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KINETICS OF THE REACTION

$OH(v=0) + O_3 \rightarrow HO_2 + O_2$

BY

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SPONSORED BY
ADVANCED RESEARCH PROJECTS AGENCY
ARPA ORDER NO. 826

SRCC REPORT NO. 183

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PITTSBURGH, PENNSYLVANIA

FEBRUARY 1973

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Unclassified
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* University of Pittsburgh Pittsburgh, PA 15213	**2a. REPORT SECURITY CLASSIFICATION** Unclassified **2b. GROUP**

3. REPORT TITLE

Kinetics of the Reaction OH(v=o) + $O_3 \rightarrow HO_2 + O_2$

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Scientific paper - issued January 1973

5. AUTHOR(S) *(First name, middle initial, last name)*

James G. Anderson and Frederick Kaufman

6. REPORT DATE January 1973	**7a. TOTAL NO. OF PAGES** 12	**7b. NO. OF REFS** 12
8a. CONTRACT OR GRANT NO. DA-31-124-ARO-D-440 **b. PROJECT NO.** **c.** **d.**	**9a. ORIGINATOR'S REPORT NUMBER(S)** **9b. OTHER REPORT NO(S)** *(Any other numbers that may be assigned this report)*	

10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES Monitored By: U. S. Army Research Office-Durham	**12. SPONSORING MILITARY ACTIVITY** Advanced Research Projects Agen 1400 Wilson Blvd. Arlington, Va. 22209

13. ABSTRACT

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DD FORM 1 NOV 65 1473 REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

Unclassified
Security Classification

Unclassified
Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Hydroxyl						
Kinetics						
Ozone						
Resonance Fluorescence						
Flow System						

Unclassified

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(Submitted to Chemical Physics Letters)

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Kinetics of the Reaction*

$OH(v=o) + O_3 \rightarrow HO_2 + O_2$

Technical Report

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U. S. Army Research Office-Durham

Sponsored by

Advanced Research Projects Agency
ARPA Order No. 826

and

The National Science Foundation
Washington, D. C.

Contract No. DA-31-124-ARO-D-440
and
NSF Grant No. GA 27638

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(I) INTRODUCTION

Bates and Nicolet introduced the subject of atmospheric water vapor photochemistry in a classic paper[1] more than twenty years ago. A basic step in the chain mechanism proposed in that paper and in later studies[2-5] is the reaction

$$OH + O_3 \xrightarrow{k_1} HO_2 + O_2 \quad .$$

Recently, intense interest in those steps which control the ozone concentration in the stratosphere[6-8] has developed out of a concern for possible photochemical effects resulting from the deposition of combustion products at stratospheric levels, principally from high altitude aircraft flights.

Measurement of the hydroxyl-ozone reaction rate constant, k_1, has to date eluded observation. Kaufman[9] recommended an upper limit of 5×10^{-13} cm³/sec which has often been quoted as a measured rate constant and used as such in model calculations. Langley and McGrath[10] inferred an upper limit of 10^{-16} cm³/sec from observing the effects of water vapor on the decay of ozone following the flash photolysis of an Ar-O_3-H_2O mixture. For a comprehensive review of data pertaining to k_1, see Hampson et al.[11]

The previous development of molecular resonance fluorescence as a method for detecting OH radicals[12] has provided the required sensitivity to directly observe the first order decay of ground state OH in the presence of O_3. A fast flow reactor tube operating in the 2 to 5 torr pressure range was used in this study to determine k_1 over the temperature range $220°K \leq T \leq 450°K$.

(II) EXPERIMENTAL

The pyrex flow tube 1 meter in length and 2.5 cm in diameter, coupled with a fixed position quartz fluorescence cell, used in this study, was identical to the system previously described.[12]

Hydroxyl radicals were formed in the reaction

$$H + NO_2 \rightarrow OH + NO$$

by the addition of NO_2 through a fixed loop injector at the upstream end of the main flow tube to H atoms formed in a microwave discharge of H_2 and He (see Figure 1).

Detection of OH was accomplished by observing photons resonantly scattered at 3090Å ($A^2\Sigma \rightarrow X^2\Pi$ (0-0)) in a direction perpendicular to a collimated beam of resonance radiation from an H_2O-Ar discharge lamp which was aligned so as to illuminate the center of the fluorescence cell.

A 0.3 cm o.d. polished stainless steel movable injector tube, concentric with the main flow tube, was used to add ozone at any desired point upstream of the fluorescence cell. Stable temperature control over the range $220° \leq T \leq 450°K$ was achieved using a hollow copper cooling jacket surrounded by a heating mantle, both of which extend over the full length of the main flow tube.

The apparatus for the production, handling and measurement of ozone is also displayed in Figure 1. A cold trap containing 500 grams of silica gel (Davidson, 6-12 mesh), immersed in an isopropanol-dry ice bath at -78°C, was used to selectively adsorb ozone from a 4 percent O_3 to O_2 mixture taken directly from a Welsbach ozonizer (Model T-408). A second isopropanol immersion bath maintained at some higher temperature (e.g. -55°C) could be inserted in place of the dry ice bath. Argon diluent, the flow of which was monitored by a capillary flow meter, was passed through the trap in order to elute O_3. The O_3 concentration was determined by absorption photometry at a point immediately before the argon-ozone mixture passed into the sliding injector using a quartz cell, a mercury discharge lamp (Oriel Model 13-61) coupled with a 2540Å filter (Baird-Atomic) and a photomultiplier (RCA 1P28). The total pressure in the quartz absorption cell, typically 40 torr, was measured with a pressure transducer (Validyne, Model DP7).

(III) PROCEDURE

Hydroxyl radicals were produced by adding NO_2 in slight excess through the fixed loop injector to atomic hydrogen as described previously.[12] Since that report, the first order wall decay constant has been reduced from $40 \pm 5\ \mathrm{sec}^{-1}$ to $15 \pm 3\ \mathrm{sec}^{-1}$ by aging the phosphoric acid wall coating at elevated temperatures (~440°K). This allows a reduction in the flow velocity for kinetic experiments.

The flow rates of reactants added to the system were such that the concentration of OH ($\leq 3 \times 10^{11}\ \mathrm{cm}^{-3}$) in the reaction zone was three orders of magnitude smaller than that of the injected O_3 concentration ($1 - 6 \times 10^{14}\ \mathrm{cm}^{-3}$) which in turn was nearly three orders of magnitude smaller than the carrier gas concentration ($2 \times 10^{17}\ \mathrm{cm}^{-3}$). The O_3 mole fraction in the injector was about 0.2, so that the flow entering through the sliding injector was normally less than one percent of the total flow. The ozone handling system was arranged such that a constant flow of argon could enter the sliding injector by either of two routes: (a) through the silica gel trap containing the adsorbed O_3 or (b) through a by-pass loop. Therefore, changes in the OH concentration at the fluorescence cell as a function of injector position with: (a) a measured mole fraction of argon-ozone or (b) pure argon added through the injector, constitute the fundamental experimental data.

In order to verify that no ozone was lost in the injector assembly, the OH resonance lamp was replaced by a mercury discharge lamp and an O_3 absorption experiment was performed in the fluorescence cell at the downstream end of the flow tube. The O_3 concentrations measured at the two locations agreed within the experimental uncertainty (± 10 percent).

(IV) RESULTS

Figure 2 presents a typical example of the OH decay as a function of injector position for two cases, one with argon alone added through the injector and another with an ozone-argon ratio of 1:5. The negligible effect of the injector and of added Ar on the OH decay is apparent, as is the linearity of the logarithmic decay of OH concentration over an order of magnitude in the presence of O_3, verifying the pseudo-first order nature of the removal process.

The first order rate constant calculated from the OH decay plots was found to be independent of total pressure in the range of study (2 to 5 torr), independent of the NO_2 excess flow through the loop injector, and exactly proportional to the O_3 concentration within the experimental uncertainty of the O_3 concentration measurement. At 297°K the bimolecular rate constant was found to be $5.5 \pm 1.5 \times 10^{-14}$ cm^3/sec.

The possibility of OH regeneration by the reaction

$$HO_2 + O_3 \xrightarrow{k_2} OH + 2O_2$$

was considered. Hydroxyl decay profiles encompassing the range $0 < k_1/k_2 < \infty$ were calculated and compared with the observed decay profiles. As the ratio k_1/k_2 becomes less than about ten, distinct curvature in the logarithmic decay plots of OH results, which is clearly inconsistent with the observations. It can thus be inferred that $k_2 \leq 5 \times 10^{-15}$ cm^3/sec.

Preliminary results over the temperature range 220 to 450°K, presented in Figure 3, indicate an activation energy of 1.9 kcal/mole and lead to the Arrhenius expression $k_1 = 1.3 \times 10^{-12} \exp(-1900/RT)$ cm^3 sec^{-1}.

The room temperature reaction rate constant $k_1 = 5.5 \pm 1.5 \times 10^{-14}$ cm^3/sec is in strong disagreement with the upper limit of 10^{-16} cm^3/sec reported by Langley and McGrath[10] from flash photolysis studies. We suggest that the reaction $OH + OH \rightarrow H_2O + O$, which was not taken into account in their analysis, greatly decreases the OH concentration in their experiments and makes it impossible to set limits for k_1.

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*This research was supported in part by the National Science Foundation, Atmospheric Sciences Division (Aeronomy) under Grant No. GA 27638 and by the Advanced Research Projects Agency, The Department of Defense, and was monitored by U. S. Army Research Office-Durham, Box CM, Duke Station, Durham, N. C. 27706, under Contract No. DA-31-124-ARO-D-440.

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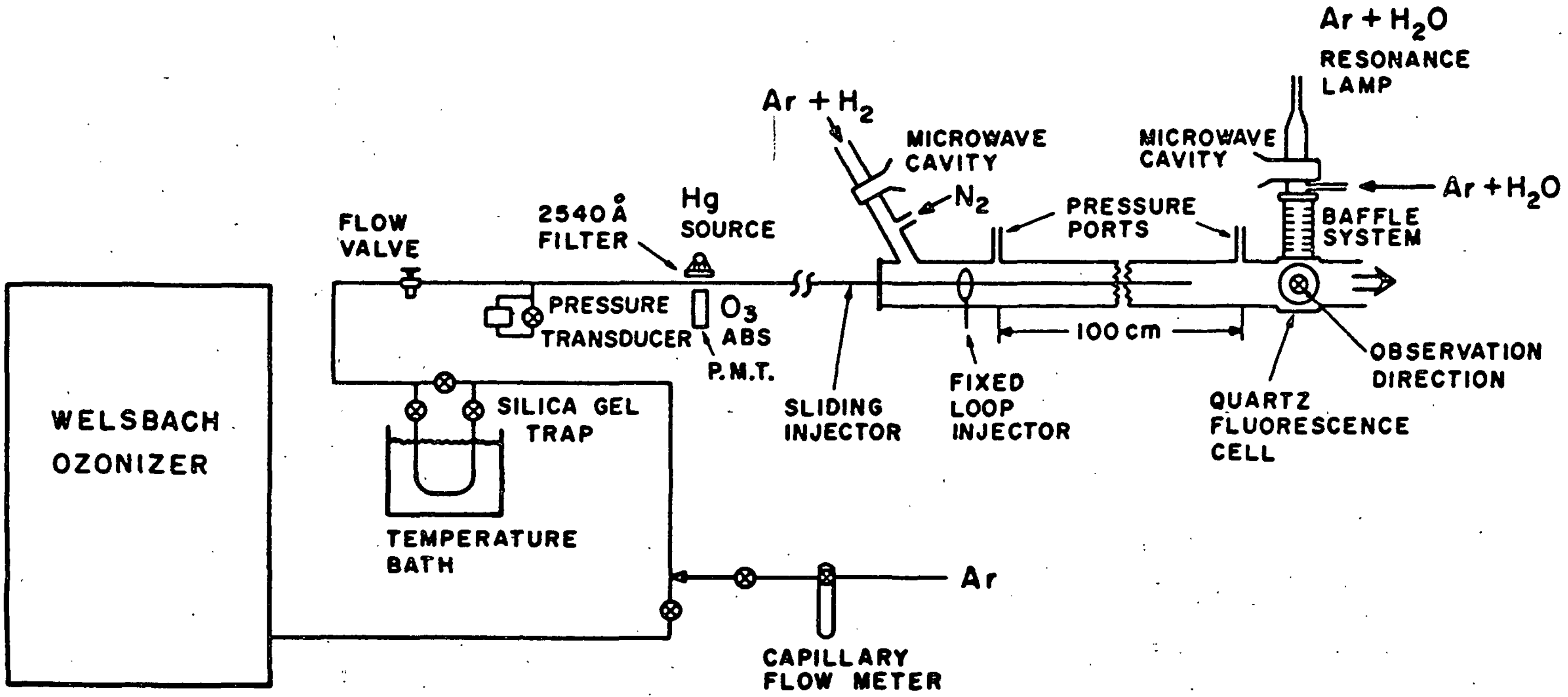
LIST OF FIGURE CAPTIONS

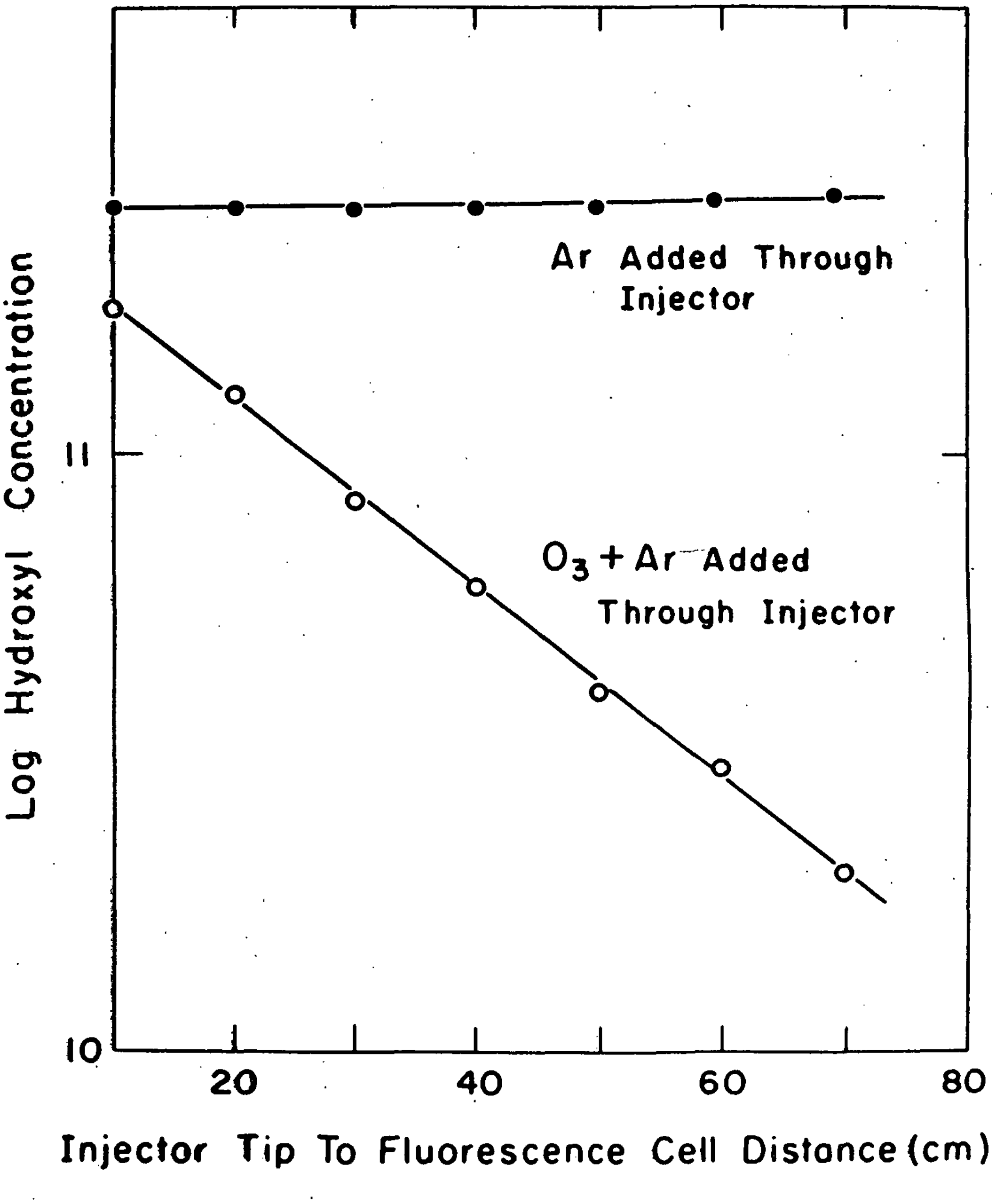
Figure 1. Schematic description of the ozone system, main reaction tube, fluorescence cell and resonance lamp.

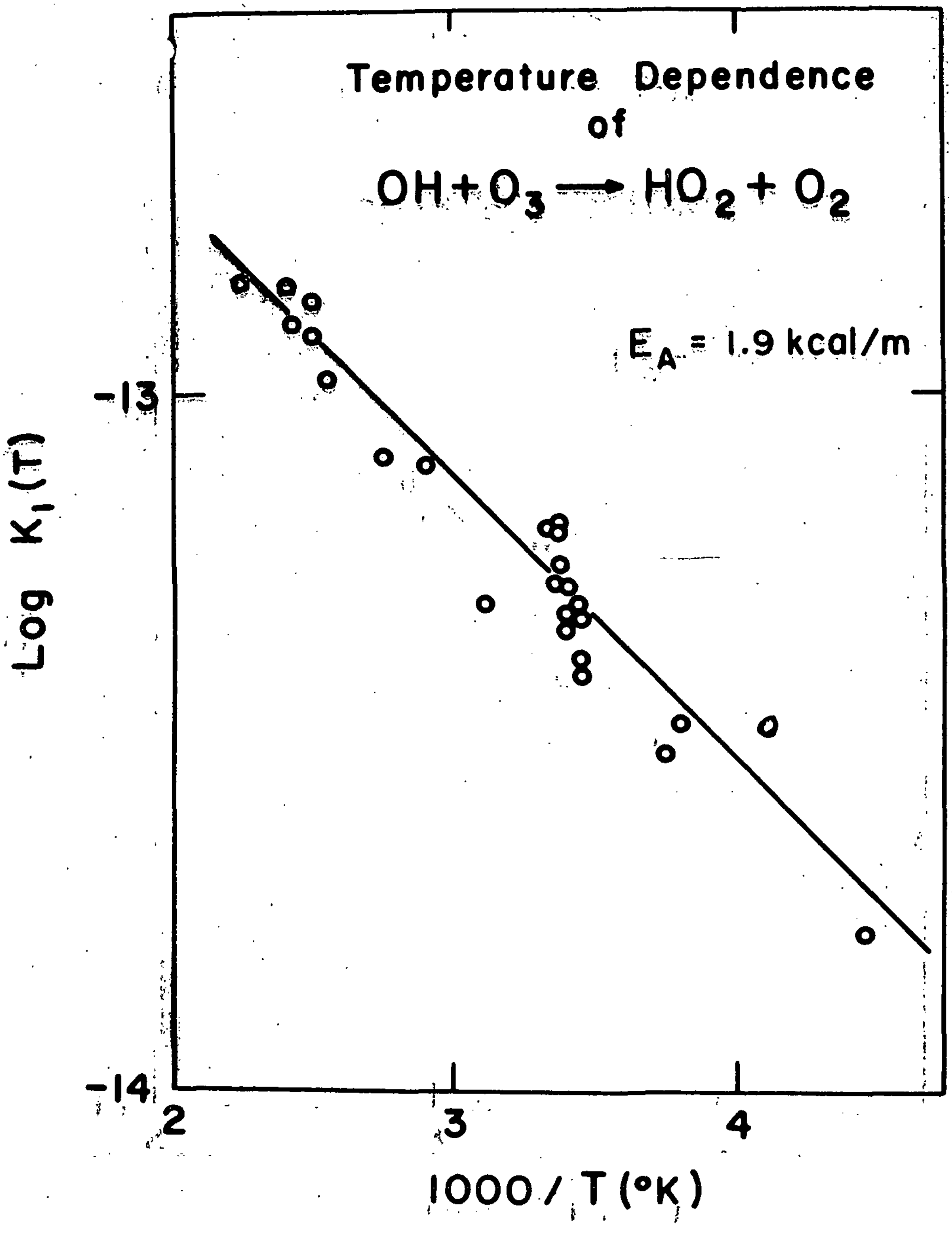
Figure 2. Hydroxyl decay resulting from the addition of pure argon and an argon-ozone mixture through the sliding probe.

Figure 3. Arrhenius plot of $k_1(T)$ versus 1/T from 220 to 450°K.



Ar + H_2O
RESONANCE LAMP
MICROWAVE CAVITY
Ar + H_2O
BAFFLE SYSTEM
Ar + H_2
MICROWAVE CAVITY
N_2
PRESSURE PORTS
FLOW VALVE
2540 Å FILTER
Hg SOURCE
PRESSURE TRANSDUCER
O_3 ABS
P.M.T.
100 cm
OBSERVATION DIRECTION
WELSBACH OZONIZER
SILICA GEL TRAP
SLIDING INJECTOR
FIXED LOOP INJECTOR
QUARTZ FLUORESCENCE CELL
TEMPERATURE BATH
Ar
CAPILLARY FLOW METER


Log Hydroxyl Concentration
11
10
20
40
60
80
Injector Tip To Fluorescence Cell Distance (cm)
Ar Added Through Injector
O_3 + Ar Added Through Injector


Temperature Dependence
of
OH + O3 → HO2 + O2
EA = 1.9 kcal/m
-13
-14
2
3
4
Log K1(T)
1000 / T (°K)