

## Reaction of Triplet Oxygen Atom with Halogenated Ethylenes: Discharge Flow/Chemiluminescence Method

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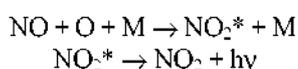
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The reaction of oxygen atom  $O(^3P)$  with halogenated ethylenes has been extensively studied since the reaction has an important role in the atmospheric and environmental chemistry. Halogenated ethylenes are the main primary products in photodecomposition reaction of the CFCs (chlorofluorocarbons) and HCFCs (hydrochlorofluorocarbons) at VUV (vacuum ultraviolet) region.<sup>1-3</sup> HCFCs are removed by sequential radical processes which are initiated by the H abstraction of OH in the troposphere.<sup>4</sup> However, the halogenated ethylenes from photodecomposition reaction have longer life times than the HCFC or CFC. The  $O(^3P)$  atom reaction with halogenated ethylenes is able to initiate radical processes and enhance removal of the halogenated compounds.<sup>5</sup>

The reaction rates have been measured by the discharge flow chemiluminescence imaging technique which is proved to have advantages in data treatment, detection of the chemiluminescence, and controlling the flow conditions.<sup>5</sup> In this work, we modified the imaging system by one-dimensional diode array detector. Since the sensitivity of diode array is higher than that of CCD (charge coupled device), we could get reasonable kinetic data in the course of experiment. The effects of molecular structure on the reaction rates were also studied by computational work.

### Experimental Section

Experiments were carried out under pseudo-first order condition,  $[\text{olefin}] \gg [\text{O}]$ . The reaction was monitored by the discharge flow chemiluminescence imaging method. The experimental setup was described in detail previously.<sup>6</sup> The inner diameters of reaction tube were 15.5 mm for the fast reaction and 26.0 mm for the slow reaction. The amounts of ethylenes, NO/He, and  $O_2$ /He were controlled by mass flow controller (MKS 1179A). The flow velocity was determined from a combination of the inner diameter of the tube, amounts of the reactants, and pressure in the reaction tube. Capacitance pressure gauge (MKS 626A) was used for monitoring the pressure in reaction tube. The flow velocities were 2.0 m/s and 2.4 m/s at  $P_{\text{total}} \approx 1$  Torr.  $O(^3P)$  atom was developed by microwave discharge of 0.14%  $O_2$  in helium at 1 Torr. The concentration of oxygen atom is proportional to the intensity of chemiluminescence. The chemiluminescence process is given by:



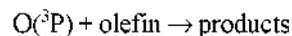
The  $\text{NO}_2$  chemiluminescence was observed by MOS-LIS (metal oxide semiconductor linear image sensor: Hamamatsu

S3903-1024Q) equipped with data acquisition system.

The 0.14%  $O_2$  in He (Korea Research Institute of Standards Science), 10.6% NO in He (Korea Industrial Gas Co.), and 99.99% He (Praxair Korea) were used without further purification.  $\text{CH}_2=\text{CFCl}$  (97%, PCR),  $\text{CHF}=\text{CHCl}$  (*E/Z* mixture, PCR),  $\text{CF}_2=\text{CCl}_2$  (97%, PCR),  $\text{CFCl}=\text{CFCl}$  (*E/Z* mixture, PCR),  $\text{CHCl}=\text{CCl}_2$  (99.5%, Aldrich), and  $\text{CH}_2=\text{CH}_2$  (99%, Lancaster) were purified by several cycles of the freeze-thaw procedure. The 3.0-7.0% ethylenes in helium were used in this work to optimize the chemiluminescence intensity.

### Results and Discussion

The reaction rates were determined from the decay curve of oxygen atom concentration during the reaction in the flow tube. At a constant flow velocity, the reaction time  $t$  corresponds to the distance of reaction point from the injection point along the flow tube. The oxygen atom is consumed by reaction with ethylenes to products and by collision with wall of the tube.



The oxygen atom concentration is given by the rate expression:

$$[O(t)]_0/[O(t)]_R = I_0(t)/I_R(t) = \exp[(k_{\text{wall}} + k_{\text{bi}}[\text{olefin}])t]$$

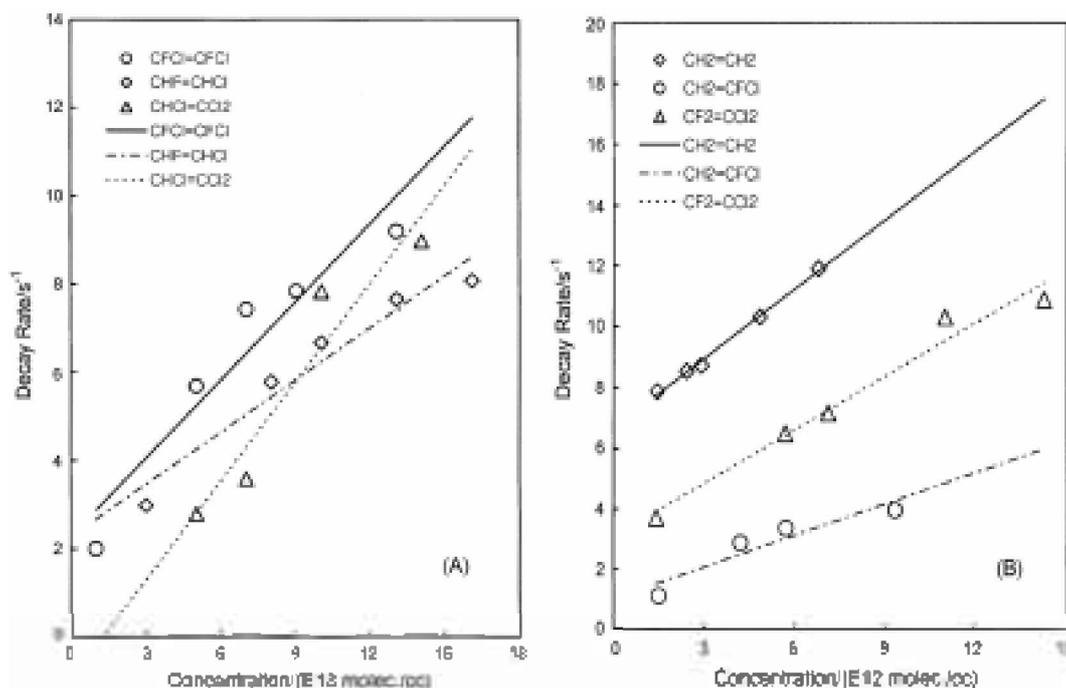
$[O(t)]_0$  is the concentration of  $O(^3P)$  atoms in the absence of olefin, while  $[O(t)]_R$  is that in the presence of olefins at time  $t$ .  $I_0(t)$  and  $I_R(t)$  are the corresponding chemiluminescence intensities.  $k_{\text{bi}}$  is the bimolecular reaction rate constant and the first order rate coefficient  $k_{\text{wall}}$  is for the removal of  $O(^3P)$  atoms from the observing zone by collision with impurities and  $O_2$  in the absence of any added olefins.

The exponential decay rate of chemiluminescence is given by the expression:

$$k_{\text{decay}} = k_{\text{wall}} + k_{\text{bi}}[\text{olefin}] = t^{-1} \ln I_0(t)/I_R(t)$$

The decay constant  $k_{\text{decay}}$  is linearly dependent on the concentration of olefin and the bimolecular rate constant  $k_{\text{bi}}$  was determined by the slope of Figure 1. The experimental results were summarized in Table 1.

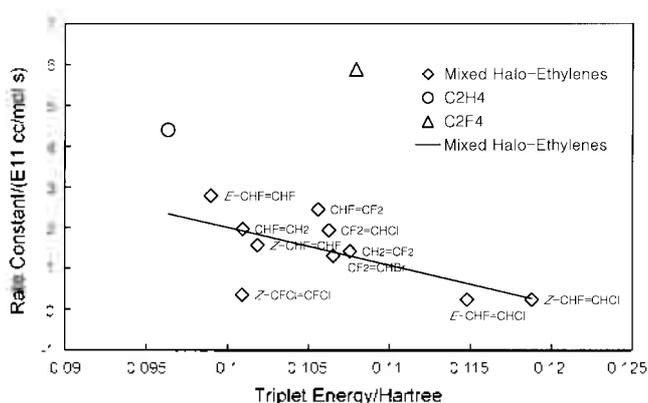
$O(^3P)$  atom reactions with olefins are known to be electrophilic addition.<sup>7</sup> The primary step of the reaction was proposed that the electrophilic oxygen atom addition to  $\pi$  electron of olefins to form a triplet diradical intermediate, oxirane (C-C-O).<sup>8,9</sup> The chlorine or bromine substituted olefins form a relatively stable oxirane intermediate by oxygen



**Figure 1.** Dependence of  $O(^3P)$  atom decay rates on the concentration of ethylenes at room temperature for (A)  $CFC1=CFC1$ ,  $CHF=CHCl$ , and  $CHCl=CCl_2$  at flow velocity =  $2.0 \text{ ms}^{-1}$ ; (B)  $CH_2=CH_2$ ,  $CH_2=CFC1$ , and  $CF_2=CCl_2$  at flow velocity =  $2.4 \text{ ms}^{-1}$ .

**Table 1.** The bimolecular reaction rate constants for the reaction of  $O(^3P)$  with olefins

Olefins	$k_{bi}/10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ sec}^{-1}$	
	This work	Reference value
$CH_2=CH_2$	7.6	$6.81^6$ ; $7.37^{15}$ ; $5.73^{15}$
$CH_2=CFC1$	3.49	
$CHF=CHCl(E/Z)$	0.39	
$CFC1=CFC1(E/Z)$	0.59	
$CF_2=CCl_2$	5.89	$6.48^{15}$
$CHCl=CCl_2$	0.74	$0.98^{15}$



**Figure 2.** The bimolecular rate constants,  $k_{bi}$ , as a function of the triplet energy of halogenated ethylenes. The kinetic data are from this work and Ref. 15.

atom addition.<sup>10</sup> There have been many challenges to find a correlation of reaction rate and the properties of halogenated ethylenes such as electron density of double bond,<sup>11</sup> ioniza-

tion energy,<sup>6,12</sup> and the energy of oxirane diradicals.<sup>9</sup> However, the reactivity has been correlated for only some limited series of halogenated ethylenes. To estimate the correlation between the rate and property of olefins, the energy of triplet state of halogenated olefins were calculated using UCIS/6-311G by Gaussian 94.<sup>13</sup> As shown in Figure 2, one can find that the reaction rate is correlated to the energy of triplet state of ethylenes. The rate for  $CF_2=CF_2$  is apart from the tendency since the reaction of  $CF_2=CF_2$  with  $O(^3P)$  has a reaction channel of direct C-C bond cleavage due to the weakened bond by highly electronegative substituents while the other halogen substituted ethylenes have oxirane intermediate.<sup>14</sup>

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