ORO-3106-54

"RADIATION CHEMISTRY OF HYDROCARBON AND ALKYL HALIDE SYSTEMS"

PROGRESS REPORT

ROBERT J. HANRAHAN

UNIVERSITY OF FLORIDA
GAINESVILLE, FLORIDA

JULY 1, 1974 - JULY 31, 1975

PREPARED FOR

THE U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
UNDER CONTRACT NO. AT-(40-1)-3106

I. Introduction

This report describes the progress of our research during the period July 1, 1974 through July 31, 1975. During this period, two papers were published in the Journal of Physical Chemistry[1,2] and one in the Journal of Chemical Physics;[3] ~~Reprints are included with this report~~. Two manuscripts have been written dealing with recently completed work,[4,5] and will be submitted for publication in the near future. ~~Preprints of these manuscripts are also included with the report~~. A contributed paper was presented at the Southeastern Regional Meeting of the American Chemical Society in October 1974, and an invited paper was given at the Eighth Caribbean Chemical Congress held in Georgetown, Guyana, in January 1975. Additional papers have been submitted for the 170th National Meeting of the American Chemical Society in August 1975, and for the First All North American Chemical Congress to be held in Mexico City in late November.

Due to a grant from the University of Florida Division of Sponsored Research, we were able to acquire a major new instrument for the use of the radiation chemistry group, a Febetron 706 pulsed electron accelerator. Several accessories for use in pulse radiolysis experiments have also been obtained. Negotiations for reloading of our Cobalt 60 gamma irradiator to its 600 curie capacity were completed in the fall of 1974, and the new source was installed in May 1975.

II. Progress of Experimental Work

A. Gas Phase Radiolysis of C_2F_6 - C_2H_6 Mixtures

Previous work on this system is summarized in our annual reports of 1972, 1973, and 1974,[6-8] as well as in abstracts of papers presented at the 21st Annual Meeting of the Radiation Research Society, St. Louis, 1973 and at the 5th International Congress of Radiation Research, Seattle, 1974.[9,10]

Work completed during the past year includes measurement of the effect of 10% added oxygen on major products of the radiolysis (H_2, CH_4, C_2H_2, C_2H_4, C_3H_8, and C_4H_{10}, CF_3H, and C_2F_5H) in the pure fluorocarbon, pure hydrocarbon, and five intermediate compositions. Results of this work are presented in Figures 1 - 3. Additionally, the yields of HF, both with and without added oxygen, were measured at five mixture concentrations. These results are shown in Figure 4.

We will not present a detailed discussion of these results at this time, since final write up of the work is currently in progress. It will be noted, however, that n-butane is decreased to the extent of about 85% by added oxygen, propane by about 60%, methane by about 50%, and hydrogen by 40%. The yield of CH_3CF_3 and CF_2CH_2 are completely eliminated, indicating that these products arise exclusively by radical-radical reactions. The yield of ethylene increases five fold with added oxygen, and acetylene three fold; probably, oxygen protects these products from further attack by free radicals species. The yields of HF, CF_3H, and C_2F_5H are essentially unaffected by 10% added oxygen. On the basis of related mass spectrometric work from this laboratory,[3] we strongly suggest that CF_3H and C_2F_5H are formed via hydride ion

transfer from C_2H_6 to CF_3^+ and $C_2F_5^+$ ions, respectively. Consistent with this interpretation, yields of both of these products maximize when about 90% of the energy is deposited in C_2F_6, and the yield decreases essentially in "direct effect" fashion as the fluorocarbon is diluted with added hydrocarbon. We believe that the HF yield is a simple hydrogen atom abstraction reaction; fluorine atoms are such a vigorous reagent that the hydrocarbon substrate is essentially a "scavenger" as far as fluorine atoms are concerned. It is reasonable that added oxygen would have little net effect on the production of HF from this process, although there may be some transient formation of a fluorine - oxygen complex.

B. Gas Phase Radiolysis and Photolysis of Ethyl Bromide

Work on this system was completed in February 1975. Two manuscripts, dealing respectively with the photolysis and radiolysis of ethyl bromide, have recently been completed and are included with this report.[4,5] Although these manuscripts can be consulted for a detailed discussion of our work on this subject, we give a few highlights of our results below.

At short light exposure, photolysis of ethyl bromide at 253.6 nm gives hydrogen bromide as a major product (the initial quantum yield equals 0.36). The complementary product ethylene is also found with a maximum quantum yield at short photolysis time, but a straightforward material balance is not observed; the initial quantum yield of ethylene is only 0.03. At long photolysis times, both HBr and ethylene reach plateau values, and the major products are C_2H_6 and a mixture of 1,1 and 1,2 dibromoethanes. We suggest that there are two main elementary reactions in ethyl bromide photolysis, giving $C_2H_5^{\cdot}$ + Br·, and C_2H_4 + HBr, respectively. Production of CH_4 and CH_2Br_2 provides evidence for a minor

process involving rupture of the C-C bond. Accordingly, this photolysis system involves an elaborate steady state kinetic competition involving HBr, Br·, Br_2, C_2H_4, and substrate ethyl bromide, which is subject to free radical attack. We attempted an analysis of the steady state kinetics using numerical integration on an IBM 370-165 computer. Results were not completely successful, but were sufficiently encouraging to suggest that the reactions scheme includes a majority of the relevant processes.

The radiolysis of ethyl bromide is remarkably similar to the photolysis; in both cases, no net Br_2 is formed, although (as suggested above) it is probably present at low concentration under steady state conditions. All of the main products seen in the photolysis are also observed under radiolysis conditions; indeed, the shape of yield-dose graphs are similar in most cases. Additional products from the radiolysis include hydrogen and acetylene; it is clear that production of these species involves high energy reaction pathways, not accessible in the 253.7 nm photolysis. An examination of known ionic fragmentation pathways and established ion-molecule reactions in the ethyl bromide system gives a straightforward interpretation of the differences observed between the photolysis and the radiolsis of this system.

The results of our investigation of the radiolysis of ethyl bromide form the basis of an interesting comparison with work published earlier by Schindler and others on ethyl chloride and iodide.[11,12] Although a manuscript on this subject has not been prepared for publication, the comparison between the radiolytic behavior of the the three compounds is discussed at some length in the Ph.D. dissertation of Dr. Arthur J. Frank.[13]

C. Radiolysis and Mass Spectrometry of CF_3I and C_2F_5I.

Identification of major and minor products from the gamma radiolysis of C_2F_5I, and quantitative measurement of radiolytic yields, is nearly complete. Result of our work to date are summarized in Table 1. Some additional work is necessary on the measurement of relative flame ionization detector response of the various products. Although several of the needed compounds are available as standards, simple syringe injection into the gas chromatograph is impractical due to the fact that these compounds cause a severe skin allergy. An indirect procedure involving vacuum line preparation of standards is being carried out. A study of the behavior of this radiolysis system in the presence of a free radical scavenger will be undertaken in the near future; we will probably utilize hydrogen iodide, since it reacts in a straightforward fashion, furnishing a hydrogen atom to the radical site.

Quantitative experiments on the radiolysis of CF_3I have not yet been accomplished, but identification of major and minor radiolysis products is complete. Products observed include CF_4, C_2F_6, C_2F_4, C_3F_8, C_2F_5I, C_2F_3I, CF_2I_2, and I_2. Three of these products (C_3F_8, C_2F_5I, and C_2F_3I) had not been reported by earlier workers.[14,15]

A discussion on ion-molecule reactions of C_2F_5I as studied by high pressure time-of-flight mass spectrometry was included with the 1973 Annual Report.[7] Recently, the opportunity arose to carry out studies of ion-molecule reactions in CF_3I and C_2F_5I using a Varian Model V 5900 ICR mass spectrometer in the laboratory of Prof. John Eyler of the U.F. Department of Chemistry. Tables 2 and 3 indicate reaction pathways definitely established or inferred, on the basis of ICR single resonance, ICR double resonance (ICDR), or high pressure

time-of-flight mass spectrometry (in the case of C_2F_5I). It is noteworthy that a number of the reactions definitely identified by the ICDR technique would be endoergic for ground state ions. The energy deficit is high as 20 to 30 kcal/mole in some instances. Marcotte and Tiernan[16] reported previously on the participation of excited reactant ions during ion-molecule reactions of fluorocarbon species. It appears that attempts to calculate bond energies in fluorocarbon systems, using the assumption that all observable ion-molecule reactions must be exothermic or thermoneutral, are of doubtful validity.

In the case of C_2F_5I, the ICR, ICDR, and high pressure time-of-flight measurements appear to be straightforward and in good agreement. There is an anomaly, however, concerning the reaction pathways confirmed for CF_3I by the double resonance technique, on the one hand, and straightforward measurements of relative ion intensities using single resonance techniques, on the other hand. Several measurements taken by the latter technique are shown in Figure 5. It should be noted that there is a sharp decrease of the intensity of CF_3I^+ between 1×10^{-6} and 2×10^{-5} torr, and a clearly correlated increase in the intensity of CF_3^+ over the same pressure range. This observation strongly suggests a reaction channel in which CF_3I^+ disappears and CF_3^+ is formed. Surprisingly, the reaction demonstrated by ICDR, and listed in Table 2 has exactly the opposite consequence -- CF_3^+ interacts with parent CF_3I, and CF_3I^+ is formed. We are forced to conclude that a collisionally induced dissociation of CF_3I^+ must occur. It is necessary to assume that the CF_3I^+ is excited either vibrationally or electronically, so that the dissociation process would be nearly thermoneutral, since the reaction is not seen by the double resonance technique.

D. Radiolysis, Photolysis, and Mass Spectrometry of Tetrafluorocyclobutane

A study of ionization and appearance potentials of fragment ions from 1,1,2,2-tetrafluorocyclobutane was completed last year; the results have been published, and a reprint is included with this report.[2] We have also carried out a series of experiments on ion-molecule reactions in this system, using both high pressure time-of-flight mass spectrometry and ion-cyclotron techniques. Typical ion intensity graphs are shown in Figure 6, and related kinetic plots in Figure 7.

There is an interpretational difficulty with the high pressure work, since the overall mass spectra seen at the lowest usable pressures in our ion-molecule reaction source (approximately 5 microns) are significantly different from those seen under normal analytical conditions (about 10^{-6} torr). Relative intensities of $C_2F_4^+$ and $C_2H_2F_2^+$ are quite small at 5 microns, whereas the relative intensity of $C_2H_4^+$ is very large compared with the normal 10^{-6} torr spectrum. The system seems to be well behaved, and gives reasonable kinetic plots (Figure 7). We can only suggest that $C_2F_4^+$ and $C_2H_2F_2^+$ undergo efficient charge transfer reactions with the parent tetrafluorocyclobutane. In the reactions observed in the 5-40 micron pressure regeim (Figure 6), $C_2H_4^+$ is a reactant ion, and is destroyed with concommitant formation of $C_2F_4^+$ and $C_2H_2F_2^+$. There are also a number of interesting high molecular weight ions in this system, as seen by time-of-flight mass spectrometry and/or ICR techniques. The following two reaction channels have been identified by the ICDR method:

$$C_2H_2F_2^+ + c\text{-}C_4H_4F_4 \longrightarrow C_5H_6F_4^+ + CF_2$$

$$C_2H_2F_2^+ + c\text{-}C_4H_4F_4 \longrightarrow C_6H_6F_6^+$$

The second reaction was seen in both time-of-flight and ICR

experiments, and the first only by ICR. An ion of mass 164, corresponding to $C_4H_2F_6^+$, was seen only in the time-of-flight mass spectrometer; the route to its formation had not yet been identified.

We have also completed a series of investigations of the gamma radiolysis of tetrafluorocyclobutane, with and without added oxygen. The results of this work are presented in Table 3. It will be seen that a large number of products are formed, but the majority of the observed G values are quite small. A similar pattern was seen in the radiolysis of the related compounds cyclobutane and perfluorocyclobutane.[16,17] In all three cases it appears that a portion of the olefinic yield undergoes polymerization and is deposited on the vessel walls. Consistent with this suggestion, we found a marked evolution of fluorine containing organic fragments when a vessel which had been used for the radiolysis of tetrafluorocyclobutane was attached directly to the mass spectrometer and flamed strongly with a hand torch.

A number of measurements have also been made on the mercury sensitized photolysis of tetrafluorocyclobutane at 253.7 nm. Identification of both low and high molecular weight products has been completed, and yield-vs-photolysis time curves have been measured for low molecular weight species. Work remaining to be done includes yield measurements for the high molecular weight products, as well as HF measurements and scavenger studies. Upon completion of the photolysis, radiolysis, and mass spectrometric experiments, we expect to be in a position to make some reasonable suggestions concerning the overall mechanism of the radiolytic decomposition of tetrafluorocyclobutane.

E. Other Work

Since last summer, Dr. James Fanning has spent most of his time on reprogramming of our mass spectrometer data acquisition and reduction routines. The existing system was written shortly after we obtained our General Automation SPC 12 Minicomputer, and does not incorporate many improvements in software made since that time. In particular, it utilizes a double precision (15 bit + sign + exponent) floating point mathematics package, which is really not sufficiently precise for the data reduction computations. The new version will utilize our quadruple precision (31 bit + sign + exponent) mathematics package. In addition, we are making some changes in the data reduction algorithm, which is currently based upon a theoretically correct quadratic term and an arbitrary cubic term, added to correct for a known drift in the machine calibration with increasing mass. Recently, we have found that two separate quadratic expressions, splined together at approximately mass 130, are much more satisfactory. Other changes being made include provision for normalizing each spectral peak, as it is scanned, against the total ion intensity as measured on a separate electrometer unit design for this purpose. This correction is particularly convenient during MS-GLC experiments, since it allows normalizing out the chromatographic peak envelope. A further refinement being added is a provision for monitoring the total output intensity signal during GC runs, automatically initiating mass spectrometer scan if a GC peak is detected, and storage of the resulting spectrum on magnetic tape.

It was our original intention that Dr. Fanning would also undertake some experimental work concerning effects of oxygen on the radiolysis

of propane in the gas phase. Only limited progress was made in this direction, since the programming work has taken longer than expected. However, there has been some progress in this area, particularly reconstruction of a vacuum line and refurbishing of a gas chromatograph for the work. We expect to make good progress in this area during the fall months.

F. Facilities and Equipment

Improvements in laboratory facilities during the year include reloading of our Cobalt 60 gamma irradiator to its nominal capacity of 600 curies; negotiations for this work were completed in October 1974, and the source arrived in May 1975. An irradiator essentially identical to ours has recently been constructed by the research group of Prof. Phillip Achey in radiation biology, using the original working drawings for our facility. The new unit, which was installed on the ground floor of the Nuclear Science Center, was loaded at the same time as our irradiator, with corresponding saving in shipping cost. Since the two irradiators are essentially identical in geometry and intensity, they can be shared between both research groups, with a resulting evening of the work load. This is likely to be especially useful to the radiation chemistry group, since individual irradiations on gas phase systems frequently require from 10 to 50 hours.

A major addition to the facilities of the laboratory is a Febetron 706 pulse electron accelerator, purchased with funds made available by the University of Florida Division of Sponsored Research. This unit has been installed and tested, and we are now in the process of building up equipment to undertake experiments in the pulse radiolysis

of gases. To date, we have fabricated a sample chamber and obtained a Tektronix oscilloscope, an oscilloscope camera, and a 3 Kv. power supply, mostly from Government Surplus. A Biomation Model 8100 transient digitizer was purchased with contract funds. Remaining components of the photomultiplier light detection system will be ordered in the near future, and initial experiments should be undertaken by fall.

In order to afford components for the photomultiplier light detection system, we have put off the purchase of a new flame ionization electrometer, listed in the budget for the present year. It is possible that we will be able to get along without this item indefinitely, due to a shift of activities towards the pulse radiolysis area.

IV. Publications, Meetings Attended

In January, a paper dealing with the gas phase photolysis of carbon tetrachloride at 253.7, 184.9, 147.0, and 106.7 nm was published in the Journal of Physical Chemistry; co-authors are Drs. Douglas D. Davis, John F. Schmidt, and Charles H. Neeley.[1] Publication of this paper was quite timely, in light of considerable current interest in the pnotochemistry of the chlorofluoromethanes. We reported a substantial production of dichlorocarbene (CCl_2) from the photolysis of CCl_4 at 184.9 nm and lower wavelengths; it is very likely that CF_2 is formed in the photolysis of CF_2Cl_2, and possibly in the case of CF_3Cl. If this is so, it will be significant with respect to the potential ozone destroying reactions of these molecules in the stratosphere.

In Febraury a paper on ion-molecule reactions in the systems CF_4 - CH_4 and CF_4 - C_2H_6, co-authored by Prof. Edgar Heckel, was published in the Journal of Chemical Physics.[3] A paper with Mr. A.R. Ravishankara, on an electron impact investigation of 1,1,2,2-tetrafluorocyclobutane,

was published in the Journal of Physical Chemistry in April.[2] A paper on the same work was also read at the Southeastern Regional Meeting of the American Chemical Society in Norfolk, Virginia, in October 1974. Finally, Prof. Hanrahan attended the 8th Caribbean Chemical Congress in Georgetown, Guyana, in January, and gave an invited lecture on the radiolysis of fluorocarbon - hydrocarbon systems in a symposium organized by Prof. Larry Kevan.

Two manuscripts dealing with Dr. Arthur Frank's recently completed work on the photolysis and radiolysis of ethyl bromide in the gas phase have been completed, ~~and are included with this report.~~[4,5] Two papers dealing with this work have been submitted to the American Chemical Society 170th National Meeting in Chicago this September, and to the First All North American Chemical Congress in Mexico City this coming October, respectively.

Table 1. Yields in the Gamma Radiolysis of C_2F_5I

Product	G-Value[a]	Detector Response
CF_4	(3-4)[b]	4×10^{-4}
C_2F_4	1.16[e]	0.122
C_2F_6	0.298	0.186
C_3F_8	0.055	1
C_3F_6	0.369	0.695
C_4F_{10}	0.417[c,e]	1.095
CF_3I	0.196[e]	1.05
C_2F_3I	0.012	(2.10)[d]
n-C_3F_7I	0.028	(3.16)
i-C_3F_7I	0.001	(3.16)
n-C_4F_9I	0.005	(4.21)
i-C_4F_9I	0.014	(4.21)
$C_2F_2I_2$	0.095	1.05
1,2-$C_2F_4I_2$	0.127	1.60
1,1-$C_2F_4I_2$	0.166	1.60
I_2	present	—

(a) Yields measured at a dose of 5.10×10^{19} ev/gram except as noted.

(b) Based on one measurement

(c) Measured at an absorbed dose of 3.22×10^{19} ev/gram

(d) Relative detector response values in parenthesis are estimates based on carbon number.

(e) Higher yields of C_2F_4, n-C_4F_{10}, and CF_3I listed in the 1974 report were an artifact due to impurities of these species in the starting material.

Table 2. Ion - Molecule Reactions in CF_3I

Reaction	ΔH, Kcal/mole	Method[a]
(1) $CF_3^+ + CF_3I \longrightarrow CF_3I^+ + CF_3$	+33.54	ICDR
(2) $I^+ + CF_3I \longrightarrow CF_3I^+ + I$	+ 3.5	ICDR
(3) $CF_3^+ + CF_3I \longrightarrow CF_2I^+ + CF_4$	- 3.9	ICDR
(4) $CF_3I^+ + M \longrightarrow CF_3^+ + I + M$		ICRPP

(a) ICDR refers to Ion Cyclotron Double Resonance; ICRPP indicates a plot of ion intensity versus pressure in single - resonance ICR.

Table 3. Ion - Molecule Reactions in C_2F_5I

	Reaction	ΔH Kcal/mole	Method[a]
(1)	$CF_3^+ + C_2F_5I \longrightarrow C_2F_5I^+ + CF_3\cdot$	+34.24	ICDR
(2)	$CF_3^+ + C_2F_5I \longrightarrow C_2F_4I^+ + CF_4$	exo	ICDR
(3)	$C_2F_4^+ + C_2F_5I \longrightarrow C_2F_5I^+ + C_2F_4$	+12.7	ICDR
(4)	$C_2F_5^+ + C_2F_5I \longrightarrow C_2F_5I^+ + C_2F_5\cdot$	+22.7	ICDR
(5)	$C_2F_5^+ + C_2F_5I \longrightarrow C_2F_4I^+ + C_2F_6$	exo	Both
(6)[b]	$I^+ + C_2F_5I \longrightarrow C_2F_5I^+ + I\cdot$	+ 4.24	Both
(7)[b]	$I^+ + C_2F_5I \longrightarrow I_2^+ + C_2F_5\cdot$	-16.6	Both
(8)	$CF_2I^+ + C_2F_5I \longrightarrow C_2F_5I^+ + CF_2I$		ICDR
(9)	$CF_2I^+ + C_2F_5I \longrightarrow C_2F_4I^+ + CF_3I$	endo	ICDR
(10)[b,c]	$C_2F_5I^+ + C_2F_5I \longrightarrow C_2F_5I_2^+ + C_2F_5\cdot$		TOF
(11)[b,c]	$C_2F_5I^+ + C_2F_5I \longrightarrow C_4F_{10}I_2^+$		TOF

(a) ICDR refers to Ion - Cyclotron Double Resonance; TOF indicates high pressure time-of-flight mass spectrometry. "Both" indicates that reaction was seen by ICDR and TOF methods.

(b) Rate constants were measured by high pressure TOF method, as follows ($k \times 10^{10}$ cc molecule^{-1} sec^{-1}): Reaction 6, 0.237; Reaction 7, 0.279; Reaction 10, 0.836; Reaction 11, 1.11.

(c) Mass of product ion beyond range of ICR instrument.

Table 4a

Yields in the Radiolysis of 1,1,2,2-Tetrafluorocyclobutane; Products Eluting on Silica Gel Column.

	UNSCAVENGED SYSTEM		O_2 SCAVENGED SYSTEM	
Product	Initial	Linear[a]	Initial	Linear
H_2	0.52	0.52	0.205	0.682
HF	2.3	2.3	8.6	8.6
CH_4	0.0082	0.0082	0.008	0.0
C_2H_6	0.0057	0.0129	0.0057	0.0057
C_2F_4	0.093	0.171	0.109	0.109
C_2H_4	0.0	0.0	0.053	0.125
$1,1\text{-}C_2H_2F_2$	(~.47)	0.0464	0.471	0.471
C_2H_2	0.0853	0.196	0.0186	0.114
C_2H_3F	0.0125	0.0	0.024	0.0397
$1,2\text{-}C_2H_2F_2$	0.0071	0.0071	0.0	0.0
$C_3H_4F_2$	0.023	0.0487	0.0	0.0
$1,2\text{-}C_2H_2F_2$	0.0546	0.0546	$\leq$0.001	$\leq$0.001
C_2F_3H	0.01[c]	0.01[c]	—[b]	—
$C_3F_4H_2$	0.0035	0.0165	$\leq$0.001	$\leq$0.001
CF_3H	0.01[d]	0.01[d]	—	—

(a) Linear region reached at a dose of ca. 1×10^{19} ev. except for C_2H_6, which required 2 x 10 ev.

(b) Dash indicates product not measured

(c) C_2F_3H eluted with C_2H_2; yield estimated from mass spectrometry analysis

(d) CF_3H elutes with $1,1\text{-}C_2H_2F_2$; yield estimated from mass spectrometric analysis.

Table 4b

Yields in the Radiolysis of 1,1,2,2-Tetrafluorocyclobutane; Products Eluting on SE-30 Column

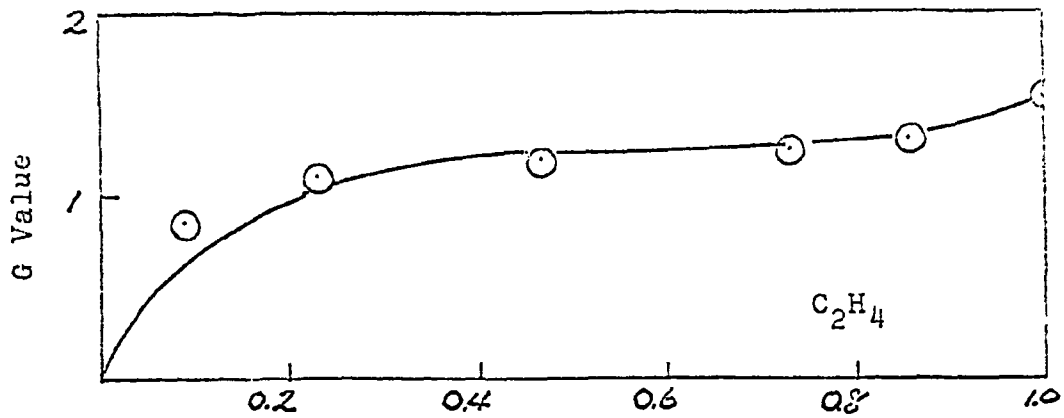
	UNSCAVENGED SYSTEM		O_2 SCAVENGED SYSTEM
Product	Initial	Linear	
$C_3H_4F_2$[a]	0.032	0.047	0.005
$C_3H_2F_2$	0.013	0.021	0.005
$C_4H_2F_4$	0.0062	0.017	<<0.001
$C_4H_2F_2$	0.013	0.013	<<0.001
$C_4H_3F_3$	0.063	0.197	0.13
$C_5H_6F_4$	0.007	0.05	—[c]
?	0.01	0.01	—
?	—	0.05	—
$C_6H_4F_6$	0.05	0.09	~0.05[d]
$C_6H_4F_6$	0.02	0.06	~0.05[d]
?	0.0	0.015	<<0.001
$C_8H_6F_8$	0.01	0.0	0.0

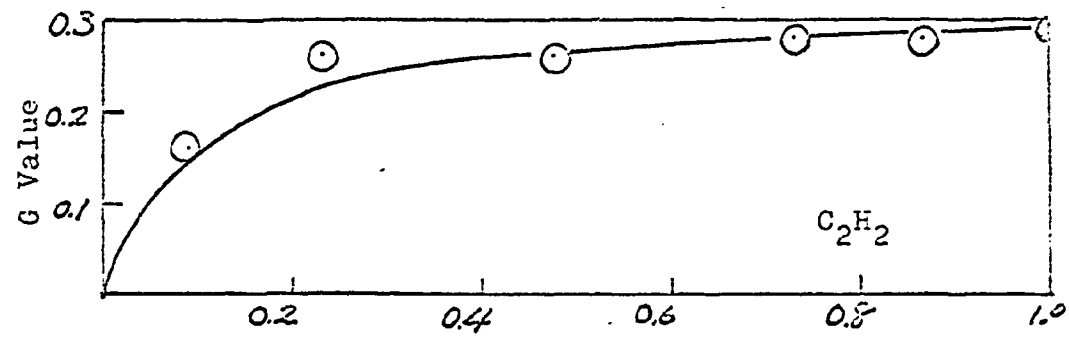
(a) Measured on silica gel column also

(b) Based on the first three points. (The yield at longer doses becomes zero and then becomes negative)

(c) Dash indicates product not measured

(d) Irreproducible





Fraction of Energy Absorbed by C_2H_6

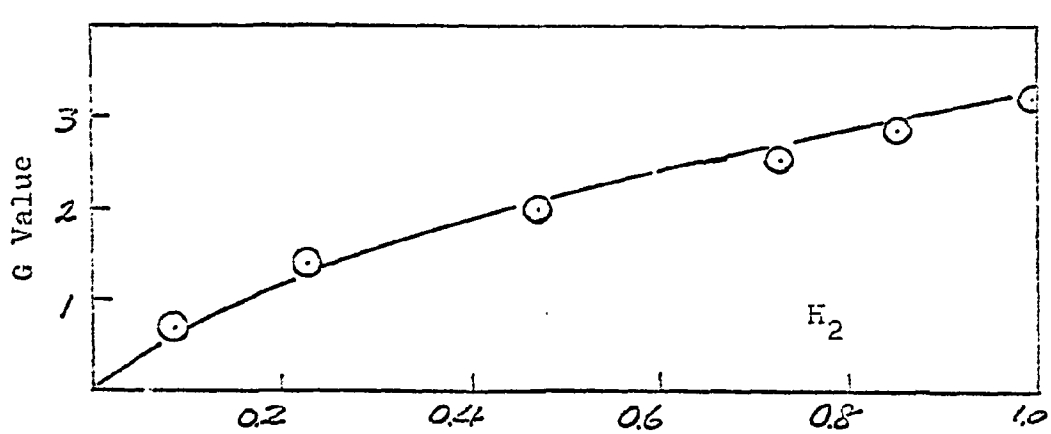


Figure 1: Production of H_2, C_2H_2, and C_2H_4 in the radiolysis of C_2F_6-C_2H_6 mixtures with 10% added O_2.

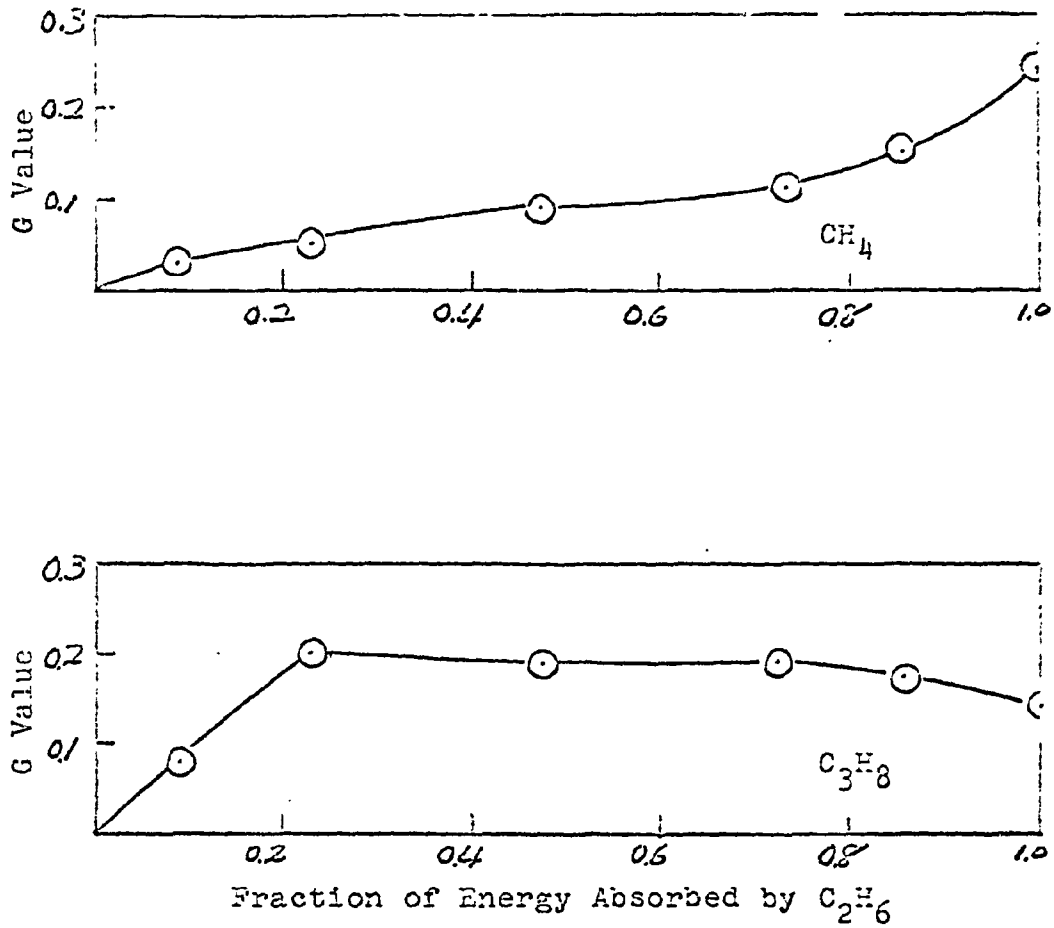
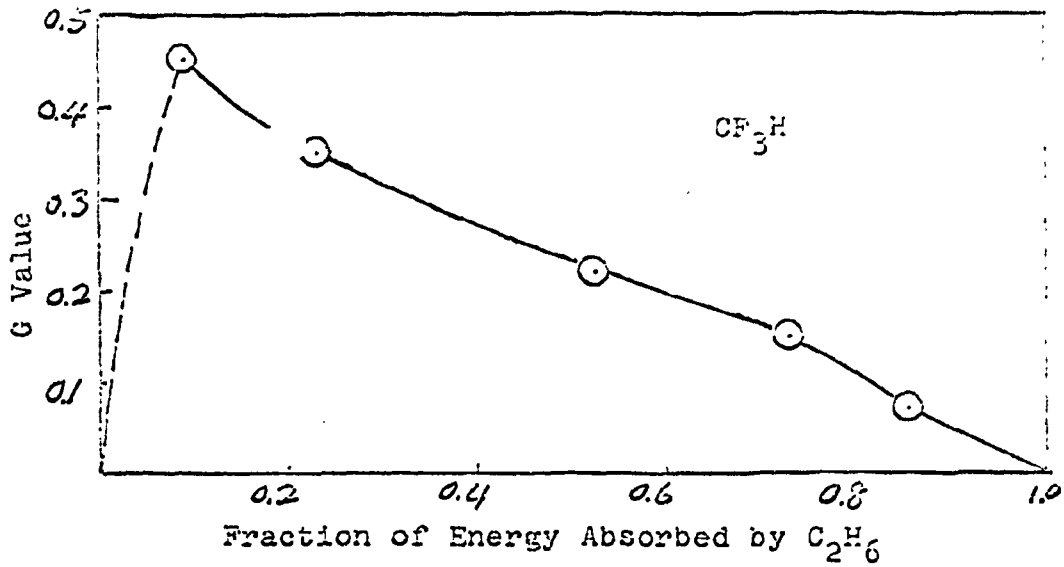


Figure 2: Production of CH_4, C_3H_8, and $n\text{-}C_4H_{10}$ in the radiolysis of C_2F_6-C_2H_6 mixtures with 10% added O_2.



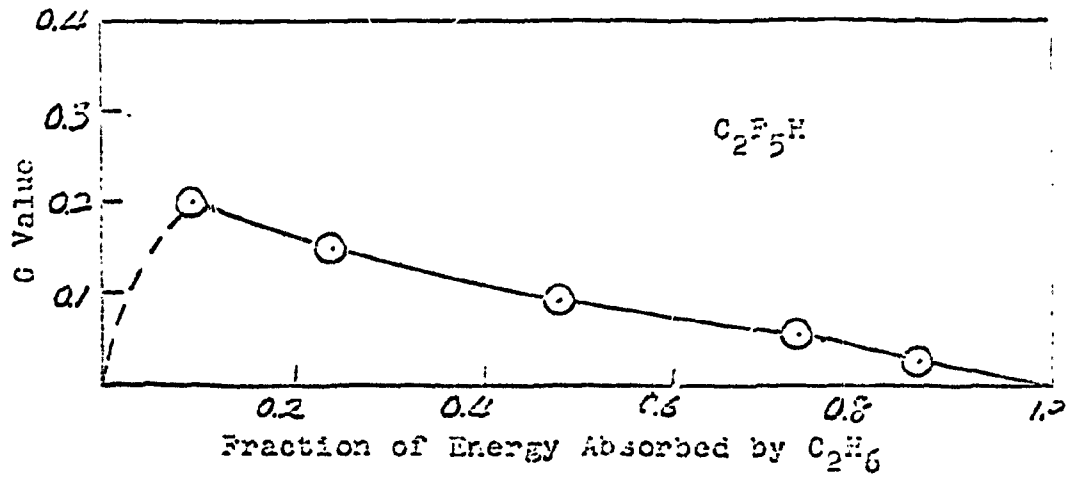
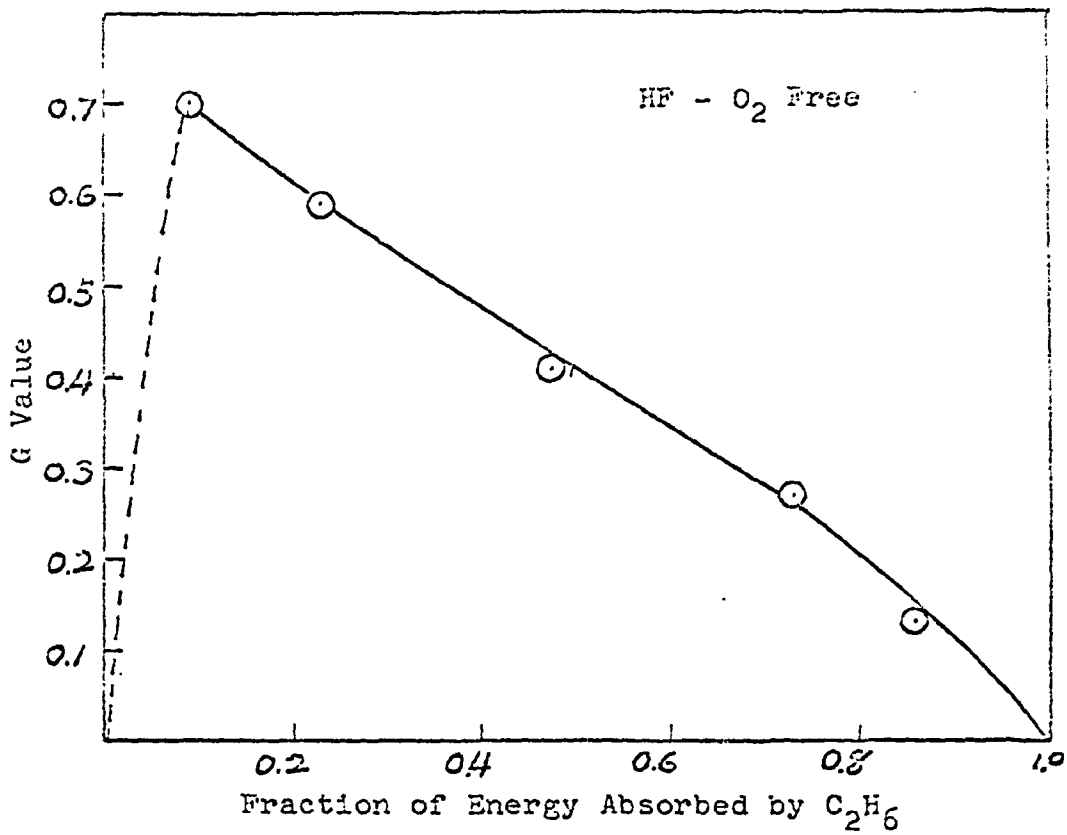


Figure 3: Production of CF_3H and C_2F_5H in the radiolysis of C_2F_6-C_2H_6 mixtures with 10% added O_2.



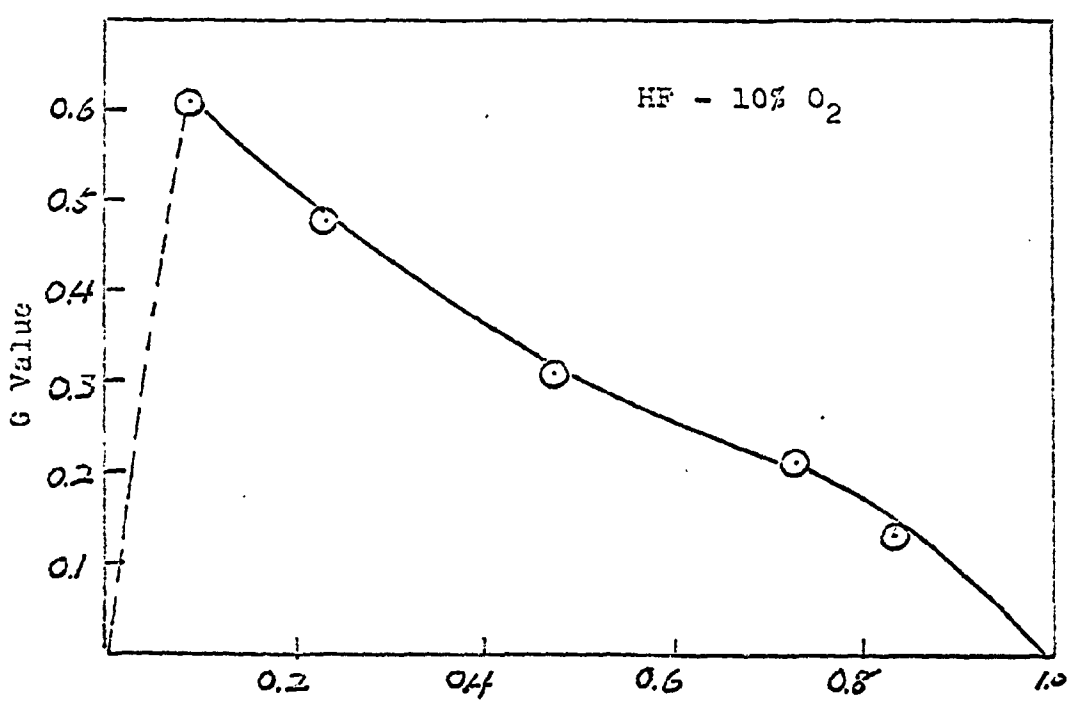


Figure 4: Production of HF in the radiolysis of C_2F_6-C_2H_6 mixtures with and without 10% added O_2.

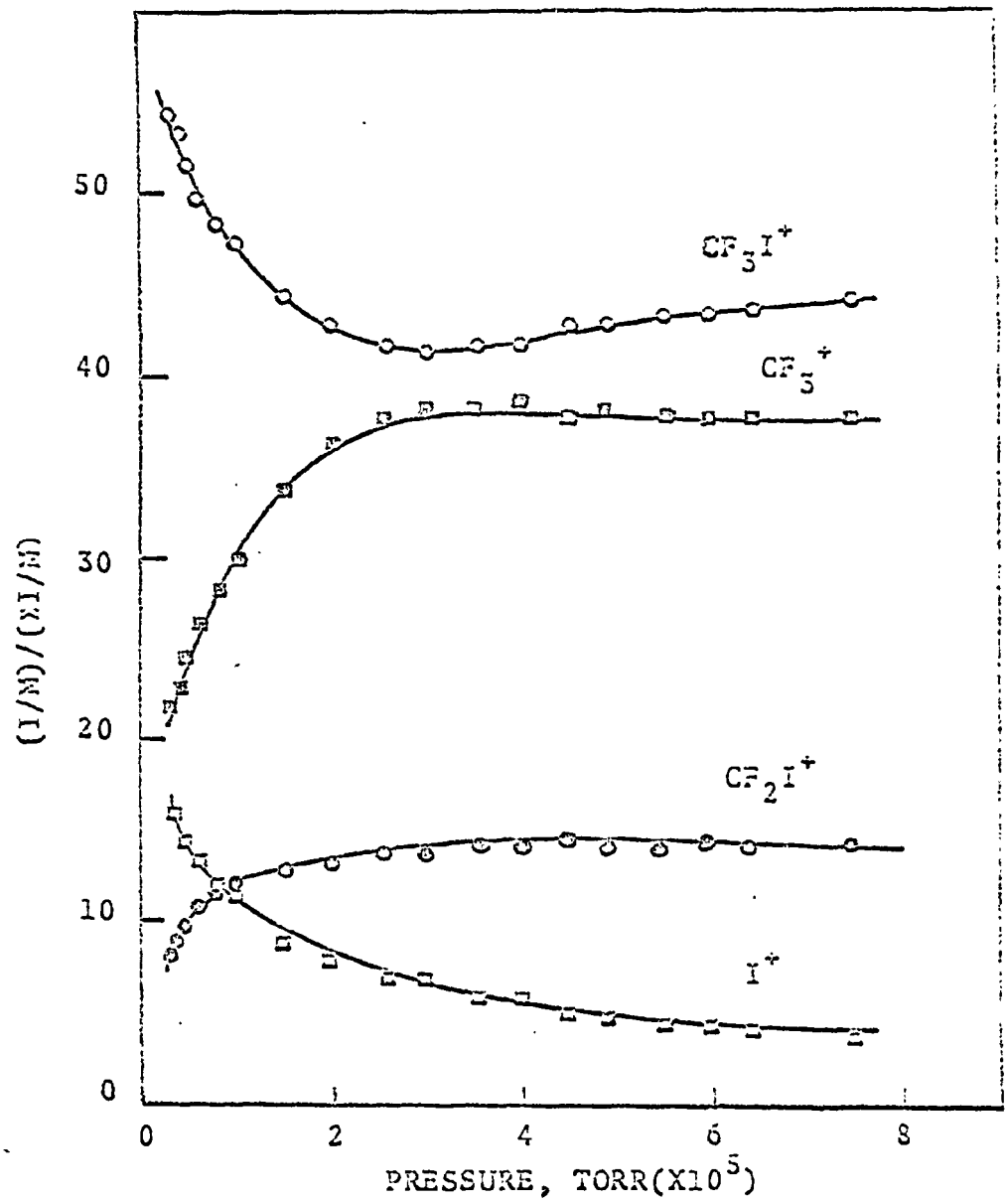


Figure 5: Variation of ion single-resonance intensities with pressure of CF_3I at 25 eV. (O) CF_3I^+, (□) CF_3^+, (○) CF_2I^+, (□) I^+. Measurements made using Varian V5900 ICR mass spectrometer.

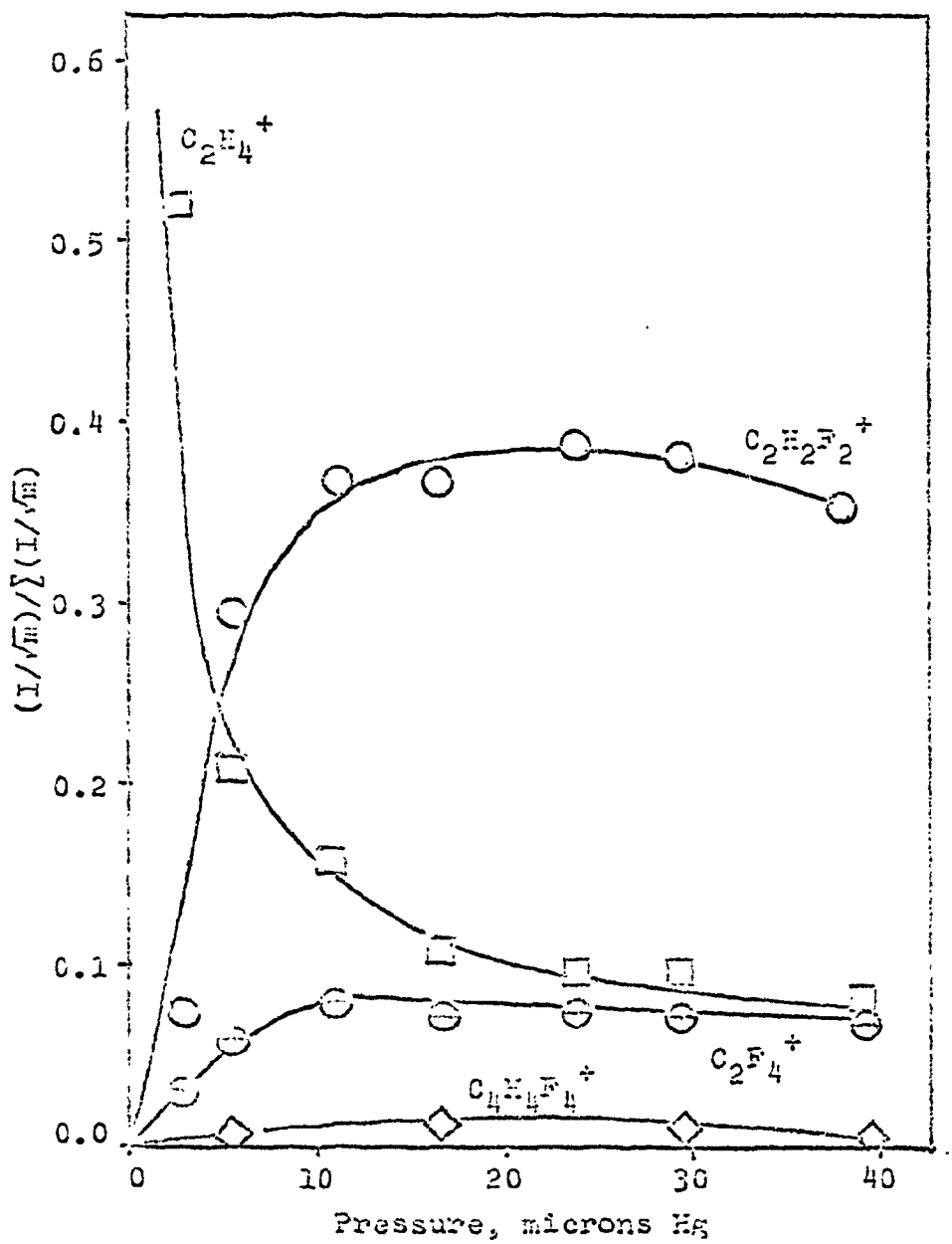


Figure 6: Normalized ion intensities as a function of pressure in the TOF spectrum of 1,1,2,2-tetrafluorocyclobutane.

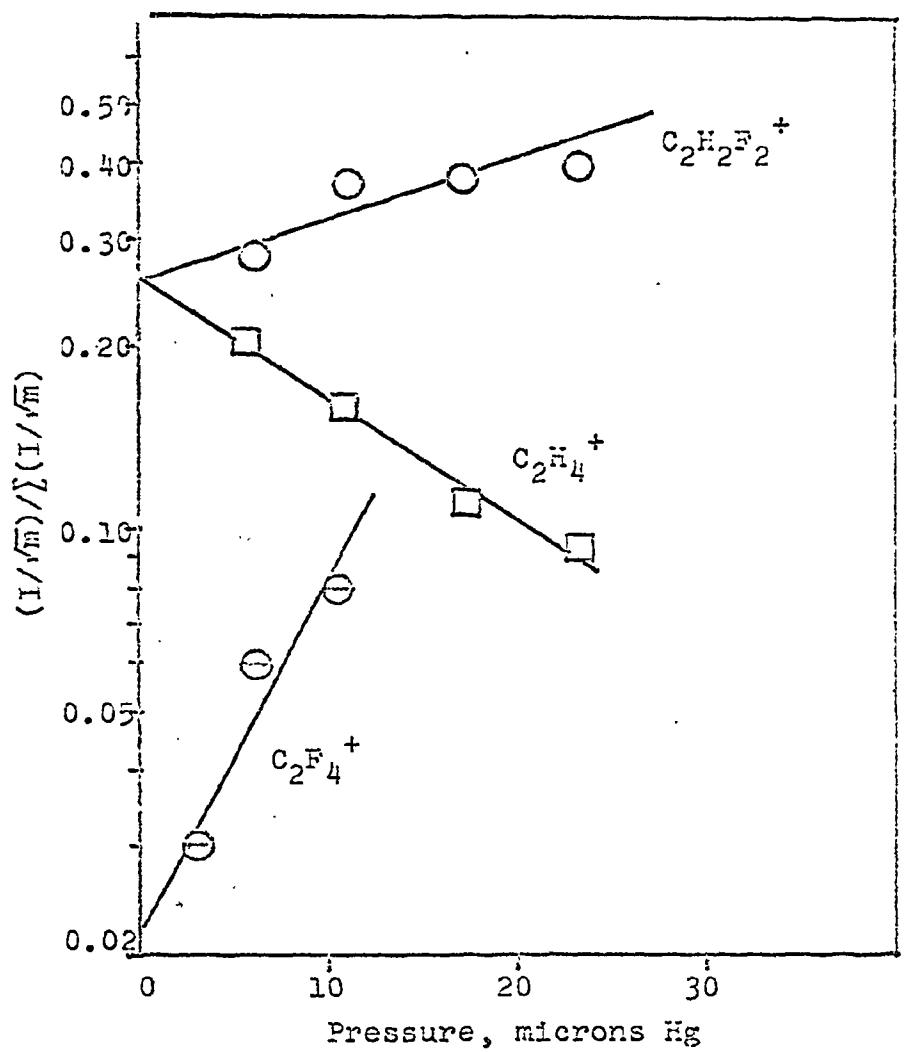


Figure 7: Semilogarithmic plots of normalized ion intensities versus pressure in the high pressure TOF spectrum of 1,1,2,2-tetrafluorocyclobutane. Measured rate constants ($k \times 10^{10}$ cc molec^{-1} sec^{-1}) are as follows: $C_2H_2F_2^+$ formation, 0.94; $C_2F_4^+$ formation, 0.94; $C_2H_4^+$ consumption, 2.0.

Reprints & Preprints Included

References

1. D. D. Davis, J. F. Schmidt, C. H. Neeley and R. J. Hanrahan, "Effect of Wavelength in the Gas Phase Photolysis of Carbon Tetrachloride at 253.7, 184.9, 147.0, and 106.7 nm," J. Phys. Chem., 79, 11 (1975).

2. A. R. Ravishankara and R. J. Hanrahan, "An Electron Impact Investigation of 1,1,2,2-Tetrafluorocyclobutane," J. Phys. Chem., 79, 876 (1975).

3. E. Heckel and R. J. Hanrahan, "Ion-Molecule Reactions in the Systems CF_4 - CH_4 and CF_4 - C_2H_6," J. Chem. Phys. 62, 1027 (1975).

4. A. J. Frank and R. J. Hanrahan, "The Gas Phase Photolysis of Ethyl Bromide at 253.7 nm," to be submitted for publication (1975).

5. A. J. Frank and R. J. Hanrahan, "The Gas Phase Radiation Chemistry of Ethyl Bromide," to be submitted for publication (1975).

6. R. J. Hanrahan, Ninth Annual Report of Progress under AEC Contract AT-(40-1)-3106, "Radiation Chemistry of Hydrocarbon and Alkyl Halide Systems," University of Florida, Gainesville, Fla., July 1972.

7. R. J. Hanrahan, Tenth Annual Report of Progress under AEC Contract AT-(40-1)-3106, "Radiation Chemistry of Hydrocarbon and Alkyl Halide Systems," University of Florida, Gainesville, Fla., July 1973.

8. R. J. Hanrahan, Eleventh Annual Report of Progress under AEC Contract AT-(40-1)-3106, "Radiation Chemistry of Hydrocarbon and Alkyl Halide Systems," University of Florida, Gainesville, Fla. July 1974.

9. M. D. Scanlon and R. J. Hanrahan, "A Comparative Investigation of the Gas Phase Radiation Chemistry of C_2F_6 and C_2H_6," Paper Gd-8, 21 st. Annual Meeting of the Radiation Research Society, St. Louis, Mo., April 29-May 3, 1973.

10. M. D. Scanlon and R. J. Hanrahan, "The Gamma Radiolysis of Mixture of Ethane and Hexafluoroethane in the Gas Phase," Vth International Congress of Radiation Research, Seattle, Washington, July 14-20, 1974.

11. (a) R. N. Schindler, Radiochim. Acta, 2, 62 (1963). (b) T. O. Tiernan and B. M. Hughes, Advances in Chemistry Series, 82, American Chemical Society, Washington, D.C., 1968.

12. R. N. Schindler and M. H. J. Wijnen, Z. Physik Chem. Neue Folge, 38, 285 (1963).

13. Arthur J. Frank, "The Radiation Chemistry and Photochemistry of Ethyl Bromide in the Gas Phase," Ph.D. Dissertation, University of Florida, Gainesville, February 1974. Available from University Microfilms, Ann Arbor, Michigan.

14. I. McAlpine and H. Sutcliffe, "The Radiolysis of Trifluoroiodomethane in the Gas Phase," J. Phys. Chem. 73, 3215 (1969).

15. P. G. Shah, D. R. Stranks, and R. Cooper, "The Radiolysis of Gaseous Trifluoromethyl Iodide," Aust. J. Chem. 23, 253 (1970).

16. E. Heckel and R. J. Hanrahan, "The X-Radiolysis of Perfluorocyclobutane and Mixtures of Perfluorocyclobutane and Methane in the Gas Phase," Adv. Chemistry Series, 82, 120 (1968).

17. E. Heckel and R. J. Hanrahan, "The Gamma Radiolysis of Cyclobutane in the Gas Phase", Int. J. Radiat. Phys. Chem., 5, 271 (1973).