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Absolute determinations of the addition rate constants for the reactions of $O(^3P)$ atoms with halogenated propenes and butenes. A structure–activity relationship for the estimation of rate constants[†]

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ABSTRACT: The kinetics of the reactions of $O(^3P)$ atoms with $CF_3CH{=}CH_2$, $CF_3CCl{=}CCl_2$, $CF_3CF{=}CClCF_3$ and $CF_3CCl{=}CClCF_3$ were studied at 298 K using a discharge flow tube system. This is the first absolute kinetic study of these reactions. The overall rate constants based on the measured afterglow reactions were $(3.4 \pm 0.4) \times 10^{-14}$, $(3.3 \pm 0.6) \times 10^{-14}$, $(1.3 \pm 0.3) \times 10^{-14}$ and $(1.9 \pm 0.4) \times 10^{-14}\,\mathrm{cm^3\ molecule^{-1}\,s^{-1}}$, respectively. The experiments were carried out under pseudo-first-order conditions with $[O(^3P)]_0 \ll [\text{alkene}]_0$. The effect of substituent atoms or groups on the reactivity was analyzed. A simple method, using a structure–activity relationship based on the structure of the alkene, was applied for the first time to the reactions of $O(^3P)$ with haloalkenes. It is shown that this approach is useful in obtaining an initial estimate of unknown rate constants for reactions of $O(^3P)$ with alkenes. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: reaction rate constants; haloalkenes; oxygen atom; structure–activity relationship

INTRODUCTION

Reactions of ground-state oxygen atoms, $O(^3P)$, with alkenes are of both fundamental and practical importance. $O(^3P)$ reactions are necessary to model accurately the early stages of smog formation in urban areas and are often important in atmospheric pressure chamber studies of alkene reactions with OH. Although there have been many studies of O atom reactions with a variety of unsaturated hydrocarbons, only limited information is available for halogenated alkenes, most of which was reviewed by Cvetanovic.[1] Studies of fluoroalkene reactivity towards O atoms are even more scarce[2–6] and the database for perhaloalkenes is still smaller.[7] Most of these studies were indirect measurements of the rate coefficients by the relative rate method.

As part of a systematic study of $O(^3P)$ atom reactivity and a prototype system for the addition reactions to the C=C bond, we report here the absolute rate constants at room temperature for the reactions of $O(^3P)$ with $CF_3CH{=}CH_2$, $CF_3CCl{=}CCl_2$, $CF_3CF{=}CClCF_3$ and $CF_3CCl{=}CClCF_3$. These reactions were measured using a conventional discharge flow-tube apparatus at 298 K. Reliable rate constant values for these reactions are of interest regarding the role of chemical oxidative processes in atmospheric and combustion chemistry and the investigation of the reactivity of halogenated alkenes provides an opportunity to examine halogen substituent effects as a function of the extent and positioning about the double bond.

The development and use of *a priori* predictive techniques for the estimation of rate constants for the reactions of different atoms and radicals with organic compounds has received some attention as a means of cost effectively assessing the lifetimes of organic compounds emitted into the atmosphere.[8,9] However, the development of such estimation techniques depends on the existence of an accurate kinetic database for a wide variety of organic classes and structures.

We used a structure–activity relationship (SAR) developed by Atkinson[10] to estimate the rate constants for the $O(^3P)$ atom addition reactions to alkenes. This is the first

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time that this SAR method has been applied to oxygen atom addition reactions.

EXPERIMENTAL

The experiments were conducted at 298 K in a discharge flow system using the air afterglow chemiluminescence to monitor the oxygen atom concentration. Briefly, the reactor consisted of a Pyrex tube (1.00 m long and 2.50 cm i.d.) coupled to a sliding injector used to introduce the reactant at one end of the reaction tube.

Oxygen atoms, O(^{3}P), were generated by an electrodeless microwave discharge (30 W, 2.5 GHz.) on a 2% O_2–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. The 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 10 to 50 cm from the center of the detection zone, giving contact times in the range 6–39 ms. The system was evacuated by a rotary pump (Edwards 80 $m^3 h^{-1}$) and a capacitance manometer [MKS Baratron, 0–10 Torr (1 Torr = 133.3 Pa)] was used to measure the pressure in the flow tube. The experiments were carried out at total pressures of 2.2 Torr for the reaction with $CF_3CH{=}CH_2$, 1.95 Torr with $CF_3CCl{=}CCl_2$, 3.25 Torr with $CF_3CF{=}CClCF_3$ and 3.15 Torr with $CF_3CCl{=}CClCF_3$.

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. Typical linear flow velocities under our experimental conditions were 1110, 1180, 1390 and 1230 cm s^{-1} for O(^{3}P) with $CF_3CH{=}CH_2$, $CF_3CCl{=}CCl_2$, $CF_3CF{=}CClCF_3$ and $CF_3CCl{=}CClCF_3$ respectively.

The plug-flow conditions[11,12] in the flow tube allowed us to follow the reaction kinetics of the O(^{3}P) atoms in a known excess of the alkene in order to assume the pseudo-first-order approximation.

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*).[13] A constant flow of NO was added 8 cm before the photomultiplier tube detector (Hamamatsu R636) and the chemiluminescence from NO_2* passed through a wide-bandpass filter ($\lambda < 500$ nm) before reaching the photomultiplier tube. The output signal, S_t, of the detector, which was proportional to the light intensity of chemiluminescence, was amplified and displayed on an oscilloscope. In all experiments the background signal obtained when [NO] = [alkene] = 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.[14] The initial concentrations of O atoms ranged from 4×10^{12} to 5×10^{12} molecule cm^{-3}.

The commercial gases used in this study had the following stated minimun purities: He (AGA, 99.999%), O_2 (AGA, 99.999%), NO (AGA 99,5%), $CF_3CH{=}CH_2$ (Apollo Scientific, 99%), $CF_3CCl{=}CCl_2$ (Apollo Scientific, 99%), $CF_3CF{=}CClCF_3$ (Apollo Scientific, 99%) and $CF_3CCl{=}CClCF_3$ (Apollo Scientific, 98%). Nitric oxide was purified by passing it through a trap held at 153 K to remove NO_2. Helium was flowed through traps containing silica gel and molecular sieves (BDH Type 4A) at 77 K to remove water. Alkenes were degassed prior to use and oxygen was used as supplied.

RESULTS

Absolute values of the rate constants at 298 K for the reactions of O(^{3}P) atoms with $CF_3CH{=}CH_2$, $CF_3CCl{=}CCl_2$, $CF_3CF{=}CClCF_3$ and $CF_3CCl{=}CClCF_3$ were determined as described below.

Experiments were carried out under pseudo-first-order conditions, $[\text{alkene}]_0/[O(^3P)]_0$ always >40. In the absence of secondary reactions that significantly deplete the transient O(^{3}P) atoms, the concentration of oxygen atoms varies in an exponential manner with time:

$$[O(^3P)]_t = [O(^3P)]_0 \exp[-(k[\text{alkene}]_0 + k_x)t] \qquad (1)$$

$$= [O(^3P)]_0 \exp(-k't) \qquad (2)$$

$$\ln\{[O(^3P)]_0/[O(^3P)]_t\} = k't \qquad (3)$$

where $[O(^3P)]_0$ is the oxygen atom concentration in the absence of alkene and $[O(^3P)]_t$ is the concentration after reaction with the alkene 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) disapperance by diffusion out of the detection zone, reaction with background impurities or wall losses.

The concentration of O(^{3}P) was monitored by adding a known excess of NO to produce electronically excited NO_2*, whose chemiluminescence was checked 8 cm downstream of the NO inlet port, following the air afterglow reaction:

$$NO + O(^3P) + M \rightarrow NO_2^* + M \qquad (4)$$

$$NO_2^* + M \rightarrow NO_2 + M + h\nu \qquad (5)$$

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(^{3}P)]. The O(^{3}P) loss between the entrance of NO and the detection zone was calculated as $<4\%$.

The first-order kinetic analysis 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 t. Hence

$$\ln(S_0/S_t) = k't \tag{6}$$

The pseudo-first-order rate coefficient, k', was calculated, for a specific concentration of the alkene, from the slope of a plot of $\ln(S_0/S_t)$ as a function of contact time t. The second-order rate constants were obtained from the slopes of the lines of plots of k' vs $[\text{alkene}]_0$ (Figs 1–4), weight fitting the experimental values within 95% confidence. The precision of the individually measured second-order rate coefficients, k, may be derived from the standard propagation of random error analysis of the various flow tube parameters that determine k. The resultant uncertainties in the values of k for $CF_3CH{=}CH_2$, $CF_3CCl{=}CCl_2$, $CF_3CF{=}CClCF_3$ and $CF_3CCl{=}CClCF_3$ are $\sim$12, 18, 23 and 21%, respectively. 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%.[12]

The pseudo-first-order rate coefficients were corrected for axial and radial diffusion, resulting in $<5\%$ upward correction of the k' values.[12] The linearity of the data points, especially in the low $[\text{alkene}]_0$ range in our plots, suggests that the contribution to the decay of O(^{3}P) atoms due to secondary reactions with the products of the reactions is negligible. Also, the fact that the plots show small intercepts (between 2 and 6 s^{-1}) is consistent with a negligible loss of oxygen atoms by wall reactions.

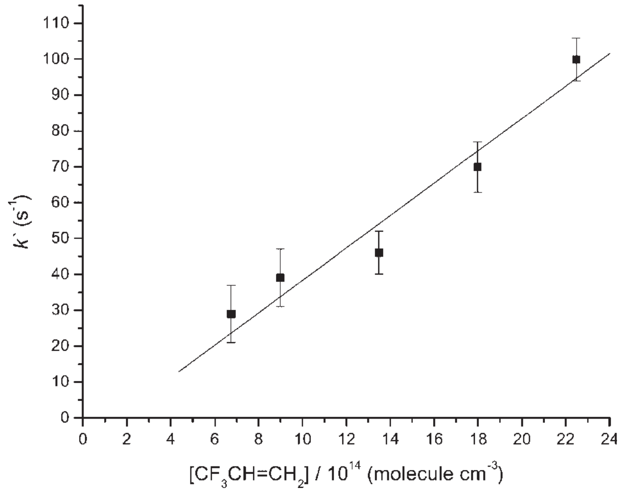

Figure 1. Second-order plot for the O(^{3}P) + $CF_3CH{=}CH_2$ reaction at 298 K

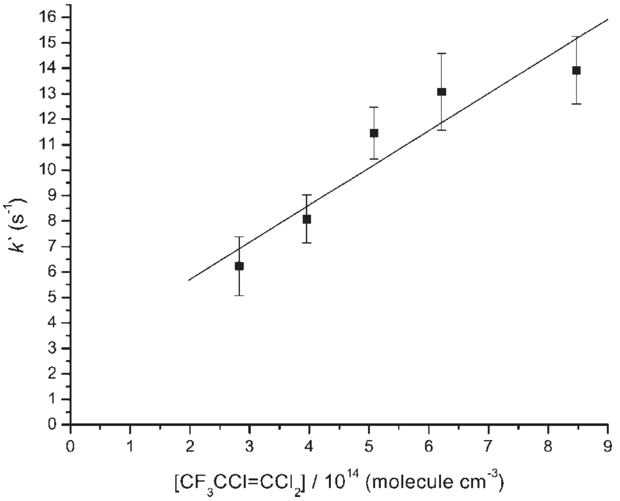

Figure 2. Second-order plot for the O(^{3}P) + $CF_3CCl{=}CCl_2$ reaction at 298 K

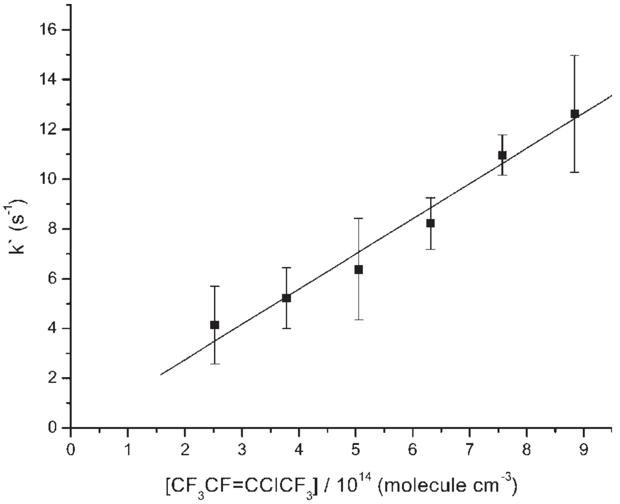

Figure 3. Second-order plot for the O(^{3}P) + $CF_3CF{=}CClCF_3$ reaction at 298 K

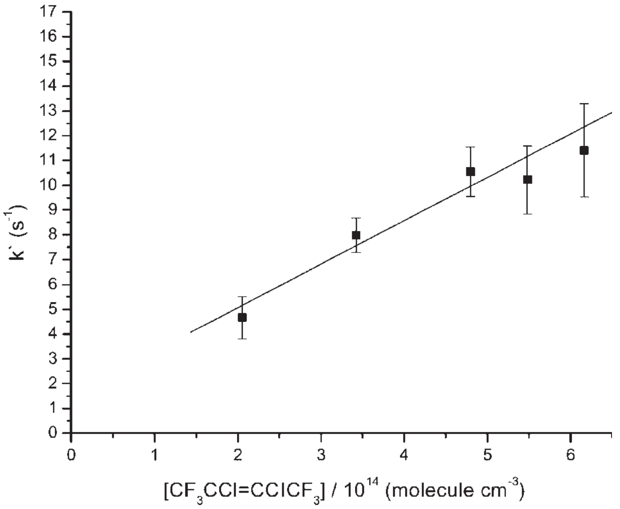

Figure 4. Second-order plot for the O(^{3}P) + $CF_3CCl{=}CClCF_3$ reaction at 298 K

DISCUSSION

The literature database for these reactions is scarce. There has been only one other previous measurement of the O(^{3}P) + $CF_3CH{=}CH_2$ reaction, by Moss and Jennings.[15] They reported a relative rate constant value which was subsequently recalculated by Cvetanovic[1] to be 4.2×10^{-14} cm^3 molecule^{-1} s^{-1} at 296 K. The present absolute value of the rate constant at 298 K of $(3.4 \pm 0.4) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} is therefore ~20% lower than the relative value, which is in good agreement within the experimental errors of both techniques.

To the best of our knowledge, there are no other previously reported values of the rate constants for the reactions of O atoms with $CF_3CCl{=}CCl_2$, $CF_3CF{=}CClCF_3$ and $CF_3CCl{=}CClCF_3$.

A general observation can be made about the presence of halogen atoms as substituents in alkenes, namely that the room temperature reactivity towards O atoms decreases relative to that of ethene, propene or butene.[1,16] Specifically, the presence of the CF_3 group results in an approximately two orders of magnitude decrease in the rate coefficient relative to those of propene ($k_{298\,K} = 4.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1})[1] and butene ($k_{298\,K} = 2.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1})[1].

Fluorination or chlorination of the olefinic carbon atoms in propenes and butenes results in only small additional changes in reactivity. For the propenes, $CF_3CCl{=}CCl_2$ [$k_{298\,K} = (3.3 \pm 0.6) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}] and $CF_3CF{=}CF_2$ [$k_{298\,K} = (3.0 \pm 0.3) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}][16a] are slightly less reactive than $CF_3CH{=}CH_2$ [$k_{298\,K} = (3.4 \pm 0.4) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}]. With butenes, a small change in reactivity is also observed when F is substituted by Cl on going from $CF_3CF{=}CClCF_3$ [$k_{298\,K} = (1.3 \pm 0.3) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}] to $CF_3CCl{=}CClCF_3$ [$k_{298\,K} = (1.9 \pm 0.4) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}]. These results can be rationalized by considering the factors that affect the rate of addition of the electrophilic O(^{3}P) atom to the double bond.

The strong electron-withdrawing capacity of the F and Cl atoms and the CF_3 group reduce the charge density on the carbon atoms next to the double bond and also the polarizability of the π-electrons, leading to a decrease in the rate constants. Substitution of F by Cl, however, would favor an increase in the π-electron density in the double bond through contributions of the chlorine atom lone pair, thus leading to a smaller decrease in the rate coefficients as F atoms are substituted by Cl.

In general, halogenation of any olefinic carbon atom results in small reactivity decreases in ethenes,[16] propenes and butenes. However, fluorination of the CH_3 group in propene and butene results in a more pronounced decrease in O atom reactivity (a factor of two orders of magnitude in the case of CF_3). Hence these results for O atom addition studies suggest that halogenation of olefinic carbon atoms does not affect the π-electron density in the double bond very much, in contrast with fluorination of the carbon adjacent to the olefinic group in propenes and butenes.

Structure–activity relationships (SAR) for O(^{3}P) atom addition to alkenes

A number of correlations between atom or radical reaction rate constants and physical or chemical properties of the organic reactants have been investigated.[10] Such estimation techniques can be classified in two general

Table 1. Group rate constants (k_{basic}) at 298 K for O(^{3}P) addition reactions to haloalkene structural basic units

Basic structure	Alkene	$k_{exp} \times 10^{12}$ (cm^3 molecule^{-1} s^{-1})[a]	$k_{basic} \times 10^{12}$ (cm^3 molecule^{-1} s^{-1})[b]
$CH_2{=}CHR$	Propene	4.0	4.38
		4.8	
		4.35	
$CH_2{=}CR_2$	2-Methylpropene	16.9	17.6
		17.5	
		17.8	
(*Z*)-RHC=CHR	(*Z*)-2-Butene	17.6	17.2
		16.1	
		18.3	
(*E*)-RHC=CHR	(*E*)-2-Butene	22.0	21.0
		20.0	
		21.8	
$RHC{=}CR_2$	2-Methyl-2-butene	56.0	55.0
		53.9	
$R_2C{=}CR_2$	2,3-Dimethyl-2-butene	76.0	77.7
		78.2	
		78.9	

[a] The rate constant values (k_{exp}) are taken from Ref. 7.
[b] Derived from the average reaction rate constants of the alkenes shown in the table.

Table 2. Substituent factors $C_{(X)}$ at 298 K

Substituent X	$C_{(X)}$	Substituent X	$C_{(X)}$
F	0.15[a]	CH_2F	0.19[e]
Cl	0.13[b]	CH_2Cl[f]	0.099
Br	0.13[c]	CH_2CH_3[g]	0.84
CF_3	0.009[d]		

[a] Derived from the experimental reaction rate constants of the $O(^3P)$ atom with $CH_2{=}CHF$, $CH_2{=}CF_2$, $CHF{=}CF_2$, (*Z*)-$CHF{=}CHF$ and (*E*)-$CHF{=}CHF$.

[b] Derived from the experimental reaction rate constants of the $O(^3P)$ atom with $CH_2{=}CHCl$, $CH_2{=}CCl_2$, $CHCl{=}CCl_2$, (*E*)-$CHCl{=}CHCl$.

[c] Derived from the experimental reaction rate constants of the $O(^3P)$ atom with $CH_2{=}CHBr$.

[d] Derived from the experimental reaction rate constants of the $O(^3P)$ atom with $CH_2{=}CHCF_3$.

[e] Derived from the experimental reaction rate constants of the $O(^3P)$ atom with $CH_2{=}CHCH_2F$.

[f] Derived from the experimental reaction rate constants of the $O(^3P)$ atom with $CH_2{=}CHCH_2Cl$.

[g] Derived from the experimental reaction rate constants of the $O(^3P)$ atom with $CH_2{=}CHCH_2CH_3$.

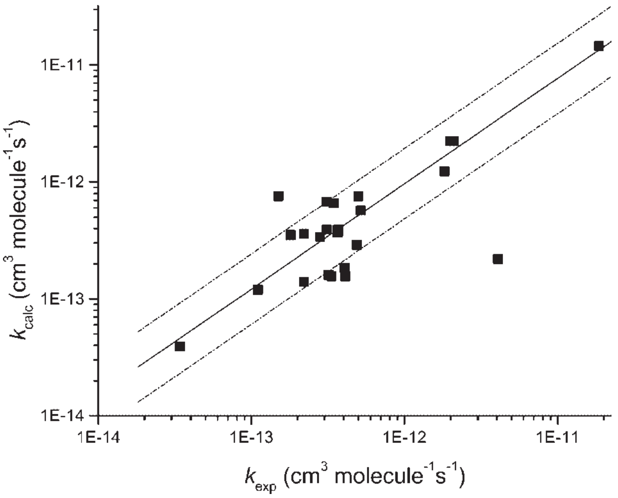

Figure 5. Comparison of the calculated and experimental room-temperature $O(^3P)$ atom addition rate constants for haloalkenes and substituted alkenes (dashed lines denote disagreement by a factor of 2)

categories: those which rely solely on the structure of the organic compound (SARs) and those which utilize a physical or chemical property such as the ionization potential or bond dissociation energy.[17]

In this work, we applied for the first time the SAR approach developed by Atkinson[10] for OH radical reactions to the $O(^3P)$ atom reactions. The method is based on the structure of the alkene, the number of unconjugated double bonds or conjugated double bonds and the degree, identity, position and configuration of the substitution around these double bonds.

The rate constants for the 'basic structures' are calculated from the average of the experimental rate constants for the parent alkenes given in Table 1, taking the reactivity factor for CH_3, as unity. The group factors $[C_{(X)}]$ given in Table 2 are defined by the equation

$$k = k(\text{basic}) \times \prod_{i=1}^{i=1-4} [C_{(X)i}]$$

The group factors given in Table 2 are the energies of the contributions selected on the basis of the reliability of the data as expressed in recent reviews.[1,7] A correlation between the calculated and experimental room temperature $O(^3P)$ atom reaction rate constants for organic compounds with C=C bonds is given in Fig. 5. The corresponding values are shown in Table 3.

Of the 29 haloalkenes listed in Table 3, for only seven is the disagreement between the calculated and experimental room temperature addition rate constants more than a factor of 2.

The reasonable agreement between the calculated and experimental rate coefficients, within three orders of magnitude variation of the rate constants, demonstrates the potential power and usefulness of the SAR method in

Table 3. Comparison of the experimental (k_{exp}) and calculated (k_{calc}) room-temperature rate constants for haloalkenes and substituted alkenes

Haloalkene or substituted alkene	k_{calc} (cm^3 molecule^{-1} s^{-1})	k_{exp} (cm^3 molecule^{-1} s^{-1})[a]
$CH_2{=}C(CH_3)C_2H_5$	1.46×10^{-11}	1.86×10^{-11}
$CF_2{=}CFCF{=}CF_2$	3.71×10^{-13}	3.65×10^{-13}
$CH_2{=}C(CF_3)CH_3$	1.57×10^{-13}	4.1×10^{-13}
$CF_2{=}CHF$	1.86×10^{-13}	4.05×10^{-13}
$CH_2{=}CCl_2$	2.9×10^{-13}	4.88×10^{-13}
$CH_2{=}CF_2$	3.9×10^{-13}	1.63×10^{-13}
(*Z*)-$CHF{=}CHF$	3.9×10^{-13}	3.7×10^{-13}
$CH_3CH{=}CF_2$	1.24×10^{-12}	1.82×10^{-12}
$CH_2{=}CHBr$	5.69×10^{-13}	5.64×10^{-13}
$CH_2{=}CHCl$	5.69×10^{-13}	5.95×10^{-13}
$CH_2{=}CHF$	6.57×10^{-13}	3.44×10^{-13}
$CH_3CHCF{=}CF_2$	2.2×10^{-13}	3.32×10^{-12}
(*E*/*Z*)-$CHF{=}CHF$	3.89×10^{-13}	3.65×10^{-13}
$CH_3CH{=}CHCl$	2.25×10^{-12}	2.1×10^{-12}
$CH_3CF{=}CH_2$	2.26×10^{-12}	1.99×10^{-12}
$CF_3CH{=}CH_2$	3.94×10^{-14}	3.4×10^{-14} [b]
$CF_3CF{=}CF_2$	2.62×10^{-15}	3.0×10^{-14} [c]
$CF_3CCl{=}CCl_2$	1.71×10^{-15}	3.3×10^{-14} [b]
$CF_3CF{=}CClCF_3$	1.5×10^{-16}	1.3×10^{-14} [b]
$CF_3CCl{=}CClCF_3$	1.3×10^{-16}	1.9×10^{-14} [b]
$CF_2{=}CFCl$	7.5×10^{-13}	4.5×10^{-13} [d]
$CF_2{=}CCl_2$	6.8×10^{-13}	3.1×10^{-13} [c]
(*E*/*Z*)-$CFCl{=}CFCl$	7.6×10^{-13}	1.5×10^{-13} [d]
$CHCl{=}CCl_2$	1.2×10^{-13}	1.4×10^{-13} [c]
(*E*/*Z*)-$CHCl{=}CHCl$	3.6×10^{-13}	2.2×10^{-13} [c]
(*E*/*Z*)-$CHF{=}CHCl$	3.5×10^{-13}	1.8×10^{-13} [d]
$CH_2{=}CFCl$	3.4×10^{-13}	2.8×10^{-13} [d]
(*E*/*Z*)-$CHCl{=}CFCl$	1.4×10^{-13}	2.2×10^{-13} [d]
$CF_2{=}CHCl$	1.61×10^{-13}	3.2×10^{-13}

[a] The experimental rate constant values at room temperature (k_{exp}) are taken from Ref. 7.

[b] This work.

[c] The experimental rate constant values at room temperature (k_{exp}) are taken from Ref. 16.

[d] To be published.

the prediction of the reactivity towards O(^{3}P) of a wide range of alkenes. However, we must point out that the halopropenes and halobutenes are the compounds which show disagreement by more than a factor of 2 between the calculated and experimental values (Fig. 5), probably because this method does not take into account certain factors such as the interactions of the substituent with the oxygen atom or with the double bond, which would significantly influence the reactivity in comparison with the other haloalkenes.

In addition to the good agreement obtained with this *a priori* technique, it should be emphasized that this is the first attempt to apply these relationships to the reactions of O(^{3}P) atoms, and a much larger kinetic database is required to establish a more comprehensive and reliable set of rate constants for basic structures and group factors. This limitation is particularly marked for compounds with more than one chlorine atom attached to the double bond and for the perhalogenated alkenes.

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