# Absolute Rate Constants for the Gas-Phase Reactions of O(<sup>3</sup>P) Atoms with CF<sub>2</sub>=CFCl and (*E*/*Z*)-CFCl=CFCl at 298 K. Reactivity Trends of the Halogen-Substituted Ethenes Series

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ABSTRACT: Absolute rate coefficients for the gas-phase reactions of CF<sub>2</sub>=CFCl and (*E/Z*)-CFCl=CFCl with O(<sup>3</sup>P) atoms have been measured at 298 K using a discharge flow tube coupled to a chemiluminescence detection system. The observed rate constant values are  $(4.5 \pm 0.4) \times 10^{-13}$  and  $(1.5 \pm 0.3) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively. The experiments were carried out under pseudo-first-order conditions with  $[O(^{3}P)]_{0} \ll [alkene]_{0}$ . These results are compared to those of O atom reactions with other chlorine- and fluorine-substituted ethenes. Different factors that affect the rate of addition to the double bond are considered. The  $O(^{3}P)$ /chloroethenes reactions do not obey the reactivity trend with the ionization potential, as is the case in the alkene and methyl-substituted alkene reactions. © 2004 Wiley Periodicals, Inc. Int J Chem Kinet 36: 525–533, 2004

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## INTRODUCTION

The gas-phase reactions of ground-state oxygen atoms,  $O({}^{3}P)$ , with alkenes are of both fundamental and practical importance. While there are many studies of O atom reactions with a variety of unsaturated hydrocarbons, only limited information is available for halogenated alkenes, most of which has been reviewed by

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Cvetanovic [1]. The database for perhaloalkenes is even more scarce [2–7], and fluoroalkene reactivity studies toward O atoms are still less [8–11]. Most of these studies have been relative measurements of the rate coefficients.

Mitchell and Simons used the long wavelength flash photolysis of NO<sub>2</sub> as the O(<sup>3</sup>P) atom source and studied its reactions with  $CF_2 = CF_2$  and a series of 1,1difluoroethylenes [4]. The reactants were subjected to continuous photolysis and the final products analyzed by IR spectroscopy. In the reaction with  $CF_2=CF_2$ , a strong signal from the CF2 radical in its ground state  $(X^1A_1)$  was observed by its ultraviolet absorption in the region of 250 nm. CF<sub>2</sub>O was the predominant product. Conversely, in the reaction with CF<sub>2</sub>=CFCl, CF<sub>2</sub>O was also the predominant product, but the CF<sub>2</sub> absorption signal was very weak, implying that Cl atom substitution inhibits the formation of CF2 but enhances that of CF<sub>2</sub>O. Mitchell and Simons did not report the reaction rate constants. Tyerman [5], using the same experimental approach, also did not observe the absorption signal for CF<sub>2</sub> in the CF<sub>2</sub>=CFCl and CF<sub>2</sub>=CCl<sub>2</sub> reations with  $O({}^{3}P)$ . In addition, and contrary to Mitchell and Simons' observations, Tyerman did not find CF2O as a reaction product. However, this author was able to measure the rates of disappearance of these alkenes in reaction with O atoms using a competitive method.

Huie, Herron, and Davis [6], using a discharge flow system coupled to a mass spectrometer, studied the reactions of atomic oxygen with several haloethylenes. The main product in the reactions with  $CF_2=CCl_2$  and  $CF_2=CFCl$  was  $CF_2O$ , and CFCIO in the reaction with CFCI=CFCI. The corresponding rate constants, however, were not reported.

As part of a systematic study of  $O(^{3}P)$  atom reactivity and a prototype system for the addition reactions to the C=C bond, we report in this work absolute rate constants for the reactions of  $O({}^{3}P)$  with the two title perhaloalkenes, measured in a conventional discharge flow tube apparatus at 298 K, as an extension of our earlier measurements of the rate coefficients for the reactions of  $O({}^{3}P)$  with CF<sub>2</sub>=CCl<sub>2</sub> and CF<sub>3</sub>CF=CF<sub>2</sub> [10].

In addition, and in order to clarify whether  $CF_2O$  is, in fact, formed in the reaction with  $CF_2$ =CFCl in view of the discrepancy between Mitchell and Simons' and Tyerman's observations, we conducted several experiments to determine the products of this reaction in an attempt to shed light into its mechanism, i.e., if O atom attack on  $CF_2$ =CFCl occurs exclusively at the  $CF_2$  group.

Reliable rate constant values for these reactions are of interest for the role of chemical oxidative processes in atmospheric and combustion chemistry. In particular, the reactions of  $O(^{3}P)$  atoms with fluorinated alkenes have attracted considerable attention because of their general usefulness in the chemical etching processes of the semiconductor industry. The presence of electronwithdrawing substituents in the alkene is expected to modify the electron distribution considerably, and this should be reflected in the reactivity of the alkene toward the O atoms, thus providing an opportunity to examine halogen substituent effects as a function of extent and positioning about the double bond.

# **EXPERIMENTAL**

The experiments were conducted in a discharge flow system using the air afterglow chemiluminescence signal to follow the oxygen atom concentration. The schematic representation of the discharge flow tube employed in this work is shown in Fig. 1. Briefly, the reac-



Figure 1 Schematic diagram of the discharge flow chemiluminescence system used in  $O(^{3}P)$  atom reaction studies. PM: photomultiplier tube; MFC: mass flow controller; MFM: mass flow meter; MW: microwave discharge; CM: capacitance manometer.

tor consisted of a Pyrex tube (1.00 m long and 2.50 cm i.d.) coupled with an axially sliding injector (0.25 cm i.d.) used to introduce the olefin into the reactor.

Oxygen atoms, O(<sup>3</sup>P), were generated by an electrodeless microwave discharge (30 W, 2.5 GHz) on a 2% O<sub>2</sub>/He mixture and were flowed into the tube through a fixed side-arm port. Initial concentrations of O atoms ranged from  $4 \times 10^{12}$  to  $5 \times 10^{12}$  atom cm<sup>-3</sup>.

Reaction times could be varied by adjusting the distance of the sliding injector with respect to the fixed position of the photomultiplier tube. The system was evacuated by a rotary pump (90  $\text{m}^3 \text{h}^{-1}$ ) and a capacitance manometer (MKS Baratron, 0-10 torr) was used to measure the pressure in the tube. Electronic mass flow controllers (MKS 179 A, 1259 C), previously calibrated for each gas mixture, were used to control and measure the gas flows in the reaction tube. The total linear flow velocity for the reaction with CF2=CFCl was between 1503 and 1610 cm s<sup>-1</sup> and the total pressure was 3.8 torr; for the reaction with (E/Z)-CFCl=CFCl the total linear flow velocity was between 1056 and 1609 cm s<sup>-1</sup> and the total pressure was varied between 1.86 and 5.50 torr. The experiments were conducted at 298 K and 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" [12,13] is satisfied.

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

The position of the injector could be changed from 9 to 50 cm from the center of the detection zone, giving contact times of the  $O(^{3}P)$  atoms with the alkene in the range of 6–20 ms.

The concentration of O(<sup>3</sup>P) atoms was monitored by measuring the chemiluminescence from the air afterglow reaction in which O(<sup>3</sup>P) atoms react with NO to produce electronically excited nitrogen dioxide (NO<sub>2</sub>\*) [14]. A constant flow of NO was added 8.5 cm before the photomultiplier tube detector (Hamamatsu R636) so that NO concentration was ca. (5–9) × 10<sup>14</sup> molecule cm<sup>-3</sup> and the chemiluminescence from NO<sub>2</sub>\* passed through a wide band pass filter ( $\lambda < 500$  nm) before reaching the photomultiplier tube, the output signal of which was amplified and displayed on an oscilloscope. The signal, *S*, was proportional to the light intensity of chemiluminescence. In all experiments, the background signal obtained when [NO] = [alkene] = 0, arising from scattered light in the reaction tube, was subtracted from *S* before further analysis. Concentrations of O(<sup>3</sup>P) atoms in the kinetic experiments were estimated by the fast reaction with NO<sub>2</sub> under secondorder conditions [15].

Several experiments were carried out measuring the chemiluminescence signal in the absence of added alkene, introducing O atoms at different contact times, in order to assess wall losses of O atoms. The measured values of  $k_w$  were always <15 s<sup>-1</sup>.

In order to determine the products of the reaction of  $O(^{3}P)$  atoms with  $CF_2$ =CFCl, several experiments were performed at ambient temperature under static conditions, generating the oxygen atoms,  $O(^{3}P)$ , by the mercury-photosensitized decomposition of  $N_2O$  [16]. The cylindrical Pyrex cell of 250-cm<sup>3</sup> volume, sealed with quartz windows, was illuminated by two lowpressure mercury lamps. In each experiment, a new drop of Hg was admitted into the cell, after which the CF<sub>2</sub>=CFCl and N<sub>2</sub>O were measured manometrically and introduced into the reaction cell. Typically, the pressure of N<sub>2</sub>O was about 100 torr, and that of CF<sub>2</sub>=CFCl about 10 torr.

The analytical techniques employed for qualitative identification of the products formed after irradiation was terminated were infrared spectroscopy using a Buck Scientific model 500 infrared spectrometer and GC-mass spectrometery on a Shimadzu GC-MS QP 5050 spectrometer equipped with a 30 m by 0.12 mm DB-5 MS column.

Calculations of the carbon atomic charges of the alkenes were carried out using the semiempirical method PM3 and ab initio HF and B3LYP/NBO levels of theory with the 6-31G\*\* basis set, using the Gaussian-98 suite of programs [17]. All geometries were fully optimized by minimizing the energy with respect to all geometrical variables. The stationary points were characterized as the minimun-energy structures when the number of imaginary frequencies was zero by calculations of the corresponding Hessian matrix. The ionization potential of the alkenes was taken from the literature [18]. The corresponding values for CFCI=CCl<sub>2</sub> and (E/Z)-CFCI=CFCl that were not available in the literature were calculated in this work using the PM3 semiempirical method.

#### Materials

The commercial gases used in this study had the following stated minimum purity: He (AGA 99.999%), O<sub>2</sub>(AGA 99.999%), NO (AGA 99.5%),

N<sub>2</sub>O (AGA 99.5%), CF<sub>2</sub>=CFCl (PCR 99%), and (E/Z)-CFCl=CFCl (PCR 97%). Nitric oxide was purified by passing it through a trap held at 140 K to remove NO<sub>2</sub>. Helium was flowed through traps containing silica gel and molecular sieves (BDH Type 4 A) at 77 K, to remove water. The alkenes were purified by successive trap-to-trap distillations under vacuum, and oxygen was used as supplied. Nitrous oxide was used without further purification.

## Results

Using the above-mentioned technique the rate constants, k, for the following reactions at 298 K were obtained:

$$O(^{3}P) + CF_{2} = CFCl \rightarrow Products$$
 (1)

$$O(^{3}P) + (E/Z)$$
-CFCl=CFCl  $\rightarrow$  Products (2)

All experiments were carried out under pseudofirst-order conditions with a ratio,  $[alkene]_0/[O(^3P)]_0$ , always greater than 40.

Therefore, in the absence of secondary reactions that significantly deplete the transient  $O(^{3}P)$  atoms,  $O(^{3}P)$  concentration varied with time according to the following expression:

$$[O(^{3}P)]_{t} = [O(^{3}P)]_{0} \exp[-(k[alkene]_{0} + k_{x})t]$$
(3)

$$\ln\{[O(^{3}P)]_{0}/[O(^{3}P)]_{t}\} = k't$$
(4)

where  $[O({}^{3}P)]_{0}$  is the concentration in the absence of olefin,  $[O({}^{3}P)]_{t}$  is the concentration after reaction with the olefin over time *t*, *k'* is the measured pseudo-first-order rate coefficient, and  $k_{x}$  is the first-order rate coefficient for  $O({}^{3}P)$  atom disappearance by diffusion out of the detection zone, reaction with background impurities or wall losses.

In order to monitor the  $O({}^{3}P)$  concentration, a known excess of NO was added to produce electronically excited NO<sub>2</sub>\*, the chemiluminescence of which was checked downstream of the NO inlet port, following the air afterglow reaction:

$$O(^{3}P) + NO + M \rightarrow NO_{2}^{*} + M$$
 (5)

$$NO_2^* \to NO_2 + h\nu$$
 (6)

It has been shown that the intensity, S, of the air afterglow is proportional to the product of the NO and O concentrations [14]. Since NO concentration is constant, the intensity of the air afterglow at selected points down the tube is a relative measure of O(<sup>3</sup>P) concentration.

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 a reactant and  $S_t$  is the signal after addition of a reactant at a fixed time of contact. The O(<sup>3</sup>P) 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 and Eq. (4), it is possible to write

$$\ln(S_0/S_t) = k[\text{alkene}]_0 t \tag{7}$$

The pseudo-first-order decay rate coefficient, k', was computed from the slope of a plot of  $\ln(S_0/S_t)$  vs time of contact, which was linear for approximately three 1/e lifetimes. The second-order rate coefficient for reactions (1) and (2),  $k_1$  and  $k_2$ , were obtained from the slope of the line of a plot of k' vs. [alkene]<sub>0</sub> (Figs. 2 and 3). A linear least-squares fit to the data points yields values of  $k_1 = (4.5 \pm 0.5) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup>s<sup>-1</sup> and  $k_2 = (1.5 \pm 0.3) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Thus, the resultant uncertainties in the values of  $k_1$  and  $k_2$  are about 11 and 20%, respectively. The error limits are one standard deviation from the least-squares analysis. The pseudo-first-order rate coefficients were corrected for axial and radial diffusion [12], using the following expression:

$$k'_{\rm corr} = k'_{\rm exp} (1 + k'_{\rm exp} D/v^2 + k'_{\rm exp} R^2/48D) \quad (8)$$

where D (cm<sup>2</sup> s<sup>-1</sup>) is the diffusion coefficient of O(<sup>3</sup>P) in He, v (cm s<sup>-1</sup>) 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 130–380 cm<sup>2</sup> s<sup>-1</sup>. This procedure resulted in <5% upward correction of the k' values, which means that the second and third



**Figure 2** Second-order plot for the  $O(^{3}P) + CF_{2}=CFCI$  reaction at 298 K.



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

terms in Eq. (8), 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 (Figs. 2 and 3), 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 show practically no intercepts is consistent with a negligible loss of oxygen atoms by wall reactions  $(k_w = 9-15 \text{ s}^{-1})$ . Therefore no corrections for the velocity profile effect were required [12]. The pressure of the reactor for the  $O({}^{3}P) + (E/Z)$ -CFCl=CFCl experiments was changed from 1.9 to 5.5 torr and no variation in the global rate constant was observed.

In order to check the performance of our flow system in obtaining reliable results, we also measured the overall rate constant for the reaction of CH=CH with O(<sup>3</sup>P), obtaining a value of  $(1.4 \pm 0.3) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, which is in excellent agreement with the literature value of  $(1.4 \pm 0.4) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [19].

The products identified by IR spectroscopy and GCmass spectrometry from experiments of the reaction of  $O(^{3}P) + CF_{2}=CFCl$ , generating the O atoms by the Hg-photosensitized decomposition of N<sub>2</sub>O were CF<sub>2</sub>O, CFCl=CFCl, and *c*-C<sub>3</sub>F<sub>4</sub>Cl<sub>2</sub>. The formation of these products suggests that the O atom attaches to the CF<sub>2</sub> group of the alkene, producing CF<sub>2</sub>O and leaving the CFCl radicals to recombine and form CFCl=CFCl and *c*-C<sub>3</sub>F<sub>4</sub>Cl<sub>2</sub> by reaction with the reactant CF<sub>2</sub>=CFCl.

### DISCUSSION

The rate constant values at 298 K for the reactions of O atoms with  $CF_2$ =CFCl and (E/Z)-CFCl=CFCl found

in the literature for comparison are scarce. Tyerman [5] studied the reaction with CF2=CFC1. Huie, Herron, and Davis [6] reported the product carbonyl halide of the reaction of O + CFCl = CFCl, but the corresponding rate coefficient was not reported. Tyerman obtained a value of 0.51 for the ratio of the rates of reaction of oxygen atoms with CF2=CFCl relative to CF2=CF2 at 298 K [5]. If the value recommended by Cvetanovic [1] for the reference reaction rate constant,  $O(^{3}P) +$  $CF_2 = CF_2, k_{298} = 9.76 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$ is used, the rate constant for the reaction of interest is  $4.98 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, based on the value of 0.51 for the relative rates. Thus, our value of  $k_1 = (4.5 \pm 0.5) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is in good agreement with the previous one obtained from relative measurements.

More recently, Yi et al. [11], using the chemiluminescence imaging technique, determined the rate coefficients at room temperature for O(<sup>3</sup>P) + CF<sub>2</sub>=CFCl and O(<sup>3</sup>P) + CFCl=CFCl as  $(5.04 \pm 0.14) \times 10^{-13}$ and  $(2.67 \pm 0.07) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively. Again, our value of  $k_1$  for CF<sub>2</sub>=CFCl is in good agreement, within the combined uncertainties of both investigations, whereas for CFCl=CFCl our value of  $k_2 = (1.5 \pm 0.3) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> is almost a factor of two lower.

The room-temperature rate constants for the reactions of the ethenes studied in this work and some other fluorine- and chlorine-substituted ethenes with the O atom are listed in Table I. Whenever hydrogen is replaced by fluorine or chlorine at any position in the molecule, the reactivity of the substituted ethene to O atoms is less than that of the unsubstituted ethene, the only exception being that  $CF_2=CF_2$  is more reactive than  $CH_2=CH_2$ .

For the sake of clarity and order of this discussion, we will first analyze the fluoroethenes, then the chloroethenes, and finally the perhalogenated ethenes. The rate constant values for the reactions of the fluoroethenes show that (a) The magnitude of the effect of hydrogen substitution by fluorine varies considerably with the position of substitution, and (b) as the number of fluorine atoms attached to the carbon atoms of the double bond increases, the reactivity of the ethene does not continue to decrease but appears to pass through a minimum. Asymmetric fluorination of the olefinic carbon atom seems to lessen reactivity, whereas further fluorination (more symmetric substitution) compensates for the original deactivation, so much so that  $CF_2 = CF_2$  has a rate coefficient greater than that of CH<sub>2</sub>=CH<sub>2</sub>. This suggests that alkene reactivity toward O atoms depends on the geometrical localization of the  $\pi$ -electron density. The  $\pi$ -electron density localization in the center of the C=C bond ( $CH_2$ = $CH_2$ ,  $CF_2$ = $CF_2$ )

$\frac{\text{Alkene}}{\text{C}^{(1)}=\text{C}^{(2)}}$	Method of Calculation	Total Atomic Charges		$k_{(298 \text{ K})} (\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1})$		
		C <sup>(1)</sup>	C <sup>(2)</sup>	$O(^{3}P) + alkene$	Ref.	$IP^{a}$ (eV)
CH <sub>2</sub> =CH <sub>2</sub>	PM3	-0.3196	-0.3196	$7.31 \times 10^{-13}$	[1]	10.51
	RHF	-0.2544	-0.2544	$7.40 \times 10^{-13}$	[20]	
	B3LYP/NBO	-0.4347	-0.4347	$7.38 \times 10^{-13}$	[11]	
CH <sub>2</sub> =CHF	PM3	-0.3841	-0.0797	$3.25 \times 10^{-13}$	[1]	10.36
	RHF	-0.3610	0.2977			
	B3LYP/NBO	-0.5517	0.2272			
CH <sub>2</sub> =CF <sub>2</sub>	PM3	-0.4074	0.1681	$2.34 \times 10^{-13}$	[1]	10.29
	RHF	-0.4382	0.7647			
	B3LYP/NBO	-0.6392	0.7969			
(E/Z)-CHF=CHF	PM3	-0.1311	-0.1311	$4.48 \times 10^{-13}$	[1]	10.18
	RHF	0.2038	0.2038			
	B3LYP/NBO	0.1307	0.1307			
CHF=CF <sub>2</sub>	PM3	-0.1394	0.1252	$5.73 \times 10^{-13}$	[1]	10.15
	RHF	0.1321	0.6933	$4.05 \times 10^{-13}$	[8]	
	B3LYP/NBO	0.0466	0.7087			
CF <sub>2</sub> =CF <sub>2</sub>	PM3	0.1247	0.1247	$9.76 \times 10^{-13}$	[1]	10.14
	RHF	0.6366	0.6366			
	B3LYP/NBO	0.6336	0.6336			
CH <sub>2</sub> =CHCl	PM3	-0.3314	-0.3314	$5.94 \times 10^{-13}$	[1]	9.99
	RHF	-0.2445	-0.2103	$5.19 \times 10^{-13}$	[21]	
	B3LYP/NBO	-0.4540	-0.2474		[]	
CH <sub>2</sub> =CCl <sub>2</sub>	PM3	-0.3270	-0.2355	$4.88 \times 10^{-13}$	[21]	9.81
	RHF	-0.2257	-0.2054	$9.79 \times 10^{-13}$	[1]	,
	B3LYP/NBO	-0.4629	-0.1176	<i></i>	[+]	
(E)-CHCl=CHCl	PM3	-0.2928	-0.2928	$2.20 \times 10^{-13}$	[22]	9.64
	RHF	-0.2009	-0.2009	$9.58 \times 10^{-14}$	[23]	2101
	B3LYP/NBO	-0.2810	-0.2810	21007710	[=0]	
CHCl=CCl <sub>2</sub>	PM3	-0.2979	-0.2673	$1.40 \times 10^{-13}$	[22]	9.45
	RHF	-0.1916	-0.2073	$1.10 \times 10^{-13}$	[22]	2.15
	B3LYP/NBO	-0.2950	-0.1439	1.07 × 10	[21]	
CCl <sub>2</sub> =CCl <sub>2</sub>	PM3	-0.2785	-0.2785			9 33
	RHF	-0.1935	-0.1935			7.55
	B3LYP/NBO	-0.1643	-0.1643			
CF <sub>2</sub> =CFCl	PM3	0.1450	-0.1102	$4.5 \times 10^{-13}$	b	9.81
	RHE	0.7291	0.1522	$4.98 \times 10^{-13}$	[1]	2.01
	B3I VP/NBO	0.7099	0.1322	$5.04 \times 10^{-13}$	[1]	
CF <sub>2</sub> =CCl <sub>2</sub>	PM3	0.1795	-0.3538	$3.10 \times 10^{-13}$	[11]	0.65
	DUE	0.8536	-0.5558	$5.10 \times 10^{-13}$	[10]	9.05
	R3I VP/NBO	0.8550	-0.4149 -0.2904	0.47 × 10	[1]	
$CFCI=CCI_2$		0.7801	-0.2904	$1.36 \times 10^{-13}$	[11]	0 40¢
		-0.0443	-0.3223	1.50 × 10	[11]	9.49
	KIIF D2I VD/NDO	0.3774	-0.3218			
	DJLI P/NBU	0.0241	-0.2247	$1.5 \times 10^{-13}$	b	0.776
( <i>E</i> /Z)-CFCI=CFCI	FMI3	-0.0848	-0.0848	$1.5 \times 10^{-13}$	г [11]	9.17
		0.2478	0.2478	$2.07 \times 10^{-12}$	[11]	
	BOLI P/NBO	0.2378	0.2578			

 Table I
 Rate Constants for the Reactions of Haloalkenes with O(<sup>3</sup>P) at 298 K, Total Atomic Charges, and Ionization

 Potential (IP) for the Corresponding Haloalkenes

<sup>a</sup> Ionization potentials from Ref. [18] except where marked otherwise.

<sup>b</sup> This work.

<sup>c</sup> Calculated by PM3 method (see text).

promotes O atom addition, whereas the shift of electron density toward the carbon atom due to the high electron affinity of the F atom obstructs it. This suggests the importance of a geometrical factor, as well as the electron affinity of the substituent on the delocalization of the  $\pi$  electrons.

An analysis of the rate coefficients presented in Table I for the hydrochloroethenes shows that the addition of a single chlorine to ethene leads to a small decrease in the rate constant, while addition of a second chlorine on the same carbon results in an additional small decrease in reactivity. However, if the two chlorine atoms are located on different carbon atoms, there is a considerable reduction in the rate constant. The addition of the third chlorine leads to a further reduction in the rate constant, and a still further decrease would be expected for tetrachloroethene taking into account what is observed for OH and NO3radicals reacting with  $CCl_2 = CCl_2$  [24]. We must point out that to the best of our knowledge, the reaction of  $O + CCl_2 = CCl_2$  was studied only by Sanhueza and Heicklen [25] using a competitive method, but the corresponding rate constant was not reported.

Again, the presence of Cl atoms in the olefin produces a strong electron-withdrawing effect, which reduces the charge density on the carbon atoms next to the double bond as well as the polarizability of the  $\pi$  electrons, leading to a decrease of the rate constants. Substitution of F by Cl, however, would favor an increase of the  $\pi$  electron density in the double bond through contributions of the Cl atom lone-pair, thus leading to a smaller decrease of the rate coefficients as F atoms are substituted by Cl ( $k_{CH_2=CHF} < k_{CH_2=CHCl}$ and  $k_{CH_2=CF_2} < k_{CH_2=CCl_2}$ ).

Within the O/chloroethenes series, progressive substitution of H by Cl decreases the reaction rate, contrary to fluorine substitution in the fluoroethenes. This indicates that the reactivity change of chlorinated ethenes cannot be induced only by the electronic effect. Steric hindrance by the Cl atom appears to be a dominant factor for the change of the rate of addition. The bulky Cl atom offers significant electron density above the molecular plane compared to the F atom, inhibiting the O atom attack on the  $\pi$  orbital of the alkene. The cross-section of the Cl and F atoms has been estimated to be 7.2 and 3.8 A<sup>2</sup>, respectively [26]. In 1,2dichloroethene, addition is hindered as compared to 1,2-difluoroethene.

The reactivity of the chloro-fluoro-ethenes toward O atom addition is suppressed with respect to ethene itself because of electronic effects introduced by halogen substitution, but here again steric hindrance by increased Cl substitution seems to play a major role in the reaction rate change. It can be inferred that the steric effect rather than the electronic effect dominates when F is successively replaced by Cl. Thus,  $k_{CF_2=CF_2} > k_{CF_2=CFCl} > k_{CF_2=CCl_2} > k_{(E/Z)-CFCl=CFCl} > k_{CFCl=CCl_2}$ .

Ab initio calculations carried out in this work of the total atomic charges for the ethenes presented in Table I, reveal that the reactivity of the ethenes does not seem to correlate with the charge density on the olefinic carbon atoms. It is rather the charge density between the two carbon atoms that controls reactivity, thus suggesting the attachment of the electrophilic O atom to the double bond as pointed out by Cvetanovic [16]. This line of reasoning is consistent with the enhancement of the O addition reaction observed with the fluoroethenes for which more symmetric substitution of H by F offsets the original deactivation so that  $CF_2=CF_2$  is more reactive than  $CH_2=CH_2$ .

Recent work by Washida et al. [27] on the mechanism of the O + halogenated ethene reactions through observation of the radicals produced in the addition process, concludes that the O atom attaches to the fluorinesubstituted carbon in the fluoroethenes. In the case of chloroethenes it is not clear whether O atoms add to either side or only to the chlorine-substituted side of the double bond. This evidence is opposed to the expected orientation of addition considering the charge densities on the olefinic carbon atoms. This would confirm Cvetanovic's [16] statement that the factors which control the reactivity of the alkenes are not the same as those which control the orientation of the addition reaction.

In our study of the products of the reaction of O atoms with  $CF_2$ =CFCl, we found mainly  $CF_2O$  and traces of CFCl=CFCl and c-C<sub>3</sub>F<sub>4</sub>Cl<sub>2</sub>. Neither CFClO nor C<sub>2</sub>F<sub>4</sub> was detected, which would indicate that of the two possible reaction channels

$$CF_2$$
=CFCl + O(<sup>3</sup>P) → CF<sub>2</sub>O + CFCl  
CF<sub>2</sub>=CFCl + O(<sup>3</sup>P) → CFClO + CF<sub>2</sub>

the first is largely favored, suggesting that the O atom attaches to the carbon atom most substituted by fluorine. Thus, our findings support the observations of Mitchell and Simons [4] that attack occurs mainly at the  $CF_2$  group.

The reactivity of O atom addition to ethene and methyl-substituted ethenes has been found to correlate with the ionization potentials (IP) of the alkenes [28]. The energy required to remove a  $\pi$  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. It is evident from Fig. 4 that the observed correlation between rate constant and IP does not hold for the



Figure 4 Rate constants of O(<sup>3</sup>P) reactions as a function of the ionization potentials of the halogen-substituted ethenes. ■ fluoroethenes; ● chloroethenes; ▲ chlorofluoroethenes.

chloroethenes and chloro-fluoro-ethenes. In fact, the same behavior as for the hydrogenated ethenes is observed for the fluoroethenes, whereas for the chlorinesubstituted ethenes the opposite trend is observed, i.e., the reaction rate constants decrease as the ionization potentials decrease. The reason is probably that in the chloroethenes, the highest occupied molecular orbital (HOMO), whose energy is described by the experimental ionization potential, is composed of carbon-carbon  $\pi$  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  $\pi$ bonding [29].

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