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Gas-phase kinetics of the reactions of $O(^3P)$ atoms with (*Z*)-CHCl═CHCl, CCl_2═CH_2, CCl_2═CCl_2 and (*E*/*Z*)-CFCl═CHCl at 298 K†

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ABSTRACT: The kinetics of the gas-phase reactions of $O(^3P)$ atoms with (*Z*)-CHCl═CHCl, CCl_2═CH_2, CCl_2═CCl_2 and (*E*/*Z*)-CFCl═CHCl were studied at 298 K using a discharge flow tube system. The overall rate constants based on the measured afterglow reactions were $(2.0 \pm 0.2) \times 10^{-13}$, $(11.3 \pm 0.9) \times 10^{-13}$, $(1.9 \pm 0.3) \times 10^{-13}$, and $(1.4 \pm 0.3) \times 10^{-14}$, respectively, all in units of cm^3 $molecule^{-1}$ sec^{-1}. The experiments were carried out under pseudo-first-order conditions with $[O(^3P)]_0 \ll$ [chloroethene]. Halogen substitution in the alkenes is discussed in terms of reactivity with $O(^3P)$ and its relation to the ionization potential and the reactivity with OH radicals.
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KEYWORDS: reaction rate constants; (*Z*)-1,2-dichloroethene; 1,1-dichloroethene; tetrachloroethene; (*E*/*Z*)-1,2,-dichlorofluoroethene; oxygen atom

INTRODUCTION

Reactions of ground-state oxygen atoms, $O(^3P)$, with alkenes are of both 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 involving the C═C bond.

On the other hand, chlorinated compounds make up a significant part of wastes and the need to obtain detailed kinetic and mechanistic information on their fate has frequently been emphasized.[1] It is well known that chloroethylenes are toxic and carcinogenic and in high temperature environments, such as in incinerators, the incomplete combustion of chlorinated hydrocarbons produces trichloroethylene among the most frequently present of these compounds.

Although a substantial body of kinetic data exits 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]

The reaction of CCl_2═CCl_2 with $O(^3P)$ has been studied previously by Upadhyaya *et al.*[3] using a discharge flow tube system with chemiluminescence detection at 298 K and at pressures between 1.2 and 1.5 Torr. They also performed theoretical calculations using PM3 and CTST methods, observing that the formation of a biradical in the addition reaction of an O atom to the double bond was the main reaction pathway.

Concerning the reaction of (*E*/*Z*)-CFCl═CHCl with $O(^3P)$ there is only one previous kinetic study at 298 K performed by Lee *et al.*[4] using a discharge flow tube system coupled with a chemiluminescence imaging technique.

For the reaction of CCl_2═CH_2 with $O(^3P)$ the available kinetic data is quite scattered. Room temperature rate coefficients have been reported ranging from 4.9 to 9.8×10^{-13} cm^3 $molecule^{-1}$ sec^{-1}.[2,3,5] There is a related study by Sanhuenza and Heicklen[6] which was later reviewed by Cvetanovic,[2] and more recently two absolute studies reported by Hranisavljevic *et al.*[5] and Upadhyaya *et al.*[3] Hranisavljevic *et al.*[5] used a high temperature photochemical reactor (HTP), producing the $O(^3P)$ atoms by either flash photolysis or laser photolysis of SO_2 or O_2 and monitoring their relative concentrations by resonance fluorescence.

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To the best of our knowledge, there are no previous kinetic data on the reaction of O(^{3}P) atoms with (*Z*)-CHCl═CHCl. Therefore, this is the first determination of the rate constant for this reaction.

As part of a systematic study of O(^{3}P) atom reactivity, we report in this paper absolute rate constants for the reactions of O(^{3}P) with (*Z*)-CHCl═CHCl, CCl_2═CH_2, CCl_2═CCl_2, and (*E*/*Z*)-CFCl═CHCl measured in a discharge flow tube apparatus coupled with a chemiluminescence detection system to monitor the O(^{3}P) decay at 298 K.

The present study was undertaken to complete our previous studies on O + chloroethene reactions[7] using these reactions as a prototype system of additions to the C═C double bond. These results could be of importance in combustion chemistry and the correlations with OH addition reactions in atmospheric chemistry.

EXPERIMENTAL

The experiments were conducted in a discharge flow system (Fig. 1) using the air afterglow chemiluminescence reaction to monitor the oxygen atom concentration. Basically, the system consists of a 1.20 m long, 2.50 cm (i.d.) Pyrex tube reactor fitted with a 0.25 cm (i.d.) sliding Pyrex injector used to introduce the alkene at one end of the flow tube at different distances from the center of the observation region, giving contact times in the range of 5–18 msec.

O(^{3}P) atoms were generated by an electrode less microwave discharge (30 W, 2.5 GHz) in a 2% O_2/He mixture and introduced into the main flow of He carrier gas. The flow tube pressures were varied between 2.1 and 3.9 Torr. Helium was used as the carrier gas and under our experimental conditions, a Reynolds number of less than 50 allowed the work to be carried out under a laminar flow regime which, due to the rapid radial mixing of the gases, satisfied the condition known as 'plug flow,' allowing a linear correlation between distances and times of contact between the O(^{3}P) and the chloroethenes.[8,9]

The system was evacuated by a rotary pump (Edwards $80\,m^3\,h^{-1}$) and a capacitance manometer (MKS, 0–10 Torr) was used to measure the pressure in the tube. Electronic mass flow controllers (MKS), previously calibrated for each gas mixture, were used to control and measure the gas flows in the reaction tube. The concentration of O(^{3}P) atoms was monitored by measuring the chemiluminescence from the air afterglow reaction in which O(^{3}P) atoms react with NO to produce electronically excited nitrogen dioxide (NO_2^*).[10,11] A constant flow of NO was added, so that [NO] was *ca*. (3.4–4.9) $\times 10^{14}$ molecule cm^{-3} and the chemiluminescence from NO_2^* passed through a wide bandpass filter ($\lambda < 500$ nm) before reaching the photomultiplier tube, the output signal of which was amplified and displayed on an oscilloscope. In all experiments the background signal obtained when [NO] = [chloroethene] = 0, arising from scattered light in the reaction tube, was subtracted from S_t before further analysis. Concentrations of O(^{3}P) atoms in the kinetic experiments were estimated by the fast reaction with NO_2 under second-order conditions.[12] The initial concentrations of O atoms ranged from 1.9 to 3.6×10^{12} atom cm^{-3}. Several experiments were carried out measuring the chemiluminescence signal in the absence of added olefin, and introducing O atoms at different contact times, in order to assess wall losses of O atoms. The measured values of k_w were always less than 8 sec^{-1}, therefore, the flow tube walls were left uncoated.[8]

The commercial gases used in this study had the following stated minimum purity: He (AGA 99.999%), O_2 (AGA 99.999%), NO (AGA 99.5%), (*Z*)-CHCl═CHCl (Aldrich 97%), CCl_2═CH_2 (Aldrich 99%), CCl_2═CCl_2 (Aldrich 99%) and (*E*/*Z*)-CFCl═CHCl (Apollo Scientific 98%). Nitric oxide was purified by passing it through a trap held at 153 K to remove NO_2.

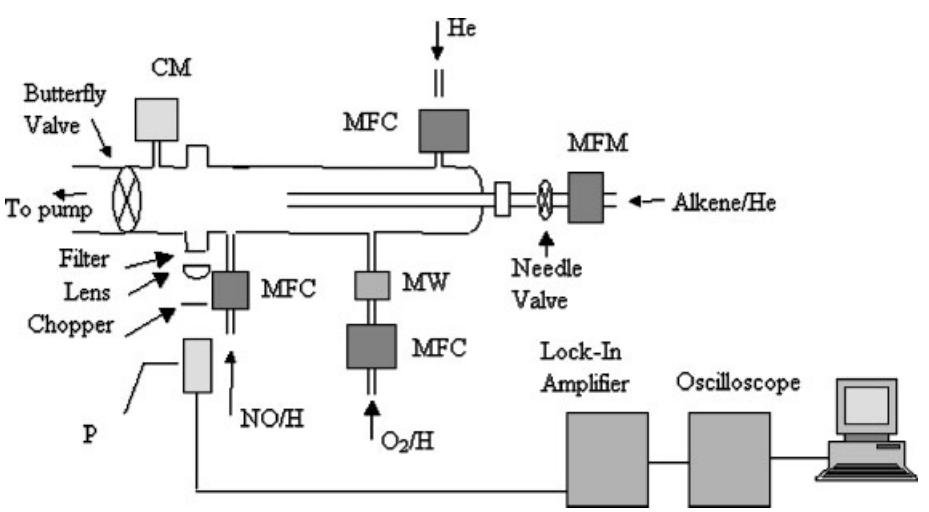

Figure 1. Schematic diagram of the discharge flow tube used to study the O(^{3}P) atom addition reaction for haloalkenes. PM: photomultiplier tube; MFC: mass flow controller; MFM: mass flow meter; MW: microwave cavity; CM: capacitance manometer; P: photomultiplier tube; MFC: mass flow controller; MFM: mass flow meter; MW: microwave cavity; CM: capacitance manometer

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The helium flowed through traps containing silica gel and molecular sieves (BDH Type 4A) at 77 K to remove water. Chloroethenes were degassed prior to use and oxygen was used as supplied.

RESULTS

The absolute rate constants, k, at 298 K were obtained for the reactions of $O(^3P)$ with (*Z*)-CHCl═CHCl, $CCl_2{=}CH_2$, $CCl_2{=}CCl_2$ and (*E*/*Z*)-CFCl═CHCl.

The experiments were carried out under pseudo-first-order conditions. The loss of O atoms may be described by the equation:

$$\ln\{[O(^3P)]_0/[O(^3P)]_t\} = (k[\text{ethene}]_0 + k_x)t = k't \quad (1)$$

where $[O(^3P)]_0$ is the concentration of O atoms in the absence of ethene and $[O(^3P)]_t$ is the concentration after reaction with the ethene over time t, k' is the measured pseudo-first-order rate coefficient and k_x is the first-order rate coefficient for $O(^3P)$ atom 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 Eqn (1), it is possible to write:

$$\ln(S_0/S_t) = k't \quad (2)$$

A plot of ln (S_0/S_t) *versus* time of contact gave the pseudo-first-order decay rate constant, k'. A typical pseudo-first-order plot for the reaction of $O(^3P)$ with $CCl_2{=}CH_2$ is shown in Fig. 2. The pseudo-first-order rate coefficients were corrected for axial and radial diffusion.[8] This procedure resulted in less than 5% upward correction of the k' values.

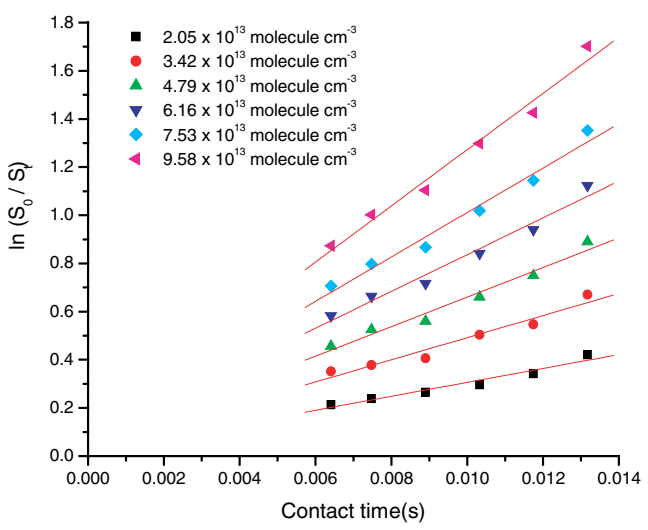

Figure 2. Typical pseudo-first-order plot for the $O(^3P) + CCl_2{=}CH_2$ reaction at 298 K with different concentrations of $CCl_2{=}CH_2$

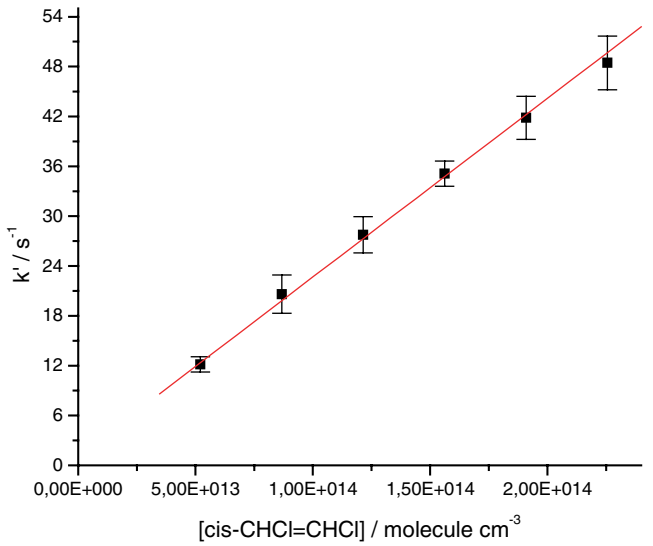

Figure 3. Second-order plot for the $O(^3P) + (Z)$-CHCl═CHCl reaction at 298 K

The second-order rate coefficient, k, was obtained from the slope of the line of a plot of k' *versus* $[\text{chloroethene}]_0$ at a given temperature. Figures 3–6 show plots of the values of k' *versus* [(*Z*)-CHCl═CHCl], $[CCl_2{=}CH_2]$, $[CCl_2{=}CCl_2]$, and [(*E*/*Z*)-CFCl═CHCl], respectively.

The rate constant 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 increase these accuracy estimates by about 10%.

The linearity of the data points, especially in the low alkene concentration range in our plots, suggests that the

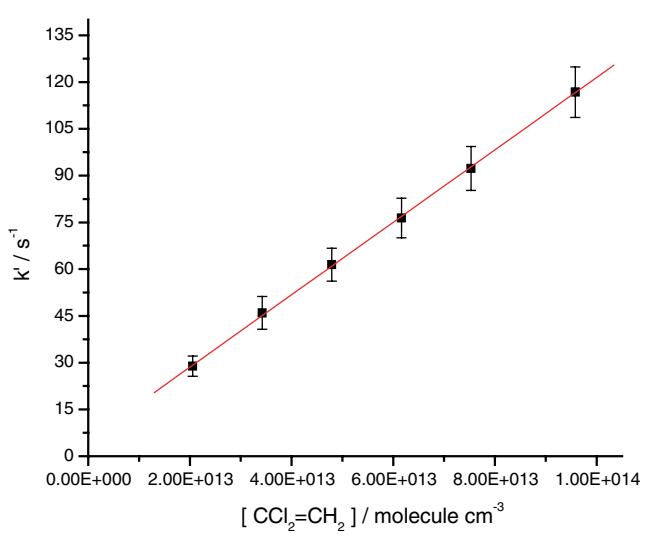

Figure 4. Second-order plot for the $O(^3P) + CCl_2{=}CH_2$ reaction at 298 K

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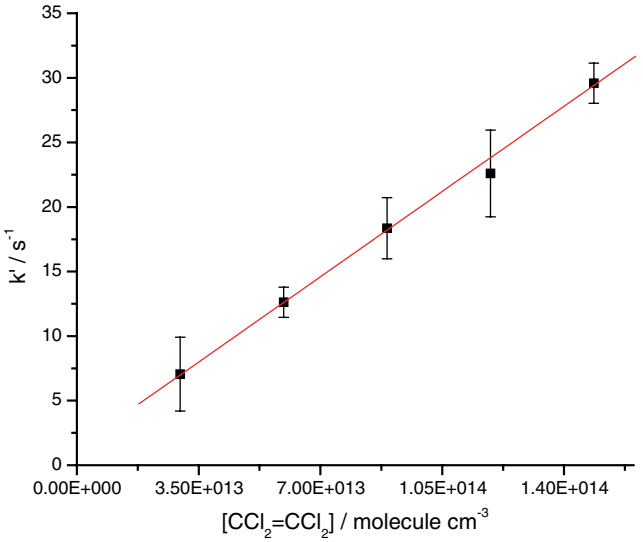

Figure 5. Second-order plot for the O(^{3}P) + $CCl_2{=}CCl_2$ reaction at 298 K

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 show practically no intercepts is consistent with a negligible loss of oxygen atoms by wall reactions ($k_w < 8\,\text{sec}^{-1}$). Therefore, no corrections for the velocity profile effect were required.[8] The bimolecular rate constants at 298 K for the reactions O(^{3}P) + Alkenes → Products, were determined as $(2.0 \pm 0.2) \times 10^{-13}$, $(11.3 \pm 0.9) \times 10^{-13}$, $(1.9 \pm 0.3) \times 10^{-13}$, and $(1.4 \pm 0.3) \times 10^{-13}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{sec}^{-1}$ for (*Z*)-CHCl=CHCl, $CCl_2{=}CH_2$, $CCl_2{=}CCl_2$, and (*E*/*Z*)-CFCl=CHCl, respectively.

DISCUSSION

Comparison with previous measurements

The rate constants obtained in this work are compared with previously reported data in Table 1. 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. However, rate coefficient data have been reported for the related compounds, $CCl_2{=}CH_2$, $CCl_2{=}CCl_2$ and (*E*/*Z*)-CFCl=CHCl.

For $CCl_2{=}CCl_2$ our value of *k* at room temperature is in excellent agreement with that previously reported by Upadhyaya *et al.*[3] using the same experimental technique.

Concerning the reaction of O atoms with (*E*/*Z*)-CFCl=CHCl, we obtained an acceptable agreement, within the experimental error, with the previous value reported by Yi *et al.* using the discharge flow technique with CCD-chemiluminescence detection.[4]

For the reaction of O(^{3}P) with $CCl_2{=}CH_2$, Table 1 shows that the value of *k* at room temperature obtained in this work is in good agreement with the value recommended by Cvetanovic.[2] However, our value of $11.3 \times 10^{-13}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{sec}^{-1}$ is 1.7 times higher than the value reported by Upadhyaya *et al.*[3] of $6.6 \times 10^{-13}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{sec}^{-1}$ and 2.3 times faster than the rate reported by Hranisavljevic *et al.*[5] of $4.98 \times 10^{-13}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{sec}^{-1}$. It is worth noting that there appears to be an upward discrepancy between our value and those of 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

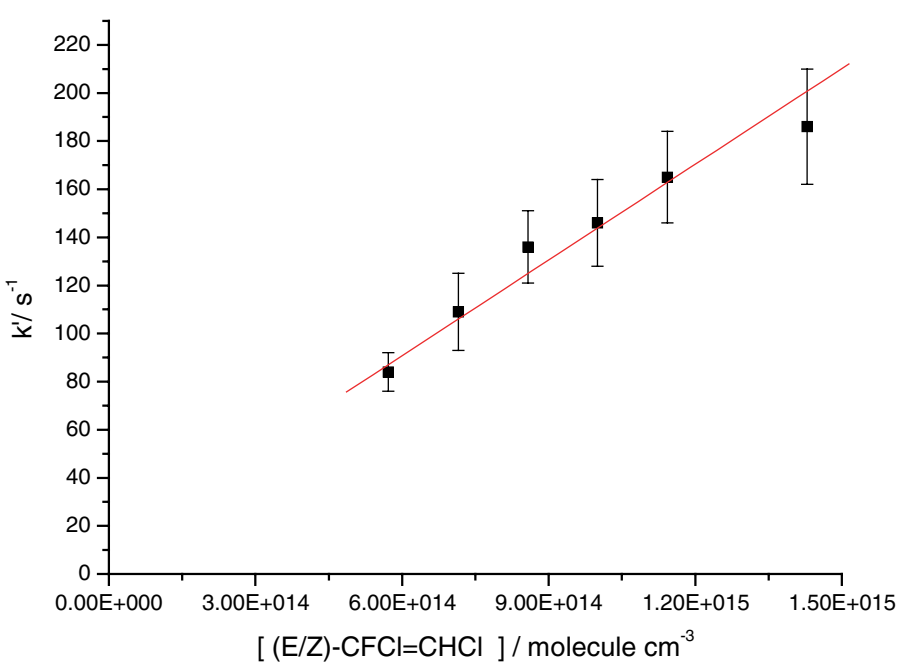

Figure 6. Second-order plot for the O(^{3}P) + (*E*/*Z*)-CFCl=CHCl reaction at 298 K

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Table 1. Rate coefficients ($k_{298\,K}$) for the reactions of O(^{3}P) with chloroalkenes

Alkene	Reference	Experimental method[a]	$k_{298\,K}/10^{-13}$ (cm^3 molecule^{-1} sec^{-1})
(*Z*)-CHCl═CHCl	This work	DF-Chem.	2.0 ± 0.2
$CCl_2{=}CH_2$	This work	DF-Chem.	11.3 ± 0.9
	3	DF-Chem.	6.6 ± 1.1
	5	FP-RF	4.96 ± 0.6
	2	ELR	9.8 ± 2.0
$CCl_2{=}CCl_2$	This work	DF-Chem.	1.9 ± 0.3
	3	DF-Chem.	1.9 ± 0.3
(*E*/*Z*)-CFCl═CHCl	This work	DF-Chem.	1.4 ± 0.3
	4	DF-Chem.	1.57 ± 0.02

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

for the reactions of the O atom with both halogenated ethenes and 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 could 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, that is, our values should be lower than theirs, if we are still in the pressure dependent regime. Furthermore, Howard[13] 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.*[14] found no pressure effect on the rate constants for OH with dichloroethenes in the range 5–50 Torr with Ar.

Reactivity trends

As we pointed out before, the initial step for the reaction of O atoms with halogenated ethenes and alkenes is the reversible electrophilic addition of the O atom to the double bond to form an excited biradical intermediate.

There are different factors that could influence the rate of addition to the double bond: substitution of H by Cl atoms on the alkene reduces the electron density of the double bond through an inductive effect, causing deactivation toward electrophilic attack. This effect can be observed in Table 2 through the following trend: $k_{CH_2=CH_2} > k_{CHCl=CH_2} > k_{CHCl=CHCl} > k_{CHClCCl_2}$. This negative effect on the rate is offset by a positive stabilizing effect on the biradical intermediate of the Cl atoms; the more stable the biradical or radical intermediate formed in the addition step, the faster the reaction rate. Chlorine atoms have a greater stabilizing effect than alkyl groups and this could be one of the main reasons for the difference in reactivity with O atoms of the two isomers, CHCl═CHCl and $CCl_2{=}CH_2$.

The presence of F atoms on the alkene produces a decrease in its reactivity towards the O(^{3}P) atoms. This effect can be attributed to the strong electron-withdrawing capacity of the F atoms which reduce the charge density on the carbon atom next to the double bond as well as the polarizability of the π electrons, leading to a decrease in the rate constant value, which is consistent with the electrophilic character of the O atoms. Thus, $k_{CH_2=CH_2} > k_{CH_2=CHF} > k_{CH_2=CF_2}$ as shown in Table 2.

The electronic density of the σ bond in the C═C bond is reduced by the inductive effect of the halogen atom, whereas the electronic density of the π bond is increased by the mesomeric effect. This is observed if F substitution by Cl is compared, thus increasing the mesomeric effect as well as the rate constant ($k_{CH_2=CHF} < k_{CH_2=CHCl}$ and $k_{CH_2=CF_2} < k_{CH_2=CCl_2}$).

Correlation of *k* with the ionization potential

The reactivity of O atom addition to ethene and methyl-substituted ethenes has been found to correlate with the ionization potentials of the olefins. The energy required to remove a π electron, the ionization potential,[18] is lowered in the olefins 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. The opposite trend, however, is observed with the chloroethenes, the reaction rate constants decrease as the ionization potentials decrease as can be noted in Table 2 for the series of $CH_2{=}CH_2$, $CH_2{=}$CHCl, CHCl═CHCl, CHCl═CCl_2 and $CCl_2{=}CCl_2$. The reason is probably that in the haloethenes, the highest occupied molecular orbital is composed of carbon–carbon π bonding and halogen atom lone-pair contributions. The attacking radical, thus, experiences greater nonbonding interactions in the transition state than it does in the alkene reactions where the HOMO involves solely carbon–carbon π bonding.[19]

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Table 2. Rate constants for the reactions of haloalkenes with O(^{3}P) at 298 K and ionization potential (IP) for the corresponding haloalkenes

Alkene	$k_{298\,K}$ (cm^3 molecule^{-1} sec^{-1})	Reference	IP (eV)	Reference
C=C	O(^{3}P) + alkene			
$CH_2{=}CH_2$	7.25×10^{-13}	2	10.51	17
$CH_2{=}CHF$	3.25×10^{-13}	2	10.36	17
$CH_2{=}CF_2$	2.34×10^{-13}	2	10.29	17
$CHF{=}CF_2$	5.73×10^{-13}	2	10.15	17
(*E*)-CHF=CHF	4.62×10^{-13}	2	10.18	17
$CF_2{=}CF_2$	9.76×10^{-13}	2	10.14	17
$CF_2{=}CFCl$	4.06×10^{-13}	15	9.81	17
$CF_2{=}CCl_2$	3.10×10^{-13}	16	9.65	17
(*E*/*Z*)-CFCl=CFCl	1.67×10^{-13}	15	9.77	a
$CCl_2{=}CCl_2$	1.9×10^{-13}	This work	9.33	17
$CH_2{=}CHCl$	5.94×10^{-13}	2	9.99	17
$CH_2{=}CCl_2$	11.3×10^{-13}	This work	9.81	17
$CHCl{=}CCl_2$	1.40×10^{-13}	7	9.45	17
(*E*)-CHCl=CHCl	2.20×10^{-13}	7	9.64	17
(*Z*)-CHCl=CHCl	2.00×10^{-13}	This work		
(*E*/*Z*)-CHF=CHCl	1.648×10^{-13}	15	9.86	a
$CH_2{=}CFCl$	2.83×10^{-13}	16	10.14	a
(*E*/*Z*)-CHCl=CFCl	1.4×10^{-13}	This work	9.67	a

[2] Calculated by PM3 method.

Linear free-energy correlations

The O(^{3}P) atom has an electrophilic character like the OH radical. It may be expected that the rate constants for these species with unsaturated carbon–carbon bonds will exhibit some degree of correlation. In this sense, Fig. 7 shows a very good correlation between $k_{O(^3P)}$ and k_{OH} for the entire series of ethenes for which measurements exist, with a least-squares expression of (with the rate constants in units of cm^3 molecule^{-1} sec^{-1}):

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

The correlation between the reaction rate constants for OH and O(^{3}P) atoms is sufficiently good for estimations of the rate constants to be made for reactions that have not yet been measured. Moreover, this correlation shows that the mechanism of alkene reactions with O(^{3}P) atoms is similar to that observed for OH-alkene reactions, this is, that the addition to the alkene double bond 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).[21]

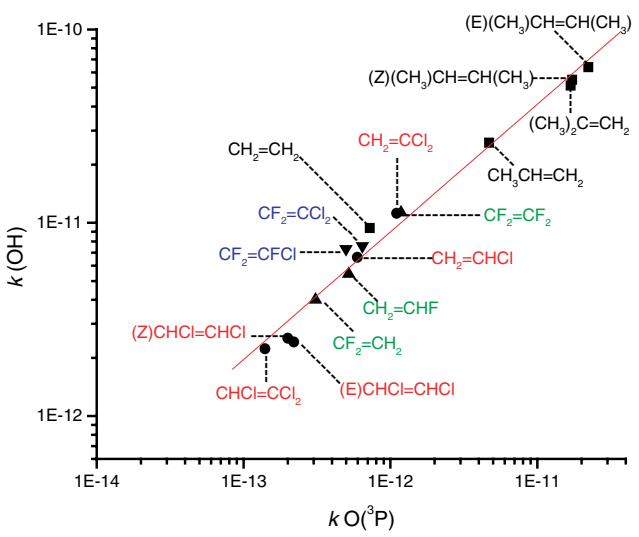

Figure 7. Linear free energy plot of $\log k^{O(^3P)}$ against $\log k^{OH}$ at room temperature for a series of chlorinated (●), fluorinated (▲), chlorofluorinated (▼) and hydrogenated (●) alkenes. Room temperature rate coefficients for the reactions of O + (*Z*)-CHCl=CHCl, $CCl_2{=}CH_2$, $CCl_2{=}CCl_2$, and (*E*/*Z*)-CFCl=CHCl are from this work. Rate constants for the rest of the alkenes with O atoms and for the OH reactions were taken from Ref. 20

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