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# Measurements of $HO_2$ Chemical Kinetics with a New Detection Method

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## I. Introduction

This report covers the period from December 1, 1985 to May 31, 1986 for the research program currently supported by NASA under Grant No. NAGW-661 basic. In this program, the reaction rate constant of $HO_2+O_3$ has been measured with a discharge-flow-tube apparatus. The $HO_2$ radical was detected by the OH(A-X) photofragment emission produced from photodissociative excitation of $HO_2$ at 147 nm. In the meantime, the optical emissions produced by the vacuum ultraviolet excitation of chemical species in the flow tube were investigated and used to examine the possibility for their interference with the $HO_2$ detection. The research results are summarized below.

## II. Research Accomplished

### A. Reaction Rate Constant of $HO_2+O_3$

A discharge-flow-tube apparatus has been constructed and used to measure the reaction rate constant of $HO_2+O_3$. The flow tube consisted of three coaxial tubes. The innermost tube was a movable Teflon tube of 2 mm ID, and the second tube was a movable Teflon coated Pyres tube of 1 cm ID and 70 cm long. The main reactor was a Teflon coated Pyres tube. Two sizes of tubes were used - one 4.8 cm ID and the other 2.2 cm ID.

$HO_2$ was produced by the reaction sequence:

$Cl + CH_3OH \rightarrow CH_2OH + HCl$

$CH_2OH + O_2 \rightarrow HO_2 + CH_2O$

The Cl atom was produced by microwave discharge of a trace amount of $Cl_2$ in He. The $HO_2$ was detected by monitoring the

$OH(A-X)$ emission from photodissociative excitation of $HO_2$ by a Xe resonance light at 147 nm,

$$HO_2 + h\nu(147\ \mathrm{nm}) \rightarrow OH(A^2\Sigma^+) + O$$

$$OH(A^2\Sigma^+) \rightarrow OH(X^2\Pi) + h\nu\ (306\text{-}320\ \mathrm{nm}).$$

The concentrations of Cl and the consequent reaction products (such as $CH_2OH$, $CH_2O$ and $HO_2$) were limited to low values such that the requirements for the pseudo-first-order reaction were satisfied. $HO_2$ could be regenerated by the reaction sequence:

$$HO_2 + O_3 \rightarrow OH + 2O_2$$

$$OH + O_3 \rightarrow HO_2 + O_2$$

The regeneration was greatly reduced by adding $C_2F_3Cl$ or $C_3H_8$ as the OH scavenger.

The reaction rate of $HO_2 + O_3$ at room temperature was measured as a function of reaction time and $O_3$ concentration. The reaction rate constants measured with different flow tubes sizes and different OH scavengers are consistent to be $(1.9 \pm 0.3) \times 10^{-15}\ \mathrm{cm^3/s}$. A computer simulation modeling for the reaction kinetics occurring in the flow tube was carried out to confirm that the secondary reactions were negligible at the low $HO_2$ concentrations used in the experiment. This current reaction rate constant agrees very well with the value of $2 \times 10^{-15}\ \mathrm{cm^3/s}$ measured by the Laser-magnetic-resonance technique. Our results are described in more detail in a paper entitled "Reaction Rate Constant of $HO_2+O_3$ Measured by Detecting $HO_2$ from Photofragment Fluorescence" which is attached in this report as Appendix A.

We are measuring the $HO_2+O_3$ reaction rate constant in the temperature range of 200-350 $^oC$. The result will be presented in the next report.

## B. Photofragment Emissions for VUV Excitation of Chemical Species in the Flow Tube

When the chemical species in the flow tube are excited by the 147 nm photons, they may produce UV light to interfere with the OH(A-X) emission from photoexcitation of $HO_2$. Thus, the optical emissions from the vacuum ultraviolet (VUV) excitation of chemical species in the flow tube are needed to interpret our data. The fluorescence spectra of various chemical species were investigated using synchrotron radiation as a light source. The emission spectra were also produced by excitation of the chemical species with intense atomic lines, and they were dispersed to identify the emitting species.

The OH(A-X) emission from photoexcitation of $CH_3OH$ has been observed and the result has been reported in an earlier paper (J. B. Nee, M. Suto and L. C. Lee, Chem. Phys. 98, 147 (1985)). The result for photoexcitation of $Cl_2$ has been recently published in the Journal of Chemical Physics which is attached in this report as Appendix B. The spectroscopic data of HCl, $CH_2O$, $C_3H_8$ and $C_2F_3Cl$ have been obtained and analyzed. Their results will be summarized in papers and published in scientific journals. Among all these molecules studied, only $C_2F_3Cl$ emits at 147 nm. The cross section for the emission in the 300-330 nm region is, however, quite small such that this emission does not seriously disturb the measurement of $HO_2$ concentration by the photofragment emission method.

In summary, the photofragment emissions of all chemical species in the flow tube have been investigated, and their possible interferences to the OH(A-X) emission produced by photoexcitation of $HO_2$ have been examined. It is concluded that the possible optical emissions from other chemical species do not interfere the measurement of $HO_2$ concentration by the photofragment emission method. Thus, our measurement of the $HO_2$+$O_3$ reaction rate constant is not affected by the optical emissions from chemical species other than $HO_2$.

# Appendix A

"Reaction Rate Constant of $HO_2+O_3$ Measured by Detecting $HO_2$ from Photofragment Fluorescence"

# Reaction Rate Constant of $HO_2+O_3$ Measured by Detecting $HO_2$ from Photofragment Fluorescence

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## ABSTRACT

The rate constant for the reaction $HO_2+O_3 \rightarrow OH+2O_2$ was investigated in a discharge-flow system at room temperature. $HO_2$ was produced from the reaction sequence: $Cl+CH_3OH \rightarrow CH_2OH+HCl$ and $CH_2OH+O_2 \rightarrow HO_2+CH_2O$. $HO_2$ was detected by the OH(A-X) fluorescence produced from photodissociative excitation of $HO_2$ at 147 nm. A computer modeling of the reaction kinetics occurring in the flow tube was carried out to confirm that contributions from secondary reactions were negligible at low $HO_2$ concentrations. The rate constant was determined from first order decay of $HO_2$ in excess $O_3$. The measured reaction rate constant of $HO_2+O_3$ is $(1.9 \pm 0.3)\times10^{-15}$ $cm^3/s$, which agrees well with published data.

## I. INTRODUCTION

The reaction of odd hydrogen radicals, in particular, the reaction sequence

$$HO_2 + O_3 \rightarrow OH + 2O_2 \quad (1)$$

$$OH + O_3 \rightarrow HO_2 + O_2 \quad (2)$$

has been implicated as major depletion reactions for $O_3$ in the lower stratosphere and important radical reactions in the troposphere. Several direct measurements of $k_2$ have been undertaken[1-3] but to date only the laser magnetic resonance (LMR) detection[4] of $HO_2$ has been employed to directly measure $k_1$. In this present study, we demonstrate that the discharge-flow technique with photofragment emission (DF-PE) detection[5,6] of $HO_2$ can be used to directly measure the rate constant of reaction (1).

$HO_2$ was produced by microwave discharge of $Cl_2$, which then reacted with $CH_3OH$ and $O_2$ by[6]

$$Cl + CH_3OH \rightarrow CH_2OH + HCl \quad (3)$$

$$CH_2OH + O_2 \rightarrow HO_2 + CH_2O \quad (4)$$

$HO_2$ was detected by monitoring the $OH(A^2\Sigma^+ \rightarrow X^2\Pi)$ emission from photodissociative excitation of $HO_2$ by a Xe resonance light at 147 nm,[6]

$$HO_2 + h\nu \text{ (147 nm)} \rightarrow OH(A^2\Sigma^+) + O \quad (5)$$

$$OH(A^2\Sigma^+) \rightarrow OH(X^2\Pi) + h\nu \text{ (306-320 nm)} \quad (6)$$

The experimental conditions were such that the requirements for psuedo-first order reaction were satisfied. Regeneration of $HO_2$ via reaction (2) was greatly reduced by adding OH scavengers.[4,7] Two reagents, $C_2F_3Cl$ and $C_3H_8$, were used as OH scavengers in our experiments.

Since the measurement of reaction rate constant involves many experimental parameters, it is essential to apply different techniques to verify agreement among reported values. Both the methods of production and detection of $HO_2$ for the study of reaction (1) in this experiment are different from previously reported experiments.[4,7-9] This work reports the second direct measurement for the rate constant of reaction (1).

## II. EXPERIMENTAL

The schematic diagram of the experimental apparatus is shown in Fig. 1. The experimental chamber consisted of a flow tube assembly and a gas cell. The flow tube consisted of three coaxial tubes. The innermost tube was a movable teflon tube of 2 mm i.d. through which $CH_3OH$ and $O_2$ were fed. The second tube, a teflon coated Pyrex, was also a movable injector of 1 cm i.d. and 70 cm long. Chlorine atoms were produced upstream by a microwave discharge of a trace of $Cl_2$ in He. Helium was also used as a carrier gas and its flow rate ($Q_1$) was regulated by a mass flow controller (MKS instruments). The production of $HO_2$ was completed in this tube.

The main reactor was also a teflon coated Pyrex tube. Two sizes were used, one of 4.8 cm i.d. and the other 2.2 cm i.d. both 60 cm long. $O_3$ and the OH scavenger, $C_2F_3Cl$ or $C_3H_8$, were introduced into the flow tube upstream. $O_3$ was produced, prior to use, by a high voltage a.c. discharge of $O_2$ at atmospheric pressure and stored on two silica gel traps at 195 $^{o}K$. The $O_3$ was purified before use by pumping on the silica gel $O_3$ traps down to a few torr, where the $O_3$ concentration measured by absorption of 253.7 nm agreed with the pressure measured by an MKS Baratron manometer. $O_3$ was introduced into the flow tube with He as a carrier gas with the He flow rate ($Q_2$) regulated by another controller. The elution rate of $O_3$ was controlled by varying both the flow rate and the temperature of the trap. The partial pressure of $O_3$ was monitored by the attenuation of the 253.7 nm Hg line at two positions, upstream of the flow tube and downstream after the gas cell. Both measurements agreed within experimental uncertainty, indicating $O_3$ loss in the flow tube was negligible.

$HO_2$ radicals reacted with $O_3$ in the main reaction tube. The partial pressure of all gases were fixed, and the reaction times were varied by moving the position of the $HO_2$ injector tube. The reaction time is a function of the linear flow velocity which in turn is dependent on the total flow rate. The total flow rate (discussed in detail below) was determined for the flow conditions of each experimental run. The pressures in the flow tube and in the gas cell were monitored separately by two Baratron manometers (MKS). The ratio of total pressures $(P_{tube}-P_{cell})/P_{cell} \sim 0.05$. Since the pressure drop was so small, no corrections for Poiseuille drop were made (discussed in Section C of Results).

The carrier gas was in excess over the reactants, so the total flow rate was dependent largely on the He flow rate. The total flow rate was determined as follows. First, the volume of the chamber, $V_T$, was determined using Boyle's Law with a calibrated (at room temperature) 1000 $cm^3$ container as a reference volume, $V_1$. A known pressure of He, $P_1$, was contained in $V_1$ and then expanded to the total volume, $V_2 = V_T + V_1$, and the pressure in $V_2$, $P_2$, was recorded. Thus, $V_2 = P_1V_1/P_2$ in $cm^3$. With the flow rates of He, $Q_1$ and $Q_2$, kept constant, the chamber was isolated from the pump and the increase in pressure per min, $\Delta P/\Delta t$ in torr/min, was recorded. The total standard flow rate, $Q_T$, was obtained using:

$$Q_T = V_2\,(273/760)\,(\Delta P/\Delta t)/T \qquad (8)$$

where T is temperature in K, and $Q_T$ is the flow rate in standard cubic centimeter per minute (SCCM). This equation was used to verify the instrumental flow rate settings $Q_1$ and $Q_2$. For the kinetic experiments, the ratio of $\Delta P/\Delta t$ was determined for each individual run with all the major reactants in the flow as well.

The linear flow velocity in the tubes was derived from:

$$v = V_2\,[(\Delta P/\Delta t)/(60P)]\,(1/\pi r^2) \qquad (9)$$

where P is the total pressure, $P = (P_{tube}+P_{cell})/2$, at which the experiment was performed, r is the radius of the flow tube and v is in cm/sec. The error estimates at 95% confidence level[10] are: $V_2$ (± 2%), T (± 1%), P (± 5%), $\Delta P/\Delta t$ (± 7%), and r (± 1%). The resultant error in $Q_T$ or v is ± 9%. The total flow rates were typically in the range of 150-250 SCCM with the 4.8 cm i.d. and 80-100 SCCM with the 2.2 cm i.d., for which the linear flow velocities in the main reaction flow tube were in the range 100-130 cm/s and 150-200 cm/s, respectively.

The gas cell was a six-way-stainless steel-cross of 3 inch o.d. $HO_2$ radicals were detected by monitoring its OH(A → X) photofragment emission. A sealed Xe resonance lamp with a $MgF_2$ window was used as a light source. The light source intensity was monitored by a CsI photodiode (Hamamatsu R1187). A gas filter (1% $CH_4$ in Ar at atmospheric pressure) was used to cut-off the 129.5 nm line in the Xe lamp so that only the 147 nm line transmitted into the gas cell.[6] The OH(A-X) emission from $HO_2$ was detected at the direction perpendicular to both the light source and the gas flow by a cooled PMT (EMI 9558 QB). A narrow band pass filter (310 ± 10 nm) was used to isolate the OH(A-X) band. The signal from the PMT was processed by an ORTEC counting system and the output fed to an IBM PC. The carrier gas flow rates, the total pressure, and the intensities of the 147 nm and 253.7 nm light sources were also simultaneously recorded by the computer.

The gas mixture of 2.0% $Cl_2$ in He and the lecture bottles of C.P. grade $C_2F_3Cl$ ( > 99.0%) and $C_3H_8$ ( > 99.0%) were supplied by Matheson. The $CH_3OH$ (supplied by Fisher, purity > 99.9%) vapor was carried by He into the gas cell. The concentration of $CH_3OH$ was determined from the ratio of the $CH_3OH$ vapor pressure (120 torr at room temperature) to the pressure of the carrier gas. $O_2$ was supplied by Amerigas and He of UHP grade (99.999%) was supplied by M.G. Scientific. Gases were used as delivered.

## III. RESULTS AND DISCUSSION

### A. Detection of $HO_2$ Radicals

The photofragment emission intensity can be described by,

$$I_f = C\sigma_f[HO_2]\, I_o \exp(-\sigma_i n_i \ell)/(1 + \tau\sum_i n_i k_i), \qquad (7)$$

where C is a constant including the geometric factor and the PMT detection efficiency, $\sigma_f$ is the cross section for the OH(A → X) fluorescence produced from excitation of $HO_2$ at 147 nm, $[HO_2]$ is the $HO_2$ concentration, $I_o$ is the light source intensity of the Xe lamp, $\ell$ is the path length of the light source from the $MgF_2$ window to the center of the PMT view region, $\tau$ is the radiative lifetime of the OH(A-X) transition; $n_i$, $\sigma_i$ and $k_i$ are the concentrations, the absorption cross sections at 147 nm, and the quenching rate constants of OH*(A) by various species in the flow tube, respectively. The exponential term represents the attenuation of the light source intensity at 147 nm by various species in the flow tube. The denominator represents the reduction in OH emission by the quenching of OH*(A) by the various gases.

The absorption cross sections for $O_2$, $O_3$, $CH_3OH$, $C_2F_3Cl$, and $C_3H_8$ at 147 nm were determined from the slope of the linear plot of absorbance versus pressure for each gas and are $1.4 \times 10^{-17}$, $4.41 \times 10^{-18}$, $1.30 \times 10^{-17}$, $1.80 \times 10^{-17}$ and $7.67 \times 10^{-18}$ $cm^2$, respectively. The absorption cross-section[11] of $Cl_2$ is $< 10^{-18}$ $cm^2$. The attenuation of light source intensity by all gases for the optical path from the $MgF_2$ window to the detection region of about 1 cm was estimated to be about 10% at a typical experimental condition such as $[O_3] = 2.5 \times 10^{15}$ $cm^{-3}$, $[O_2] = 1.0 \times 10^{15}$ $cm^{-3}$, $[CH_3OH] = 1.0 \times 10^{14}$ $cm^{-3}$, $[Cl_2] = 6.5 \times 10^{13}$ $cm^{-3}$ and $[C_2F_3Cl] = 4 \times 10^{15}$ $cm^{-3}$ (or $[C_3H_8] = 6.5 \times 10^{15}$ $cm^{-3}$).

The quenching term $(\tau \sum_i n_i k_i)$ of OH*(A) by all gases in the flow tube is estimated to be about 1.6 and 2.6 with $C_2F_3Cl$ and $C_3H_8$ as scavengers, respectively, assuming that the quenching rate constants of OH*(A) by all the gases are equal to the gas kinetic constant ($3 \times 10^{-10}$ $cm^3/s$). The OH(A-X) emission intensity may thus be reduced by a factor of 2.6 or 3.6, depending on $C_2F_3Cl$ or $C_3H_8$ being used as the OH scavenger. With such attenuation, the light source intensity was still strong enough for the detection of $HO_2$ radicals.

The photofragment emissions in the UV region from photoexcitation of various gases used in this experiment were also studied. The OH(A-X) emission was observed from excitation of $CH_3OH$ at 147 nm with fluorescence cross section[12] of $3\times10^{-21}$ $cm^2$. An intense photofragment emission in the UV region (280-380 nm) was observed from excitation of $C_2F_3Cl$ at 147 nm. The fluorescence cross section of $C_2F_3Cl$ has been measured in the 105-170 nm region;[13] however, when a narrow bandpass filter (310 ± 10 nm) was used, the fluorescence signal was greatly reduced such that it only contributed a small constant background. The other molecules do not fluoresce in the UV region when excited at 147 nm.

From the above results, it is conclusive that the relative $HO_2$ concentration in the gas cell can be measured from the OH(A-X) emission. The estimated minimum detectable $[HO_2]$ is $\sim 10^9$ molecule/$cm^3$. In each measurement of the $HO_2 + O_3$ reaction rate, flow conditions, which included gas flow velocities, gas flow rates, gas pressures, and microwave discharge power were fixed, except for the reaction time which was varied by changing the position of the movable injector. Since the gas pressures in each measurement were kept constant, the light attenuation, quenching, and emission due to species other than $HO_2$ were constant so that the relative $[HO_2]$ is proportional to the OH(A-

X) fluorescence intensity observed. For a fixed [$O_3$], relative [$HO_2$] was measured as a function of the reaction time.

B. $HO_2$ Concentrations and Secondary Reactions

The calibration of $HO_2$ by reaction with NO to give $NO_2$ and OH, where the [OH] was measured by OH(A-X) resonance fluorescence,[5] proved difficult for this chemical system. Instead, the [$HO_2$] was estimated by a titration method using $CH_3OH$ as titrant and the data were compared with a kinetic model. For [$Cl_2$] = $5.5 \times 10^{13}$ $cm^{-3}$ and [$O_2$] = $1.3 \times 10^{15}$ $cm^{-3}$ kept constant, the data of $I_f$ versus [$CH_3OH$] are plotted in Fig. 2 for two reaction times, 45 and 65 msec, inside the central tube (1 cm i.d.) and for an additional 10 and 20 msec to the detection region, respectively. The error bars in $I_f$ represent one standard deviation and that in [$CH_3OH$] is the instrumental uncertainty of the pressure manometer. The reactions for the kinetic model are summarized in Table 1. The calculations were carried out using a program which uses the Gear routine for the solution of differential equations.[14]

The reactions in the model are similar to those considered by Takacs and Howard in their modeling of the self-reaction of $HO_2$.[15] The estimates for the wall losses were deduced from other experimental data. Wall loss rate for $HO_2$ was not greater than 1.5 $s^{-1}$ in the central tubing (deduced from the intercepts of Figs. 9-11 as discussed later). When the $O_2$/$CH_3OH$ injector was positioned so that the residence time of Cl was about 40 msec before interacting with $CH_3OH$ and $O_2$, no fluorescence from $HO_2$ was detected, thus an upper limit to Cl loss rate is 25 $s^{-1}$. The wall loss rate of $CH_2OH$ was estimated to be 185 $s^{-1}$ for a halocarbon wax coated tube of 1.24 cm i.d. at comparable flow velocities used in our experiments.[6]

In the modeling, at each [$CH_3OH$], the [$O_2$] was given and [Cl] was varied to give the best fit to the data. Best agreement was obtained between computer calculations and experiments when $1\times10^{11}$ < [Cl] < $2\times10^{11}$ $cm^{-3}$ and wall loss rate of Cl was 10 $s^{-1}$. Wall loss rates of $HO_2$ and $CH_2OH$ contributed insignificantly to the curve fitting. Experimental and calculation data were normalized at [$CH_3OH$] = $1\times10^{14}$ $cm^{-3}$ and compared in Fig. 2.

First, ignoring wall losses of $HO_2$, Cl and $CH_2OH$, plots (a) and (b) of Fig. 2 are the simulation curves with [Cl] = $1\times10^{11}$ and $2\times10^{11}$ $cm^{-3}$, respectively. Plot (c) is with $k_w(HO_2)$ = 1.5 $s^{-1}$ for [Cl] = $1\times10^{11}$ $cm^{-3}$. There is no substantial change in the simulation curve when $k_w(HO_2)$ is considered. The same curve as (c) was obtained when $k_w(CH_2OH)$ = 200 $s^{-1}$ was included in the modeling. Curve (d) is obtained when $k_w(Cl)$ = 10 $s^{-1}$ and $k_w(CH_2OH)$ and $k_w(HO_2)$ were set at zero. Including $k_w(Cl)$ improved the curve fitting at smaller [$CH_3OH$]. However, the change in curve (d) was not significant when wall losses from $HO_2$ and $CH_2OH$ were considered. The [Cl] represents the Cl entering the central reactor. The amount of Cl formed in the discharge region is possibly high but wall losses and atom recombination can also be high so that the resulting [Cl] is low.

Complications in the treatment of our kinetic data for the $HO_2$ + $O_3$ reaction could arise from (i) interference of the OH fluorescence from photodissociation of $H_2O_2$ and (ii) contributions from secondary reactions. These are discussed below.

$H_2O_2$ is produced in the reaction of $HO_2+HO_2$. $H_2O_2$ is also photodissociated when irradiated by 147 nm photons:

$$H_2O_2 + h\nu\ (147) \rightarrow OH^*(A^2\Sigma^+) + OH(A^2\Pi) \qquad (10)$$

Thus, the OH(A-X) emission (reaction 6) from $H_2O_2$ will also be detected. The $H_2O_2$ fluorescence cross section[17] at 147 nm is $(H_2O_2) = 5\times10^{-19}\ cm^2$.[16] The fluorescence from photodissociation of $H_2O_2$ will add a background that may interfer with the data analysis. However, this additional signal in a typical experimental condition was quite small such that it is negligible as discussed below.

A summary of the experimental conditions are given in Table II. The flow velocities correspond to an average reaction time of 80 msec in the central tube. The typical concentrations of reactants are: $[CH_3OH] = 1.2\times10^{14}$, $[O_2] = 1.3\times10^{15}$ and $[Cl_2] = 5.5\times10^{13}$. Using these concentrations and assuming that wall losses for $HO_2$, $CH_2OH$ and Cl are neglible so that the maximum contribution from secondary reactions can be obtained, the modeling predicts an $9.7\times10^{10} \leq [HO_2] \leq 1.9\times10^{11}\ cm^{-3}$ and $1.1\times10^9 \leq [H_2O_2] \leq 4.5\times10^9\ cm^{-3}$ after 80 msec of reaction for $1\times10^{11} \leq [Cl] \leq 2\times10^{11}\ cm^{-3}$. Since $[H_2O_2]$ is two-orders of magnitude smaller than $[HO_2]$, the contribution of $H_2O_2$ to the fluorescence is expected to be quite small if the fluorescence cross sections of $HO_2$ and $H_2O_2$ are the same order of magnitude. This is indeed true as justified below.

The fluorescence cross section of $HO_2$, $\sigma(HO_2)$, can be deduced from the current experimental data. $CH_3OH$, like $HO_2$ and $H_2O_2$, is also photodissociated by 147 nm photons to give $OH^*(A)$

which subsequently emits in the 310 ± 10 nm region. The $\sigma(HO_2)$ can be obtained by calibration against the $CH_3OH$ emission whose fluorescence cross section[12] at 147 nm is known, $\sigma(CH_3OH) = 3\times10^{-21}$ cm$^2$. Using the $[HO_2]$ from the modeling, we have $5\times10^{-20} \leq \sigma(HO_2) \leq 1\times10^{-19}$ cm$^2$. Thus, $\sigma(HO_2)$ is about a factor of 5 to 10 smaller than $\sigma(H_2O_2)$. Considering the low $[H_2O_2]$, its contribution to the observed fluorescence is less than 10%. This percentage will be considerably reduced when the $[HO_2]$ is kept low.

To further verify that the [Cl] is indeed small in our experiments, and thus, the $[HO_2]$ and $[H_2O_2]$ are likewise small, the fluorescence intensity was monitored as a function of $[Cl_2]$ as shown in Fig. 3. The plot of $I_f$ versus $[Cl_2]$ is linear for the case without or with $O_3$. The plots (a) and (b) are fit to the respective data, where $[Cl] = 10^{11}$ cm$^{-3}$ is assumed for an initial $[Cl_2] = 5.5\times10^{13}$ cm$^{-3}$ and $\sigma(H_2O_2) = 3\ \sigma(HO_2)$. This linearity extends to about three times the $[Cl_2]$ used in the $HO_2+O_3$ experiments ($C_3H_8$ was used as the OH scavenger to inhibit reaction (2) for the data when $O_3$ was added). If $\sigma(H_2O_2) = 10\ \sigma(HO_2)$, is assumed, the dependence deviates from the linearity as shown in plots (c) and (d). When $[Cl] = 2\times10^{11}$ cm$^{-3}$ is assumed for an initial $[Cl_2] = 5.5\times10^{13}$, and $\sigma(H_2O_2) = 10\ \sigma(HO_2)$ then the dependence deviates further from the linearity as shown in plots (e) and (f). For plot (f), the $H_2O_2+O_3$ reaction rate constant is assumed equal to the $HO_2+O_3$ reaction rate constant (Section D). If the $H_2O_2+O_3$ reaction is slower, then the nonlinearity will occur sooner at lower $[Cl_2]$. To obtain the linear relationship, the $H_2O_2+O_3$ reaction must be faster than the $HO_2+O_3$ reaction, at least five times faster or at the order of $10^{-14}$ $cm^3/s$. There is no indication in the available literature that suggests this reaction rate constant to be greater than $k_1$. These results clearly indicate that the upper limit of the [Cl] is $2x10^{11}$ $cm^{-3}$ and $\sigma(H_2O_2) < 10\ \sigma(HO_2)$. For a typical experimental condition, the concentrations of reactants in the central tube, where $[CH_3OH] = 1.2x10^{14}$ $cm^{-3}$, $[O_2] = 1.3x10^{15}$ cm $cm^{-3}$, and $[Cl_2] = 5.5x10^{13}$ $cm^{-3}$, the kinetic model predicts that the signal due to $H_2O_2$ is only a few percent of $HO_2$. Thus, the analysis of the $HO_2+O_3$ reaction rate constant is not significantly interferred with by the secondary product of $H_2O_2$.

The predicted $[HO_2]$ originating from the injector is less than $1.9x10^{11}$ $cm^{-3}$ and the concentration of all other radical products formed in the central tube are negligible compared to $[HO_2]$, thus, the loss rate of $HO_2$ by other reactions is negligible when compared with the $HO_2+O_3$ reaction. Radical concentrations are small because, for the $[CH_3OH]$ and $[O_2]$ used in the experiment, all Cl atoms are readily converted to $HO_2$ within a msec and the probability for the formation of radicals involving Cl and its secondary products is thus small. The $O_3$ used is in the range $4x10^{14} \leq [O_3] \leq 3x10^{15}$ $cm^{-3}$, hence, the loss rate of $HO_2$ from $HO_2+HO_2 \rightarrow H_2O_2+O_2$ ($1.5x10^{-12}$ $cm^3/s$) is minimal when compared with $HO_2+O_3$. Analysis of our $HO_2+O_3$ reaction (Section D) at all $[O_3]$ was consistent with a psuedo-first order loss rate for $HO_2$.

## C. Flow Tube Parameters

The flow dynamics in a flow tube reactor are complicated by the change of pressure along the length of the tube and the change of transport velocity of radicals caused by diffusion.[18,19] The linear flow velocity in the central tube of 1 cm i.d. was about $10^3$ cm/s which is 4.84 times faster than that in main reactor tube of 2.2 cm i.d.. The pressure drop will be large if the linear flow velcoity, v, is fast and the tube radius, r, is small, that is, $(\Delta p/\ell) \propto (v/r^2)$ where $(\Delta p/\ell)$ is the pressure drop across the tube length. However, even if there is a pressure drop in the central tube and hence an $[HO_2]$ gradient, the initial $[HO_2]$ at the point entering the main reaction flow tube should be constant for a given experimental set-up. This assertion is supported by the evidence that in the central tube where $HO_2$ is formed, a 60% change in v does not disrupt the linear dependence of $[HO_2]$ on $[Cl_2]$ (Fig. 3). The pressure gradient in the main reactor (2.2 cm i.d. and 60 cm long) is small (about 0.05). No corrections were made for this gradient, because this does not introduce any serious problem as shown in the next section.

There is no apparent complication arising from back diffusion. When the $[Cl_2]$ was increased, the $[HO_2]$ proportionally increased. If the addition of $Cl_2$ or increased $HO_2$ production caused changes in the flow velocities of the gases or the transport velocity of the radical then the linearity would not hold.

As shown in Fig. 3, changing the linear flow velocity and addition of $O_3$ and the OH scavenger did not affect the linear dependence of $[HO_2]$ on $[Cl_2]$. This linearity held for different reaction distances. Such linearity again indicates a low $[HO_2]$ and the $[HO_2]$ is distributed uniformly in the tube. The partial pressure of the He carrier gas is at least a factor of seven greater than the sum of the partial pressures of the additive gases and at least four orders of magnitude greater than $[HO_2]$. Thus, the flow conditions and the gas pressures apparently constituted good mixing. This uniform distribution of $[HO_2]$ ensures that the reaction of $HO_2$ with $O_3$ was spatially uniform in the flow tube.

The above discussion concludes that (1) there was no substantial pressure gradient in the main reactor; (2) since the $[HO_2]$ was low (Section B), its transport velocity was the same as the carrier gas; and (3) the reactant gases were well mixed in the system. Thus, the experimental conditions were appropriate for studying the $HO_2+O_3$ reaction.

D. Reaction Rate Constant of $HO_2+O_3$

In the measurements of reaction rates, $[O_3]$ was in the $4.5\times10^{14}$ - $3x0\times10^{15}$ $cm^{-3}$ range which was much larger than the $[HO_2]$ in the reaction flow tube. With $[C_2F_3Cl]$ of about $3\times10^{15}$ $cm^{-3}$ or $C_3H_8$ of about $6\times10^{15}$ $cm^{-3}$, reaction (2) ($k_2$ = $6.5\times10^{-14}$ $cm^3/s$)[4] was negligible since it is much slower than the reaction rates of $OH+C_2F_3Cl$ ($6\times10^{-12}$ $cm^3/s$)[4] or $OH+C_3H_8$ ($1.1\times10^{-12}$ $cm^3/s$)[13] by about two-orders of magnitude. Thus, the decay of $HO_2$ due to reaction with $O_3$ can be represented by the psuedo-first-order approximation.

The psuedo-first order reaction rate, K, for a given $[O_3]$ is

$$K = - v \frac{d(\ln(I_f))}{dz}$$

where v is the linear flow velocity in the main reactor, z is the reaction distance from the tip of the 1 cm tube to the $HO_2$ detection point in the gas cell, and $I_f$ is proportional to $[HO_2]$. The bimolecular rate constant, $k_1$, is obtained from the slope of K versus $[O_3]$ since $K = k_1[O_3]$.

Sample first-order $HO_2$ decay plots, ($\ln(I_f)$ versus z) are shown in Figs. 4 and 5 with $C_2F_3Cl$ and $C_3H_8$ as the OH scavengers, respectively. For each experimental run, the movable $HO_2$ injector was moved 50 cm at 5-cm intervals. The z=0 points in Figs. 4 and 5 were set at about 6 cm from the $HO_2$ detection point. The reaction time between $HO_2+O_3$ was increased for each increase in distance. Each plot was linear for the range of $0 \leq [O_3] \leq 3\times10^{15}$ $cm^{-3}$ used in these experiments which indicate that (i) the OH product from reaction (2) was effectively removed by the scavengers, and (ii) $HO_2+HO_2$ reaction is negligible as indicated by the small decrease rate of $[HO_2]$ at $[O_3]=0$. This is consistent with predicted $[HO_2] \leq 1\times10^{11}$ molecule/$cm^3$. The experimental data is summarized in Table II.

The first-order rates of reaction (1) versus $[O_3]$ are shown in Figs. 6 and 7 for $C_2F_3Cl$ and $C_3H_8$ as OH scavengers, respectively. The vertical error bars represent one standard deviation which includes the uncertainties in the determination of v and the linear least square fit of $\ln(I_f)$ versus z (as in Figs. 4 and 5). The horizontal error bars represent the standard deviation in determining $[O_3]$. The lines are linear least squares fit. The bimolecular rate constants obtained from the slopes of Figs. 6 and 7 are $1.7\times10^{-15}$ and $2.0\times10^{-15}$ $cm^3/s$, respectively. A reasonable estimate of the precision is about

17% using a 95% confidence level from the errors: $k_1$ (±10%), K (±10%), $[O_3]$ (±5%), and v (±9%). Adding a systematic error of 10%, the experimental resultant error is 20%. The intercepts represent $HO_2$ loss to the walls of the reactor. The intercept of $K_o$ = 0.3 $s^{-1}$ in Fig. 6 and ∿ 0 in Fig. 7 are quite small, suggesting the apparent $HO_2$ loss due to the walls being quite small.

The reaction rate constants were also measured using a flow tube of 4.8 cm i.d. The results are shown in Fig. 8. With $C_2F_3Cl$ as the OH scavenger, the slope gave $k_1 = (1.5 \pm 0.4)\times10^{-15}$ $cm^3/s$, and with $C_3H_8$, $k_1 = (2.1 \pm 0.5)\times10^{-15}$ $cm^3/s$. The experimental uncertainties for the measurements with such large flow tube are relatively high. The flow velocity and the gas mixing in a large flow tube are more difficult to control than that of a small tube. Nevertheless, $k_1$ values obtained from the larger flow tube are in agreement with the small one.

## IV. CONCLUSION

The current $k_1$ value at room temperature (298 K) determined from Figs. 6 and 7 is $(1.9\pm0.3)\times10^{-15}$ $cm^3/s$, where error limit represents 95% confidence limit. This is in good agreement with the absolute rate constant of $2\times10^{-15}$ $cm^3/s$ measured by the LMR method[4] and the value of $1.7\times10^{-15}$ $cm^3/s$ indirectly measured by photolysis of dry $H_2$-$O_2$-$O_3$ mixtures.[9] In the indirect measurements , $k_1$ was determined from relative rates with the $2HO_2 \rightarrow H_2O_2 + O_2$ reaction as the competing reaction. The lower $k_1$ values derived from relative rates from early photolysis results[7,8] were reconciled to the later detemination[9] by taking into account that in the presence of water vapor the self-reaction of $HO_2$ increases.

The Arrhenius parameters in the temperature range 230-365 K indicate a low value for the A-factor ($1.3 \times 10^{-14}$ $cm^{-3}/s$) for a simple atom-transfer mechanism.[4] The reaction rate constants at different temperatures will be further measured in our laboratory to verify the Arrhenius parameters. The reaction rate constants at various temperature are needed in the stratospheric modeling, since temperature changes with height in the stratosphere.

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Table I

| Number | Reactions | Rate Constants ($cm^3$/molec. - s) |
|---|---|---|
| 1 | $CH_3OH + Cl \rightarrow CH_2OH + HCl$ | 6.30 E-11[a] |
| 2 | $CH_2OH + O_2 \rightarrow CH_2O + HO_2$ | 1.40 E-12 |
| 3 | $CH_2OH + Cl \rightarrow CH_2O + HCl$ | 3.00 E-10[b] |
| 4 | $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ | 1.50 E-12 |
| 5 | $Cl + H_2O_2 \rightarrow HCl + HO_2$ | 4.10 E-13 |
| 6 | $Cl + HO_2 \rightarrow HCl + O_2$ | 3.20 E-11 |
| 7 | $Cl + HO_2 \rightarrow ClO + OH$ | 9.10 E-12 |
| 8 | $OH + HO_2 \rightarrow H_2O + O_2$ | 7.00 E-11 |
| 9 | $OH + H_2O_2 \rightarrow H_2O + HO_2$ | 1.70 E-12 |
| 10 | $ClO + HO_2 \rightarrow HOCl + O_2$ | 5.00 E-12 |
| 11 | $OH + HCl \rightarrow H_2O + Cl$ | 6.60 E-13 |
| 12 | $ClO + OH \rightarrow Cl + HO_2$ | 1.20 E-11 |
| 13 | $ClO + ClO \rightarrow Cl + CLO_2$ | 1.60 E-14 |
| 14 | $ClO + ClO \rightarrow Cl_2 + O_2$ | 7.80 E-15 |
| 15 | $OH + HOCl \rightarrow H_2O + ClO$ | 1.80 E-12 |
| 16 | $OH + CH_3OH \rightarrow H_2O + CH_2OH$ | 1.00 E-12 |
| 17 | $Cl + CH_2O \rightarrow HCl + HCO$ | 7.30 E-11 |
| 18 | $HCO + O_2 \rightarrow CO + HO_2$ | 5.50 E-12 |
| 19 | $Cl + HOCl \rightarrow Cl_2 + OH$ | 1.90 E-12 |
| 20 | $Cl + O_2 \rightarrow ClO_2$ | 4.90 E-17[c] |
| 21 | $Cl + ClO_2 \rightarrow Cl_2 + O_2$ | 1.40 E-10 |
| 22 | $Cl + ClO_2 \rightarrow ClO + ClO$ | 8.00 E-12 |
| 23 | $OH + CH_2O \rightarrow H_2O + HCO$ | 1.00 E-11 |
| 24 | $HO_2 + CH_2O \rightarrow$ Adduct | 4.50 E-14[d] |
| 25 | $HO_2$ + wall $\rightarrow$ products | $k_w(HO_2)$[e] |
| 26 | $CH_2OH$ + wall $\rightarrow$ products | $k_w(CH_2OH)$ |
| 27 | Cl + wall $\rightarrow$ products | $k_w(Cl)$ |

(continued) Table I

[a]All reactions unless otherwise stated are similar to those considered in Reference 15 and the rate constants compared with Reference 16. The rate constant 6.30 E-11 reads $6.30 \times 10^{-11}$.

[b]Added to the list of reactions, while a negligible step in comparison to the $CH_2OH+O_2$ reaction because of our high $[O_2]$, this step was necessary in the simulation of the data in Reference 6. The gas kinetic value was assumed for the rate constant.

[c]$Cl + O_2 + M \rightarrow ClO_2 + M$ with M principally He at 1.5 torr.

[d]Added to list for completion.

[e]Wall lost rates. See text.

Table II

Summary of Experimental Conditions*

| Run | $[O_3]$ ($10^{15}$ $cm^{-3}$) | $[Cl_2]$ ($10^{13}$ $cm^{-3}$) | $[CH_3OH]$ ($10^{14}$ $cm^{-3}$) | $[O_2]$ ($10^{15}$ $cm^{-3}$) | $[C_2F_3Cl]$ ($10^{15}$ $cm^{-3}$) | p** (torr) | v (cm/s) | $d(\ln I_f)/dz$ ($10^{-2}$ $cm^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| 1 | 0 | 5.70 | 1.11 | 1.43 | 3.34 | 1.633 | 203 | 0 |
| 2 | 0.451 | 5.64 | 1.13 | 1.43 | 3.69 | 1.699 | 216 | 0.35 |
| 3 | 0.830 | 5.57 | 1.13 | 1.43 | 3.60 | 1.687 | 173 | 1.02 |
| 4 | 1.16 | 5.57 | 1.23 | 1.46 | 3.53 | 1.651 | 165 | 1.52 |
| 5 | 1.34 | 5.51 | 1.12 | 1.39 | 3.50 | 1.690 | 183 | 1.18 |
| 6 | 1.73 | 5.24 | 1.10 | 1.43 | 3.56 | 1.664 | 190 | 1.85 |
| 7 | 2.13 | 5.51 | 1.13 | 1.30 | 3.50 | 1.834 | 190 | 2.20 |
| 8 | 2.43 | 3.11 | 1.10 | 1.36 | 3.43 | 1.717 | 197 | 2.34 |
| 9 | 3.00 | 4.54 | 1.44 | 1.04 | 3.18 | 1.714 | 235 | 2.54 |
| | | | | | $[C_3H_8]$ ($10^{15}$ $cm^{-3}$) | | | |
| 10 | 0 | 5.90 | 1.21 | 1.30 | 6.40 | 1.700 | 220 | 0 |
| 11 | 0.642 | 5.51 | 1.20 | 1.33 | 4.86 | 1.820 | 197 | 0.66 |
| 12 | 1.25 | 5.44 | 1.31 | 1.26 | 5.35 | 1.882 | 198 | 1.11 |
| 13 | 1.52 | 6.80 | 1.27 | 1.39 | 5.51 | 1.916 | 189 | 1.54 |
| 14 | 1.99 | 6.03 | 1.22 | 1.52 | 6.61 | 1.890 | 171 | 2.20 |
| 15 | 2.25 | 6.03 | 1.18 | 1.30 | 6.22 | 1.960 | 172 | 2.50 |
| 16 | 2.61 | 6.22 | 1.26 | 1.33 | 6.42 | 2.051 | 175 | 3.02 |

*tube radius is 2.2 cm i.d.

**total cell pressure

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## FIGURE CAPTIONS

Figure 1 Schematic diagram of experimental apparatus.

Figure 2 Emission intensity versus $[CH_3OH]$ with $[Cl_2]$ = $5.5\times10^{13}$ $cm^{-3}$ and $[O_2] = 1.3\times10^{15}$ $cm^{-3}$, for a reaction time of 65 msec (■) and 45 msec (●) in the central tube. See text for discussion.

Figure 3 $I_f$ versus $[Cl_2]$. Concentrations in $cm^{-3}$: $[O_3] = 0$, $[CH_3OH] = 1.1\times10^{14}$. $[O_2] = 1.3\times10^{15}$, v = 292 cm/s (●); $[O_3] = 2.0\times10^{15}$, $[CH_3OH] = 1.2\times10^{14}$, $[O_2]$ = $1.3\times10^{15}$, $[C_3H_8] = 6.4\times10^{15}$, v = 183 cm/s (■), for z = 20 cm. (a) - (f) are the modeling curves (see text).

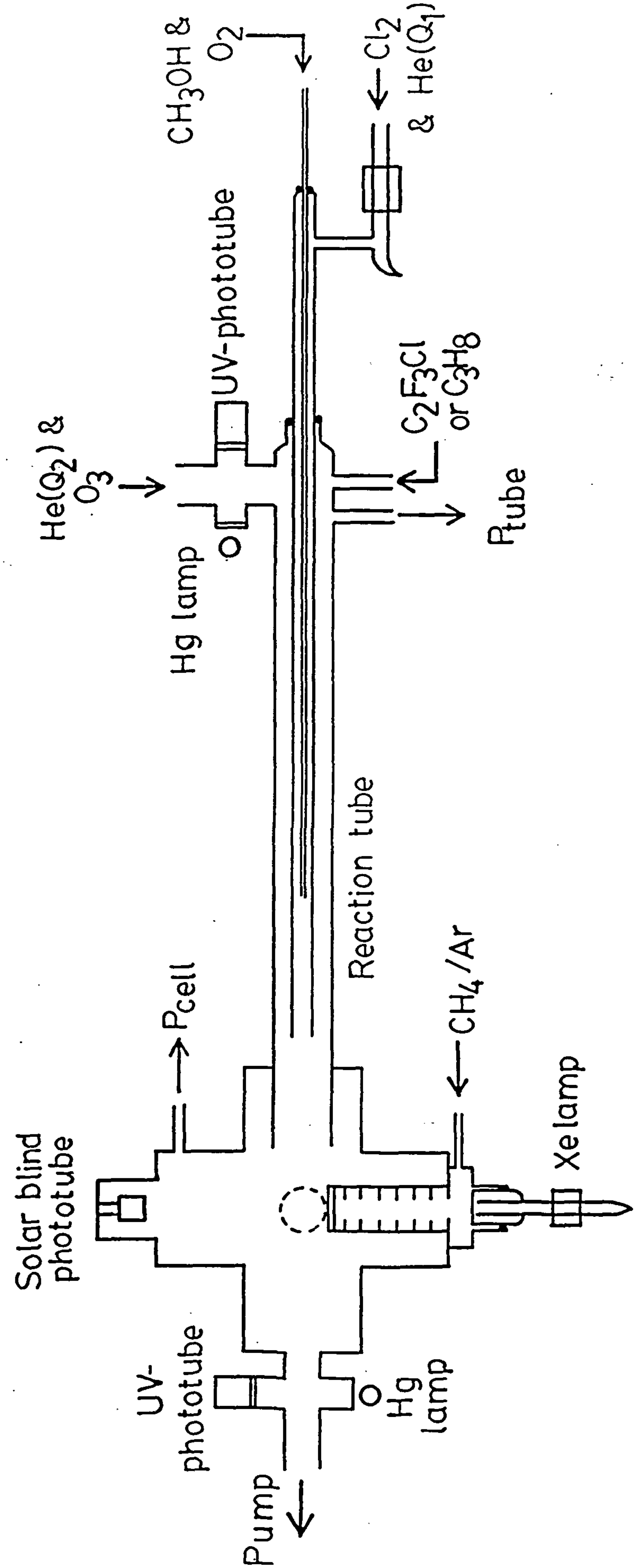
Figure 4 First order decay plots with $C_2F_3Cl$ as OH scavenger. See Table II for experimental condition: (a) run 1, $[O_3] = 0$; (b) run 3, $[O_3] = 8.30\times10^{14}$ $cm^{-3}$; (c) run 7, $[O_3] = 2.13\times10^{15}$ $cm^{-3}$.

Figure 5 First order decay plots with $C_3H_8$ as the OH scavenger. See Table II for experimental condition (a) run 11, $[O_3] = 6.42\times10^{14}$ $cm^{-3}$, (b) run 12, $[O_3] = 1.25\times10^{15}$ $cm^{-3}$, and (c) run 15, $[O_3] = 2.25\times10^{15}$ $cm^{-3}$.

Figure 6 K versus $[O_3]$ with $C_2F_3Cl$ as the OH scavenger. The tube radius was 2.2 cm i.d. The slope is $k_1$ = $1.7\times10^{-15}$ $cm^3/s$.

Figure 7 Same as Figure 6 but with $C_3H_8$ as the OH scavanger, $k_1 = 2.0\times10^{-15}$ $cm^3/s$.

Figure 8 K versus $[O_3]$. The tube radius was 4.8 cm i.d. The slope is $k_1$. Plot (a) with $C_2F_3Cl$ as the OH scavenger, $k_1 = (1.5 \pm 0.4)\times10^{-15}$ $cm^3/s$ and plot (b) with $C_3H_8$, $k_1 = (2.1 \pm 0.5)\times10^{-15}$ $cm^3/s$.



$CH_3OH$ & $O_2$
$Cl_2$ & $He(Q_1)$
UV-phototube
$He(Q_2)$ & $O_3$
$C_2F_3Cl$ or $C_3H_8$
$R_{tube}$
Hg lamp
Reaction tube
$P_{cell}$
$CH_4$/Ar
Solar blind phototube
Xe lamp
UV-phototube
Hg lamp
Pump


Fig. 1

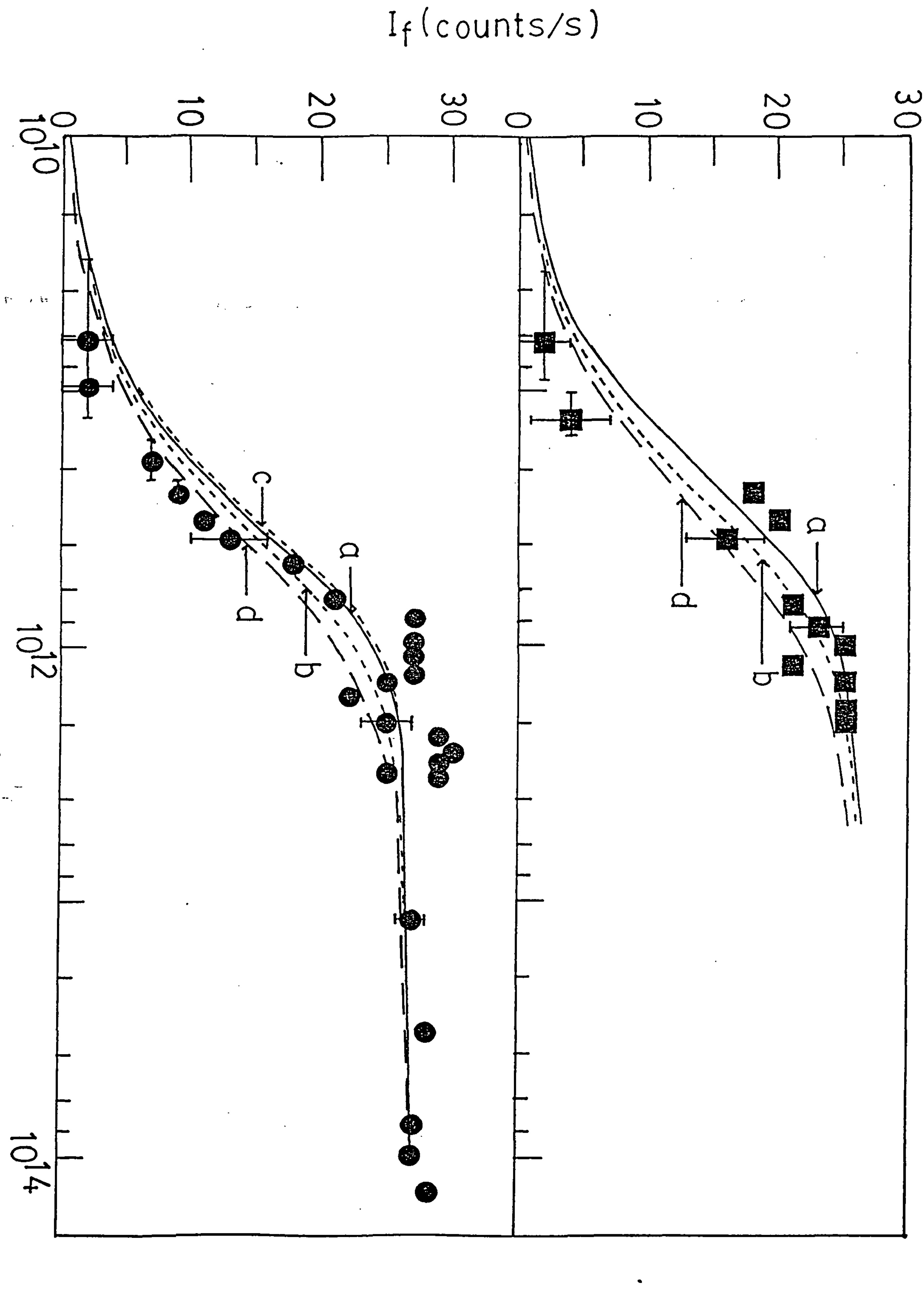
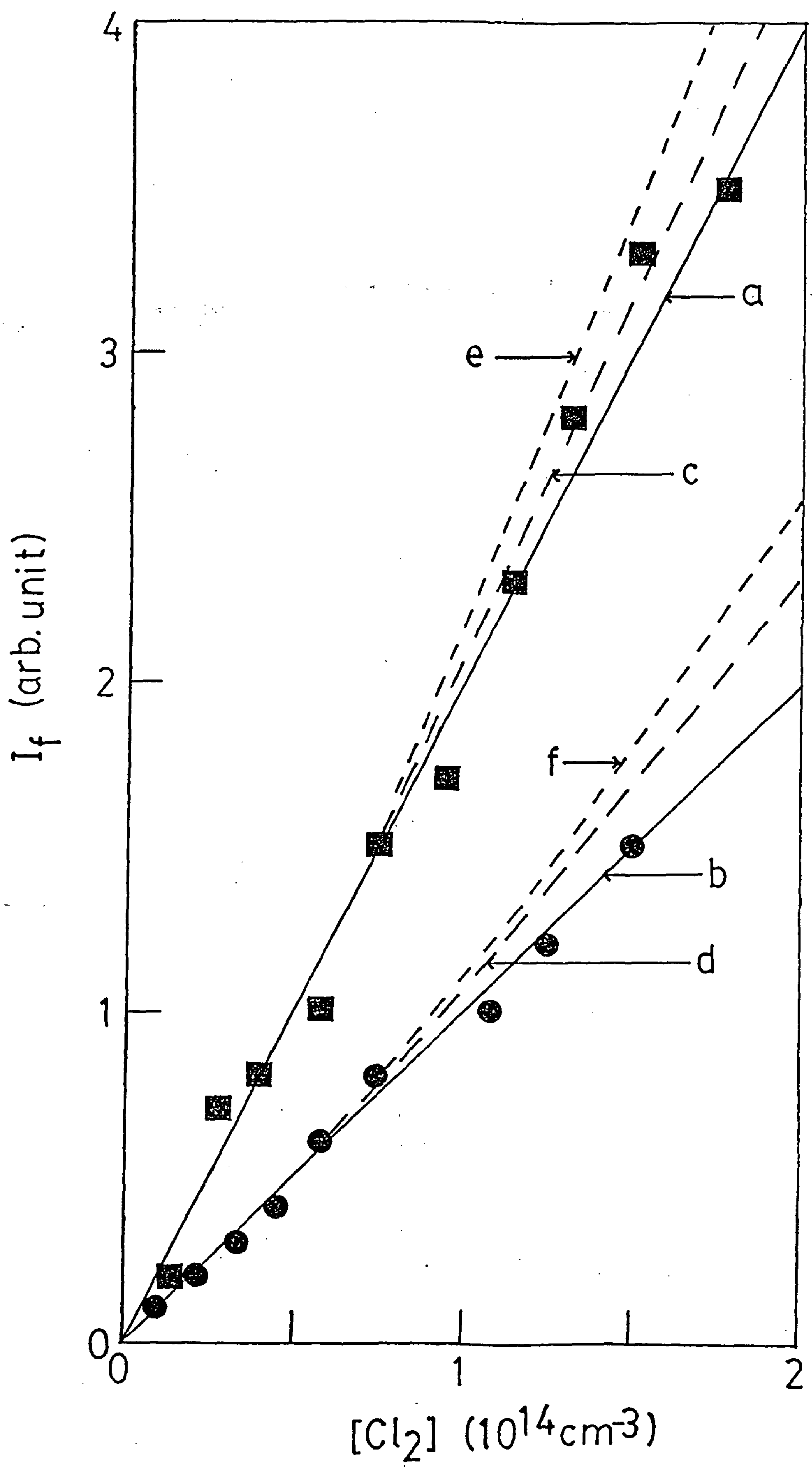
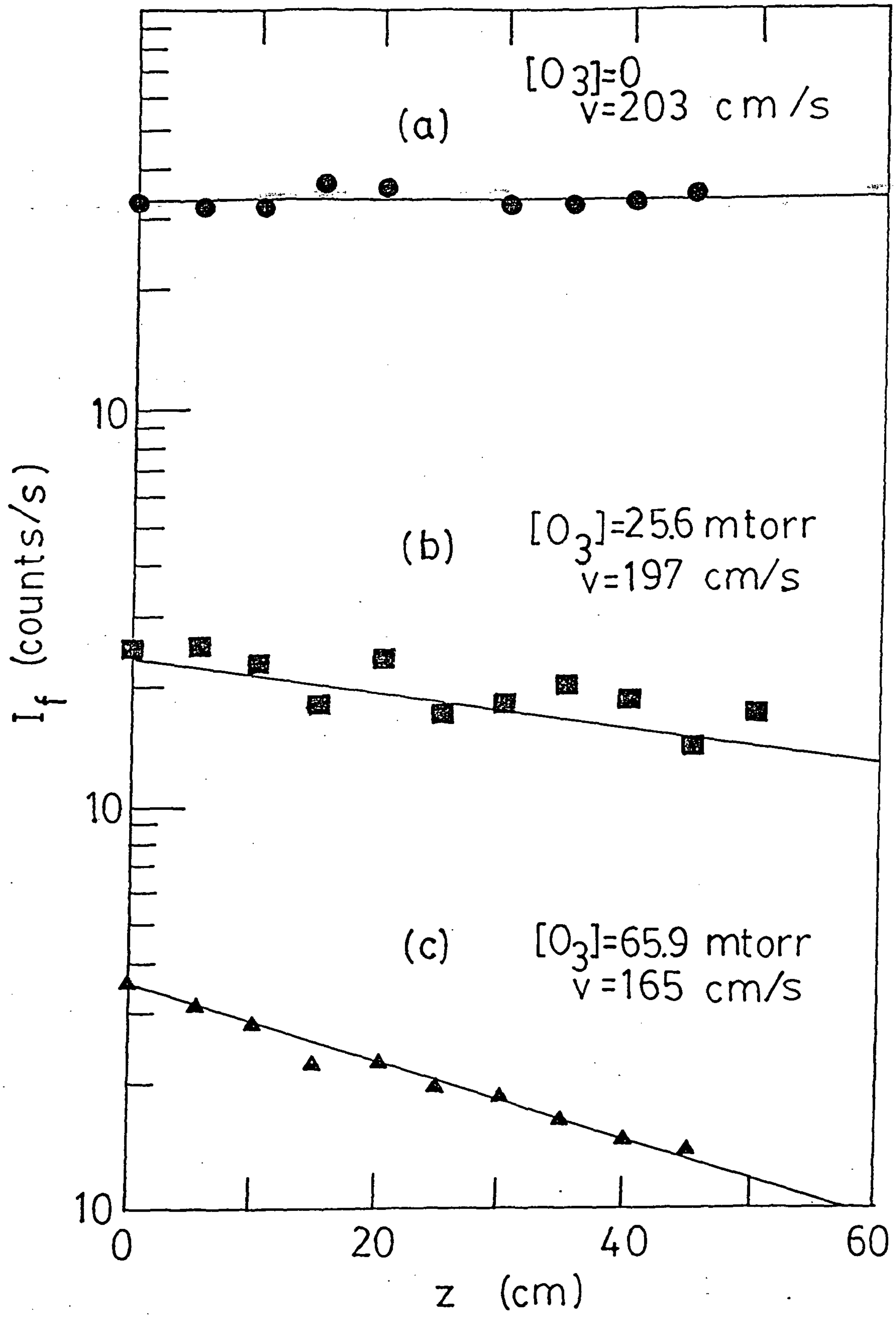



Fig. 2

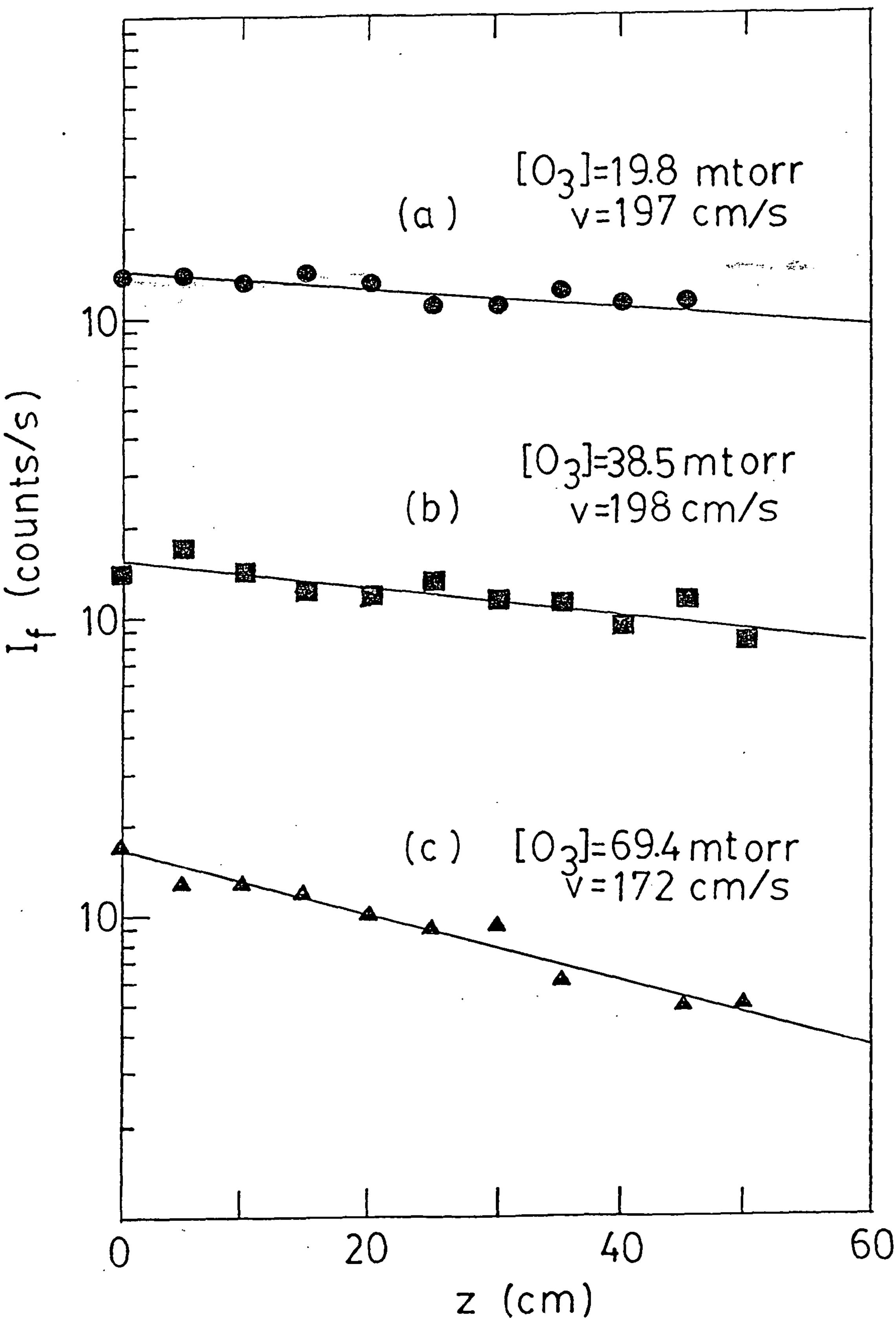


4
3
2
1
0
0
1
2
$I_f$ (arb. unit)
$[Cl_2]$ ($10^{14}$cm$^{-3}$)
a
b
c
d
e
f



[O3]=0
v=203 cm/s
(a)
10
[O3]=25.6 mtorr
v=197 cm/s
(b)
10
[O3]=65.9 mtorr
v=165 cm/s
(c)
10
I_f (counts/s)
0
20
40
60
z (cm)


Fig. 4



[O3]=19.8 mtorr
(a) v=197 cm/s
[O3]=38.5 mtorr
(b) v=198 cm/s
(c) [O3]=69.4 mtorr
v=172 cm/s
10
10
10
If (counts/s)
0
20
40
60
z (cm)


Fig. 5

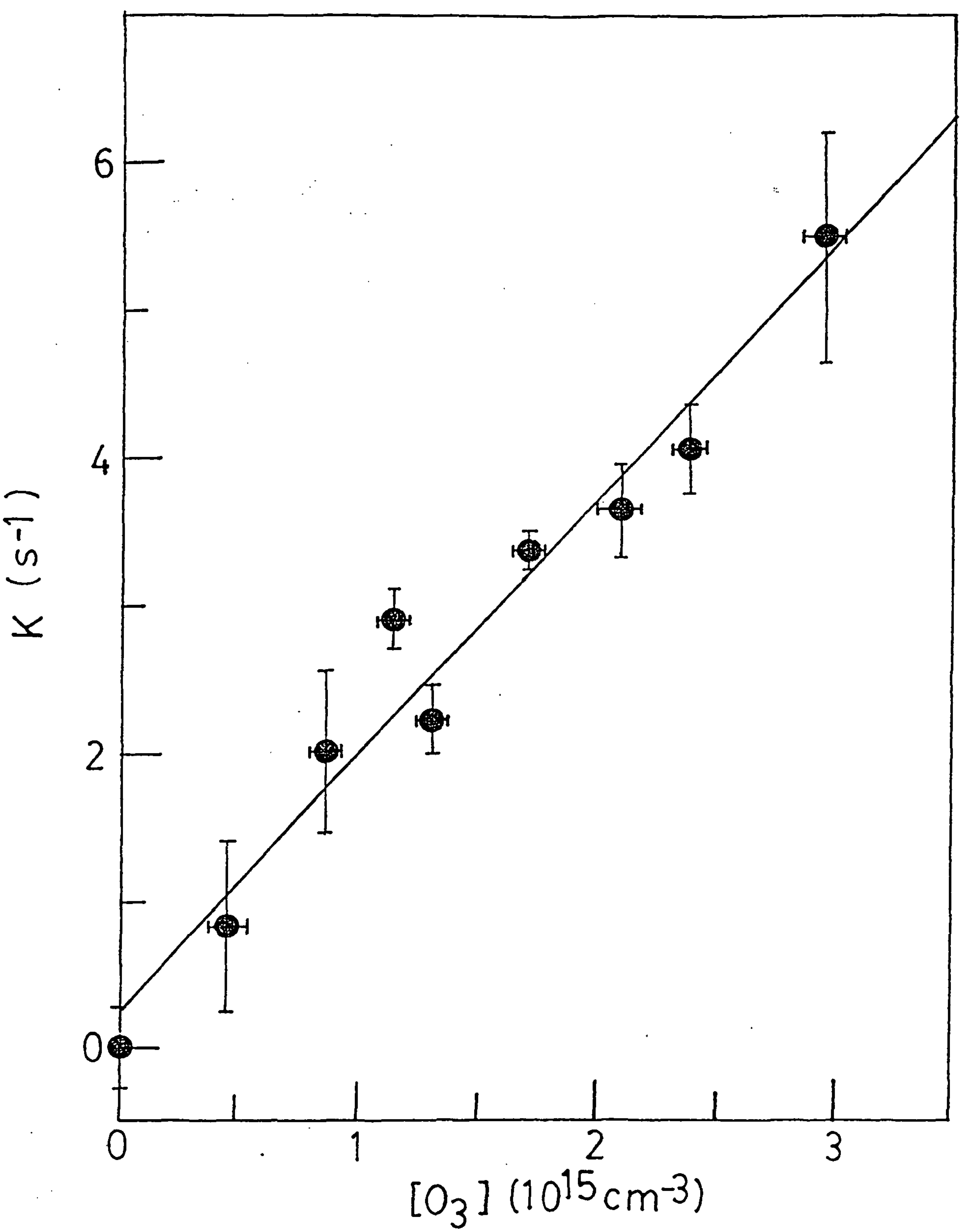



Fig. 6

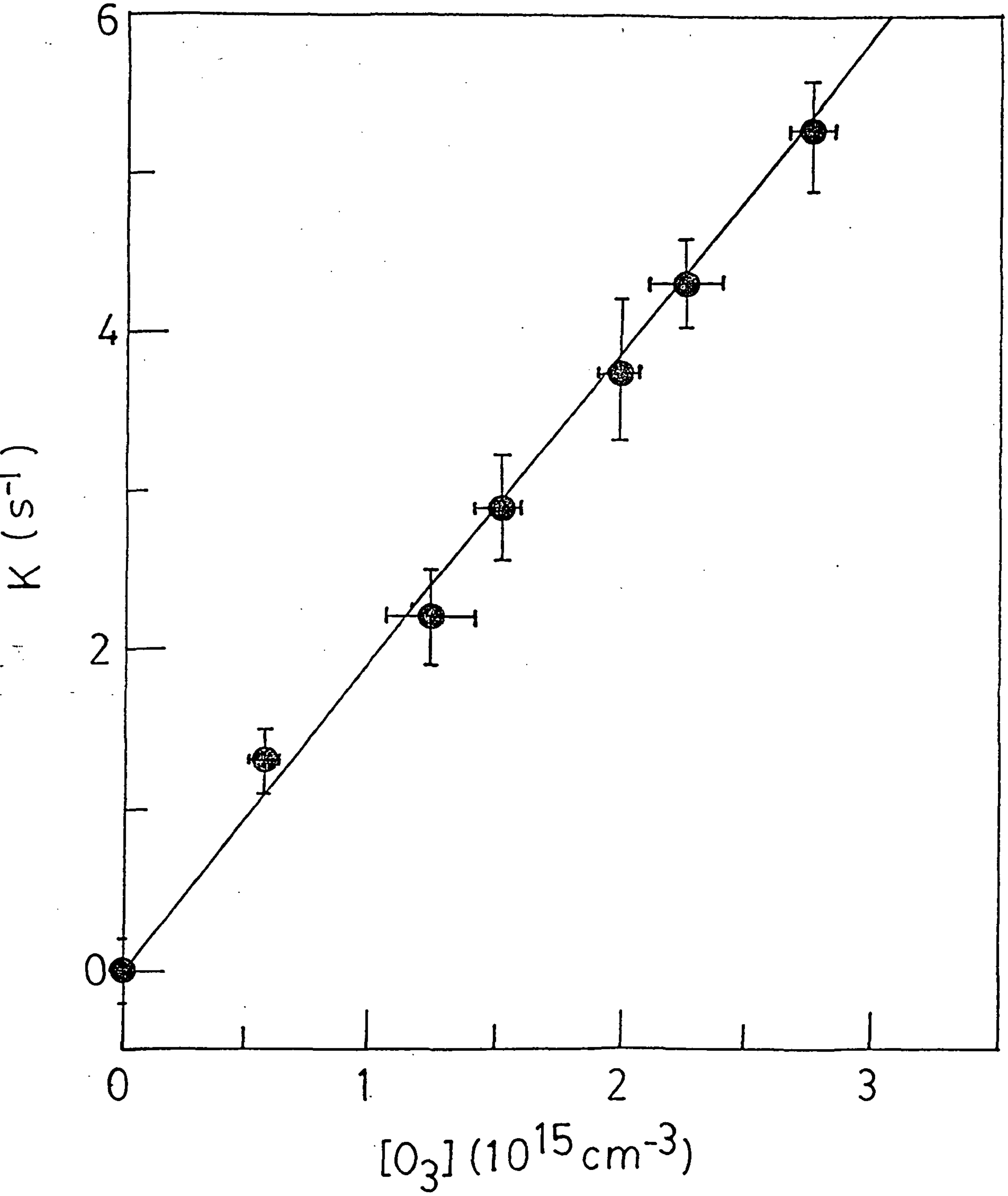



Fig. 7

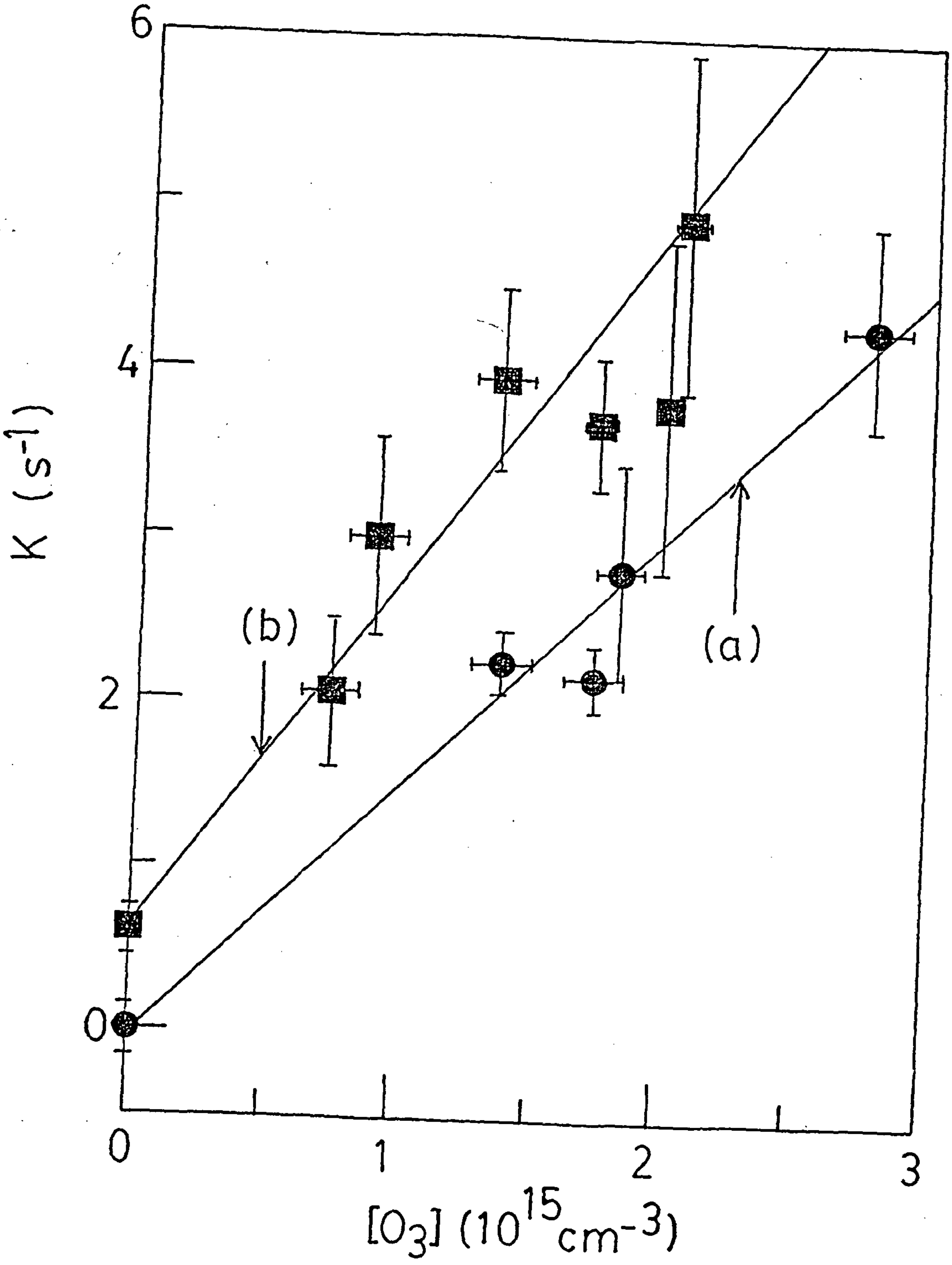



Fig. 8