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Ab Initio Study on the Mechanism of Tropospheric Reactions of the Nitrate Radical with Haloalkenes: Chloroethene

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Abstract: A mechanism for the reaction of the NO_3 radical with vinyl chloride is proposed on the basis of B3LYP and CASSCF quantum chemistry calculations. Two initial transition states lead to the Markownikoff and contra-Markownikoff addition of NO_3 to chloroethene. From the two initial adducts different interconnected pathways start. We have found epoxichloroethane, chloroethanal, nitrous acid, acetyl chloride, nitric acid, formaldehyde, formyl chloride, and NO radical as main products. The energy of the reactants, products, and all intermediates along with the barrier heights for each reaction path has been calculated. The geometry optimization and characterization of all of the stationary points found on the potential energy hypersurface was made at the B3LYP level with a 6-31G* basis set, and some of the stationary points have been reoptimized with the 6-311+G* basis set. Later, single-point CASSCF calculations were carried out with the same basis set, building the active space with seven active electrons in eight active orbitals. It can be concluded that an equilibrium distribution of formyl chloride, formaldehyde, and the NO radical will be obtained along with small proportions of epoxychloroetane and the Markownikoff radical adduct. An estimation of the reaction rate constant has also been calculated.

Introduction

The nitrate radical is known to be an important oxidant in the troposphere during night-time. The reactions of the nitrate radical with many unsaturated organic species represent a significant way for the loss of these compounds.[1] Halogenated compounds may be a major concern in local industrial areas. The chloroethenes are toxic, organic chemicals with a wide-spread use as solvents and refrigerants.

The reaction of NO_3 with haloalkenes proceeds in a similar way to that of the alkenes by electrophilic addition of the radical to the double bond. Few mechanistic studies on the reactions of the nitrate radical with halogenated organic compounds have been published. Edney et al.[2] in their study of the photooxidation of allyl chloride in the presence of NO_x propose that the formed alkoxy radical decomposes to give a Cl atom and acrolein. However, the work of Wänberg et al.[3] with chlorinated butenes suggests that, at least for this reaction, this is not an important pathway. The principal products they have found are acid chlorides, aldehydes, and NO_2 when the Cl atom is placed on the double bond. However, if the Cl atom is situated next to the double bond (vicinal or farther) the main products found are aldehydes, chlorinated carbonyl nitrate compounds, and NO_2. Recently, Noremsaune et al.,[4] studying the reactions between the nitrate radical and some haloethenes have proposed as main products formaldehyde (CH_2O), formyl chloride (HCOCl), HCl, CO, chloroacetyl chlorides, and CCl_2O, where chloroacetyl chloride can only be formed from vinylidene chloride by reaction with Cl atoms. Chlorine atoms would be released in the formation of nitrooxyacetyl chloride (NAC). These two works were performed in synthetic air. The epoxide formation is not included in these mechanism proposals.

In two previous papers,[5,6] we have studied theoretically the addition reaction mechanism of the NO_3 radical to ethene and propene. In both cases we have found as main products epoxide, aldehyde, ketone, and NO_2. In the second case, we have also found the NO radical and propenol. The epoxide is the product kinetically more favored in the ethene mechanism. In the propene mechanism an equilibrium distribution is produced, where epoxide, NO_2 radical, formaldehyde, ethanal, and NO radical are the kinetically most favored products.

One goal in this study is to compare the mechanism of the simplest chlorinated alkene with the corresponding unsubstituted alkene, the ethene, and with the methyl monosubstituted alkene, the propene, to obtain a generalized reaction mechanism to be applied to reactions of NO_3 and other alkenes and haloalkenes. This work series will be completed with the studies on other substituted alkenes ($C_2H_{4-n}Me_n$ and $C_2H_{4-n}Cl_n$, $n = 2, 3, 4$) to provide a theoretical explanation for the dependence of the rate constant on the substitution degree of the double bond, complementing thus model experiences.

This work also provides information on the whole mechanism to know the main products and possible intermediates. The knowledge of all them is very important for two reasons: on one hand, they can be themselves pollutants, and on the other hand, they would be the target for the attack of oxygen and

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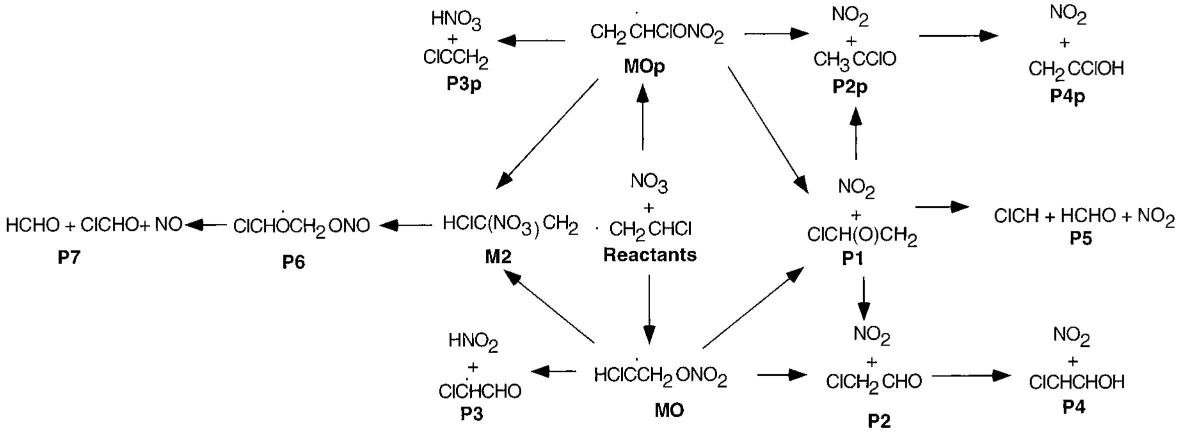

Figure 1. Reaction mechanism scheme for the addition reaction of NO_3 to cloroethene.

other molecules such as NO_2, NO_3, SO_2, etc., giving other pollutant products. Future research is open to study competition of the intramolecular rearrangements following the initial addition of NO_3 on the alkene, and the reactions with O_2 or other molecules.

In this work, we present a theoretical study on the mechanism of the reaction between the nitrate radical and the vinyl chloride molecule. After a prospective study of the potential energy hypersurface with the AM1 method, the stationary points found were optimized and characterized at the DFT level of theory with the B3LYP density functional. Then, energy single-point calculations were made at the CASSCF level using these geometries. In section 2 computational aspects are detailed; in section 3 a reaction mechanism is proposed and discussed. Section 3.1 and 3.2 describe the Markownikoff and contra-Markownikoff reaction pathways, respectively. Section 3.3 includes the common pathways in both Markownikoff and contra-Markownikoff pathways. In section 3.4 the schemes of the reaction energy profiles and the energy barriers involved for all of the reaction pathways studied are shown and discussed. Finally, the main conclusions are enumerated in section 4.

Computational Details

An AM1[7] semiempirical study of the whole potential energy surface (PES) has been performed, and the stationary points have been classified according to their significance for this reaction, in a similar way as in previous papers.[5,6] The AM1 results have not been included in the results section. Taking these geometries as starting points, all of the relevant stationary points have been reoptimized at density functional theory level, using the referred B3LYP functional. This functional is based on Becke's 3-parametrization adiabatic connection method (ACM), and consists on a combination of Slater,[8] Hartree–Fock,[9] and Becke[10] exchange, the Vosko, Wilk, and Nusair (VWN) local correlation functional,[11] and the Lee, Yang, and Parr (LYP) nonlocal correlation functional.[12]

The stationary points optimized at DFT level have been characterized as minima (number of imaginary frequencies, $NIMAG = 0$) or transition states ($NIMAG = 1$), by calculating the Hessian matrix and analyzing the vibrational normal modes. The eigen following and transition state[13] methods have been used for the minima and transition states geometry optimizations, respectively. Also to confirm that the transition states connect between designated intermediates, we performed intrinsic reaction coordinate (IRC) calculations[14] at the B3LYP/6-31G* level.

The Berny analytical gradient[15] was used for geometry optimization of the minima and transition states at B3LYP level. The basis set used in B3LYP and CASSCF calculations was 6-31G* [16,17] which has polarization functions (d-type) on non-hydrogen atoms. Some points were optimized with the basis set 6-311+G* [16] (see Figures 1 and 2) to ensure that when larger basis sets including diffuse functions are used, the geometry and the energy barrier values (see Table 1) are kept.

The active space for the CASSCF calculations was chosen in accord with aprevious SDCI calculation. Those orbitals with occupation numbers between 0.02 and 1.98[18] were selected, resulting in an active space of seven electrons in eight active orbitals.

B3LYP and CASSCF calculations were performed with the GAUSSIAN 94 series of programs.[19] The calculations were performed in the two IBM RS6000-590 and IBM SP2, of the Theoretical Chemistry Group of the University of Valencia and a SG-Origin 2000 of the University of Valencia.

Results and Discussion

A reaction mechanism has been obtained for the NO_3 + vinyl chloride reaction. Only those stationary points relating to the chemical reaction have been chosen. In the reaction mechanism two main reaction pathways have been found, resulting from the Markownikoff and the contra-Markownikoff addition. The initial radical adducts can rearrange in several ways. Both adducts can form epoxichloroethane, $ClCH(O)CH_2$ and NO_2, in one way, and a cyclic adduct in another reaction pathway. The Markownikoff radical adduct gives specifically nitrous acid, HNO_2, and chloroethanal radical, ClCHCHO, in a first way and, in a second way, chloroethanal, $ClCH_2CHO$, and NO_2. The contra-Markownikoff radical adduct gives specifically nitric acid, HNO_3, and chlorovinyl radical, $ClCCH_2$, in one way and acetyl chloride, CH_3CClO, and NO_2 in a second way. On the other hand, epoxichloroethane can react in three ways. Two of

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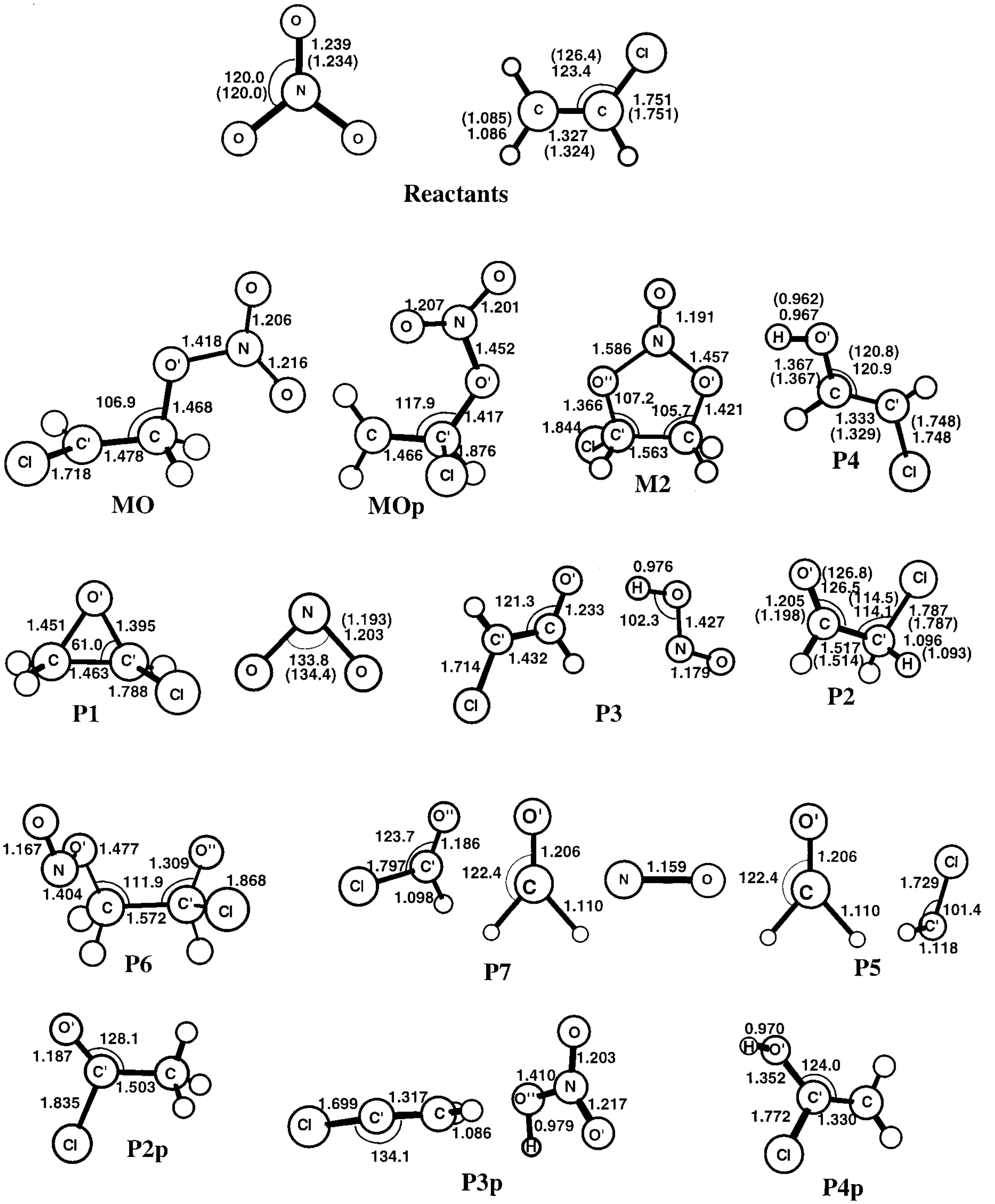

Figure 2. Optimized geometries of reactants, products, and intermediates for the NO_3 + chloroethene addition reaction, at the B3-LYP/6-31G* level of theory. White atoms correspond to nonrelevant hydrogen atoms.

them give chloroethanal and acetyl chloride, and the third, formaldehyde, CH_2O, ClCH, through a C−C bond cleavage. Chloroethanal rearranges toward 2-chloroethenol, ClCHCHOH, and acetyl chloride toward 1-chloroethenol, CH_2CClOH. Finally, the cyclic adduct gives, through N−O bond cleavage, formaldehyde and formyl chloride, ClCOH, and NO radical. A scheme of the reaction network, along with the notation used for the intermediates and products is depicted in Figure 1.

The B3LYP optimized geometries of the reactants, products, intermediates, and transition states of this reaction system are depicted in Figures 2 and 3. The energy profile of the reaction is illustrated in Figures 4 and 5, at B3LYP and CASSCF level, respectively. Table 1 describes the different transition states found in the mechanism. In this table, energy relative to the reactants, the pathway involved, the imaginary frequency, and a short description of the transition vector associated with it are shown.

3.1. Markownikoff Reaction Pathway. The starting point, MO, is the result of the Markownikoff addition of the radical to the double bond. The spin density is mainly located on the C′ atom, confirming the experimental idea of an electrophilic addition to the double bond[1] (for the notation see Figures 2 and 3). If an attack of an oxygen molecule takes place, it would oxidize the intermediate at C′, producing peroxides, due to the

Table 1: Energy Relative to NO_3 + Chloroethene, the Minima Connected by the Transition State, the Value of the Imaginary Frequency Involved, and a Short Description of the Associate Transition Vector for the Transition States Involved in the NO_3 + Chloroethene Proposed Reaction Mechanism

TS	starting point → final point	ΔE_{B3LYP} kJ/mol	ν_i cm^{-1}	main transition vector components
TSM	reactants → MO	−5.94	411*i*,15*i*	shortening O′−C
TS1	MO → P1	3.59	676*i*	closure C′−C−O′ enlargement O′−N
TS2	P1 → P2	128.41	659*i*	opening epoxide ring 1,2-H shift C−C′ shortening C−O′
TS5	P1 → P5	179.11	269*i*	cleavage C−C
TS3	MO → P2	118.04	1989*i*	1,2-H shift C−C′ enlargement O′−N
TS4	P2 → P4	49.91	2177*i*	1,2-H shift C′−O′
TS7	MO → P3	54.63	788*i*	enlargement H−C and N−O′ shortening O″−H
TS10	MO → M2	12.87	738*i*	rotation the O″−C′−C−O shortening O″−C′
TS8	M2 → P6	−118.46	140*i*	enlargement N−O″ shortening N−O′ and O″−C′
TS9	P6 → P7	−125.19	311*i*	enlargement C−C′ and N−O′ shortening C−O′ and O″−C″
TScM	reactants → MOp	8.86	294*i*	shortening O′−C′
TS0	MO → MOp	31.81	343*i*	enlargement O″−C′ shortening O″−C
TS1p	MOp → P1	6.98	620*i*	closure C−C′−O′ enlargement O′−N
TS2p	P1 → P2p	65.38	570*i*	opening epoxide ring 1,2-H shift C′−C shortening C′−O′
TS3p	MOp → P2p	49.70	592*i*	1,2-H shift C−C enlargement O′−N
TS4p	P2p → P4p	26.58	2226*i*	1,2-H shift C−O′
TS7p	MOp → P3p	135.81	921*i*	enlargement H−C′ and N−O′ shortening O−H
TS11	MOp → M2	23.12	688*i*	rotation the O″−C′−C−O′ shortening O″−C

diradical character of the oxygen molecule, in accord with that reported experimentally.[20]

The Cl atom stabilizes the radical adduct in two ways:

1. by resonance effect due to the lone electron pairs, which share electron density with the reaction center, and

2. by inductive effect, since it should decrease the electronic density on the C atom according to the higher electronegativity of the Cl atom.

Similar to that found for the NO_3 + ethene reaction mechanism,[21] we can assume that, prior to the addition, a van der Waals complex is formed and a transition state connects this complex with the Markownikoff radical adduct, MO, through a symmetric movement. Since we have not been able to optimize this transition state completely, an estimation was done by fixing the O′−C distance (see Figure 3) and optimizing the other parameters. This estimated transition state, TSM, is at −5.94 kJ/mol (in all cases the energy values correspond to B3LYP calculations) and shows two imaginary frequencies. The first one is 411*i* cm^{-1}, associated to the symmetric movement of the oxygen O′ toward the carbon C, and the second one is15*i* cm^{-1}, corresponding to the relative movement between the two fragments.

From MO four reaction paths originate. Two of them are interconnected, the first one leading to epoxide formation, and the other, to chloroethanal. The other two lead to nitrous acid formation and to formyl chloride, formaldehyde, and NO radical, respectively.

3.1.1. Chloroethanal Formation. This reaction pathway involves an exothermic step of 157.83 kJ/mol leading from MO to the chloroethanal, P2, through a transition state, TS3 (see Table 1). From this, an endothermic intramolecular reaction of 58.64 kJ/mol takes places, leading to the 2-chloroethenol formation, P4, through a transition state, TS4 (see Table 1).

The transformation of the initial adduct in the chloroethanal, P2, is carried out through a 1,2-hydrogen shift from the C to the C′ atoms and the enlargement of the O′−N bond length (see Figure 2). In the conformation of the involved transition state, TS3, the H−C and H−C′ distances are practically equal (see Figure 3). This fact is reflected in the spin density, since each carbon atom has nearly a half of the total.

From the aldehyde, a path that leads to the enol formation, P4, has been found. The reaction coordinate involves a hydrogen shift from the CH_2 group to the oxygen atom in the carbonyl group.

The optimized geometries of the TS2, P2, TS4, and P4 as well as the reactants were also calculated with a 6-311+G* basis set, to know the effect of larger basis sets and diffuse functions on the geometries. The results are depicted in brackets in Figures 1 and 2. It can be seen that no significant differences are obtained, the largest difference being 0.013 Å in the distances and 3° in the angles. Thus, larger basis sets and diffuse functions are not relevant in the calculation of the geometries of the molecules involved in this reaction mechanism.

3.1.2. Nitrous Acid Formation. The third pathway in the Markownikoff reaction mechanism involves the formation of nitrous acid and chloroethanal radical, P3.

The reaction coordinate leading to P3 from MO involves an exothermic step by 103.41 kJ/mol associated to an H abstraction

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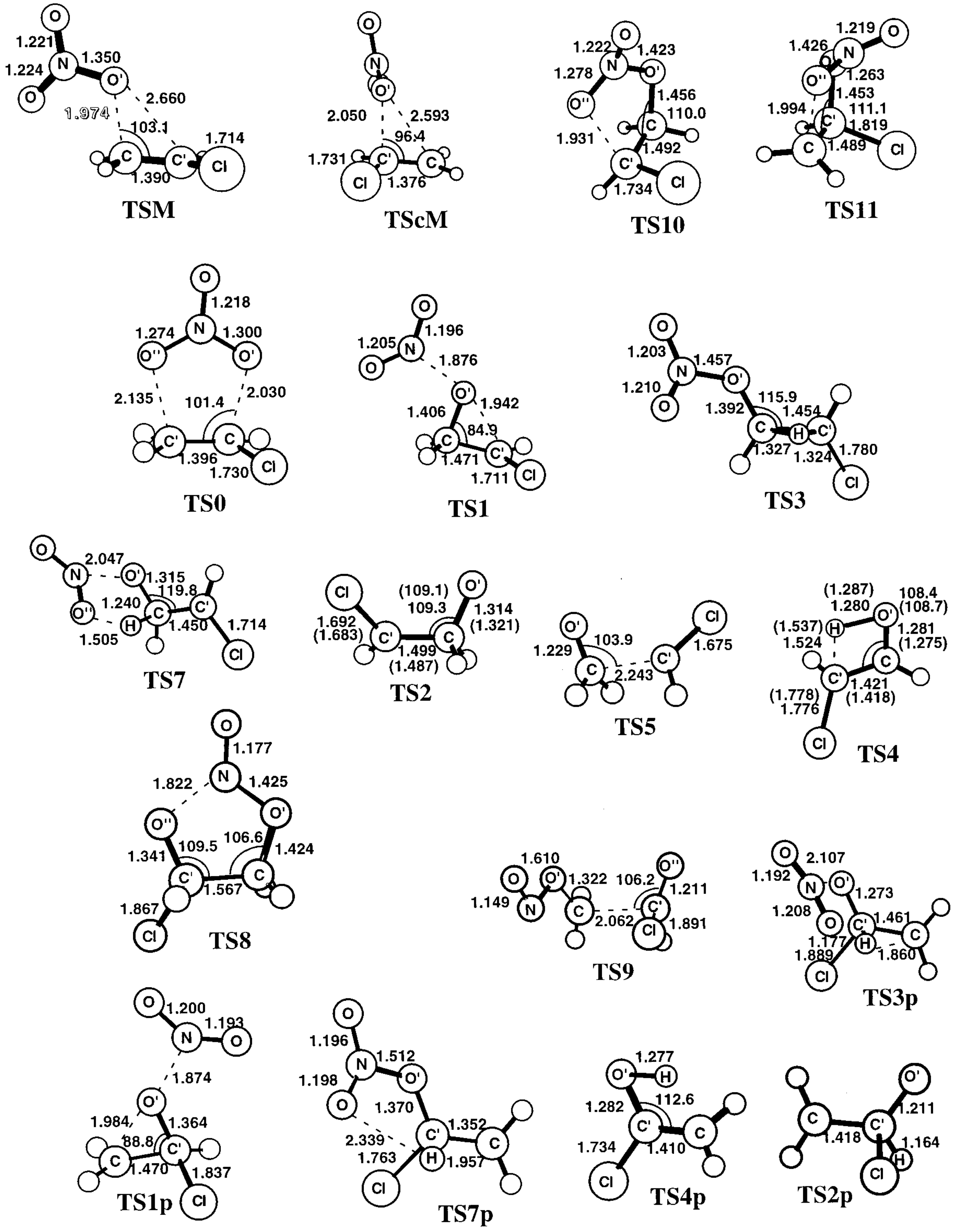

Figure 3. Optimized geometries of transition states for the NO_3 + chloroethene addition reaction, at B3-LYP/6-31G* level of theory. White atoms correspond to non relevant hydrogen atoms. Shadowed parameters correspond to fixed distances.

by the NO_2 group. The spin density in the corresponding transition state, TS7 (see Table 1), is mainly located on C′ atom.

3.2. Contra-Markownikoff Reaction Pathway. Although it is likely that the addition occurs with preference at the less substituted carbon, the other alternative must also be considered. However, the experimental ratio between the C′ and C addition reactions remains unknown, since no products confirming C′ addition have been reported.[4] Thus, the reaction pathway which forms the most unstable and less substituted radical adduct, MOp, has been found. In this conformation, the NO_3 radical attacks the most substituted carbon atom, C′. The spin density is mainly located on C atom. Thus, the radical is not stabilized by resonance and inductive effects due to the lone electron pairs and the high electronegativity of the Cl atom, in opposition to the Markownikoff addition.

In this pathway we have found the transition state, TScM (see Table 1), leading from the reactants to the contra-Markownikoff adduct. It is likely that a van der Waals complex previous to the transition state was also formed, as in the ethene[21] and propene[6] cases, but we have not been able to find

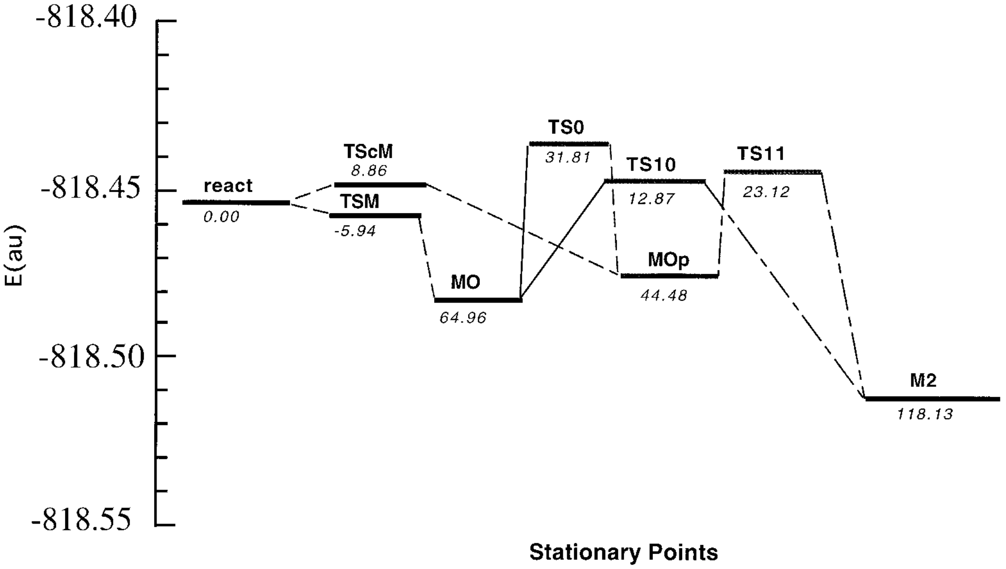

Figure 4. Scheme of the B3LYP/6-31G* reaction profile for the first steps of the reaction mechanism. Energy relative to the reactants in kJ/mol.

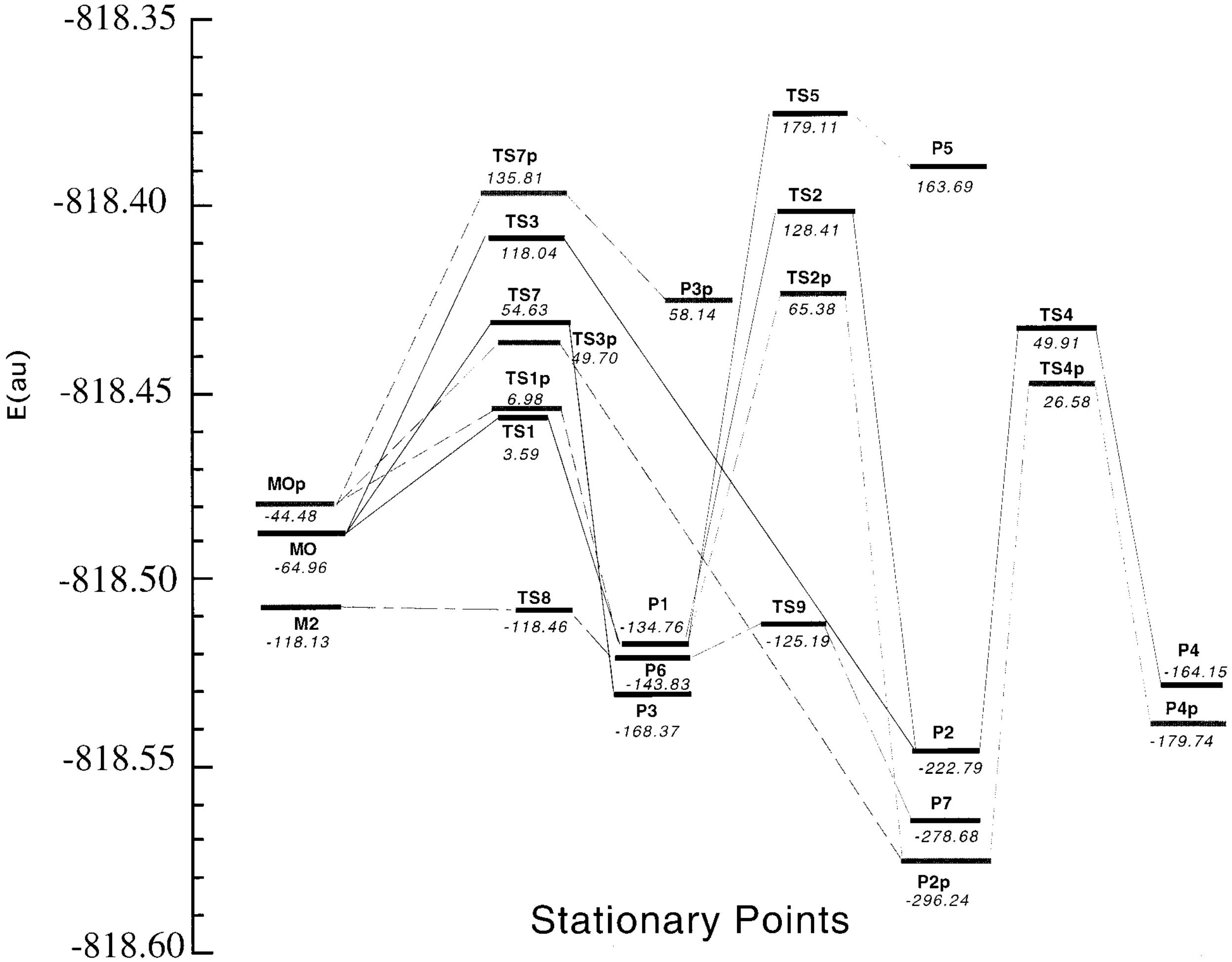

Figure 5. Scheme of the B3LYP/6-31G* reaction profile for the final steps of the reaction mechanism. Energy relative to the reactants in kJ/mol.

it; moreover it will be irrelevant with respect to the chemistry of the reaction.[22] In the TScM conformation, the NO_3 radical is placed with two oxygen atoms contained in a plane perpendicular to the double bond (see Figure 2). The spin density is mainly localized on the O′ and C atoms, and hence, the radical character is located not only on the NO_3 fragment but also on the π system.

Also, we have found a transition state, TS0 (see Table 1), connecting Markownikoff and contra-Markownikoff radical adducts.

As in the Markownikoff reaction pathway, four reaction pathways originate from the contra-Markownikoff radical ad-

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duct. They lead to epoxide, acetyl chloride, nitric acid, formyl chloride, formaldehyde and NO_2, and NO radical formation.

3.2.1. Acetyl Chloride Formation. In a similar way to the Markownikoff adduct, the contra-Markownikoff one goes directly to the formation of acetyl chloride, P2p, and then, from it to its enol, P4p, along with the NO_2 radical formation. It converges with the Markownikoff pathway in the acetyl chloride, P2p.

The reaction coordinate leading from the initial adduct, MOp, to acetylchloride, P2p, involves a 1,2-hydrogen shift from C′ to C and the enlargement of the O′−N distance (see Figure 3). This step is exothermic by 251.76 kJ/mol. In the transtion state, TS3p (see Table 1), the H−C distance is larger than the H−C′ distance, which is different from the corresponding Markownikoff transition state, TS3. Thus, it is an early reagent-like transition state. The spin density reflects this fact, since it is located mainly in C and N.

Starting from the acetyl chloride, a path that leads to the enol formation, P4p, endothermically by 116.5 kJ/mol, through a transition state, TS4p (see Table 1), has been found. The reaction coordinate involves a hydrogen shift from the CH_3 group to the oxygen atom in the carbonyl group.

3.2.2. Nitric Acid Formation. The third pathway in the contra-Markownikoff reaction mechanism leads endothermically by 102.62 kJ/mol to the nitric acid and chlorovinyl radical formation, P3p, from the contra-Markownikoff radical adduct, MOp.

The pathway leading from MOp to P3p involves the H abstraction by the NO_3 group, by enlargement of the H−C′ distance (see Figure 3). The spin density in the corresponding transition state, TS7p (see Table 1), is mainly located on the H atom. The high barrier involved in this pathway and the fact that this step is endothermic prevent its formation in the troposphere by this way.

3.3. Common Products to Markownikoff and Contra-Markownikoff Reaction Pathways. Starting from both the Markownikoff and contra-Markownikoff adducts, MO and MOp, we have found two pathways leading to an epoxide formation and a cyclic intermediate, M2.

3.3.1. Epoxichloroethane Formation. Similar to the reaction mechanism of the ethene[5] and propene,[6] there are pathways leading from the initial adducts to epoxichloroethane formation, P1. Eventually, P1, can give, by means of intramolecular rearrangements, chloroethanal, P2, or acetyl chloride, P2p, connecting with the Markownikoff and contra-Markownikoff pathways, already described, or, by means of bond cleavage, formaldehyde and chloromethylene, p5, through the corresponding transition states.

The reaction path leading from MO or MOp to epoxichloroethane, P1, andthe NO_2 radical involves the closure of the C′−C−O′ angle and the enlargement of the O′−N distance (see Figure 2). This step occurs exothermically by 69.80 and 90.28 kJ/mol for the MO and MOp pathways, respectively. The conformation of P1 shows an asymmetrical three-membered ring, with the C−O and the C−C distances nearly equal and the other C−O distance shorter, corresponding to the substituted C atom. NO_2 radical is one the products experimentally found.[3]

MO and MOp and P1 are connected through the TS1 and TS1p transition states, respectively (see Table 1), showing the spin density mainly located on the C and N atoms.

We have found three reaction pathways starting from P1. The first one is an exothermic path by 88.03 kJ/mol leading to chloroethanal, P2, through a transition state, TS2 (see Table 1). The reaction coordinate involves the opening of the epoxide ring, a 1,2-hydrogen shift from C to C′, and the shortening of the C−O′ bond to become a carbonyl group.

An endothermic reaction pathway by 298.45 kJ/mol leads from the epoxichloroethane to formaldehyde and chloromethylene formation, P5, through a transition state, TS5 (see Table 1). Formaldehyde is one of the products experimentally found by Noremsaune et al.[4] The reaction coordinate involves the C′−C bond cleavage and the opening of the three-membered ring.

The reaction coordinate leading from P1 to acetyl chloride, P2p, through the corresponding transition state, TS2p (see Table 1), involves the opening of the three-membered ring, a 1,2-hydrogen shift from C′ to C, and the shortening of the O′−C′ distance to become a carbonyl group. This step is exothermic by 161.48 kJ/mol. It is noteworthy that acetyl chloride is one of the products experimentally found.[4]

3.3.2. Formaldehyde, Formyl Chloride, and NO Radical Formation. A reaction pathway leading exothermically by 213.72 kJ/mol to formaldehyde, formyl chloride, and NO radical from the Markownikoff adduct, MO, has been found. In this pathway there are two intermediates, M2 and P6, and three transition states, TS10, TS8, and TS9, between MO and the final products.

The first intermediate is a five-membered ring structure, M2, formed exothermically by 53.17 kJ/mol. In M2, the distances on the ring structure are slightly distorted due to the presence of the Cl atom, which breaks the symmetry of the molecule. Thus, the O″−C′ distance is shorter than the O′−C one and, in the same way, the N−O″ distance is ∼0.13 Å larger than the N−O′ distance. The C−C distance indicates a long single bond. This asymmetry in the molecule shows the weak points where the molecule may break to give different products. The spin density is delocalized on the NO_3 system, mainly in the N and the out-of-ring O atoms. The reaction coordinate leading from MO to M2, involves the rotation of the O″−C′−C−O′ dihedral angle and the shortening of the O″−C′ distance. The geometry of the transition state involved, TS10 (see Table 1), shows the NO_3 system placed with two oxygen atoms in a near-bridge conformation over the C−C bond. The spin density is located on the C′ atom.

We have also found a pathway leading from the contra-Markownikoff radical adduct, MOp, to M2. This step occurs exothermically by 73.65 kJ/mol. The reaction coordinate leading from MOp to M2 involves the rotation of the O″−C′−C−O′ dihedral angle and the shortening of the O″−C distance. The geometry of the transition state connecting both minima, TS11 (see Table 1 and Figure 3), is similar to that described before. The spin density is located on the C atom.

The intermediate, M2, breaks exothermically by 25.70 kJ/mol giving an alkoxy radical intermediate, P6. Cleavage of the C−C bond gives the final products, P7.

The reaction coordinate leading from M2 to P6, involves the enlargening of the N−O″ distance and a small shortening of the N−O′ and O″−C′ distances. The spin density is located mainly on O″. In the transition state connecting both intermediates, TS8 (see Table 1), the spin density is placed on the N, O, and O″ atoms, showing double value in O″ than in the other two atoms.

The final elementary step in this reaction pathway involves the formation of formaldehyde, formyl chloride, and NO radical. The step from P6 to the final products involves mainly the

Table 2: Experimental Enthalpies of Formation, where Available, and B3LYP (6-31G* and 6-311+G*), CASSCF (6-31G*), and Experimental Energy Relative to Reactants (in kJ mol^{-1})[a]

PES Points	ΔH_f^o	ΔE		ΔH_r^o	ΔE[b]	PES Points	ΔH_f^o	ΔE		ΔH_r^o	ΔE[b]
		B3LYP	CASSCF					B3LYP	CASSCF		
reactants	111.00[c]	0.00	0.00	0.00	0.00	P2p	−210.30[d]	−296.24	−362.16	−321.32	
TSM		−5.94	−83.18			TS3p		49.70	141.12		
TScM		8.86	19.56			TS4p		26.58	52.00		
MO		−64.96	−166.57			P4p		−179.74	−200.51		
TS1		3.59	12.00			TS7p		135.81	96.31		
P1		−134.76	−195.71			P3p		58.14	−29.64		
TS2		128.41	16.34		110.18	TS10		12.87	4.77		
P2	−157.80[d]	−222.79	−296.99	−268.82	−227.78	TS11		23.12	16.74		
TS3		118.04	139.36			M2		−118.13	−132.09		
TS4		49.91	35.45		50.71	TS8		−118.46	−156.16		
P4		−164.15	−246.79		−171.53	P6		−143.83	−292.64		
TS7		54.63	71.39			TS9		−125.19	−167.45		
P3	−167.79[d]	−168.37	−292.43	−278.81		P7		−278.68	−464.69		
TS5		179.11	140.45								
P5		163.69	43.01								
TS0		31.81	42.26								
MOp		−44.48	118.75								
TS1p		6.98	66.67								
TS2p		65.38	91.71								

[a] Reactants were calculated as a supermolecule. Zero-point correction has been included in B3LYP and CASSCF energy differences. [b] B3LYP 6-311+G* calculations. [c] Reference 24. [d] Reference 23.

homolytic cleavage of the C−C bond to form formyl chloride and formaldehyde. The spin density in P6 is located on the NO molecule. In the transition state involved, TS9 (see Table 1), the spin density is located on C and O″.

3.4. Scheme of the Reaction Profiles and E_a. Table 1S shows the B3LYP and CASSCF calculated energies, and Table 2, the experimental formation enthalpies[23,24] of reactants and intermediates, where available, and the B3LYP, CASSCF, and experimental energies relative to the reactants. Zero-point energy correction has been included in the theoretical relative energy values. Schemes of the B3LYP reaction energy profiles are depicted in Figures 4 and 5.

The transition state involved in the initial step of the Markownikoff radical adduct formation is lower in energy than the formation of the reactants. Thus, this step is kinetically favored. In both reaction profiles, the Markownikoff radical adduct is more stable than the contra-Markownikoff one. This is due to the stabilizing effect of the Cl atom by resonance and inductive effects. Moreover, under aerobic conditions, the attack of this adduct by the O_2 molecules would be enhanced, obtaining peroxides, in agreement with experimental results.[1]

The lowest barrier to be overcome is the one leading to epoxichloroethane and NO_2 radical. As there are different energy barriers leading to different products, the reaction is kinetically controlled, the main products obtained in the reaction being the epoxide and NO_2 radical, according to this mechanism. Some experimental works agree with the proposal of the epoxide formation,[25] while others do not discard its formation.[26]

For increasing temperatures, other reaction pathways are available. The one leading to formyl chloride, formaldehyde, and NO radical involves a barrier height of 12.87 kJ/mol at B3LYP level, these products being thermodynamically more stable than the epoxide and the NO_2 radical. These are the products experimentally found by Noremsaune et al.[4] and Wängberg et al.[3] Then, in these conditions, an equilibrium distribution will be produced between the products of both reaction pathways.

Both levels of theory agree in obtaining acetyl chloride, formaldehyde, formyl chloride, and NO radical as the most stable products from the thermodynamics point of view, but not in the relative order among them. At the B3LYP level, the most stable is the acetyl chloride, while at the CASSCF level the most stable are formyl chloride, formaldehyde, and NO radical. The height of the barrier leading to acetyl chloride prevents its formation but for high temperatures.

In this proposal of reaction mechanism, no chlorine atoms are released. Noremsaune et al.[4] proposed the formation of nitroxy acetyl chloride (NAC) by reaction with Cl atoms. In the theoretical proposal of the reaction mechanism presented in this work, acetyl chloride can be formed at higher temperatures, and NAC would simply be obtained by the attack of a NO_3 molecule. This reaction is very probable in experimental condition when model chemical kinetics studies are carried out, since there is a great excess of NO_3 in these conditions. Also, at higher temperatures, HONO, chlorovinyl radical, and chloroethanal may be produced.

The experimental activation energy, E_a, is to be compared with the relative-to-reactants energy for the transition state involved in the disappearance of the NO_3 radical, which is −5.94 kJ/mol at the B3LYP level and −83.18 kJ/mol at the CASSCF level. The experimental activation energy is 15 kJ/mol.[26] The B3LYP result is within the confidence margin of 0.5 eV estimated for theoretical calculations of this level of theory. Thus, our mechanism can be assumed to be in good agreement with the experimental studies at this point.

There are large differences between the energy barriers at the B3LYP and CASSCF levels, and, in some cases, the order of the barriers are exchanged. The B3LYP results seem to be more reliable than CASSCF ones since the geometries are not optimized at the CASSCF level and the active spaces are not completely balanced along all the potential energy hypersurface. However, qualitatively, the reaction mechanism is the same in whole, as can be seen in Figures 6 and 7, where schemes of the CASSCF reaction energy profiles are depicted.

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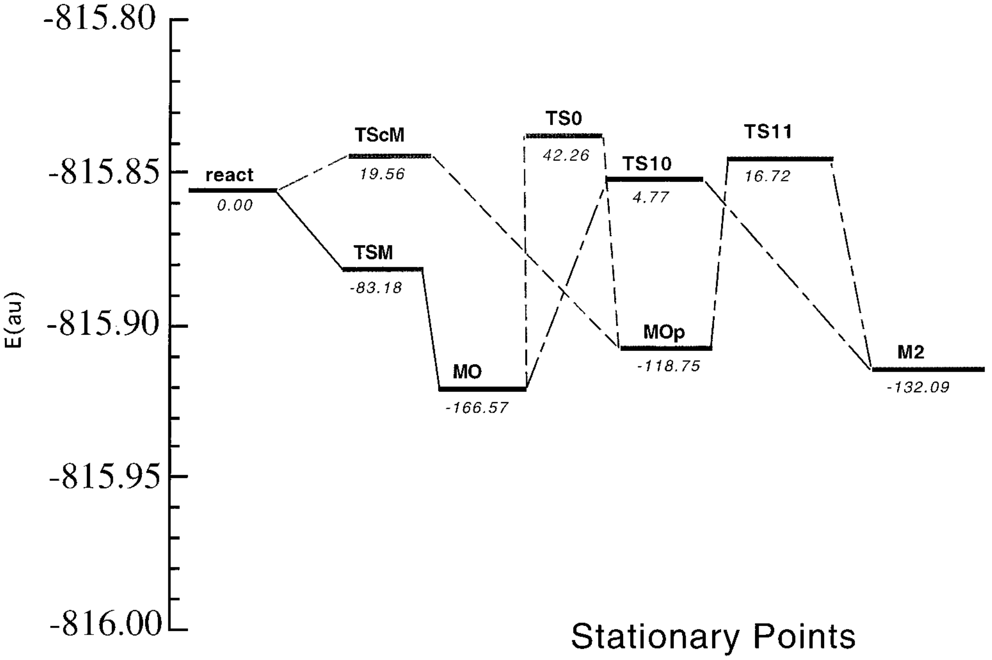

Figure 6. Scheme of the CASSCF/B3LYP/6-31G* reaction profile for the first steps of the reaction mechanism. Energy relative to the reactants in kJ/mol.

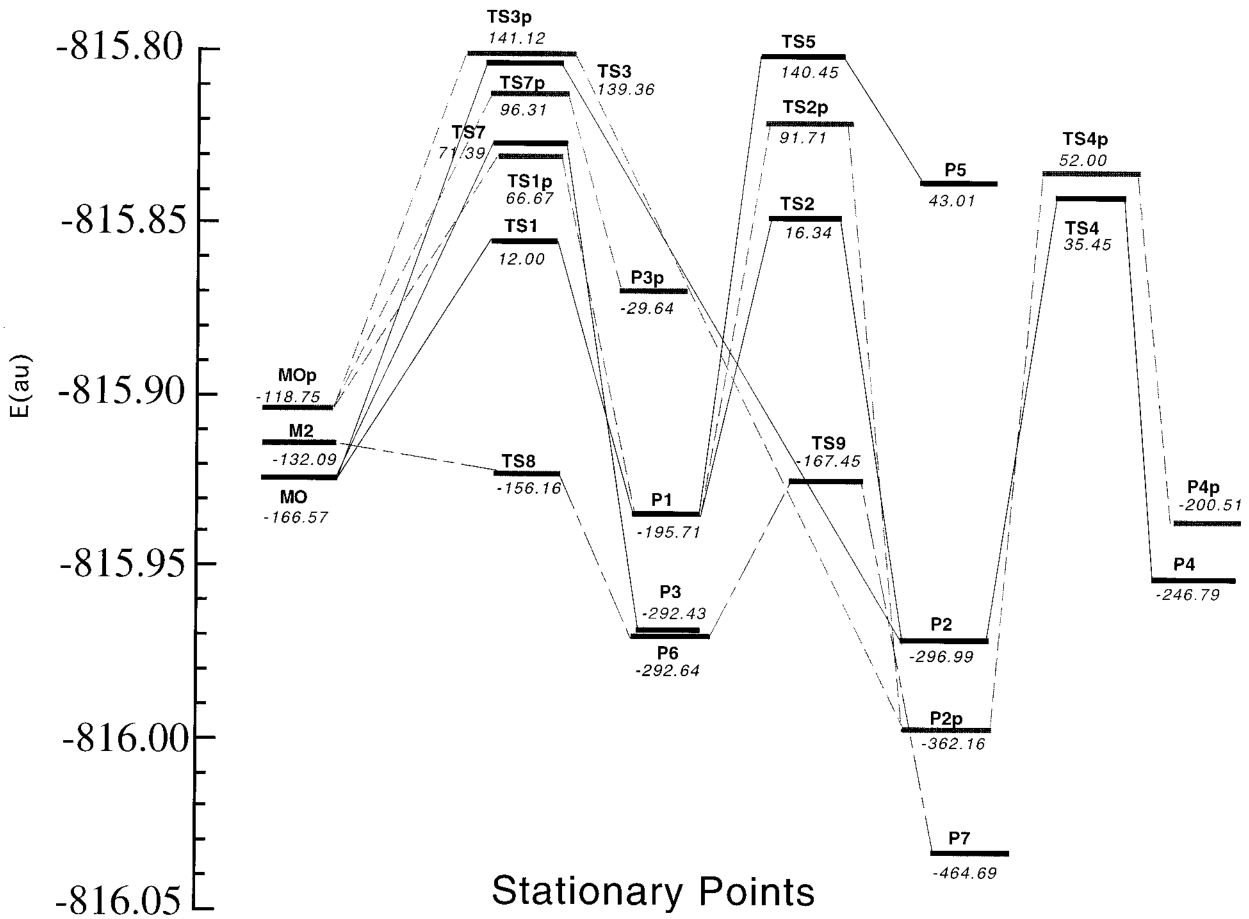

Figure 7. Scheme of the CASSCF/B3LYP/6-31G* reaction profile for the final steps of the reaction mechanism. Energy relative to the reactants in kJ/mol.

B3LYP total and relative-to-reactants optimal geometry energies obtained with a 6-311+G* basis set, have been included for five stationary points in Tables 1S and 2, respectively. No significant differences are shown, the highest corresponding to the TS2 transition state, and the difference is smaller than 20 kJ/mol. Thus, the effect in the whole energy profile of including diffuse functions is only slight.

Also, in this table, enthalpies of formation and reaction are shown.There are a few experimental data on chlorine molecules. On the basis of these results one could say that the CASSCF ones are closer to the experimental ones. The largest difference at B3LYP is on the nitrous acid and chloroethanal radical, P3, ∼110 kJ/mol, while in CASSCF the maximum error is ∼41 kJ/mol. It is to point out that, in the case of the theoretical study of reaction mechanism of the propene with NO_3,[6] the B3LYP energies were closer to the experimental reaction enthalpies than the CASSCF energies, where the geometries are optimized at this level. Thus, maybe the larger coincidence of the CASSCF results in the reaction studied in this work with the few experimental data available is due to a compensation of errors.

Also, the values of the rate coefficients have been estimated, taking into account molecular parameters, in agreement with transition-state theory according to the expression:[27]

$$k = \frac{kTQ^{\ddagger}}{hQ} e^{-E_0/RT}$$

where Q and $Q^{\ddagger}$ are the partition functions of the reactants and transition state, respectively, and E_0 is the theoretical activation energy.

The resulting value for the rate coefficient of disappearance of NO_3 and chloroethene through the estimated transition state, TSM, placed at −5.94 kJ/mol, at B3LYP level, is

$$k = 10.0 \times 10^{-15}\ \mathrm{cm^3{\cdot}molec^{-1}{\cdot}s^{-1}} \quad \text{at} \quad T = 298,\ 15\ \mathrm{K}$$

Also, the rate coefficient through the contra-Markownikoff transition state has been estimated, where the transition state considered is the TScM, at 8.86 kJ/mol, at the B3LYP level. The rate coefficient is

$$k = 2.2 \times 10^{-17}\ \mathrm{cm^3{\cdot}molec^{-1}{\cdot}s^{-1}} \quad \text{at} \quad T = 298,\ 15\ \mathrm{K}$$

Since the value of the barrier leading to the Markownikoff radical adduct, TSM, is an estimation, the obtained values of the rate coefficients for both pathways can be considered as the upper and lower limit to the true rate constant. Indeed, the experimental value of the rate constant is $k = (3.73 \pm 0.82) \times 10^{-16}\ \mathrm{cm^3{\cdot}molec^{-1}{\cdot}s^{-1}}$ at $T = 298$ K[26] and lies between the two theoretical values.

To evaluate the effect of the chlorine atom as a substituent on the reaction rate, we point out that the reaction rate coefficient is of the same order as the ethene + NO_3 reaction ($k = (1.1 \pm 0.5) \times 10^{-16}\ \mathrm{cm^3{\cdot}molec^{-1}{\cdot}s^{-11}}$), while if the substituent on the double bond is a methyl group, the reaction rate coefficient is larger, $k = (4.2 \pm 0.9) \times 10^{-16}\ \mathrm{cm^3{\cdot}molec^{-1}{\cdot}s^{-11}}$. Obviously, the energy of the involved transition states is related to the reaction rate. In the propene + NO_3 reaction mechanism theoretical study,[6] the initial transition-state energy (relative to reactants) is lower than in the vinyl chloride case by 4.01 kJ/mol.

In this work, the obtained mechanism for the $NO_3 + C_2H_3Cl$ reaction is similar to the mechanisms proposed in the theoretical studies on the $NO_3 + C_2H_4$[5] and $NO_3 + C_2H_3Me$[6] reactions, allowing us to propose a generalized reaction mechanism for the addition of the NO_3 radical to a double bond and the eventual intramolecular rearrangements. In this generalized mechanism, we can assume that the first step is the NO_3 radical addition to the double bond and that it goes through the formation of a van der Waals complex in the long-distances range. The theoretical determination of this complex can be very difficult with standard quantum chemical methods in rather large molecular systems, but this is not an actual problem, since the complex is not chemically relevant. The van der Waals complex gives an initial adduct through a transition state, very close to the van der Waals complex. The energy of this transition state, relative to reactants, is to be related with the experimental activation energy, although they cannot be compared directly. In systems asymmetrically substituted, two adducts can be formed, one according to the Markownikoff rule and the other in the opposite way. Then, from this adduct (Markownikoff or contra-Markownikoff) three different pathway are obtained:

1. In the first pathway, (halo)epoxides are formed by closing the C−C−O ring, and NO_2 radical is also formed.
2. In the second path, acid chlorides, (halo)aldehydes, or ketones are formed, through a 1,2-H shift from the adduct.
3. In the third reaction path, a new intermediate is formed, containing a five-membered ring. Then, from it, the succesive cleavage of the N−O and C−C bonds give (halo)aldehydes and NO radical.

3.5. Atmospheric Implications. The main products found, epoxichloroethane and NO_2 radical as well as the possibly formed formaldehyde, formyl chloride, and NO, play an important role on atmospheric chemistry.[28] Thus, the NO radical is involved with the stratospheric ozone depletion, and it is an important source of the OH radical, also involved in the ozone layer hole. The NO_2 radical reacts with OH radicals, giving nitric acid. This reaction is one of the guilty ones for the acid rain. The fundamental source of HO_2 radicals is the aldehyde and ketone photolysis, mainly formaldehyde. Formaldehyde is also involved in a reaction cycle where CO is produced, contributing to the greenhouse effect.[29] The formyl chloride produces Cl atoms by photolysis, which are also involved in the ozone depletion and in the formation of ClO.[30] On the other hand, epoxides are carcinogenic and mutagenic compounds.[31] At high temperatures and pressures, such as in combustion reactions, other products such as chlorinated radicals and acetyl chloride will be produced. These are highly reactive and pollutive compounds, since they can produce chlorine atoms.[28]

4. Conclusions

A theoretical study of the addition reaction of the nitrate radical to chloroethene has been carried out. The study includes geometry optimization and characterization of the stationary points in the framework of the density functional theory, using the B3LYP functional. Also, single-point energy calculations at these geometries were made at the CASSCF level, including seven active electrons in eight active orbitals.

In the obtained mechanism, two main reaction pathways, resulting from the Markownikoff and contra-Markownikoff have been localized. Different products have been found. These are: epoxichloroethane, $ClCH(O)CH_2$, chloroethanal, $ClCH_2CHO$, nitrous acid, HNO_2, chloroethanal radical, ClCHCHO, NO_2, formaldehyde, CH_2O, ClCH, formyl chloride, ClCOH, and NO radical, nitric acid, HNO_3, chlorovinyl radical, $ClCCH_2$, acetyl chloride, CH_3CClO.

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Taking into account the mechanism proposed in this work, we can conclude that, at lower temperatures, the main products found would be epoxichloroethane and NO_2 radical as well as the Markownikoff radical adduct. At higher temperatures an equilibrium distribution between the epoxichloroethane, the Markownikoff and contra-Markownikoff radical adducts, and formyl chloride, formaldehyde, and NO radical will be produced, in agreement with Noremsaune et al.[4] and Wängberg et al.[3] The reaction has a kinetic control, being the formation of other products avoided due to higher energy barriers.

This work is one more step trying to answer the question of what is the role played by organics and what reactions are responsible for the rapid loss of organics in the atmosphere.

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Supporting Information Available: B3LYP/6−31 G* and CASSCF/6-31G* total energies in hartrees for all of the structures studied and B3LYP/6-311+G* total energies for the structures corrresponding to reactants, TS2, P2, TS4, and P4 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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