

Reaction of $O(^3P)$ atoms with $CF_2 = CXY$ ($X, Y = H, F, Cl, Br$). Discharge flow-chemiluminescence imaging technique

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Abstract

The chemiluminescence imaging technique has been introduced to study kinetics in the discharge flow system. Concentration profile of $O(^3P)$ atom in the reaction with $CF_2 = CXY$ ($X, Y = H, F, Cl, Br$) has been monitored using NO_2 chemiluminescence imaging from the entire reaction zone by a charge-coupled device camera. The observed rate coefficients of $O(^3P)$ with $CH_2 = CH_2$, $CF_2 = CHF$, $CF_2 = CHCl$, $CF_2 = CHBr$, $CF_2 = CFBr$, and $CF_2 = CBr_2$ at 298 ± 2 K are (6.81 ± 0.66) , (4.05 ± 0.20) , (3.21 ± 0.41) , (2.16 ± 0.18) , (3.39 ± 0.23) and $(1.40 \pm 0.27) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. The present method gives reasonably good results and can therefore be considered as an acceptable new tool for kinetic studies.

1. Introduction

The reactions of $O(^3P)$ atoms with partially fluorinated olefins have attracted considerable attention recently because of their unusual kinetic behaviors and general usefulness in the chemical etching processes of the semiconductor industry.

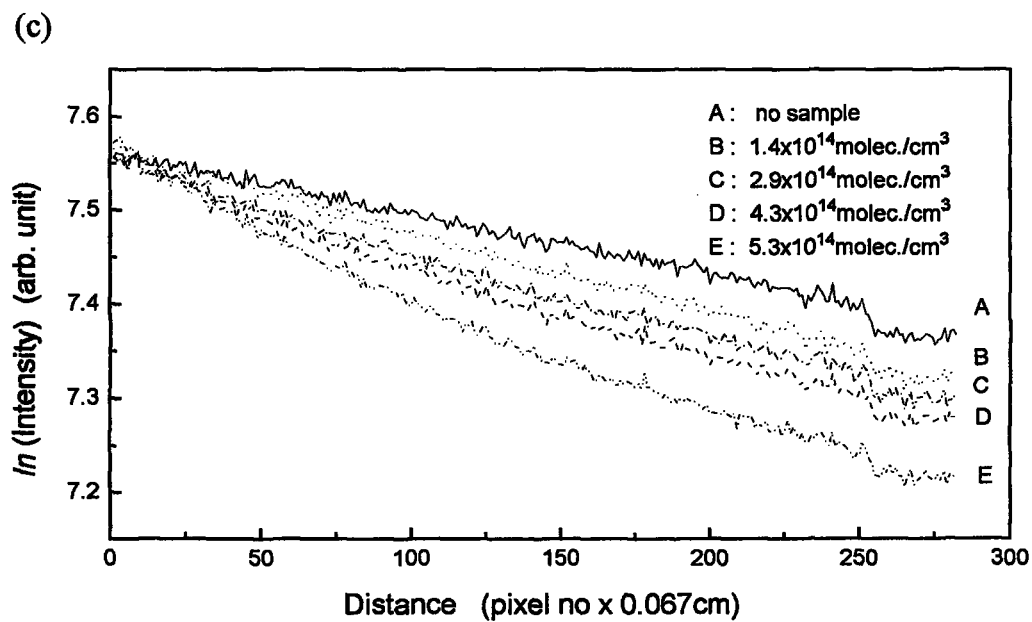
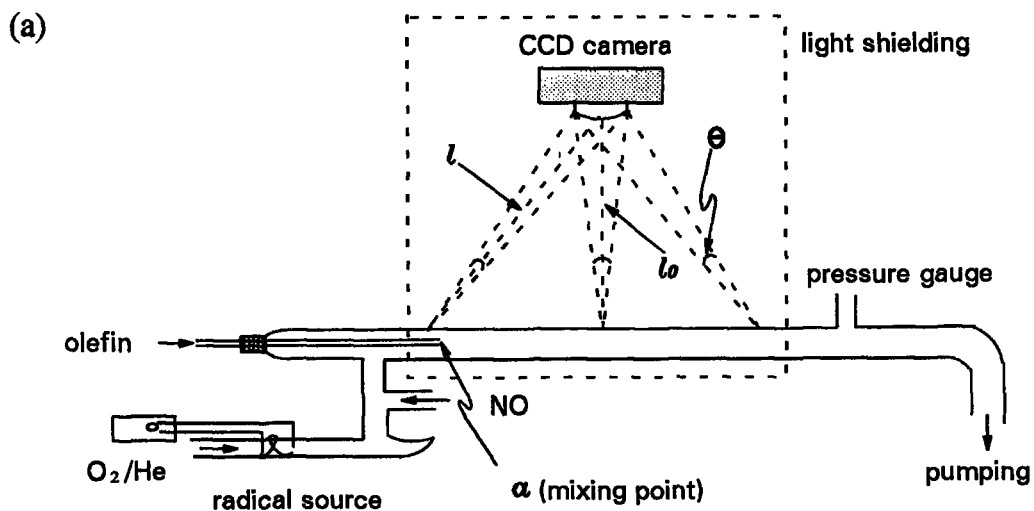
The reactions have been studied using the discharge flow method [1–3], flash photolysis– NO_2 chemiluminescence [4–6], flash photolysis–resonance fluorescence [7] and modulation–phase shift methods [8]. For discharge flow method, the decay concentration of $O(^3P)$ atoms with reaction time is

measured to determine the rate constants. The reaction time is usually achieved by changing the reaction zone length and the distance of the mixing spot of the reactants from the detection point. The zone length is varied by moving either the detection spot or the reactant inlet, along the flow tube. Since disruption of the velocity profile and the development of a pressure gradient by the movable inlet are unavoidable, the measured kinetic data also inherit the serious intrinsic errors present in the conventional flow method [9].

In this work, we propose a new technique to study the flow system by observation of the concentration decay of oxygen atoms with a charge-coupled device (CCD) camera. Since the whole chemiluminescence image in the flow tube can be observed at one time, without changing the location of a movable inlet, use of this method can elucidate the turbulence effect from the reaction system.

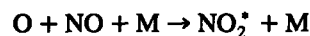
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2. Experimental

Experiments were carried out at room temperature under discharge flow conditions (Fig. 1a). $O(^3P)$ atoms are formed at the upstream end of the apparatus by means of a microwave discharge through dilute O_2 in He gas. The two-dimensional NO_2 chemiluminescence image (Fig. 1b) is used to obtain $O(^3P)$ atom concentrations using a CCD camera (Photometrics CH250, 512×512). The chemiluminescence process is given by



The signal from the camera is fed into an image capturing board with a 16 bit memory for accumulations.

Ethene and $CF_2=CXY$ ($X, Y = H, F, Cl, Br$) gases pass into the flow tube about 30 cm downstream from the atomic oxygen source (see Fig. 1a, mixing point). All reagent gas flows are regulated by a mass flow controller while pressure in the flow tube is monitored with a capacitance manometer. The total pressure is about 1 torr and the flow velocity is about 1100 cm s^{-1} .

Oxygen (99.999%) and He (99.999%) were obtained from Dong-Jin Co. The fluorinated ethylenes (PCR Inc, 99 + %) were purified by several cycles of the freeze–thaw procedure. Ethene (99.995%) and NO (99.9%) were obtained from Matheson. The NO was purified before use, using the trap–thaw method to freeze out NO_2 molecules.

3. Results and discussion

The reactions of $O(^3P)$ atoms with ethylene and $CF_2=CXY$ were carried out under pseudo-first order conditions, $[\text{olefin}] \geq 100[O]$,



The decay of the oxygen atom concentration, $C(t)$, is given by the rate expression

$$\begin{aligned} C_0(t)/C_R(t) &= I_0(t)/I_R(t) \\ &= \exp[(k_w + k_{bi}[\text{olefin}])t]. \end{aligned}$$

At a constant flow velocity, time t corresponds to the distance from the starting point of the reaction to the detector along the flow tube. The $C_0(t)$ is the concentration of $O(^3P)$ atoms in the absence of olefins while $C_R(t)$ is that in the presence of olefins, at time t . The $I_0(t)$ and $I_R(t)$ are the corresponding NO_2 chemiluminescence intensities. The first order rate, k_w , is the removal of $O(^3P)$ atoms (attributed to diffusion out of the viewing zone to the wall) and reaction with impurities and O_2 in the absence of any added olefin, and k_{bi} is the bimolecular reaction rate coefficient.

The observed exponential decay of NO_2 chemiluminescence is put into the decay rate expression below:

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

where the decay constant is linearly dependent on the concentrations of added olefin, at constant total pressure and NO concentration (Fig. 1c). Fig. 2 shows a typical plot of the $O(^3P)$ decay constant against olefin concentrations at room temperature. The bimolecular reaction rate constants, k_{bi} , are obtained from slopes of plots of the k_{decay} versus the olefin concentrations. The k_{bi} for ethylene and various $CF_2=CXY$ molecules are listed in Table 1. Secondary reactions of $O(^3P)$ atoms with reaction products have been found to have negligible effects on the measured rate constants in this study.

The imaging method has several advantages over the conventional flow system. In the conventional flow system, the random errors [10] are caused by frequent movement of the movable inlet to control the reaction time, and the fluctuation in detector sensitivity during the operation. Such random errors are considerably reduced with the imaging method,

Fig. 1. Decay signals of the NO_2 chemiluminescence for the reaction of $O(^3P)$ with various $CF_2=CHF$ concentration. (a) A schematic diagram of experimental setup. a : the mixing point (time = 0.0), l : the distance from the camera (ca. 101 cm), l_0 : the central distance (ca. 100 cm), and θ : the view angle (2.5°). (b) The projection of the NO_2 chemiluminescence intensity (Y axis) vs. distance (X axis, reaction time). (c) The averaged data plot: $\ln(\text{intensity})$ vs. distance.

Table 1
The reaction rates of $O(^3P)$ with ethylene, $CF_2=CXY$

Reagent	k_{bi} ($10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Reference values
C_2H_4	6.81 ± 0.66	7.31 ± 0.93 [12]
CF_2CHF	4.05 ± 0.20	5.73 ± 1.99 [12]
		4.48 [13]
CF_2CHCl	3.21 ± 0.41	
CF_2CHBr	2.16 ± 0.18	
CF_2CFBr	3.39 ± 0.23	
CF_2CBr_2	1.40 ± 0.27	

The indicated errors are the least square one standard deviations.

since the decay rate of oxygen atoms is obtained from one observation only, and without the use of a moveable injector. This method has an additional advantage of reducing the systematic errors, caused by different levels of operator expertise. Control of experimental parameters such as total pressure and mixing ratio is achieved by the direct observation of oxygen atom distribution in the reaction tube. Additionally, the disruption of the velocity profiles caused by the moveable injector is removed, and it takes less time for each experimental run compared with the conventional flow method. Overall therefore, the systematic errors due to fluctuations of microwave

generator power and the flow controller are reduced. Above all, the imaging method enables the reaction to be directly and simultaneously monitored throughout the entire reaction region compared with only part of the reaction region in the conventional flow system. For calculation of the decay constant, the numbers of chemiluminescence data points (512×30 in our system) are much larger than those used in a conventional system. These large numbers of data points serve to enhance the accuracy and precision of kinetic measurements.

As a check on the experimental system, the rate coefficients for the systems of $O(^3P)$ with $CH_2=CH_2$ and $CF_2=CHF$ were determined and found to be $k_{bi}(C_2H_4) = (6.81 \pm 0.66) \times 10^{-13}$, and $k_{bi}(C_2F_3H) = (4.05 \pm 0.20) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (at room temperature) and are thus in good agreement with the reference values [11,4]. The rate coefficients for the systems of $O(^3P)$ with $CF_2=CHCl$, $CF_2=CHBr$, $CF_2=CFBr$, and $CF_2=CBr_2$ were found to be (3.21 ± 0.41) , (2.16 ± 0.18) , (3.39 ± 0.23) , and $(1.40 \pm 0.27) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (at room temperature).

Two different types of reactions have been identified for the $O(^3P)$ reaction with halogenated olefins. In the first type a normal addition of an O atom to

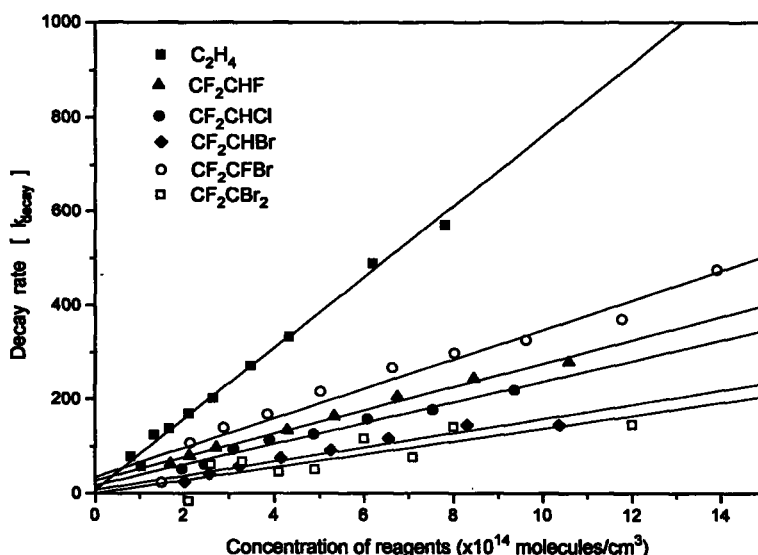
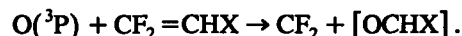


Fig. 2. $O(^3P)$ atom decay rates as a function of ethylene, $CF_2=CXY$ ($X, Y = H, F, Cl, Br$) concentrations at the room temperature. Total pressure ≈ 1 torr. Flow velocity $\approx 1100 \text{ cm s}^{-1}$.

the olefin forms an epoxide as a primary reaction product. The second type involves the formation of two fragments by direct C–C double bond cleavage [12]. The O atom is usually attached to the carbon atom with higher electron density. This suggestion has been confirmed in some halogenated olefins [14–16] as given by an example:



The direct C–C bond cleavage reaction rate of halogenated ethylenes has been found to be related to the number and type of substituted halogen atoms.

The direct cleavage of fluorinated ethylenes has been interpreted by Gutman [3] in terms of an electronic inductive effect due to the higher electron negativity of its substituents which causes a weakening of the C–C π bond strength and which leads to direct bond breakage. Direct C–C bond cleavage usually occurs in halogenated olefins with two or more fluorine atoms.

The reactivity of O atom addition to ethylene and methyl- or chlorine-substituted ethylenes has been found to have some correlation with the ionization

Table 2

The ionization potentials of halogenated olefins

Olefin	Ionization potential (eV)
$\text{CF}_2=\text{CF}_2$	10.805
$\text{CF}_2=\text{CHF}$	10.678
$\text{CF}_2=\text{CH}_2$	10.757
$\text{CH}_2=\text{CHF}$	10.597
$\text{CHF}=\text{CHF}(\text{trans})$	10.545
$\text{CHF}=\text{CHF}(\text{cis})$	10.535
$\text{CF}_2=\text{CHBr}$	10.508
$\text{CF}_2=\text{CHCl}$	9.935
$\text{CF}_2=\text{CFBr}$	10.635
$\text{CF}_2=\text{CBr}_2$	10.398

potentials of the olefins [17]. The electron density of the double bond of olefins, is increased by substitution of an H atom with an alkyl group while the ionization potential, (the energy required to remove a π electron), is lowered by the substitution. Reaction rates of molecules with electrophilic O atoms increase as a result of the increased negative character of the double bond [18]. On the contrary, with the chloro- and alkyl-substituted ethylenes however, the reactivity of O atom addition reaction has shown quite opposite trends in fluorinated olefin systems. Fig. 3 illustrates the relationships between reaction rates and the ionization potentials of fluorinated olefins. The reaction rate coefficients lower as the ionization potential decrease in the $\text{O}(^3\text{P})$ -halogenated olefin systems. The ionization potentials are calculated using the PM3 method [19], MOPAC 93 package [20] and are listed in Table 2.

In conclusion, the chemiluminescence imaging technique introduced in this work has been proven to have several advantages over the conventional flow technique for kinetic studies. These are, (1) a considerable reduction of systematic and random errors by monitoring the entire reaction zone directly and simultaneously, and (2) faster data acquisition.

The reactivities of $\text{O}(^3\text{P})$ with fluorinated ethylenes are strongly dependent on the properties of C–C double bond. These rate enhancements are caused by (1) the higher ionization potentials of the olefins, (2) the reduced electron densities of the carbon atoms in the double bond, and (3) the steric effects of substituted groups, and the decrease of van der Waals radii (as from bromine to fluorine).

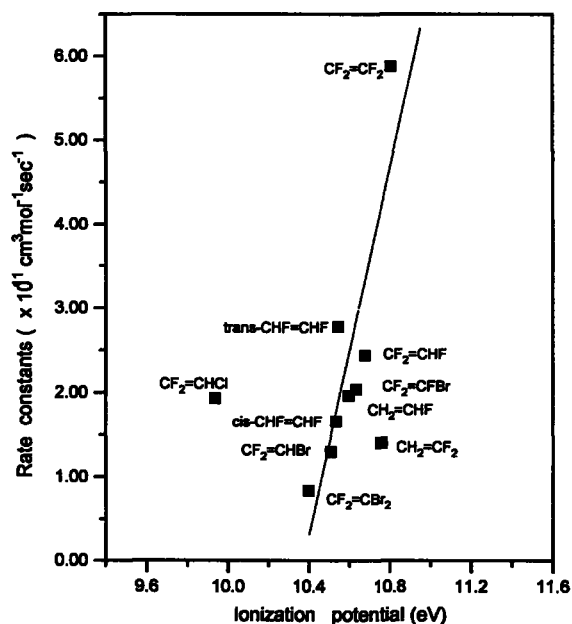


Fig. 3. The rate constants of $\text{O}(^3\text{P})$ atom reactions as a function of the ionization potentials of halogenated olefins. Rate constants other than those of $\text{CF}_2=\text{CHX}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$), $\text{CF}_2=\text{CFBr}$ and $\text{CF}_2=\text{CBr}_2$ are obtained from Ref. [12].

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References

- [1] R.E. Huie, J.T. Herron and D. Davis, *Intern. J. Chem. Kinet.* 4 (1972) 521.
- [2] I.R. Slagle, D. Gutman and J.R. Gilbert, *Symp. Combustion* 19 (Combustion Institute, Pittsburgh, 1974) 785.
- [3] J.R. Gilbert, I.R. Slagle, R.E. Graham and D. Gutman, *J. Phys. Chem.* 80 (1976) 14.
- [4] K. Sugawara, K. Okazaki and S. Sato, *Bull. Chem. Soc. Japan* 54 (1981) 358.
- [5] H. Umemoto, K. Sugiyama, S. Tsunashima and S. Sato, *Bull. Chem. Soc. Japan* 58 (1985) 1228.
- [6] R. Atkinson and J.N. Pitts, Jr., *J. Chem. Phys.* 67 (1977) 2488.
- [7] J. Hranisavljevic and A. Fontijn, *J. Phys. Chem.* 99 (1995) 12809.
- [8] R. Atkinson and J.N. Pitts, Jr., *Intern. J. Chem. Kinet.* 8 (1976) 475.
- [9] J.H. Carleton, *J. Phys. Chem.* 83 (1979) 3.
- [10] R.J. Cvetanovic, D.L. Singleton and G. Paraskevopoulos, *J. Phys. Chem.* 83 (1979) 50.
- [11] D.L. Singleton and R.J. Cvetanovic, *J. Am. Chem. Soc.* 98 (1976) 6812.
- [12] R.J. Cvetanovic, *J. Phys. Chem. Ref. Data* 16 (1987) 261.
- [13] J.T. Herron and R.E. Huie, *J. Phys. Chem. Ref. Data* 2 (1973) 467.
- [14] R.E. Huie, N.J.T. Long and B.A. Thrush, *Chem. Phys. Letters* 51 (1977) 197.
- [15] H. Meunier, J.R. Purdy and B.A. Thrush, *J. Chem. Soc. Faraday II* 76 (1980) 1304.
- [16] R.C. Mitchell and J.P. Simons, *J. Chem. Soc. (B)* (1968) 1005.
- [17] R.E. Huie and J.T. Herron, *Prog. React. Kinet.* 8 (1975) 1.
- [18] G.Y. Adusei and A. Fontijn, *J. Phys. Chem.* 98 (1994) 3732.
- [19] J.J.P. Stewart, *J. Compt. Chem.* 10 (1989) 209.
- [20] J.J.P. Stewart, *Quantum Chemistry Program Exchange*, 1993.