2

SECURITY CL

AD-A207 138

ATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

3. DISTRIBUTION / AVAILABILITY OF REPORT
Approved for public release;
distribution unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

5. MONITORING ORGANIZATION REPORT NUMBER(S)
AFOSR-TR- 89-0505

6a. NAME OF PERFORMING ORGANIZATION
University of Pittsburgh
Department of Chemistry

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
AFOSR

6c. ADDRESS *(City, State, and ZIP Code)*
Pittsburgh, PA 15260

7b. ADDRESS *(City, State, and ZIP Code)*
BLDG 410
BAFB DC 20332-6448

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
AFOSR

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
F49620-79-C-0155

8c. ADDRESS *(City, State, and ZIP Code)*
BLDG 410
BAFB DC 20332

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO	WORK UNIT ACCESSION NO.
61102F	2303	B1	

11. TITLE *(Include Security Classification)*
Measurement of Rate Constants of Elementary Gas Reactions of Importance to Upper Atomosphere And Combustion System

12. PERSONAL AUTHOR(S)
Frederick Kaufman

13a. TYPE OF REPORT
FINAL

13b. TIME COVERED
FROM ________ TO ______

14. DATE OF REPORT *(Year, Month, Day)*
31 Aug 80

15. PAGE COUNT
8

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

DTIC
ELECTE
APR 26 1989
S H D

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL
Dr. Donald Ball

22b. TELEPHONE *(Include Area Code)*
767-4960

22c. OFFICE SYMBOL
NC

DD Form 1473, JUN 86 *Previous editions are obsolete.* SECURITY CLASSIFICATION OF THIS PAGE

89 4 25 025

5 NOV 1980

AFOSR-TR- 80-0505

University of Pittsburgh
Department of Chemistry

Final Scientific Report
Submitted to the

Air Force Office of Scientific Research

Directorate of Chemical Sciences

MEASUREMENT OF RATE CONSTANTS OF ELEMENTARY GAS REACTIONS OF IMPORTANCE TO UPPER ATMOSPHERE AND COMBUSTION SYSTEMS

Principal Investigator: Frederick Kaufman
University Professor of Chemistry
Contract No. F49620-79-C-0155 for the period
1 July 1979 to 31 August 1980

I. INTRODUCTION

This Final Scientific Report is submitted for administrative reasons only, because the work continues as an AFOSR Grant No. 5-34503, but was started as a contract No. F49620-79-C-0155 which, after a two-months', no-cost extension for July and August 1980, terminated on 31 August 1980. This report will therefore be unusually brief, since it covers the very initial planning and building stages of a major, exciting project. Furthermore, its early progress was delayed by late delivery of a high power, high repetition rate CO_2 laser (Lumonix, Model 820) required for the generation of radical species, and by the late arrival of the postdoctoral research associate, Dr. Jay B. Jeffries who will carry out much of the planned experimental work.

Fortunately, a parallel research investigation on collisional relaxation of highly excited HCl and HF, formerly supported by the Advanced Research Projects Administration, and of great scientific research and development interest to AFOSR was able to be continued with modest support from this contract and has provided valuable information on relaxation rate measurements for HCl (v = 1 to 7) colliding with a large number of other molecules and some preliminary rate measurements for HF (v = 1 to 7). The present report will therefore be subdivided into two sections dealing with these two topics, but it must be kept in mind that that this is essentially a progress report covering the initial 14-months building-up period of a major project.

II. DESIGN OF REACTION FLOW SYSTEM WITH MULTIPHOTON LASER DISSOCIATION RADICAL SOURCE

Becuase of the above mentioned delays of laser delivery (April 1980) and Dr. Jeffries's arrival (August 1980), the building of our flow reactor has also been delayed, but all major components are now on hand. A large Roots Blower (Leybold Heraeus, Model RO2400) backed by a rotary pump (Heraeus E225) formerly used in ion-molecule reaction studies[1-3] is used to provide the required pumping velocity. A smaller pump is used when large flow velocities are not required, since the large pumping system is also used to pump the vibrational relaxation apparatus (Section III below).

The flow tube allows the facile placement or removal of a liner tube of 2 to 3 cm i.d. whose inner surface can be treated or coated to inhibit surface reaction or recombination of the radicals generated along a side-arm by IR laser dissociation. The partly dissociated radical precursor stream enters either through a fixed upstream port as shown in the original proposal and reproduced here (see Figure 1) or through a movable, coaxial injector tube that permits the variation of radical-to-detector transit time without major changes in other flow parameters. The flow tube is also fitted with a thin, movable injector tube (o.d. ∿3 mm) and with up-stream ports for the introduction of inert diluent gases and of stable reactants, as well as with microwave discharge cavities placed on fixed and/or movable injector tubes for the purpose of introducing atom or simple radical species. The length of and flow velocity in the laser dissociation tube are so chosen as to provide a "slug" of radicals of sufficient length and repetition rate to minimize the problem of axial diffusion. The tube and liner are surrounded by a heating/cooling enclosure to allow operation over the 200–600 K range initially and later probably to about 1000 K.

The detection of radicals, precursors, and other species is accomplished by mass spectrometry using the available quadrupole mass filter assembly[1-3] but including an efficient electron impact ionizer (Extranuclear Laboratories, Inc., Model 041-1) and control (Extranuclear Laboratories, Inc., Model 020-2) operating near threshold and also making use of time-of-flight techniques to discriminate against stable precursor molecules. Additionally, it is hoped that a photoionization lamp emitting, say, the Kr resonance line (123.6 nm) will be used with its mildly focussed beam traversing the electron impact ion source region such that mass peaks can first be identified using the electron impact ion source, but then monitored by photoionization making use of the low ionization potential of the radical species.

In the detection cell, upstream of the molecular beam sampling inlet to the mass spectrometer, there are ports and windows for laser-induced fluorescence detection of radicals using a Lambda Physics Nitrogen and Dye Laser (Models M1000 and FL2000) with doubling and controlled scanning capabilities. These lasers are now on order and will be delivered within one to two months. There will be further ports for u.v. and vacuum u.v. discharge resonance lamps and a 0.3 meter monochromator (McPherson, Model 218) is available for the detection of atomic species. Detection limits in this versatile, state-of-the-art flow reactor apparatus are expected to be $\approx 10^{9}$ cm^{-3} for mass spectrometer analysis (possibly lower for photoionization where background signals are very low), about 10^{9} cm^{-3} for v.u.v. resonance fluorescence of atomic species, and about 10^{7} for laser induced fluorescence of radicals with strong transitions in the visible or near u.v.

III. COLLISIONAL RELAXATION OF VIBRATIONALLY EXCITED HCl and HF (v = 1 to 7)

These measurements have as their aim to elucidate the systematics of vibrational relaxation processes as function of v-level and of collision partner over wide ranges of both parameters, i.e. for v = 1 to 7 and for a large number of added gases that are chosen to clarify the effects of energy resonance, dipole moment, and Van der Waals forces. The infrared chemiluminescence technique is used under steady-state conditions in a fast flow reactor with helium carrier gas at 0.5 to 1 torr. The collisions of $HX^{\neq}$ with He relax any non-thermal rotational distribution, but leave the vibrational distribution entirely unrelaxed. Generating reactions such as $H + ICl \rightarrow HCl^{\neq} + I$, $H + Cl_2 \rightarrow HCl^{\neq} + Cl$, $Cl + HI \rightarrow HCl^{\neq} + I$, $Cl + HBr \rightarrow HCl^{\neq} + Br$ are used to produce $HCl^{\neq}$ in different initial v-distributions. The reactions of $H + F_2 \rightarrow HF^{\neq} + F$ and $F + H_2 \rightarrow HF^{\neq} + H$ are used for $HF^{\neq}$. The chemiluminescence is monitored by a liquid N_2 cooled InSb detector using a circularly variable filter for spectral dispersion with a resultant detection limit of about 2×10^8 cm^{-3} for HCl (v = 7) and somewhat better for $HF^{\neq}$. The precursor species, say, H and ICl, are rapidly mixed in the field of view of the detector and the relaxation rates are measured by Stern-Volmer analysis in series of experiments with increasing amounts of quencher gas added upstream to the He flow. The H-atom (or Cl-atom) stream is square-wave modulated so that the chemiluminescence signal is also modulated and background emission is suppressed. The reference process with which the relaxation is compared is the very fast pumping rate out of the field of view, of order 10^3 to 10^4 s^{-1} and therefore one to two orders of magnitude larger than the Einstein coefficients, $A \sim 30$ to 100 s^{-1} used by other investigators.

Only stable, molecular quencher gases are used in this work, because it is desired to be able to consider only stepwise, $\Delta v = 1$ relaxation in the interpretation of the data. The dynamic range of relaxation rate constants is approximately three orders of magnitude, from 10^{-13} to 10^{-10} cm^3 $molecule^{-1}$ s^{-1}, where the lower limit is prescribed by the fact that no more than a few percent of quencher gas can be added to the He flow without changing the nature of the transport properties in the mixing region whose constancy is assumed in the analysis.

A very large array of experimental results has been obtained for $HCl^{\neq}$ which ranges are over diatomic (N_2, CO, NO, HCl, HF, DCl), triatomic (CO_2, N_2O, NO_2), and polyatomic (CH_4, CH_3F, CH_3Cl, CF_3Cl, CF_2Cl_2, $CFCl_3$, CF_4, SF_6, C_2H_6, C_3H_8, and C_4H_{10}) quenchers. Two large publications are in preparation that summarize and interpret these results. Several experimental checks and confirmations are still in progress. Therefore, this is not the place to present a thorough discussion of our findings, but a few highlights may be mentioned: For small molecules of low dipole moment the quenching rate constants are higher for molecules with infrared active vibrations and often obey Lambert-Salter type correlations, i.e. $\log(vZ^Q_{v,0-1})$ rises linearly with ΔE where $Z^Q_{v,v-1}$ is the number of gas kinetic collisions to relax HCl^v to HCl^{0-1} and ΔE is the vibrational energy defect. For molecules such as CH_4, this correlation seems to break down no matter whether one uses the high C-H stretch or lower C-H bend frequencies for ΔE. Rotational effects may play an important role here, but the analysis is as yet incomplete. For relaxation by strongly dipolar diatomics ($HCl^{v=0}$, DCl, HF) there is clear evidence that the process is one of V → R, i.e. $HCl^{v=7} + HCl^{v=0} \rightarrow HCl^{v=6} + HCl^{v=0}$ with the large energy of the upper vibrational quantum being released as rotation (and translation). Otherwise, vibrational energy resonance, i.e. small ΔE, is important and qualitatively rationalizes why CF_4 and SF_6 are very inefficient quenchers of $HCl^{\neq}$.

Initial results for $HF^{\neq}$ quenching by CO_2 are more extensive than and compare favorably with laser excitation studies for v = 3 and 4 and show marked increases of the quenching rate constant with v from v = 1 to 6. For Q = CH_4 our early results are higher than those of Poole and Smith,[4] but lower than a recent laser study[5] for v = 4. Data have also been collected for Q = NO which is an efficient relaxer in spite of the large energy defect ($k^Q \simeq 4, 21, 39, 61$, and 37×10^{-12} cm^3 s^{-1}) for v = 3 to 7. Much more experimental work will, of course, be performed in order to produce a large and reliable array of quenching rate parameters for $HF^{\neq}$ in the continuation of this contract under our new AFOSR grant.

IV. REFERENCES

1. Water Cluster Formation Rates of NO^+ in He, Ar, N_2, and O_2 at 296° K, C. J. Howard, H. W. Rundle, and F. Kaufman, J. Chem. Phys., 55, 4772 (1971).

2. Kinetics and Mechanism of the Formation of Water Cluster Ions from O_2^+ and H_2O, C. J. Howard, V. M. Bierbaum, H. W. Rundle, and F. Kaufman, J. Chem. Phys., 57, 3491 (1972).

3. Kinetics of the Reactions of N_2H^+, N_4^+, and N_3^+ with H_2O in the Gas Phase, V. M. Bierbaum and F. Kaufman, J. Chem. Phys., 61, 3804 (1974).

4. P. R. Poole and I. W. M. Smith, J. Chem. Soc. Faraday Trans. II, 73, 1447 (1977).

5. J. K. Lambert, G. M. Jurisch, and F. F. Crim, Chem. Phys. Lett., 71, 258 (1980).