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Absolute Rate of the Reaction of Hydrogen Atoms With Ozone From 219-360K

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Abstract

Absolute rate constants for the reaction of atomic hydrogen with ozone were obtained over the temperature range 219-360 K by the flash photolysis-resonance fluorescence (FP-RF) technique. The results can be expressed in Arrhenius form by $k = (1.33 \pm 0.32) \times 10^{-10} \exp(-449 \pm 58/T)$ cm^3 molecule^{-1} s^{-1} (two standard deviations). The present work is compared to two previous determinations and is theoretically discussed.

Introduction

The possibility of anthropogenic modification of the earth's ozone layer[1] has prompted considerable research into the chemical and physical processes which occur in the upper atmosphere. One dimensional models have combined transport, solar photochemical, and chemical kinetic concepts[2,3] in an attempt to understand both the stratospheric and mesospheric regions of the atmsphere. These models have considered the chemical reactions of various atomic, radical, and molecular species with ozone. One such mesospheric reaction is

$$H + O_3 \rightarrow OH + O_2 \qquad (1)$$

Reaction (1), which is 77 kcal/mole exothermic, was first proposed as the source of the presumed OH overtone bands (Meinel bands)[4] in order to explain some features in the night airglow spectrum[5]. Subsequent laboratory studies have shown that vibrationally and rotationally excited $OH(^2\pi)$ up to $v' = 9$ is produced in reaction (1). There have been many spectroscopic studies of the resulting overtone bands[6]. Reaction (1) as the source of vibrationally hot OH has also been used for kinetic studies of OH $(v' \leq 9)$ reactions[7].

Subsequent airglow studies[8] confirm that reaction (1) is occurring in the mesosphere where $T \sim 200$ K. From model calculations which include the rate constant for reaction (1), the mesospheric hydrogen atom density can be estimated[8b,9].

Reaction (1) and the resulting hot hydroxyl radicals have been additionally studied by the "arrested relaxation" technique[10] in order

to ascertain the energy partitioning which occurs in the reaction. These studies ultimately relate to understanding the potential energy surface for the reaction.

Thus, there has been a great deal of interest in reaction (1), but, to date, there have been only two determinations of the reaction rate constant[11,12]. Both studies have utilized the discharge-flow technique. One is at room temperature only[11] while the other reports rate constant measurements at three temperatures: 298, 479, and 638 K[12]. Because of the documented continuing interest in reaction (1) and the paucity of data particularly at low temperatures, we have undertaken the present study. Here we report rate constant measurements at five temperatures from 219-360 K.

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Experimental

The technique employed in the present study is flash photolysis-resonance fluorescence (FP-RF). The apparatus and general techniques have been described previously[13], and the application to hydrogen atom with molecule reactions has also been reported[14]. Thus, only those procedures specific to the present study will be discussed.

H atoms ($\sim 10^{11}$ atoms cm^{-3}) were generally produced by the flash photolysis of H_2O or HCN at $\lambda > 110$ nm (LiF cut off). However, some comparative experiments were performed at 300 K with a suprasil filter ($\lambda > 165$ nm) in order to test for the possible effects of higher energy initiating radiation. The results were identical to those obtained with LiF flash source filtration. Lyman α resonance radiation was obtained from a 2450 MHz microwave driven discharge lamp in 1 Torr of helium, and the scattered photons were observed at right angles through 5 cm of flowing dry air at atmospheric pressure.

Ozone was generated by an electrical discharge in O_2, collected on silica gel, and was purified as described previously[15]. The present apparatus has been modified so that $[O_3]$ could be determined photometrically by absorption at 253.7 nm. The absorption coefficient at this wavelength is well known[16]. The details of this modification have also been recently presented[15]. The optical path length is 154.5 cm, and the measured transmittances for $[O_3]$ levels necessary in the present study were $0.83 \leq T \leq 0.96$. Due to signal to noise errors and their effect on absolute accuracies at these high transmittances, the freshly prepared

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experimental ternary mixtures of O_3, H_2O or HCN, and Ar with a constant

mole fraction of O_3 (X_{O_3}) were typically analyzed at higher pressures

than usable (i.e., higher $[O_3]$ than usable) in order to determine X_{O_3}

accurately. The ternary mixtures were then analyzed for long term

$[O_3]$ stability and were found to be stable for periods of hours. $[O_3]$

exiting from the cell was then measured continuously as rate data

were taken at the higher transmittances, and the derived X_{O_3} values

at the experimental pressures were always in agreement with the

high pressure determination within experimental error. However, in

the present report we elected to use the $[O_3]$ values as obtained from

continuous monitoring at the experimental conditions rather than scaling

the accurate X_{O_3} value down to the experimental pressures. Thus, the

$[O_3]$ values presented reflect the signal to noise errors in the high

transmittance values and are inherently only accurate to $\sim \pm$ 5%. This

introduces a definite systematic error into the rate constant measure-

ments of reaction (1).

In preliminary experiments, CH_4 was used as the source molecule

for H atoms. CH_4, O_3, and Ar ternary mixtures were stable; however,

the observed decay plots were not linear and the extent of non-linearity

depended on the CH_4 concentration. The effect indicated that some un-

known H atom reformation process was occurring at longer times during

the decay. Since the effect is dependent on $[CH_4]$ and is therefore

dependent on the extent of photolysis, we believe it is associated

with the ozone oxidation of methyl radicals to yield H atoms. One such

exothermic overall process is

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$$CH_3 + O_3 \rightarrow H_2CO + H + O_2 \quad . \tag{2}$$
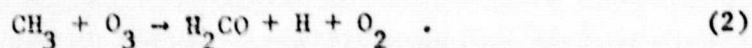
We note that if reaction (2) can occur, possibly through the intermediate formation of vibrationally hot methoxy radicals, it would be complicating for initially equal H atom and CH_3 concentrations in the way that is observed.

Similar experiments with H_2O as the source molecule showed no such complications. Also no dependence on flash energy (i.e., initial [H]) was observed on the strictly linear first order decay constants. Additionally, in order to confirm that H_2O and/or its photolysis products were not complicating, a complete determination of k_1 with HCN as the source molecule was carried out at room temperature. Experiments were then carried out at the other experimental temperatures with H_2O as the source molecule. We were limited to 219 K as the lowest temperature by the saturation vapor pressure of H_2O and to 360 K as the highest temperature because of the thermal decomposition of ozone.

Regardless of which source molecule was used, the diffusional correction term with no ozone was routinely determined under exactly the same conditions as the reaction experiments. The correction never exceeded 20% and for most of the reported results it was 2-10% of the observed decay constant.

Argon (Matheson, 99.9995%) and helium (Airco, 99.9999%) were used without further purification. Ozone was synthesized daily from O_2 (Airco, 99.5%) and was thoroughly outgassed at 250 K in a silica gel trap before usage. Laboratory distilled water was further purified

by bulb-to-bulb vacuum disillation at 260 K, the middle third being retained. HCN was obtained as a 1.02% mixture in Ar (99.998%) from Precision Gas Products, Inc.

Results

The present results were obtained under pseudo-first-order conditions with $[O_3] \gg [H]$. The decay of $[H]$ can then be represented by

$$\ell n\, [H] = -k_{observed}\, t + \ell n\, [H]_o \tag{3}$$

where $k_{observed}$ is given by

$$k_{observed} = k_1\, [O_3] + k_d . \tag{4}$$

k_1 is the reaction rate constant for reaction (1) and k_d represents the first order rate constant due to diffusional loss out of the reaction viewing zone. $k_{observed}$ was obtained by linear least squares methods from the exponential decay of the fluorescent photon count which is proportional to $[H]_t$. The correctness of Eq. (3) is seen in typical decay plots in Fig. 1. $k_{observed}$ in the absence of reactant ozone gives the diffusional loss constant, k_d, unambiguously. Then k_1 is obtained according to Eq. (4) by linear least squares methods from the reactant experiments with a knowledge of k_d and $[O_3]$.

The results at room temperature are shown in Table I for experiments in which H_2O and HCN were respectively used as source molecules for H atoms. The values obtained are in excellent agreement and indicate the high probability of no secondary reaction complications. Results with H_2O as the source molecule at four additional temperatures ranging from 219-360 K are given in Table II and are plotted in Fig. 2. A linear least squares treatment yields the Arrhenius expression $k_1 = (1.33 \pm 0.32) \times 10^{-10}\, exp(-449 \pm 58/T)\, cm^3\, molecule^{-1}\, s^{-1}$. The indicated errors are two standard deviations in order to account the lack of accuracy in $[O_3]$ ($\sim \pm 5\%$).

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Discussion

The present results are compared to those of Phillips and Schiff[11] and Clyne and Monkhouse[12] in Fig. 2. At 298 K these authors report values of $(2.6 \pm 0.5) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} and $(1.76 \pm 0.21) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, respectively.

The present result at 300 K of $(2.9 \pm 0.2) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} is in good agreement with that of Phillips and Schiff,[11] but this agreement may be fortuitous in view of the fact that these authors used second order kinetic conditions and therefore required both accurate and absolute knowledge of [H] and [O_3], and used only 1-4 ms of dwell time for their kinetic runs. As pointed out by Clyne and Monkhouse,[12] an inaccurate knowledge of [H] and [O_3] can lead to large systematic errors; however, we would suggest that their method of [H] analysis is accurate and has been used elsewhere.[17] On the other hand, mixing can take ~ 2 mx for single reactant inlet flow reactors operating at low pressure.[18] To be sure, these authors used a multi-inlet probe which should accentuate faster mixing. However, we agree with Clyne and Monkhouse[12] who point out that the extent of reaction with distance was sufficiently large that the system may not have been isothermal.

The room temperature comparison of the present result with that of Clyne and Monkhouse[12] shows the present value to be higher by about 60%. In fact, the present results are uniformly higher at all temperatures as can be seen by comparison of respective Arrhenius expressions for reaction (1). $k_1 = (9.89 \pm 2.62) \times 10^{-11} \exp(-516 \pm 60/T)$ cm^3 $molecule^{-1}$ s^{-1} (two standard deviations) is reported by Clyne and Monhouse whereas the present value is $k_1 = (1.33 \pm 0.32) \times 10^{-10}$

$\exp(-449 \pm 58/T) \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (two standard deviations). Both expressions are plotted in Fig. 2. We note that the quoted expression of Clyne and Monkhouse[12] does not agree with their Fig. 6(b). Fig. 6 (b) was drawn from a preliminary analysis, and these authors prefer their quoted Arrhenius expression as the appropriate representation of their data[19]. Though there is agreement within combined errors in the energy and A factors, the discrepancy arises from a combination of both terms and is significant at 200 K where the present result $(1.41 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ would be 2.1 times larger than that from Clyne and Monkhouse.

Atomic hydrogen densities in the mesosphere ($\sim 10^7$ atoms cm^{-3}) have been inferred from airglow measurements of both $OH(^2\pi, v' \leq 9)$[8] and $O_2(b^1\Sigma_g)$ emissions[9]. The conclusions are dependent on an accurate knowledge of k_1 at mesospheric temperatures (~ 200 K). Noxon[9] used the temperature invariant value of $k_1 = 2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ whereas Evans and Llewellyn[8b] used the value preferred by Nicolet[20], $k_1 = 1.5 \times 10^{-12} T^{1/2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ($2.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 200 K). Since the present value extrapolated to 200 K is 50-100% smaller than used in these calculations, the predicted mesospheric hydrogen atom densities would be somewhat larger.

Since reaction (1) produces vibrationally excited OH radicals it has been previously used for spectroscopic[6], kinetic[7], and dynamical experiments[10]. Of particular interest is the internal energy distribution of the initially produced radicals and what fraction of the available energy (77 kcal/mole) goes into vibrational degrees of freedom of the products. The "arrested relaxation" experiments of Polanyi and Sloan[10] indicate that nearly all of the energy channels into the OH fragment

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with 90% and 3% in vibration and rotation, respectively. The remaining 7% apparently channels into translation and internal energy of O_2, the other fragment.

By analogy with theoretical dynamical calculations[21], the observations led these workers[10] to suggest that the potential surface for the reaction was attractive; i.e., the energy was released before the turning point was attained. Furthermore, the absence of substantial release into rotation suggested a narrow range of impact parameters with little deviation from collinear H-O-O. Collinear approach is enhanced even more if the activation energy (E_a = 892 $\pm$ 115 cal/mole measured here) can be associated with a barrier on the surface[21]. Thus, the observations suggest the necessity of preferred orientations and the possibility of elastic collisions particularly in a thermalized system with a distribution of relative velocities and angular approach.

If the Lennard-Jones collision rate constant, calculated as Z_{LJ} = $\sigma_{LJ}^2 \, \Omega^*(2,2) \, (8\pi kT/\mu)^{1/2}$[22], is taken as a measure of the total number of encounters, then we find $Z_{LJ} \simeq 9 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for the temperature range 219-360 K. (σ,ϵ/k) values for H[17] and O_3[22] were taken as (1.67,217) and (4.2,200), respectively. The experimental A factor, 1.33×10^{-10} cm^3 molecule^{-1} s^{-1}, is about 15% of Z_{LJ}. Though there is some ambiguity in the choice of Lennard-Jones parameters, quite unreasonable values would have to be chosen to duplicate the experimental A factor. Thus, there may be a steric factor which is less than unity for the present reaction. We further note that this may be due to the aforementioned suggestion of preferred orientations.

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22) $\sigma_{LJ} = (\sigma_H + \sigma_{O_3})/2$, $\epsilon_{LJ} = (\epsilon_H \epsilon_{O_3})^{1/2}$ and $T^* = kT/\epsilon_{LJ}$. $(\sigma, \epsilon/k)$ for O_3 is assumed to be similar to other triatomics. $\Omega^*(2,2)(T^*)$ integrals and $(\sigma, \epsilon/k)$ values for triatomics are from tabulations in J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids", Wiley, New York, 1964.

TABLE I. Rate Data for H + O_3 at 300 K

O_3 mTorr	H_2O mTorr	Ar Torr	F.E.[b] J	No. of Expts.	k_1[a] $10^{-11} cm^3 molecule^{-1} s^{-1}$
2.6	75	10	56	1	3.1_0
0.7	75	10	127,144	2	$2.9_4 \pm 0.1_6$
0.6	75	10	56-182	4	$3.2_3 \pm 0.2_6$
1.4	150	20	56-182	5	$2.6_5 \pm 0.1_8$
1.2	150	20	20-182	4	$2.7_0 \pm 0.1_2$
1.8	225	30	20-182	4	$2.8_9 \pm 0.0_9$
2.4	300	40	20-182	4	$2.8_4 \pm 0.0_7$
2.8	300	40	20-127	3	$2.8_6 \pm 0.0_4$
				27	$2.8_7 \pm 0.2_3$
	HCN mTorr				
1.8	115	30	127	1	3.0_7
1.4	115	30	110-225	3	$2.9_5 \pm 0.1_3$
2.4	153	40	127,144	2	$2.9_4 \pm 0.1_8$
1.8	153	40	110-182	3	$2.6_3 \pm 0.0_6$
2.1	191	50	110-182	3	$2.7_1 \pm 0.1_9$
				12	$2.8_1 \pm 0.1_9$
		Average at 300K		39	$2.8_5 \pm 0.2_2$

a- Error limit in k_1 is one standard deviation.

b- Flash energy in Joules.

$\dfrac{T}{K}$	$\dfrac{O_3}{mTorr}$	$\dfrac{H_2O}{mTorr}$	$\dfrac{Ar}{Torr}$	$\dfrac{F.E.^b}{J}$	No. of Expts.	$\dfrac{k_1{}^a}{10^{-11}\ cm^3\ molecule^{-1}s^{-1}}$
219	1.1	15	20	56,163	4	$1.8_4 \pm 0.0_8$
	1.6	23	30	56,81	4	$1.5_2 \pm 0.1_0$
	2.1	30	40	56,81	4	$1.6_8 \pm 0.1_0$
					12	$1.6_8 \pm 0.1_6$
230	1.3	30	30	127,163	3	$1.8_1 \pm 0.0_2$
	1.6	40	40	127,163	3	$2.0_0 \pm 0.1_5$
	1.8	50	50	110,144	2	$2.1_5 \pm 0.0_7$
	2.2	60	60	127	1	2.0_4
					9	$1.9_8 \pm 0.1_6$
254	1.6	150	20	56–163	5	$2.1_3 \pm 0.1_9$
	2.4	188	25	127	1	2.3_9
	2.4	225	30	110,144	3	$2.4_6 \pm 0.1_7$
	3.3	263	35	110,127	3	$2.2_1 \pm 0.0_6$
					12	$2.2_6 \pm 0.2_0$
300	See Table I					$2.8_5 \pm 0.2_2$
360	0.8	150	20	144,163	2	$4.1_1 \pm 0.0_8$
	1.2	225	30	127,163	3	$3.9_1 \pm 0.2_5$
	1.4	300	40	110–163	3	$3.8_7 \pm 0.4_7$
	2.0	375	50	127,163	3	$3.9_5 \pm 0.2_8$
	2.4	450	60	127	1	3.8_9
					12	$3.9_4 \pm 0.2_7$

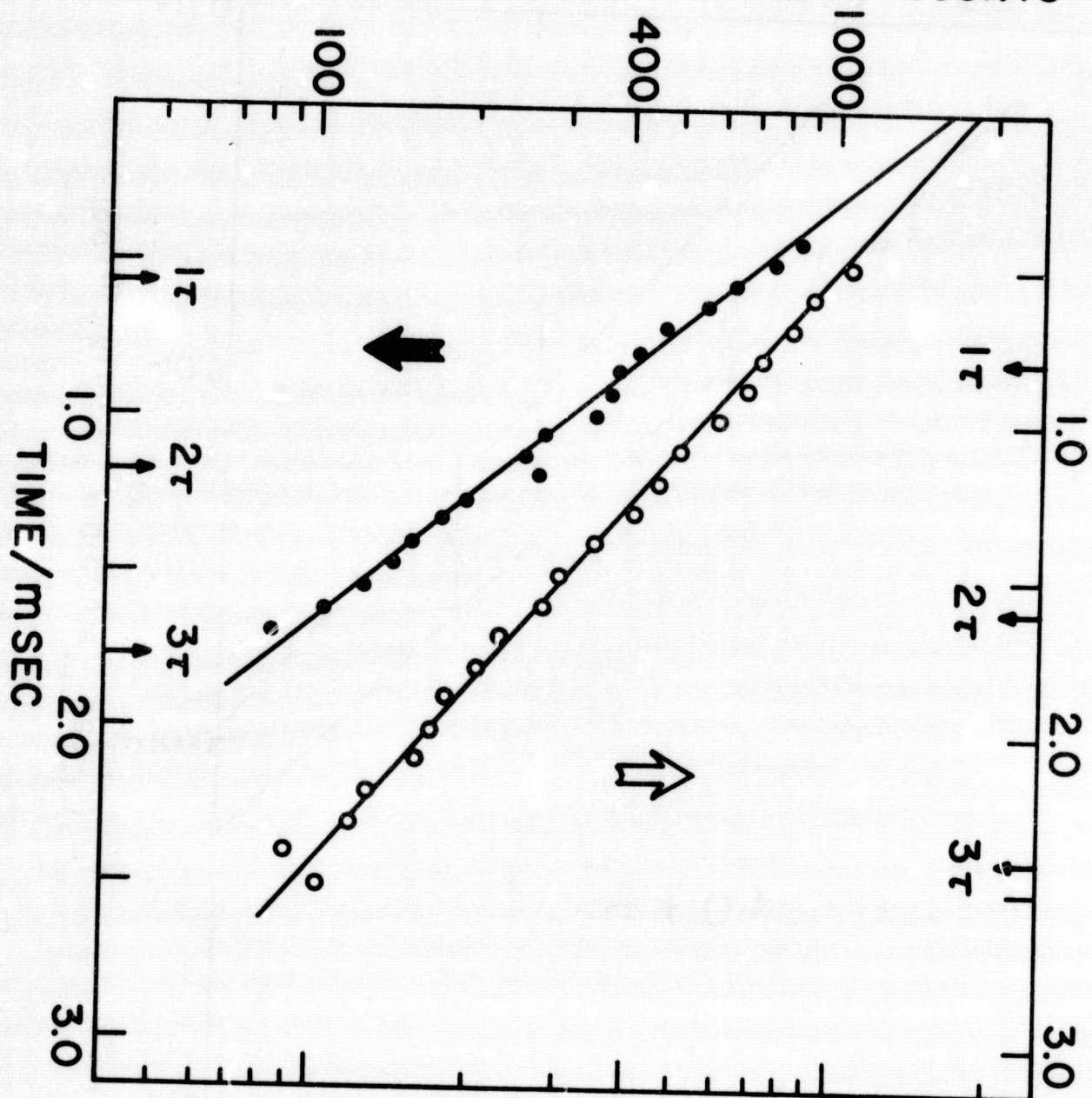a - Error limit in k_1 is one standard deviation.
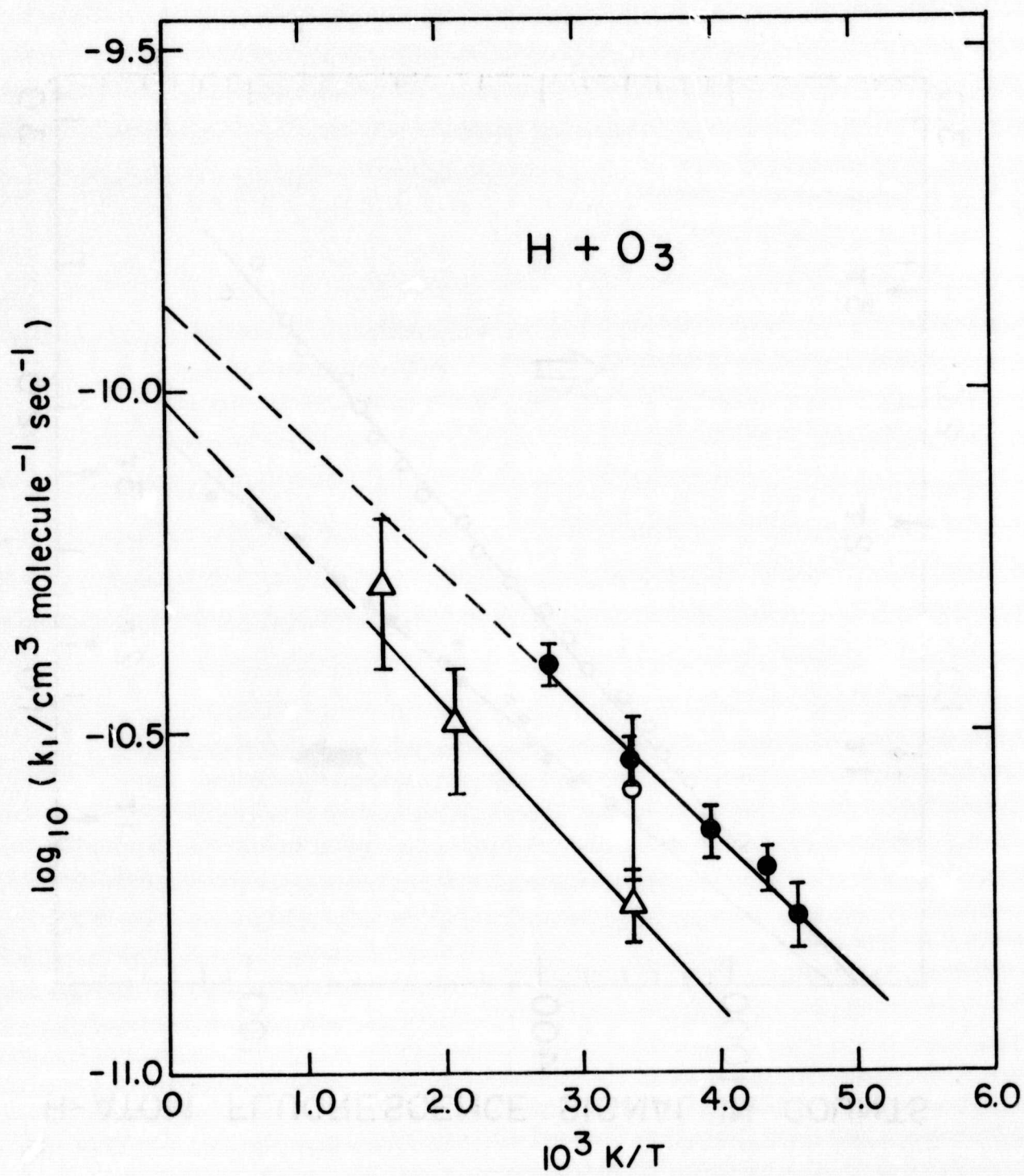
b - Flash energy in Joules.

FIGURE CAPTIONS

Fig. 1: Typical first order decay plots of $\log_{10}$ (Lyman α fluorescent count) vs. time according to Eq. (3). $O - [O_3] - 1.2$ mtorr, flash energy = 163 J, T = 298 K, and $P_T = 20$ torr. $\bullet - [O_3] - 1.8$ mtorr, flash energy = 95 J, T = 298 K, and $P_T = 30$ torr. In both experiments the source of H atoms is H_2O.

Fig. 2: Arrhenius plot for the reaction, $H + O_3 \rightarrow OH + O_2$. $\triangle$ - Clyne and Monkhouse,[12] O - Phillips and Schiff,[11] and $\bullet$ - present results. Error bars are 2σ for ref. 12 and 1σ for ref. 11 and the present study. Lines drawn through the data points are from ref. 12 and the present report.

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15. Supplementary Notes

16. Abstract

   Absolute rate constants for the reaction of atomic hydrogen with ozone were obtained over the temperature range 219-360 K by the flash photolysis-resonance fluorescence (FP-RF) technique. The results can be expressed in Arrhenius form by $k = (1.33 \pm 0.32) \times 10^{-10} \exp(-449 \pm 58/T)$ cm^3 molecule^{-1} s^{-1} (two standard deviations). The present work is compared to two previous determinations and is theoretically discussed.

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