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Progress Report

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RADIOCHEMISTRY RESEARCH

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Progress Report on work carried out during the contract year from:
October 1, 1974 to September 30, 1975

PRINCIPAL INVESTIGATOR F. S. Rowland

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RADIOCHEMISTRY RESEARCH - UNIVERSITY OF CALIFORNIA

IRVINE, F. S. ROWLAND

Progress Report, A. E. C. Contract No. AT(04-3)-34, Agreement No. 126.

Progress during the contract year October 1, 1974 - September 30, 1975

I. A major effort has been made in this year to pursue many of the details of the research on the effects of the chlorofluoromethanes in the environment. The Atomic Energy Commission report written in September, 1974, was revised and published as a review article in February 1975 in *Reviews of Geophysics and Space Physics*. This is the most detailed report of the atmospheric chemistry involved in this problem.

A shorter description without references was published in the *New Scientist* in December, 1974.

Three additional papers were published on particular aspects of the stratospheric chlorine problem, and several more are in various stages of preparation. Completion of some of these papers has been slowed down by the time required for testimony at various legislative hearings.

Testimony was provided by the principal investigator at the following hearings during the contract year (Dr. Molina also appeared at the December 11 hearings in Washington, D. C., and the May 19 hearings in Oregon).

October 26, 1974. Member, Ad Hoc Committee of the National Academy of Science on Fluorocarbon Problem.

December 11, 1974. Sub-committee of U. S. House Interstate and Foreign Commerce Committee, Washington, D. C.

January 14, 1975. Public Hearings for the Attorney General of the State of New York, New York City.

February 20, 1975. California State Senate, Health Committee.

February 27, 1975. Hearings of I. M. O. S. Committee, Council on Environmental Quality and Federal Council for Science and Technology, Washington, D. C.

March 20, 1975. Sub-Committee of U. S. House Interstate and Foreign Commerce Committee, Washington, D. C.

April 20, 1975. California State Senate, Finance Committee.

May 19, 1975. Environment Committee, Oregon House of Representatives, Salem, Oregon.

July 24, 1975. Climatic Impact Committee of National Academy of Sciences, Snowmass, Colorado.

August 20, 1975. California State House, Sacramento.

September 8-11, 1975. Panel of World Meteorological Organization, Geneva, Switzerland.

September 16, 1975. U. S. Senate Committee on Science and Astronautics, Washington, D. C.

In addition, presentations were made at symposia given on this problem at the American Geophysical Union, San Francisco, December 12, 1974; at the American Chemical Society, Philadelphia, April 9, 1975; at I. A. G. A. in Grenoble, France, August 29, 1975.

The following articles concerning stratospheric chlorine chemistry were published during the contract year:

- (1) Predicted Present Stratospheric Abundances of Chlorine Species from Photodissociation of Carbon Tetrachloride, *Geophysical Research Letters*, 1, 205 (1974), Mario J. Molina and F. S. Rowland.

The abundances of ClX (HCl, ClO, Cl) in the stratosphere should be nearly in equilibrium with the CCl₄ concentration of the troposphere because CCl₄ has been present in the earth's atmosphere for 30-50 years (or much longer if of natural origin). These stratospheric abundances approach a mixing ratio of 10⁻¹⁰, and are almost within the range of detection of present instrumentation. Measurement of the ¹⁴C concentration of atmospheric CCl₄ may identify whether its origin is natural or anthropogenic.

- (2) Some Unmeasured Chlorine Atom Reaction Rates Important for Stratospheric Modeling of Chlorine Atom Catalyzed Removal of Ozone, *Journal of Physical Chemistry*, 79, 667 (1975), Mario J. Molina and F. S. Rowland.

Calculations were made of the possible importance of these three reactions for the stratospheric ozone problem:



(3) Quantum Yield for the Photolysis of CF_2Cl_2 in O_2 , Journal of Physical Chemistry, 79, 669 (1975), Richard Milstein and F. S. Rowland.

The quantum yield for decomposition of CF_2Cl_2 was measured to be 1.0 at 1849 Å, indicating complete photodissociation is to be expected in the stratosphere.

Several other papers are nearly completed, with the following titles:

(4) The Stratospheric Chemistry of Cosmogenic Chlorine Radionuclides.

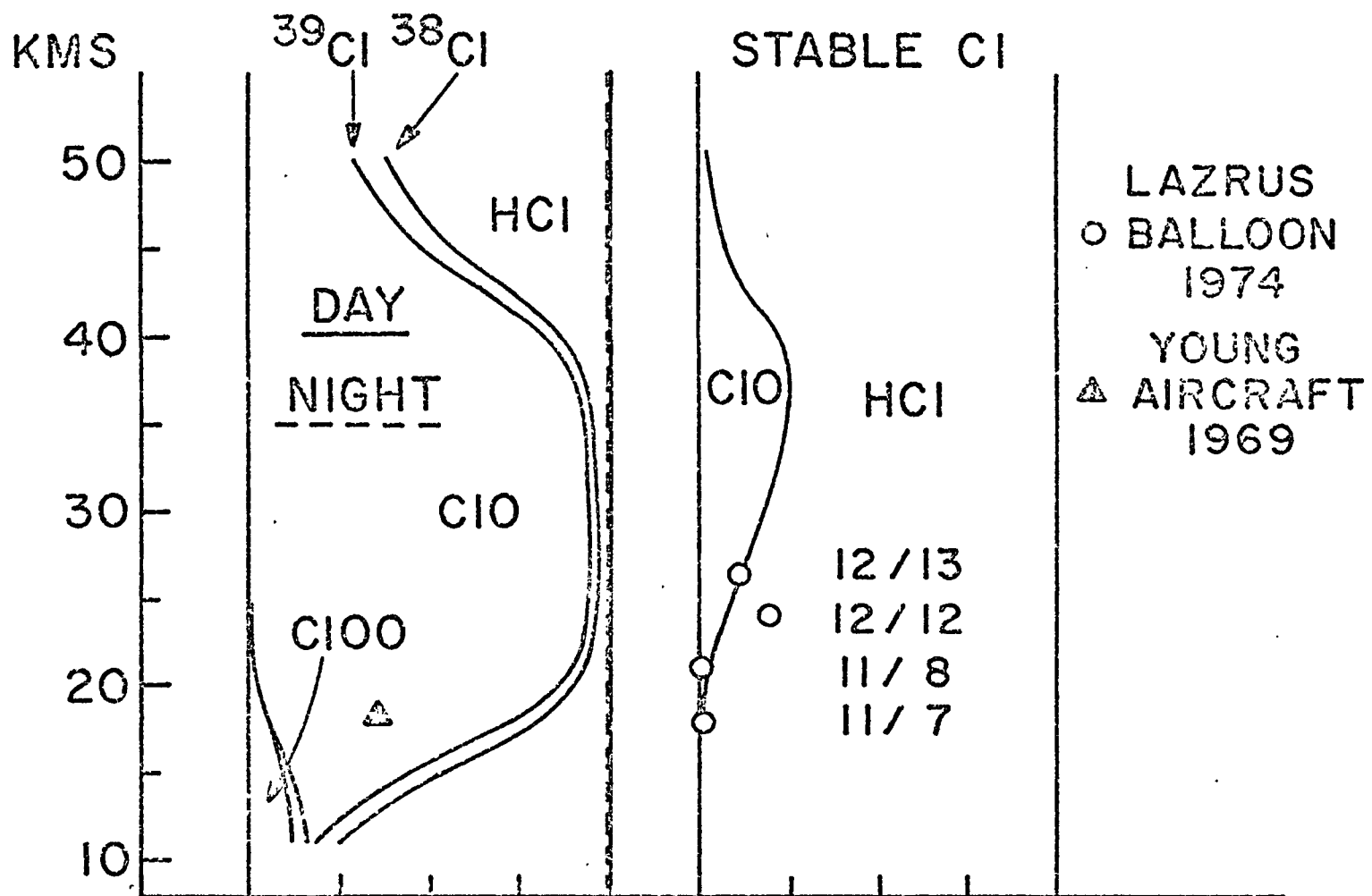
The significance of this paper is summarized in Figure 1, which shows the differences expected in the chemistry of cosmogenic ^{38}Cl and ^{39}Cl from that of stable chlorine. The chemical reactions are the same, but the radiochlorine isotopes do not form HCl at most altitudes because they decay before reaction occurs. Some useful stratospheric experiments are suggested involving measurements with ^{38}Cl and ^{39}Cl .

(5) Stratospheric Photodissociation of Several Chlorofluorocarbon Compounds of Current Technological Interest--Fluorocarbons 13, 113, 114, 115.

The stratospheric removal processes and atmospheric residence times have been calculated for several molecules which parallel CCl_2F_2 and CCl_3F in composition. These include CClF_3 (FC-13), $\text{CCl}_2\text{FCClF}_2$ (FC-113), $\text{CCl}_2\text{FCCl}_2\text{F}$ (FC-114), CClF_2CF_3 (FC-115). FC-113 is removed primarily by direct photolysis, but reaction with $\text{O}(^1\text{D})$ is also important for FC-114, and is dominant for FC-13 and FC-115 because of the very low photochemical absorption cross-sections.

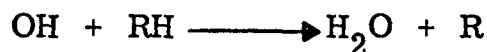
All of these molecules are predicted to have long lifetimes in the atmosphere.

FIGURE 1



(6) Relative Stratospheric Chlorine Releases from Chlorofluorocarbon Compounds--
 CHClF_2 , CHCl_2F , and CH_2ClF

The chlorofluorocarbon compounds containing C-H bonds can be removed from the atmosphere by the reaction

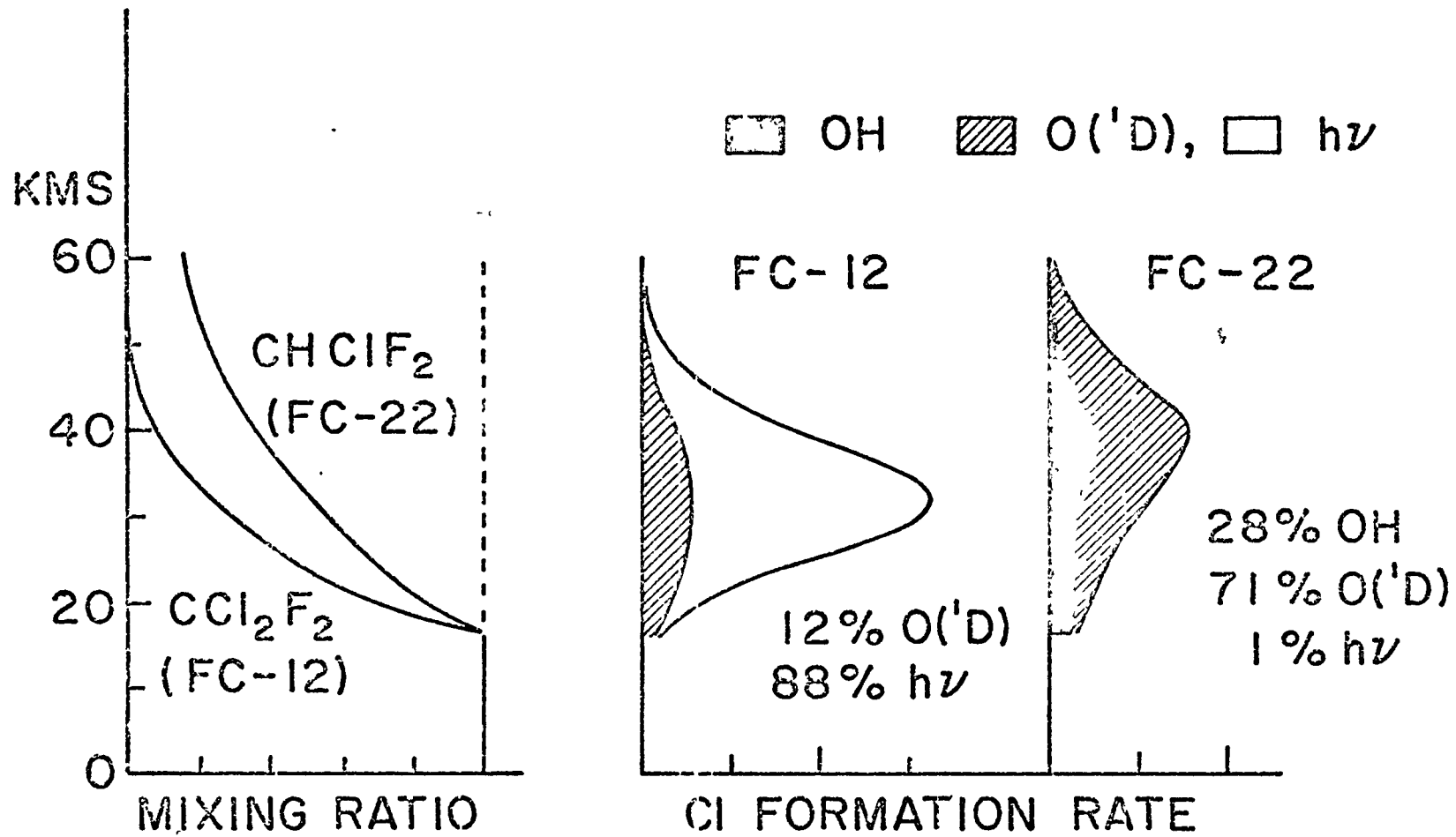


occurring in the troposphere, and consequently have much shorter atmospheric lifetimes than molecules without C-H bonds. Since many such molecules are already in widespread technological use, the lesser stratospheric hazard makes them desirable as substitutes for the more hazardous CCl_2F_2 and CCl_3F .

Figure 2 illustrates the processes removing CHClF_2 (FC-22) in the stratosphere--predominantly attack by $\text{O}({}^1\text{D})$. However, since its tropospheric lifetime is only about 10 years, it is less hazardous in the stratosphere than CCl_2F_2 by about a factor of 15-25. With a stratospheric lifetime of 100 years for CCl_2F_2 , the steady state concentration ratio of $\text{CHClF}_2/\text{CCl}_2\text{F}_2$ for equal input rates would be $10/100 = 0.1$. The Cl release rate (1 atm in CHClF_2 , 2 in CCl_2F_2) would lower this to $1/20$, and the differences in amount decomposed around 35-45 kms would make it about $1/30$ -or 30 times less hazardous for CHClF_2 than CCl_2F_2 . With outside limits of 14 years for CHClF_2 and 70 years for CCl_2F_2 , the factor is about 15.

For CHCl_2F and CH_2ClF , the stratospheric hazard is even less.

FIGURE 2



(7) Subsequent Reactions of CF_2O Formed in the Stratosphere by Photolysis of CCl_2F_2 .

The absorption cross-sections for CF_2O have been measured in the 1850-2250 Å range, and its rate of photodissociation calculated as a function of altitude. The absorption is small enough that the CF_2O lifetime at each altitude is relatively long. Appreciable fractions of CCl_2F_2 already photolyzed in the stratosphere should still be present now as CF_2O . Stratospheric spectroscopic searches should be directed toward both CF_2O and HF. Figure 3 shows the expected distributions with altitude for CF_2O and HF in 1975 for two different eddy diffusion coefficients.

(8) Stratospheric Eddy Diffusion Coefficients as Tested by Stratospheric Measurements of CCl_3F and CCl_2F_2 .

The measurements of CCl_2F_2 and CCl_3F versus altitude in the stratosphere agree quite well with the predictions for this profile made in July, 1974, as shown in Figure 4. The differences between a steady-state model (solid line) and a time-dependent model (dotted line) are negligible.

Calculations with several choices of eddy diffusion coefficients all agree reasonably well with the observational data, as in Figure 5, permitting no choice among them. These same diffusion models predict quite different fluxes of dissociated ClX (HCl, ClO, Cl), as indicated by the variations in the models in Figure 6. However, no ClX flux data are available.

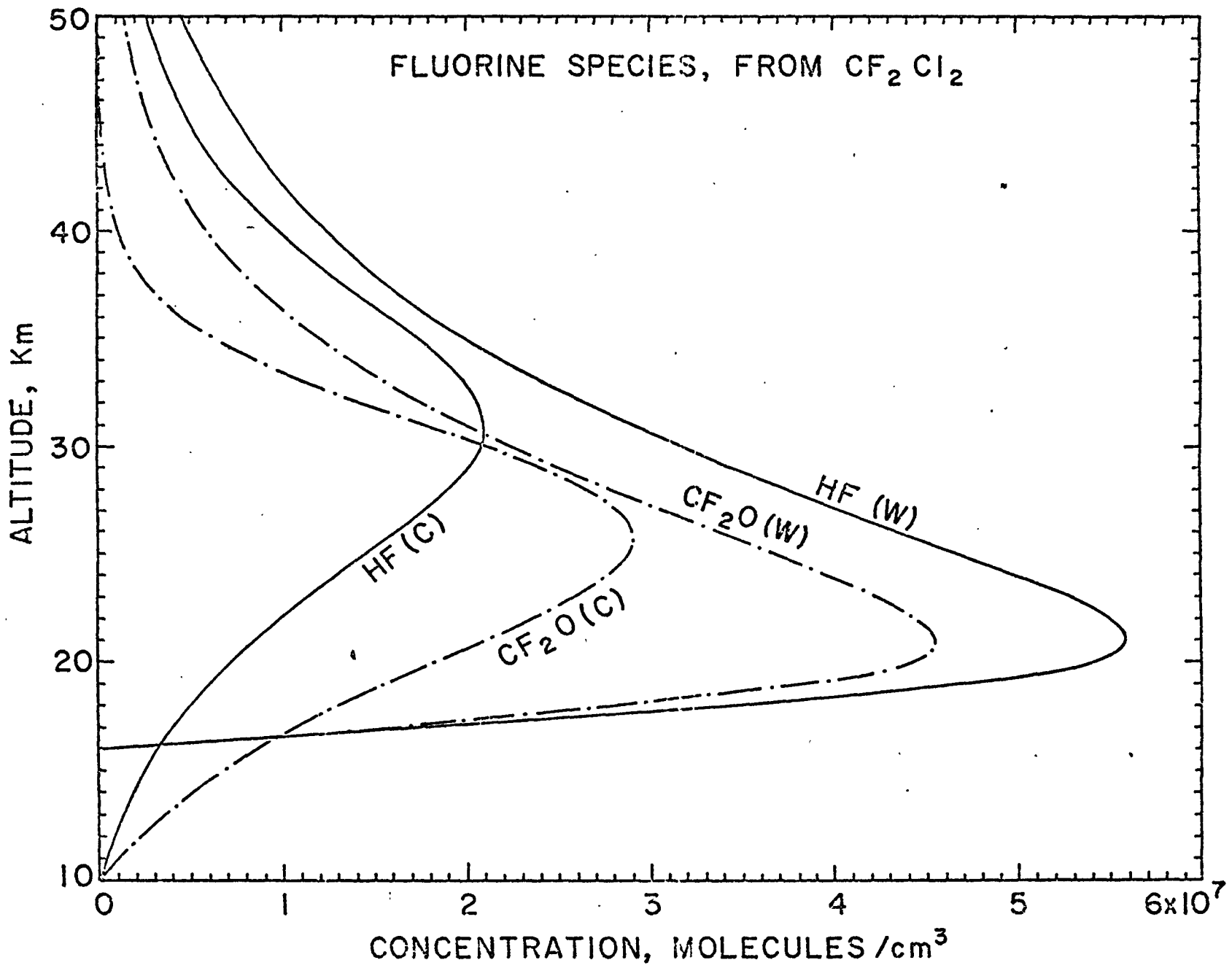
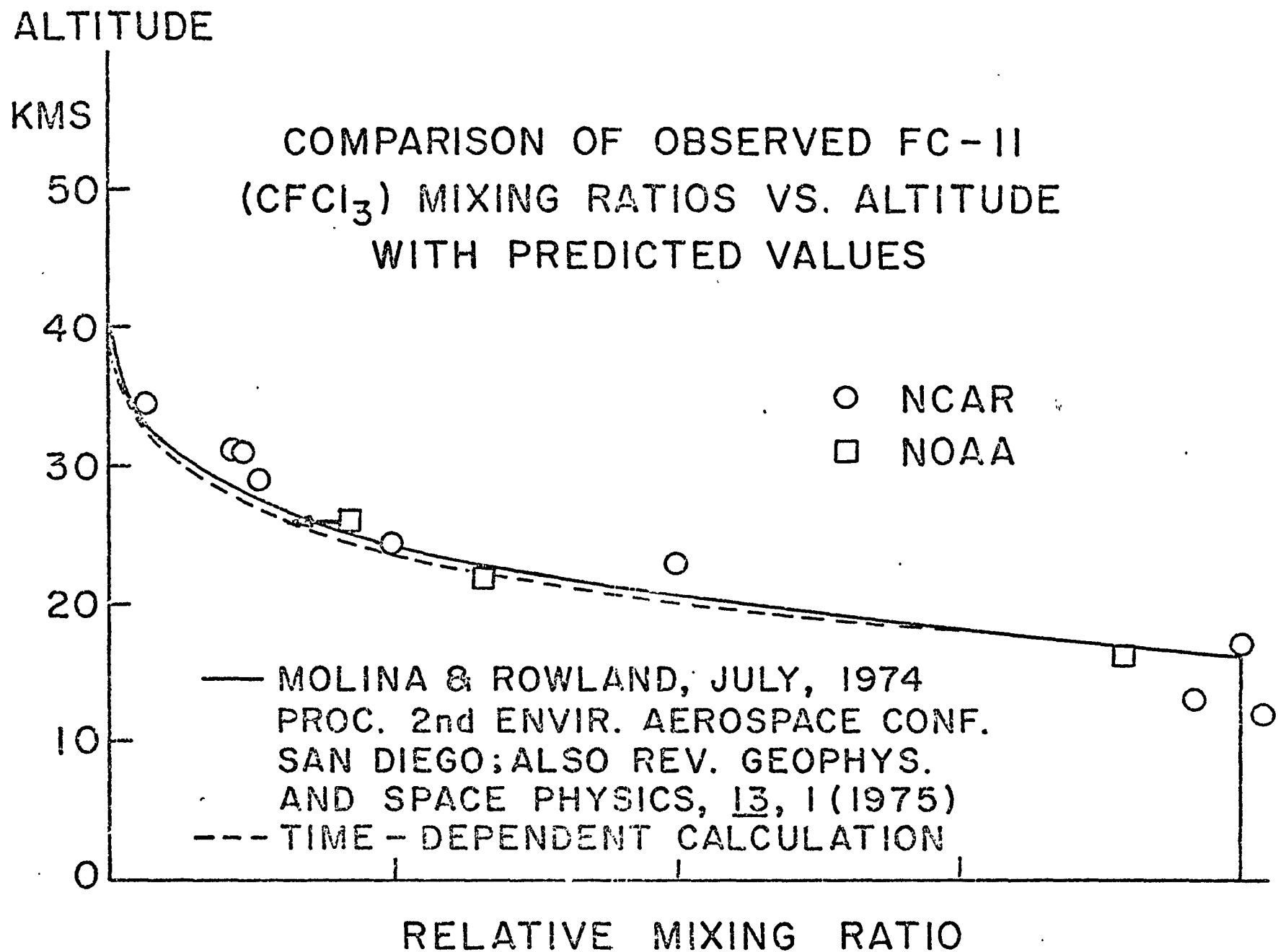


FIGURE 3

COMPARISON OF OBSERVED FC-II
(CFCI₃) MIXING RATIOS VS. ALTITUDE
WITH PREDICTED VALUES

Figure 4



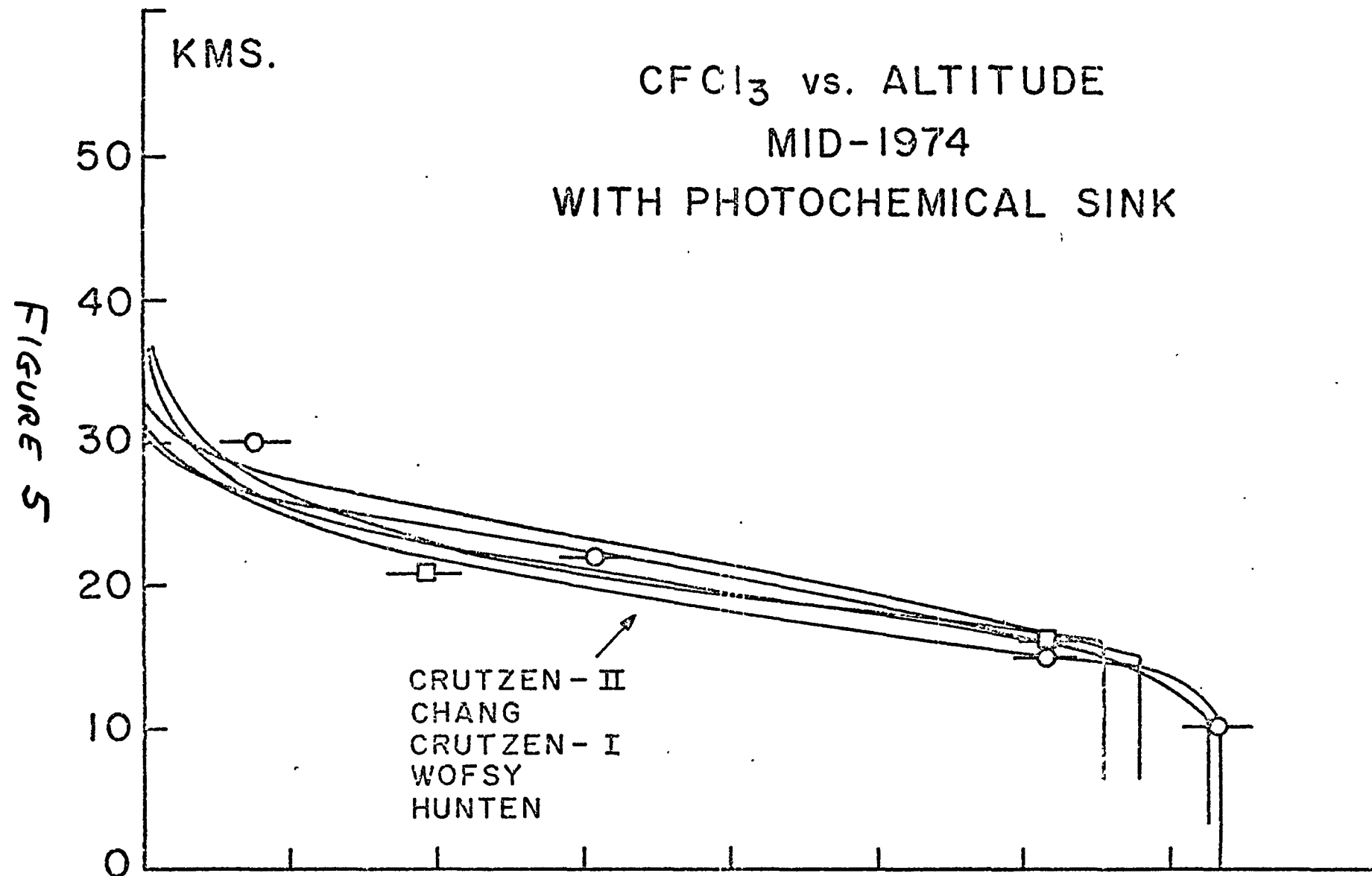
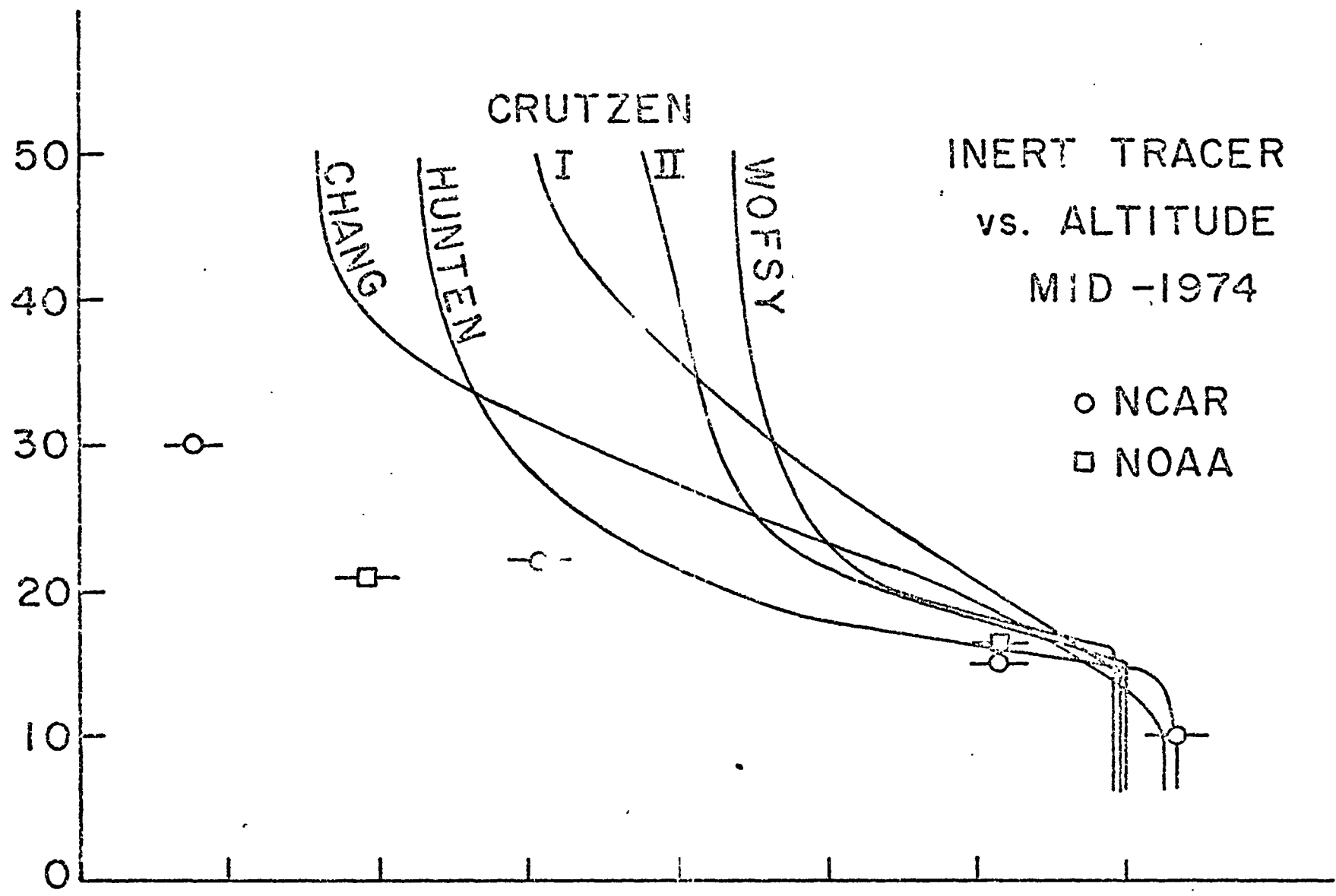


Figure 6



(9) Estimated Atmospheric Residence Times for Chlorocarbons and their Contributions to Stratospheric Chlorine Atom Concentrations

The atmospheric residence time for chlorocarbons containing C-H and/or C=C bonds has been estimated from the amounts present in the atmosphere (Figure 7) and the ratio of concentrations in the northern to southern hemispheres (Figure 8). These measurements give a good approximation for global average tropospheric OH concentrations.

FIGURE 7

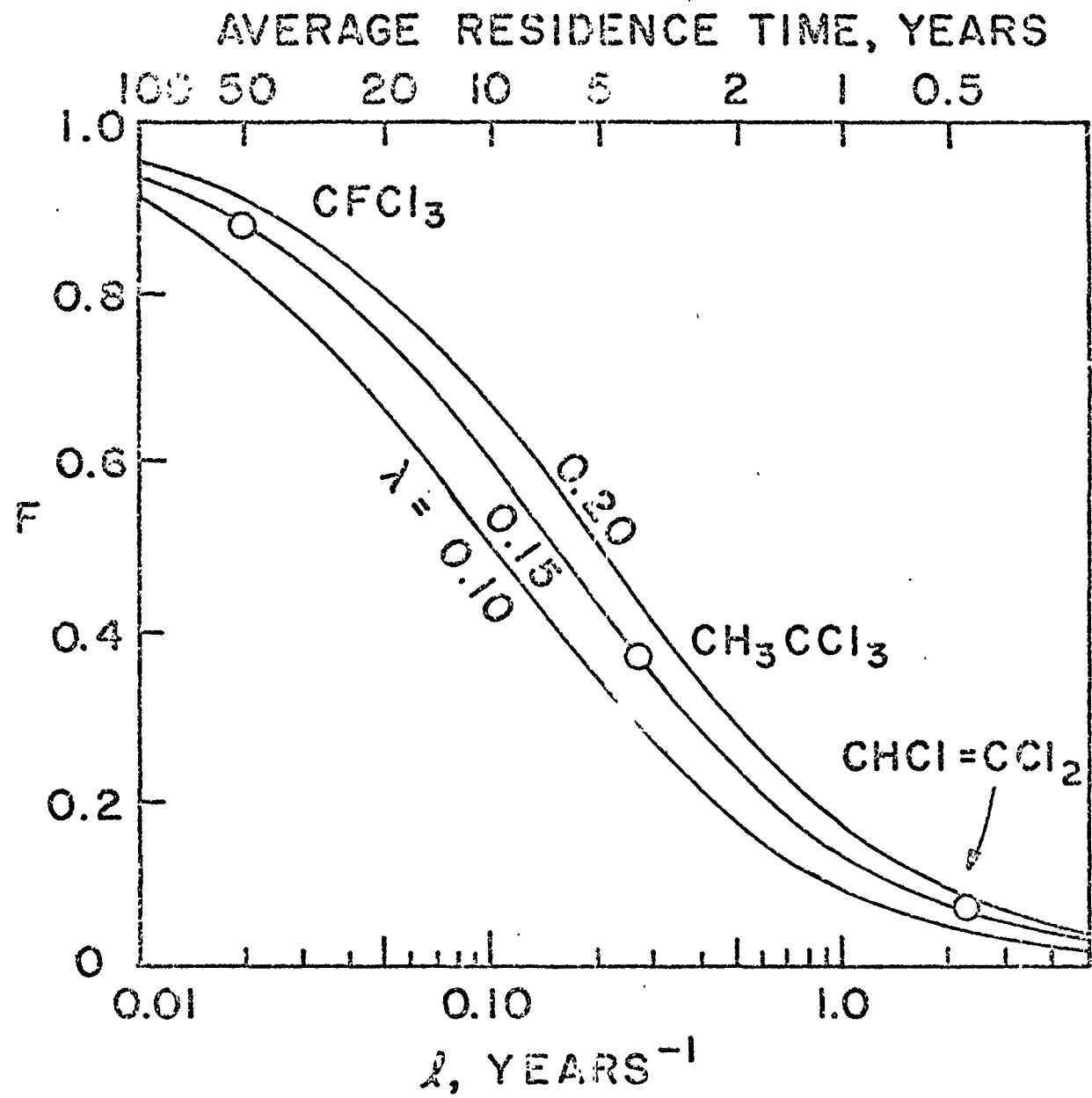
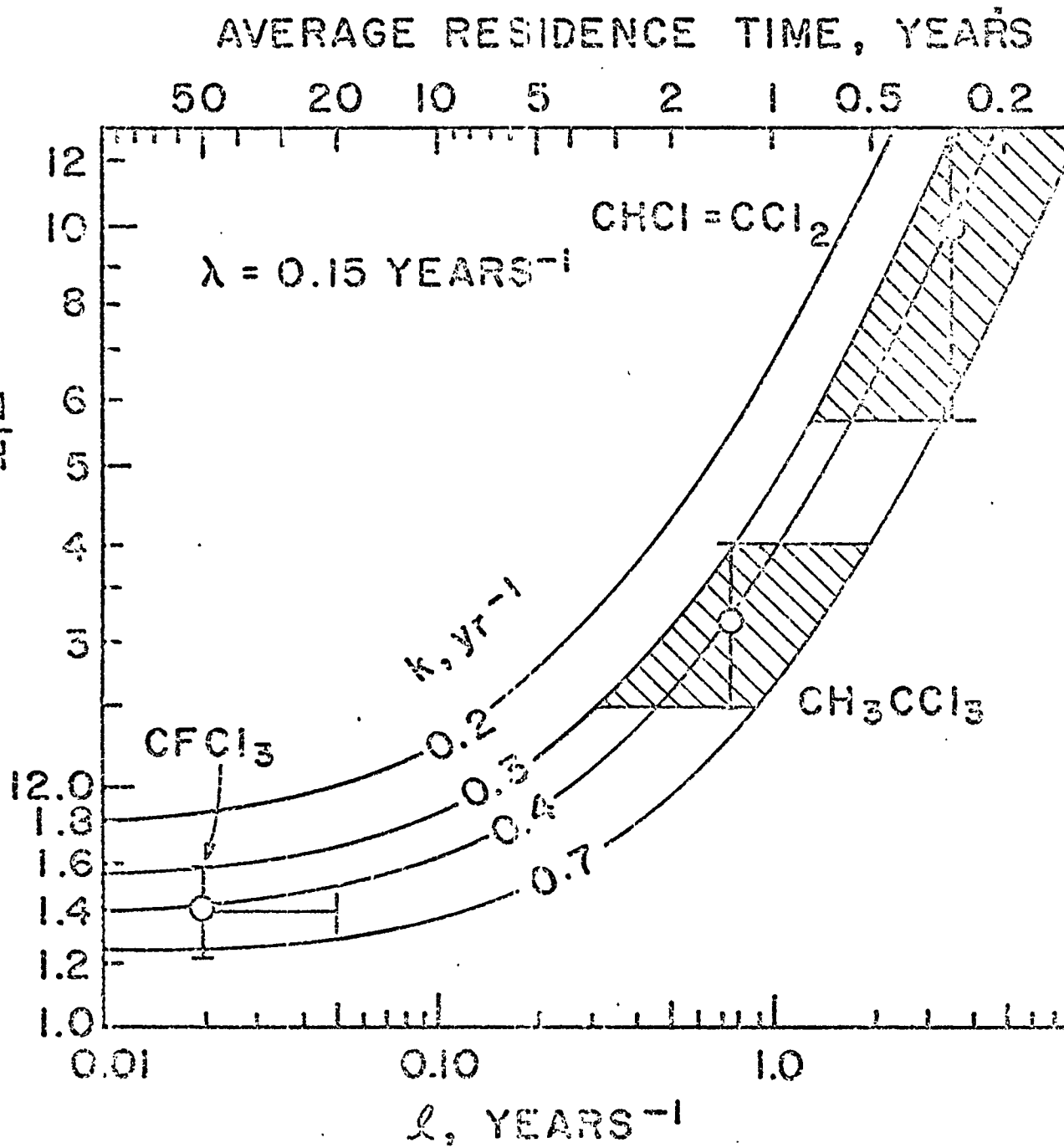


FIGURE 8



II. (B) Several papers about various aspects of hot atom chemistry have either been published or are in press. Progress in publication of our results in the past 2 or 3 years has been especially slow this year because of the press of work on the fluorocarbon/ozone problem. Abstracts of these papers are given in the succeeding pages.

(1) GAS PHASE REACTIONS OF ATOMIC TRITIUM,
 FLUORINE AND CHLORINE

Proceedings of I. A. E. A. Panel on Chemical Effects of Nuclear Transformations
Vienna, to be published.

F. S. Rowland

ABSTRACT

The hot atom reactions of tritium, chlorine and fluorine were reviewed with special emphasis on stereochemistry of substitution, excitation energies of products, substituent influences on reactions, bond energy effects and thresholds.

(2) GAS PHASE FLUORINATION OF BENZENE, FLUOROBENZENE,
m-DIFLUOROBENZENE AND TRIFLUOROMETHYLBENZENE
BY REACTIONS OF THERMAL ^{18}F ATOMS

Journal of the American Chemical Society

John A. Cramer and F.S. Rowland

ABSTRACT

Thermal fluorine-18 atoms have been reacted in the gas phase with benzene, fluorobenzene, m-difluorobenzene, and trifluoromethylbenzene. The ^{18}F atoms were formed at high kinetic energies by the $^{19}\text{F}(n, 2n)^{18}\text{F}$ nuclear reaction, and then thermalized by multiple collisions with SF_6 . The yields of $^{18}\text{F}/\text{H}$ are small, and pressure-independent in the absence of oxygen. With O_2 present, the yields increase substantially, reaching > 60% for $\text{C}_6\text{H}_5^{18}\text{F}$ from C_6H_6 . The yield from substitution of thermal ^{18}F for H ortho to another F substituent is decreased by O_2 , while that in meta and para positions is substantially increased. No such diminution of yield in the ortho position is found for CF_3 as a substituent. The substitution of thermal ^{18}F for aromatically-bonded F atoms is observed in low yields only.

(3) MOLECULAR ACTIVATION ANALYSIS

Proceedings of I. A. E. A. Panel on Chemical Effects of Nuclear Transformations Vienna, to be published.

Patrick M. Grant and F.S. Rowland

ABSTRACT

Thermal neutron capture by ^{37}Cl forms radioactive ^{38}Cl in the close vicinity of the original ^{37}Cl site. In standard neutron activation analysis procedures, only the total amount of ^{38}Cl formed -- and thereby the number of ^{37}Cl atoms present -- is determined, while the physical location and molecular form of the ^{37}Cl in the sample is not measured. The organic nature of the ^{37}Cl -containing molecular target has been demonstrated for trace solutions (0.3 to 500 PPM) of chloranilic acid in water through neutron irradiations of the frozen ice at -196°C . Approximately 12% of all of the ^{38}Cl is separable as organically bound at all concentrations. In comparable samples irradiated as liquids at 20°C , the organically-bound product yield rapidly decreases to zero with decreasing concentration. Negligible yields of organically-bound ^{38}Cl are formed when ^{37}Cl is originally present as chloride ion.

Molecular neutron activation analysis may be useful in the determination of organically-bound chlorine, such as that found in pesticide residues.

Three additional reports have been presented to the American Chemical Society meeting in Chicago, August, 1975.

(1) ISOTOPE EFFECTS IN THE DECOMPOSITION OF $C_2H_4^{18}F^*$ and $C_2D_4^{18}F^*$ RADICALS FOLLOWING ADDITION OF THERMAL ^{18}F TO ETHYLENE.

Joan P. Frank, Fleet Rust and F. S. Rowland

Thermalized ^{18}F atoms moderated in an excess of an inert molecule (e. g. $SF_6/NF_3/CF_4/C_2F_6$) after formation by the $^{19}F(n, 2n)^{18}F$ reaction have been reacted with C_2H_4 and with C_2D_4 in the presence of HI. The decomposition/stabilization ratio ($CH_2=CH^{18}F$ vs. $CH_3CH_2^{18}F$; $CD_2=CD^{18}F$ vs. $CD_2HCD_2^{18}F$) has been measured for each fluoroethyl radical and the isotopic ratio of half-stabilization pressures for the two radicals in each moderator has been determined.

A two-part theoretical calculation of the rate constants for decomposition of fluoroethyl radical and its deuterated counterpart has been executed for purposes of comparison with the experimental results: A) The frequencies of both radicals have been calculated using a computer program based on Wilson's FG matrix method. For this a knowledge of the atomic masses, geometries and valence force constants for both fluoroethyl radicals and for both critical complexes was necessary. This approach ensures that the frequencies of the isotopic species obey the Teller-Redlich product rule. B) The decomposition rate constants were obtained using the general RRKM computer program. Moments of inertia and detailed thermochemical information were also required.

The significance of the excellent agreement between theory and experiment will be discussed.

(2) THE TRACER REACTIONS OF ^{38}Cl ATOMS IN THE GAS PHASE
STUDIED BY A NUCLEAR RECOIL METHOD.

Frank S. C. Lee and F. S. Rowland

Energetic ^{38}Cl atoms formed via the $^{37}\text{Cl}(n, \gamma) ^{38}\text{Cl}$ nuclear reaction in the gas phase, and are thermalized by multiple moderating collisions with CF_3Cl or CF_2Cl_2 in excess. These thermalized ^{38}Cl atoms can then react with minor amounts of substrate molecules included in the sample.

Studies on the addition of ^{38}Cl to ethylene, acetylene and propylene will be reported in detail. The addition reaction leads to excited adduct radicals, which competitively either are stabilized by collision or else decomposed by ^{38}Cl loss. After H abstraction from HI, the stabilized radicals have been identified as the corresponding saturated molecules. The half-stabilization pressure (in Torr) for the radicals are $\text{C}_2\text{H}_4 ^{38}\text{Cl}$ (800 ± 120), $\text{C}_2\text{H}_2 ^{38}\text{Cl}$ (840 ± 80) and $\text{C}_3\text{H}_6 ^{38}\text{Cl}$ (<200), respectively. Direct competition experiments between C_2H_4 and C_2H_2 show that the rate of addition to C_2H_4 is 1.49 ± 0.02 times faster than such addition to C_2H_2 . Both $\text{CH}_3\text{CH}^{38}\text{ClCH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2 ^{38}\text{Cl}$ are observed from addition to propylene, with terminal addition favored by a factor of ≥ 6

Mechanistic and stereochemical studies on the addition of ^{38}Cl to several other unsaturated molecules, will be briefly discussed. The formation of $\text{CH}_3 ^{38}\text{Cl}$ by reaction with gaseous molecules such as $\text{Sn}(\text{CH}_3)_4$ and $\text{Pb}(\text{CH}_3)_4$ has also been observed. The advantages of thermalized nuclear recoil atoms for the study of atomic chlorine reactions will be summarized.

(3) PRODUCTION OF ^{18}F USING ENERGETIC NEUTRONS
FROM THE LAMPF BEAM STOP

R. S. Iyer, W. S. Smith, P. Grant, and F. S. Rowland

The energetic neutrons produced at the LAMPF (Los Alamos Meson Physics Facility) proton beam stop offer the possibility of investigating the chemistry of atomic fluorine using the $^{19}\text{F}(n, 2n)^{18}\text{F}$ reaction. At full beam current (mA) this method might prove to be of potential application for the synthesis of mCi levels of ^{18}F -labelled radiopharmaceuticals. In our preliminary experiments we have irradiated gas samples containing excess (>90%) SF_6 with one of the following substrate molecules: C_2H_2 , C_2H_4 , $\text{CH}_3\text{CH}\equiv\text{CH}_2$, C_6H_6 , and $\text{C}_6\text{H}_5\text{F}$. HI or O_2 scavengers were also included in order to observe the extent of radiation damage in the samples.

The average proton beam currents for these irradiations were $\sim 5 \mu\text{A}$. The yields of ^{18}F -labelled products from each of these systems have been measured by radio gas chromatography. The results are compared with those previously obtained in our experiments using a Kaman A-711 neutron generator. The results obtained at LAMPF resemble the neutron generator runs and no additional ^{18}F -labelled products were observed. It was concluded that appreciable amounts of radiation damage have not been produced at the $5 \mu\text{A}$ level.