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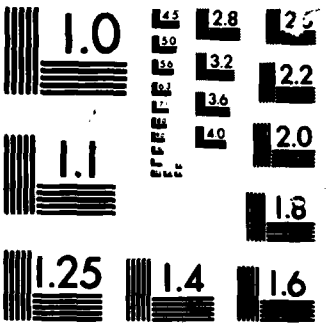

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)
At the conclusion of our DOD instrumentation grant, we have assembled our enhanced flow reactor. The LEF system, utilizing an excimer pumped dye laser, has been used in preliminary studies of the OH + CH_3OH reaction. The mass spectrometer has been installed in the new UHV envelope and is undergoing final testing.

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Final Report

AFOSR-85-0044

University of Pittsburgh

Frederick Kaufman

14 December 1984 - 13 December 1985

Measurement of Rate Constants of Elementary Gas-Reactions of Importance to Upper Atmosphere and Combustion Systems

24 February 1986

DOD FINAL REPORT

At the conclusion of our DOD instrument grant, we are in possession of all the components for our new, versatile flow reactor system. The major items purchased were a bakeable, differentially pumped, UHV envelope to interface our mass spectrometer to our flow tube and an excimer pumped dye laser system for laser excited fluorescence (LEF) detection of radicals in our flow tube. Our LEF system, employing a Lambda Physik excimer pumped dye laser (EMG 103 MSC/FL 2001), has been operational since mid-autumn. It has already been used in preliminary studies of our new methoxy radical source. Completion of our mass spectrometer system was delayed by a variety of problems. However, by late October the required parts were on hand, and the vacuum envelope, sans mass spectrometer, was successfully pumped down. The complete system is currently assembled and undergoing final testing.

Keywords: Hydroxyl radical, Chemical reactions

We are using the Extranuclear Laboratories quadrupole mass spectrometer from our previous system with the spectrometer axis oriented perpendicular to the molecular beam extracted from the flow tube. This geometry was chosen to minimize interference from He metastables formed in the ionizer. The molecular beam can be chopped with a tuning fork chopper, allowing us to use phase sensitive detection. Additionally, measurement of the neutral beam time-of-flight (as reflected in the phase delay) allows us to selectively detect ions arising from parent neutrals of arbitrary mass. We have also redesigned the ionizer to accept the larger beam expected from our glass capillary array beam source. The ion source utilizes an inhomogeneous electric field to correct for initial beam velocity transverse to the spectrometer axis, thus increasing the spectrometer's throughput.

The presence of both LEF and mass spectrometric detectors on one flow tube greatly enhances our capabilities for detailed kinetic studies of radical-radical reactions. For example, we can monitor total (CH_3O/CH_2OH) (m/e =31) mass spectrometrically, while

selectively detecting only CH_3O using LEF. Additionally, cross calibration between the mass spectrometer and LEF system will enhance our abilities to measure absolute radical concentrations.

A major thrust in our work with the new system will center on reactions of methyl, methoxy, and methylperoxy radicals. Our first studies have been devoted to developing and characterizing methoxy radical sources. A particularly interesting source is based on work carried out by Dr. Denis Bogan at Naval Research Laboratory. The source utilizes hydrogen abstraction from methanol by atomic fluorine; this abstraction produces approximately 75% methoxy radical. The remaining 25% of the reaction goes to form hydroxymethyl radicals, which react with excess molecular fluorine to produce a fluorinated methanol and a fluorine atom. This chain continues until all of the hydroxymethyl radicals have been indirectly converted to methoxy radical. This source is a useful alternative to our earlier source, the methyl + NO_2 prereaction.

Before beginning our study of the O + CH_3O reaction, we examined the possible interferences arising from O + CH_3OH and OH + CH_3OH reactions. We will be able to avoid these interference by a careful choice of O atom and F_2 concentrations. Of interest, however, is our observation that the OH + CH_3OH reaction goes to give essentially 100% hydroxymethyl. In contrast, the analogous, isoelectronic F atom reaction produces predominantly methoxy radical. The importance of (CH_3O/CH_2OH) species in combustion is well established; the large differences in hydroxymethyl and methoxy reactivity, especially with oxygen, makes it quite important that we understand the mechanisms which govern the branching between the two channels.

We are also applying our expertise to reactions of NF_2. NF_2, produced by pyrolysis of N_2F_4, will be detected mass spectrometrically. Once this radical source is characterized,

we will re-examine the NF_2 + O reaction. Previous rate measurements disagree by about a factor of ten.

Our final equipment acquisitions conform closely to those proposed originally, with the modifications outlined in our budget revision. The major differences to be noted are: (1) the change in suppliers, to Kurt J. Lesker, for a larger fraction of our vacuum hardware, because of lower prices; (2) the change to a Radio Shack TRS-100 microcomputer with a Polar Engineering Assembler/Debugger for dye laser control, replacing an equivalent, but more expensive system from Lambda Physik, and 3) the rejection of an Extranuclear Laboratories "counting/preamplifier" because we felt it offered us no real improvement in performance compared to the signal-conditioning electronics we were already using. With the resulting savings incurred by these changes, we were able to enhance our system by purchase of several additional items. Hardware was purchased from the Unistrut Pittsburgh Service Company to upgrade the framework supporting our UHV envelope. Additional money was spent to purchase a set of bakeable, "Kal-Rez" "O"-rings for the vacuum envelope, allowing us to obtain excellent ultimate vacuum without sacrificing the ease of "O"-ring assembly. We also purchased laser beam steering optics from Newport Corporation and CVI Laser to enhance our LIF system. Finally, a high purity gas regulator was purchased from the Harvey Company for sample introduction into the mass spectrometer envelope. It should again be emphasized that no capabilities of the flow reactor system were sacrificed in the reallocation of money and that the cost to the grant remained essentially unchanged.

LIST OF EQUIPMENT

LEYBOLD HERAEUS VACUUM PRODUCTS, INC.
5700 Mellon Road
Export, PA 15632
Bill Ritter (412) 327-5700

Turbovac 1000 turbomolecular pump with 10" OD (8" ID) conflat flange, inlet screen and modification for corrosive gas use. Includes NT1000 solid-state frequency converter	$12,100.00
Bake-out jacket for 115 volt use	225.00
Cryopump with 10" OD conflat flange and 2 3/4" OD conflat forevacuum connection	3,850.00
Compressor for pump	3,475.00
Ten-foot flexlines for pump	375.00
Corrosive application series dual stage rotary pump 36.7 CFM displacement direct drive, for 208 V 3 phase operation	4,375.00
Al_2O_3 type adsorption trap	595.00
Corrosive application series dual stage rotary pump	1,805.00
Adsorption trap	460.00
Activated Al_3O_3 for traps	57.00
Hot cathode ionization gauge pkg	1,875.00
Ionization gauge tube	405.00
Three-station gauge controller	490.00
Thermovac gauge tube	250.00
Thermovac gauge tube	240.00
Thirty-two-foot cable for tubes	75.00
Corrosion resistant diaphragm gauge	450.00
Misc. vacuum hardware	
Actuated air inlet valve	267.00
Stainless steel elbow	62.00
Stainless steel bellows	68.00
Stainless steel hose adapter	27.00
Stainless steel centering rings	59.10
Wing nut clamps	50.40
Clamp for sealing disc	39.00
KF25 to CF35 adapter	60.00
Stainless steel reducing cross	192.05
Stainless steel hose	126.00
Stainless steel hose adapter	23.00
Stainless steel centering rings	34.75

Wing nut clamps	34.75
Stainless steel centering rings	31.80
Stainless steel centering rings	29.75
Wing nut clamps	40.95
Stainless steel weld stub	39.00
Thermocouple gauge adapter	20.50
Replacement viton o-ring	3.70
Replacement viton o-ring	3.60
UHV sealing discs	30.00
Support ring for sealing disc	5.00
Stainless steel blank flange	12.30
KF-10 stainless steel flanges	20.55
Freight	149.36
Sub-Total	$ 32,531.56

MDC VACUUM PRODUCTS CORPORATION
23842 Cabot Boulevard
Hayward, CA 94545
(415) 887-6100

Tube tee with del-seal flanges	$ 590.00
Two-conductor electrical feedthru	320.00
Dual bakeable electrical feedthrus	270.00
Single MHV electrical feedthru	110.00
Sorption pump with del-seal flange	380.00
Molecular sieve material	30.00
Dewar for sorption pump	55.00
Wrap-around bakeout heater	160.00
Electropneumatically operated right angle valve	340.00
Misc. vacuum hardware	
Stainless steel tubing	39.00
Mitered elbow without flanges	210.00
Formed bellows, type 321	310.00
Del-seal bellows assembly	220.00
Del-seal blank flange	34.00
Bolts for tapped 10" flanges	116.00
Thru-bolts, washers, nuts for 8" flanges	66.00
Thru-bolts, washers, nuts for 6" flanges	30.00
Thru-bolts, washers, nuts for 3 3/8" flanges	30.00
Thru-bolts, washers, nuts for 2 3/4" flanges	64.00
Bolts for 2 3/4" flanges	28.00
Thru-bolts, washers, nuts for 1 1/3" flanges	22.00
Bolts for tapped 1 1/3" flanges	22.00
Thru-bolts, washers, nuts for 10" flanges	132.00
10" double-sided flange	235.00

Thru-bolts for 10" flange	33.00
Credit for above	-33.00
Replacement for above	33.00
Bolt set for 3 3/8" flanges	29.00
8" blank del-seal flange	100.00
Flexible coupling	330.00
Dodecagon bolts	29.00
Freight	106.40
Discount	-43.67
Sub-Total	$ 4,396.73

HUNTINGTON MECHANICAL LABS, INC.
1040 L'Avenida
Mountain View, CA 94043
Bob Cooke (800) 227-8059

Custom five-way cross	$ 3,570.00
Freight	1.74
Sub-Total	$ 3,571.74

VARIAN/VACUUM PRODUCTS DIVISION
333 Babbit Road
Euclid, OH 44123
Art Shivers (216) 289-6365

Triode Vacion pump with magnet	$ 1,585.00
Medium Vacion pump control unit	1,100.00
Twelve-foot bakeable cable	190.00
Rack mount chassis kit	210.00
Bakeout unit	499.00
Fel-pro thread lubricant	9.00
Rotary motion feedthru	296.00
Freight	100.19
Sub-Total	$ 3,994.19

PITTSBURGH VALVE AND FITTING COMPANY
49 Mead Avenue
P. O. Box 4155
Pittsburgh, PA 15202
761-3212

Bellows-sealed butterfly vacuum valve (3)	$ 1,245.60
O-ring sealed butterfly vacuum valve (4)	976.80

Bolt set for 304 series vacuum valve	62.40
"B" series valves (4)	457.20
Stainless steel fine metering valve	73.00
Misc. vacuum hardware	
3/8" stainless steel elbows	71.00
3/8" stainless steel tees	22.60
3/8" stainless steel cross	19.20
3/8" VCR glands	17.20
1/2" VCR male nut	5.70
1/2" VCR female nut	6.90
1/2" VCR copper gasket	5.00
1/4" to 3/8" stainless steel adapter	8.60
Freight	7.86
Discount	-29.70
Sub-Total	$ 2,949.36

EXTRANUCLEAR LABORATORIES
P. O. Box 11512
Pittsburgh, PA 15238
Chuck Kunkel 782-3884

Counting preamplifier, including power cable	$ 1,200.00
Returned for credit	-1,200.00
Freight	1.59
Sub-Total	$ 1.59

KURT J. LESKER COMPANY
5635 Horning Road
Pittsburgh, PA 15236
George Hanyo (412) 655-9500

Stainless steel sliding gate valve with flanges	$ 7,082.00
Ten-conductor feedthru	234.00
Single BNC feedthru	90.39
1 1/2" OD tube 2 3/4" six-way cross	400.00
Vacuum generator adapter assembly	172.00
Vacuum generators MD6 leak valve	662.00
Vacuum generator adaptor assembly	210.00
Misc. vacuum hardware	
10" CF blank flange	350.00
10" double-sided blank flange	225.00
10" CF to 8: CF adapter flange	270.00
8" CF blank flange	100.00
2 3/4" CF, 1 1/2" bore flange	39.00

1 1/3" CF, 3/4" bore necked flange	64.08
Credit for above two items, returned	-103.08
Replacement for above two items	154.54
1 1/3" CF blank flange	40.00
2 3/4" CF, 1 1/2" tube elbow	165.00
2 3/4" CF bellows assembly	210.00
2 3/4" CF half nipple	60.00
2 3/4" CF blank flange	67.90
2 3/4" CF to 1 1/3" adapter flange	55.00
2 3/4" CF rotatable blank flange	30.00
1 1/2" CF, 1/4" bore flange	42.72
10" CF gasket	48.00
8" CF gasket	38.00
6" CF gasket	13.50
2 3/4" CF gasket	70.00
1 1/3" CF gasket	24.00
Copper gaskets for 10" flange	24.00
Vacuum generator feedthru	165.00
Bakeable external connector	113.00
Vacuum generator linear motion thimble	566.00
3 3/8" to 2 3/4" adapter flange	60.00
1 1/3" non-rotatable blank flange	11.00
1 1/3" equpped 3/4" nipple	45.00
Screws, washers	13.00
2 3/4" bellows assembly	105.00
Credit for above	-105.50
1 1/3" blank flange	44.00
3 3/8" copper gasket	9.50
Freight	89.24
Credit	-211.00
Sub-Total	$ 11,742.29

HARVEY COMPANY
421 Regis Avenue
P. O. Box 18086
Pittsburgh, PA 15236
834-9200

Single state, high purity regulator	$ 594.00
Sub-Total	$ 594.00

MILLER SALES
1240 Trapp Road
Eagan, MN 55121
Jamie Hayes (612) 452-2250

PAI#1-006 "o"-ring	$	28.20
PAI#1-022 "o"-ring		25.70
PAI#1-252 "o"-ring		233.00
Freight		2.02
Sub-Total	$	288.92

UNISTRUT PITTSBURGH SERVICE COMPANY
711 Parkway View Drive
Pittsburgh, PA 15205
(412) 322-3124

Unistrut joint 90° elbow	$	13.09
Unistrut joint flat plate		1.60
Unistrut joint wing shape left		10.44
Unistrut joint wing shape right		3.48
Unistrut joint corner 3 way		75.90
Unistrut joint corner 3 way, light		16.92
Unistrut joint flat plate		14.04
Unistrut joint u-shape		4.51
Unistrut joint z-shape		16.72
Unistrut joint z-shape		1.21
Unistrut joint flat plate		6.00
Unistrut joint hook, right		4.42
Unistrut joint hook, left		4.42
Unistrut joint L-shape		16.87
Unistrut joint L-shape		4.82
Ten-foot length strut		41.58
Spring nuts for 1/2"-13 bolts		63.60
Spring nuts for 1/2"-13 bolts		29.25
1/2"-13 x 15/16" bolts		44.80
Freight		19.18
Discount		-3.75
Sub-Total	$	389.12

LAMBDA PHYSIK
289 Great Road
Acton, MA 01720
Thomas Hutches (216) 327-6581

Excimer laser with intelligent laser control option	48,800.00
Deflection mirrors	1,160.00
50/50 Beamsplitter	300.00
Dye laser with etalon	19,900.00
Xenon chloride pumping kit with optics and dye selector	2,900.00
Asynchronous controller	2,950.00
Frequency doubler control	3,750.00
KDP-590 doubling crystal	1,880.00
KPB-492 doubling crystal	2,280.00
Compensator for FL30T	110.00
Compensator for FL32T	110.00
Freight	541.00
Sub-Total	$ 84,681.00

RADIO SHACK
Monroeville Mall
Monroeville, PA 15146
Bill Synder 373-0630

Model 100 microcomputer	$ 599.00
AC adapter	11.90
Cassette recorder	49.95
Parallel interface cable	14.95
Model 100 technical reference	9.95
20% educational discount	-137.15
Sub-Total	$ 548.60

POLAR ENGINEERING
P. O. Box 7188
Nikishka, AL 99635
(907) 776-5529

ROM2 assembly/debugger for computer	$ 98.00
Sub-Total	$ 98.00

NEWPORT CORPORATION
18235 Mount Baldy Circle
Fountain Valley, CA 92708
(714) 963-9811

Five-axis lens positioner	372.00
1" optic holder	15.00
Translating post holder	252.00
Credit due for above item	-252.00
Replacement post holder	234.00
Support post (4")	36.00
Support post (2")	10.00
Freight	3.40
Sub-Total	$ 670.40

CVI LASER CORPORATION
922 Stafford Road
Storrs, CT 06268
(203) 486-0633

1.0" right angle prism	$ 225.00
Freight	2.96
Sub-Total	$ 227.96

TOTAL	$146,685.46
TOTAL OF GRANT	146,698.00
REMAINING	$ 12.54

END

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