

**THE HALOGEN-SUBSTITUENT EFFECT ON THE REACTIONS OF  
O(<sup>3</sup>P) WITH HALOCARBONS:  
THE REACTION RATES FOR O(<sup>3</sup>P) + FLUOROETHANE REACTIONS**

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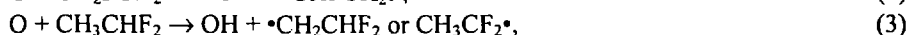
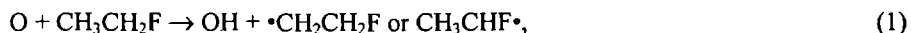
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### Introduction

Recently, the formation mechanism of dioxins, polychlorodibenzo-*p*-dioxins (PCDDs) and polychlorodibenzofurans (PCDFs), via recombination reactions has attracted less attention than that via suit. However, in order to achieve the higher control of discharge, the knowledge of the reactivity of halocarbons is important under the good combustion conditions where the suit formation is not dominant. Although extensive investigations have been reported on the rate constants for the reaction with OH radicals and their atmospheric degradation mechanisms [1,2], much less information is available on the high-temperature oxidation mechanism of halocarbons in combustion.

Recent improvement of the kinetic studies using a shock tube apparatus, especially the development of the (laser) flash photolysis – shock tube technique (LFP-ST), has provided a reliable and powerful tool for the high-temperature kinetics. In the present study, the rate constants for the reactions of oxygen atoms with fluoroethanes,



**Table 1.** Fluorine-substitution effect on the C-H bond dissociation energy of ethanes.

C-H bond	$D^\circ_{298} / \text{kJ mol}^{-1}$ <sup>a)</sup>	$\Delta D^\circ_{298} / \text{kJ mol}^{-1}$ <sup>b)</sup>	C-H bond	$D^\circ_{298}$	$\Delta D^\circ_{298}$
CH <sub>3</sub> CH <sub>2</sub> -H	422.2 <sup>c)</sup>	0.0	( <i>β</i> -substitution)		
( <i>α</i> -substitution)			CH <sub>2</sub> FCH <sub>2</sub> -H	434.2 <sup>d)</sup>	+12.0
CH <sub>3</sub> CHF-H	414.8 <sup>d)</sup>	-7.4	CHF <sub>2</sub> CH <sub>2</sub> -H	442.4 <sup>d)</sup>	+20.2
CH <sub>3</sub> CF <sub>2</sub> -H	423.1 <sup>d)</sup>	+0.9	CF <sub>3</sub> CH <sub>2</sub> -H	446.8 <sup>d)</sup>	+24.6
( <i>α</i> - and <i>β</i> -substitution)					
CH <sub>2</sub> FCHF-H	416.7 <sup>d)</sup>	-5.5			

<sup>a)</sup> enthalpy change ( $\Delta H^\circ_{298}$ ) of the bond dissociation reaction,  $\text{RH} \rightarrow \text{R} + \text{H}$ .

<sup>b)</sup> difference of the  $D^\circ_{298}$  relative to non-substituted ethanes.

<sup>c)</sup> calculated from the  $\Delta H^\circ_{298}$  of C<sub>2</sub>H<sub>5</sub> radical in ref.3. <sup>d)</sup> results of BAC-MP4 calc. in ref.4.

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have been directly measured by LFP-ST at temperatures above 1000 K. The C-H bond dissociation energy (BDE) of hydrofluorocarbons (HFCs) has been the subject of many experimental and theoretical investigations. The fluorine-substitution effect to the C-H BDEs of fluoromethanes, which looks strange, was questioned [5], but now it has been well established [6]. The characteristic fluorine-substitution effect to the C-H BDEs of fluorinated ethanes is summarized in Table 1. The fluorine-substitution effect on the rate constant is discussed combined with the previous measurements for  $O + CH_4$  and  $C_2H_6$  [7], and  $O +$  fluoromethanes [8].

### Methods

A 5-cm inner diameter, 4.8-m long diaphragmless stainless-steel shock tube was used in the present experiments. Details of the apparatus have been described elsewhere [9]. Sample gas mixture of  $SO_2$  and fluoroethane diluted in Ar was irradiated by an ArF excimer laser light (193 nm) after 100  $\mu s$  delay to the arrival of reflected shock wave at the observation port. Oxygen atoms were generated by the photolysis of  $SO_2$ ,



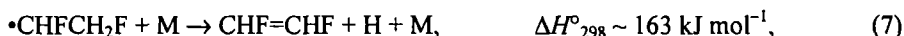
The laser light was introduced to the shock tube through a suprasil quartz window located at the end of the shock tube. The initial oxygen-atom concentration was kept low enough to satisfy the pseudo first-order condition,  $[O]_0 \ll [\text{fluoroethane}]_0$ .

Atomic resonance absorption spectrometry (ARAS) was used to monitor the  $O(^3P)$  atom concentrations. A microwave discharge in 1%  $O_2$  in He was used as a light source. Triplet resonance lines around 130.6 nm were filtered by a 20-cm vacuum ultraviolet monochromator and detected with a solar-blind photomultiplier (Hamamatsu R976). Transient ARAS signals were recorded with a storage oscilloscope. The signal was converted to the concentration of oxygen atoms with a calibration curve constructed by the separate experiments using the thermal decomposition of  $N_2O$ .

All errors indicated with experimental values are at the level of two standard deviations.

### Results and Discussion

The time profile could be well fitted by a single exponential function and the rate constant was derived by a least-squares method. Arrhenius plots of the derived rate constants are shown in Figure 1. For the reactions of mono- and di-fluoroethanes, the product fluoroethyl radicals quickly decomposes via C-H bond fission,



and the effects of subsequent reactions of oxygen atoms with these radicals are negligible. Further, this has been confirmed by the experiments with 2–3 times smaller initial O-atom concentration (open symbols in Figure 1). The derived rate constant did not change significantly by changing the initial O-atom concentration. The contribution of the other side reactions,  $O + OH$  and  $O +$  fluoroethene, was also estimated to be minor, less than 5% of the total O-atom decay rate.

The Arrhenius parameters derived from the plots in Figure 1 are summarized in Table 2.

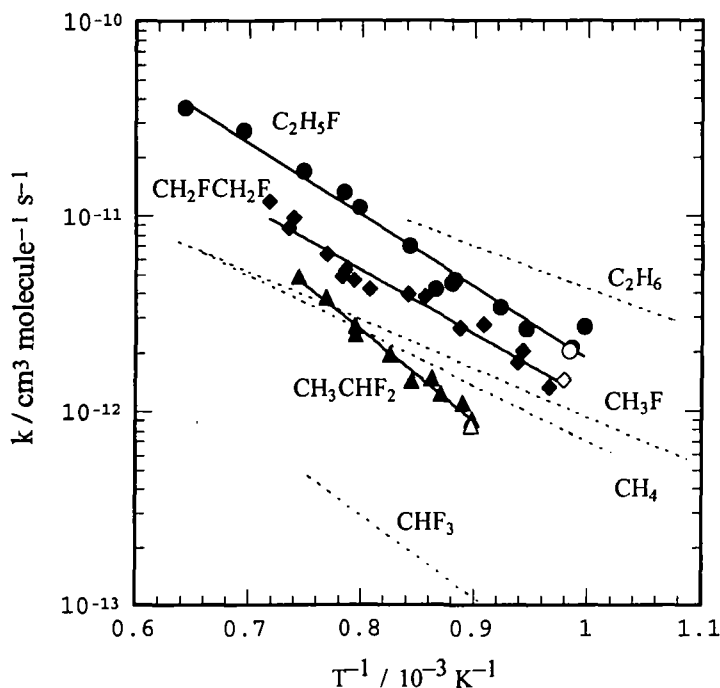
**Table 2.** Arrhenius parameters for O + fluoroethane reactions.

Reaction	$k = A \exp(-E_a/RT)$		$F^a)$	temp. range (K)
	$A$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	$E_a$ ( $\text{kJ mol}^{-1}$ )		
O + CH <sub>3</sub> CH <sub>2</sub> F	$9.23 \times 10^{-9}$ (2.02) <sup>b)</sup>	$70.9 \pm 6.8$	1.38	1000–1560
O + CH <sub>2</sub> FCH <sub>2</sub> F	$2.12 \times 10^{-9}$ (1.99)	$62.4 \pm 6.8$	1.32	1020–1390
O + CH <sub>3</sub> CHF <sub>2</sub>	$1.24 \times 10^{-8}$ (2.16)	$88.2 \pm 7.6$	1.17	1110–1340
O + C <sub>2</sub> H <sub>6</sub>	$6.61 \times 10^{-10}$ <sup>c)</sup>	$42.0$ <sup>c)</sup>		930–1190

<sup>a)</sup> F is the uncertainty factor (at 2 $\sigma$  level) for the rate constants evaluated by the Arrhenius expression in specified temperature range.

<sup>b)</sup> Values in parentheses denote uncertainty factors of A-factors.

<sup>c)</sup> results of ref. 7.



**Figure 1.** Arrhenius plots for the reaction of O + fluoroethanes: Open symbols indicate the experimental data with reduced (1/2 – 1/3) initial O-atom concentration. Solid lines are the results of Arrhenius fit. Dotted lines indicate the experimental data for O + CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> [7], and O + CH<sub>3</sub>F and CHF<sub>3</sub> [8], reported previously.

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As shown in Figure 1 and Table 2, all the measured rate constants for O + fluoroethanes are smaller than that for O + C<sub>2</sub>H<sub>6</sub>, and the derived activation energy was larger than that of C<sub>2</sub>H<sub>6</sub>. This result seems strange since the C-H BDE of singly substituted -CH<sub>2</sub>F group in CH<sub>3</sub>CH<sub>2</sub>F or CH<sub>2</sub>FCH<sub>2</sub>F is smaller than that of C<sub>2</sub>H<sub>6</sub> as shown in Table 1. Also the observed activation energy for O + CH<sub>3</sub>CHF<sub>2</sub> is higher than that for O + C<sub>2</sub>H<sub>6</sub> by ~30 kJ mol<sup>-1</sup> while the weaker α-C-H BDE of CH<sub>3</sub>CHF<sub>2</sub> is only 0.9 kJ mol<sup>-1</sup> larger than C<sub>2</sub>H<sub>6</sub>.

This behavior might be interpreted by considering the difference of the substituent effects between -CH<sub>3</sub> and -F substitutions. Although the -CH<sub>3</sub> substitution is simply interpreted by its σ electron donating character, the fluorine substitution effect has been reported as the complex combination of the σ electron withdrawing effect and the π electron donating effect [10]. Since the π electron donation requires the planer •CX<sub>3</sub> geometry, this effect may not stabilize the transition state, while it significantly stabilizes the product fluoroethyl radical. The hypothetical interpretation presented above should be subject to further experimental and theoretical investigations.

Another remarkable difference from alkane reactions was found in the Arrhenius preexponential factors (*A*-factors). As shown in Table 2, the *A*-factors for the O + fluoroethanes are larger than that for O + C<sub>2</sub>H<sub>6</sub>. This may be explained by the enhanced activation entropy due to the substitution of heavier fluorine atoms. Another possible interpretation is to assume a complex formation mechanism which has been well understood for the reaction of O + iodoalkanes. For the reaction of O + CH<sub>3</sub>I or C<sub>2</sub>H<sub>5</sub>I, product channels to produce IO or HOI are known [11,12],



From theoretical investigations [13,14], these reactions are known to proceed via singlet alkyl hypoiodite (ROI) complexes. Although, for fluoroalkanes, the FO and HOF product channels are energetically much less favored than the case of iodoalkanes, the singlet hypofluorite (ROF) complex or a weak triplet complex (reported for C<sub>2</sub>H<sub>5</sub>IO [14]) may play a role in the enhancement of *A*-factors. Theoretical investigation on this hypothesis is planned as a future work.

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