

MASTER

ORO-3106-69

**"RADIATION CHEMISTRY OF HYDROCARBON
AND ALKYL HALIDE SYSTEMS"**

PROGRESS REPORT

MASTER

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AUGUST 1, 1977 - AUGUST 1, 1978

PREPARED FOR

THE U.S. DEPARTMENT OF ENERGY
UNDER CONTRACT NO. EY-76-S-05-3106

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UNLIMITED

I. Introduction

This report describes research progress for the period August 1, 1977 thru July 31, 1978. Two papers which were in press at the time of the previous report have been published, and reprints are included here.^{1,2} Four manuscripts which were submitted for publication at the time of the previous annual report have subsequently been accepted for publication.³⁻⁶ One additional paper is still in route through the editorial processes.⁷ Three new manuscripts have recently been completed; copies are included with this report.⁸⁻¹⁰

A survey paper describing several years of work of this laboratory on fluorocarbon-hydrocarbon systems was presented in a symposium at the National Meeting of the American Chemical Society held in Chicago, Illinois in August 1977.¹¹ A paper describing the pulse radiolysis work done by the senior investigator while on sabbatical leave in Berlin will be presented in the forthcoming Miami Beach ACS meeting in September, 1978.¹² The project director also attended the 1978 Gordon Conference on Radiation Chemistry, and served as Chairman for a session on gas phase pulse radiolysis and ion-molecule reactions.

Developments of the laboratory facilities during the year have largely centered on the gas phase pulse radiolysis experiment. A Jarrell-Ash monochromator was added to the optical train, several new components were obtained for the data reduction computer, and various modifications were made to improve the signal/noise situation. Transisterized power supplies for the Bendix mass spectrometer were also obtained. An order for a new research gas chromatograph will be placed before the end of August, utilizing \$3,000.00 in contract funds plus \$2,500.00 generously provided by the University of Florida Graduate School.

II. Progress of Experimental Work

A. Pulse Radiolysis of Simple Alkyl Halides in the Gas Phase.

At the time of the previous report, we were operating our pulse radiolysis equipment with interference filters, since the monochromator had not yet been delivered. In addition, the atomic iodine resonance lamp had not as yet been checked out. In consequence, we were able to observe only broad band fluorescence signals at that time, which were not very definitive.

A Jarrell-Ash model 84-215 one-quarter meter Ebert monochromator was delivered in the fall of 1977. The unit was modified for use in the range 1500-2000 Å by providing air-tight flanges at the entrance and exit face plates to allow inert gas flushing, and by equipping the optical path with a black flag to remove so-called re-entrant spectra which are a problem with this type of instrument.¹³ These modifications were completed in the winter of 1978.

Initial efforts to operate the atomic iodine resonance lamp with an open dish type A antenna were not entirely satisfactory, since the light intensity was rather low. Replacement of the open antenna by an Evenson cavity (borrowed from another experiment in the laboratory) gave greatly enhanced intensities.

It is found that the iodine lamp always produces a molecular I₂ band system near 200 nm when first turned on (Fig. 1). After several minutes warmup however, the atomic iodine spectrum is observed (Fig. 2) identified by lines at 184.4, 187.7 and 206.2 nm as described by Donohue et.al.¹⁴ Operating a model 9750QB EMI photomultiplier tube (10 stage venetian blind type, S-20 spectral response, quartz envelope) at 1100 volts, we are able to obtain 0.7 x 10⁻³ amps of anode current at the 206.2 nm line. Under optimal conditions, the 184.4 and 187.7 lines are about 2/3 as intense as the higher emission. The lower level for all of these lines is the excited iodine atom ²P_{1/2}. We have not as yet been successful in reliably observing the lower wavelength iodine

lines at 178.3, 179.9, and 183.0 nm, apparently due to insufficiently pure nitrogen flushing gas and/or an insufficient quality quartz window on the reaction chamber. We are in the process of building a liquid nitrogen cooled, molecular sieve trap to further purify the nitrogen. (Use of argon flushing gas proved to be a disaster. The breakdown voltage of argon is too low to allow the necessary high voltages in the photomultiplier tube base, leading to electrical breakdown.)

Work with the pulse radiolysis of methyl iodide using the three atomic iodine lines mentioned above, in the atomic absorption mode, has provided interesting preliminary results. An absorption signal is observed at 184.4 or 187.7 nm which disappears by pseudo-first order kinetics (rate constant dependant upon methyl iodide pressure), and showing a half-life of about 15 microseconds with a CH_3I pressure of 2 Torr (Fig. 3). From these data it can be calculated that the total rate constant for disappearance of iodine atom is 7×10^{-13} cc/mole s, in surprisingly good agreement (probably somewhat fortuitous at this point) with the result of 5.7×10^{-13} cc/mole s reported by Donohue and Wiesenfeld.¹⁴

It is possible to make a straightforward measurement only at the two lower wavelengths (184.4, 187.7 nm) because an additional feature appears at 206.2 nm. In particular, at the higher wavelength the absorption signal shows an apparent faster decay rate, and is followed by an emission signal with a half-life ca. 3 or 4 times longer than the absorption (Fig. 4). This signal appears to be an induced emission, since it is not seen with the light out. We do not as yet have sufficient experience with the entire setup to be certain that the emission is not an artifact. However, all aspects of the experiment seem to be well behaved, and at this point the emission seems to be real. The phenomenon does not appear at other strong lamp wavelengths, e.g. molecular I_2 or Ar lines.

Although it is tempting to suggest that the emission is due to a population inversion between the two stages involved in the 206.2 nm iodine line ($6(^2P_{3/2})$ and $5(^2P_{1/2})$) this interpretation appears to be unlikely because of the long lifetime of the signal (half-life about 85 μ sec at 2 Torr). In any event, we intend to pursue this feature of the system further.

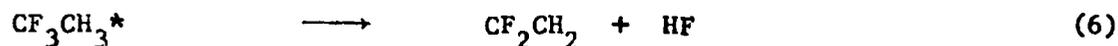
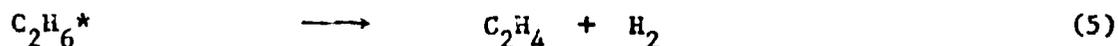
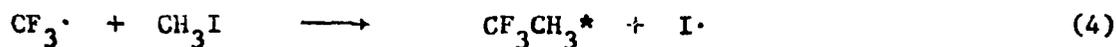
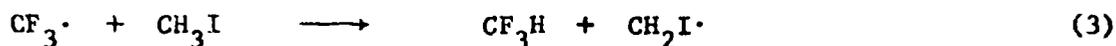
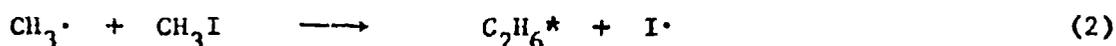
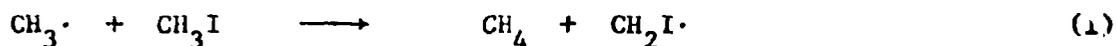
It should be pointed out that Figs. 3 and 4 were not selected for cosmetic purposes; they are somewhat noisier than is typical of the apparatus. These figures were photographed on Polaroid transparency film, then projected and traced. Many other shots recorded on regular film show a better signal-to-noise ratio. In any event, the computer system which is now under development will allow averaging several successive shots along with least-square fitting of the data, and should give greatly improved results.

Work on a data acquisition system for pulse radiolysis work has progressed in parallel with development of the radiolysis facility and experiments on CH_3I as the initial system. In the period since the last report was submitted, we have purchased, installed (in some cases constructed) and checked out the following equipment: Peripheral Vision Co. 8 inch floppy-disk system; North Star Co. floating point mathematics board; MiniTerm Associates video display board, equipped with George Risk Co. keyboard and Tandy Corporation 12 inch video display. A commercially available BASIC interpreter¹⁵ was modified to allow interaction with the disk, the floating point board, and the video display system, and is now working well. An interface between the Biomation and the IMSAI 8080 computer was also checked out, and special software to receive data from the Biomation and display it on the video screen has been completed. A supervisory program in BASIC is being written at the present time; this will allow us to place the entire system in use. At a later stage, we hope to add facilities to control all aspects of the experiment, including firing the Febetron, from the TV typewriter.

B. Gas Phase Radiolysis of CF₃I-CH₃I Mixtures.

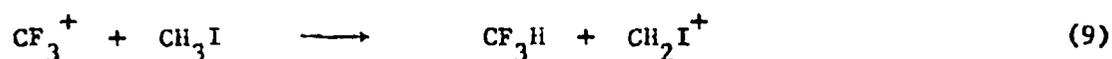
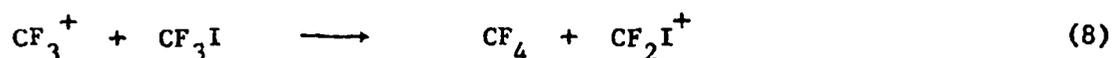
A limited study of the gas phase radiolysis of equimolar CF₃I-CH₃I mixtures was undertaken by Mr. Dawit Teclemariam as a Masters Degree research. This work is now nearly complete, and the results will be prepared for publication in the near future.

The gas phase gamma radiolysis of equimolar mixtures of CH₃I and CF₃I was carried out at 200 Torr pressure. For the pure system, 21 products were identified and their G values measured, as listed in Table 1. The major products and their G values are: HI, 0.69; HF, 0.47; I₂, 0.34; H₂, 0.19; CH₄, 0.16; C₂H₆, 0.13; CF₃H, 0.16; and C₂H₂F₂, 0.28. Yield-dose graphs for the major products are shown in Figs. 5 - 10. Formation of several of the major products is readily interpreted on the basis of attack by CF₃ or CH₃ radicals on the CH₃I substrate:



Reactions (2) and (4) are analogous to processes which have been postulated in the Casper-Pimentel photochemical iodine laser.^{16,17} Reactions (1) and (3) are obviously feasible branches available to the same reactant pair. Attack of CF₃ radical on the CF₃I substrate also occurs, producing the minor product CF₄ and C₂F₆. Reactions (2) and (4) are strongly exoergic, since the C-C bond formed is ca. 50 kcal/mole stronger than the C-I bond which is broken. Accordingly, the product ethane can be excited with as much as 50 kcal/mole,

in addition to any initial excitation energy carried by the attacking radical. Fragmentation of the product ethane can be expected, as shown in Reactions (5) and (6). This simple reaction sequence accounts for at least part of the yield of seven major products including CH_4 , C_2H_6 , CF_3H , H_2 , and HF as well as the minor products CF_3CH_3 and C_2F_4 . An additional component of the yields of CH_4 , CF_4 , and CF_3H is ascribed to ion-molecule reactions:



Reactions (7) and (8) have previously been observed in connection with high pressure or ICR mass spectrometry studies of ion-molecule reactions in the CH_3I and CF_3I systems.^{3,18} Reaction (9) is conjectural. We hope to carry out experimental investigation of ion-molecule reactions in the $\text{CF}_3\text{I}-\text{CH}_3\text{I}$ mixtures in the near future.

The observed yield of HI is attributed primarily to iodine atom abstractions from CF_3I or CH_3I by H atoms arising from primary processes on CH_3I . The HF yield is due in part to Reaction (6) above as well as to attack of fluorine atoms on CH_3I substrate. Undoubtedly, a large fraction of the energy deposited in this system leads to direct rupture of C-I bonds in CF_3I and CH_3I ; the iodine atoms will then combine to form I_2 . A large portion of the molecular iodine (ca. 80-90%) is expected to back react with radicals in the system; net molecular iodine accumulates only to the extent that methyl radicals are stabilized in C_2 or higher products, by a process such as Reactions (2) or (4).

Many of the minor products are most readily interpreted as arising from carbene insertion into substrate; several processes are possible, involving

insertion of either CF_2 or CH_2 into the weak C-I bond on either substrate. Small amounts of very minor products may involve the less stable carbenes CFI and CHI . Other minor products may involve addition of HI or I_2 to olefinic products such as C_2F_4 .

Since substantial yields of both fluorocarbon and hydrocarbon products were observed, as well as mixed fluorohydrocarbon species, the presence of each reactant has only a moderate influence on the primary radiolytic decomposition of the other. The C-I bonds in CF_3I and CH_3I have similar strengths, so that primary C-I bond rupture of both compounds is comparably efficient. However, whereas 62% of the energy deposited in these mixtures resides initially in the fluorocarbon, the yields of the hydrocarbons products exceed those of perfluorocarbon products by 3 or 4 times. It is concluded that attack of perfluoro intermediates on the CH_3I substrate is considerably more likely than the inverse situation.

C. Gamma Radiolysis of the System CO/H_2 .

Work described in the previous Annual Report consisted of gamma radiolysis of 3:1 mixtures of H_2 and CO in the gas phase. Subsequent work has concentrated on study of similar mixtures adsorbed on various active surfaces. Substrates examined to date include chromatographic grade alumina, Alfa-Ventron brand nickel on alumina catalyst, 60-65% nickel, catalog number 89049, and Alfa-Ventron brand palladium on alumina catalyst, 0.5% palladium, catalog number 89114. Extensive product formation was observed with all three catalysts. The palladium/alumina resembled pure alumina, however, possibly because of the small percentage of palladium involved. On the other hand, the nickel/alumina catalyst showed considerably different results, with a shift in the product distribution towards lower molecular weight hydrocarbons, see Figs. 11 and 12. The products are predominately n-alkanes (notably ethane but

also propane and n-butane) with smaller yields of branched and higher alkanes. This catalyst system seems to be particularly active. When it is balanced to show formation of methane as product, the associated chemical reaction indicated formation of 1 mole of water per each mole of methane formed;



This reaction is clearly not entirely indicative of the chemistry of the system, since CO_2 is also formed as an inorganic product, and since apparently some oxygenated organics are produced. However, it is notable that the amount of water formed from this system in a 24 hour radiolysis (400 curie Co-60 irradiator, dose rate ca. 0.5 megarad/hr) is sufficient to be readily observable visually. Considering that effective power output of the cobalt irradiator is only a few milliwatts, the possibility that practical quantities of product could be formed by such reactions is certainly not inconceivable. It would probably be necessary to utilize radiation produced as a byproduct of generating electricity or heat, however, so that the effective cost of the radiation itself would be minimal.

We are presently engaged in carrying out dosimetry measurements on the empty radiolysis vessels, in order to obtain a feeling for the G values involved. It will probably not be possible to place yield measurements on an entirely quantitative basis, since there will be uncertainties concerning the partitioning of the reactants between the gas and adsorbed state, and also between various type of active sites on the surface. However, it should be possible to calculate two limiting types of G values: one set based only upon energy absorbed by the gas itself, ignoring the presence of the substrate, and a second set based upon total energy absorbed by the reactant gas plus substrate. By comparing these numbers, it should be possible to gain some idea of the extent of energy transfer from the substrate to the reactants.

Some tentative product identification information was included in the previous report. Efforts to obtain further identification using the mass spectrometer-gas chromatograph combined technique have met with only limited success, since the amount of material produced in a 24 hour radiolysis is relatively small. Unfortunately, extending the radiolysis time does not produce larger quantities of the same set of products, but rather causes a shift of the product distribution towards higher molecular weights. The spark discharge technique frequently used in this laboratory to obtain "mock radiolysis mixtures" to aid in identifying products is of course not applicable, since the behavior of the adsorbed system is not equivalent to the gas phase system, either in principle or in fact. We intend to proceed in the direction of carrying out the necessary identification by combining together product yields from several successive irradiations - although this technique is tedious.

Not unexpectedly, the system involving the active surfaces shows some tendency towards irreproducibility. It will be necessary for us to work on a standard sequence of operations involving sample preparation, sample removal for analysis, and catalyst regeneration which leads to the most nearly reproducible results which we can obtain. (Considerable work in this direction has already been accomplished.) It will then be possible to carry out systematic variation of mixture composition, catalyst loading and temperature in order to determine the way in which product yields respond to these variables.

D. Other Work

Dr. James E. Fanning has been employed on the project for only one month during the past year, which was devoted to further work on our mass spectrometer data acquisition software package. We have funds available to employ Dr. Fanning for one additional month (Aug. 15- Sept. 15) which will be used to finish up and document that work.

Mrs. S.F. Becht has continued to work (without financial remuneration) on aspects of the radiolysis of chlorofluorocarbons in the gas phase. However, due to continued family problems, she was able to put in only about one months time during the past year. Some progress was made, however, on improving gas chromatographic purification procedures for CF_2Cl_2 , and in refining our previous product G values for that system.

Other possible projects as mentioned in the previous renewal proposal could not be implemented. due to unavailability of additional personnel.

III. Facilities and Equipment

In order to improve the operating stability of the Bendix time-of-flight mass spectrometer, we have obtained transistorized power supplies to replace the original tube-type units on the main power supply chassis number 1. The units selected were Elasco model 2L150-300-050 to provide +300 volts, and Elasco model 2L50-150-030 to provide the -150 volts supply. These units were recently delivered and will be installed in the near future.

In the original budget for the present year, we provided \$2,000.00 to be used toward the purchase of new gas chromatography equipment. Due to the availability of some additional carry-over funds, we recently budgeted an additional \$1,000.00 for this purpose, with the approval of the Oak Ridge Operations office. However, the sum of \$3,000.00 is still considerably short of the minimum price of a suitable research gas chromatograph. Fortunately, Dean H.H. Sisler of the University of Florida Graduate School has recently made \$2,500.00 available for this purchase, and a dual column, temperature programmed flame ionization gas chromatograph will be ordered in the near future.

Following plans presented last year, we have made several improvements in our gas phase pulse radiolysis facilities. A Jarrell-Ash model 82-415

quarter-meter Ebert monochromator was delivered in the fall, and was extensively modified for our needs. The entrance and exit face plates were replaced by O-ring sealed flanges, which required rebuilding the entrance and exit slits. A remote drive motor was added to the unit. Also, a special modification consisting of a black "flag" suitably placed in the light path, was constructed following plans supplied by Jarrell-Ash. This modification is necessary when using an Ebert type monochromator in the low wave length region.¹³ In order to prevent a problem called "re-entrant spectra", which for instance will cause light of ca. 5000 Å° in the second order to be transmitted, when the monochromator is set at approximately 3000 Å° in the first order. An aluminum light pipe arrangement was constructed to allow inert gas flushing of the entire optical path from the light beam exit window of the sample cell through the monochromator and to the photomultiplier system. Following installation of the monochromator in its intended final position, a two inch lead brick wall was arranged between the working head of the Febetron and the monochromator/photomultiplier area. In order to prevent X-ray transmission along the light path itself, a lead window was installed in the monochromator exit slit region, of approximately 1/2 inch thickness, with a 1/8 inch slit to accommodate the emerging light beam.

Work has continued on the development of the data reduction computer for pulse radiolysis work. During the past year, we acquired and installed the following additional components: 8 inch hard-sectored floppy disk system; "Merlin" high density graphics video display unit, with attached keyboard and 12 inch video display; North Star floating point arithmetic board; and 16K additional memory. An interface was designed and constructed to allow transfer of digital data from the Biomation 610B transient digitizer to the computer memory. All these components have been checked out and are fully operational.

A major part of the data acquisition computer project is writing of the necessary software. It was necessary to make several modifications in the floppy disk operating system (FDOS) to accommodate certain features of the operation of the graphics display and floating point hardware boards. It was also necessary to write a special package of graphics routines to allow scientific graphs to be displayed on the video screen.

A major problem concerned the availability of an appropriate BASIC language interpreter. Due to the numerous special needs of this project, we found it necessary to have a BASIC interpreter which was fully documented (i.e., source listings had to be available). Since no adequate quality, fully documented BASIC interpreter was available, we undertook to modify a low level BASIC which has been published by Processor Technology Inc.¹⁵ This program was modified to include log, exponential, and trigonometric functions, to provide loading and storing from absolute memory locations out of the range of the BASIC interpreter (the so-called "Peek" and "Poke" commands) and to allow calls to assembly language subroutines. According to a partial copywrite waiver provided by Processor Technology Inc., it would be possible for us to give copies of this software to other scientific and educational institutions.

All of the software described above has been written and debugged, and is operational. The project in hand at the present time is writing the actual BASIC language supervisory software, which will allow carrying out data entry and data reduction during a pulse radiolysis experiment in a conversational mode. We expect to have this work completed within about 6 weeks.

IV. Publications, Meetings Attended

In the period since the last Annual Report, two papers from the University of Florida Radiation Chemistry group have been published, dealing respectively

with mercury sensitized photolysis and gamma radiolysis of 1,1,2,2-tetrafluorocyclobutane.^{1,2} Reprints are included with this report. Two papers co-authored by Tacheng Hsieh dealing respectively with the gas phase gamma radiolysis of CF_3I and $\text{C}_2\text{F}_5\text{I}$ have been accepted for publication in Radiation Physics and Chemistry.^{3,4} They should appear sometime during the fall. A paper co-authored by Tacheng Hsieh and John Eyler of the University of Florida, Department of Chemistry, describing our work on ion-molecule reactions in CF_3I and $\text{C}_2\text{F}_5\text{I}$, is in press at the International Journal of Mass Spectrometry and Ion Physics.⁵ A revised version of the manuscript describing photolysis work on $\text{C}_2\text{H}_5\text{Br}$ has been accepted for publication by the Journal of Physical Chemistry,⁶ and a briefer version of the manuscript on pulse radiolysis on carbonate solutions, co-authored by J. Lilie and A. Henglein of the Hahn-Meitner Institute in Berlin, has been submitted to Radiation Physics and Chemistry.⁷

Three manuscripts deriving from the doctoral research of M.D. Scanlon are included with this report. The main paper describes radiolysis of $\text{C}_2\text{F}_6 - \text{C}_2\text{H}_6$ mixtures in the gas phase, as a function of mixture composition and added scavengers.¹⁰ In connection with that work, it was necessary to reinvestigate the gas phase radiation chemistry of C_2F_6 and C_2H_6 , both pure and with added scavengers, in order to establish "end-points" for yield-composition graphs in the mixtures. Two brief papers were written to record those results and are also included with this report.^{8,9}

In August 1977, the project director participated in a symposium on radiation chemistry at the 174th National Meeting of the American Chemical Society, in Chicago Illinois. A paper was presented surveying work of this laboratory in the area of radiolysis of perfluorocarbons and fluorocarbon-hydrocarbon mixtures.¹¹ A paper describing work done in Berlin on radiolysis

of aqueous carbonate solutions will be given at the forthcoming ACS meeting in Miami Beach, Florida in September 1978.¹² Additionally, Dr. Hanrahan attended the Gordon Conference on radiation chemistry held in Plymouth, New Hampshire in July 1978, and served as Chairman of a session on gas phase radiolysis and ion-molecule reactions.

Table 1 Radiolysis Yield for Equimolar Mixture $\text{CH}_3\text{I} - \text{CF}_3\text{I}$

G values								
Major Yield			Semi-major Yield			Minor Yield		
Product	Pure	10% O	Product	Pure	10% O	Product	Pure	10% O
HI	0.69	—	CF_4	0.052	0.017	$\text{C}_2\text{F}_3\text{H}$	0.0016	0.0017
HF	0.47	—	C_2F_6	0.07	0.047	$\text{C}_2\text{F}_3\text{I}$	0.0013	0.0009 ⁴
I_2	0.34	0.50	C_2F_4	0.038	0.013	$\text{C}_2\text{H}_2\text{F}_3\text{I}$	0.0029	0.0017
H_2	0.19	—	C_2H_4	0.013	0.022	$\text{C}_2\text{F}_4\text{I}_2$	0.002	0.0015
CH_4	0.164	0.087	C_2H_2	0.089	0.041			
C_2H_6	0.128	0.082	CH_3CF_3	0.021	0.0091			
CF_3H	0.159	0.185	$\text{C}_2\text{F}_2\text{HI}$	0.031	0.003			
$\text{C}_2\text{H}_2\text{F}_2$	0.28	0.016	$\text{C}_2\text{F}_5\text{I}$	0.012	0.0051			
			$\text{C}_2\text{H}_2\text{F}_2\text{I}_2$	0.018	0.0056			

^a — means not measured.

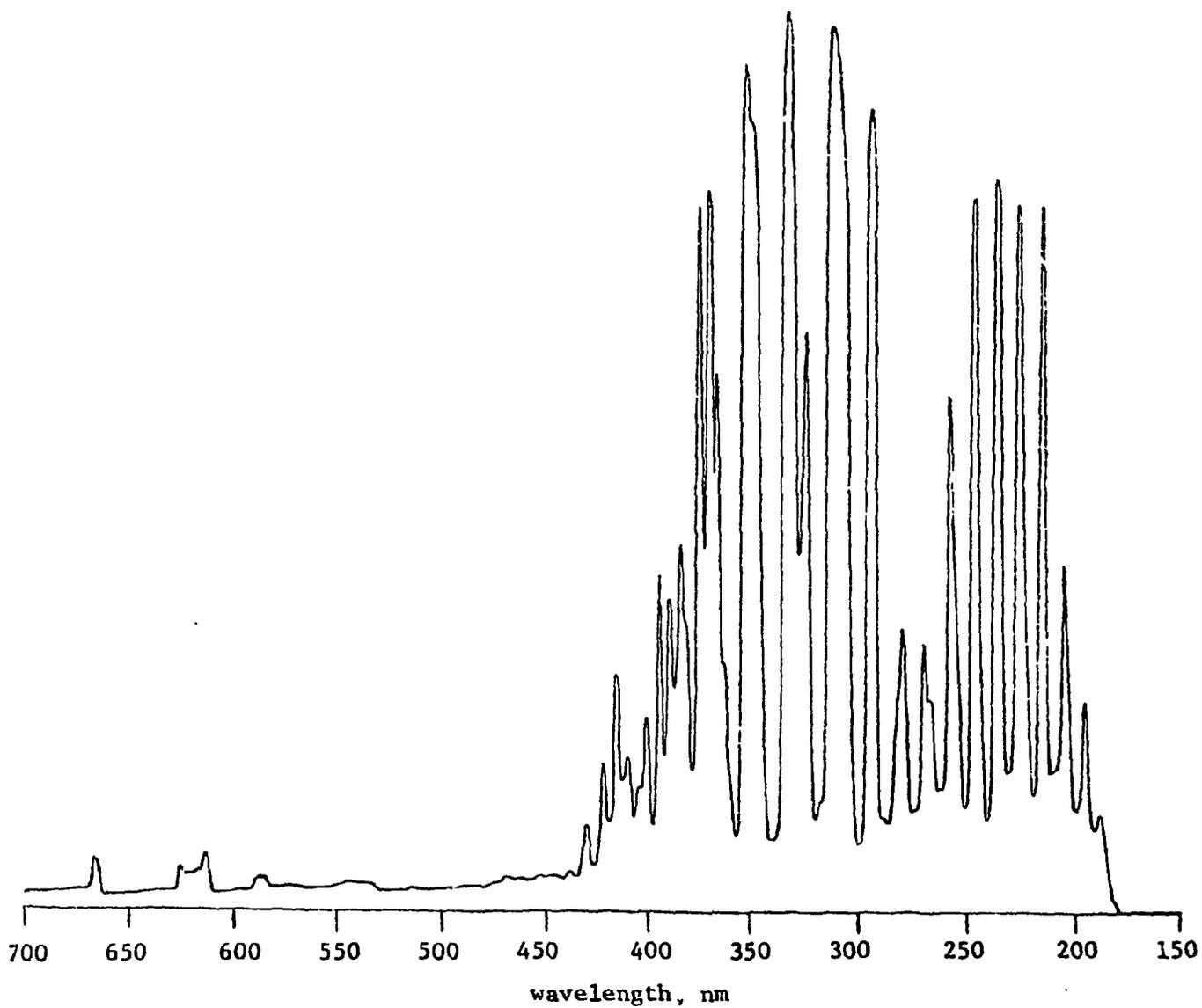


Fig. 1 Molecular iodine spectrum produced by microwave discharge Ar-I₂ lamp, Total pressure ca. 8 Torr.

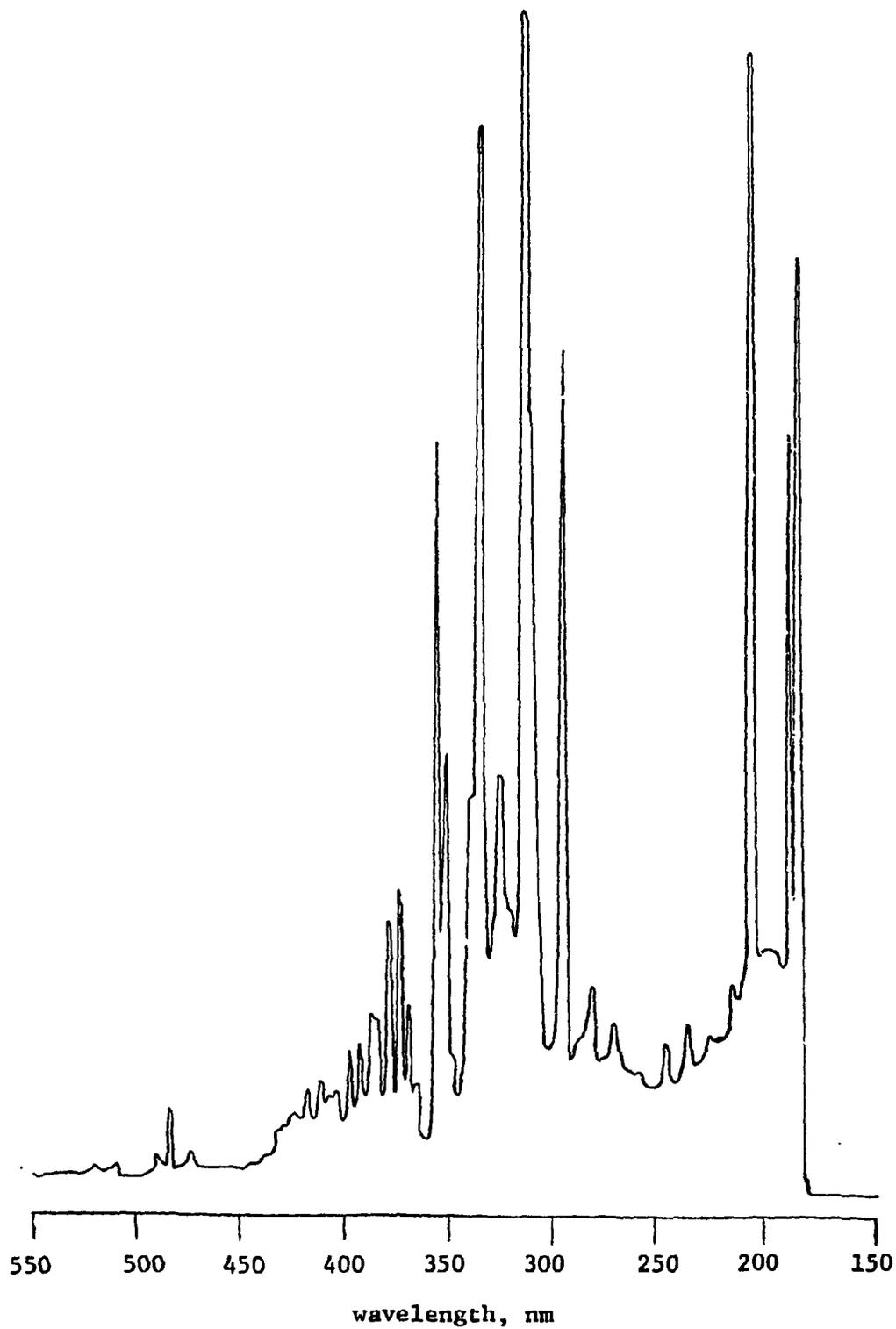
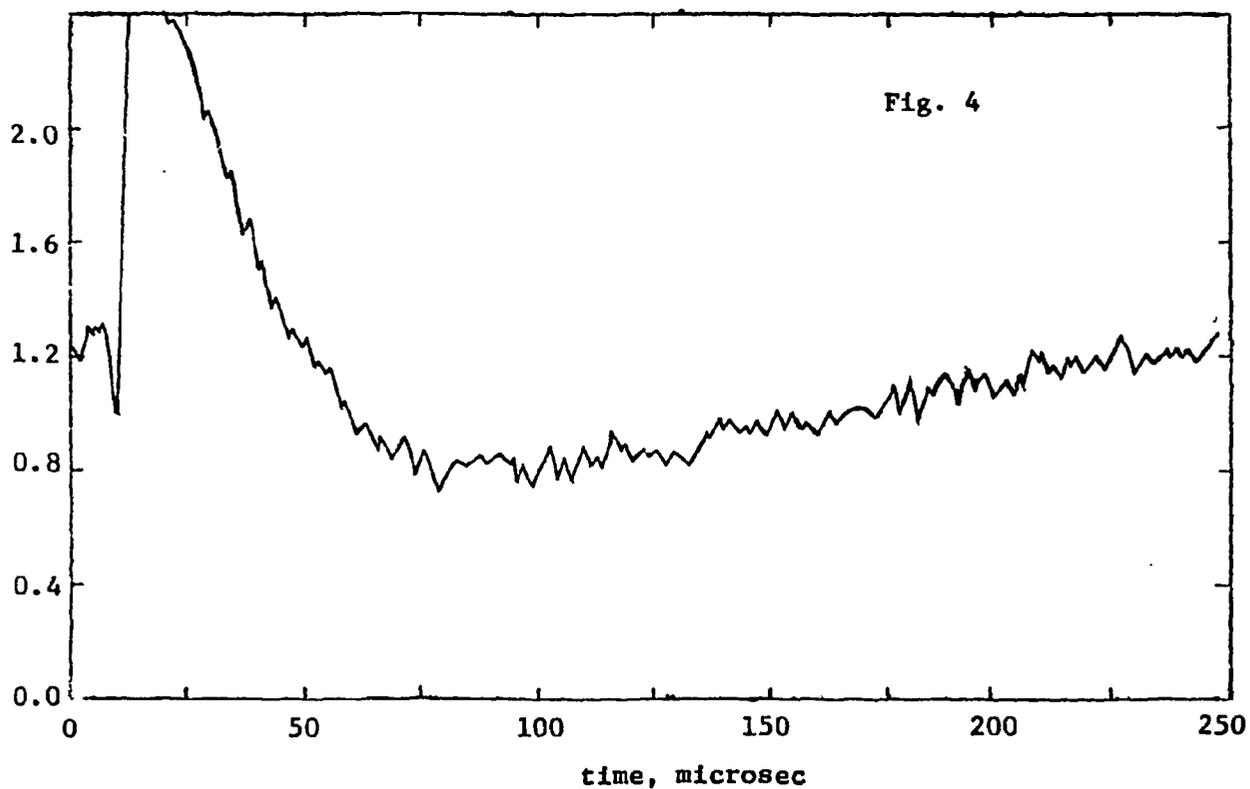
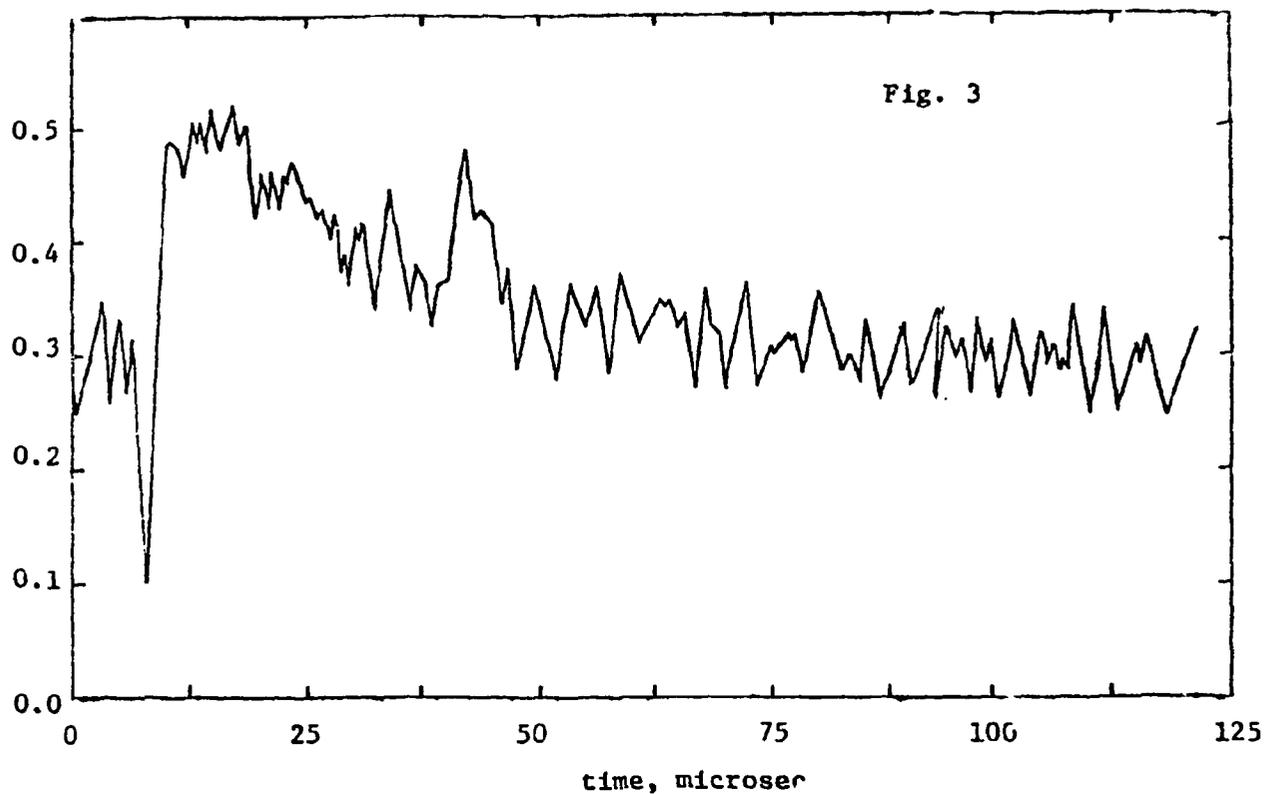


Fig. 2 Atomic iodine spectrum produced by microwave discharge Ar-I₂ lamp after warmup. Total pressure ca. 2 Torr.



Figs. 3 and 4 Light absorption at 184.4 nm (upper curve) and 206.2 nm (lower curve) following Febetron pulse in 2.0 Torr CH_3I plus 100 Torr Ar.

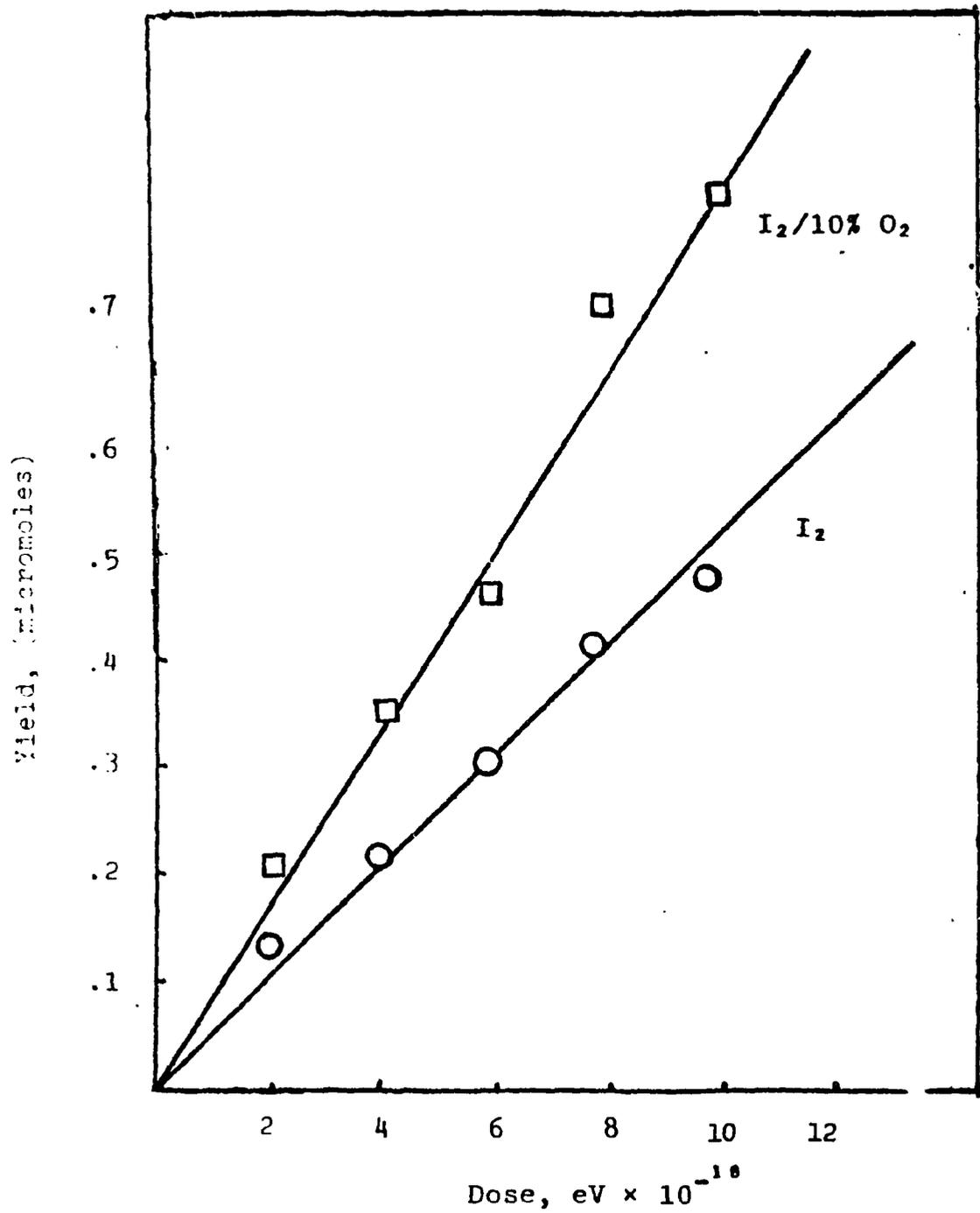


Fig. 5. Production of I_2 (pure, ○; 10% O_2 , □) as a function of dose in the $CF_3I - CH_3I$ system.

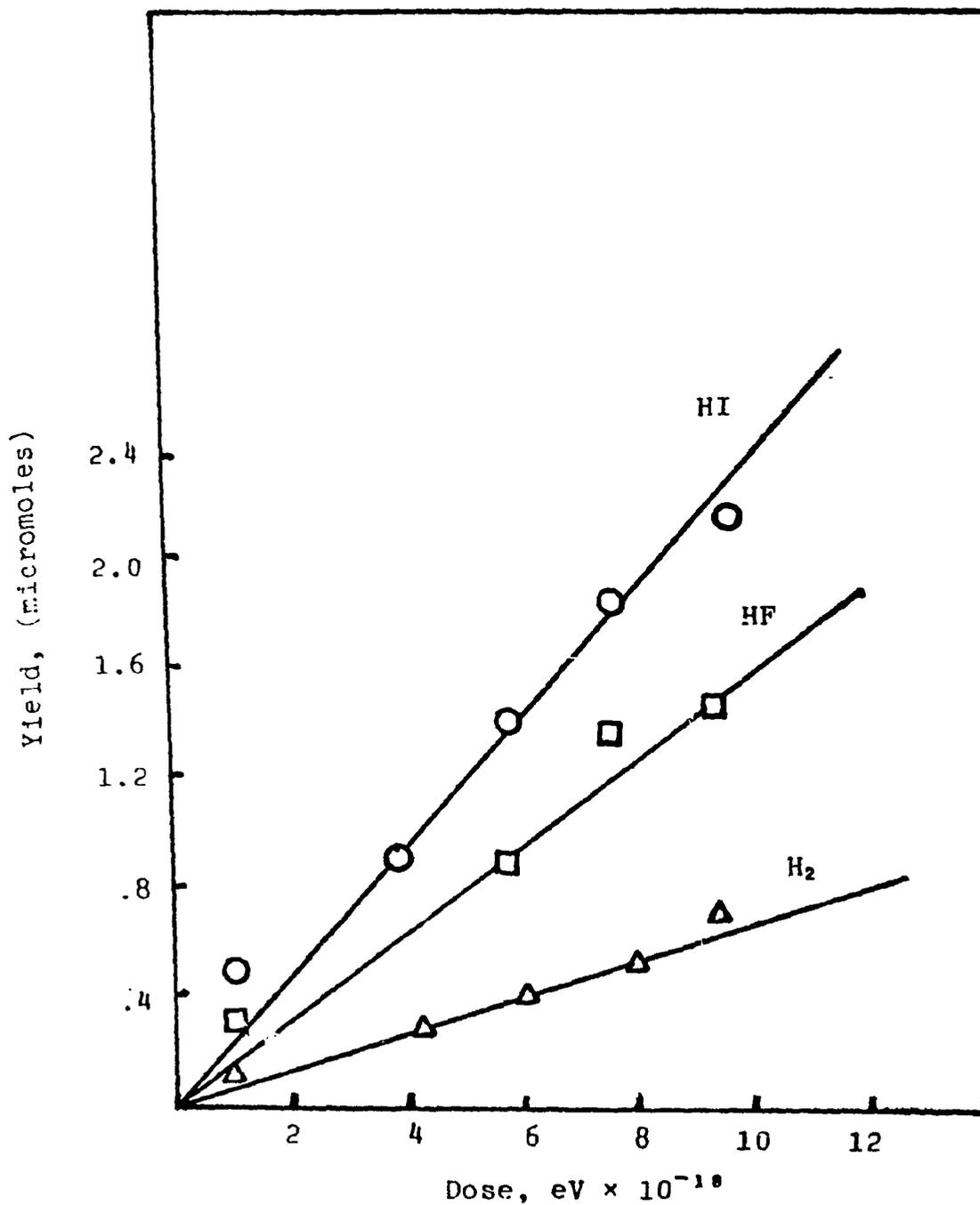


Fig. 6. Production of HI (pure, ○); HF (pure, □); H₂ (pure, △); as a function of dose in the CF₃I - CH₃I system.

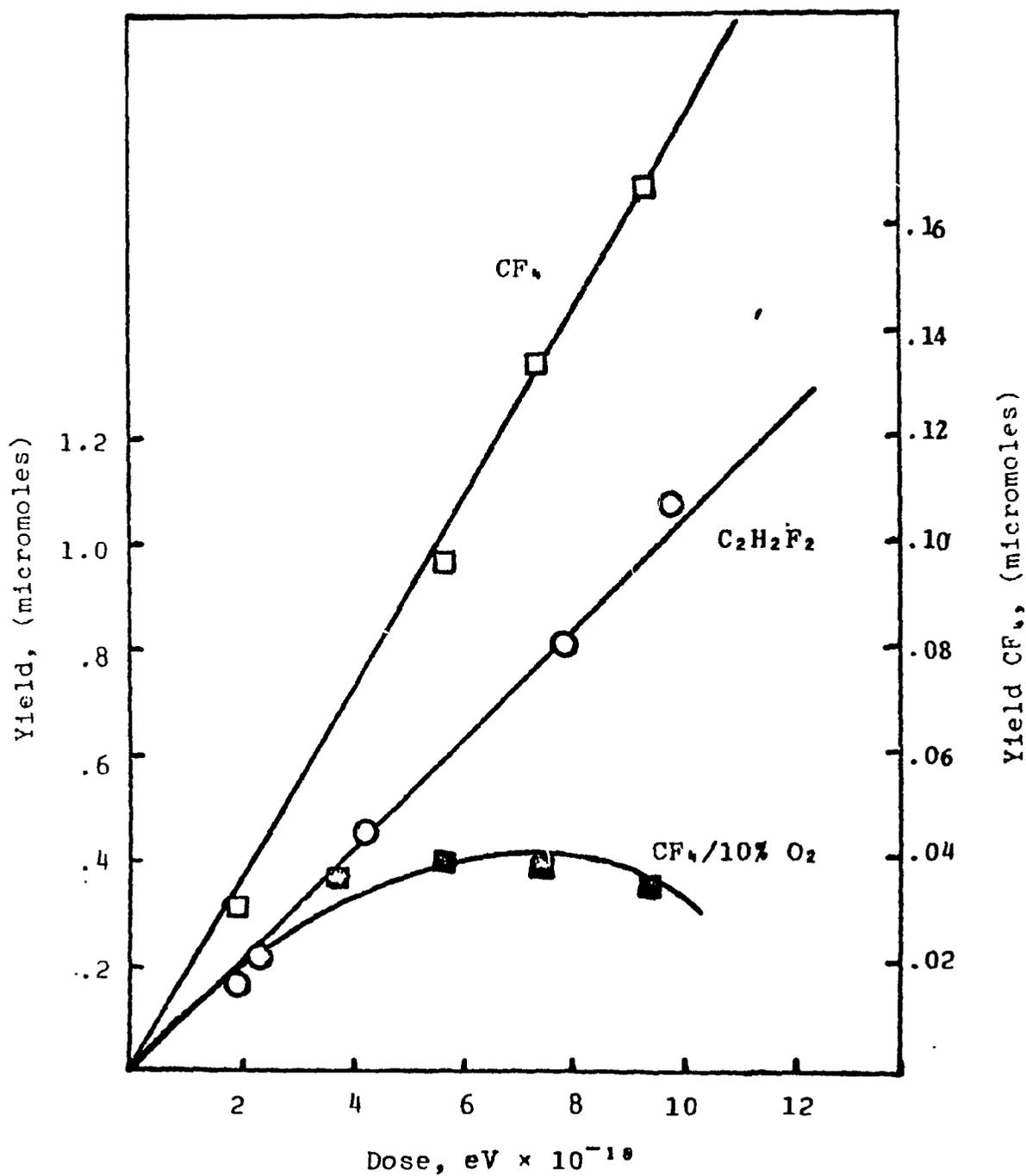


Fig. 7. Production of CF_4 (pure, \square ; 10% O_2 , \blacksquare); $\text{C}_2\text{H}_2\text{F}_2$ (pure, \circ) as a function of dose in the $\text{CF}_3\text{I} - \text{CH}_3\text{I}$ system.

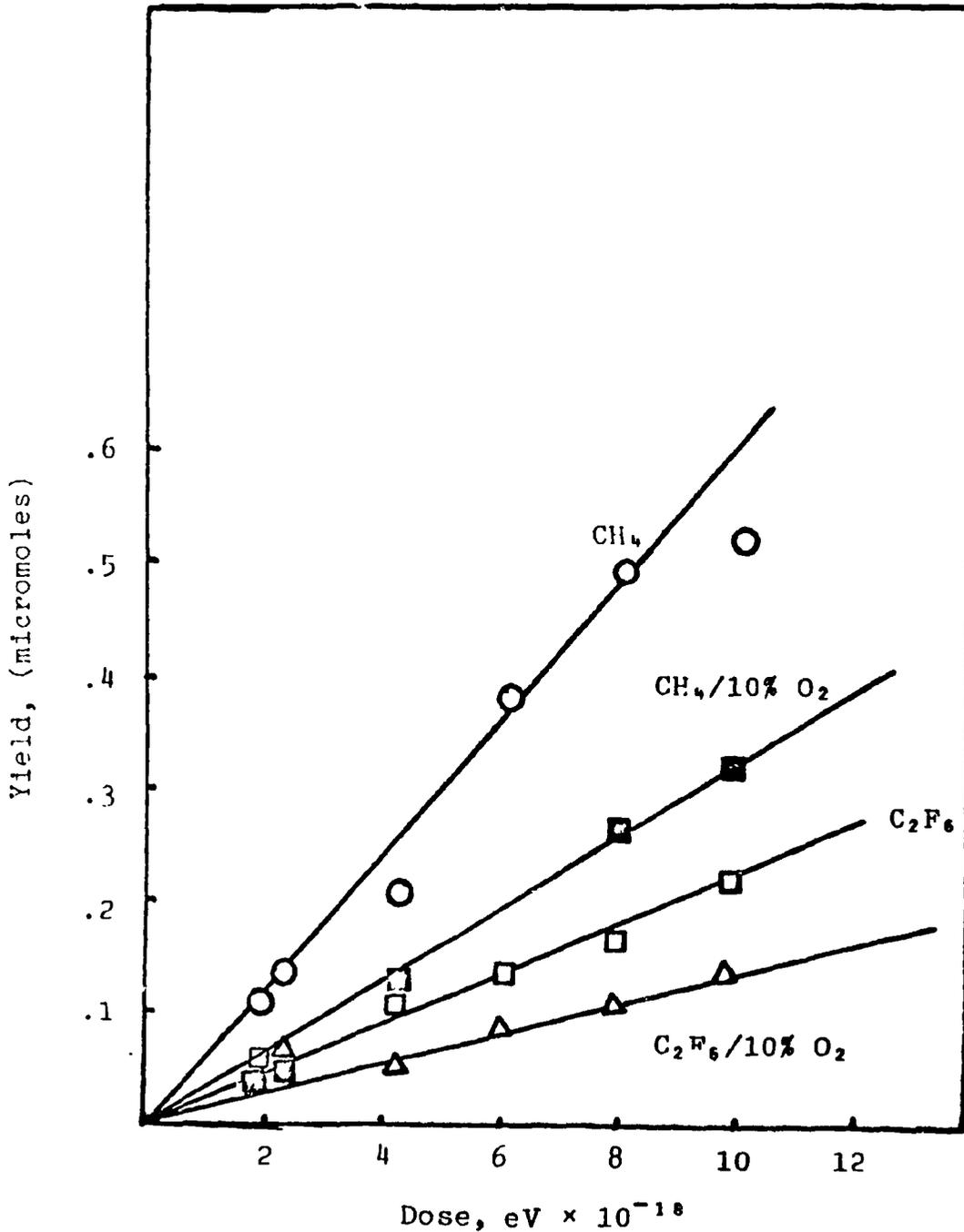


Fig. 8. Production of CH₄ (pure, ○; 10% O₂, ■); C₂F₆ (pure, □; 10% O₂, △) as a function of dose in the CF₃I - CH₃I system.

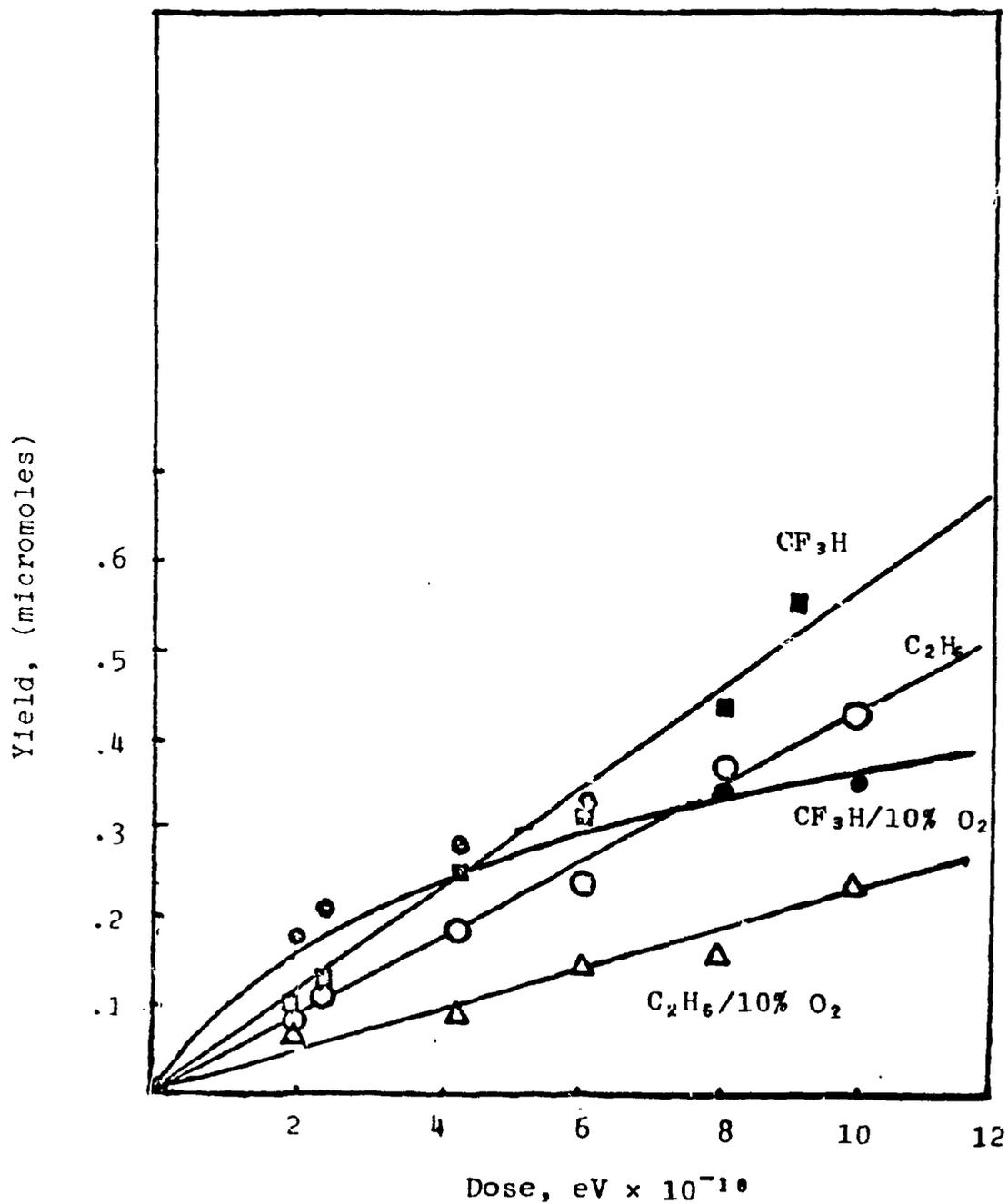


Fig. 9. Production of CF₃H (pure, ■ ; 10% O₂, ●); C₂H₆ (pure, ○; 10% O₂, △) as a function of dose in the CF₃I - CH₃I system.

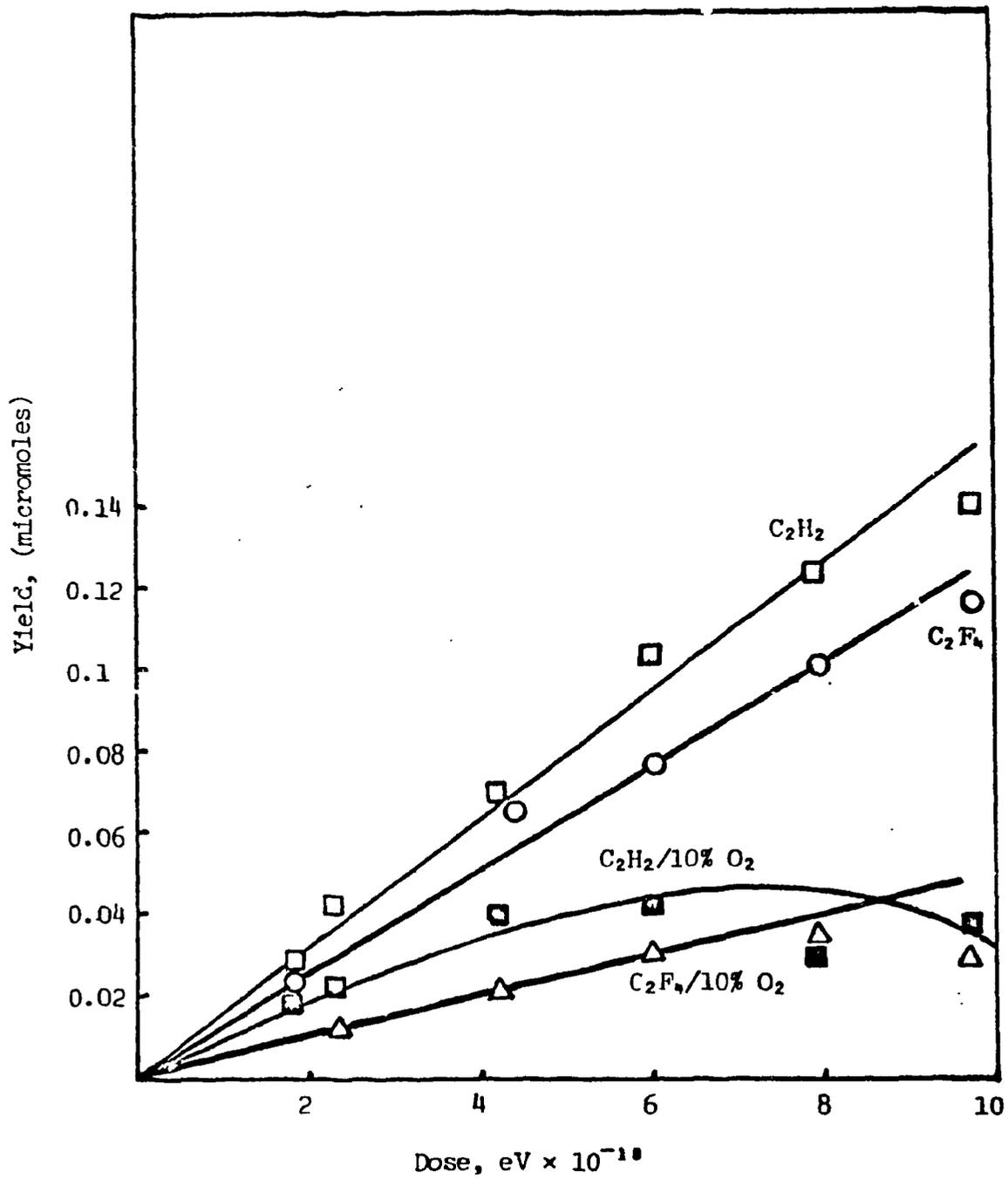


Fig. 10. Production C₂H₂ (pure, □; 10% O₂, ■); C₂F₄ (pure, ○; 10% O₂, △) as a function of dose in the Cl₂I - Cl₂I system.

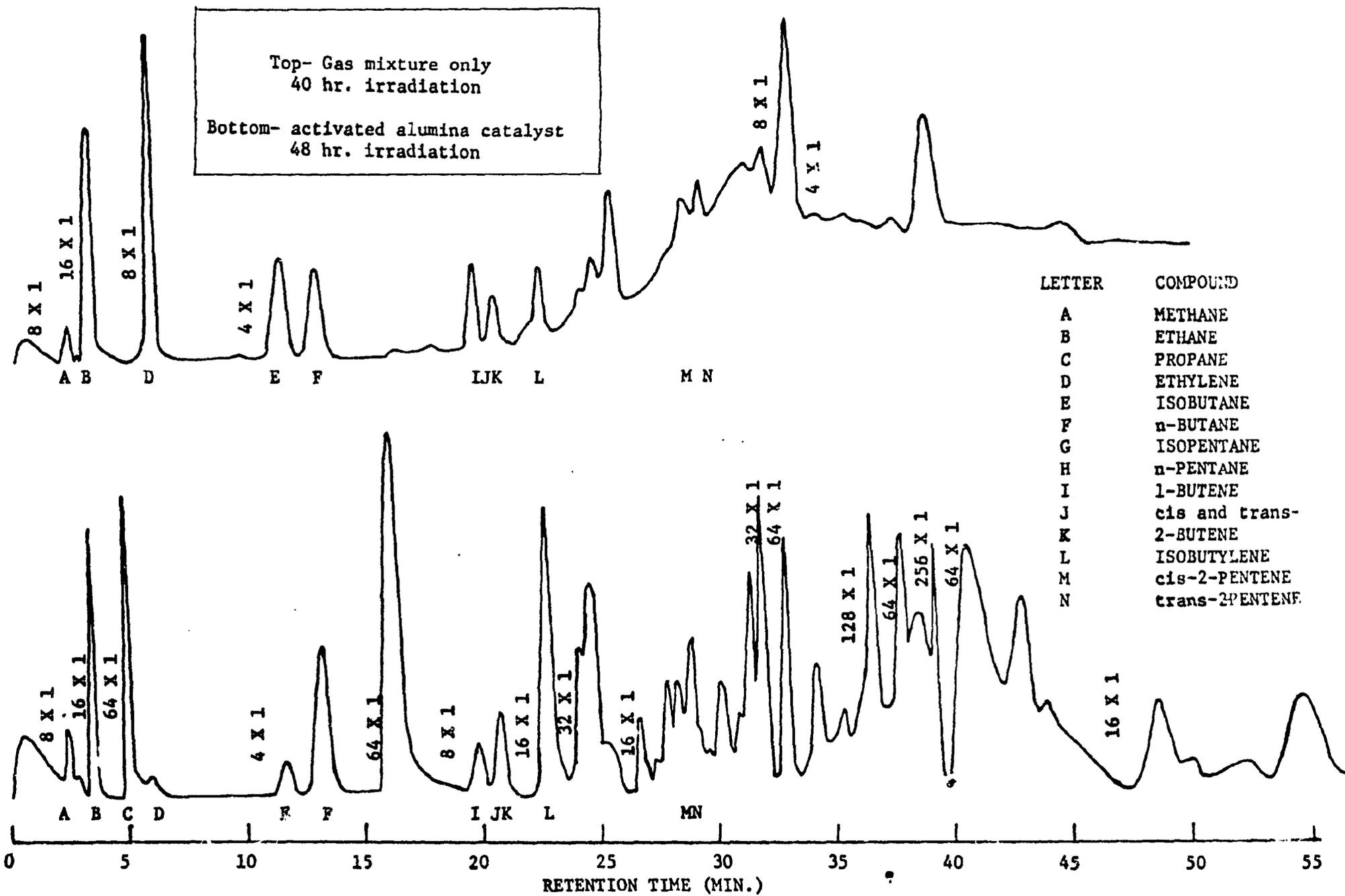


Fig. 11. Gas Chromatograms of irradiated $H_2 - CO$ mixtures.

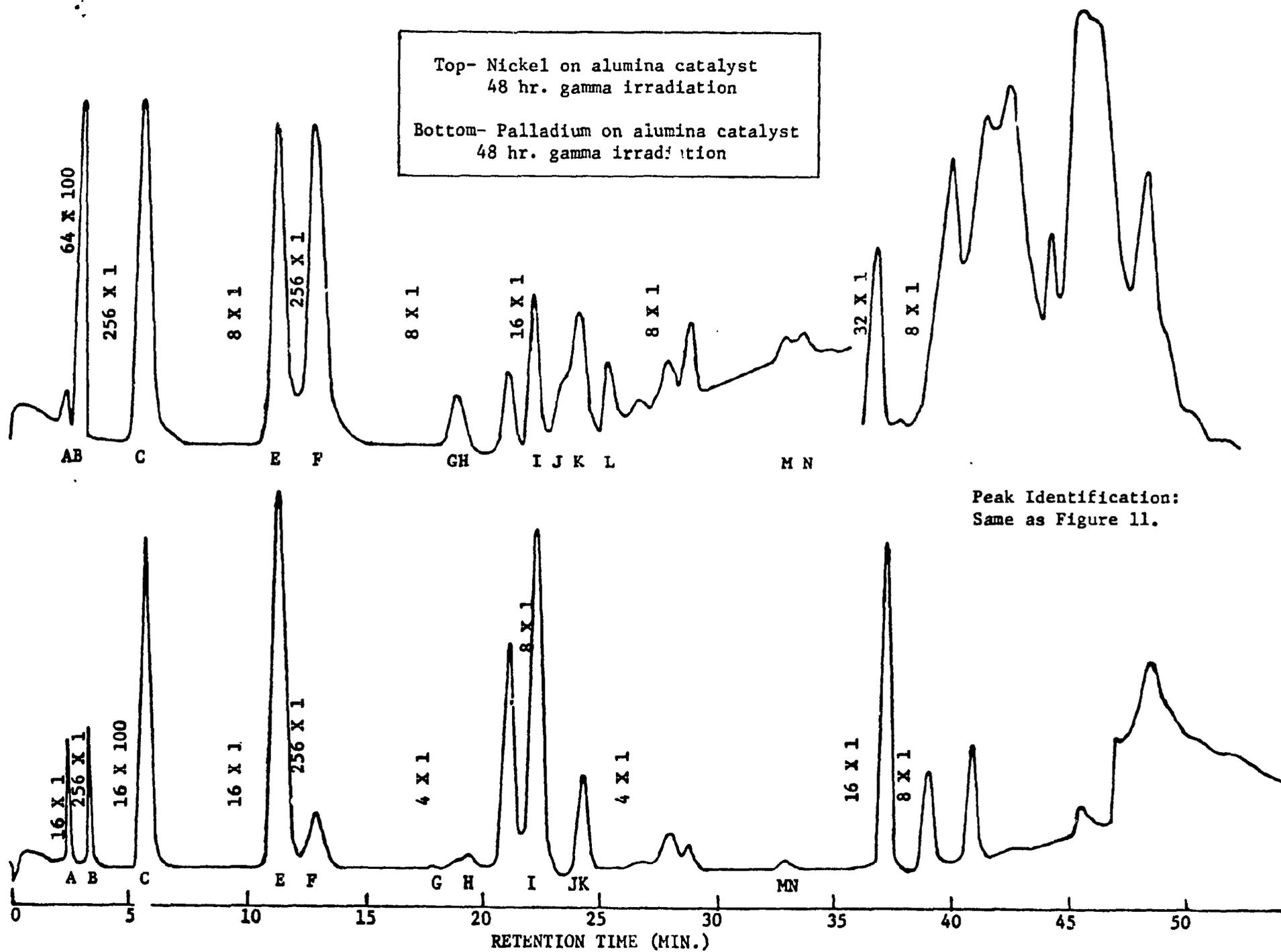


Fig. 12. Gas Chromatograms of irradiated $H_2 - CO$ mixtures.

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