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Kinetics of the Reactions of O(^{3}P) with CCl$_2$=CH$_2$, (Z)-CHCl=CHCl, and CCl$_2$=CCl$_2$: A Temperature Dependence Study

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Absolute rate coefficients for the gas-phase reactions of ground-state oxygen atoms with CCl$_2$=CH$_2$ (1), (Z)-CHCl=CHCl (2) and CCl$_2$=CCl$_2$ (3) have been measured directly using the fast flow discharge technique. The experiments were carried out under pseudo-first-order conditions with [O(^{3}P)]$_0$ ≪ [chloroethene]$_0$. The temperature dependences of the reactions of O(^{3}P) with CCl$_2$=CH$_2$, (Z)-CHCl=CHCl and CCl$_2$=CCl$_2$ were studied in the range 298–359 K. The kinetic data obtained were used to derive the following Arrhenius expressions (in units of cm^3 molecule^{-1} s^{-1}): k_1 = (1.82 ± 1.29) × 10^{-11} exp[−(12.63 ± 0.97) × 10^3/RT], k_2 = (1.56 ± 0.92) × 10^{-11} exp[−(16.68 ± 1.54) × 10^3/RT], k_3 = (4.63 ± 1.38) × 10^{-11} exp[−(19.59 ± 3.21) × 10^3/RT]. This is the first temperature dependence study of the reactions of O(^{3}P) atoms with (Z)-CHCl=CHCl and CCl$_2$=CCl$_2$. All the rate coefficients display a positive temperature dependence and pressure independence, which points to the importance of the irreversibility of the addition mechanism for these reactions. The obtained rate coefficients are compared with previous studies carried out mainly at room temperature. The rates of addition of O atoms and OH radicals to the double bond of alkenes at 298 K are related by the expression: log k_{OH} = 0.57278 log $k_{O(3P)}$ − 4.095. A correlation is presented between the reactivity of chloroethenes toward O atoms and the second-order perturbational term of the frontier molecular orbital theory which carries the contribution of the different atomic orbitals to the HOMO of the chloroethene. To a first approximation, this correlation allows room-temperature rate coefficients to be predicted within ±25–30% of the measured values.

Introduction

Chlorinated organics have extensively been used in different industries. Specifically chloroethenes are widely used as solvents, metal degreasing, dry cleaning, and paint stripping agents. They are also employed in the extraction of chemicals, as intermediates in the manufacture of polymers and in the circuit-board manufacture.[1-3] They are toxic and volatile and may be of major concern in local industrial areas. Substantial amounts of chlorinated compounds are continually introduced into the atmosphere, and the kinetics and degradation pathways under atmospheric conditions of many of these compounds are still largely unknown.

Even though the addition reactions of O(^{3}P) to alkenes are of little importance in atmospheric chemistry, they can become significant in laboratory irradiations of NO$_x$−alkene−air mixtures, especially as an initial source of radicals, and probably also in plumes that contain high concentrations of NO$_2$.[4,5] The addition reaction of O(^{3}P) to alkenes constitutes a prototype of an electrophilic addition to the C=C double bond. Several authors have proposed a linear correlation between the rate coefficients of O(^{3}P) addition reactions and those of other tropospheric oxidants like OH and NO$_3$ radicals or O$_3$ molecules, suggesting the possibility of similar reaction mechanisms.[6-8]

The reaction of CCl$_2$=CCl$_2$ with O(^{3}P) has been previously studied only by Upadhyaya et al.[9] using a discharge flow tube system with chemiluminescence detection at 298 K and at pressures between 1.2 and 1.5 Torr. In addition, through PM3 and conventional transition state theory (CTST) calculations, they propose that the formation of a biradical in the addition reaction of an O atom to the double bond is the main reaction pathway.

For the reaction of CCl$_2$=CH$_2$ with O(^{3}P), the available kinetic data are quite scattered. Room-temperature rate coefficients have been reported ranging from 4.9 to 9.8 × 10^{-13} cm^3 molecule^{-1} s^{-1}.[9-11] Cvetanovic[10] has reported a recommended value based on an evaluation of an early relative kinetic study by Sanhuenza and Heicklen[12] and more recently there have been two absolute studies by Hranisavljevic et al.[11] and Upadhyaya et al.[9] Hranisavljevic et al. used a high-temperature photochemical reactor (FP−RF) to study the temperature dependence of the reaction of O(^{3}P) with CCl$_2$=CH$_2$ in the temperature range of 295−1220 K and at pressures between 0.14 and 0.53 Bar.

As part of a systematic study of O(^{3}P) atom reactivity, we report in this work absolute rate coefficients and the Arrhenius parameters for the reactions of O(^{3}P) with CCl$_2$=CH$_2$, (Z)−CHCl=CHCl, and CCl$_2$=CCl$_2$ in the temperature range 298−359 K. The kinetic determinations were performed using a discharge flow tube apparatus coupled with chemiluminescence detection of O(^{3}P) atoms.

To the best of our knowledge, the temperature dependences of the reactions of O(^{3}P) with (Z)-CHCl=CHCl and CCl$_2$=CCl$_2$ have not been reported previously; hence, the present work

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is the first temperature dependence study of these reactions, as well as the first kinetic determination of the reaction of O(^{3}P) with (Z)-CHCl=CHCl.

The aim of this study was to extend our earlier work on the reactivity of chlorinated and fluorinated ethenes[13-15] and to determine the temperature dependences of these reactions, to predict the corresponding rate constants in the temperature range studied. Additionally, the reactivity of the chlorinated ethenes with O(^{3}P) atoms was correlated with the reactivity of the chloroethenes toward OH radicals and with the complete interaction HOMO−SOMO of the frontier molecular orbital theory (FMOT). To this end, the contribution of the different atomic orbitals to the HOMO of the chloroethene through the atomic orbital coefficients was taken into account.

Kinetic data for these O(^{3}P) reactions are needed to gain a better understanding of the role of chlorinated ethenes in combustion chemistry and smog chambers and to develop a reliable structure−reactivity relationship for these chlorinated compounds.

Experimental Section

Detailed descriptions of the apparatus and the experimental methods used to measure the rate coefficients for the reactions of chloroethenes with O(^{3}P) are given in previous papers;[15,16] therefore, only a brief description is presented here.

All the kinetic experiments were conducted in a fast flow discharge system with chemiluminescence detection of the O(^{3}P) atoms.

Briefly, the flow tube consisted of a 1.20 m long, 2.50 cm (i.d.) Pyrex tube fitted with a 0.25 cm (i.d.) axially sliding Pyrex injector. Oxygen atoms, O(^{3}P), were generated in a sidearm tube by an electrodeless microwave discharge (2450 MHz) on a 0.5 to 2% O$_2$/He mixture that was slowly flowed through an Evenson cavity and introduced into the main flow of helium carrier gas through a fixed sidearm port. Initial concentrations of O atoms ranged from 1.9 to 3.6 × 10^{12} atoms cm^{-3}, the total linear flow velocities were in the range of 1320 to 2411 cm s^{-1} and the time of contact varied between 5 × 10^{-3} and 18 × 10^{-3} s. The experiments were conducted between 298 and 359 K for CCl$_2$=CH$_2$, (Z)-CHCl=CHCl, and CCl$_2$=CCl$_2$. The total pressure in the flow tube was varied between 2.1 and 3.9 Torr. The pressure drop along the tube was estimated as negligible, considering the viscosity of He. Helium was used as the carrier gas because of its inertness and excellent diffusion coefficient, thus ensuring rapid radial mixing of all reactants with the bulk of the flow. Under our experimental conditions, the Reynolds number is <50; therefore, the flow can be considered laminar. When the flow is laminar and the radial diffusion of the gases occurs very quickly such that there is no radial concentration gradient or radial velocity gradient, the condition known as "plug-flow"[17,18] is satisfied.

The sliding Pyrex injector was used to introduce the chloroethene at one end of the uncoated reaction tube which was evacuated by a rotary pump (Mariotte, 90 m^3/h). A capacitance manometer (MKS Baratron, 0−10 Torr), and electronic MKS mass flow controllers (179A, 1259 C), previously calibrated, were used to measure the pressure and gas flows in the reaction zone. The plug flow conditions[17,18] established in the flow tube allowed us to follow the reaction kinetics of the O(^{3}P) atoms in a known excess of the chloroethenes in order to assume the pseudo-first-order approximation.

The concentration of O(^{3}P) was monitored by measuring the chemiluminescence from the air afterglow reaction in which O(^{3}P) reacts with NO to produce electronically excited nitrogen

dioxide (NO$_2$*).[19,20] A constant flow of NO was added 8.5 cm before the photomultiplier tube detector (Hamamatsu R636) so that [NO] was ca. (3−5) × 10^{14} molecules cm^{-3}, and the chemiluminescence from NO$_2$* passed through a wide band-pass filter (λ < 500 nm) before reaching the photomultiplier tube, the output signal of which was amplified and displayed on an oscilloscope. The signal, S_t, was proportional to the light intensity. In all experiments, the background signal obtained when [NO] = 0, arising from scattered light in the reaction tube, was subtracted from S_t before further analysis. The background was checked at each contact time, with and without the addition of the chloroethene, and the same negligible background signal, on the order of the sensitivity of the detection system, was obtained under both conditions.

To ensure pseudo-first-order conditions, the absolute concentrations of O(^{3}P) were estimated, before each set of kinetic experiments, by the fast titration reaction of O atoms with NO$_2$ at a fixed contact time.[21]
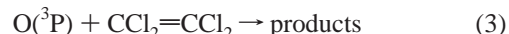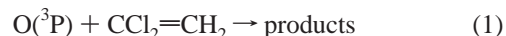
Several experiments were carried out measuring the chemiluminescence signal in the absence of added alkene, introducing O atoms at different contact times, to assess wall losses of O atoms. The measured values of k_w were always <10 s^{-1}.

Materials

The gases and chloroethenes used in this study had the following minimum purity: He (AGA 99.999%), O$_2$ (AGA 99.999%), NO (AGA 99.5%), CCl$_2$=CH$_2$ (Aldrich 97%), (Z)-CHCl=CHCl (Aldrich 99%), and CCl$_2$=CCl$_2$ (Aldrich 99%). All samples were used after several freeze/pump/thaw cycles. The NO was purified by passing it through a trap held at 153 K to remove NO$_2$. Helium was flowed through traps containing molecular sieves (Type 4A) at 77 K to remove water. Oxygen was used as supplied.

Results

Absolute reaction rate coefficients, k, for the following reactions were determined:

$$O(^3P) + CCl_2{=}CH_2 \rightarrow products \quad (1)$$

$$O(^3P) + (Z)\text{-}CHCl{=}CHCl \rightarrow products \quad (2)$$

$$O(^3P) + CCl_2{=}CCl_2 \rightarrow products \quad (3)$$

The experiments were carried out under pseudo-first-order conditions with a ratio, [chloroethene]$_0$/[O(^{3}P)]$_0$, between 11 and 47. Therefore, in the absence of secondary reactions that significantly deplete the transient O(^{3}P) atoms, the loss of O atoms may be described by the equation

$$\ln\{[O(^3P)]_0/[O(^3P)]_t\} =$$
$$(k[\text{chloroethene}]_0 + k_x)t = k't \quad (I)$$

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

The first-order kinetic analysis is based on the ratio S_0/S_t which is applicable to our system. S_0 is the chemiluminescence signal without reactant and S_t is the signal after addition of reactant at a fixed time of contact. Taking into account the above considerations and eq I, it is possible to write:

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$$\ln(S_0/S_t) = k't \quad \text{(II)}$$

A plot of $\ln(S_0/S_t)$ vs time of contact gives the pseudo-first-order decay rate constant, k'. A typical pseudo-first-order plot for the reaction of O(^{3}P) with $CCl_2{=}CH_2$ is shown in Figure 1. The second-order rate coefficient, k, was obtained from the slope of the line of a plot of k' vs [chloroethene]$_0$ at one given temperature. Figures 2–4 show plots of the values of k' vs [$CCl_2{=}CH_2$], [(Z)-CHCl=CHCl], and [$CCl_2{=}CCl_2$], respectively. The rate coefficient values for the reactions studied were determined from a linear least-squares fit to the data points, and the error limits are one standard deviation from the least-squares analysis. Consideration of possible systematic errors in calibration and measurements would probably raise these accuracy estimates by about 10%.[17]

The pseudo-first-order rate coefficients were corrected for axial and radial diffusion,[17] using the following expression:

$$k'_{corr} = k'_{exp}\,(1 + k'_{exp}D/v^2 + k'_{exp}R^2/48D) \quad \text{(III)}$$

where D (cm^2 s^{-1}) is the diffusion coefficient of O(^{3}P) in He, v (cm s^{-1}) is the linear flow velocity, and R (cm) is tube radius. The values of D calculated for our experimental conditions were in the range of 187–348 cm^2 s^{-1}. This procedure resulted in a <6% upward correction of the k' values, which means that the second and third terms in eq III, representing the corrections for axial and radial diffusion, respectively, are negligible.

The linearity of the data points, especially in the low alkene concentration range in our plots (Figures 1 and 2), suggests that the contribution to the decay of O(^{3}P) atoms due to secondary reactions with the products of the title reactions is negligible. Also, the fact that the plots have near zero intercepts is consistent with a negligible loss of oxygen atoms by wall reactions ($k_w <$ 10 s^{-1}). Therefore, no corrections for the velocity profile effect were required.[17] A summary of the absolute second-order rate coefficients obtained for the reactions studied as a function of temperature is given in Table 1. For all three compounds, the reaction rate coefficients were found to increase with increasing temperature in the temperature range of 298–359 K, as shown by plotting $\ln k$ vs $1/T$ (Figure 5). A linear least-squares analysis of the data yields the activation energy and the preexponential factor for each reaction. The rate coefficients at different temperatures for the reactions studied with the corresponding activation energy (E_a) and preexponential factor (A) are summarized in Table 1. According to these experimental results, the following Arrhenius expressions, derived from Figure 5, were obtained in the range of 298–359 K:

$$k_{(CCl_2{=}CH_2)} = (1.82 \pm 1.29) \times$$
$$10^{-11}\exp[-(12.63 \pm 0.97) \times 10^3/RT] \quad \text{(IV)}$$

$$k_{((Z)-CHCl{=}CHCl)} = (1.56 \pm 0.92) \times$$
$$10^{-11}\exp[-(16.68 \pm 1.54) \times 10^3/RT] \quad \text{(V)}$$

$$k_{(CCl_2{=}CCl_2)} = (4.63 \pm 1.38) \times$$
$$10^{-11}\exp[-(19.59 \pm 3.21) \times 10^3/RT] \quad \text{(VI)}$$

where the units of A are cm^3 molecule^{-1} s^{-1} and E_a is in J mol^{-1}. The errors in the activation energies and the preexponential factors are 2σ random only by the fit to the data presented in Table 1. These expressions can predict the rate coefficients of the reactions of O atoms with $CCl_2{=}CH_2$, (Z)-CHCl=CHCl, and $CCl_2{=}CCl_2$, respectively, in the range of temperature cited
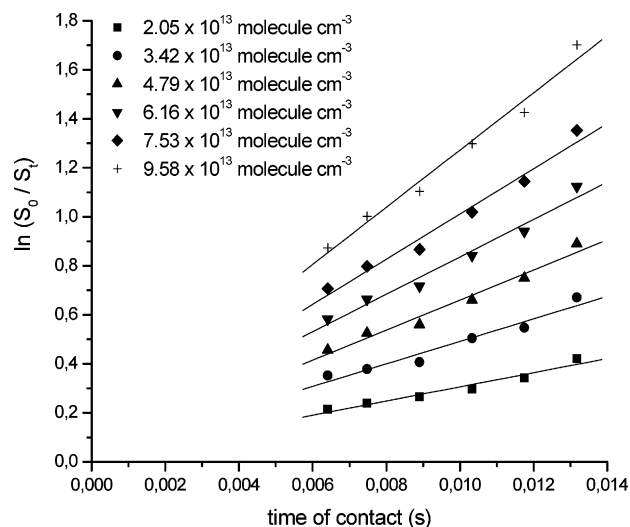

Figure 1. Example of a 298 K pseudo-first-order plot for the O(^{3}P) + $CCl_2{=}CH_2$ reaction at different concentrations of $CCl_2{=}CH_2$.
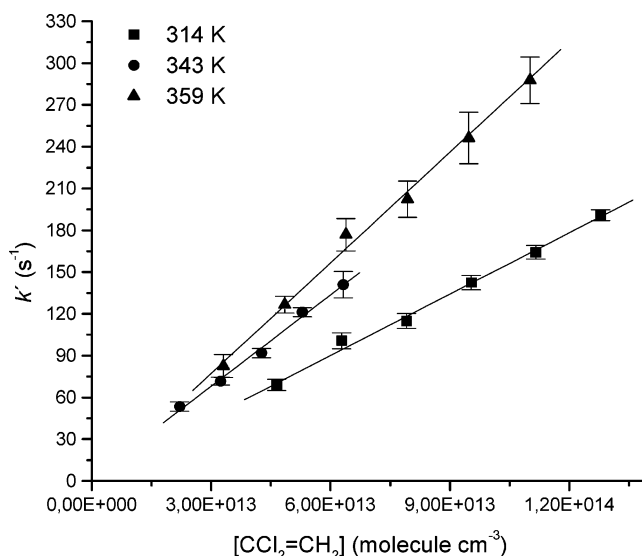

Figure 2. Second-order plot for the reaction of O(^{3}P) with $CCl_2{=}CH_2$ at different temperatures.

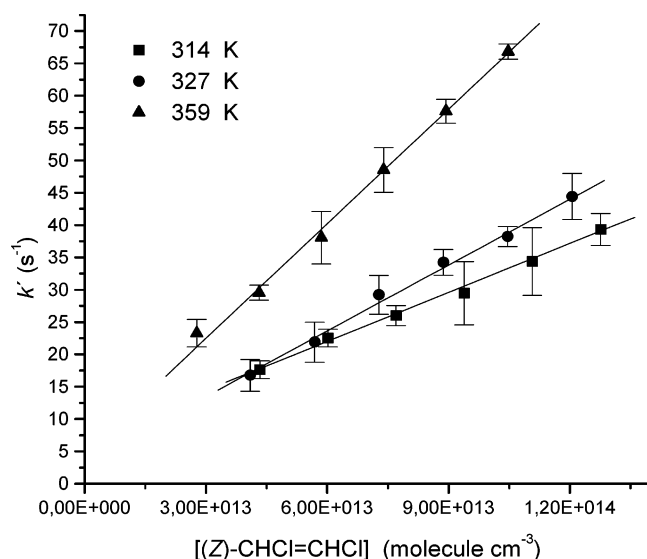above. In the pressure range used for each reaction, no variation in the global rate coefficients was observed.

Discussion

In this work, accurate kinetic data for the reactions of O(^{3}P) with $CCl_2{=}CH_2$, (Z)-CHCl=CHCl, and $CCl_2{=}CCl_2$ at temperatures between 298 and 359 K have been obtained. To the best of our knowledge this is the first reported room-temperature rate coefficient for the reaction of O atoms with (Z)−CHCl=CHCl and therefore, no direct comparison with the literature can be made.
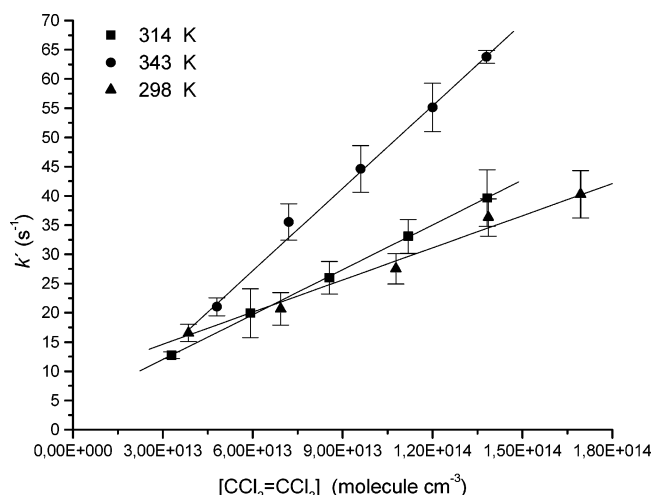
In Table 2, we compare our results with the available previous measurements of the rate coefficients for the reactions studied, most often at room temperature. For $CCl_2{=}CCl_2$ our value of k at room temperature is in excellent agreement with that reported earlier by Upadhyaya et al. using the same experimental technique.[9] For the reaction of O(^{3}P) with $CCl_2{=}CH_2$, Table 2 shows that the obtained value of k at room temperature in this work is in good agreement with the recommended value of Cvetanovic[10] and moreover, if we consider the ratio of 1.0

TABLE 1: Summary of the Measured Rate Coefficients for the Reactions of O(^{3}P) with Selected Chloroethenes as a Function of Temperature

T (K)	$k/10^{-13}$ (cm^3 molecule^{-1} s^{-1})	[chloroethene]/10^{13} (molecule cm^{-3})	$E_a/10^3$ (J mol^{-1})	$A/10^{-11}$ (cm^3 molecule^{-1} s^{-1})
		CCl$_2$=CH$_2$		
298	11.3 ± 0.9	$2.1-9.6$	12.63 ± 0.97	1.82 ± 1.29
314	14.5 ± 0.9	$2.7-6.8$		
328	17.8 ± 1.3	$2.4-5.1$		
343	21.8 ± 1.6	$2.2-7.6$		
359	26.1 ± 2.3	$3.3-7.9$		
		(Z)-CHCl=CHCl		
298	2.04 ± 0.22	$5.2-15.7$	16.68 ± 1.54	1.56 ± 0.92
314	2.50 ± 0.23	$4.3-12.7$		
328	3.45 ± 0.23	$4.1-12.1$		
343	4.59 ± 0.44	$2.4-7.2$		
359	5.79 ± 0.47	$2.8-10.0$		
		CCl$_2$=CCl$_2$		
298	1.90 ± 0.30	$2.8-16.9$	19.59 ± 3.21	4.63 ± 1.38
314	2.54 ± 0.34	$3.3-13.8$		
328	3.70 ± 0.39	$2.8-12.9$		
343	4.61 ± 0.40	$4.8-13.8$		
359	6.55 ± 1.16	$3.3-11.8$		

Figure 3. Second-order plot for the reaction of O(^{3}P) with (Z)-CHCl=CHCl at different temperatures.

Figure 4. Second-order plot for the reaction of O(^{3}P) with CCl$_2$=CCl$_2$ at different temperatures.

relative to the rate coefficient of O + CF$_2$=CF$_2$ obtained by Sanhueza et al., taking into account the last experimental value reported in the literature by Young et al.[22] of 1.2×10^{-12} cm^3 molecule^{-1} s^{-1} for the rate coefficient of O + CF$_2$=CF$_2$, the obtained rate coefficient for the reaction O + CCl$_2$=CH$_2$ of 1.2×10^{-12} cm^3 molecule^{-1} s^{-1} is even closer to the value obtained in this work. However, our value of 11.3×10^{-13} cm^3 molecule^{-1} s^{-1} is 1.7 times higher than the value reported by Upadhyaya et al. of 6.6×10^{-13} cm^3 molecule^{-1} s^{-1} [9] and 2.3 times faster than the value reported by Hranisavljevic et al. of 4.98×10^{-13} cm^3 molecule^{-1} s^{-1}.[11] It is worth noting that there appears to be an upward discrepancy between our value and those reported by Upadhyaya et al. and Hranisavljevic et al. for this reaction. We have, at present, no satisfactory explanation for this apparent difference aside from the fact that, taking into account that the initial step for the reactions of O atoms with halogenated alkenes is the reversible electrophilic addition of the O atom to the double bond to form an excited biradical intermediate, the observed rate constant may be pressure dependent. Because the results of the present study, although performed at a few Torr of total pressure in the range considered

in this work at room temperature, demonstrate no observable pressure dependence, we can assume that the rate constants offered here reflect the high-pressure limit values and can therefore be directly compared with those of Hranisavljevic et al. which were obtained at much higher pressures. Moreover, since the work of Hranisavljevic et al. was carried out at higher pressures than the present investigation, the opposite trend should be observed, i.e. our values should be lower than theirs, if we were still in the pressure dependent regime. Furthermore, Howard [23] found, in a low-pressure discharge flow system, that for the reaction of OH + CHCl=CCl$_2$, the rate constant levels off at only a few Torr of total pressure and Zhang et al. [24] found no pressure effect on the rate coefficients for OH with the dichloroethenes in the range 5−50 Torr with Ar.

The only temperature-dependent study of the reaction of O(^{3}P) atoms with CCl$_2$=CH$_2$ reported so far is that of Hranisavljevic et al. [11] They show curvature in the Arrhenius plot in the temperature range of 295−1127 K. In Figure 6, for comparative purposes, we have represented their data between 298 and 359 K along with the present results obtained in this work. It can be observed that the rate constants obtained in this work are always higher than their values, although both follow the same trend for the temperature dependence of the rate constants. So
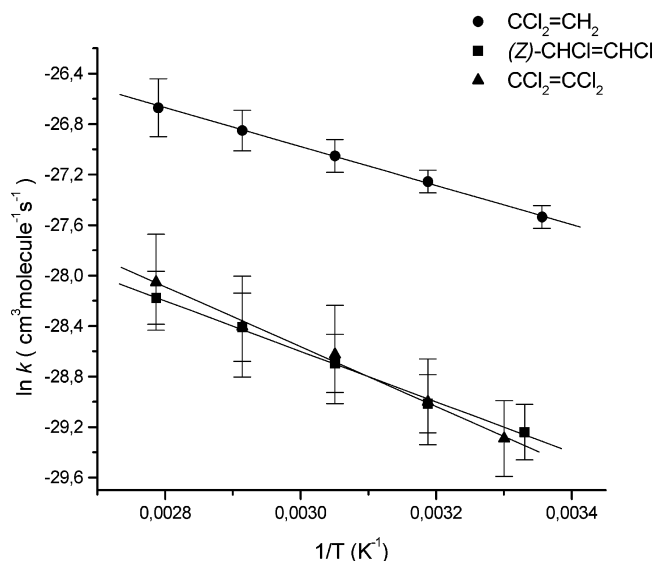
Figure 5. Arrhenius plots for the reactions of O(^{3}P) with CCl$_2$=CH$_2$- (●), (Z)-CHCl=CHCl (■), and CCl$_2$=CCl$_2$ (▲) between 298 and 359 K.
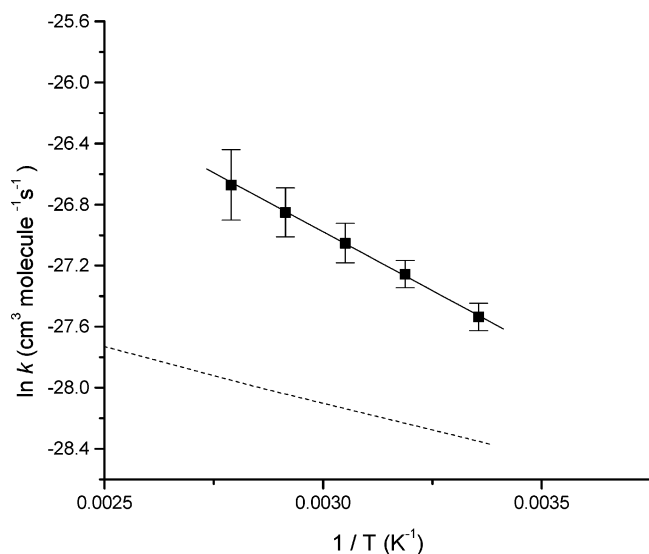

Figure 6. Arrhenius plot for the reaction of O(^{3}P) with CCl$_2$=CH$_2$ from the present study compared with the recommended Arrhenius equation reported by Hranisavljevic[11] (dashed line).
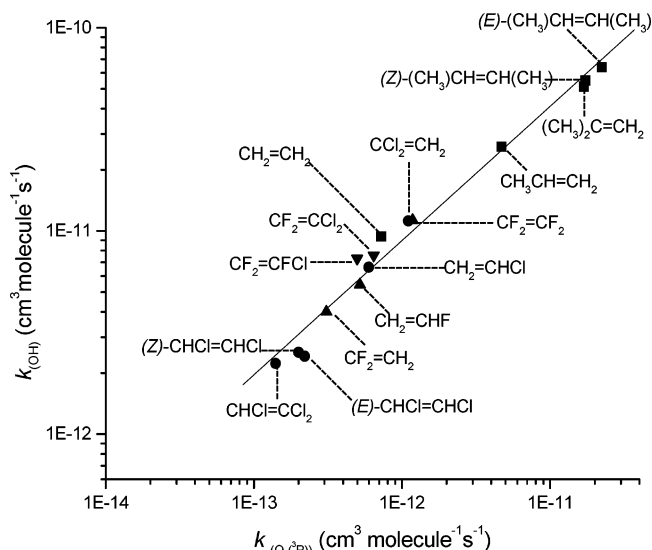

Figure 7. Linear free energy plot of log $k^{O(3P)}$ against log k^{OH} at room temperature for a series of chlorinated (●), fluorinated (▲), chlorofluorinated (▼), and hydrogenated (■) alkenes. Room-temperature rate coefficients for the reactions of O atoms with CCl$_2$=CH$_2$, (Z)−CHCl=CHCl, and CCl$_2$=CCl$_2$ are from this work. Rate constants for the rest of the alkenes with O atoms and for the OH reactions with the same alkenes were taken from ref 26.
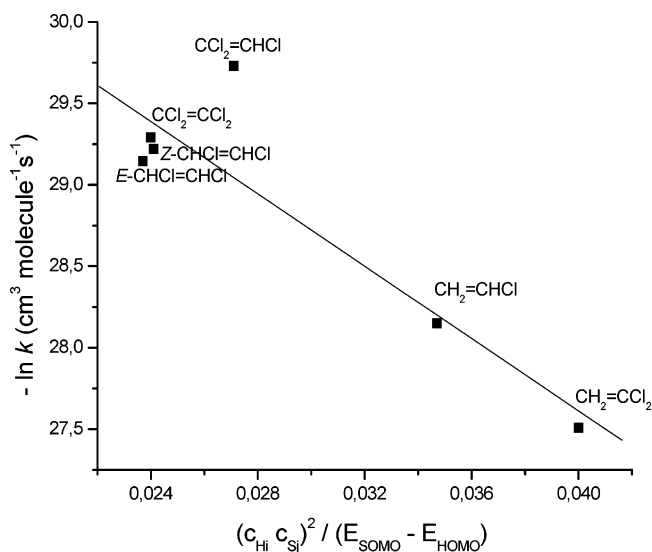

Figure 8. Correlation plot of −ln(k/cm^3 molecule$^{−1}$ s$^{−1}$) vs calculated $(c_{Hi}c_{Sj})^2/(E_{SOMO} − E_{HOMO})$ for the reactions of O(^{3}P) with chloroethenes.

far, we do not have an explanation for the discrepancies. All three reactions studied here show positive activation energies with increasing rate coefficients as the temperature increases between 298 and 359 K. Upadhyaya et al. reported activation energy values, obtained by PM3 calculations, for the reactions of O(^{3}P) with CCl$_2$=CH$_2$ and CCl$_2$=CCl$_2$ to be 14.64 and 22.18 kJ/mol, respectively. These are in very good agreement with our experimental results of 12.63 ± 0.97 and 19.59 ± 3.21 kJ/mol for the same reactions.

There are no prior experimental determinations of the Arrhenius parameters for the reactions of O(^{3}P) with (Z)-CHCl=CHCl and CCl$_2$=CCl$_2$. Hence, this is the first temperature dependence study for these reactions.

The values of rate coefficients and activation energies obtained in the present work appear entirely consistent with the available literature data for the reactions of O(^{3}P) atoms with other halogenated alkenes.[10,13,15,16] Kinetics and products analysis for the reactions of O(^{3}P) with alkenes show that the initial

step proceeds mainly via electrophilic addition of the O(^{3}P) atoms to the double bond to form an energy-rich biradical which may either collisionally stabilize or unimolecularly decompose to products.[25] The positive activation energies obtained in this work and the pressure independence of the reactions, suggest that the dissociation of the triplet biradical will be a fast process compared with the formation of the adduct. Consequently, collisional relaxation will be negligible and the effective rate-determining step will be passage through the entrance channel transition state.

Several correlations between structure and reactivity of alkenes have been suggested.[6,7] The good correlation between the rate coefficient measured for O(^{3}P) atoms reacting with a given alkene to that for the OH radical reacting with the same alkene is shown in Figure 7. A least-squares treatment of the data points in Figure 7 yields the following expression (with

TABLE 2: Experimental Rate Coefficient at 298 K (k_{298K}) and Arrhenius Parameters (E_a and A) for the Reactions of O(^{3}P) Atom with Chloroethenes

chloroethene	experimental method[a]	k_{298K}/ 10^{-13} (cm^3 molecule^{-1}s^{-1})	E_a/10^3 (J mol^{-1})	A/10^{-11} (cm^3 molecule^{-1}s^{-1})	T (K)	P (Torr)	ref
CCl$_2$=CH$_2$	DF−Chem.	11.3 ± 0.9	12.63 ± 0.97	1.82 ± 1.29	298−359	2.1−3.9	this work
	DF−Chem.	6.6 ± 1.1			298	1.2−1.5	9
	FP−RF	4.96 ± 0.60			295−1220	109−411	11
	ELR	9.8 ± 2.0			298	1.2−17.8	10
(Z)-CHCl=CHCl	DF−Chem.	2.04 ± 0.22	16.68 ± 1.54	1.56 ± 0.92	298−359	2.3−3.4	this work
CCl$_2$=CCl$_2$	DF−Chem.	1.90 ± 0.30	19.59 ± 3.21	4.63 ± 1.38	298−359	2.1−3.2	this work
	DF−Chem.	1.90 ± 0.30			298	1.2−1.5	9

[a] Method: DF−Chem., discharge flow−chemiluminescence; FP−RF, flash photolysis−resonance fluorescence; ELR, extensive literature review.

TABLE 3: Rate Coefficients, Perturbation [$(c_{Hi}c_{Sj})^2/(E_{SOMO} - E_{HOMO})$], c_{C1}, c_{C2}, and Ionization Potentials (IP) of the Chloroethenes Series

chloroethenes	$-\ln k_{exp}$ (cm^3 molecule^{-1}s^{-1})	$(c_{Hi}c_{Sj})^2/(E_{SOMO} - E_{HOMO})$ [d]	c_{C1} [e]	c_{C2} [e]	IP(exp) (eV) [f]
CH$_2$=CHCl	28.150[a]	0.0347	0.539	0.392	10.0
CH$_2$=CCl$_2$	27.509[b]	0.0400	0.575	0.377	9.86
(E)-CHCl=CHCl	29.145[c]	0.0237	0.437	0.437	9.63
(Z)-CHCl=CHCl	29.221[b]	0.0241	0.439	0.439	9.66
CCl$_2$=CHCl	29.730[c]	0.0271	0.463	0.411	9.45
CCl$_2$=CCl$_2$	29.292[b]	0.0240	0.432	0.432	9.33

[a] The experimental rate coefficient value at room-temperature (k_{exp}) was taken from ref 10. [b] This work. [c] The experimental rate coefficient values at room-temperature (k_{exp}) were taken from ref 13. [d] A constant value of β^2_{ij} equal to 1 was taken for the homologous series of chloroethenes reacting with O atoms and E_{SOMO} (−1.47 eV) was taken to be numerically identical to the electron affinity of the O atom. The coefficient of the SOMO is 1 for the O(^{3}P) atom. [e] Suffix refers to carbon atom of double bond. C$_1$ is designated as the less substituted carbon atom. [f] The experimental IP values were taken from ref 30.

the rate coefficients in units of cm^3 molecule^{-1} s^{-1}):

$$\log k_{OH} = 0.57278 \log k_{O(3P)} - 4.095 \quad \text{(VII)}$$

The good quality of the correlation between OH and O(^{3}P) atoms reaction rate coefficients is such that estimation can be made of the rate coefficients for reactions which have not yet been investigated. Moreover, this correlation shows that the mechanism of alkene reactions with O(^{3}P) atoms is similar to that observed for OH-alkene reactions, i.e. that the addition to the double bond of the alkene occurs in the primary step, forming a radical (in the case of OH additions) or a biradical (in the case of O(^{3}P) additions).[6]

The reactivity of O atom addition to alkenes and methyl-substituted alkenes has been found to correlate with the ionization potentials (IP) of the alkenes.[27,28] The energy required to remove a π-electron, the ionization potential, is lowered in the alkenes by substitution of an H atom by an alkyl group, while the electron density of the double bond is increased by the substitution leading to an increase in the reaction rates. Previously, we pointed out that the correlation between rate coefficient and IP does not hold for the chloroethenes and chlorofluoroethenes.[13,29] In fact, the same behavior as for the hydrogenated ethenes is observed for the fluoroethenes, whereas for the chlorine substituted ethenes the opposite trend is observed; i.e., the reaction rate constants decrease as the ionization potentials decrease (Table 3). The same tendency is observed for the chloropropenes.[31] Probably, the reason is that in the chloroalkenes, the highest occupied molecular orbital (HOMO), whose energy is described by the experimental ionization potential, is composed of carbon−carbon π-bonding and chlorine−atom lone pairs. Consequently, the HOMO spreads out covering both the double bond and the chlorine atom or atoms and the energy of that orbital (the ionization potential) by itself is insufficient to reflect the reactivity of the molecule. The attacking O atom thus experiences greater nonbonding

interactions in the transition state than it does in the alkene reactions, where the HOMO is solely carbon−carbon π-bonding.[32]

In a previous work,[14] we pointed out that the frontier molecular orbital (FMO) theory appears as a reasonable starting point to establish reactivity trends of similar types of reactions. Considering that the addition mechanism operates for the reaction of different chloroethenes with O(^{3}P), i.e., formation of a single new bond at one end of the π-bond system, asymmetry in substituents around the double bond will bring about asymmetry or nonequivalence in the size of the HOMO orbital coefficients. These are related, in terms of the FMO approach, with the energy change involved in the reaction as follows[33]

$$\ln(k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) \propto \Delta E \propto \frac{c_{Hi}^2 c_{Sj}^2 \beta_{ij}^2}{E_{SOMO} - E_{HOMO}} \quad \text{(VIII)}$$

where c_{Hi} is the atomic orbital coefficient of atom i in the HOMO of the chloroethene, c_{Sj} is the coefficient of the atomic orbital SOMO of the electrophile and β_{ij} is the resonance integral between atoms i and j.

Thus, if an orbital coefficient is taken to be directly related to the size of the orbital, then the change in reactivity of a chloroalkene toward a radical as compared to a simple alkene can be expected to be related, according to eq VIII, to the product of the squared values of the coefficients, of the carbon atom with the highest coefficient in each chloroethene and the coefficient of the SOMO orbital of each electrophile.

Table 3 lists the rate constants at 298 K for the reactions of O(^{3}P) with a series of chloroethenes including the rate coefficients, obtained in the present work, for the reactions of O(^{3}P) atoms with CCl$_2$=CH$_2$, (Z)-CHCl=CHCl and CCl$_2$=CCl$_2$ together with the corresponding orbital coefficients computed by the PM3 method. In Figure 8, a linear correlation can be

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observed between ln k and the second-order perturbational term, ($[c_{Hi}^2 c_{Sj}^2]/[E_{SOMO} - E_{HOMO}]$). It is also evident from Table 3 that the greater the disparity between orbital coefficients, the higher the reactivity of the chloroethene, and the greater the value of the C_1 coefficient of the chloroethene, the greater the rate constant which means that the overlap HOMO−SOMO will be more effective for reaction to occur. The fact that the addition takes place at the carbon atom of the double bond with the highest coefficient allows a more quantitative description of the experimental observation, based on analysis of the reaction products,[12,34−36] that the electrophilic attack of the O(^{3}P) will be at the less substituted carbon atom of the alkene or that chlorine substitution deactivates the carbon on which it is attached toward radical attack while activating the carbon on the other side of the double bond.

The correlation based on eq VIII can be described mathematically by the following equation:

$$-\ln(k/\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}) = a\frac{c_{Hi}^{\;2}\,c_{Sj}^{\;2}}{E_{SOMO} - E_{HOMO}} + b \tag{IX}$$

A standard linear-squares regression of the fitting of the data shown in Table 3 and in Figure 8 yields the values of a and b which are 110.95 ± 25.13 and 32.05 ± 0.74, respectively in good agreement with the ones previously reported of 115.15 ± 31.39 and 32.44 ± 1.00.[14] Errors are quoted at 95% confidence level. Thus, considering the experimental value of the rate constants obtained in this work for the reaction of O(^{3}P) with $CCl_2{=}CH_2$ and for the first time with (Z)-CHCl=CHCl and $CCl_2{=}CCl_2$, we have updated the previously reported expression[14] for the correlation between the rate constants and the second-order perturbation term for this kind of reactions.

To a first approximation, this correlation allows room-temperature rate coefficients to be predicted within ±25−30% of the measured values.

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