

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/233614534>

DFT and Ab-initio study on the reaction mechanisms of the homogeneous, unimolecular elimination kinetics of selected 1- chloroalkenes in the gas phase

ARTICLE *in* INTERNATIONAL JOURNAL OF QUANTUM CHEMISTRY · JANUARY 2012

Impact Factor: 1.43

READS

20

5 AUTHORS, INCLUDING:



Mora J.R

Venezuelan Institute for Scientific Research

52 PUBLICATIONS 148 CITATIONS

SEE PROFILE



Jesus Lezama

Universidad de Oriente (Venezuela)

20 PUBLICATIONS 58 CITATIONS

SEE PROFILE



Tania Cecilia Cordova-Sintjago

University of Florida

99 PUBLICATIONS 256 CITATIONS

SEE PROFILE



Gabriel Chuchani

Venezuelan Institute for Scientific Research

245 PUBLICATIONS 1,224 CITATIONS

SEE PROFILE

Density Functional Theory and *Ab Initio* Study on the Reaction Mechanisms of the Homogeneous, Unimolecular Elimination Kinetics of Selected 1-Chloroalkenes in the Gas Phase

Jose R. Mora,^[a] Jesus Lezama,^[a] Neydher Berroteran,^[b] Tania Cordova,^{*,[c]} and Gabriel Chuchani^[a]

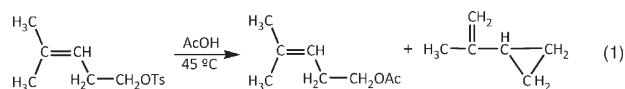
The mechanisms for the unimolecular elimination kinetics of selected 1-chloroalkenes in the gas phase were studied at MPW1PW91/6-31G(d,p), MPW1PW91/6-31++G(d,p), G3, and G3MP2 levels of theory. Two possible unimolecular mechanisms were considered: mechanism A as a concerted 1,2 elimination process through four-membered cyclic transition state (TS). mechanism B describing the anchimeric assistance of the double bond in HCl elimination previously suggested in the literature. Calculated parameters suggest that the elimination reactions of 1-chloroalkenes proceed through mechanism A, in view of the higher energy of activation associated with mechanism B. Density functional method MPW1PW91/6-31G(d,p) calculated parameters gave a better agreement with the experimental values than G3 and G3MP2.

The changes along the reaction path of mechanism A were followed by geometric parameters, natural bond orbital charges, and bond order analysis, suggesting the rate-determining process is the breaking of C—Cl bond in the TS. The dehydrochlorination of chloroalkenes occurs in a concerted nonsynchronous fashion with stabilization of the TS by π -electron delocalization from the neighboring bond. Isomerization reactions for 4-chloro-1-butene, 4-chloro-2-methyl-1-butene, and 4-chloro-1-butene are unlikely at the experimental reaction condition because of the higher the enthalpies and energies of activation. © 2012 Wiley Periodicals, Inc.

DOI: 10.1002/qua.24175

Introduction

A classical work of neighboring olefinic double bond participation in organic chemistry was the reaction describing the acetolysis of 4-methyl-3-penten-1-yl *p*-toluene sulfonate.^[1] The π -bond of the vinyl system enhanced significantly the rate to about 1200 times faster than that of the parent compound ethyl tosylate. Both the rate and the formation of a cyclic product suggested an unequivocal evidence of anchimeric assistance of the aliphatic double bond [reaction (1)].



An additional support of aliphatic π -bond participation is the work describing the solvolysis of 3-buten-1-yl *p*-toluene sulfonate.^[2]

In view of the polar nature of the four-centered cyclic transition state (TS) of alkyl halide pyrolysis in the gas phase,^[3] Mac-coll and Thomas proposed the ion-pair mechanism where both *cis*- and *trans*-elimination may occur,^[4,5] while Benson and Bose's semi-ion-pair TS is limited to *cis*-elimination.^[6] Because of these postulations, many number of investigations had been performed to prove the ion-pair theory in the gas phase.^[7] A study of the thermal decomposition of *threo*- and *erythro*-2-bromo-3-deuteriobutane using deuterium isotopic

effect reported that the elimination in these compounds occurs predominantly via a *syn* TS, while the *anti*-elimination is negligible.^[8] The TS structure in 1,2-hydrogen halide eliminations from ethyl halides has been studied using Hartree–Fock and perturbation theory methods.^[9] The TS was found to be strongly asymmetric with the C—X bond almost broken.

Investigations of the elimination reaction mechanism of alkyl halides, using computational methods, were reported recently: a theoretical study on chlorocyclohexane, 3-chlorocyclohexene, and 4-chlorocyclohexene eliminations in the gas phase, and the neighboring carbonyl group participation of chloroketones pyrolysis and on neopentyl halides thermal decomposition.^[10–12] The elimination reactions of neopentyl chloride and neopentyl bromide were examined by using density functional theory (DFT) method of calculation to describe the changes in electronic structure, geometrical parameters, and bond orders. These

[a] J. R. Mora, J. Lezama, G. Chuchani

Lab Fisicoquímica Organica, Centro de Química, Instituto Venezolano de Investigaciones Científicas (I.V.I.C.), Apartado 21827, Caracas, Venezuela

[b] N. Berroteran

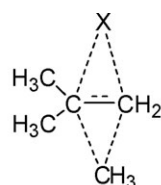
Departamento de Química, Escuela de Química, Facultad de Ciencias, Universidad Central de Venezuela, Apartado 1020-A, Caracas, Venezuela
E-mail: taniacsintjago@ufl.edu

[c] T. Cordova

Department of Medicinal Chemistry, College of Pharmacy, University of Florida, P.O. Box 100485, Gainesville, Florida 32610
E-mail: taniacsintjago@ufl.edu

© 2012 Wiley Periodicals, Inc.

elimination reactions proceed through a common first step that is rate determining, in which a molecular rearrangement Wagner–Meerwein occurs. The rearranged intermediates, for example, 2-chloro-2-methyl-butane or 2-bromo-2-methyl-butane undergo elimination of HCl or HBr in parallel fast steps to give two olefins; the Sayzeff and Hoffmann products. The TS of the rate-determining step was explained in terms of an intimate ion-pair, where halide has a negative charge, and the migration of the methyl group to the terminal carbon occurs in concerted fashion to the breaking of the carbon–halide bond.

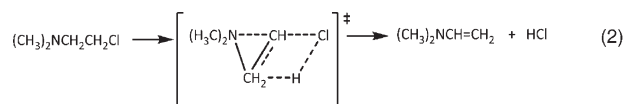


X = Cl, Br

Transition state of neopentyl halides

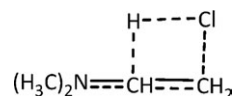
The 1,2-interchange mechanism in the eliminations reactions of neopentyl chloride and neopentyl bromide has also been recently reported.^[13]

The gas-phase elimination kinetics of 2-(dimethylamino)ethyl chloride [reaction (2)] was examined, where dehydrohalogenation was found to be 560 times greater in rate than the parent compound ethyl chloride.^[14] This difference in reactivity was believed to be due to the assistance of the nitrogen atom of the dimethylamino group to the C^{δ+}(Cl)^{δ-} bond polarization in the TS. Therefore, the mechanism was thought to take place via the anchimeric assistance of the nitrogen atom of the dimethylamino group as shown in reaction (2).

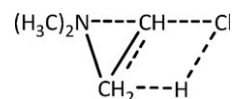


To support or modify the mechanism suggested in reaction (2), a DFT study on the elimination reaction path of 2-(dimethylamino)ethyl chloride and ethyl chloride was recently published.^[15] The results of the calculations implied that the most probable mechanism occurs in unimolecular fashion through a TS that is stabilized by electron delocalization from the amino

group (Scheme 1), rather than by direct participation of the dimethylamino group (Scheme 2).



Scheme 1. Transition state with electron delocalization from the dimethylamino group.



Scheme 2. Transition state with direct participation (anchimeric assistance) by the dimethylamino group.

Because of the reported absence of direct neighboring group participation by the nitrogen atom of the dimethylamino group,^[15] this work is aimed at examine whether or not there is anchimeric assistance by the olefinic double bond, in the HCl elimination of the alkenyl halides listed in Table 1, and if pi-electron delocalization from the olefinic bond group is involved in the transition state.^[16,17]

Consequently, the present situation of the elimination kinetics of chloroalkenes suggested an interesting study through theoretical calculations to elucidate a reasonable mechanism of these reactions. To this aim, the reaction paths of dehydrochlorination of 4-chlorobut-1-ene, 4-chloro-2-methylbut-1-ene, 5-chloro-2-methylpent-2-ene, 5-chloropent-1-ene, and 6-chlorohex-1-ene were examined at different levels of theory. In this way, it is possible to examine whether direct neighboring participation or the stabilization through delocalization of the double bond eliminates the HCl from the aforementioned substrates. The results are analyzed using calculated geometrical parameters, natural bond orbital (NBO) charges, and bond orders from DFT and G3 and G3MP2 calculations.

Computational Methods and Models

The theoretical study of the gas-phase elimination reactions of 4-chlorobut-1-ene, 4-chloro-2-methylbut-1-ene, 5-chloro-2-methylpent-2-ene, 5-chloropent-1-ene, and 6-chlorohex-1-ene was performed using the DFT methods: MPW1PW91/6-31G(d,p), MPW1PW91/6-31++G(d,p), G3, and G3MP2 using

Table 1. Kinetic and thermodynamic parameters of the gas-phase elimination kinetics of 1-chloroalkenes at 440°C.^[a]

| Z | $k_1 \times 10^4$ (s ⁻¹) | $k_H \times 10^4$ (s ⁻¹) | Rel. rate per hour | E_a (kJ/mol) | log A (s ⁻¹) | ΔS^\ddagger (J/mol K) | ΔH^\ddagger (kJ/mol) | ΔG^\ddagger (kJ/mol) | Ref. |
|---------------------------------------------------------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------|-------------------|-----------------------------|----------------------------------|---------------------------------|---------------------------------|-------|
| CH ₃ CH ₂ Cl | 1.35 | 0.45 | 1 | 241.8 | 13.84 | 4.20 | 236.2 | 233.4 | 16(a) |
| CH ₂ =CHCH ₂ CH ₂ Cl | 25.12 | 12.56 | 27.9 | 223.8 | 13.79 | 3.52 | 217.9 | 215.4 | 16(a) |
| CH ₂ =CHCH ₂ CH ₂ CH ₂ Cl | 10.61 | 5.30 | 11.8 | 230.0 | 13.65 | 0.85 | 224.1 | 223.5 | 16(b) |
| CH ₂ =C(CH ₃)CH ₂ CH ₂ Cl | 26.92 | 13.46 | 29.9 | 201.6 | 12.20 | -26.93 | 195.7 | 214.9 | 18 |
| (CH ₃) ₂ C=CHCH ₂ CH ₂ Cl | 47.86 | 23.93 | 53.2 | 215.0 | 13.43 | -3.33 | 209.1 | 211.4 | 17 |
| CH ₂ =CHCH ₂ CH ₂ CH ₂ Cl | 6.17 | 3.09 | 6.9 | 238.4 | 14.25 | 12.37 | 232.5 | 223.6 | 16(a) |
| CH ₂ =CHCH ₂ CH ₂ CH ₂ CH ₂ Cl | 10.72 | 5.36 | 11.9 | 209.6 | 12.38 | -23.43 | 203.6 | 220.3 | 16(a) |

[a] Experimental Arrhenius data taken from Refs. [16–18]. ΔS^\ddagger , ΔH^\ddagger , and ΔG^\ddagger have been estimated in this work.

Table 2. Thermodynamic and Arrhenius parameters of HCl elimination at 440°C.

| | Method | E_a (kJ/mol) | $\log A$ (s ⁻¹) | ΔH^\ddagger (kJ/mol) | ΔS^\ddagger (J/mol K) | ΔG^\ddagger (kJ/mol) | Ref. |
|------------------------------------|------------------------|----------------|-----------------------------|------------------------------|-------------------------------|------------------------------|------|
| <i>Ethyl chloride</i> | | | | | | | |
| | Experimental | 241.8 | 13.80 | 236.2 | 4.20 | 233.4 | 16 |
| Mechanism A | MPW91PW91/6-31G(d,p) | 243.8 | 14.10 | 238.2 | 10.0 | 231.5 | [a] |
| | MPW91PW91/6-31++G(d,p) | 237.9 | 14.10 | 232.2 | 9.9 | 225.7 | [a] |
| <i>4-Chloro-1-butene</i> | | | | | | | |
| | Experimental | 223.8 | 13.79 | 217.9 | 3.52 | 215.4 | 16 |
| Mechanism A | MPW1PW91/6-31G(d,p) | 226.0 | 14.11 | 220.1 | 9.66 | 213.2 | [a] |
| | MPW1PW91/6-31++G(d,p) | 221.3 | 14.11 | 215.4 | 9.80 | 208.4 | [a] |
| | MPW1PW91/6-31G(d,p) | 277.3 | 14.09 | 271.4 | 9.22 | 264.8 | [a] |
| Isomerization | B3LYP/6-31G(d,p) | 326.1 | 13.40 | 320.1 | -3.91 | 322.9 | [a] |
| <i>4-Chloro-2-methyl-1-butene</i> | | | | | | | |
| | Experimental | 201.6 | 12.20 | 195.7 | -26.93 | 214.9 | 18 |
| Mechanism A | MPW1PW91/6-31G(d,p) | 228.0 | 13.92 | 222.1 | 5.98 | 217.8 | [a] |
| | MPW1PW91/6-31++G(d,p) | 223.3 | 14.02 | 217.4 | 7.84 | 211.8 | [a] |
| | MPW1PW91/6-31G(d,p) | 287.2 | 14.00 | 281.2 | 7.52 | 275.9 | [a] |
| Mechanism B | MPW1PW91/6-31G(d,p) | 319.1 | 13.62 | 313.2 | 0.21 | 313.0 | [a] |
| Isomerization | B3LYP/6-31G(d,p) | 319.1 | 13.62 | 313.2 | 0.21 | 313.0 | [a] |
| Reaction 6, step 2 | MPW91PW91/6-31++G(d,p) | 150.2 | 13.01 | 145.5 | -9.56 | 150.9 | [a] |
| <i>5-Chloro-2-methyl-2-pentene</i> | | | | | | | |
| | Experimental | 215.0 | 13.43 | 209.1 | -3.33 | 211.4 | 17 |
| Mechanism A | MPW1PW91/6-31G(d,p) | 214.4 | 14.28 | 208.5 | 12.92 | 199.3 | [a] |
| | MPW1PW91/6-31++G(d,p) | 209.4 | 14.32 | 203.4 | 13.60 | 193.7 | [a] |
| | MPW1PW91/6-31G(d,p) | 254.9 | 13.95 | 248.9 | 6.66 | 244.2 | [a] |
| Mechanism B | MPW1PW91/6-31G(d,p) | 254.9 | 13.95 | 248.9 | 6.66 | 244.2 | [a] |
| Isomerization | B3LYP/6-31G(d,p) | 349.1 | 13.42 | 343.1 | -3.48 | 345.6 | [a] |
| <i>5-Chloro-1-pentene</i> | | | | | | | |
| | Experimental | 238.4 | 14.25 | 232.5 | 12.37 | 223.6 | 16 |
| Mechanism A | MPW1PW91/6-31G(d,p) | 239.1 | 14.34 | 233.2 | 14.11 | 223.1 | [a] |
| | MPW1PW91/6-31++G(d,p) | 233.7 | 14.31 | 227.8 | 13.41 | 218.2 | [a] |
| | MPW1PW91/6-31++G(d,p) | 233.7 | 14.31 | 227.8 | 13.41 | 218.2 | [a] |
| <i>6-chloro-1-hexene</i> | | | | | | | |
| | Experimental | 209.6 | 12.38 | 203.6 | -23.43 | 220.3 | 16 |
| Mechanism A | MPW1PW91/6-31G(d,p) | 237.8 | 13.93 | 231.9 | 6.27 | 227.4 | [a] |
| | MPW1PW91/6-31++G(d,p) | 223.0 | 14.15 | 217.1 | 10.42 | 209.7 | [a] |
| | MPW1PW91/6-31++G(d,p) | 223.0 | 14.15 | 217.1 | 10.42 | 209.7 | [a] |

[a] This work.

Gaussian 03 program.^[19] We have used the default parameters for convergence, that is, the Berny analytical gradient optimization routine, convergence on the density matrix was 10^{-9} atomic units, threshold value for maximum displacement was 0.0018 Å, and maximum force was 0.00045 Hartree/Bohr. The structures of stationary points, minimum energy, and TSs were verified by frequency calculations. Location of TS structures was performed using the quadratic synchronous transit (QST) protocol. The TS structures were identified using normal-mode analysis by having a single imaginary frequency and the corresponding transition vector is associated to the reaction products formation. The reaction paths were confirmed using intrinsic reaction coordinate calculations.

Frequency calculations have been used to determine the thermodynamic quantities, that is, zero-point vibrational energy, temperature corrections ($E(T)$), and absolute entropies ($S(T)$), assuming ideal gas behavior from the harmonic frequencies and moments of inertia by standard methods.^[20] Frequencies values, moments of inertia, and thermochemistry results are included as Supporting Information. We have used the average temperature and pressure values within the experimental range in the calculations. Scaling factors for frequencies and zero point energies were taken from the literature.^[21,22]

The canonical Transition state Theory was used for calculation of rate constants. The experimental enthalpy, entropy, and free energy of activation are obtained from the energy of activation

and $\log A$ using Arrhenius and Eyring equations.^[23] Theoretical energies of activation, $\log A$, and rate coefficients are derived from the enthalpy and entropy of activation obtained in the frequency calculations. Detailed description and equations are described in previous works and also included as Supporting Information.^[24,25]

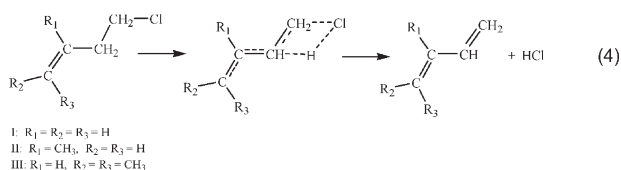
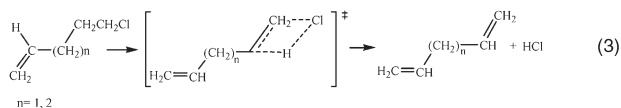
Results and Discussions

Kinetic and thermodynamic

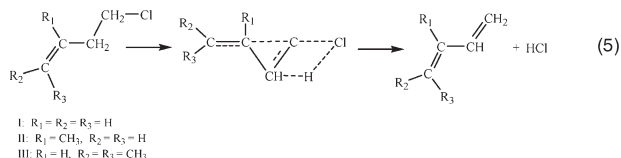
The study of the kinetic and mechanism of the elimination of hydrogen chloride from 4-chlorobut-1-ene, 4-chloro-2-methylbut-1-ene, 5-chloro-2-methylpent-2-ene, 5-chloropent-1-ene, and 6-chlorohex-1-ene was undertaken to determine a reasonable reaction mechanism. The calculated kinetic and thermodynamic parameters for these reactions are summarized in Table 2. Two possible mechanisms have been investigated as shown in reactions (3), (4), and (5). Mechanism A is 1,2-elimination reaction, while mechanism B considers the participation of the double bond assisting the exit of chlorine in the rate-determining step. The possible isomerization reactions in (6) were also investigated. Examination of the calculated and experimental parameters shown in Table 2, illustrates mechanism A to be favored for all the compounds in this study. In mechanism B, the enthalpies and consequently the energies of

activation are 30–60 kJ/mol greater than experimental values. Isomerization reactions for 4-chloro-1-butene, 4-chloro-2-methyl-1-butene, and 4-chloro-1-butene are unlikely, the enthalpies and energies of activation being higher still.

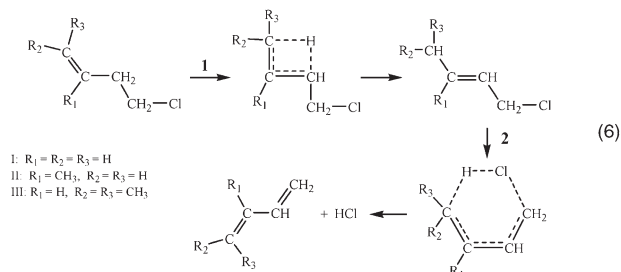
Mechanism A:



Mechanism B:



Isomerization reactions:



The present results suggest that the elimination reaction occurs through mechanism A 1,2-elimination, with possible π electron delocalization, rather than mechanism B, where anchi-

meric assistance through space by π -electrons was suggested. The following sections describe the changes occurring in the reactant, TSs, and products, using geometrical parameters, NBO charges, and bond orders.

Better enthalpy of activation and consequently the energy of activation was obtained when using MPW1PW91/6-31G(d,p) and MPW1PW91/6-31++G(d,p). Calculations results using the G3 and G3MP2 methods gave overestimated values of enthalpy of activation and consequently the energy of activation by 12–20 and 15–21 kJ/mol, respectively. G3 and G3MP2 results are given as Supporting Information Material. Perturbation methods truncated at MP2 are known to recover about 95% of the correlation energy and consequently are not adequate to describe these processes. We have obtained overestimated enthalpies of activation, and therefore overestimated energies of activation using G3 and G3MP2 methods. Higher levels such as MP3 and MP4 may be required at much higher computational cost.^[26] We have found that MPW1PW91 methods provide a reasonable description of these reactions.

The QST method allowed locating the TS structures for the above reactions; TS are shown in Figures 1–5. We have selected the MPW1PW91/6-31G(d,p) method for the analysis of geometrical parameters, NBO charges, and bond orders described in the following sections.

The present results suggest that the elimination reaction occurs through mechanism A 1,2-elimination, where π electron delocalization may be involved, rather than mechanism B, where anchi-

meric assistance through space by π -electrons was suggested. Regarding the entropy of activation, the calculated values are reasonable, however, about 6–7 J/mol K higher and a more positive than the experimental entropy values for 4-chloro-1-butene and 4-chloro-2-methyl-1-butene. In the case of 5-chloro-2-methyl-2-pentene and 6-chloro-1-hexene, the calculated entropies are higher by about 15 and 11 J/mol K, respectively. For 5-chloro-1-pentene, good agreement was found for calculated and experimental entropy of activation. The divergences observed are possibly due to the use of the harmonic approximation and the existence of low-frequency modes. These vibrational modes are highly unharmonic and may contribute significantly to the entropy.

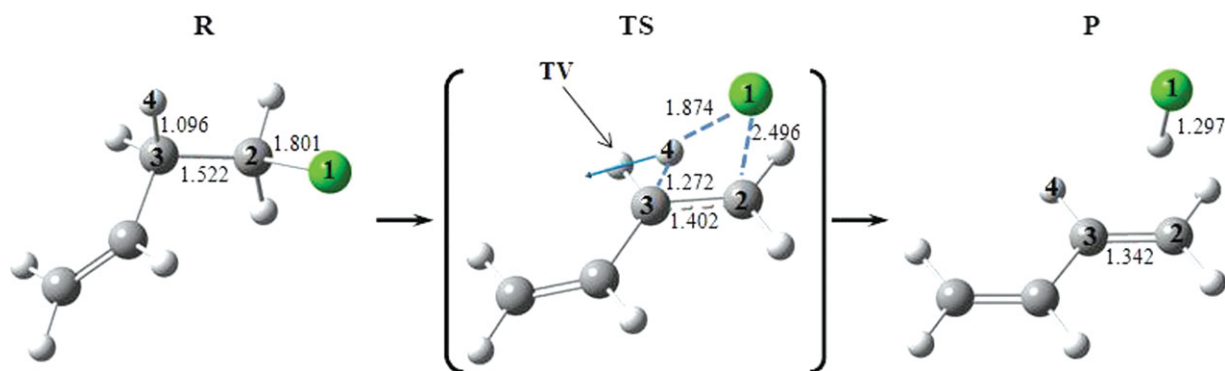


Figure 1. Optimized structures for reactant R, transition state TS, and product P in the gas phase elimination of HCl from 4-chloro-1-butene through mechanism A at MPW1PW91/6-31G(d,p). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

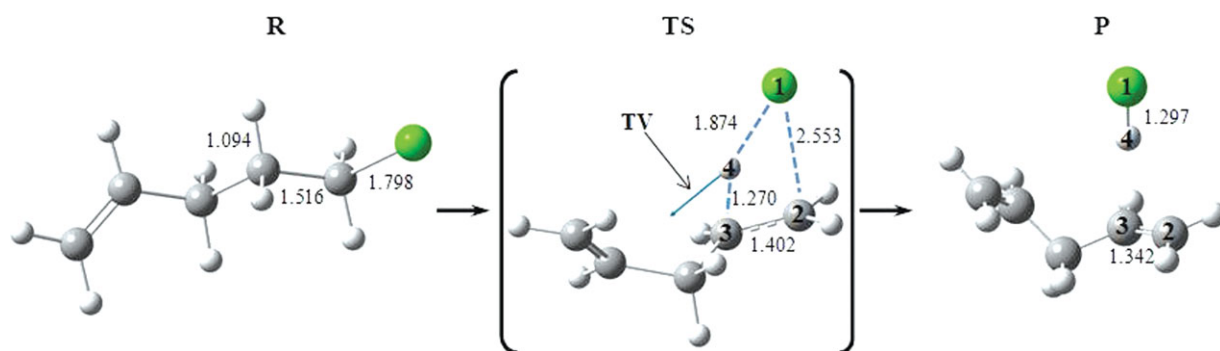


Figure 2. Optimized structures for reactant R, transition state TS, and product P in the gas phase elimination of HCl from 5-chloro-1-pentene through mechanism A at MPW1PW91/6-31G(d,p). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

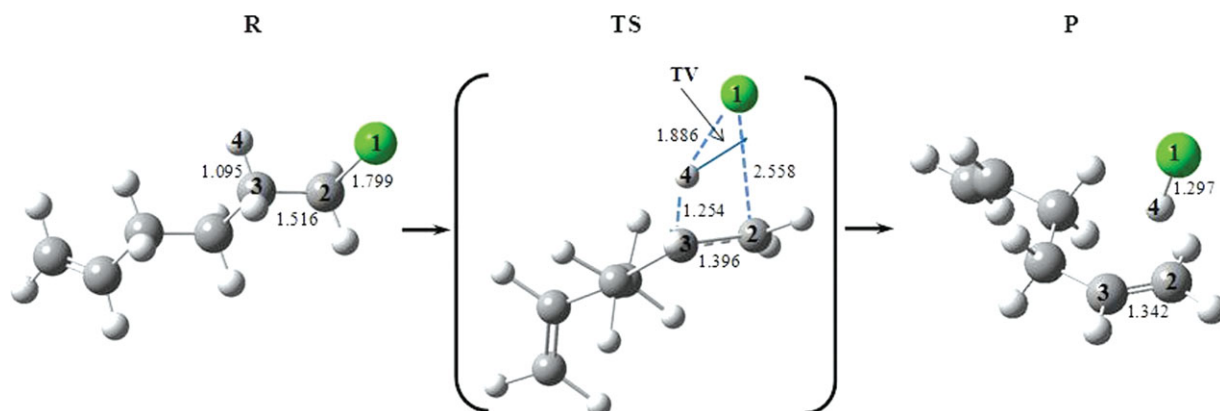


Figure 3. Optimized structures for reactant R, transition state TS, and product P in the gas phase elimination of HCl from 6-chloro-1-hexene through mechanism A at MPW1PW91/6-31G(d,p). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

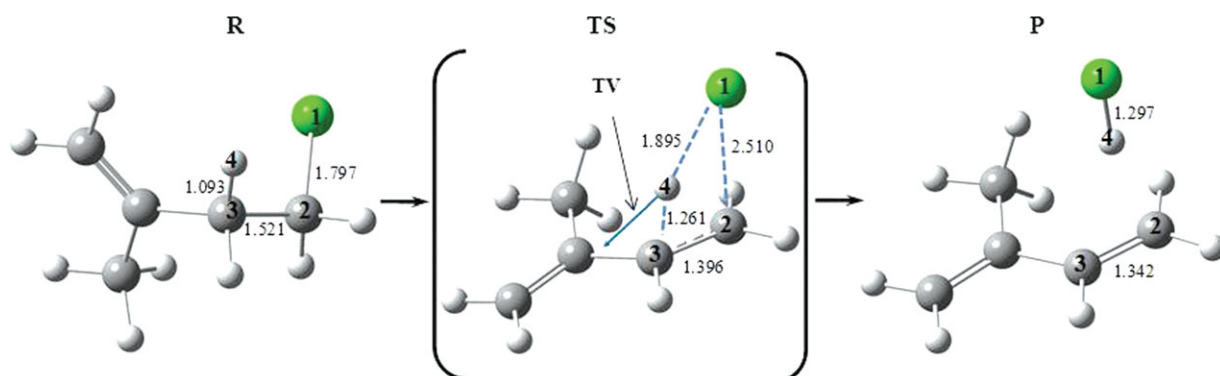


Figure 4. Optimized structures for reactant R, transition state TS, and product P in the gas phase elimination of HCl from 4-chloro-2-methyl-1-butene through mechanism A at MPW1PW91/6-31G(d,p). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

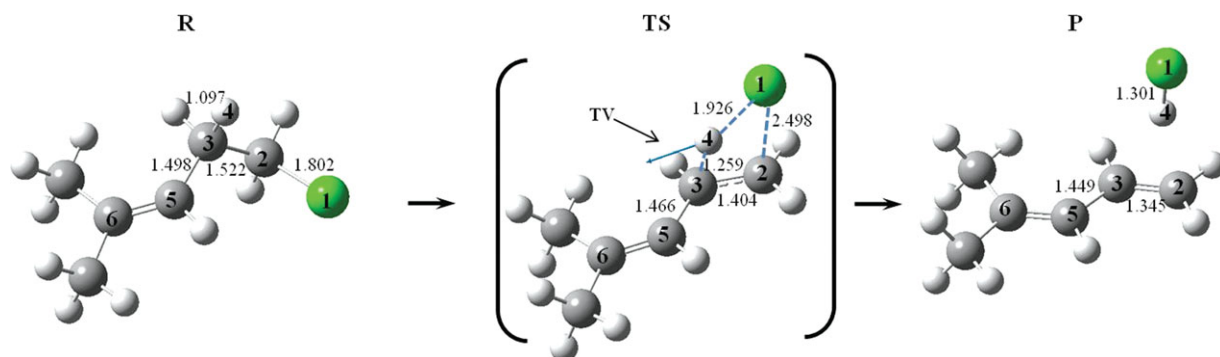


Figure 5. Optimized structures for reactant R, transition state TS, and product P in the gas phase elimination of HCl from 5-chloro-2-methyl-2-pentene through mechanism A at MPW1PW91/6-31G(d,p). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

It has been reported that the use of the harmonic approximation in frequency calculation has more impact in entropy calculations and therefore on the A factor than enthalpy calculations. Consequently, activation enthalpies and energies correlate closer to experimental values than entropies of activation.^[26] In this respect, we have chosen to compare enthalpies or energies of activation instead of calculated rates. The limitations of the harmonic approximations are described in a number of publications as a consequence the use of scaled frequency in spectroscopy studies.^[27,28]

Other methods had been used in an effort to obtain better entropies, such as anharmonic frequency calculations, hindered-rotor, and free-rotor models. In this study, we found that enthalpies of activation and consequently the energies of activation can be used to explain the preferred reaction path because of the low impact on enthalpy calculations using the harmonic approximation. Tunneling was not considered. The observed temperature dependence of rates in these reactions which follows Arrhenius behavior was an indication that tunneling was not of great impact particularly on energies of activation, although A values can be affected. In McGrath and Rowland's work on ethyl chloride, correction for tunneling effects gave better calculated rates compared to the experimental values.^[29] Tunneling becomes especially important at low temperatures,^[30] that is, at low-temperature regimes in which the reaction rate is independent of temperature, tunneling becomes important; however, this behavior was not observed. We were able to analyze the reactions mechanisms by comparing calculated enthalpies and energies of activation with experimental values.

Further analysis of nature of the TS found in this elimination reaction is needed to learn the role of π -electrons in the TS for mechanism A. In the following sections, a comparative description of the optimized structures of reactants, TS, and products is given in terms of geometrical parameters and NBO charges and bond orders.

TS and mechanism

Optimized structures for reactants, TS, and products of the hydrogen chloride elimination from 4-chlorobut-1-ene, 4-chloro-2-methylbut-1-ene, 5-chloro-2-methylpent-2-ene, 5-chloropent-1-ene, and 6-chlorohex-1-ene are shown in Figures 1–5. The struc-

tures of the TSs are four-centered geometries comprising atoms Cl₁, C₂, C₃, and H₄ (Scheme 3). Structural parameters of reactant, TS, and product of these elimination reactions are reported in Tables 3–6 (Scheme 3). For the substrates where π -delocalization is possible, for example, 4-chlorobut-1-ene, 4-chloro-2-methylbut-1-ene, and 5-chloro-2-methylpent-2-ene, the C₃–C₅ bond (Scheme 4)—next to the four centers involved in the elimination reaction—was also studied.

Significant increase of Cl₁–C₂ distance from 1.80 to 2.5–2.6 Å was found for all substrates, indicating the breaking of Cl₁–C₂ bond in the TS. The distance C₂–C₃ is decreased from 1.52 to 1.4 Å in the TS, demonstrating the double bond formation. The elongation of C₃–H₄ is significant in the TS; from 1.09 in the reactant to 1.26–1.27 Å. The hydrogen atom H₄ is closer to Cl₁ to form hydrogen chloride, 1.86–1.92 Å in the TS. Overall, the TSs appear similar in the distances, and the dihedral angles are small considering atoms Cl₁, C₂, C₃, and H₄, implying a quasi-planar configuration in the TS for the compounds 5-chloro-1-pentene and 6-chloro-1-hexene producing nonconjugated dienes.

In the case of the compounds producing conjugated dienes in the reaction, for example, 4-chloro-1-butene, 4-chloro-2-

Table 3. Structural parameters of reactant (R), transition state (TS), and products (P) for HCl elimination of CH₂=CH(CH₂)_nCH₂CH₂Cl (*n* = 1, 2; 5-chloro-1-pentene and 6-chloro-1-hexene) at 440°C from MPW1PW91/6-31G(d,p) calculations (Scheme 3).

| | | | Atomic lengths (Å) | | | |
|--------------|----|--|-----------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|
| | | | Cl ₁ –C ₂ | C ₂ –C ₃ | C ₃ –H ₄ | H ₄ –Cl ₁ |
| <i>n</i> = 1 | R | | 1.798 | 1.516 | 1.094 | 2.927 |
| | TS | | 2.553 | 1.393 | 1.267 | 1.860 |
| | P | | 3.537 | 1.335 | 2.478 | 1.297 |
| <i>n</i> = 2 | R | | 1.799 | 1.516 | 1.095 | 2.918 |
| | TS | | 2.558 | 1.396 | 1.254 | 1.886 |
| | P | | 3.595 | 1.338 | 2.410 | 1.304 |
| | | | Dihedral angles (degrees) | | | |
| | | | Cl ₁ –C ₂ –C ₃ –H ₄ | C ₂ –C ₃ –H ₄ –Cl ₁ | C ₃ –H ₄ –Cl ₁ –C ₂ | H ₄ –Cl ₁ –C ₂ –C ₃ |
| <i>n</i> = 1 | TS | | 3.003 | –8.719 | 7.334 | –3.156 |
| <i>n</i> = 2 | TS | | 3.008 | –8.644 | 7.312 | –3.103 |
| | | | Imaginary frequency (cm ^{–1}) | | | |
| <i>n</i> = 1 | TS | | 1354.99 | | | |
| <i>n</i> = 2 | TS | | 1266.15 | | | |

Table 4. Structural parameters of reactant (R), transition state (TS), and products (P) for HCl elimination from 4-chloro-1-butene at 440°C. MPW1PW91/6-31G(d,p) calculations (Scheme 4).

| | | Atomic lengths (Å) | | | | |
|----|--|-----------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|----------------------------------------------------------------|
| | | Cl ₁ –C ₂ | C ₂ –C ₃ | C ₃ –H ₄ | H ₄ –Cl ₁ | C ₃ –C ₅ |
| R | | 1.801 | 1.522 | 1.096 | 2.921 | 1.498 |
| TS | | 2.496 | 1.402 | 1.270 | 1.874 | 1.468 |
| P | | 3.530 | 1.342 | 2.464 | 1.297 | 1.453 |
| | | Dihedral angles (degrees) | | | | |
| | | Cl ₁ –C ₂ –C ₃ –H ₄ | C ₂ –C ₃ –H ₄ –Cl ₁ | C ₃ –H ₄ –Cl ₁ –C ₂ | H ₄ –Cl ₁ –C ₂ –C ₃ | C ₂ –C ₃ –C ₅ –C ₆ |
| TS | | 1.402 | –3.870 | 3.305 | –1.445 | –165.885 |
| | | Imaginary frequency (cm ^{–1}) | | | | |
| TS | | 1308.15 | | | | |

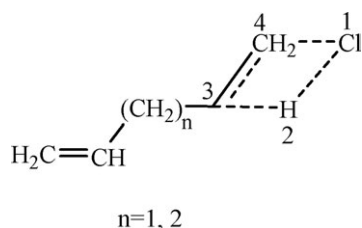
Table 5. Structural parameters of reactant (R), transition state (TS), and products (P) for HCl elimination from 4-chloro-2-methyl-1-butene at 440°C. MPW1PW91/6-31G(d,p) calculations (Scheme 4).

| | Atomic lengths (Å) | | | | |
|-----------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|----------------------------------------------------------------|
| | Cl ₁ —C ₂ | C ₂ —C ₃ | C ₃ —H ₄ | H ₄ —Cl ₁ | C ₃ —C ₅ |
| R | 1.797 | 1.521 | 1.093 | 2.970 | 1.507 |
| TS | 2.510 | 1.402 | 1.261 | 1.895 | 1.479 |
| P | 3.506 | 1.342 | 2.437 | 1.299 | 1.463 |
| | Dihedral angles (degrees) | | | | |
| | Cl ₁ —C ₂ —C ₃ —H ₄ | C ₂ —C ₃ —H ₄ —Cl ₁ | C ₃ —H ₄ —Cl ₁ —C ₂ | H ₄ —Cl ₁ —C ₂ —C ₃ | C ₂ —C ₃ —C ₅ —C ₆ |
| TS | −2.909 | 7.968 | −6.810 | 2.966 | 166.335 |
| Imaginary frequency (cm ^{−1}) | | | | | |
| TS | 1252.55 | | | | |

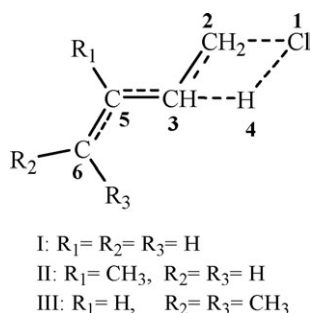
Table 6. Structural parameters of reactant (R), transition state (TS), and products (P) for HCl elimination from 5-chloro-2-methyl-2-pentene at 440°C. MPW1PW91/6-31G(d,p) calculations (Scheme 4).

| | Atomic lengths (Å) | | | | |
|-----------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|----------------------------------------------------------------|
| | Cl ₁ —C ₂ | C ₂ —C ₃ | C ₃ —H ₄ | H ₄ —Cl ₁ | C ₃ —C ₅ |
| R | 1.802 | 1.522 | 1.097 | 2.920 | 1.498 |
| TS | 2.498 | 1.404 | 1.259 | 1.926 | 1.466 |
| P | 3.483 | 1.345 | 2.432 | 1.301 | 1.449 |
| | Dihedral angles (degrees) | | | | |
| | Cl ₁ —C ₂ —C ₃ —H ₄ | C ₂ —C ₃ —H ₄ —Cl ₁ | C ₃ —H ₄ —Cl ₁ —C ₂ | H ₄ —Cl ₁ —C ₂ —C ₃ | C ₂ —C ₃ —C ₅ —C ₆ |
| TS | −1.758 | 4.726 | −4.084 | 1.766 | 172.368 |
| Imaginary frequency (cm ^{−1}) | | | | | |
| TS | 1227.38 | | | | |

methyl-1-butene, and 5-chloro-2-methyl-2-pentene, the distance C₃—C₅ diminishes from 1.50 Å to 1.47 Å, indicating partial double bond character in the TS. The dihedral



Scheme 3. Transition state with no extended pi-electron delocalization.



Scheme 4. Transition state with pi-electron delocalization from the olefinic double bond.

C₂—C₃—C₅—C₆, varying from 166 to 172, implies that the four centers Cl₁, C₂, C₃, and H₄ are in a different plane respect to C₂—C₃—C₅—C₆. For all substrates, the imaginary frequencies are associated with the motion of the hydrogen approaching the chlorine atom and a rocking motion of the substrate. Geometrical parameters alone provide a limited description of the changes occurring in the reaction. NBO charges and bond orders are used to illustrate the changes in electronic structure occurring from reactant to TS to product.

NBO charges

NBO charges have been used to describe the changes in electron distribution occurring in the reaction. The NBO charges of atoms involved in the reaction changes in the reactant, TS, and products of the compounds in this study are reported in Tables 7–10. Atom numbers are shown in Schemes 1 and 2.

Table 7 summarizes the NBO charges for CH₂=CH(CH₂)_nCH₂CH₂Cl (*n* = 1, 2), that is, 5-chloro-1-pentene and 6-chloro-1-hexene. The elimination products of these two compounds are nonconjugated dienes; consequently, no π-electron delocalization occurs in the TS. Considering the mechanism A, NBO charges show similar changes in electron distribution in the two substrates as the reaction progress from reactant to TS and to products. There is a significant increase in negative charge at Cl₁ in the TS from −0.083 to −0.574 in the TS when *n* = 1 and from −0.085 to −0.587 in the TS when *n* = 2. Carbon C₂ decreases in electron density in the TS to similar extent on both substrates. Equivalent changes also occur at C₃ and

Table 7. NBO charges of reactant (R), transition state (TS), and products (P) for HCl elimination of CH₂=CH(CH₂)_nCH₂CH₂Cl (*n* = 1, 2; 5-chloro-1-pentene and 6-chloro-1-hexene) at 440°C. MPW1PW91/6-31G(d,p) calculations (Scheme 3).

| | NBO charges | | | |
|--------------|-----------------|----------------|----------------|----------------|
| | Cl ₁ | C ₂ | C ₃ | H ₄ |
| <i>n</i> = 1 | | | | |
| R | −0.083 | −0.452 | −0.500 | 0.261 |
| TS | −0.574 | −0.190 | −0.517 | 0.389 |
| P | −0.316 | −0.490 | −0.208 | 0.284 |
| <i>n</i> = 2 | | | | |
| R | −0.085 | −0.449 | −0.505 | 0.256 |
| TS | −0.587 | −0.191 | −0.520 | 0.389 |
| P | −0.323 | −0.498 | −0.215 | 0.280 |

Table 8. NBO charges of reactant (R), transition state (TS), and products (P) for HCl elimination from 4-chloro-1-butene at 440°C. MPW1PW91/6-31G(d,p) calculations (Scheme 4).

| | NBO charges | | | | | |
|----|-----------------|----------------|----------------|----------------|----------------|----------------|
| | Cl ₁ | C ₂ | C ₃ | H ₄ | C ₅ | C ₆ |
| R | −0.089 | −0.451 | −0.532 | 0.268 | −0.236 | −0.450 |
| TS | −0.549 | −0.220 | −0.539 | 0.399 | −0.252 | −0.420 |
| P | −0.318 | −0.477 | −0.250 | 0.285 | −0.272 | −0.406 |

Table 9. NBO charges of reactant (R), transition state (TS), and products (P) for HCl elimination from 4-chloro-2-methyl-1-butene at 440°C. MPW1PW91/6-31G(d,p) calculations (Scheme 4).

| | NBO charges | | | | | |
|----|-----------------|----------------|----------------|----------------|----------------|----------------|
| | Cl ₁ | C ₂ | C ₃ | H ₄ | C ₅ | C ₆ |
| R | −0.083 | −0.456 | −0.520 | 0.264 | −0.024 | −0.444 |
| TS | −0.565 | −0.220 | −0.530 | 0.402 | −0.037 | −0.424 |
| P | −0.320 | −0.489 | −0.238 | 0.284 | −0.064 | −0.404 |

Table 10. NBO charges of reactant (R), transition state (TS), and products (P) for HCl elimination from 5-chloro-2-methyl-2-pentene at 440°C. MPW1PW91/6-31G(d,p) calculations (Scheme 4).

| | NBO charges | | | | | |
|----|-----------------|----------------|----------------|----------------|----------------|----------------|
| | Cl ₁ | C ₂ | C ₃ | H ₄ | C ₅ | C ₆ |
| R | −0.092 | −0.446 | −0.523 | 0.266 | −0.254 | −0.008 |
| TS | −0.573 | −0.235 | −0.522 | 0.408 | −0.271 | 0.030 |
| P | −0.321 | −0.494 | −0.236 | 0.282 | −0.289 | 0.042 |

H₄; C₃ develop into more negative charge in the TS, charge about −0.52, while H₄ becomes more positive and charge 0.389.

Compounds in Tables 9 and 10, that is, 4-chloro-1-butene, 4-chloro-2-methyl-1-butene, and 5-chloro-2-methyl-2-pentene, produce conjugated dienes in the hydrogen chloride elimination; consequently π -electron delocalization occurs. The changes in electron density in the neighboring atoms were studied as shown in charges at C₅ and C₆ (Scheme 4). For these three substrates, there is an important increase in negative charge at Cl₁ in the TS, changes are in the order: 4-chloro-1-butene < 4-chloro-2-methyl-1-butene < 5-chloro-2-methyl-2-pentene. At carbon, C₂ charges are identical in the TS for 4-chloro-1-butene and 4-chloro-2-methyl-1-butene; however, in the case of 5-chloro-2-methyl-2-pentene, C₂ is more negative in the TS compared to 4-chloro-1-butene and 4-chloro-2-methyl-1-butene. NBO charge for C₃ in the TS shows this atom is less negative in the case of 5-chloro-2-methyl-2-pentene. H₄ becomes more positive in the TS in the order: 4-chloro-1-butene < 4-chloro-2-methyl-1-butene < 5-chloro-2-methyl-2-pentene, as observed in the increase in negative charge at Cl₁. Changes in electron density at C₅ and C₆ are also observed, interestingly, charges at C₅ are smaller for 4-chloro-2-methyl-1-butene, with a methyl substituent at C₅, compared to the

other two substrates. To further investigate the nature of the TS, we studied the changes in bond orders from NBO calculations.

Bond order analysis

We used NBO bond order calculations to describe the progress of along different reaction coordinates.^[31–33] Wiberg bond indexes^[34] were computed using the NBO program^[35] as implemented in Gaussian 03. The reaction mechanism involving bond breaking and making process may be accounted through the Synchronicity (Sy) concept proposed by Moyano et al.^[36] as described in the following equations:

$$Sy = 1 - \left[\sum_{i=1}^n |\delta Bi - \delta Bav| / \delta Bav \right] / 2n - 2$$

δBi indicates change in i bond order, and n is the number of bonds directly involved in the reaction and the relative variation of the bond index is obtained from

$$\delta Bi = [B_i^{TS} - B_i^R] / [B_i^P - B_i^R]$$

The superscript R, TS, and P indicate reactant, TS, and product, respectively.

The bond indexes of Wiberg, B_{ij} , were calculated for the bonds involved in the reaction, changes, that is, Cl₁–C₂, C₂–C₃, C₃–H₄, and H₄–Cl₁, for 5-chloro-1-pentene and 6-chloro-1-hexene (CH₂=CH(CH₂)_nCH₂CH₂Cl, $n = 1, 2$), reported in Table 11, and for 4-chloro-1-butene, 4-chloro-2-methyl-1-butene, and 5-chloro-2-methyl-2-pentene (Tables 12–14), bond order C₃–C₅ was also considered.

Table 11. Wiberg bond index of reactant (R), transition state (TS), and products (P) for HCl elimination of CH₂=CH(CH₂)_nCH₂CH₂Cl ($n = 1, 2$) at 440°C. MPW1PW91/6-31G(d,p) calculations (Scheme 3).

| | Cl ₁ –C ₂ | C ₂ –C ₃ | C ₃ –H ₄ | H ₄ –Cl ₁ | S _y |
|-----------------|---------------------------------|--------------------------------|--------------------------------|---------------------------------|----------------|
| $n = 1$ | | | | | |
| B_i^R | 1.0040 | 1.0225 | 0.8991 | 0.0021 | 0.813 |
| B_i^{TS} | 0.3277 | 1.3886 | 0.4230 | 0.2549 | |
| B_i^P | 0.0106 | 1.9456 | 0.0164 | 0.8796 | |
| %E _v | 68.08 | 39.66 | 53.94 | 28.81 | |
| $n = 2$ | | | | | |
| B_i^R | 1.0030 | 1.0234 | 0.9010 | 0.0022 | 0.803 |
| B_i^{TS} | 0.3232 | 1.3758 | 0.4368 | 0.2365 | |
| B_i^P | 0.0170 | 1.9224 | 0.0252 | 0.8669 | |
| %E _v | 68.95 | 39.20 | 53.00 | 27.10 | |

Table 12. Wiberg bond index of reactant (R), transition state (TS), and products (P) for HCl elimination from 4-chloro-2-methyl-1-butene at 440°C. MPW1PW91/6-31G(d,p) calculations.

| | Cl ₁ –C ₂ | C ₂ –C ₃ | C ₃ –H ₄ | H ₄ –Cl ₁ | C ₃ –C ₅ | S _y |
|-----------------|---------------------------------|--------------------------------|--------------------------------|---------------------------------|--------------------------------|----------------|
| B_i^R | 0.9993 | 1.0151 | 0.8859 | 0.0027 | 1.0284 | 0.796 |
| B_i^{TS} | 0.3437 | 1.3300 | 0.4097 | 0.2360 | 1.0724 | |
| B_i^P | 0.0107 | 1.8534 | 0.0156 | 0.8766 | 1.1236 | |
| %E _v | 66.31 | 37.56 | 54.72 | 26.70 | | |

Table 13. Wiberg bond index of reactant (R), transition state (TS), and products (P) for HCl elimination from 4-chloro-2-methyl-1-butene at 440°C. MPW1PW91/6-31G(d,p) calculations.

| | Cl ₁ —C ₂ | C ₂ —C ₃ | C ₃ —H ₄ | H ₄ —Cl ₁ | C ₃ —C ₅ | S _y |
|------------------------------|---------------------------------|--------------------------------|--------------------------------|---------------------------------|--------------------------------|----------------|
| B _i ^R | 1.0009 | 1.0147 | 0.9003 | 0.0021 | 1.0122 | 0.788 |
| B _i ^{TS} | 0.3329 | 1.3297 | 0.4177 | 0.2247 | 1.0515 | |
| B _i ^P | 0.0118 | 1.8530 | 0.0168 | 0.8727 | 1.0984 | |
| %E _v | 67.54 | 37.58 | 54.62 | 25.57 | | |

Table 14. Wiberg bond index of reactant (R), transition state (TS), and products (P) for HCl elimination from 5-chloro-2-methyl-2-pentene at 440°C. MPW1PW91/6-31G(d,p) calculations.

| | Cl ₁ —C ₂ | C ₂ —C ₃ | C ₃ —H ₄ | H ₄ —Cl ₁ | C ₃ —C ₅ | S _y |
|------------------------------|---------------------------------|--------------------------------|--------------------------------|---------------------------------|--------------------------------|----------------|
| B _i ^R | 0.9978 | 1.0148 | 0.8863 | 0.0028 | 1.0177 | 0.774 |
| B _i ^{TS} | 0.3315 | 1.3191 | 0.4183 | 0.2011 | 1.0740 | |
| B _i ^P | 0.0126 | 1.8332 | 0.0172 | 0.8699 | 1.1349 | |
| %E _v | 67.63 | 37.18 | 53.85 | 22.87 | | |

Calculated bond orders for compounds CH₂=CH(CH₂)_nCH₂CH₂Cl (*n* = 1, 2) show the reaction dominated by the breaking of Cl₁—C₂ bond (68–69% in the TS). The breaking of C₃—H₄ bond shows intermediate progress, while the change in bond order C₂—C₃ and HCl bond formation are early in the reaction coordinate.

In the case of the substrates producing conjugated dienes on HCl elimination: 4-chloro-2-methyl-1-butene, 4-chloro-2-methyl-1-butene, and 5-chloro-2-methyl-2-pentene (Tables 12–14), the reaction is dominated by the breaking of Cl₁—C₂ bond showing progress of ~ 66–68%, in the order 4-chloro-1-butene < 4-chloro-2-methyl-1-butene < 5-chloro-2-methyl-2-pentene. The breaking of C₃—H₄ bond shows intermediate development, about 55–54%. Similar progress is observed for the double bond formation C₂—C₃, ~ 37%. The formation of HCl is less advanced ~ 27–23%. Small changes are observed in C₃—C₅ bond order. This bond has a small double bond character in the product, due to π -electron delocalization; a slight increase in C₃—C₅ bond order is seen in the TS.

The synchronicity concept has been used to illustrate if a reaction that occurs in a concerted fashion shows equal development along the different reaction coordinates or not. The parameter S_y varies from 1 to 0; being S_y = 1 in the case of concerted synchronic reaction, and S_y = 0 in the case of nonsynchronous process. Global synchronicity is a general concept, nevertheless, analysis of bond order in the different reaction coordinates describes the extension to which any particular bond involved in the reaction is formed or broken in the TS. Accordingly, the reaction can be described as more advanced in some reaction coordinates than others.

The hydrogen chloride elimination from the compounds in this study appears to proceed through mechanism A 1,2-elimination with some involvement of π -electron delocalization in the case of the substrates producing conjugates dienes. The reactions with S_y = 0.8 can be described as nonsynchronous and moderately polar. This is more apparent for the substrates

with π -electron delocalization in the order 4-chloro-1-butene < 4-chloro-2-methyl-1-butene < 5-chloro-2-methyl-2-pentene.

Conclusions

The dehydrochlorination of selected 1-chloroalkenes was studied using DFT, G3, and G3MP2 methods to establish a reasonable reaction mechanism. Two model reaction mechanisms have been considered: mechanism A, a 1,2-elimination with possible π -electron delocalization for the substrates yielding conjugated diene product and mechanism B, where the anchimeric assistance of π -electrons aiding the leaving group Cl was proposed. We have analyzed here the possible reaction mechanisms by comparing the calculated enthalpies and energies of activation with the corresponding experimental values. Calculated parameters suggest mechanism A to be more reasonable. Good agreement of activation parameters was obtained using MPW1PW91/6-31G(d,p) and MPW1PW91/6-31++G(d,p) levels of theory. G3 and G3MP2 methods gave overestimated enthalpies and energies of activation. The DFT method MPW1PW91 with relatively small basis set is able to provide reasonable enthalpies and energies of activation. The rate-determining process in these reactions is the cleavage of C—Cl bond. However, breaking of C—H shows also an important progress in the TS. The TS shows some involvement of π -electron delocalization for the substrates producing product conjugated dienes and do not support the anchimeric assistance by π electrons in the dehydrochlorination reaction of the compounds in this study.

Keywords: 1-chloroalkenes • mechanism • elimination kinetics • density functional theory • G3 and G3MP2 method

How to cite this article: JR. Mora, J. Lezama, N. Berroteran, T. Cordova, G. Chuchani, *Int. J. Quantum Chem.* **2012**, 112, 3729–3738. DOI: 10.1002/qua.24175

Additional Supporting Information may be found in the online version of this article.

- [1] J. B. Rogan, *J. Org. Chem.* **1962**, 27, 3910.
- [2] K. L. Servis, J. D. Roberts, *J. Am. Chem. Soc.* **1964**, 86, 3773.
- [3] A. Maccoll, *Chem. Rev.* **1969**, 69, 33.
- [4] A. Maccoll, P. J. Thomas, *Nature* **1955**, 176, 392.
- [5] A. Maccoll, P. J. Thomas, *Prog. React. Kinet.* **1967**, 4, 119.
- [6] S. W. Benson, A. H. Bose, *J. Chem. Phys.* **1963**, 39, 3463.
- [7] G. Chuchani, *The Chemistry of Halides, Pseudo-Halides and Azides*; S. Patai and Z. Rapoport, Eds., Chapter 19; Wiley: New York, **1995**; p. 1069–1119.
- [8] S. D. Paisley, B. E. Holmes, *J. Phys. Chem.* **1983**, 87, 3042.
- [9] J. L. Toto, G. O. Pritchard, B. Kirtmann, *J. Phys. Chem.* **1994**, 98, 8359.
- [10] J. R. Mora, E. Márquez, J. R. Mora, T. Córdoba, G. Chuchani, *J. Mol. Struct. Theochem.* **2009**, 916, 17.
- [11] J. R. Mora, J. Lezama, E. Márquez, L. Escalante, T. Córdoba, G. Chuchani, *J. Phys. Org. Chem.* **2011**, 24, 229.
- [12] J. R. Mora, E. Márquez, J. Lezama, T. Córdoba, G. Chuchani, *Int. J. Quant. Chem.* **2011**, 111, 4011.
- [13] C. E. Lisowski, J. R. Duncan, A. J. Ranieri, G. L. Heard, D. W. Setser, B. E. Holmes, *J. Phys. Chem. A* **2010**, 114, 10395.

- [14] G. Chuchani, I. Martin, G. Martin, D. B. Bigley, *Int. J. Chem. Kinet.* **1979**, *11*, 109.
- [15] A. Maldonado, J. R. Mora, T. Cordova, G. Chuchani, *J. Mol. Struct. Theochem.* **2010**, *961*, 55.
- [16] (a) G. Chuchani, J. A. Hernandez, I. Martin, *Int. J. Chem. Kinet.* **1979**, *11*, 1279; (b) P. Cadman, M. Day, A. F. Trotman-Dickenson, *J. Chem. Soc. A* **1970**, 2058.
- [17] G. Chuchani, I. Martin, M. E. Alonso, P. I. Jano, *Int. J. Chem. Kinet.* **1981**, *13*, 1.
- [18] J. Mauger, J. Maurin, *Bull. Soc. Chim. Fr.* **1970**, *6*, 2332.
- [19] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, D. A. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, Revision C.02; Gaussian, Inc.: Wallingford, CT, **2004**.
- [20] D. McQuarrie, *Statistical Mechanics*; Harper & Row: New York, **1986**.
- [21] J. B. Foresman, ó. Frish, *Exploring Chemistry with Electronic Methods*, 2nd ed.; Gaussian, Inc.: Pittsburg, PA, **1996**.
- [22] (a) Scale factors. Available at: <http://cccbdb.nist.gov/vibscalejust.asp>; (b) Database of Frequency Scaling Factors for Electronic Structure Methods. Available at: http://comp.chem.umn.edu/truhlar/freq_scale.htm. Accessed May 2011.
- [23] S. W. Benson, *The Foundations of Chemical Kinetics*; Mc-Graw-Hill: New York, **1960**.
- [24] J. Lezama, E. Marquez, J. R. Mora, T. Cordova, G. Chuchani, *J. Mol. Struct. Theochem.* **2009**, *916*, 17.
- [25] E. Marquez, R. M. Dominguez, J. R. Mora, T. Cordova, G. Chuchani, *J. Phys. Chem. A* **2010**, *114*, 4203.
- [26] A. Rastelli, M. Bagatti, R. Gandolfi, *J. Am. Chem. Soc.* **1995**, *117*, 4965.
- [27] A. P. Scott, L. Radom, *J. Phys. Chem.* **1996**, *100*, 16502.
- [28] G. M. Chaban, J. O. Jung, R. B. Gerber, *J. Chem. Phys.* **1999**, *111*, 1823.
- [29] M. P. McGrath, F. S. Rowland, *J. Phys. Chem. A* **2001**, *106*, 8191.
- [30] P. R. Schreiner, *Science* **2011**, *332*, 1300.
- [31] G. Lendvay, *J. Phys. Chem.* **1989**, *93*, 4422.
- [32] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735.
- [33] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899.
- [34] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083.
- [35] a. NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold. b. A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.*, **1985**, *83*, 735.
- [36] A. Moyano, M. A. Pericá, E. Valenti, *J. Org. Chem.* **1989**, *54*, 573.

Received: 19 March 2012
Revised: 19 March 2012
Accepted: 5 April 2012
Published online on 24 May 2012