



Experimental and theoretical study of the reactions of O(³P) with 3-chloropropene and 2-chloropropene between 298 and 359 K

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ARTICLE INFO

Article history:

Received 7 September 2009

In final form 21 October 2009

Available online 24 October 2009

ABSTRACT

The temperature dependences of the rate coefficients of the gas-phase reactions of O(³P) atoms with CH₂=CHCH₂Cl and CH₂=CClCH₃ were studied in the range 298–359 K, using the discharge flow-chemiluminescence technique. The Arrhenius expressions obtained (in units of cm³ molecule⁻¹ s⁻¹) were: $k_1 = (1.96 \pm 0.33) \times 10^{-10} \exp[(-1476 \pm 56)/T]$ and $k_2 = (9.11 \pm 0.17) \times 10^{-11} \exp[(-1007 \pm 61)/T]$ with E_a in J mol⁻¹. Theoretical calculations at different levels of theory were carried out. Both, theoretical and experimental results, support the conclusion that addition of O(³P) to the less substituted carbon atom of the double bond of the studied chloropropenes, is the main pathway of the reactions.

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1. Introduction

The electrophilic addition of the oxygen atom, O(³P), to halogenated alkenes is of interest in the context of chemical oxidative processes in atmospheric and combustion chemistry [1].

Reactions of ground-state oxygen atoms, O(³P), with alkenes are both of fundamental and practical importance. O(³P) reactions are necessary to accurately model the early stages of smog formation in urban areas and are often important in atmospheric pressure chamber studies of alkene reactions with OH. O(³P) reactions are also of central importance in combustion chemistry and serve as prototype systems for the addition reactions to the C=C bond. Although a substantial body of kinetic data exists for O atom reactions with a variety of alkenes, only limited information is available for haloalkenes, most of which has been reviewed by Cvetanovic [2].

Halogenated alkenes are volatile organic compounds (VOCs) widely used as degreasing agents and industrial solvents, as well as in the PVC and PVCD industry making up a significant part of disposable wastes [3].

As part of a systematic study of O(³P) atom reactivity, we report here the temperature dependence of the absolute rate coefficients for the following reactions:



The experiments were carried out in a conventional discharge flow-tube apparatus between 298 and 359 K, in order to obtain absolute values of the reaction rate coefficients for these reactions and to compare these values with previously reported rate measurements when available.

To improve our understanding of the reactions of O(³P) atom with the chloropropenes, we have conducted *ab initio* calculations of the kinetics and mechanism of the reactions (1) and (2). The required electronic structure information for the stationary points and a series of extra points along the minimum energy path (MEP) were obtained directly from *ab initio* electronic structure calculations. These results allowed us to calculate the activation energies for the addition and abstraction reactions as well as the pre-exponential factors and rate constants at 298 K for the addition channels using the Canonical Transition State Theory. Experimental and theoretical results are compared and the temperature dependence of the rate coefficients is discussed.

2. Experimental

The experiments were conducted in a discharge flow system using the air afterglow chemiluminescence to monitor the oxygen atom concentration. The apparatus has been described previously [4,5]. Briefly, the reactor consisted of a Pyrex tube (1.00 m long and 2.50 cm i.d.) coupled with a sliding injector used to introduce the chloropropene reactant at one end of the reaction tube.

Oxygen atoms, O(³P), were generated by an electrodeless microwave discharge (30 W, 2.5 GHz) on a 2% O₂/He mixture that was slowly flowed through an Evenson cavity and introduced into the main flow of He carrier gas through a fixed side-arm port.

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Reaction times could be varied by adjusting the distance of the sliding injector with respect to the fixed position of the photomultiplier tube detector. The position of the injector could be changed from 7.5 to 25 cm from the center of the detection zone, giving contact times in the range of 4.4–14.2 ms. The system was evacuated by a rotary pump (90 m³ h⁻¹) and a capacitance manometer (MKS Baratron, 0–10 Torr) was used to measure the pressure in the flow tube.

Electronic mass flow controllers, previously calibrated for each gas mixture, were used to control and measure the gas flows in the reaction tube. Typical linear flow velocities under our experimental conditions were between 1760 and 1857 cm s⁻¹ for the O(³P) + CH₂=CHCH₂Cl reaction and between 1364 and 1750 cm s⁻¹ for the O(³P) + CH₂=CClCH₃ reaction.

The experiments were conducted between 298 and 359 K and the flow tube pressures were varied in the range of 2.98–4.26 Torr in experiments with CH₂=CHCH₂Cl and from 2.82 to 4.05 Torr with CH₂=CClCH₃. Helium was used as carrier gas.

The pressure drop along the tube was estimated, considering the viscosity of He, as negligible. The plug-flow conditions [6,7] in the flow tube, allowed us to follow the reaction kinetics of the O(³P) atoms in a known excess of the chloropropene in order to assume the pseudo-first-order approximation.

The concentration of O(³P) atoms was monitored by measuring the chemiluminescence from the air afterglow reaction in which O(³P) atoms react with NO to produce electronically excited nitrogen dioxide (NO₂^{*}) [8]. A constant flow of NO was added 8.5 cm before the photomultiplier tube detector (Hamamatsu R636) so that [NO] was ca. (0.9–9.8) × 10¹³ molecule cm⁻³, and the chemiluminescence from NO₂^{*} passed through a wide band pass filter (λ < 500 nm) before reaching the photomultiplier tube. The output signal, S_t, of the detector that was proportional to the light intensity of chemiluminescence, was amplified and displayed on an oscilloscope. In all experiments the background signal obtained when [NO] = [chloropropene] = 0, arising from scattered light in the reaction tube, was subtracted from S_t before further analysis. Concentrations of O(³P) atoms in the kinetic experiments, estimated by the fast reaction with NO₂ under second-order conditions [9], ranged between 0.8 and 1.7 × 10¹² atoms cm⁻³ and no variations in the obtained results were observed.

3. Theoretical calculations

The *ab initio* molecular orbital calculations were performed with the GAUSSIAN 03 suite of programs.

All equilibrium and transition state (TS) structures were fully optimized at the MP2/6-31G(d) (restricted or unrestricted) level of theory. At the same level of theory, the minimum energy path (MEP) was obtained by the intrinsic reaction coordinate (IRC) theory to confirm that the transition states really connect to the minimum along the reaction path.

Energies were improved by using one of the variants of the CBS-RAD procedure: the CBS-RAD(MP2, MP2). The CBS-RAD is a modification of the CBS-Q method in which the geometries and scaled (at 0.9776) zero-point vibrational energy corrections (ZPE), are obtained at the QCISD(fc)/6-31G(d) level, and CCSD(T)/6-31+G⁺ single-point energy calculations are used to recover the errors that result from spin-contamination in open-shell systems. The CBS-RAD(MP2, MP2) modification uses geometries and scaled (at 0.9676) MP2(fc)/6-31G(d) ZPEs, and is useful for larger systems. The CBS-RAD(MP2, MP2) calculation sequence in this study was performed on the geometry and frequencies determined by an MP2(fc)/6-31G(d) calculation; B3-LYP/6-31G(d) is the suggested method for frequency calculation with CBS-RAD(MP2, B3-LYP) [10]. The full sequence of calculations required

to obtain the total energies by these procedures is described in Ref. [10].

The rate coefficient, *k*(*T*), at temperature *T* for a bimolecular reaction as a function of the activation energy, *E*_a, and the pre-exponential factor, *A*(*T*), is expressed as: *k*(*T*) = *A*(*T*)exp(-*E*_a/*RT*). In particular, the *A*-factor formulation that results from the TST in terms of the partition functions of the reactants and species involved at the transition state is

$$A(T) = (k_B T/h) \kappa [Q^{TS}(T)/(Q^{O(^3P)}(T)Q^{CH_2=R}(T))]$$

where, *Q*^{O(³P)}(*T*), *Q*^{CH₂=R}, and *Q*^{TS}(*T*), are the total partition functions, at temperature *T*, of the atomic oxygen in its ground electronic state, the chloropropene of the type CH₂=R with R = CClCH₃ or CHCH₂Cl and transition state, respectively; *κ*, is the transmission coefficient; *k*_B is Boltzmann's constant, and *h* is Planck's constant. The total partition function of all species can be cast in terms of the translational (*Q*_T^X), rotational (*Q*_R^X), electronic (*Q*_E^X), and vibrational (*Q*_V^X), partition functions. Vibrational partition functions are evaluated with explicit consideration of the hindered internal rotation of the different tops involved in the chloropropenes and transition state structures, using the method described by Ayala and Schlegel [11]. The evaluation of the electronic partition function, *Q*_E^X(*T*), for the ground state of the oxygen atom, O(³P), is a little more complicated than for the other atoms. The lowest state is ³P₂, but there are two states very close to it: ³P₁ and ³P₀, which are 157.4 cm⁻¹ and 226.1 cm⁻¹ respectively, above the lowest level. Higher states, however, can be neglected at all but the highest temperatures. The degeneracies of the three levels are 5, 3 and 1, respectively. Therefore, on computing the electronic partition function for the oxygen atom all these contributions were taken into account [12,13].

4. Materials

The commercial gases used in this study had the following stated minimum purity: He (AGA 99.999%), O₂ (AGA 99.999%), NO (AGA 99.5%), CH₂=CClCH₃ (Aldrich 98%) and CH₂=CHCH₂Cl (Fluka 98%). Nitric oxide was purified by passing it through a trap held at 140 K to remove NO₂. Helium was flowed through traps containing silica gel and molecular sieves (BDH Type 5 A) at 77 K, to remove water. Chloropropenes were vacuum-distilled before use and oxygen was used as supplied.

5. Results

5.1. Experimental

Using the discharge flow-chemiluminescence technique, the following Arrhenius expressions were obtained for reactions (1) and (2):

$$k_1 = (1.96 \pm 0.33) \times 10^{-10} \exp[(-1476 \pm 56)/T]$$

$$k_2 = (9.11 \pm 0.17) \times 10^{-11} \exp[(-1007 \pm 61)/T]$$

with *k* in units of cm³ molecule⁻¹ s⁻¹ and *E*_a in units of J mol⁻¹. The errors in the activation energy and the pre-exponential factor are 2σ random only by the fit to the data presented in Table 1.

Absolute rate coefficients, *k*₁ and *k*₂ for these reactions, were obtained as follows. All the experiments were carried out under pseudo-first-order conditions, [chloropropene]₀/[O(³P)]₀ always greater than 10.

In the absence of secondary reactions that significantly deplete the transient O(³P) atoms, the concentration of O(³P), [O(³P)], varied in an exponential manner with time:

Table 1Rate constants, experimental conditions and Arrhenius parameters of $O(^3P) + CH_2=CHCH_2Cl$ and $O(^3P) + CH_2=CClCH_3$ reactions.

<i>T</i> (K)	<i>k</i> /10 ⁻¹² (cm ⁻³ molecule ⁻¹ s ⁻¹)	[Chloropropene]/10 ¹³ (molecule cm ⁻³)	<i>E</i> _a (kJ mol ⁻¹)	<i>A</i> /10 ⁻¹¹ (cm ³ molecule ⁻¹ s ⁻¹)
<i>CH</i> ₂ = <i>CHCH</i> ₂ <i>Cl</i>				
298	1.35 ± 0.09	0.9–6.8	12.3 ± 0.5	1.96 ± 0.33
314	1.90 ± 0.13	1.5–7.5		
328	2.22 ± 0.13	2.1–7.1		
343	2.65 ± 0.16	1.9–6.3		
359	3.15 ± 0.14	2.0–6.5		
<i>CH</i> ₂ = <i>CClCH</i> ₃				
298	3.15 ± 0.17	1.3–4.8	8.37 ± 0.5	0.91 ± 0.17
314	3.59 ± 0.22	1.1–4.5		
328	4.10 ± 0.22	1.4–4.3		
343	4.97 ± 0.25	0.8–3.8		
359	5.48 ± 0.28	1.2–3.9		

$$[O(^3P)]_t = [O(^3P)]_0 \exp[-(k[\text{chloropropene}]_0 + k_x)t] \quad (3)$$

$$= [O(^3P)]_0 \exp(-k't) \quad (4)$$

$$\ln[O(^3P)]_0/[O(^3P)]_t = k't \quad (5)$$

where $[O(^3P)]_0$ is the concentration observed at the detector in the absence of chloropropene after wall losses and $[O(^3P)]_t$ is the concentration after reaction with the chloropropene over time t , k' is the measured pseudo-first-order rate coefficient and k_x is the first-order rate coefficient for $O(^3P)$ disappearance by diffusion out of the detection zone, reaction with background impurities or wall losses.

In order to monitor the $O(^3P)$ concentration, a known excess of NO was added to produce electronically excited NO_2^* whose global chemiluminescence was checked 8.5 cm downstream of the NO inlet port, following the air afterglow reaction:



If O atoms react via reaction (6) under our experimental conditions, the NO_2 molecules formed rapidly consume O atoms to reform NO via reaction (7) ($k_{298\text{ K}} = (9.7 \pm 1.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) [14]:



Thus, every time an NO molecule changes to NO_2 in reaction (6), it is almost immediately regenerated by reaction (7). The effect is that the concentration of nitric oxide does not decay along the flow tube. It can be shown that the intensity, S , of the air afterglow is proportional to the product of the NO and O concentrations. Since $[NO]$ is constant, the intensity of the signal at selected points down the tube is a relative measure of $[O(^3P)]$.

The first-order kinetic analysis considered in this work is based on the ratio S_0/S_t , where S_0 is the chemiluminescence signal without reactant and S_t is the signal after addition of reactant at a fixed time of contact. The $O(^3P)$ loss between the NO entrance and the detection zone for the reaction with the NO was calculated as less than 4%.

Taking into account the above considerations, equation (5), can be written as:

$$\ln(S_0/S_t) = k't \quad (8)$$

For a specific concentration of chloropropene, the pseudo-first-order decay rate coefficient, k' , was computed from the slope of a plot of $\ln(S_0/S_t)$ as a function of contact time which was linear for approximately 0.5–3 $1/e$ lifetimes. An example of pseudo-first-order plot for the $O(^3P) + CH_2=CClCH_3$ reaction is shown in the Fig. 1. The second-order rate coefficients, k , for reactions (1) and (2), were obtained from the slopes of the lines of the plots of k'

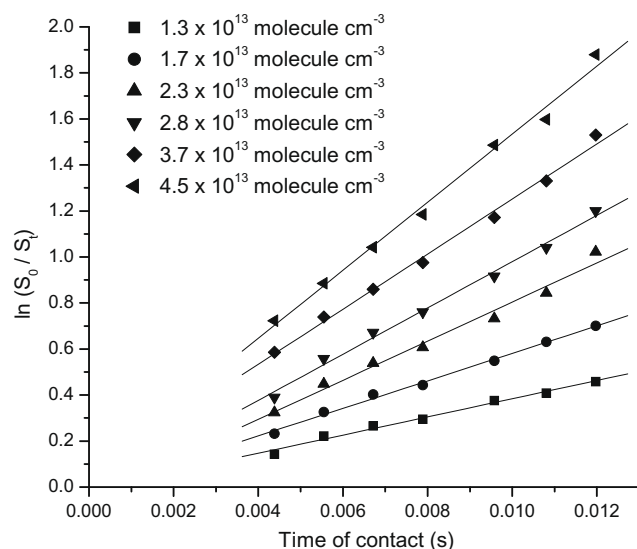


Fig. 1. Pseudo-first-order plot of the $O(^3P) + CH_2=CClCH_3$ reaction at different concentrations of $CH_2=CClCH_3$.

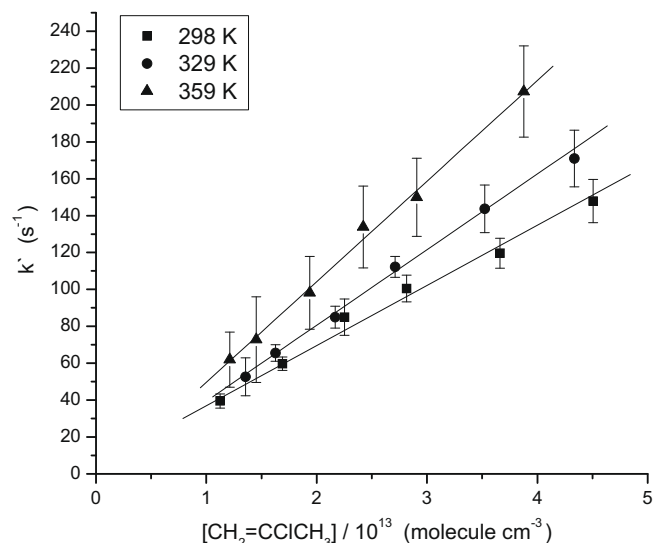


Fig. 2. Second-order plots for the $O(^3P) + CH_2=CClCH_3$ reaction at three different temperatures.

vs [chloropropene]₀. An example of second-order plot for the $O(^3P) + CH_2=CClCH_3$ reaction is shown in the Fig. 2. Linear least-squares fits to the data points yield the values of $k_1 = (1.35 \pm 0.08) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_2 = (3.15 \pm 0.17) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. The error limits are one standard deviation from the least-squares analysis. An estimated 10–20% uncertainty should be added for possible systematic errors [7]. The pseudo-first-order rate coefficients were corrected for axial and radial diffusion [7], and this procedure resulted in <5% upward correction of the k' values.

The linearity of the data points, (Figs. 1 and 2) suggests that the contribution to the decay of $O(^3P)$ atoms due to secondary reactions with the products of the title reactions or with impurities are negligible. Also, the fact that the plots show practically zero intercepts is consistent with a negligible loss of O atoms by wall reactions ($k_w = 4\text{--}10 \text{ s}^{-1}$). As the wall losses of O atoms were negligible no corrections for velocity profile effect were required [7]. The pressure of the reactor was varied for both reactions as indicated in the experimental section and the observed rate coefficient values remained unchanged.

Arrhenius plots were linear in the experimental temperature range as shown in (Fig. 3). Experimental conditions, rate coefficients and Arrhenius parameters for both reactions, are summarized in the Table 1.

5.2. Calculations

Bond distances of the reactants, transition states and products for the reactions of $O(^3P)$ with $CH_2=CClCH_3$ and $CH_2=CHCH_2Cl$ are shown in Fig. 4.

The calculated scaled harmonic vibrational frequencies for reactants, products and the corresponding transition states at the MP2(full)/6-31G(d) level of theory are shown in Table 2, together with the only available experimental values for $CH_2=CHCH_2Cl$ [15].

The computed vibrationally adiabatic barriers, VAB are shown in Table 3 for the reactions under study at the two levels of theory here used. The following equation was used to determine these barriers:

$$VAB = E_{TS} - E_R + ZPE_{TS} - ZPE_R$$

where, E_{TS} and E_R are the *ab initio* energies of the transition states and reactants, respectively and ZPE_{TS} and ZPE_R are the correspond-

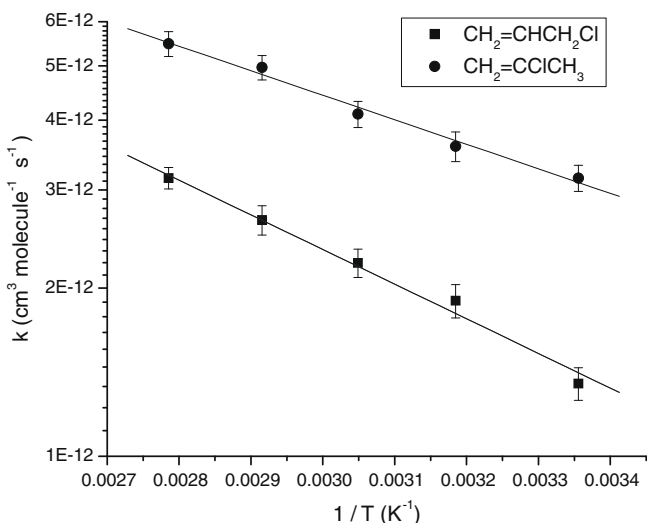


Fig. 3. Arrhenius plots for the $O(^3P) + CH_2=CClCH_3$ and $O(^3P) + CH_2=CHCH_2Cl$ reactions between 298 and 359 K.

ing zero-point energy corrections. The experimental activation energies, E_a , obtained in this work, for the addition reactions are also listed in Table 3 for comparison purposes.

The $O(^3P)$ atom may either add to the double bond of the chloropropene or abstract a H atom. For the reaction of $O(^3P)$ with $CH_2=CHCH_2Cl$ we have located two transition states TS1 and TS2 (Fig. 4) which lead to the addition of the O atom to the double bond of the 3-chloropropene at the C¹ and C² carbon atoms, respectively.

On the other hand, for the H-abstraction reactions, we distinguish four different types of H atoms in $CH_2=CHCH_2Cl$. If abstraction occurs from the terminal $=CH_2$ group, transition states TS3 and TS4 were found which correlate with the products $CHCHCH_2Cl$ (I) and $CHCHCH_2Cl$ (II) shown in Fig. 4. The relative energies of these two transition states calculated at the CBS-RAD(MP2/MP2) level of theory are quite high, 58.03 and 56.48 kJ mol^{-1} , respectively as observed in Table 3. If, however, abstraction takes place from the H atoms of the $-CH_2Cl$ group via TS5 with 27.45 kJ mol^{-1} of energy above that of reactants, the $CH_2=CHCHCl$ radical is formed. Finally, abstraction from the $=CH-$ group via TS6 has a barrier of 64.94 kJ mol^{-1} to form the CH_2CCH_2Cl radical. The imaginary frequencies, presented in Table 2, associated to the different transition states are 2051i, 2038i, 2600i and 1993i cm^{-1} for TS3, TS4, TS5 and TS6, respectively.

For the reaction between $O(^3P)$ and $CH_2=CClCH_3$, two addition channels were also considered on each of the two carbon atoms of the double bond, $=CH_2$ and $=CCl-$, through transition states TS1a and TS2a, respectively (Fig. 4).

Regarding the abstraction channels, three different H atoms were considered; two reaction pathways for the H atoms of the $=CH_2$ group leading to the radicals $CHCClCH_3$ (I) and $CHCClCH_3$ (II) via TS3a and TS4a (Fig. 4) with relative energies of 72.22 and 62.13 kJ mol^{-1} , respectively as shown in Table 3. Abstraction from the $-CH_3$ group corresponds to the formation of the $CH_2=CClCH_2$ radical via TS5a with 29.29 kJ mol^{-1} of energy. Table 2 contains the imaginary frequencies of 1896i, 1942i and 2551i cm^{-1} corresponding to TS3a, TS4a and TS5a, respectively.

6. Discussion

To the best of our knowledge, this Letter presents the first study of the temperature dependence of the reactions of $O(^3P)$ atoms with $CH_2=CHCH_2Cl$ and $CH_2=CClCH_3$.

The reaction of $CH_2=CHCH_2Cl$ with $O(^3P)$ atoms was studied previously by Park et al. [16] using the discharge flow-mass spectrometry technique and reviewed later by Cvetanovic [2]. The rate constant obtained in the present work for this reaction of $1.35 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is in acceptable agreement, with-in experimental error, with the recommended value of Cvetanovic of $1.01 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature, considering an estimated accuracy of around $\pm 20\%$ in both cases. The 3-chloropropene was also studied at room temperature with other atmospheric oxidants, OH [17], Cl [18], O_3 [19] and NO_3 [20]. There are only three systematic studies at different temperatures, one is with the OH radical [17] another with NO_3 radical [21] and the third with the O_3 molecule [22].

On the other hand, this is the first study of the reaction of $O(^3P)$ with $CH_2=CClCH_3$. Previous works involve two theoretical studies of the kinetics of this molecule with Cl atoms [23] and NO_3 radicals [24].

The dependence of $\ln k$ with $1/T$ for the two reactions studied is shown in Fig. 3. A linear variation is observed over the temperature range investigated, suggesting that the reactions proceed via a single elementary pathway over the temperature range of our study and furthermore, that this channel is addition of $O(^3P)$ to the dou-

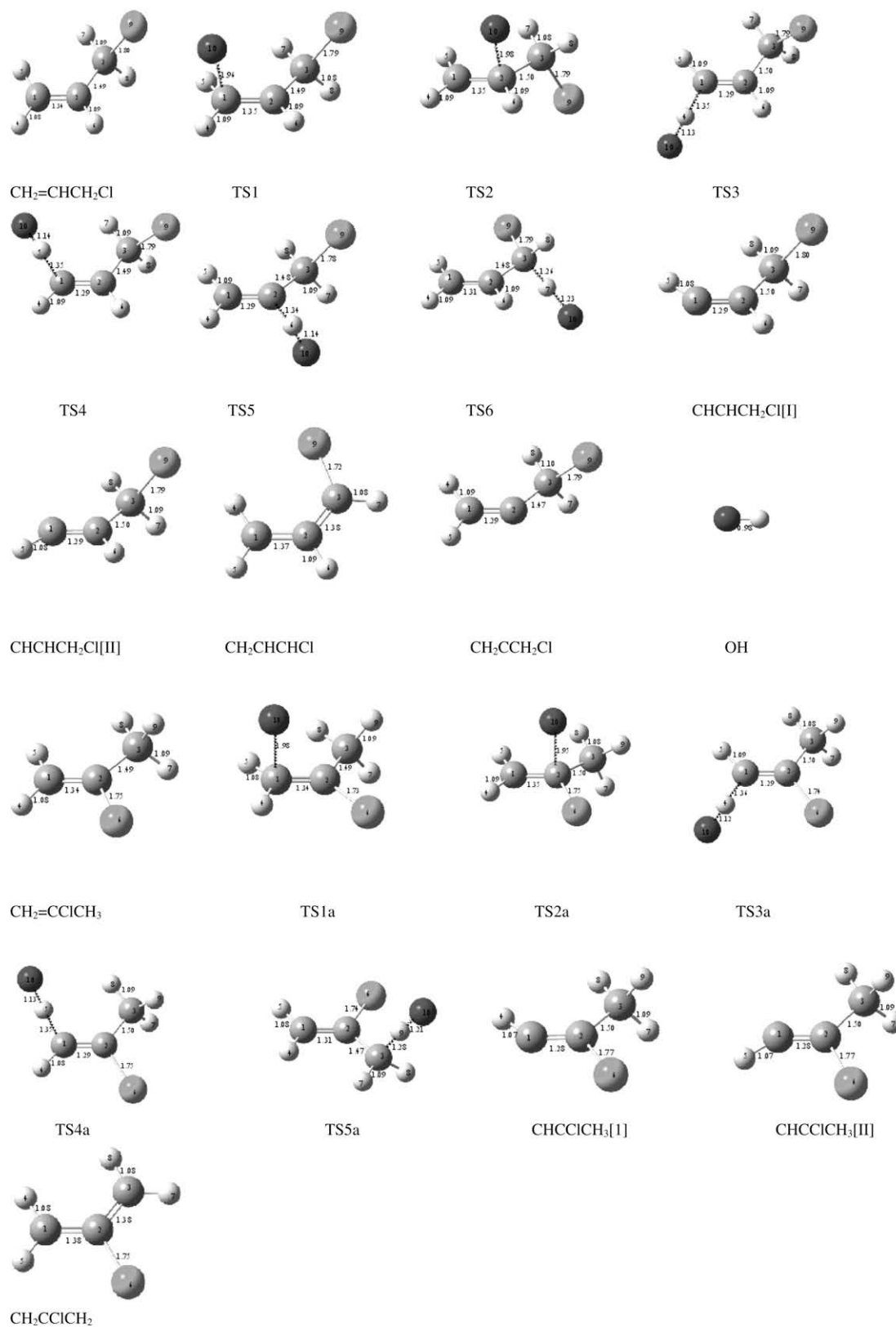


Fig. 4. Optimized geometries for reactants, transition structures and products of the $O(^3P) + CH_2=CHCH_2Cl$ and $O(^3P) + CH_2=CClCH_3$ reactions. Bond lengths are given in angstroms.

ble bond of the chloropropenes. Both reactions show positive activation energies with increasing rate coefficients as the temperature increases between 298 and 359 K.

The measured rate constants, on the order of $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and the small temperature dependences detected for both chloropropenes ($E_a < 13 \text{ kJ mol}^{-1}$), suggest a general mecha-

Table 2
Scaled harmonic frequencies^a calculated at the MP2(full)/6-31G(d) level of theory.

CH ₂ =CHCH ₂ Cl ^b	290	409	590	938	987	1050	1100	1412	1642	3109	3112	3131	3204	3155	3212
CH ₂ =CHCH ₂ Cl	102	285	399	602	770	908	917	951	1001	1126	1230	1299	1320	1447	1494
TS1	646i	106	219	333	402	673	779	914	932	1000	1027	1132	1234	1296	1311
TS2	607i	83	169	204	305	405	578	707	908	922	1031	1123	1237	1290	1307
TS3	2051i	52	99	116	295	345	498	615	748	848	931	977	1047	1111	1197
TS4	2038i	56	104	156	299	420	505	661	767	844	921	954	1012	1106	1197
TS5	2600i	85	90	204	246	466	542	618	797	957	1067	1083	1103	1125	1254
TS6	1993i	60	86	173	289	389	582	648	793	894	979	1015	1056	1140	1240
OH ^c	3618														
CHCHCH ₂ Cl [I]	114	297	377	696	801	875	941	1011	1076	1197	1284	1323	1489	1841	3052
CHCHCH ₂ Cl [II]	121	299	398	669	788	840	931	982	1096	1200	1281	1327	1490	1852	3057
CH ₂ CHCHCl	233	323	552	561	650	798	805	975	1030	1143	1185	1386	1407	1520	3128
CH ₂ CCCH ₂ Cl	119	268	352	576	774	892	956	1017	1073	1208	1309	1430	1472	1922	3011
CH ₂ =CClCH ₃	199	341	394	430	649	700	859	933	1016	1071	1204	1409	1436	1483	3103
TS1a	630i	101	127	185	347	403	458	666	824	946	1021	1069	1223	1401	1430
TS2a	717i	152	220	244	349	379	395	649	656	875	934	1012	1059	1208	1401
TS3a	1896i	84	109	221	327	383	509	559	656	727	899	933	1028	1075	1091
TS4a	1942i	108	131	220	307	359	495	634	678	723	854	928	1010	1095	1117
TS5a	2551i	57	91	352	389	448	493	517	668	760	954	1002	1016	1034	1195
CHCClCH ₂ [I]	213	334	378	486	620	790	833	1018	1067	1125	1416	1483	1498	1854	3013
CHCClCH ₂ [II]	211	330	372	477	634	818	823	1022	1082	1108	1419	1484	1497	1878	3017
CH ₂ CClCH ₂	374	401	574	545	555	658	752	770	953	1052	1200	1307	1466	1521	3139

^a Unit: in cm⁻¹. Scaled by a factor of 0.9676 to account for the anharmonic effects.

^b Experimental frequencies taken from Ref. [15] shown in italics.

^c M.W. Chase, J. Phys. Chem. Ref. Data (1998), Monograph 9.

Table 3

Experimental and calculated Vibrationally Adiabatic Barriers^a at the MP2/6-31G(d) and CBS-RAD(MP2/MP2) levels of theory.

Addition or abstraction reactions by O(³ P)	MP2/6-31G(d)	CBS-RAD (MP2/MP2)	Experimental ^b
<i>C</i> ¹ H ₂ =C ² HC ³ H ₂ Cl			
CH ₂ =CHCH ₂ Cl	24.48	10.33	12.30
CH ₂ =CHCH ₂ Cl	23.35	11.25	
CH ₂ =CHCH ₂ Cl (I)	92.76	58.03	
CH ₂ =CHCH ₂ Cl (II)	92.17	56.48	
CH ₂ =CHCH ₂ Cl	59.04	27.45	
CH ₂ =CHCH ₂ Cl	83.55	64.94	
<i>C</i> ¹ H ₂ =C ² ClC ³ H ₃			
CH ₂ =CClCH ₃	20.54	8.24	8.37
CH ₂ =CClCH ₃	32.59	15.77	
CH ₂ =CClCH ₃ (I)	97.15	72.22	
CH ₂ =CClCH ₃ (II)	88.32	62.13	
CH ₂ =CClCH ₃	62.89	29.29	

^a Units are in kJ mol⁻¹. The addition or abstraction takes place on the C or H atom indicated in bold letters.

^b This work.

nism for the reactions consisting of an electrophilic addition of the O atom to the π -electron system of the chloropropenes to form an energy-rich complex, a triplet biradical, which may either collisionally stabilize or unimolecularly decompose to form products [2,25]. The observed activation energies should then be for the process that leads to the formation of the triplet biradical. The reactions exhibit positive temperature dependences, suggesting that dissociation of the triplet biradical would be a fast process, due to the excess energy involved in its formation, so that the lifetime of the metastable adduct is sufficiently short that collisional relaxation does not occur. This would be supported by the experimentally observed pressure independence of these reactions, meaning that upon formation of adduct, the reverse dissociation to reactants does not occur so that the effective rate determining step is passage through the entrance channel transition state.

The proposed mechanism is also supported by the theoretical calculations. Agreement between the computed adiabatic barriers by the CBS-RAD(MP2/MP2) method and the experimental activation energies for the addition reactions is reasonably good as observed in Table 3. It can also be seen in Table 3 that for CH₂=CHCH₂Cl, even though the difference between the VABs is not very significant (0.92 kJ mol⁻¹), the VAB for addition to C¹ is lower than that for addition to C². For CH₂=CClCH₃, the difference is larger (7.53 kJ mol⁻¹) and there is still better agreement between the calculated and experimental activation energies for addition to C¹. The fact that addition to C¹ seems to be favoured, in both cases, the calculated VAB values are lower for addition to C¹, could be explained taking into account steric hindrance by the bulky Cl atom which would orient the O atom addition to the less substituted C atom of the chloropropene. This would support Cvetanovic's [26,27] general conclusion that addition of O atoms to the double bond, is primarily to the less substituted carbon atom.

Considering the electrophilic nature of O atom attachment to the double bond, this line of reasoning is also consistent with the *ab initio* calculations carried out in this work of the total atomic charges of the C¹ and C² atoms in CH₂=CHCH₂Cl and CH₂=CClCH₃. For 3-chloropropene the corresponding values are: -0.381 and -0.121 for C¹ and C², respectively, whereas for 2-chloropropene these are: -0.387 and -0.0486, respectively.

Furthermore, both experimental and theoretical values, calculated at the CBS-RAD(MP2/MP2) level of theory of activation energy, pre-exponential factors and rate constants at 298 K, shown in Table 4, are in good agreement if addition occurs at C¹ of both chloropropenes, leading to the more stable and more substituted triplet biradical adduct. In fact, from the calculated values of the

Table 4Calculated kinetics parameters E_a (kJ mol⁻¹), A -factors and rate coefficients, k , at 298 K (cm³ molecule⁻¹ s⁻¹) for the O(³P) + CH₂=CHCH₂Cl and O(³P) + CH₂=CClCH₃ reactions.^a

Addition reactions by O(³ P) to the chloropropenes	MP2/6-31G(d)			CBS-RAD(MP2, MP2)			Experimental		
	E_a	$A/10^{-10}$	$k/10^{-16}$	E_a	$A/10^{-10}$	$k/10^{-12}$	E_a	$A/10^{-10}$	$k/10^{-12}$
C ¹ H ₂ =C ² HC ³ H ₂ Cl	24.48	1.45	9.99	10.33	1.45	2.23	12.30	(1.96 ± 0.33)	(1.35 ± 0.08)
C ¹ H ₂ =C ² HC ³ H ₂ Cl	23.35	0.153	1.68	11.25	0.153	0.163			
C ¹ H ₂ =C ² ClC ³ H ₃	20.54	2.23	76.1	8.24	2.23	8.00	8.37	(0.91 ± 0.17)	(3.15 ± 0.17)
C ¹ H ₂ =C ² ClC ³ H ₃	32.59	0.00149	0.000390	15.77	0.00149	0.000255			

^a The addition takes place on the C atom indicated in bold letters.

rate constants at 298 K, it can be concluded that 93% of the addition reaction goes to C¹ for 3-chloropropene and almost 100% for 2-chloropropene. This again is in accordance with Cvetanovic [26,27], who carried out an extensive study of the products of O(³P) reactions with alkenes pointing out that addition takes place on the less substituted carbon atom of the double bond of the alkene.

It was mentioned previously that H-abstraction is the other possible pathway for the reaction of O atoms with the chloropropenes of this study. It is clear from Table 3 that abstraction cannot compete with the major channel, identified as the addition to C¹ of both chloropropenes.

According to the data shown in Table 3, for the reaction of O(³P) with CH₂=CHCH₂Cl the relative energies of the transition states for the H-abstraction channels are between 34.56 and 68.28 kJ mol⁻¹ calculated at the MP2/6-31G(d) level of theory and between 17.12 and 54.61 kJ mol⁻¹, calculated at the CBS-RAD(MP2/MP2), above the energy of the transition state of the addition to C¹.

Likewise, for the reaction of O(³P) with CH₂=CClCH₃, the energy barriers for the abstraction channels are 42.35–76.61 kJ mol⁻¹ and 21.05–63.98 kJ mol⁻¹ higher than the corresponding values for C¹ addition, calculated at the MP2/6-31G(d) and CBS-RAD(MP2/MP2) levels of theory, respectively. Thus, abstraction cannot compete with the addition steps at low to fairly high temperatures.

Acknowledgements

The authors wish to acknowledge CONICET (Argentina), ANPCyT (Préstamo BID PICT No. 38044), Agencia Córdoba Ciencia, and SECyT-UNC (Córdoba, Argentina) for financial support of this research. Facultad de Ingeniería, Universidad Nacional de Jujuy, S.S. de Jujuy, Argentina and Centro de Supercomputación de Galicia (CESGA) for infrastructure and technical support are also acknowledged.

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