The Reactions of O(^{3}P) Atom with Halomethanes: Discharge Flow-Chemiluminescence Imaging Method[†]

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The reactions of triplet oxygen atom with halomethanes as a potential fire extinguisher were studied by a discharge flow-chemiluminescence imaging method. The experiments were carried out under second order conditions. The bimolecular atom-molecule reaction rate constants were determined in terms of the initial rate method. The initial concentration of oxygen atom was also determined under second order rate law instead of the pseudo-first order conditions with $[O(^3P)]_0 << [sample]_0$. The second order conditions were more reliable than pseudo-first order conditions for the determinations of rate constants. The rate constants of the reactions $CF_3I + O(^3P)$, $CH_3I + O(^3P)$, and $CHBrCl_2 + O(^3P)$ were determined to be 5.0×10^{-12}, 1.1×10^{-11}, and 1.9×10^{-14} cm^{3}molecule^{-1}s^{-1}, respectively.

Keywords : CF_3I, CH_3I, $CHBrCl_2$, $O(^3P)$, Chemiluminescence imaging method.

Introduction

The reactions of oxygen atom with halomethanes are important in atmospheric chemistry and fire suppression processes. The sources of halomethanes are natural or man-made.[1] Bromine compounds are able to reach the stratosphere and acts as a catalytic species in ozone chemistry due to a long lifetime.[1,2] CH_3I and CF_3I are photolyzed to produce iodine atoms. The iodine atoms produced by photolysis and their oxides could participate in tropospheric chemistry.[3] There are few kinetic data for the reactions of $O(^3P)$ with these compounds by direct measurements in spite of their important feature in atmospheric chemistry. The difficulties in direct measurements are due to the formation of fluorescent products and secondary reactions. The methods by product analysis such as discharge-flow system coupled to a mass spectrometer,[4,5] a gas chromatograph.[6] laser induced fluorescence (LIF).[7] chemical ionization mass spectrometry (CIMS).[7] and laser photolysis/cavity ring down spectroscopy[8] could give us a rate coefficient for a specific channel. Direct method that observes the consumption of reactants is required to estimate lifetime of halomethanes.

The experimental method in this work, the discharge flow-chemiluminescence imaging method, has an excellent advantage in data treatment since we could get enough number of data especially at starting point of reaction zone.[9,10] The decay profile of oxygen atom concentrations near the starting point of sample injector makes it possible to use an initial rate method in second order rate equation instead of pseudo first order equation. In this paper, we determined the bimolecular rate constants for the reactions of $O(^3P)$ with

CF_3I, CH_3I, and $CHBrCl_2$ by using second order rate equations.

Experimental Section

The discharge flow-chemiluminescence imaging system is shown in Figure 1. Flow rates in the reaction tube (32 mm inner diameter) were controlled by mass flow controllers (MKS. 1179A), and the velocity of the flowing gases was determined to be 100 cm s^{-1} from the flow rates and pressure in the flow tube. The pressure of the reaction zone was monitored by a capacitance gauge (MKS. 626).

The concentrations of the samples in the reaction zone were calculated from the measured flow velocity and the injected volume of the sample mixtures. Ground state $O(^3P)$ atoms were generated by the microwave discharge (Opthos MPG-4M) of 1.0% O_2 in He. The concentration of oxygen atom is proportional to the chemiluminescence intensity of NO_2. The chemiluminescence process is given by reactions 1 and 2.

$$O + NO + M \rightarrow NO_2^* + M \qquad (1)$$

$$NO_2^* \rightarrow NO_2 + h\nu \qquad (2)$$
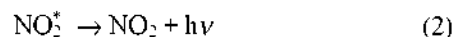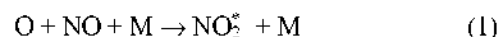
The chemiluminescence was monitored by a charge coupled device (CCD) camera (Princeton Instruments. CCD-763) equipped with a personal computer for data accumulation. The chemiluminescence signals were accumulated fifty times. Figure 2 illustrates decay signals of NO_2 chemiluminescence for the reactions of $O(^3P)$ atom with various concentrations of C_2H_4.

After purifying by the freeze-thaw method. C_2H_4 (99%, Aldrich). CF_3I (99%, Aldrich). CH_3I (99.5%, Tokyo Kasei) and $CHBrCl_2$ (98%, Aldrich) were diluted to 1.0%, 1.0%, 1.0%, and 4.0% in He, respectively. O_2 (0.98% in He, Korea Industrial Gas) and NO (1.0% in He, PRAXAIR Korea) were purchased as a pre-mixture.
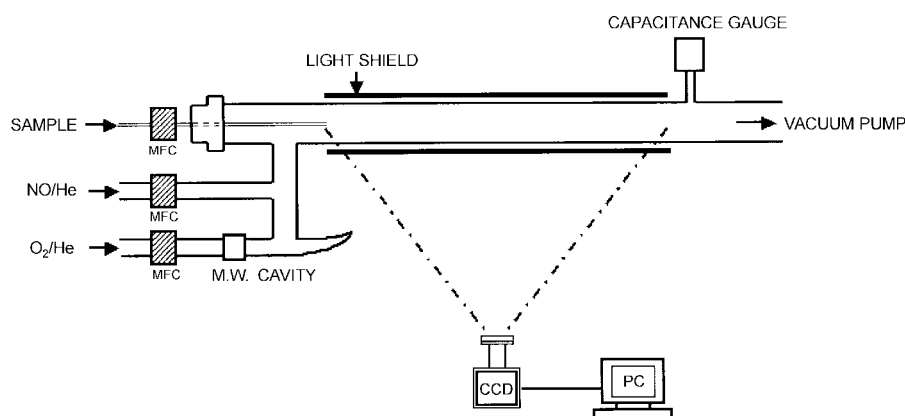
Figure 1. Experimental set-up of the discharge flow-chemiluminescence imaging system.
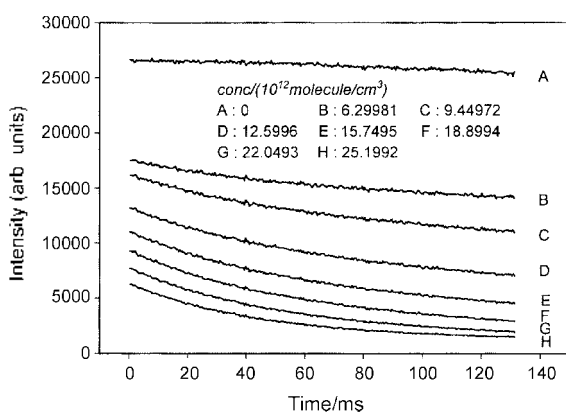

Figure 2. Decay signals of the NO_2 chemiluminescence for the reactions of $O(^3P)$ atom with various C_2H_4 concentrations. Without sample, the chemiluminescence intensity is nearly constant over the entire reaction zone as plotted in A.

Figure 3. Plot of $\ln(I/I_o)$ versus reaction time at different concentrations of ethylene at 298 K. The $O(^3P)$ atom decay rates, k_{decay}, were obtained from the slope of this plot.

Results and Discussion

The bimolecular rate constants were calculated by using the initial rate method. The concentrations of oxygen atom are comparable to halomethanes in second order rate equations. Major processes of oxygen consumption are written by reactions 3 and 4.

$$O + A \xrightarrow{k_{bi}} \text{products} \tag{3}$$

$$O + \text{wall} \xrightarrow{k_w} \text{products} \tag{4}$$
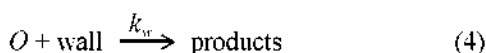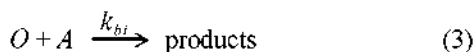
The rate equation is

$$-\frac{d[O]}{dt} = k_w[O] + k_{bi}[O][A] = k_w[O] + k_{bi}[O]([O]+[A]_0-[O]_0) \tag{I}$$

We can get integrated rate expression by solving the equation I as follows:

$$\ln\frac{[O]_t}{[O]_0} = -(k_w + k_{bi}a)t + \ln\frac{[A]_t + k_w/k_{bi}}{[A]_0 + k_w/k_{bi}} \tag{II}$$

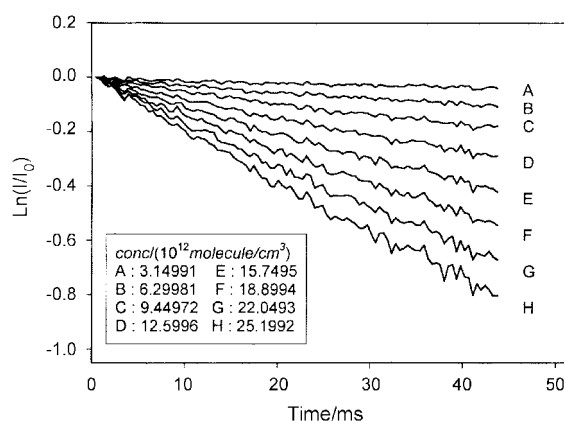where. $a = [A]_0-[O]_0$, k_{bi} is the bimolecular reaction rate

constant. and k_w is the first order rate coefficient for the removal of $O(^3P)$ atoms from the observing zone by collision with impurities and O_2. $[A]_0$ and $[O]_0$ are the initial concentrations of sample and $O(^3P)$ atom. $[A]_t$ and $[O]_t$ are those at time t, respectively. $[A]_t$ goes to $[A]_0$ near the starting point of reaction. Therefore, the equation II is approximated to

$$\ln\frac{[O]_t}{[O]_0} = \ln\frac{I_t}{I_o} = -(k_w + k_{bi}a)t . \tag{III}$$

where, I_o and I_t are the chemiluminescence intensities at initial point and time t. respectively. $[O]_0$ was determined in terms of the equation IV:

$$[O]_0 = \frac{[A]_0}{1 - [O]_\infty/[O]_0} , \tag{IV}$$

where, $[O]_\infty$ is the concentration of remaining $O(^3P)$ after the sample is consumed completely.

The plot of $\ln(I_t/I_o)$ versus t for ethylene is shown in Figure 3. The decay constant, $k_{decay}=-(k_w + k_{bi}a)$, is obtained from a slope at $t = 0$ by the equation III. This result is similar to the equation in pseudo-first order conditions except $a = [A]_0-[O]_0$ instead of [A].[9] The k_{decay} is linearly
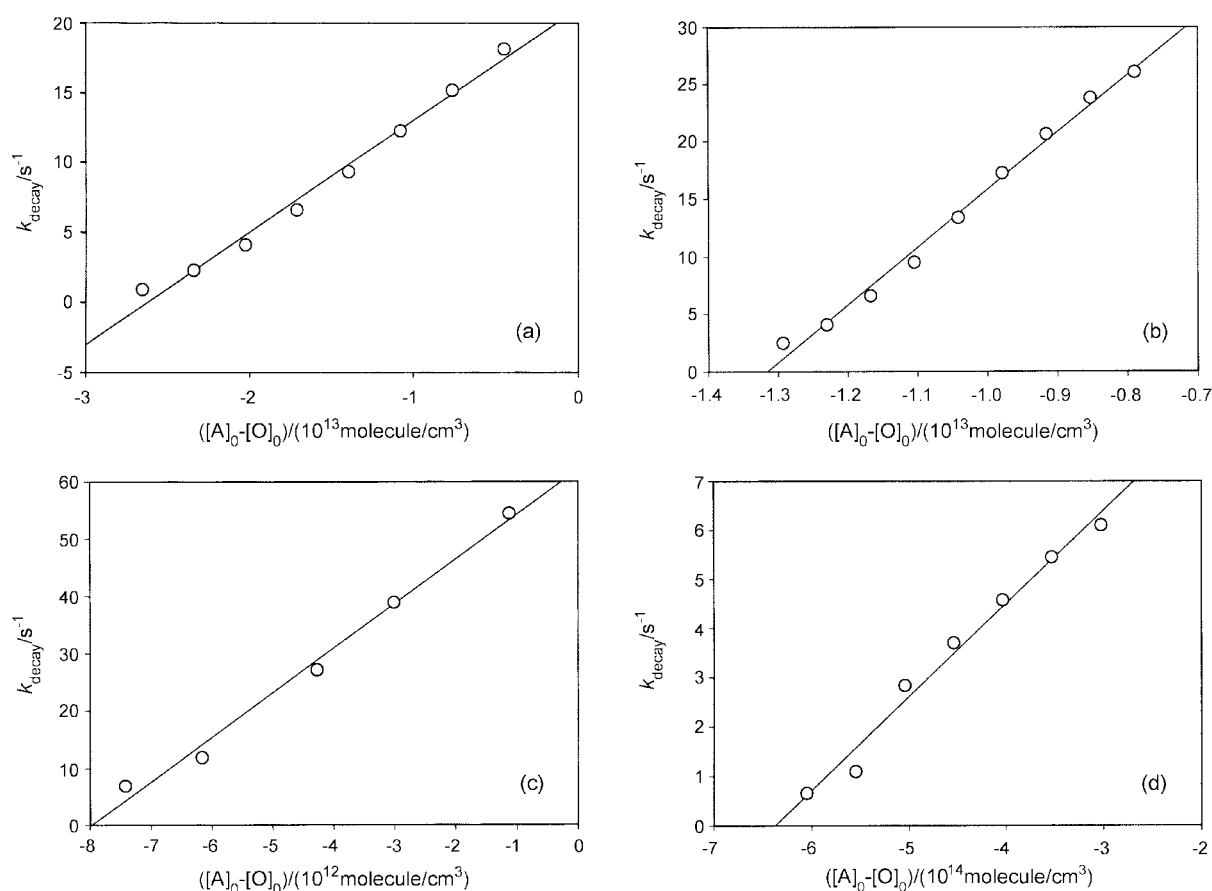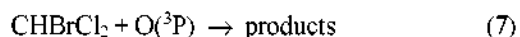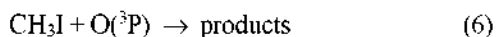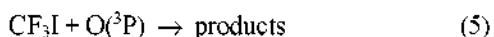
Figure 4. Plot of the second-order decay rate coefficient, k_{decay}, versus [sample]$_0$-[O]$_0$ at 298 K: (a) C_2H_4; (b) CF_3I; (c) CH_3I; (d) $CHBrCl_2$.

dependent on [A]$_0$-[O]$_0$ and the bimolecular rate constant, k_{bi}, was determined by the plot of $-(k_w + k_{bi}a)$ versus [A]$_0$-[O]$_0$ at various initial concentrations of samples as shown in Figure 4. The reaction of O(^{3}P) with C_2H_4 was tested using this method. The bimolecular rate constant was determined to be 8.0×10^{-13} cm^{3}molecule^{-1}s^{-1}, which is in good agreement with the reference values.[9-11]

This method under second order conditions has an advantage over the pseudo-first order conditions, because much stronger chemiluminescence signal is observable due to the high O(^{3}P) concentrations. Moreover, the strong chemiluminescence could effectively eliminate the disturbance caused by fluorescent products and secondary reactions because this method adopts a data at starting point. These conditions give a reliable kinetic data. On the other hand, under pseudo-first order condition, chemiluminescence is very weak because of the low concentration of oxygen atoms compared with reactants. Also, the interfering fluorescence signal from the products could not be ignored.

Measured bimolecular rate constants for the reactions 5-7 were summarized in Table 1.

$$CF_3I + O(^3P) \rightarrow \text{products} \qquad (5)$$

$$CH_3I + O(^3P) \rightarrow \text{products} \qquad (6)$$

$$CHBrCl_2 + O(^3P) \rightarrow \text{products} \qquad (7)$$

For the reaction 5, overall reaction rate constant, 5.0×10^{-12} cm^{3}molecule^{-1}s^{-1}, by the direct observation is comparable to the reference values from the analysis of product IO. Therefore, the IO production is the major channel in the reaction 5 as reported by Gilles *et al.*[7]

$$CF_3I + O(^3P) \rightarrow CF_3 + IO \qquad (5a)$$

$$CH_3I + O(^3P) \rightarrow CH_3 + IO \qquad (6a)$$
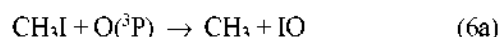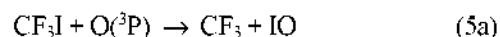
For the reaction 6, the rate constant was measured to be 1.1×10^{-11} cm^{3}molecule^{-1}s^{-1}. This value is twice as fast as that of the reaction 5. However, the value is slightly smaller than the reference value.[7] The mechanism and products of reaction 6 are uncertain. The reaction 6a is less favorable than 5a energetically. However, other pathways such as OH production are thermodynamically allowed as suggested by Gilles *et al.*[7]
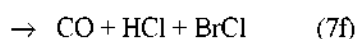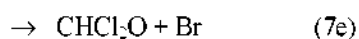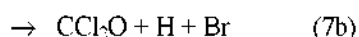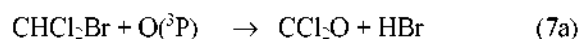
For the reaction of O(^{3}P) with CHCl$_2$Br, the rate constant is determined to be 1.9×10^{-14} cm^{3}molecule^{-1}s^{-1}. The hydrogen abstraction reaction by oxygen atom from bromine or chlorine substituted methanes are known to be 5 orders of magnitude slower than reaction 6.[6] The rate of reaction 7 in this work is much faster than that of CH$_3$Br + O.[5,6] The OBr or OH formation pathway in the reaction 7 is not feasible at room temperature since the pathways are estimated to be highly endothermic by comparing the reaction CF$_2$HBr +

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

Reagent	$k_{bi}/(cm^3molecule^{-1}s^{-1})$	
	This work	Others
C_2H_4	8.0×10^{-13}	$(7.3 \pm 0.9) \times 10^{-13a}$
		7.6×10^{-13b}
CF_3I	5.0×10^{-12}	$(4.5 \pm 1.0) \times 10^{-12c}$
CH_3I	1.1×10^{-11}	$(1.8 \pm 0.6) \times 10^{-11c}$
$CHBrCl_2$	1.9×10^{-14}	

^{a}ref(11), ^{b}ref(10), ^{c}ref(7).

$O(^1D)$.[12] No kinetic and thermodynamic data are available for $CHCl_2Br$ and its reaction with $O(^3P)$. The thermodynamically possible pathways which enhance the overall reaction, not accounting the spin conservation, could be proposed by comparing the $CF_2HBr + O(^1D)$ as reactions 7a-7f:

$$CHCl_2Br + O(^3P) \rightarrow CCl_2O + HBr \qquad (7a)$$

$$\rightarrow CCl_2O + H + Br \qquad (7b)$$

$$\rightarrow CHClO + BrCl \qquad (7c)$$

$$\rightarrow CHClO + Br + Cl \qquad (7d)$$

$$\rightarrow CHCl_2O + Br \qquad (7e)$$

$$\rightarrow CO + HCl + BrCl \qquad (7f)$$

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