Ab Initio Study on the Mechanism of the Reactions of the Nitrate Radical with Haloalkenes: 1,2-Dichloroethene, 1,1-Dichloroethene, Trichloroethene, and Tetrachloroethene

M. Pilar Pérez-Casany, Ignacio Nebot-Gil,* and José Sánchez-Marín

Institut de Ciència Molecular, Departament de Química Física, Universitat de València, C/ Dr. Moliner, 50, 46100 Burjassot (València), Spain

Received: March 20, 2000; In Final Form: September 18, 2000

A general mechanism for the reactions of the NO_3 radical with 1,2-dichloroethene, 1,1-dichloroethene, trichloroethene, and tetrachloroethene is proposed from ab initio DFT calculations. The calculated mechanism shows three main parallel reaction pathways. For the systems where the two carbon atoms are differently substituted, the study includes both the attacks with Markownikoff and contra-Markownikoff orientation. The first reaction pathway leads to the formation of an epoxide along with the NO_2 radical, the second one to the formation of carbonyl compounds, and the third one leads, through the cleavage of the C−C bond, to the formation of carbonyl compounds with a lower number of carbon atoms. The stationary points on the potential energy surface (PES) were found by means of density functional theory (DFT) calculations with the B3LYP functional and the 6-31G* basis set. For each stationary point, the geometry was optimized and the obtained conformation was characterized as an equilibrium structure (reactant, product, or intermediate) or transition state structure.

1. Introduction

The reactivity of the NO_3 radical with unsaturated organic compounds is known to represent an important sink of these species in the night-time troposphere.[1] The reaction of NO_3 with haloalkenes proceeds in a similar way to that of the alkenes, through an electrophilic addition of the radical to the double bond.

Chloroethene compounds are widely used as solvents and intermediates in the manufacture of polymers. They are toxic and volatile and may be of major concern in local industrial areas. Reaction products can also be toxic and may be transported to the stratosphere where photolysis processes will eventually lead to the release of chlorine atoms.[2]

In two previous papers[3,4] we have studied, from a theoretical point of view, the addition reaction mechanism of the NO_3 radical to 2-butene, isobutene, 2-methyl-2-butene, 2,3-dimethyl-2-butene,[3] and vinyl chloride.[4] When the double bond is substituted with methyl groups, three main parallel reaction pathways are found after the formation of a radical adduct. Scheme 1 outlines some of the energetically reasonable possibilities for the decomposition of the reactants.

The first step in this proposal of reaction mechanism involves the formation of a radical adduct. In this pathway, the formation of a van der Waals complex is supposed, similarly to the case of the NO_3 radical addition reaction to ethylene.[5] From the radical adduct, three energetically main reaction pathways originate. The first one leads, through the closing of the angle O−C−C, to an epoxide and NO_2 radical. The second one gives carbonyl compounds and NO_2 radical through a 1,2-hydrogen shift, and the third reaction pathway leads to carbonyl compounds with lower number of carbon atoms and NO radical through the cleavage of the C−C bond.

When a chlorine atom substitutes a hydrogen atom of the ethylene, to give vinyl chloride, the reaction mechanism obtained with the alkyl compounds is fulfilled.[4] In this reaction mechanism, other reaction pathways appear, leading to nitrous and nitric acids, but they are very unlikely from both thermodynamic and kinetic points of view. The main products predicted in this theoretical work are epoxichloroethane, chloroethanal, nitrous acid, formaldehyde, formyl chloride, acetyl chloride, nitric acid, NO, and NO_2.

Berndt and Böge[6,7] studied the reaction between NO_3 and several monoalkenes and they found epoxides, nitroxicarbonyls, ketones, and aldehydes as main products. In these works,[6,7] a reaction mechanism is proposed in which two parallel reaction pathways lead from a radical adduct to an epoxide and NO_2, by one hand, and to carbonyl compounds and NO_2 through a 1,2-hydrogen shift, by the other hand. These reaction pathways have been also found in the theoretically proposed mechanism.[3,4] A third reaction pathway including the addition of oxygen molecules is also proposed.[6,7] After the oxygen addition, several reaction pathways are suggested, leading to the formation of nitroxycarbonyl compounds, carbonyl compounds, and NO_2, through the cleavage of the C−C bond. In our theoretical proposed reaction mechanism, these products are obtained directly, without further addition of oxygen molecules, in a third reaction pathway.[3,4] Nuremsaune et al.[8] in their experimental study of the NO_3 reaction with several chloroethenes in aerobic conditions, propose as major products formaldehyde, formyl chloride, acid chlorides, and phosgene. They do not find epoxides, but in a later study[9] in anaerobic conditions and at low pressures, they suggest its possible formation. Wängber et al.,[10] with chlorinated butenes, suggest as main products acid chlorides, aldehyde, and NO_2 when the chlorine atom is placed on the double bond.

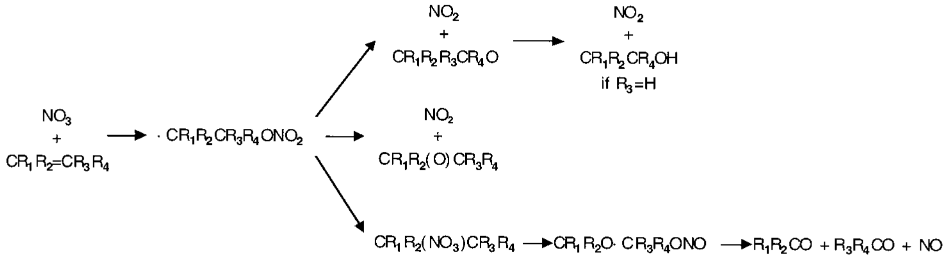
The aim of this work is to ascertain, by means of theoretical calculations, the addition mechanism of NO_3 to all the CCl_nH_{4-n}

---

* Corresponding author. E-mail: Ignacio.Nebot@UV.es; FAX: +34 398 3156.

10.1021/jp001046h CCC: $19.00

SCHEME 1



($n \geq 2$), in particular the addition step and all the unimolecular steps following the addition. This information will be valuable for the interpretation of the model kinetic studies made in anaerobic conditions and at low pressures of radical reactions with interest in tropospheric chemistry. These model studies are carried out to obtain the whole reaction rates of disappearance of atmospheric pollutants such as haloalkenes and the NO_3 itself. In this work, we present the theoretical study on the mechanism of the addition reaction of the nitrate radical to 1,2-dichloroethene, 1,1-dichloroethene, trichloroethene, and tetrachloroethene. This study intends also to ascertain whether the mechanism proposed for the methyl-substituted ethenes[3] is fulfilled in the case of the chlorine substituted unsaturated compounds. Another goal of this work is to provide a theoretical explanation for the dependence of the rate constant on the substitution degree of the double bond.

2. Computational Details

Density functional theory ab initio studies of the whole potential energy hypersurface (PES) have been performed, and the stationary points have been classified according to their significance for the reaction mechanisms, in a similar way to previous papers.[3,4,11,12] We have chosen the B3LYP functional, which is based on the Becke-3 parametrization adiabatic connection method (ACM), and consists of a combination of the Slater,[13] Hartree–Fock,[14] and Becke[15] exchange functional, the Vosko, Wilk, and Nusair (VWN) local correlation functional,[16] and the Lee, Yang, and Parr[17] nonlocal correlation functional. B3LYP has proven to be a good compromise between accuracy and the feasibility of optimizing complex structures with an all-electron methodology and several heavy atoms. In any case, we expect good energy values for equilibrium geometries. However, it is well known that DFT methods tend to give transition states energy values 4–10 kcal/mol too low, and the same is expected for the obtained barrier heights.

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 eigenfollowing and transition state techniques[18] have been used for the minima and transition states geometry optimizations, respectively. All the zero-point energy corrections have been calculated at B3LYP/6-31G* level without scaling.

The Berny analytical gradient[19] has been used for geometry optimization of the minima and transition states at B3LYP level. The basis set used in the calculations has been 6-31G*[20,21] which has polarization functions (d-type) on non-hydrogen atoms.

The calculations have been performed with the GAUSSIAN 94 series of programs[22] in the two IBM RS6000–590 and an IBM SP2 of the Theoretical Chemistry Group of the University of Valencia and with an SGI Origin 2000 of the University of Valencia.

3. Results and Discussion

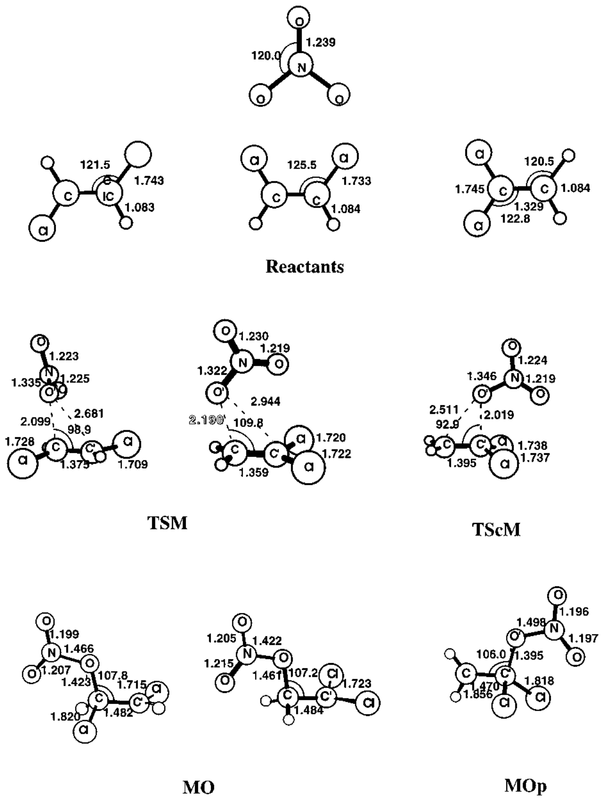
A reaction mechanism for the NO_3 addition reaction to 1,2-dichloroethene, 1,1-dichloroethene, trichloroethene, and tetrachloroethene is proposed. Only those stationary points on the PES that can be related with a chemical reaction have been included in the proposal of reaction mechanism. Because of the similarities shown by the four mechanisms studied, we have summarized them in a unique generalized proposal for the addition mechanism of the NO_3 radical to all unsaturated haloorganic compounds.

In all cases, three main reaction pathways have been found. The first one leads to an epoxide formation, the second to aldehydes and acid chloride formation, and the third one, through the cleavage of the C–C bond, leads to chloride carbonyl compounds. Which products are obtained depends on the substitution of the double bond. Thus, the products found are:

- for the 1,2-dichloroethene: 1,2-dichloroepoxiethane, dichloroethanal, chloroacetyl chloride, and chloroformyl.
- for the 1,1-dichloroethene: 1,1-dichloroepoxiethane, dichloroethanal, dichloroformyl, and formaldehyde.
- for the trichloroethene: trichloroepoxiethane, dichloroacethyl chloride, chloroformyl, and carbonyl chloride.
- for the tetrachloroethene: tetrachloroepoxiethane and carbonyl chloride.

In all of the mechanisms, NO_2 and NO are also obtained as products.

3.1. Adduct Formation. In a similar way to the case of the addition mechanism between the nitrate radical and the ethene[5] and propene[12] and several other alkyl substituted ethenes,[3] the first step in the general mechanism is the formation of a radical adduct, MO. From MO, different reaction pathways start. Prior to the adduct formation, a van der Waals complex is assumed to be formed between the reactants. We have not been able to find this complex, although this is not important, due to its small relevance in the reaction mechanism.[23] However, the transition state that leads from the hypothetical van der Waals complex to the radical adduct has been found. The transition state connecting the van der Waals complex with the Markownikoff-oriented radical adduct, TSM, for the 1,2-dichloroethene (R1), 1,1-dichloroethene (R2), trichloroethene (R3), and tetrachloroethene (R4) reactions, is at 1.63 (R1), 0.53 (R2), 0.71 (R3), and 7.29 (R4) kcal/mol relative to reactants, respectively. The notation for the different energy values along all the work will follow this same scheme. These transition states show imaginary frequencies of 274i (R1), 247i (R3), and 441i (R4) cm^{-1}, respectively. The transition vectors are related with the C–O bond formation. In the case of the 1,1-dichloroethene, we have not been able to completely optimize the TSM, so an estimation was made by fixing the O′–C distance and by optimizing the rest of the parameters (see Figure 1) and there are two imaginary frequencies. The first one, (123i cm^{-1}), corresponds to the symmetric stretching movement between the oxygen O′ and the carbon atom C, and the second one, (23i cm^{-1}), corresponds to

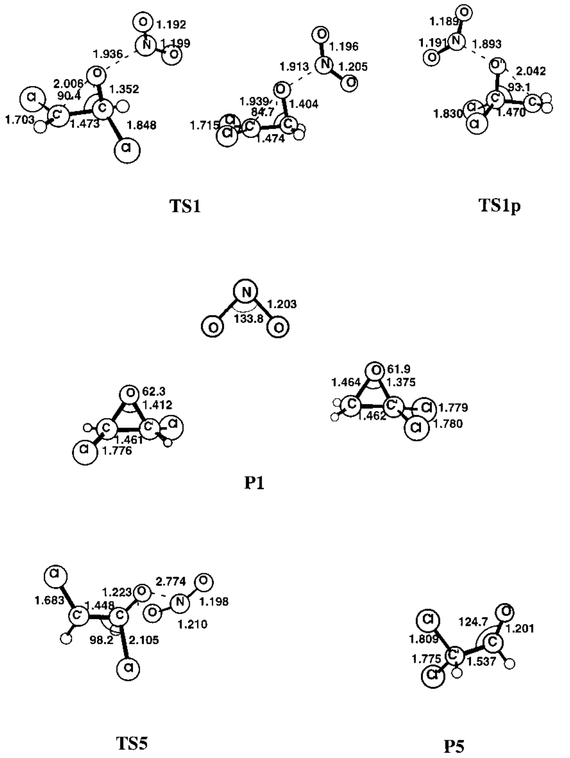


Reactants

TSM **TScM**

MO **MOp**

Figure 1. Addition reaction of NO_3 to 1,2-dichloroethene and 1,1-dichloroethene: B3LYP/6-31G* optimized geometry of the PES stationary points for the adduct formation reaction pathway. White atoms correspond to nonrelevant hydrogen atoms and the shadow parameters to fixed distances.



TS1 **TS1p**

P1

TS5 **P5**

Figure 2. Addition reaction of NO_3 to 1,2-dichloroethene and 1,1-dichloroethene: B3LYP/6-31G* optimized geometry of the PES stationary points for the epoxide, dichloroethanal, and trichloroethanal formation reaction pathway. White atoms correspond to nonrelevant hydrogen atoms.

the relative orientation between of the two fragments and can be neglected, since it appears due to the constrained optimization. For the 1,2-dichloroethene, we show only the results corresponding to the trans conformation, which is the most stable conformer. In any case, after the NO_3 addition, we can assume almost free rotation around the C−C bond.

In the compounds where the two double bond carbon atoms are differently substituted, the reaction pathway leading to the contra-Markownikoff-oriented adduct, MOp, has been also found. The transition state involved, TScM, is at 11.08 (R2) and 8.59 (R3) kcal/mol and shows an associated imaginary frequency of 510i (R2) and 468i cm^{-1} (R3). The B3LYP/6-31G* optimized geometry of all the stationary points found in this pathway is shown in Figures 1 and 1S. From either MO or MOp radical adduct, three reaction pathways start, leading different products.

3.2. Epoxide Formation. Similarly to the reaction mechanism for the alkyl substituted double bonds,[3,12] for the chlorine substituted ethenes, a reaction pathway leading exothermically by 19.41 (R1), 16.39 (R2), 17.42 (R3), and 24.12 (R4) kcal/mol from MO to epoxide and NO_2 radical, P1, is found. The transition state connecting MO with P1, TS1, is at −4.49 (R1), 0.73 (R2), −4.41 (R3), and −6.95 (R4) kcal/mol and shows an imaginary frequency of 540i (R1), 659i (R2), 504i (R3), and 310i (R4) cm^{-1}. Therefore, the barrier heights involved are 10.81 (R1), 16.68 (R2), 12.28 (R3), and 3.84 (R4) kcal/mol. The transition vectors involve the closure of the C−C−O angle and the cleavage of the NO bond.

From MOp a reaction pathway leads also to the epoxide formation in an exothermic way by 25.49 (R2) and 23.87 (R3) kcal/mol. The transition state involved, TS1p is at −2.15 (R2) and −5.13 (R3) kcal/mol and shows an imaginary frequency of 485i (R2) and 389i (R3) cm^{-1}. The barrier heights involved are then 6.16 (R2) and 5.11 (R3) kcal/mol. The contra-Markownikoff-oriented pathway leading to the epoxideis therefore more favorable than the Markownikoff pathway, in opposition to that found for the alkyl substituted double bond case.[3] This is due to both steric hindrance and electrostatic repulsion between the chlorine atoms and the oxygen atom, all of them negatively charged, which made more favorable the oxygen displacement from a Cl_2C- group toward a ClHC− or H_2C- ones, than the inverse process.

Figures 2 and 2S show the B3LYP/6-31G* optimized geometry of the stationary points involved in this step. In all four mechanisms, the reaction coordinate involves the closure of the O−C−C angle and the enlargement of the O−N distance.

3.3. Dichloroethanal and Trichloroethanal Formation. In the case of the 1,2-dichoroethene and tricloroethene, an exothermic pathway by 35.65 (R2), 31.83 (R3) kcal/mol, leading from MO to dichloroethanal and trichloroethanal formation, has been found. The reaction coordinate involves a 1,2 chlorine shift from the C′ carbon atom to the C″ one (see Figures 2 and 2S). The transition state involved, TS5, is at 6.13 (R2) and −5.07 (R3) kcal/mol and has an imaginary frequency of 307i (R2) and 306i (R3) cm^{-1}. Figures 2 and 2S show the B3LYP/6-31G* optimized geometry of the stationary points involved in this step. The transition vector involves the Cl atom migration from a carbon atom to the other and the cleavage of the N−O′ bond. However, the synchronization is not the same for R2 and R3. In R2, the N−O′ bond breaks before the Cl migration, while in R3 the order is the reverse.

3.4. Acid Chloride Formation. A second pathway leads to the formation of acid chlorides from the initial radical adduct in the cases of the 1,2-dichloroethene and trichloroethene, whereas it leads to aldehydes in the case of the 1,1-dichloro-

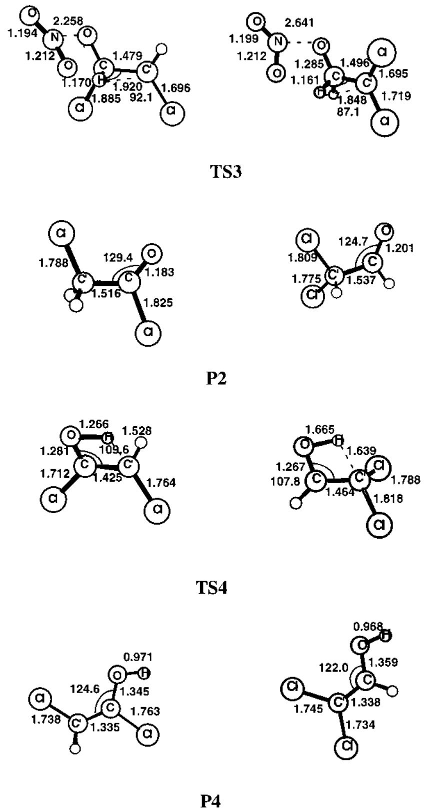


Figure 3. Addition reaction of NO_3 to 1,2-dichloroethene and 1,1-dichloroethene: B3LYP/6-31G* optimized geometry of the PES stationary points for the acid chloride formation reaction pathway. White atoms correspond to nonrelevant hydrogen atoms.

ethene. In all of the mechanisms, NO_2 is also found as a product. These products are named in the global mechanism as P2. In the case of tetrachloroethene, this reaction pathway has not been found due to the hindrance effect of the chlorine atoms when 1,2-shift is produced. From P2 a reaction pathway leading to the enol form of the carbonyl compound has been found.

The first step in this reaction pathway is produced exothermically by 50.38 (R1), 33.54 (R2), and 44.45 (R3) kcal/mol, while the second one is produced in an endothermic way by 24.04 (R1), 12.05 (R2), and 18.52 (R3) kcal/mol. The transition state that connects MO with P2, TS3, is at 10.75 (R1), 10.91 (R2), and 5.61 (R3) kcal/mol and shows an imaginary frequency of 323i (R1), 627i (R2), and 254i (R3) cm^{-1}. The transition state involved in the path from the keto form to the enol one, TS4, is at 7.35 (R1), 17.26 (R2), and 11.88 (R3) kcal/mol and has an imaginary frequency of 2193i (R1), 1761i (R2), and 1865i (R3) cm^{-1}.

The transformation of MO in P2 is carried out through a transition vector involving a C−C 1,2-hydrogen shift and the enlargement of the O−N distance (see Figures 3 and 3S). The B3LYP/6-31G* optimized geometry of the stationary points involved in this pathway is shown in Figures 3 and 3S.

The corresponding contra-Markownikoff reaction pathway in the case of the 1,1-dichloroethene and trichloroethene has not been found. This step would involve a chlorine shift, and therefore can be considered as very unlikely due to the hindrance effect.

3.5. C−C Cleavage. The third pathway in the global reaction mechanism leads in a first step to the formation of an intermediate with a five-membered ring structure, M2. Then, in a second step, it leads to the nitrite alkoxy radical formation, P6, and eventually, through the cleavage of the C−C bond, to the formation of chloroformyl, carbonyl chloride, and NO radical, P7. These three steps involve the corresponding three transition states, TS10, TS8, and TS9.

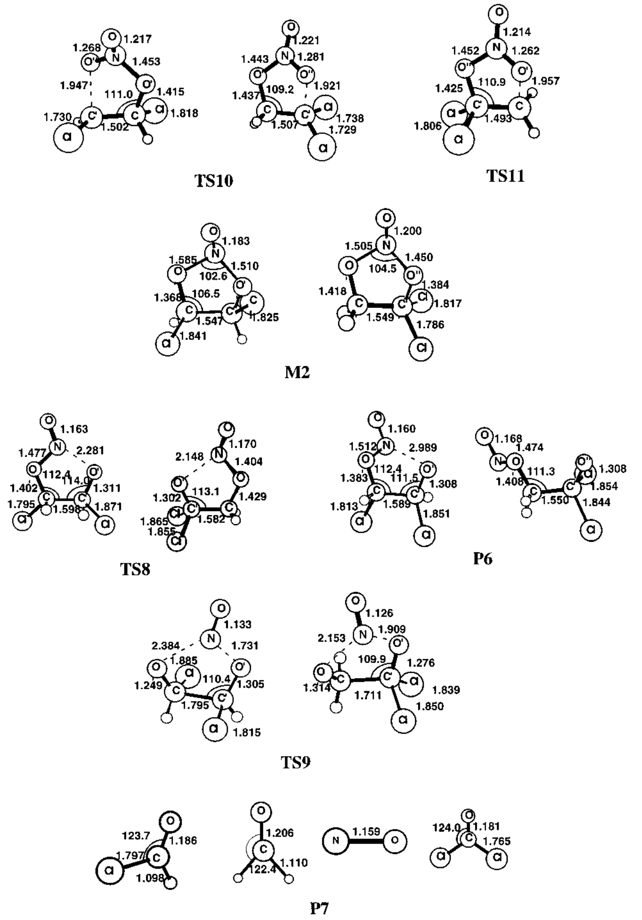


Figure 4. Addition reaction of NO_3 to 1,2-dichloroethene and 1,1-dichloroethene: B3LYP/6-31G* optimized geometry of the PES stationary points for the C−C cleavage reaction pathway. White atoms correspond to nonrelevant hydrogen atoms.

The reaction coordinate leading to M2 from MO involves mainly the change in the dihedral angle O−N−O−C. This first step is exothermic by 15.05 (R1), 17.54 (R2), 7.97 (R3), and 11.40 (R4) kcal/mol. The transition state involved, TS10, is at 2.99 (R1), 3.36 (R2), 4.80 (R3), and 8.28 (R4) kcal/mol and shows an imaginary frequency of 738i (R1), 734i (R2), 741i (R3), and 808i (R4) cm^{-1}. In the case of the 1,1-dichloroethene (R2) and trichloroethene (R3), a pathway leading from MOp to M2, through a transition state, TS11, has also been found. The reaction coordinate involved is similar to the corresponding Markownikoff reaction pathway. The transition state is at 8.01 (R2) and 8.58 (R3) kcal/mol and shows an imaginary frequency of 775i (R2) and 768i (R3) cm^{-1}.

The second step in this pathway goes from M2 to P6, and the transition vector involved can be described by the enlargement of the N−O distance (see Figures 4 and 4S). This step is endothermic for R2 by 1.81 kcal/mol and exothermic for the other cases by 1.91 (R1), 6.29 (R3), and 5.53 (R4) kcal/mol. The transition state involved, TS8, is at −27.44 (R1), −27.93 (R2), −22.11 (R3), and −22.50 (R4) kcal/mol and shows an imaginary frequency of 69i (R1), 79i (R2), 51i (R3), and 92i (R4) cm^{-1}.

The final step leading to the products involves the cleavage of the C−C bond; the geometry of the transition state involved in this step is quite similar in all the mechanisms studied. This

TABLE 1: PES Stationary Points for the $NO_3 + C_2H_{4-n}Cl_n$ ($n = 2, 3, 4$) Reaction Mechanism: Experimental Enthalpies of Formation (in kcal/mol), B3LYP/6-31G(d) Relative to Reactants Energies, ΔE_R, (in kcal/mol), and Experimental Relative to Reactants Enthalpies (in kcal/mol)[a]

PES stationary points	1,2-dichloroethene			1,1-dichloroethene			trichloroethene			tetrachloroethene		
	$\Delta H_f°$	ΔE_R (B3LYP)	$\Delta H_r°*$	$\Delta H_f°$	ΔE_R (B3LYP)	$\Delta H_r°*$	$\Delta H_f°$	ΔE_R (B3LYP)	$\Delta H_r°*$	$\Delta H_f°$	ΔE_R (B3LYP)	$\Delta H_r°*$
reactants	19.11[b] 18.73[b]	0.00 (cis) 0.10 (trans)	0.00 −0.38	18.25[b]	0.00	0.00	15.69[b]	0.00	0.00	15.02[b]	0.00	0.00
TSM		1.63			(0.53)			0.71			7.29	
TScM					11.08			8.59				
MO		−15.30			−17.41			−16.69			−10.79	
TS1		−4.49			0.73			−4.41			−6.95	
P1		−34.71			−33.80			−34.11			−34.91	
TS3		10.75			10.91			5.61			8.28	
P2		−65.68			−50.95			−61.14				
TS4		7.35			17.26			11.88				
P4		−41.64			−38.90			−42.62				
TS5		6.13						−5.07				
P5		−50.95					−39.09[b]	−48.52	−54.78			
MOp					−8.31			−10.24				
TS1p					−2.15			−5.13				
TS10		2.99			3.36			4.80				
TS11					8.01			8.58				
M2		−30.35			−34.95			−24.66			−22.19	
TS8		−27.44			−27.93			−22.11			−22.50	
P6		−32.26			−33.14			−30.95			−27.72	
TS9		−32.46			−24.65			−30.84			−27.81	
P7		−92.70		−56.56[b]	−71.12	−74.81		−86.71		−83.00[b]	−94.77	−98.02

[a] Zero point correction has been included in the B3LYP energy differences. [b] Reference 24.

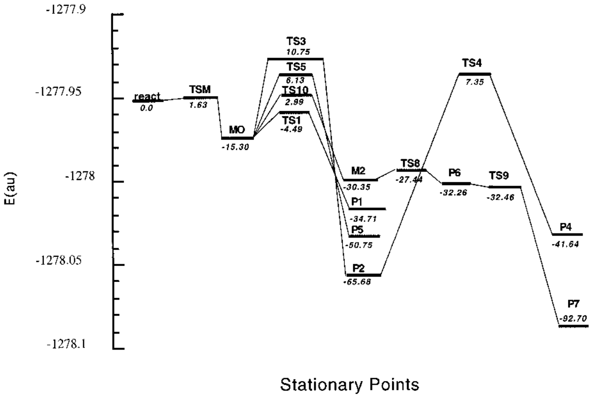


Figure 5. Schematic reaction profile for the NO_3 + 1,2-dichloroethene addition reaction. The B3LYP/6-31G* energy values (in kcal/mol) are relative to reactants.

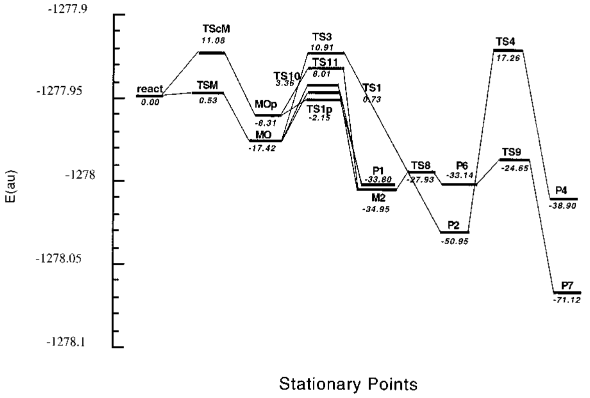


Figure 6. Schematic reaction profile for the NO_3 + 1,1-dichloroethene addition reaction. The B3LYP/6-31G* energy values (in kcal/mol) are relative to reactants.

last step leads to the formation of the final products, P7, in an exothermic way by 60.44 (R1), 37.98 (R2), 55.76 (R3), and 67.05 (R4) kcal/mol. The reaction coordinate involves the enlargement of the N−O distance in order to form NO and the shortening of the O−C distances to form the carbonyl group (see Figures 4 and 4S). The transition state connecting both minima, TS9, is at −32.46 (R1), −24.65 (R2), −30.84 (R3), and −27.81 (R4) kcal/mol and shows an imaginary frequency of 379i (R1), 364i (R2), 372i (R3), and 487i (R4) cm^{-1}. The B3LYP/6-31G* optimized geometry of the stationary points involved in these steps are shown in Figures 4 and 4S.

3.6. Reaction Profiles and E_a. Table 1S show the B3LYP/6-31G* energies of all the stationary points found in the reaction mechanism of the addition reaction of the nitrate radical to 1,2-dichloroethene, 1,1-dichloroethene, trichloroethene, and tetrachloroethene. The experimental formation and reaction enthalpies[24] of products and the relative to reactants energies are shown in Table 1. Schematic energy profiles for these reactions are depicted in Figures 5 to 8.

It must be pointed out that, as shown in all the schematic energy profiles (Figures 5−8), an initial barrier leads from the reactants to the Markownikoff-oriented radical adduct. In those mechanisms where an contra-Markownikoff-oriented reaction is also possible, an initial barrier has also been found leading to the corresponding adduct. These transition states are higher in energy than the reactants, contrary to that found for the methyl-substituted compounds.[3] Therefore, the rate coefficients for the chlorine-substituted compounds are lower than those corresponding to alkyl substituted compounds in agreement with experimental data.[1] Because the experimental E_a is obtained from the NO_3 disappearance reaction, the barrier leading to the radical adduct is the theoretically determined one to be compared with it. The experimental E_a for the 1,2-dichloroethene, 1,1-dichloroethene, and trichloroethene reactions are, respectively, 4.78[25] (R1), 3.59[25] (R2), and 4.04[9] (R3) kcal/mol. The theoretically determined energy barriers for the Markownikoff reaction pathway are 1.63 (R1), 0.53 (R2), and 0.71 (R3) kcal/mol. The B3LYP results follow the same trend as the experimental results,

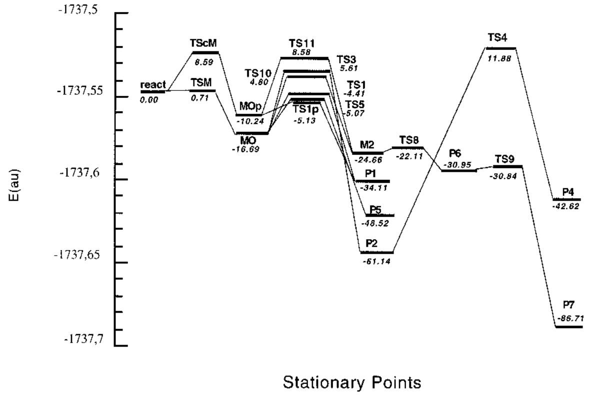


Figure 7. Schematic reaction profile for the NO_3 + trichloroethene addition reaction. The B3LYP/6-31G* energy values (in kcal/mol) are relative to reactants.

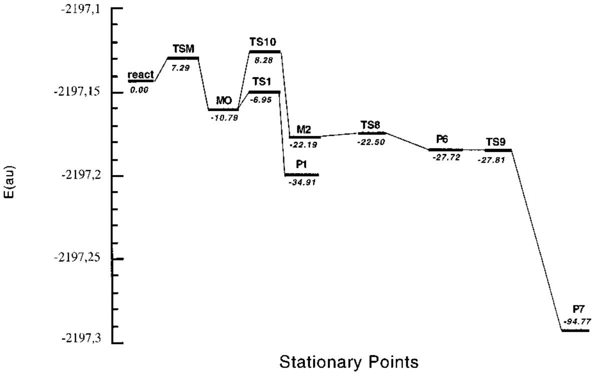


Figure 8. Schematic reaction profile for the NO_3 + tetrachloroethene addition reaction. The B3LYP/6-31G* energy values (in kcal/mol) are relative to reactants.

and they are within the confidence margin of 0.5 eV of the experimental values. So, the theoretically proposed mechanism can be assumed to be in good agreement with the experimental studies.

It is also to point out that the transition states TScM (R2 and R3) and TSM (R4) have larger energies than the TSM transition states for R1, R2, and R3. Therefore, we can conclude that when the NO_3 addition takes place on a carbon atom which is substituted with *two* chlorine atoms, steric hindrance as well as electrostatic interactions between negatively charged groups govern this addition process. This explains also why the tetrachloroethene shows the slowest reaction rate.[1]

In all cases, among all the possible reaction steps starting from each adduct, the lowest energy barrier corresponds to the pathway leading to the formation of epoxide and NO_2; therefore, these are the more kinetically favored products. This way, the system will require an initial energy to overcome the first energy barrier to give the radical adduct and, then, epoxide and NO_2. In aerobic conditions, the radical adduct would be attacked by oxygen molecules giving peroxides.[7] The most stable products from a thermodynamic point of view correspond in all cases to those products resulting from the cleavage of the C−C bond. However, the energy barriers involved are higher than the initial one. Then, only at higher temperatures an equilibrium distribution between the epoxide, NO_2, the radical adduct, and the products resulting of the C−C bond cleavage will be obtained. This equilibrium will be displaced to these last products due to their higher stability. The height of the barriers leading to the acid chlorides and halo aldehydes prevents its formation, except at high temperatures, and this step will not be very probable in the troposphere.

The reaction control is then based on barrier differences, i.e., the reaction will be kinetically controlled. If the experimental conditions made available other products, the thermodynamic stability will play the role of determining the yield of each of them.

The four mechanisms studied show no qualitative differences due to the effect of the number of chlorine substituents on the double bond, beyond the possibility of a contra-Markownikoff-oriented pathway, possible only for 1,1-dichloroethene and trichloroethene. In general, as the substituent number on the double bond increases, the higher the initial barriers are and, then, lower the rate constants, in agreement with experimental data.[26] The analogous methyl substituted compounds also follow this trend.[3] However, the 1,2-dichloroethene is an exception to this rule, because the experimental E_a as well as the theoretically determined energy barrier value that leads from reactants to the Markownikoff-oriented radical adduct are greater than the one that a priori would correspond to this compound. Thus, the reaction rate trend is 1,1-Dichloroethene> Trichloroethene> 1,2-Dichloroethene> Tetrachloroethene.

It is to point out the agreement of the theoretical results with the experimental results in this point, contrary to the results obtained from a frontier orbital analysis,[9] that gives the tetrachloroethene as more reactive toward the NO_3 than the trichloroethene.

As in a previous work,[4] the rate coefficient values calculated from molecular parameters have been estimated following the transition state theory, as[27]

$$k = \frac{kT}{h}\frac{Q^{\neq}}{Q}\mathrm{e}^{-E_0/RT}$$

where Q and $Q^{\neq}$ are the partition functions for the reactants and transition state, respectively, and E_0 the theoretically determined energy barrier for the disappearance of NO_3, which is the process followed in the experimental kinetic studies. Table 2 shows the theoretically determined values for the rate coefficient at 298.15 K for this reaction leading to the formation of the radical adduct, through the TSM and the TScM transition

TABLE 2: B3LYP/6-31G* Energy Barriers, E_0, Theoretically Estimated Rate Coefficients at B3LYP/6-31G*, Experimental Activation Energy, E_a, and Experimental Rate Constants for the Reactions between the NO_3 and 1,2-Dichloroethene, 1,1-Dichloroethene, Trichloroethene, and Tetrachloroethene, Respectively[a]

mechanism	orientation	E_0 (kcal/mol)	k_{AB}(theor) ($cm^3 molec^{-1} s^{-1}$)	E_a(exp) (kcal/mol)	k_{AB}(exp) ($cm^3 molec^{-1} s^{-1}$)
1,2-dichloroethene		1.63	0.3×10^{-16}	4.78 ± 0.1^{b}	$(1.2 \pm 0.5) \times 10^{-16\,b}$
1,1-dichloroethene	Markownikoff	(0.53)	(0.1×10^{-15})	3.59 ± 0.5^{b}	$(1.2 \pm 0.3) \times 10^{-15\,b}$
	contra-Markownikoff	11.08	1.6×10^{-24}		
trichloroethene	Markownikoff	0.71	0.4×10^{-16}	4.04 ± 0.4^{c}	$(1.06 \pm 0.08) \times 10^{-16\,c}$
	contra-Markownikoff	8.59	0.6×10^{-22}		
tetrachloroethene		7.29	3.9×10^{-22}		$<4 \times 10^{-17\,d}$

[a] Values in parentheses correspond to estimated stationary points (see text). [b] Reference 24. [c] Reference 9. [d] Reference 1.

states, where the two orientations are available. In Table 2 are also included the calculated value for the considered barrier energy, the experimental activation energy values, and the experimentally obtained rate constants.

The theoretical values of the rate coefficients are in good agreement with the experimental values. The contra-Markownikoff-oriented attack is practically forbidden from the kinetic point of view, in relation to the corresponding Markownikoff one, especially for the 1,1-dichloroethene case, because the difference between the involved energy barriers is greater. Thus, the rate constants for the contra-Markownikoff-oriented reactions are several orders of magnitude smaller than the Markownikoff-oriented reactions. Therefore, the attack of the nitrate radical to a carbon atom where two chlorine atoms are present as substituents is very slow when compared with the attack on other carbon atoms not substituted or where the substituents are methyl groups. In tetrachloroethene, both carbon atoms are doubly substituted with chlorine atoms, and this justify why the experimental value of the rate constant is very small and not well determined experimentally, representing only an upper limit to the real value.[9] Since the rate coefficient value that has been theoretically obtained is 5 orders of magnitude lower than this limit, we can also conclude that this value is in agreement with the experimental estimations.

4. Conclusions

A theoretical study of the addition reaction of the NO_3 radical to 1,2-dichlroethene, 1,1-dichloroethene, trichloroethene, and tetrachloroethene has been carried out. This study includes geometry optimization and characterization of the PES stationary points with the density functional theory by using the B3LYP functional. In the proposed general reaction mechanism, three main reaction pathways have been found. Where possible, both the Markownikoff- and contra-Markownikoff-oriented attacks have been obtained. The first reaction pathway leads to the epoxide and NO_2 radical formation, which are the experimentally proposed products,[28] in anaerobic conditions and at low pressures. The second one leads to the aldehyde and acid chloride formation, and the third, through the cleavage of the C−C bond, to chloride carbonyl compounds. An initial transition state leads from the reactants to a radical adduct. In all four cases, the transition state involved is higher in energy than the reactants. The energy of the initial barrier is linked to the number of chlorine atoms linked to carbon atom, due to steric effects and to electrostatic repulsion between negatively charged groups (Cl atoms and NO_x group). The products found are:

- for the 1,2-dichloroethene: 1,2-dichloroepoxiethane, dichloroethanal, chloroacetyl chloride, and chloroformyl.
- for the 1,2-dichloroethene: 1,1-dichloroepoxiethane, dichloroethanal, dichloroformyl, and formaldehyde.
- for the trichloroethene: trichloroepoxiethane, dichloroacethyl chloride, chloroformyl, and carbonyl chloride.
- for the tetrachloroethene: tetrachloroepoxiethane and carbonyl chloride. In all the mechanisms, NO_2 and NO are also obtained as products.

Taking into account experimental data and the mechanism proposed in this study we can conclude that, at low temperatures, epoxides, NO_2, and the radical adducts will be formed. In aerobic conditions, oxygen molecules will add to the radical adduct to form peroxides. At higher temperatures, the reaction pathway leading to C−C cleavage products becomes available, and then an equilibrium distribution is produced between the epoxide, NO_2, radical adducts, and the products resulting from the C−C bond cleavage, i.e., carbonyl chloride compounds and NO. Because the latter products are the most stable from a thermodynamic point of view, they will be the main products. This mechanism could then explain the experimental data.[7,28]

If the temperature becomes still higher, as in the combustion processes, the system could have enough energy to overcome the barrier to form carbonyl compounds through a 1,2-hydrogen shift, but this pathway will not be very probable in the troposphere.

Acknowledgment. M.P.P. thanks the Ministerio de Educación y Ciencia for a personal grant. This work was supported by Spanish DGICYCT (project PB97-1381 and INF99-02-134).

Supporting Information Available: Figures 1S to 4S including the optimized geometries of the PES stationary points for the reaction mechanism of the NO_3 addition to trichloroethene (R3), and tetrachloroethene (R4), and Table 1S including the B3LYP/6-31G(d) total energies, in a.u., for all the stationary points found. This information is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Wayne, R. P.; Barnes, I.; Biggs, P.; Burrows, J. P.; Canosa-Mas, C. E.; Hjorth, J.; Bras, G. L.; Moortgat, G. K.; Perner, D.; Poulet, G.; Restelli, G.; Sidebottom, H. *Atmos. Environ.* **1991**, *25A*, 1−203.

(2) Wilson, S. R.; Crutzen, P. J.; Schuster, G.; Griffith, D. W. T.; Helas, G. *Nature* **1988**, *334*, 689−691.

(3) Pérez-Casany, M. P.; Nebot-Gil, I.; Sánchez-Marín, J. *J. Phys. Chem. A*, in press.

(4) Pérez-Casany, M. P.; Nebot-Gil, I.; Sánchez-Marín, J. *J. Am. Chem. Soc.*, in press.

(5) Pérez-Casany, M. P.; Nebot-Gil, I.; Sánchez-Marín, J.; Crespo-Crespo, R., to be published.

(6) Berndt, T.; Böge, O. *Ber. Bunsen-Ges. Phys. Chem.* **1994**, *98*, 869−871.

(7) Berndt, T.; Böge, O. *J. Atmos. Chem.* **1995**, *21*, 275−291.

(8) Noremsaune, I. M. W.; Hjorth, J.; Nielsen, C. J. *J. Atmos. Chem.* **1995**, *21*, 223−250.

(9) Noremsaune, I. M. W.; Langer, S.; Ljungström, E.; Nielsen, C. J. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 525−531.

(10) Wängberg, I.; Ljungström, E.; Hjorth, J.; Ottobrini, G. *J. Phys. Chem.* **1990**, *1990*, 8036−8040.

(11) Pérez-Casany, M. P.; Nebot-Gil, I.; Sánchez-Marín, J.; Tomás-Vert, F.; Martínez-Ataz, E.; Cabañas-Galán, B.; Aranda-Rubio, A. *J. Org. Chem.* **1998**, *63*, 6978−6983.

(12) Pérez-Casany, M. P.; Nebot-Gil, I.; Sánchez-Marín, J., *J. Phys. Chem.* **2000**, *104*, 6277.

(13) Slater, J. C. *Quantum Theory of Molecules and Solids*; McGraw-Hill: New York, 1974; Vol. 4.

(14) Fock, V. *Z. Physic* **1930**, *61*, 126.

(15) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(16) Vosko, S. H.; Wilk, L.; Nusair, M. *J. Chem. Phys.* **1987**, *87*, 5968.

(17) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 385.

(18) Baker, J. *J. Comput. Chem.* **1986**, *7*, 385.

(19) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.

(20) Hariharan, P.; Pople, J. *Chem. Phys. Lett.* **1972**, *16*, 217.

(21) Hehre, W.; Radom, L.; Schleyer, P.; Pople, J. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

(22) 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.; González, C.; Pople, J. A.; revision d.3. ed.; Technical report, Gaussian Inc.: Pittsburgh, PA, 1995.

(23) García-Cruz, I.; Ruiz-Santoyo, M. E.; Alvarez-Idaboy, J. R.; Vivier-Bunge, A. *J. Comput. Chem.* **1999**, *20*, 845.

(24) Lide, D. R. *Handbook of Chemistry and Physics*; CRC Press: 1996.

(25) Cabañas-Galán, B.; Marston, G.; Wayne, R. P. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1185−1189.

(26) Atkinson, R.; Baulch, D. L.; Cox, R. A.; R. F. Hampson, J.; Kerr, J. A.; Rossi, M. J.; Troe, J. *J. Phys. Chem. Ref. Data* **1997**, *26*, 1329−1499.

(27) Benson, S. W. *Thermochemical Kinetics*; Wiley-Interscience: 1976.

(28) Wille, U.; Schindler, R. N. *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 1447−1453.