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Mechanistic Aspects of the Abstraction of an Allylic Hydrogen in the Chlorine Atom Reaction with 2-Methyl-1,3-Butadiene (Isoprene)

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Abstract: The different channels for the abstraction of an allylic hydrogen in the chlorine atom reaction with isoprene were explored using ab initio methodology. It is shown that the metathesis reaction proceeds through an *association−elimination* mechanism in which a weakly bound intermediate ($HCl\cdots C_5H_7^{\bullet}$) is formed first (formal *addition*). Further evolution by HCl elimination leads to the final $C_5H_7^{\bullet}$ radical. QCISD(T)/aug-cc-pVDZ//MP2/6-31G(d,p) calculations show that for two of the possible pathways the barrier heights involved are moderate and the formation of the intermediates are exergonic ($\Delta G < 0$). Therefore, the mechanism proposed is both kinetically and thermodynamically feasible. The pressure dependence experimentally observed for the Cl + isoprene reaction can be rationalized in terms of the association−elimination mechanism proposed.

Introduction

It has been recently reported[1−4] that 2-methyl-1,3-butadiene (isoprene) is produced in seawater by phytoplankton. On the other hand, the possibility that atomic chlorine contributes to the oxidation of organics in the marine boundary layer has also been discussed in the recent literature.[5−7]

The reaction between chlorine atoms and alkenes proceeds primarily by addition to a double bond to form a chlorine-containing alkyl radical, which then adds O_2 to ultimately generate characteristic chlorine-containing oxygenated products.[8] However, a small portion of the reaction proceeds via abstraction of the allylic hydrogen.[9] Particularly, in the case of the isoprene reaction it has been shown that about 15% of the overall reaction at 1 atm pressure and room temperature proceeds by abstraction of an allylic hydrogen.[10]

The mechanism of these reactions is not fully understood.[10] Indeed, we focus on the reaction between Cl and isoprene:

$$\mathrm{Cl} + \text{isoprene} \rightarrow \mathrm{HCl} + C_5H_7^{\bullet} \qquad \textit{abstraction} \qquad (1)$$

$$\mathrm{Cl} + \text{isoprene} \rightleftarrows [\mathrm{Cl}\cdots\text{isoprene}]^* \xrightarrow{[M]} C_5H_8Cl \qquad \textit{addition} \qquad (2)$$

with k_{abs} and $k_{add}(P)$ denoting the rate constants for the abstraction and addition reactions, respectively (it has been assumed that, as in the case of the alkanes, the abstraction reaction of chlorine atoms with isoprene is pressure independent).[10] Chart 1 summarizes the expected values of the observed rate constant (k_{obs}) for the reaction using either isoprene or fully deuterated isoprene (isoprene-d_8) at different pressures. It should be noted[10] that, on one hand, the addition reaction is expected to have a negligible isotope effect and that, on the other hand, the assumption that abstraction becomes negligible for the fully deuterated compound is reasonable. According to this scheme, one would expect that k_{obs} for the reactions involving isoprene and isoprene-d_8 should differ by a constant amount (k_{abs}) no matter the pressure under which the experiments were carried out. However, the experimental results showed that whereas at 760 Torr the two values of k_{obs} are different, at low-pressure conditions they coincide within the experimental uncertainty. Ragains and Finlayson-Pitts[10] speculated that a possible explanation is that the formation of HCl is not a direct bimolecular abstraction but rather involves addition followed by elimination of HCl,

$$\mathrm{Cl} + \text{isoprene} \rightleftarrows [\mathrm{Cl}\cdots\text{isoprene}]^* \xrightarrow{[M]} \mathrm{HCl} + C_5H_7^{\bullet} \qquad \textit{addition} + \textit{elimination} \qquad (3)$$

Ragains and Finlayson-Pitts[10] made the reasonable proposal that a likely mechanism coherent with the experimental facts would consist of the addition of the chlorine atom to the double bond, formation of a six-membered ring transition structure with the methyl group hydrogen, and the elimination of HCl.

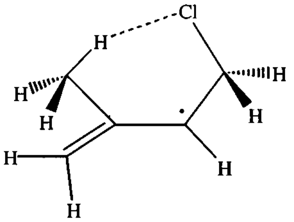

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Chart 1. Contributions to the Observed Rate Constants (k_{Obs}) for the Isoprene + Cl and Isoprene-d_8 (Fully Deuterated) + Cl Reactions at High (760 Torr) and Low (0.2−5 Torr) Pressures

Pressure Reaction	**P=760 Torr**	**P=0.2–5 Torr**
Isoprene + Cl	k_{add} (P=760) + k_{abs}	k_{add} (P=0.2–5) + k_{abs}
Isoprene-d_8 + Cl	k_{add} (P=760)	k_{add} (P=0.2–5)

A similar conclusion was reached by Kaiser and Wallington in their study on the pressure dependence of the reaction Cl + C_3H_6.[11]

Under this hypothesis, Chart 1 is still valid with the only change that the rate constant for the abstraction reaction (eq 3) is now pressure dependent; i.e., $k_{abs} = k_{abs}(P)$. At $P = 760$ Torr, k_{obs} for the two reactions should be different, whereas, as Ragains and Finlayson-Pitts concluded, in the case that $k_{abs}(P{=}0.2{-}5) \approx 0$, the values of k_{obs} for the reactions involving isoprene and isoprene-d_8 should be the same, in agreement with the experimental findings.

Bedjanian and co-workers[12] carried out a low-pressure study of the same reaction at different temperatures (233−320 K) and found that k_{abs} is greater than the corresponding value in reactions involving alkanes. These authors concluded that two possible explanations can be invoked: (a) in addition to the direct hydrogen atom transfer channel that occurs in Cl + alkane reactions, the addition−elimination process suggested by Ragains and Finlayson-Pitts can operate, and/or (b) the allylic hydrogen abstraction can proceed faster than the hydrogen abstraction in alkanes as a consequence of the fact that the C−H bond for allylic hydrogens is weaker than the C−H bond for alkanes. This latter point could be questioned by realizing that although the activation barrier predicted by these authors for the abstraction reaction Cl + isoprene is rather small (0.22 ± 0.35 kcal/mol),[12] it is still greater than the barrier associated with the direct hydrogen abstraction in the Cl + butane reaction which is predicted to be nil.[8] In any case, as concluded by Bedjanian and co-workers,[12] since the k_{abs} they report was not measured as a function of pressure (only the pressure dependence of $k_{obs} = k_{abs} + k_{add}$ was studied), the distribution between hydrogen atom direct abstraction and addition−elimination mechanism was not possible.

In the present work we carried out an ab initio study of the different channels through which the abstraction of an allylic hydrogen in the chlorine atom reaction with 2-methyl-1,3-butadiene (isoprene) proceeds. As remarked in previous experimental works,[10] the study of that process is of fundamental mechanistic and kinetics interest since its understanding is critical for assessing the sinks of both isoprene and atomic chlorine in the marine boundary layer.

Methodology

The potential energy surface (PES) corresponding to the abstraction of an allylic hydrogen in the reaction between chlorine atom and isoprene was extensively explored at the MP2/6-31G(d,p) level of theory. A previous study[13] on a similar reaction involving a smaller alkene (ethylene), where the use of larger basis sets and more sophisticated theoretical methods were feasible, allowed us to conclude that, in general, such a level provides reliable structural information.

All the geometrical parameters were fully optimized and all the structures located on the PES were characterized at the MP2/6-31G-(d,p) level by computing the corresponding Hessian matrix, examining the number of imaginary frequencies from it.

The reaction paths of the different channels (see below) were followed starting from the geometries of the transition structures by using the intrinsic reaction coordinate (IRC) algorithm in the mass-weighted internal coordinates.[14,15]

It is well-established (see refs 16−19 and references cited therein) that the use of the coupled-cluster method with singles, doubles, and a quasi-perturbative estimate of the contributions of triple excitations provides, in general, quite accurate energetics. Accordingly, QCISD-(T)//MP2 single-point calculations were carried out in order to improve the energy predictions. On the other hand, it is well-known that the presence of diffuse functions in the basis set allows for an appropriate representation of the dispersion forces which may play an important role in the stabilization of the weakly bound complexes.[13,20] Since some of the structures in the present work belong to this latter class, we used Dunning's correlation-consistent augmented basis set[21] to perform QCISD(T)/aug-cc-pVDZ//MP2/6-31G(d,p) single-point calculations on the structures located in the different channels. Each such calculation for a Cl−isoprene structure (214 basis functions) required about 111 h of CPU time on a SGI Origin 2000 computer running with 700 MB RAM.

All the MP2 energy values reported in this work correspond to spin projected calculations (PMP2) to correct for spin contamination.[22] Regarding the QCISD(T) energies, Stanton[23] has shown that, even in CCSD, all spin contamination is esentially removed from the coupled-cluster wave functions.

The thermodynamic functions (ΔH, ΔS, and ΔG) were estimated within the ideal gas, rigid-rotor, and harmonic oscillator approximations,[24] as implemented in Gaussian 98[25] which was the package of programs employed to carry out all the calculations reported in this work. A temperature of 298.15 K and a pressure of 1 atm. were assumed.

Results and Discussion

Chart 2 shows the four different channels (A−D) located on the PES through which a chlorine atom abstracts an allylic hydrogen atom from isoprene, and Figures 1−4 depict two views of the structures involved in each channel (in what follows we will use the notation introduced in these figures to denote the different structures). An exhaustive search on the PES failed to locate a transtion structure like that proposed by Ragains and Finlayson-Pitts[10] (see structure 4 above). Therefore, according to our MP2/6-31G(d,p) calculations, an addition−elimination mechanism involving the transition structure 4 can be ruled out.

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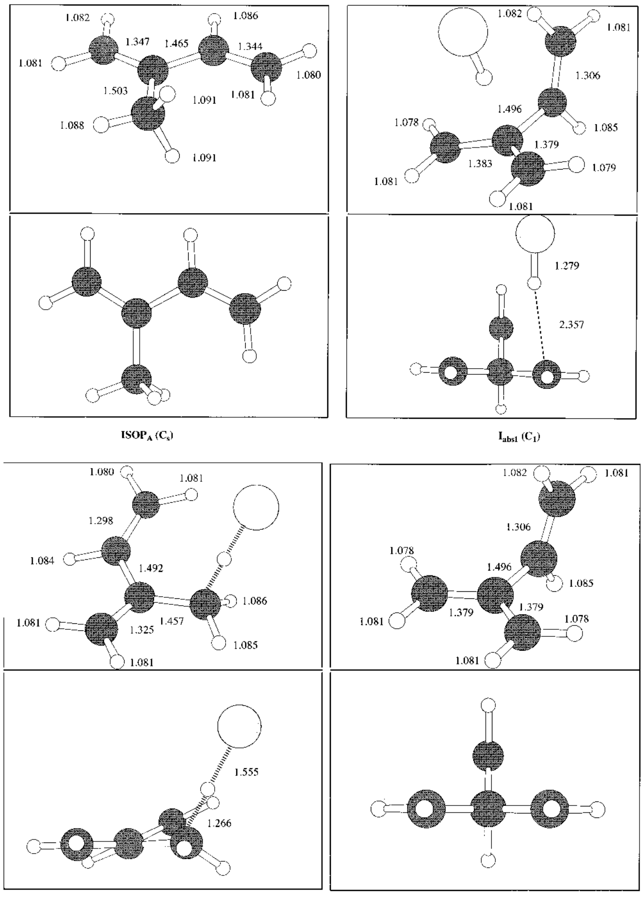
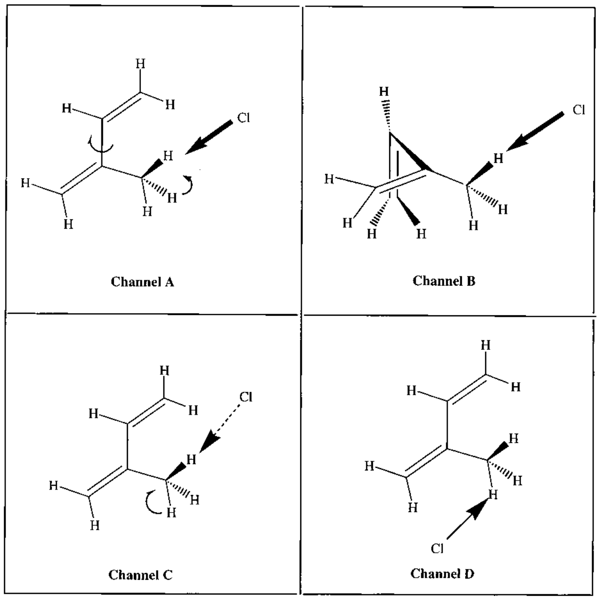


$ISOP_A$ (C_s) I_{abs1} (C_1)

TS_{abs1} (C_1) P1 (C_s)

Figure 1. Reactive ($ISOP_A$), intermediate (I_{abs1}), transition structure (TS_{abs1}), and product (P1) for the abstraction reaction (channel A; see Chart 3) between chlorine atom and isoprene.

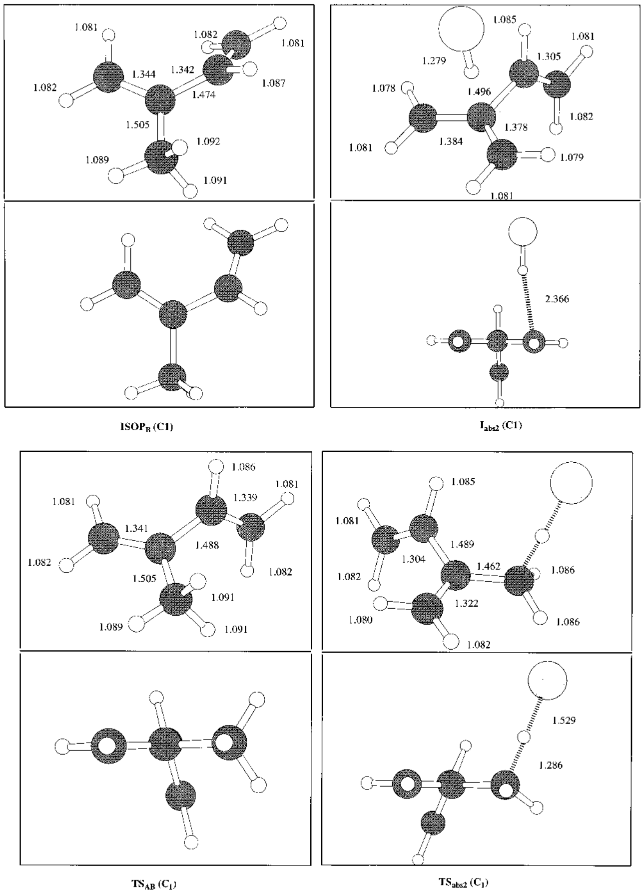
Chart 2. Different Channels for the Allylic Hydrogen Abstraction in the Cl + Isoprene Reaction



Channel A Channel B

Channel C Channel D

Table 1 collects the relative electronic energies and changes in enthalpy, entropy, and Gibbs free energy corresponding to all the structures in channels A−D, and in Chart 3 the energy profiles (electronic energies) of these four pathways are represented (it should be noted that P1 is common to channels A and B, and TS_{24} allows a connection to P2 in channel C with P4 in channel D).



$ISOP_B$ (C1) I_{abs2} (C1)

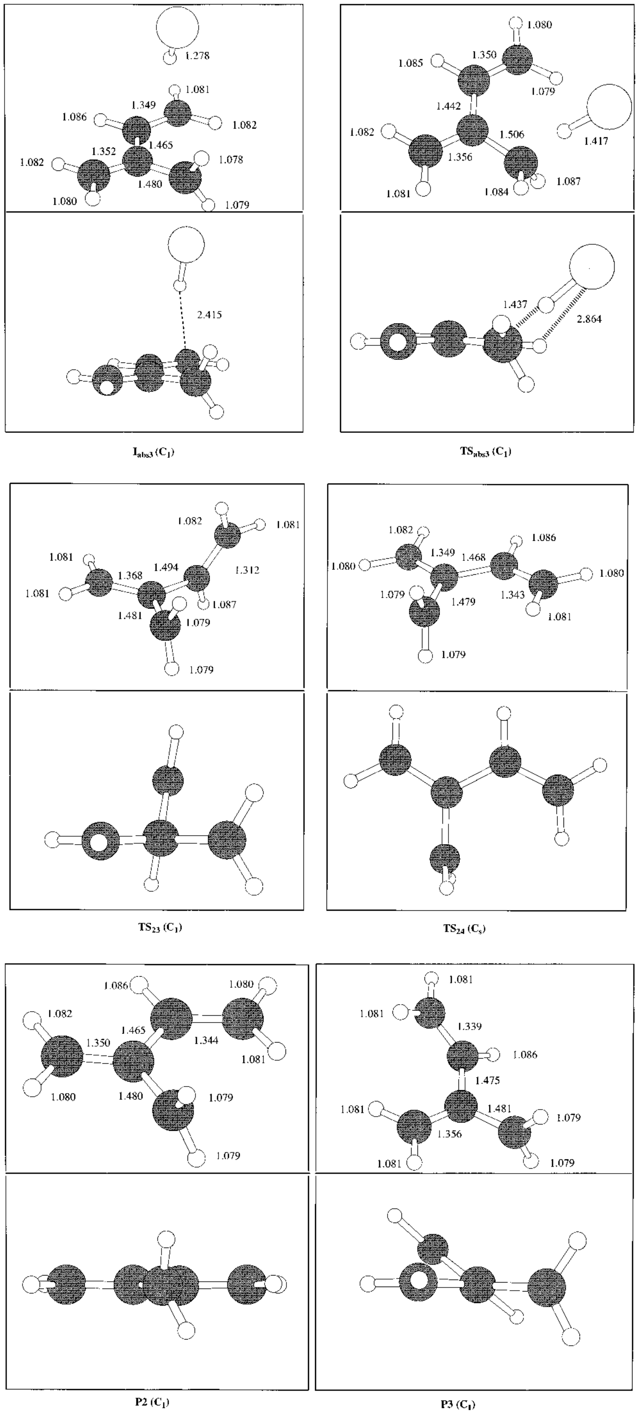
TS_{AB} (C_1) TS_{abs2} (C_1)

Figure 2. Reactive ($ISOP_B$), intermediate (I_{abs2}), transition structures (TS_{AB}, TS_{abs2}), and product (P1) for the abstraction reaction (channel B; see Chart 3) between chlorine atom and isoprene.

In the first channel (see channel A in Chart 3), the chlorine atom approaches isoprene, forming an angle of about 75° with the quasi-planar carbon skeleton of the isoprene moiety (see TS_{abs1} in Figure 1). As the chlorine atom approaches, the allylic hydrogen below the plane of the paper (see channel A in Chart 2) moves up in such a way that the $H_2C{=}C{-}CH_2^{\bullet}$ moiety becomes planar, with the remaining $-CH{=}CH_2$ perpendicular to it (see TS_{abs1} and P1 in Figure 1). After overcoming a moderate barrier ($\Delta E^{\ddagger} = 4.4-5.2$ kcal/mol; $\Delta G^{\ddagger} = 8.5-10.0$ kcal/mol) the intermediate I_{abs1} is obtained.

Figure 1 shows that I_{abs1} is a weakly bound complex that can be formally viewed as a long-distance interaction (2.357 Å) between HCl and $C_5H_7^{\bullet}$ moieties. As shown by the ΔH values in Table 1, formation of I_{abs1} is an exothermic process. Our best estimate of ΔG using the QCISD(T)/aug-cc-pVDZ electronic energy suggests that, despite the remarkable entropy contribution $-T\Delta S$ (+4.8 kcal/mol), the formation of I_{abs1} is a spontaneous process ($\Delta G = -2.1$ kcal/mol). I_{abs1} evolves toward P1 + HCl. This latter process is endothermic but, of course, entropy favored. The overall process of formation of P1 + HCl from the reaction between chlorine atom and isoprene is thus exergonic ($\Delta G = -5.4$ kcal/mol). The presence of I_{abs1} suggests that channel A is formally an addition (I_{abs1})−elimination (P1 + HCl) pathway (we can denote it association−elimination) represented by eq 3, with an expected pressure dependence in agreement with the experimental evidence.[10]

In channel B (see Chart 3), isoprene ($ISOP_A$) previously transforms into a different conformer ($ISOP_B$) with a nonplanar



I_{abs3} (C_1) TS_{abs3} (C_1)

TS_{23} (C_1) TS_{24} (C_s)

P2 (C_1) P3 (C_1)

Figure 3. Intermediate (I_{abs3}), transition structures (TS_{abs3}, TS_{23}, TS_{24}), and products (P2, P3) for the abstraction reaction (channel C; see Chart 3) between chlorine atom and isoprene.

carbon skeleton (see $ISOP_B$ in Figure 2). Such a conformational transformation involves a rather small energy barrier (TS_{AB}; $\Delta E^{\ddagger} = 5.4-5.5$ kcal/mol; $\Delta G^{\ddagger} = 5.1-5.3$ kcal/mol). Then, the chlorine atom approaches isoprene in a way similar to that in channel A (compare TS_{abs1} and TS_{abs2} in Figures 1 and 2), surmounting a moderate barrier ($\Delta E^{\ddagger} = 3.4-5.1$ kcal/mol; $\Delta G^{\ddagger} = 8.9-10.6$ kcal/mol) and leading to the intermediate I_{abs2}. As in the case of I_{abs1}, I_{abs2} can be formally considered as a molecular association with HCl and $C_5H_7^{\bullet}$ moieties interacting at a long distance (2.366 Å). As a matter of fact, Figures 1 and 2 show that I_{abs1} and I_{abs2} represent two conformational varieties of the same molecular complex.

Formation of I_{abs2} is a spontaneous process ($\Delta G = -2.2$ kcal/mol), and the subsequent, entropy favored, abstraction of HCl finally leads to P1, the same product as in channel A.

In channel C (see Chart 3), the chlorine atom attacks the methyl group of isoprene ($ISOP_A$), forming a smaller angle (about 40°) with the quasi-planar carbon skeleton of isoprene than in channels A and B (see TS_{abs3} in Figure 3 and compare with TS_{abs1} and TS_{abs2} in Figures 1 and 2). This process involves a moderate barrier ($\Delta E^{\ddagger} = 4.5-10.5$ kcal/mol; $\Delta G^{\ddagger} = 8.0-12.8$ kcal/mol) and leads to the intermediate I_{abs3} that is a weakly bound complex in which HCl and $C_5H_7^{\bullet}$ moieties are 2.415 Å apart. An important difference with I_{abs1} and I_{abs2} is that the carbon skeleton in $C_5H_7^{\bullet}$ is for I_{abs3} quasi-planar (see Figure 3). As a consequence, I_{abs3} becomes more endergonic than I_{abs1} and I_{abs2} ($\Delta G = +2.3$ kcal/mol). Further evolution to obtain a planar conformer of $C_5H_7^{\bullet}$ (P2) and HCl is enthalpy disfavored but entropy favored ($\Delta G = -0.7$ kcal/mol). P2 transforms into another conformer (P3; see Figure 3) passing through TS_{23} ($\Delta E^{\ddagger} = 7.1-7.4$ kcal/mol; $\Delta G^{\ddagger} = 11.0-11.2$ kcal/mol). Table 1 shows that this latter step is enthalpy disfavored and the overall process of formation of P3 is endergonic ($\Delta G = +2.9$ kcal/mol).

In channel D (see Chart 3), the chlorine atom abstracts that allylic hydrogen lying quasi-planar with the carbon skeleton of the isoprene moiety (see TS_{abs4} in Figure 4), overcoming a moderate barrier ($\Delta E^{\ddagger} = 5.5-10.7$ kcal/mol; $\Delta G^{\ddagger} = 7.6-14.0$ kcal/mol) and leading to the weakly bound complex I_{abs4} with a distance between HCl and $C_5H_7^{\bullet}$ moieties of 2.272 Å. This intermediate is more endergonic than any other of the intermediates found in channels A−C ($\Delta G = +3.9$ kcal/mol). Further evolution gives a $C_5H_7^{\bullet}$ conformer (P4) quite similar to P2 (compare P2 and P4 in Figures 2 and 4) plus HCl. These two latter conformers convert into each other through a transition structure (TS_{24}) involving a practically negligible barrier.

Taking into account the above energy results, it can be concluded that channels A and B represent favorable pathways for the abstraction of an allylic hydrogen in the reaction between chlorine atom and isoprene. Indeed, the barriers involved (TS_{abs1}, TS_{AB}, TS_{abs2}) are moderate ($\Delta E^{\ddagger} < 6$ kcal/mol; $\Delta G^{\ddagger} < 11$ kcal/mol) and the formation of the final product (P1 + HCl) is an exergonic process ($\Delta G = -5.4$ kcal/mol). Therefore, both kinetic and thermodynamic considerations support the viability of such channels. The two pathways involve the formation of intermediates I_{abs1}, I_{abs2}, which can be considered as the products of an exergonic addition reaction between chlorine atom and isoprene ($\Delta G \approx -2$ kcal/mol). Further evolution of these intermediates leads to the elimination of HCl and formation of $C_5H_7^{\bullet}$ (P1). Consequently, these channels represent association−elimination pathways which may be responsible for the pressure dependence experimentally observed. The two remaining channels involve similar barriers (TS_{abs3}, TS_{abs4}, TS_{23}; see Table 1) but less stable intermediates (I_{abs3}, I_{abs4}; see Table 1), although the formation of the $C_5H_7^{\bullet}$ radical P4 in channel D, after eliminating HCl, is exergonic ($\Delta G = -0.7$ kcal/mol). In any case, channels C and D represent less favorable routes than channels A and B.

It should be stressed that, as pointed out by Molina and coworkers,[26] the presence of weakly bound complexes such as the intermediates described in the present work are expected to play a more and more relevant role as the temperature lowers and the entropy contributions become smaller (upper troposphere regions).

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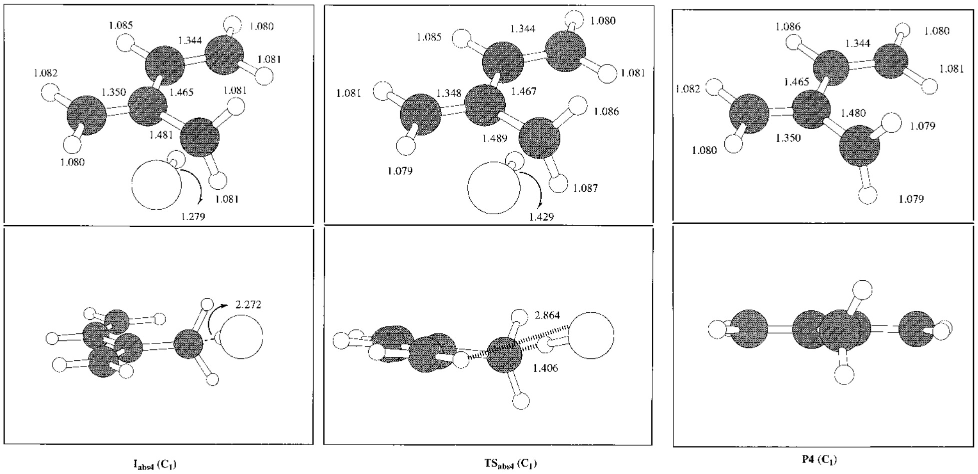


I_{abs4} (C_1) TS_{abs4} (C_1) P4 (C_1)

Figure 4. Intermediate (I_{abs4}), transition structure (TS_{abs4}), and product (P4) for the abstraction reaction (channel D; see Chart 3) between chlorine atom and isoprene.

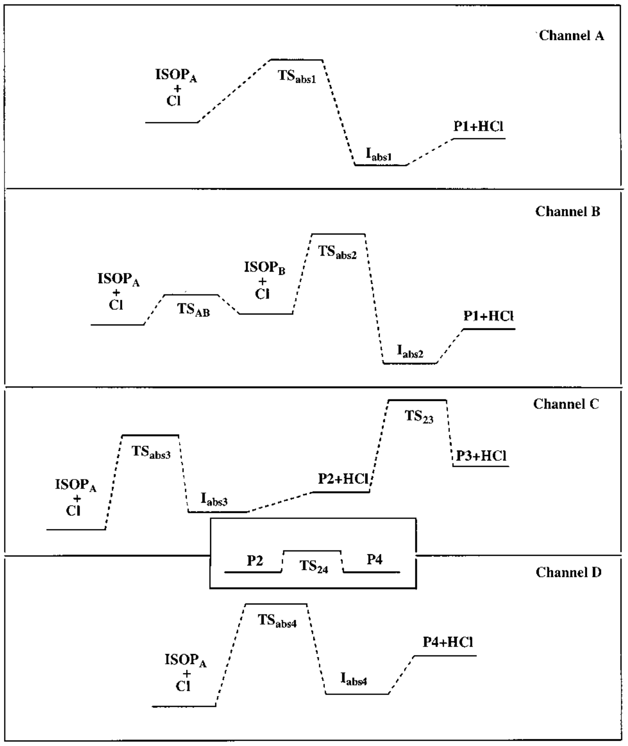
Table 1. PMP2/6-31G(d,p) (ΔE_{PMP2}) and QCISD(T)/aug-cc-pVDZ//MP2/6-31G(d,p) ($\Delta E_{Qcisd(T)}$) Relative Electronic Energies (kcal/mol) for the Structures Located on the Potential Energy Surface of the Different Channels for the Abstraction Reaction between Chlorine Atom and Isoprene[a]

system	channel[b]	ΔE_{PMP2}	$\Delta E_{QCISD(T)}$	ΔH^c	ΔS	ΔG^c
TS_{abs1}	A	5.2	4.4	3.1 (1.7)	−25.2	10.0 (8.5)
I_{abs1}	A	−4.8	−6.2	−4.9 (−6.9)	−16.0	−0.8 (−2.1)
P1 + HCl	A, B	−1.0	−1.3	−2.1 (−3.0)	7.9	−5.1 (−5.4)
TS_{AB}	B	5.4	5.5	4.6 (4.7)	−2.0	5.1 (5.3)
$ISOP_B$	B	2.3	2.9	2.2 (2.8)	0.8	2.0 (2.6)
TS_{abs2}	B	7.4	6.3	6.0 (4.3)	−24.0	12.6 (11.5)
I_{abs2}	B	−4.6	−5.9	−4.7 (−6.5)	−14.6	−1.0 (−2.2)
TS_{abs3}	C	10.5	4.5	7.0 (0.3)	−25.7	12.8 (8.0)
I_{abs3}	C	5.5	1.1	3.1 (−2.1)	−15.0	7.0 (2.3)
P2 + HCl	C	10.0	6.0	6.3 (1.8)	8.5	3.2 (−0.7)
TS_{23} + HCl	C	17.1	13.4	16.4 (12.1)	5.4	14.2 (10.5)
P3 + HCl	C	12.6	9.4	9.2 (5.5)	8.7	6.0 (2.9)
TS_{abs4}	D	10.7	5.5	6.2 (0.5)	−24.1	14.0 (7.6)
I_{abs4}	D	7.1	2.3	4.7 (−0.7)	−15.3	8.6 (3.9)
P4 + HCl	D	10.0	6.0	6.3 (1.8)	8.5	3.2 (−0.7)
TS_{24} + HCl	C, D	10.3	6.4	5.9 (1.5)	6.9	3.3 (−0.6)

[a] All the energies are referred to isoprene ($ISOP_A$) + Cl except TS_{AB} and $ISOP_B$ which are referred to $ISOP_A$. Relative enthalpies (ΔH^c, kcal/mol), entropies (ΔS, cal/(K·mol)), and Gibbs free energies (ΔG^c, kcal/mol) are also given (298.15 K and 1 atm were assumed). [a] See Scheme 3. [b] Using ΔE_{PMP2} and $\Delta E_{QCISD(T)/aug-cc-pVDZ}$ (parentheses) electronic energies and MP2/6-31G(d,p) frequencies.

Before ending, we would like to make a short comment on the reliability of the energetics collected in Table 1. In a previous work[13] we have shown that the QCISD(T)/aug-cc-pVDZ//MP2/6-31G(d,p) level provides estimates for the activation barriers and exo-/endothermicities which were consistent with the experimental data available. As mentioned in the Introduction section, Bedjanian and co-workers[12] estimated the activation barrier for the abstraction reaction Cl + isoprene to be 0.22 ± 0.35 kcal/mol. Our best theoretical estimate of this experimental parameter ($E_a = \Delta H^{\ddagger} + 2RT$), using the QCISD(T)/aug-cc-pVDZ//MP2/6-31G(d,p) electronic energy in Table 1 for the abstraction barrier in channel A (TS_{abs1}), is 2.9 kcal/mol. Bearing in mind the limitations inherent in our calculations, especially the use of harmonic frequencies for the highly anharmonic intermolecular vibrations in TS_{abs1},[13] as well as the experimental uncertainties,[12] the agreement is acceptable. This rather small activation energy contrasts with the clearly higher barrier found using a similar level of theory for the hydrogen abstraction in the Cl + ethylene reaction, 9.4 kcal/mol[13] (experimental estimate: 3−7 kcal/mol).[27−30]

Chart 3. Energy Profiles for the Different Routes of the Cl + Isoprene Abstraction Reaction



Conclusion

An exhaustive exploration of the different possible channels for the abstraction of an allylic hydrogen in the chlorine atom reaction with isoprene has been carried out at the MP2/6-31G(d,p) level. Further QCISD(T)/aug-cc-pVDZ//MP2/6-31G(d,p) calculations were performed in order to improve the energy predictions.

Four different pathways were characterized. In all of them abstraction proceeds through an association−elimination mech-

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anism. In a first step, the chlorine atom approaches isoprene forming a weakly bound intermediate after overcoming a moderate barrier. In particular, the activation energy theoretically estimated for the most favorable channel is 2.9 kcal/mol. This barrier, which is consistent with the experimentally estimated value of 0.22 ± 0.35 kcal/mol, is substantially smaller than that for the hydrogen abstraction in the Cl + ethylene reaction [QCISD(T)//MP2 estimate, 9.4 kcal/mol; experimental estimate, 3−7 kcal/mol]. For two of the pathways, this first step, that can be formally considered to be an addition, is exergonic ($\Delta G < 0$). Further entropy favored evolution leads to a $C_5H_7^{\bullet}$ radical, after elimination of HCl. Therefore, the proposed association−elimination mechanism, which is both kinetically and thermodynamically favored, allows for the rationalization of the pressure dependence experimentally observed for the reaction of chlorine atom with isoprene.

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Supporting Information Available: Tables of absolute energies, absolute entropies, enthalpies, and Gibbs free energies, and Cartesian coordinates (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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