7.82×10^{-13}	1.41×10^{-11}
275	4.62×10^{-12}	5.50×10^{-12}	8.23×10^{-13}	1.09×10^{-11}
298	4.00×10^{-12}	4.27×10^{-12}	8.62×10^{-13}	9.13×10^{-12}
300	3.96×10^{-12}	4.19×10^{-12}	8.67×10^{-13}	9.01×10^{-12}
325	3.50×10^{-12}	3.39×10^{-12}	9.06×10^{-13}	7.80×10^{-12}
350	3.17×10^{-12}	2.84×10^{-12}	9.52×10^{-13}	6.96×10^{-12}
375	2.93×10^{-12}	2.47×10^{-12}	9.89×10^{-13}	6.39×10^{-12}
400	2.73×10^{-12}	2.18×10^{-12}	1.04×10^{-12}	5.95×10^{-12}

533 * All the values are in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

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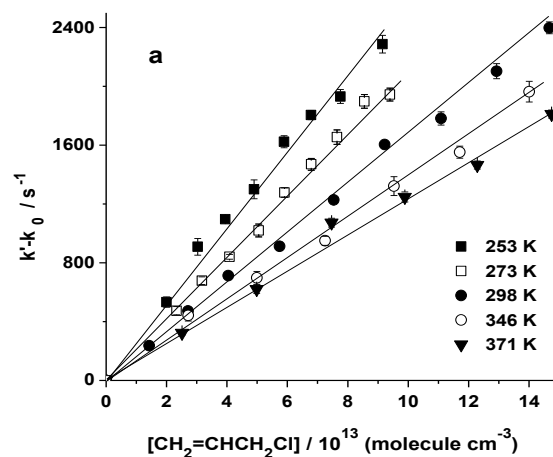
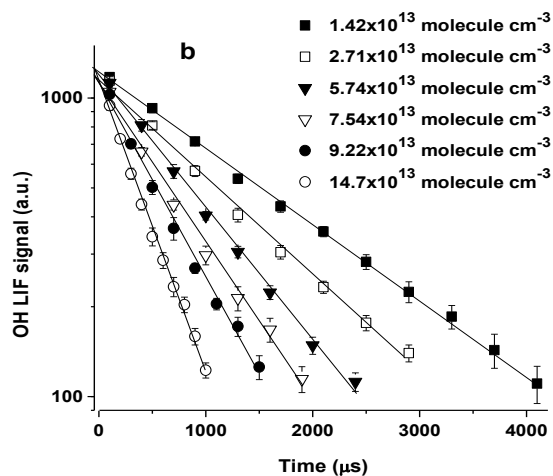
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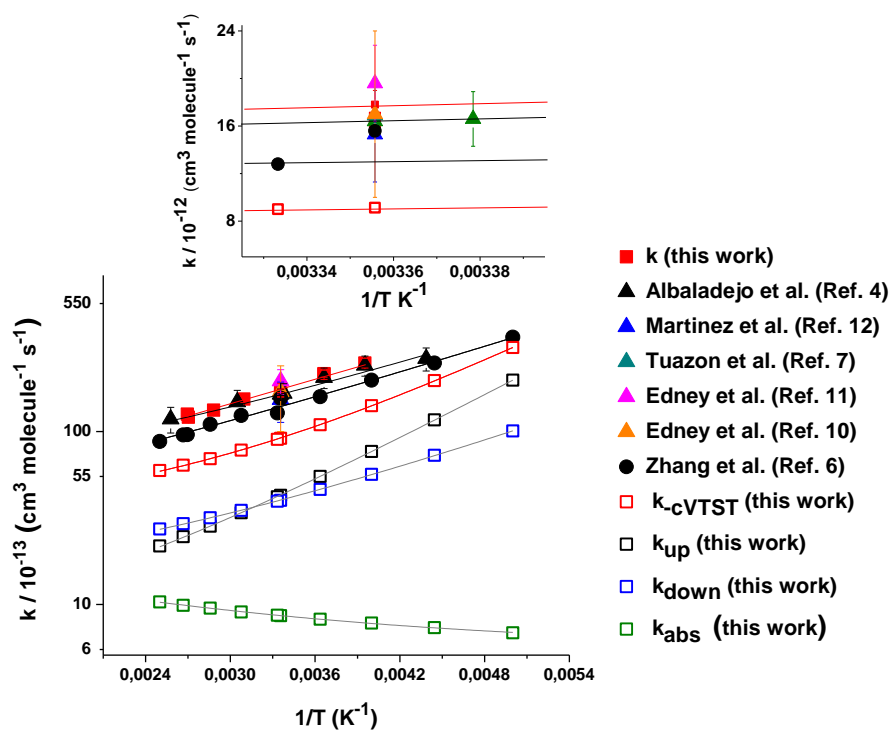
547 **Figure 1:** **a.** Example of pseudo-first-order plots for the OH radical signal decay at

548 298 K and four $\text{CH}_2\text{ClCH}=\text{CH}_2$ concentrations. **b.** Examples of plots of the

549 rate of disappearance of the OH radical ($k'-k'_0$) vs. $\text{CH}_2\text{ClCH}=\text{CH}_2$

550 concentration at different temperatures.

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555 **Figure 2.** Plot of k_1 as function of $1/T$ for the OH reaction with $\text{CH}_2\text{ClCH}=\text{CH}_2$ in the
 556 temperature range 263-369 K, compared with previous results in literature.

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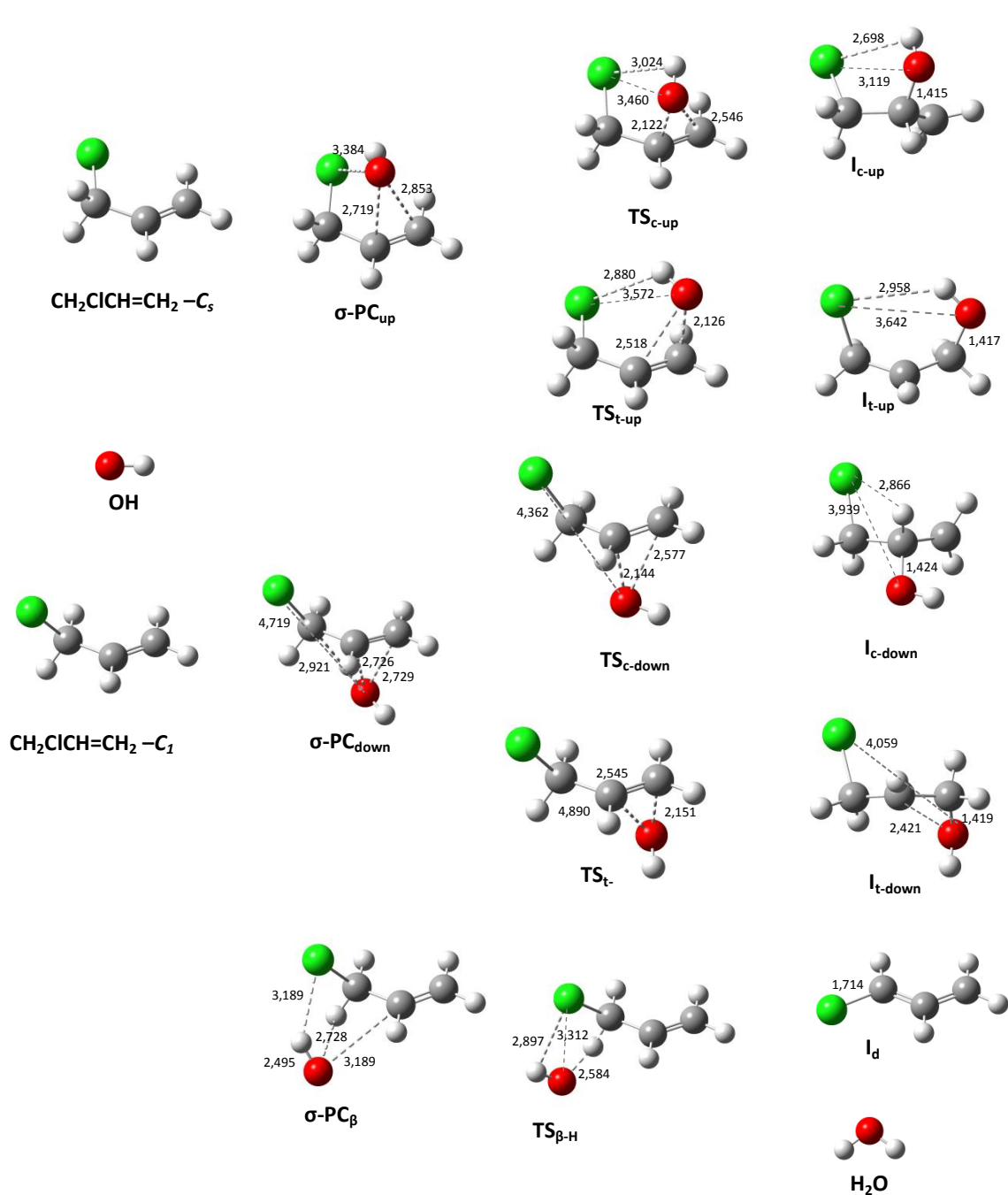
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584 **Figure 3.** Geometries of the stationary points found along the studied reaction

585 pathways

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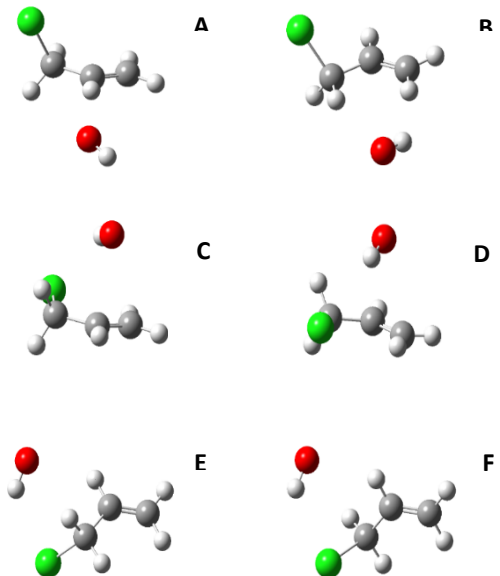
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602 **Figure 4:** Geometries obtained for the 2 stereoisomers of σ -PC_{down} (a-b), σ -PC_{up} (b-c)
603 and σ -PC _{β} (e-f).

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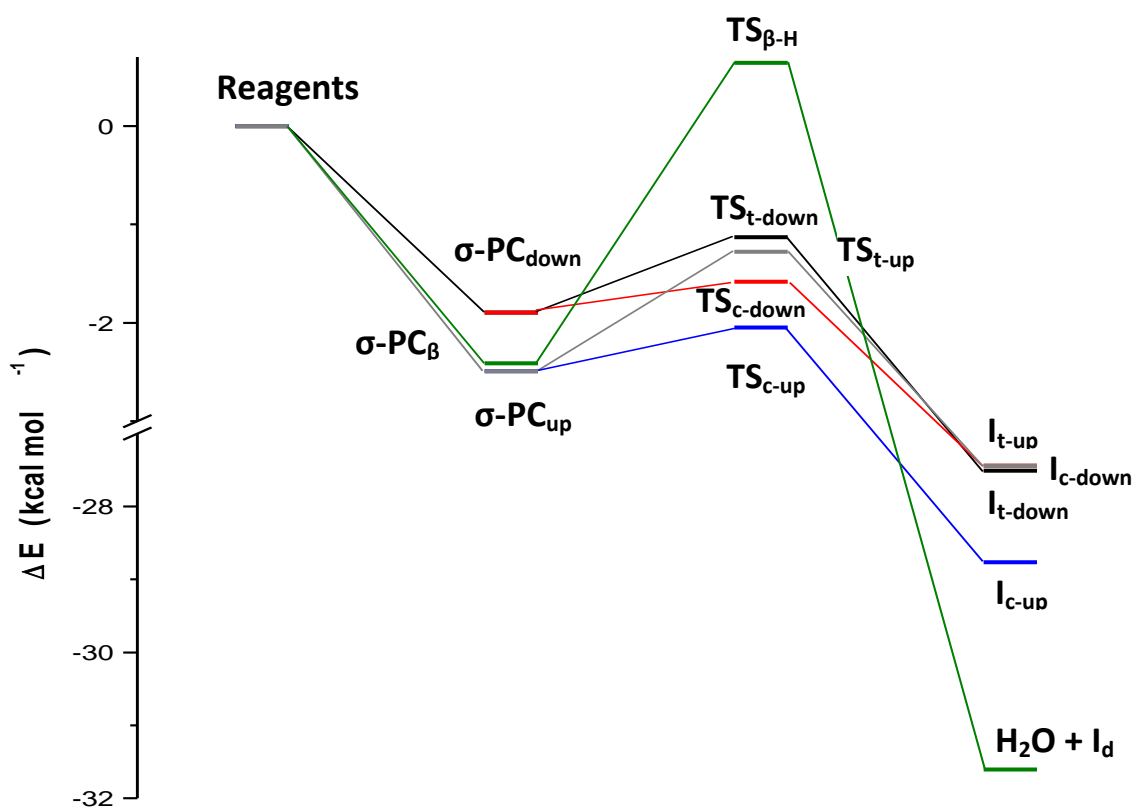


Figure 5. Relative energy of the stationary points of the studied reaction pathways.