J. Phys. Chem. A **2002,** *106,* 6415−6420

Theoretical Study of Chloroalkenylperoxy Radicals

Wenfang Lei,[†] Renyi Zhang,*[,†] Luisa T. Molina,[‡] and Mario J. Molina[‡]

Department of Atmospheric Sciences, Texas A&M University, College Station, Texas 77843, Department of Earth, Atmospheric, and Planetary Sciences and Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received: March 20, 2002; In Final Form: April 30, 2002

DFT and ab initio molecular orbital calculations have been performed to investigate the structures and energetics of the Cl−O_2−isoprene peroxy radicals arising from the Cl-initiated oxidation of isoprene. Geometry optimizations of the chloroalkenylperoxy radicals were performed using density function theory (B3LYP), and the energies were computed with the single-point calculation using different levels of theory for electron correlation and basis set effects. At the CCSD(T)/6-31G(d) level of theory corrected with zero-point energy (ZPE), the chloroalkenylperoxy radicals are about 39 to 43 kcal mol^{-1} more stable than the separated reactants (i.e., O_2 + Cl + isoprene). We find no evidence for an energetic barrier to O_2 addition and have calculated rate constants for the O_2 addition step using canonical variational transition state theory (CVTST) based on Morse potentials to describe the reaction coordinate. The results provide the isomeric branching between the six Cl−O_2−isoprene peroxy radicals, indicating that the two β-chloroalkenylperoxy radicals with initial Cl addition at C1 and C4 positions and subsequent O_2 addition at C2 and C3 positions,respectively, play an important role in determining the reaction pathways and final product distributions of the Cl−isoprene reaction system.

Introduction

Isoprene (2-methyl-1,3-butadiene, $CH_2{=}C(CH_3)CH{=}CH_2$) is one of the most abundant hydrocarbons emitted by the terrestrial biosphere,[1] and is sufficiently reactive to influence oxidation levels over large portions of the continental troposphere.[2] The isoprene source strength exceeds that of the nonmethane hydrocarbons of anthropogenic origin.[3] In addition, there are indications that isoprene is produced by human activities,[4] and also by phytoplankton in seawater.[5,6] On the other hand, reactive chlorine is present in the atmosphere not only as a consequence of direct emissions, but also is produced by multiphase chemical processes, i.e., from oceanic and terrestrial biogenic emissions, sea-salt production and de-chlorination, biomass burning, and anthropogenic emissions.[7] A recent study has indicated the importance of anthropogenic sources of chlorine molecules and the related ozone formation in the urban atmosphere:[8] the presence of chlorine radicals significantly enhances the ozone production rate. Also, chlorinated hydrocarbons such as trichloroethene (C_2HCl_3), tetrachloroethene (C_2Cl_4), and dichloromethane (CH_2Cl_2), are used in a wide variety of industrial, commercial, and consumer applications; emissions of trichloromethane ($CHCl_3$) are also important in urban areas, with sources from water treatment and pulp, paper, and other facility product manufacturing.[9,10] Once released into the atmosphere, the organic chlorinated molecules are broken down by direct photolysis or by hydroxyl radical attack, either case leading to the release of atomic chlorine.[11] Chlorine production from ion-enhanced heterogeneous reactions on aqueous sea salt aerosols has also been recently realized.[12] Hence, the oxidation of isoprene initiated by reaction with chlorine atoms may play an important role in the urban and regional atmosphere as well as in the marine planetary boundary layer.[8,12−14] In addition, it is proposed that the Cl−isoprene reactions lead to some unique chlorine-containing compounds which can be used as a tracer for chlorine chemistry in the atmosphere.[15]

The initial reaction between isoprene and Cl proceeds mainly by Cl-addition, yielding a Cl−isoprene adduct radical (reaction 1a):

$$\mathrm{Cl} + C_5H_8 \rightarrow C_5H_8Cl \qquad (1a)$$

$$\rightarrow C_5H_7 + \mathrm{HCl} \qquad (1b)$$

Alternatively, isoprene also undergoes methyl-hydrogen abstraction to form HCl (reaction 1b). Under atmospheric conditions, the Cl−isoprene adduct reacts primarily with oxygen molecules to form the chloroalkenylperoxy radicals. Subsequently, the reaction between the chloroalkenylperoxy radical with NO leads to the formation of chloroalkenylalkoxy radicals. The dominant tropospheric reaction pathway of the chloroalkenylalkoxy radicals is decomposition or reaction with oxygen molecule, leading to the formation of various oxygenated organic compounds. The mechanistic complexity arises from the isomeric branching which occurs in these initial two steps. Figure 1 shows a mechanistic diagram for the formation of the Cl−isoprene adduct and the chloroalkenylperoxy radicals.

Recently, several laboratory studies have investigated the kinetics and mechanism of the oxidation reactions of isoprene initiated by Cl atoms. The rate constants between isoprene and Cl have been studied using a relative rate method[16−18] or absolute rate measurements.[19−21] The branching ratio of the initial reaction between Cl and isoprene has been inferred from the HCl formation yield, with a value between 0.13 and 0.18.[16,20,21] Some of those studies have identified the final products of the isoprene reactions, including CO, CO_2, formyl

---

* Author to whom correspondence should be addressed.

[†] Texas A&M University.

[‡] Massachusetts Institute of Technology.

10.1021/jp025799a CCC: $22.00

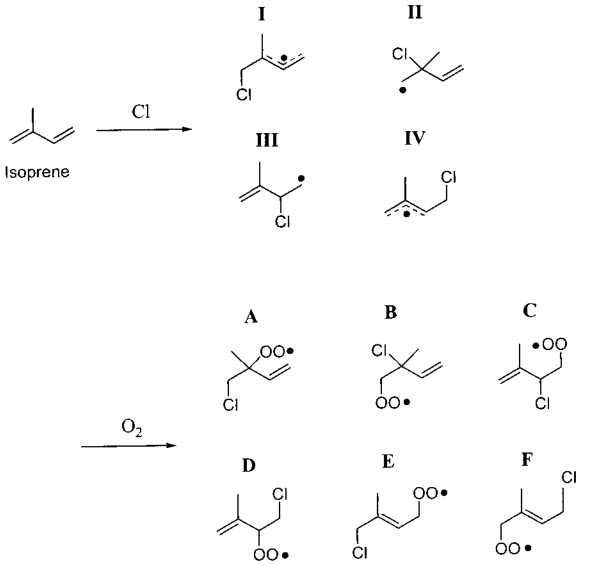

Figure 1. Mechanistic diagram for the reactions of Cl with isoprene and the Cl−isoprene adduct with O_2.

chloride (HCOCl), formic acid, methyl-glyoxal, hydrogen chloride, and 1-chloro-3-methyl-3-buten-2-one (CMBO).[15,16,17,22] In particular, CMBO has been suggested as a possible tracer for chlorine chemistry in the atmosphere.[15,22] At present, however, direct experimental data concerning the intermediate processes of the oxidation reactions of isoprene are very limited, largely due to the lack of efficient detection schemes for these species. The application of the chlorine marker method using CMBO relies on precise information of the rate constants and isomeric branching ratios of the intermediate steps.

In our previous work, we have investigated the equilibrium structures, energies, and formation rates of the four energetically favored Cl−isoprene isomeric radicals using DFT and ab initio calculations and the canonical variational transition state theory (CVTST).[23,24] In this work, we report a study of the peroxy radicals arising from the Cl-initiated oxidation reaction of isoprene. The equilibrium structures and energetics of the Cl−O_2−isoprene peroxy radicals were investigated. We have also performed calculations using the CVTST theory to determine the rate constants associated with O_2 addition to the Cl−isoprene peroxy radicals on the basis of the ab initio binding energies. The calculated rate constants provide the relative isomeric branching between the six peroxy radicals and, when combined with our previous results for the formation of the isoprene−Cl adduct, the overall branching. Implications of the present results for the atmospheric degradation mechanism of isoprene are discussed.

Theoretical Approach

Ab initio molecular orbital calculations were performed on an SGI Origin 2000 supercomputer using the Gaussian 98 software package.[25] We have recently evaluated the level of ab initio theory that applies to complex organic radical species, on the basis of computational efficiency and accuracy.[26] Our results indicated that electron correlation did not affect the geometries of organic radicals appreciably. Better convergence behavior and considerably higher computational efficiency were achieved using the nonlocal gradient density functional theory (NLDFT) as the method of geometry and frequency calculations. Also, it was noticed that beyond the split valence polarized level of description there was little improvement in the molecular geometry when the size of the basis set was further increased (i.e., triple split, diffuse functions, expansion of the polarization portion of the basis set, etc.). In addition, a basis set correction method has been developed to determine the energetics of the organic radicals. We have adopted the following methods in the present calculations: the molecular calculations were executed with geometry optimization using Becke's three parameter hybrid method employing the LYP correction function (B3LYP) in conjunction with the split valence polarized basis set 6-31G(d,P). Single-point energy calculations were carried out using the second-order Møller−Plesset perturbation theory (MP2) and coupled-cluster theory with single and double excitations including perturbative corrections for the triple excitations (CCSD(T)) and various basis set sizes. Harmonic vibrational frequency calculations were made using B3LYP/6-31G(d,p).

Results and Discussion

Geometries and Energies of Cl−O_2−Isoprene Peroxy Radicals. For the C−isoprene adduct, the addition of O_2 occurs only at the β-carbons to the Cl position for radicals II and III, but takes places at two centers (β or δ to the Cl position) for radicals I and IV. Hence O_2 addition to the Cl−isoprene adduct results in the formation of four β-chloroalkenylperoxy radicals (A to D) and two δ-chloroalkenylperoxy (E and F) radicals (Figure 1). For each structural isomer of the peroxy radicals, we performed calculations to explore possible (typically five to six) conformers. A total of about thirty conformations were considered, but we report only the lowest energy conformer for each structural isomer. The lowest energy conformers of the six structural isomers of the Cl−O_2−isoprene peroxy radicals are depicted in Figure 2, calculated at the B3LYP/6-31G(d,p) level of theory. The geometries were confirmed as minima on the potential energy surfaces by frequency calculations.

It is interesting to compare the geometries of the Cl−O_2−isoprene peroxy radicals shown in Figure 2 to those of the Cl−isoprene adduct radicals calculated previously.[23] Addition of O_2 to the four Cl−isoprene adduct isomers causes a change in the structures of the Cl−isoprene adduct radicals. For the six peroxy radicals addition of O_2 to the Cl−isoprene adduct results in a shortening of the C−Cl bond length. The C−C bond lengths adjunct to the site of O_2 addition are increased, due to an increased σ character of the C−C bond as electron density in the π bond is transferred to the newly formed C−O(O) bond. For example, addition of O_2 to carbon 2 for the Cl−isoprene adduct **A** increases the C−C carbon bond lengths by 0.06 and 0.11 Å between carbons 1 and 2 and between 2 and 3, respectively. The C−C carbon length associated with the methyl substitute is also increased by about 0.03 Å. On the other hand, the bond length between carbons 3 and 4 is reduced by about 0.05 Å. Similar changes in the C−C bond characteristics occur for all radicals upon O_2 addition.

Single-point energies of the chloroalkenylperoxy radicals were determined using MP2 and CCSD(T) at the B3LYP optimized geometries. The results of the computed energies of the peroxy radicals are listed in Table 1. Table 1 reveals that both electron correlation and basis set effects have an impact on the calculated energetics. For the six isomers of the Cl−O_2−isoprene peroxy radical the relative energies computed at the MP2 level of theory are generally lower when using a larger basis set size (i.e., 6-311++G(d,p)), with the exception for radical **F**. For isomers **B**, **C**, and **D**, the relative energies obtained using the basis sets of 6-31G(d) and 6-31+++G(d,p) differ by 1.0, 0.8, and 1.1 kcal mol^{-1}, respectively, and for isomers **E** and **F** the relative energies calculated using the two basis sets differ by 0.4 and

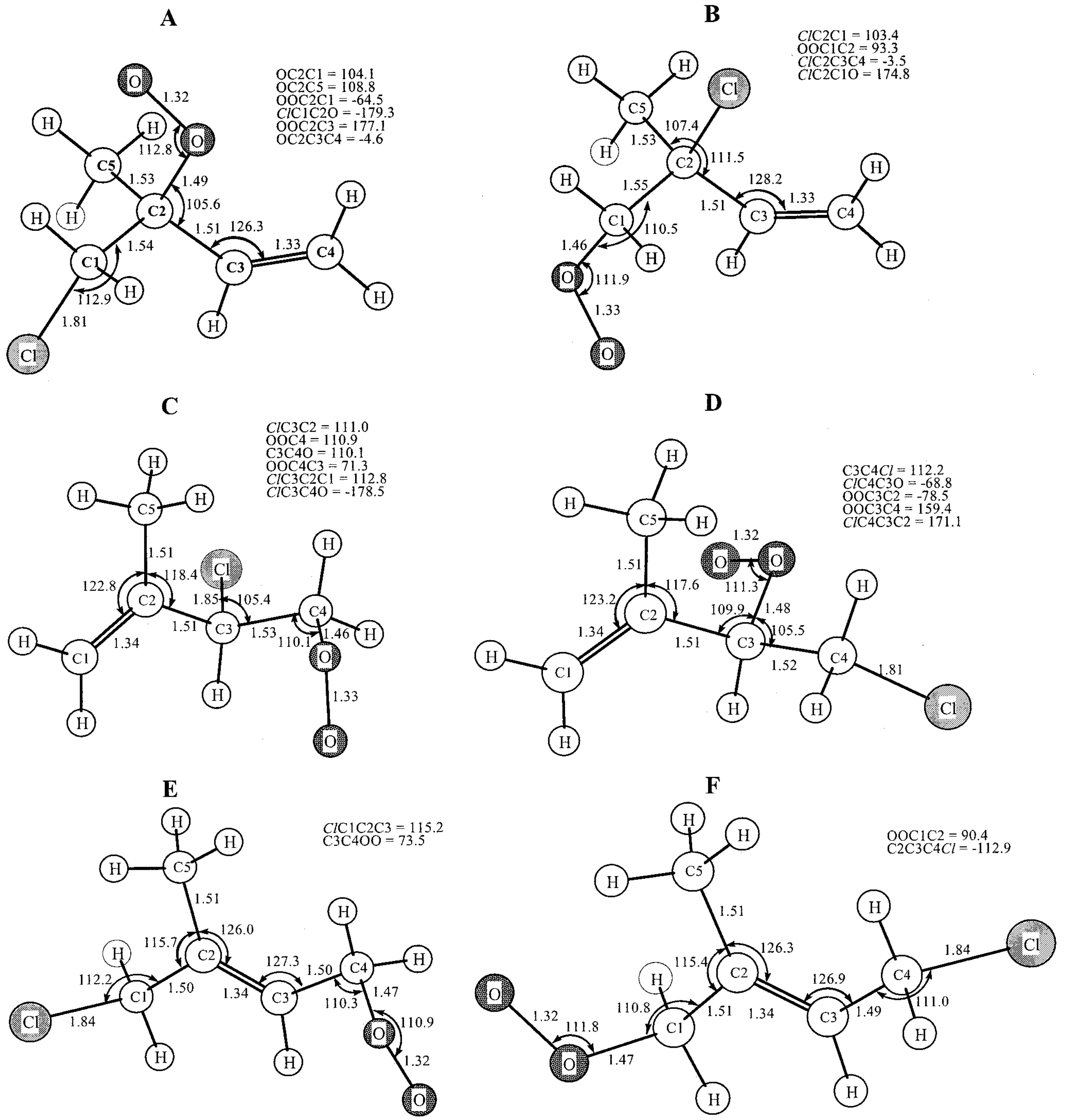

Figure 2. Optimized geometries of the six isomers of the chloroalkenylperoxy radicals calculated at the B3LYP/6-31G(d,p) level of theory (bond lengths in angstroms and angles in degrees).

TABLE 1: Calculated Total Energy (in hartrees), Relative Energies (RE) (kcal mol^{-1}), and Basis Set Correction Factors (CF) (kcal mol^{-1}) of the Cl−O$_2$−Isoprene Peroxy Radicals

isomer	energy[a]	RE[a]	energy[b]	RE[b]	energy[c]	RE[c]	CF[d]
A	−804.159209	0.0	−804.410953	0.0	−804.276199	0.0	0.0
B	−804.155350	2.4	−804.408675	1.4	−804.273000	2.0	−1.0
C	−804.158087	0.7	−804.411129	−0.1	−804.274768	0.9	−0.8
D	−804.155698	2.2	−804.409257	1.1	−804.273846	1.5	−1.1
E	−804.154421	3.0	−804.406762	2.6	−804.272181	2.5	−0.4
F	−804.155849	2.1	−804.406727	2.7	−804.272651	2.2	0.5

[a] Calculated at the MP2/6-31G(d)//B3LYP/6-31G(d,p) level of theory. [b] Calculated at the MP2/6-311++G(d,p)//B3LYP/6-31G(d,p) level of theory. [c] Calculated at the CCSD(T)/6-31G(d)//B3LYP/6-31G(d,p) level of theory. [d] Estimated from the energy difference between MP2/6-311++G(d,p) and MP2/6-31G(d).

0.6 kcal mol^{-1}, respectively. Using the basis set of 6-31G(d), the highly correlated method (i.e., CCSD(T)) produces noticeably different relative energies, with the largest relative energy difference of about 0.7 kcal mol^{-1}. Table 1 indicates that the

TABLE 2: Calculated Relative Energies[a] (RE) (kcal mol^{-1}) and Standard Heats of Formation (kcal mol^{-1}) of the Cl−O$_2$−Isoprene Peroxy Radicals

isomer	RE[b]	RE[c]	RE[d]	RE[e]	ΔH_f^0 [f]	ΔH_f^0 [g]
A	−36.7	−38.2	−40.8	−42.3	−11.0	−14.5
B	−34.2	−36.7	−38.7	−41.2	−9.5	−12.3
C	−35.6	−37.9	−39.5	−41.8	−10.7	−12.5
D	−34.3	−37.0	−39.1	−41.8	−9.7	−14.2
E	−33.2	−35.1	−37.8	−39.7	−7.8	−11.8
F	−34.0	−35.0	−38.0	−39.0	−7.7	−11.4

[a] Energy difference between the peroxy radicals and the reactants (i.e., Cl + O$_2$ + isoprene). Zero-point energy (ZPE) corrections are included. [b] Calculated at the MP2/6-31G(d)//B3LYP/6-31G(d,p) level of theory. [c] Calculated at the MP2/6-311++G(d,p)//B3LYP/6-31G(d,p) level of theory. [d] Calculated at the CCSD(T)/6-31G(d)//B3LYP/6-31G(d,p) level of theory. [e] Calculated at the CCSD(T)/6-31G(d) + CF//B3LYP/6-31G(d,p) level of theory. [f] Calculated at the MP2/6-311++G(d,p)//B3LYP/6-31G(d,p) level of theory. [g] Calculated at the CCSD(T)/6-31G(d) + CF//B3LYP/6-31G(d,p) level of theory.

most energetically favorable peroxy radicals are those with Cl addition to C1 and C3 positions and subsequent O$_2$ addition to C2 and C4 positions. The relative stability of the peroxy radicals is almost independent of basis set and electron correlation effects: isomers **A** and **C** have the lowest energies and isomers **E** and **F** have the highest energies (by about 1 to 3 kcal mol^{-1} higher than radicals **A** and **B**).

The results from Table 1 suggest that both electron correlation and basis set affect energy calculations of the peroxy radicals of the Cl−isoprene reaction system. Similar observations have been reported recently by Trular and co-workers for other molecule−radical reactions.[27] For the Cl−O$_2$−isoprene peroxy radicals, single-point energy calculations at the CCSD(T) level of theory using a larger basis set (such as 6-311++G(d,p)) are computationally very demanding. To account for basis set and electron correlation effects, we have adopted an approach that corrects for basis set effects for the chloroalkenylperoxy radicals. This approach has been developed and validated by determining the energetics of the OH−isoprene and Cl−isoprene adduct isomers.[23,26] The procedure involved determination of a correction factor associated with basis set effects evaluated at the MP2 level and subsequent correction to the energy calculated at a higher level of electron correlation with a moderate size basis set. The basis set correction factor (CF) was determined from the calculated relative energy difference between the MP2/6-31G(d) and MP2/6-311++G(d,p) levels of theory. The values of calculated energies at the CCSD(T)/6-31G(d) level were then corrected by the correction factors, effective to the CCSD(T)/6-311++G(d,p) level of theory. As listed in Table 1, the correction factors are in the range of 0−1.1 kcal mol^{-1} for the chloroalkenylperoxy radicals, indicating that basis set effect is relatively minimal. The performance of the basis set correction method has been evaluated for several reaction systems involving isoprene, and the calculated energies agreed with those obtained using other higher level theories, including CCSD(T)/6-311G(d,p), QCISD(T)/6-311G(d,P), G(1), and G(2).[23,26,28]

Table 2 summarizes the relative energies of the Cl−O$_2$−isoprene peroxy radicals obtained using the various methods. The relative energies have been corrected for zero-point energy (ZPE). At the CCSD(T)/6-31G(d) + CF level of theory, the peroxy radicals are 39 to 43 kcal mol^{-1} more stable than the reactants (i.e., Cl + O$_2$ + isoprene). The difference in relative energies between MP2/6-311++(G(d,p) and CCSD(T)/6-31G(d) + CF ranges from 3.9 to 4.8 kcal mol^{-1}. Figure 3 shows the energy diagram of the Cl−O$_2$−isoprene reaction system. The values for the energies of the Cl−isoprene adduct isomers are taken from ref 23. The reaction energies of the Cl−isoprene adducts with O$_2$ range from 14 to 31 kcal mol^{-1}, which are close to the binding energies of an analogous system involving the OH−O$_2$−isoprene peroxy radicals.[29] It is also seen from Figure 3 that the two β-chloroalkenylperoxy radicals **A** and **D** are more stable than their corresponding δ-chloroalkenylperoxy radicals **E** and **F**, by 2.6−2.9 kcal mol^{-1}, respectively.

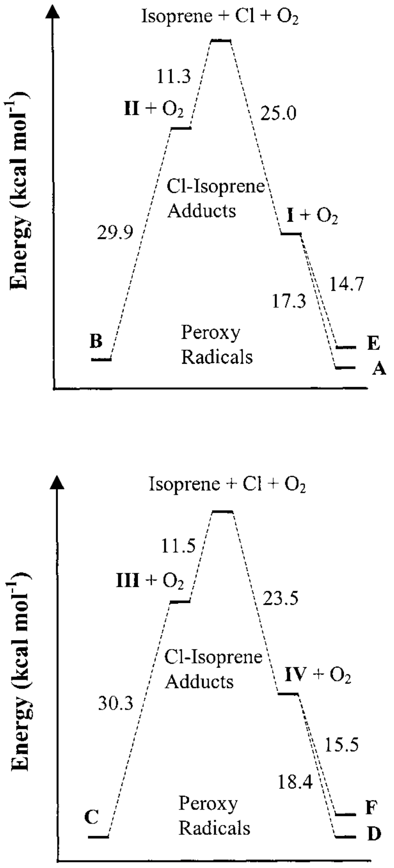

Figure 3. Schematic energy diagram of the Cl−O$_2$−isoprene reactions. The energies of the Cl−O$_2$−isoprene peroxy radicals were obtained at the CCSD(T)/6-31G(d) + CF level of theory.

We have calculated the standard heats of formation for the lowest energy isomers, estimated from the calculated total energy (*E*), the experimentally known heats of formation for the reactants, and thermal energy (TE) correction obtained from the frequency calculations. Thermal energy (TE) corrections were made through frequency calculations at the B3LYP/6-31G**//B3LYP/6-31G** level. The enthalpy of reaction (ΔH) for O$_2$ addition to the Cl−isoprene adduct at 298 K is expressed by

$$\Delta H = [E(C_5H_8ClO_2) - E(C_5H_8Cl) - E(O_2)] + [TE(C_5H_8ClO_2) - TE(C_5H_8Cl) - TE(O_2)] \quad (2)$$

Alternatively, the enthalpy of reaction for the Cl−isoprene adduct with O$_2$ is also given as

$$\Delta H = \Delta H_f^o(C_5H_8ClO_2) - \Delta H_f^o(C_5H_8Cl) - \Delta H_f o(O_2) \quad (3)$$

where the heats of formation for the Cl−isoprene adduct, $\Delta H_f^o(C_5H_8Cl)$, are taken from ref 26. The heats of formation of the chloroalkenylperoxy radicals were then calculated by equating the above two equations, with the values of −14.5, −12.3, −12.5, −14.2, −11.8, and −11.4 kcal mol^{-1} for radicals

A to **F** at the CCSD(T)/6-31G(d) + CF level of theory, respectively (Table 2).

Rate Constant Calculations. The high-pressure rate constants for the dissociation of the chloroalkenylperoxy radicals were evaluated using canonical variational transition state theory (CVTST). The dissociation rates were converted to the association rates via the equilibrium constant,[29,30]

$$\frac{k_{\mathrm{rec}}}{k_{\mathrm{uni}}} = K_{\mathrm{eq}} = \frac{Q_{\mathrm{AB}}}{Q_{\mathrm{A}}Q_{\mathrm{B}}}\exp\left(\frac{\Delta E}{kT}\right) \tag{4}$$

where Q_{AB} is the partition function of the peroxy radical, Q_{A} and Q_{B} are the partition functions of the individual products, and ΔE is zero-point corrected reaction energy. The bimolecular rate is given by[29,30]

$$k_{\mathrm{uni}} = \frac{kT}{h}\frac{Q_{\mathrm{AB}}{}^{\ddagger}}{Q_{\mathrm{AB}}}\exp\left(-\frac{\Delta E'}{kT}\right), \tag{5}$$

where $Q_{\mathrm{AB}}{}^{\ddagger}$ is the partition function of the transition state with the vibrational frequency corresponding to the reaction coordinate removed, Q_{AB} is the partition function of the adduct, and $\Delta E'$ is the zero-point corrected transition state energy relative to the separated reactants.

The partition functions required for eqs 4 and 5 were calculated by treating the rotational and translational motion classically and treating vibrational modes quantum mechanically. Unscaled vibrational frequencies and moments of inertia for the Cl−isoprene adducts were taken from our recent ab initio calculations at the B3LYP/6-31G(d,p) level.[28,29] Frequencies and moments of inertia for the peroxy radicals were obtained at the B3LYP/6-31G(d,p) level as discussed previously. The reaction energies were taken to be zero-point corrected energies calculated at the CCSD(T)/6-31G(d) + *CF*//B3LYP/6-31G(d,p) level. The conserved modes of the transition state were assumed to resemble the product modes.[29,30] The dependence of the transitional mode frequencies with C−O(O) distance were modeled using[29,30]

$$\nu(r) = \nu_0 \exp[-a(r - r_{\mathrm{e}})] + B \tag{6}$$

where ν_0 is the vibrational frequency in the reactant molecule, r_{e} is the equilibrium bond distance, B is the sum of the rotational constants of the individual isoprene−OH adduct and O_2 molecules, and a is a constant. Moments of inertia at fixed geometries were calculated by changing only the C−O(O) distance. The potential energy surface along the reaction coordinate was modeled by a Morse function including the centrifugal barrier,[29,30]

$$V(r) = D_{\mathrm{e}}[1 - \exp(-\beta r)]^2 + B_{\mathrm{ext}}(r)J(J + 1) \tag{7}$$

where D_{e} is the bond dissociation energy, $B_{\mathrm{ext}}(r)$ is the external rotational constant determined by assuming that the molecular was a symmetric top, and J was assumed to be the average rotational quantum number of a Boltzmann distribution calculated using the external rotational constant of the molecule at the equilibrium configuration.

The individual rates of formation of each isomer were obtained using eqs 4 and 5, variationally minimizing the rate as function of the C−O(O) bond distance. The value of a was determined to be 1.05 Å^{-1} based on a functional fit to the r-dependence of the zero-point energy (ZPE) evaluated at the B3LYP/6-31G(d,p) level of theory. This assumes that the largest change in ZPE is due to the decrease in transitional mode frequencies and, therefore, provides an effective dependence of these modes on bond length. We find no energy that exceeds the bond dissociation energy along the reaction coordinate in contrast to the results of the addition of O_2 to aromatic−Cl adducts, since the calculated energy relative to the equilibrium peroxy radical increased monotonically when the C−O bond length was successively increased. The β parameter for the Morse potential in eq 7 is given by $\beta = (2\pi^2\mu/D_{\mathrm{e}})^{1/2}\nu$, where μ is the reduced mass of the bonded atoms, D_{e} is the bond dissociation energy, and ν is the vibrational frequency of the reaction coordinate in the parent molecule.[29,30]

TABLE 3: CVTST Calculated High-Pressure Limit Rate Constants and Isomeric Branching Ratios for the Formation of the Cl−O_2−Isoprene Peroxy Radicals[a]

isomer	k (cm^3 molecule^{-1} s^{-1})	branching ratio (%)
A	1.58×10^{-13}	17.4
B	3.12×10^{-12}	1.9
C	3.39×10^{-12}	8.1
D	2.67×10^{-13}	30.3
E	2.03×10^{-13}	22.2
F	1.77×10^{-13}	20.1
total	7.32×10^{-12}	100

[a] Calculated at the CCSD(T)/6-31G(d) + *CF*//B3LYP/6-31G(d,p) level of theory.

The results of the CVTST rate calculations are shown in Table 3 for each peroxy isomer. The values of the high-pressure rate constants fall in the range of $1.5 \times 10^{-13} - 3.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The addition rates to form isomers **B** and **C** are comparable, while the addition rates to form isomers **A**, **D**, **E**, and **F** are much slower. Although all isoprene−OH adduct isomers will react rapidly with O_2 under ambient conditions the relative rates between the formation of isomers **A** and **E** and between **D** and **F** influence final product branching ratios in the oxidation of isoprene. We find that the **A**:**E** and **D**:**F** relative branching ratios are 0.44:0.56 and 0.60:0.40, respectively. Our previous calculations predict the relative branching ratios of 0.40, 0.02, 0.08, and 0.50 for Cl−isoprene adduct isomers **I** to **IV**, respectively. Combining those values with the calculated formation rates for the peroxy radicals yields the calculated peroxy radical branching ratios, which are also contained in Table 3.

Several laboratory experiments using the environmental smog chamber method have identified several products from the Cl-initiated reactions of isoprene, such as formyl chloride, formic acid, and methyl-glyoxal.[15,16] HCOCl is produced by the decomposition of the two β-chloroalkenylalkoxy radicals arising from peroxy radicals **A** and **D**. The same reaction pathways should also lead to the formation of methyl vinyl ketone (MVK) and methacrolein (MACR), but both MVK and MACR have been observed with very small yields.[15,16] The lack of the formation of MVK and MACR has been suggested due to the secondary reactions of the two species with Cl radical or due to photolysis. In addition, the laboratory experiments have identified 1-chloro-3-methyl-3-buten-2-one (CMBO) as another major product,[15,16] which evidently arises from peroxy radical **D**. Our present theoretical calculations are qualitatively consistent with the available experimental observations of the products of the Cl-isoprene reaction system, suggesting that the two β-chloroalkenylperoxy radicals **A** and **D** are very important in propagating the isoprene oxidation reactions. The branching ratio prediction of this study will facilitate the application of CMBO as a tracer to deduce chlorine radical concentrations in the urban and regional atmosphere.

Conclusions

In this paper we have first presented ab initio molecular orbital calculations to investigate the structures and energetics of the peroxy radicals arising from the Cl-initiated oxidation of isoprene. Equilibrium structures and energetics of the chloroalkenylalkoxy radicals were investigated. At the CCSD(T)/6-31G(d) level of theory corrected with zero-point energy (ZPE), the chloroalkenylalkoxy radicals are about 39 to 43 kcal mol^{-1} more stable than their separate reactants. Our results reveal that the two β-chloroalkenylperoxy radicals with initial Cl addition at C1 and C4 positions and subsequent O_2 addition at C2 and C3 positions (peroxy radicals **A** and **D**), respectively, play an important role in determining the reaction pathways and final product distributions of the Cl−isoprene reaction system. The present work has important implications on chlorine chemistry relevant to the urban and regional atmosphere.

Acknowledgment. This work was partially supported by the Robert A. Welch Foundation (A-1417), Texas Air Research Center (TARC), and the DOE. Additional support for this work was provided by the Texas A&M University Supercomputing Facilities. We thank Dr. Lisa Thomson for helpful discussions and acknowledge the use of Laboratory for Molecular Simulations at the Texas A&M University. Two referees provided valuable comments for improving this manuscript.

Supporting Information Available: Vibrational frequencies and zero-point energy (ZPE) of the Cl−isoprene−O_2 peroxy radicals. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Rasmussen, R. A.; Khalil, M. A. *J. Geophys. Res.* **1988**, *93*, 1417.

(2) Trainer, M., et al. *Nature* **1987**, *329*, 705.

(3) Jacob, D. J.; Wofsy, S. C. *J. Geophys. Res.* **1988**, *93*, 1477.

(4) Blake, N. J.; Penkett, S. A.; Clemitshaw, K. C.; Anwyl, P.; Lightman, P.; Marsh, A. R. W.; Butcher, G. *J. Geophys. Res.* **1993**, *98*, 2851.

(5) Moore, R. M.; Oram, D. E.; Penkett, S. A. *Geophys. Res. Lett.* **1994**, *21*, 2507.

(6) Ratte, M.; Bujok, O.; Spitzy, A.; Rudolph, J. *J. Geophys. Res.* **1998**, *103*, 5707.

(7) Graedel, T. E.; Keene, W. C. *J. Geophys. Res*. **1999,** *104*, 8331.

(8) Tanaka, P. L.; Oldfield, S.; Neece, J. D.; Mullins, C. B.; Allen, D. T. *Environ. Sci. Technol*. **2000**, *34*, 4470.

(9) McCulloch, A.; Aucott, M. L.; Graedel, T. E.; Kleiman, G.; Mideley, P.; Li, Y. F. *J. Geophys. Res*. **1999**, *104*, 8417.

(10) Aucott, M. L.; McCulloch, A.; Graedel, T. E.; Kleiman, G.; Midgley, P.; Li, Y. F. *J. Geophys. Res*. **1999**, *104*, 8405.

(11) Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*; John Wiley & Sons: New York, 1997.

(12) Knipping, E. M.; Lakin, M. J.; Foster, K. L.; Jungwirth, P.; Tobias, D. J.; Gerber, R. B.; Dabdub, D.; Finlayson-Pitts, B. J. *Science* **2000**, *288*, 301.

(13) Singh, H. B.; Thakur, A. N.; Chen, Y. E.; Kanakidou, M. *Geophys. Res. Lett*. **1996**, *23*, 1529.

(14) Spicer, C. W.; Chapman, E. G.; Finlayson-Pitts, B. J.; Plastridge, R. A.; Hubbe, J. M.; Fast, J. D.; Berkowitz, C. M. *Nature* **1998**, *394*, 353.

(15) Nordmeyer, T.; Wang, W.; Ragains, M. L.; Finlayson-Pitts, B. J. *Geophys. Res. Lett*. **1997**, *24*, 1615.

(16) Ragains, M. L.; Finlayson-Pitts, B. J. *J. Phys. Chem*. **1997**, *101*, 1509.

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

(18) Canosa-Mas, C. E.; Hutton-Squire, H. R.; King, M. D.; Stewart, D. J.; Thompson, K. C.; Wayne, R. P. *J. Atmos. Chem.* **1999**, *34*, 163.

(19) Notario, A.; Le Bras, G.; Mellouki, A. *Chem. Phys. Lett.* **1997**, *281*, 421.

(20) Bedjanian, Y.; Laverdet, G.; Le Bras, G. *J. Phys. Chem.* **1998**, *102*, 953.

(21) Suh, I.; Zhang, R. *J. Phys. Chem*. **2000**, *104*, 6590.

(22) Wang, W. H.; Finlayson-Pitts, B. J. *Geophys. Res. Lett.* **2000**, *27*, 947.

(23) Lei, W.; Zhang, R. *J. Chem. Phys*. **2000**, *113*, 153.

(24) Lei, W.; Zhang, D.; Zhang, R.; Molina, L. T.; Molina, M. J. *Chem. Phys. Lett*. **2002**, *357*, 45.

(25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 98*, Revision D.3; Gaussian, Inc.: Pittsburgh, PA, 1998.

(26) Lei, W.; Derecskei-Kovacs, A.; Zhang, R. *J. Chem. Phys*. **2000**, *113*, 5354.

(27) Chuang, Y. Y.; Coitino, E. L.; Truhlar, D. G. *J. Phys. Chem*. **2000**, *104*, 446.

(28) Zhang, D.; Zhang, R. *J. Am. Chem. Soc*. **2002**, *124*, 2692.

(29) Lei, W.; Zhang, R.; McGivern, W. S.; Derecskei-Kovacs, A.; North, S. W. *J. Phys. Chem.* **2001**, *105*, 471.

(30) Lei, W.; Zhang, R.; McGivern, W. S.; Derecskei-Kovacs, A.; North, S. W. *Chem. Phys. Lett.* **2000**, *326*, 109.