PHOTOCHEMISTRY OF 3,3,3-TRIFLUOROPROPYNE

by

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B.Sc., Simon Fraser University, 1969

A THESIS SUBMITTED IN PARTIAL FULFILMENT

OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in the Department

of

Chemistry

APPROVAL

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Degree: Master of Science

Title of Thesis: Photochemistry of 3,3,3,-trifluoropropyne

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ABSTRACT

The 1849 Å photolysis of 3,3,3,-trifluoropropyne produces trifluoromethyl and ethynyl radicals in the primary process. No evidence of a long-lived excited intermediate state was observed.

The only volatile product formed in the photolysis of neat CF_3C_2H is 1,3,5,-tris (trifluoromethyl) benzene. A brown polymeric material is also formed during the photolysis.

Secondary reactions of the CF_3 and C_2H radicals were investigated by the addition of propane and nitric oxide to the reaction system.

ACKNOWLEDGEMENTS

The author expresses his appreciation for the help and encouragement received from many members of the Simon Fraser Chemistry Department and especially to Dr. A.G. Sherwood for uncalled for displays of patience in the face of adversity. Financial assistance from the Chemistry Department, the National Research Council of Canada, and the Presidential Research Grant Committee is also gratefully acknowledged.

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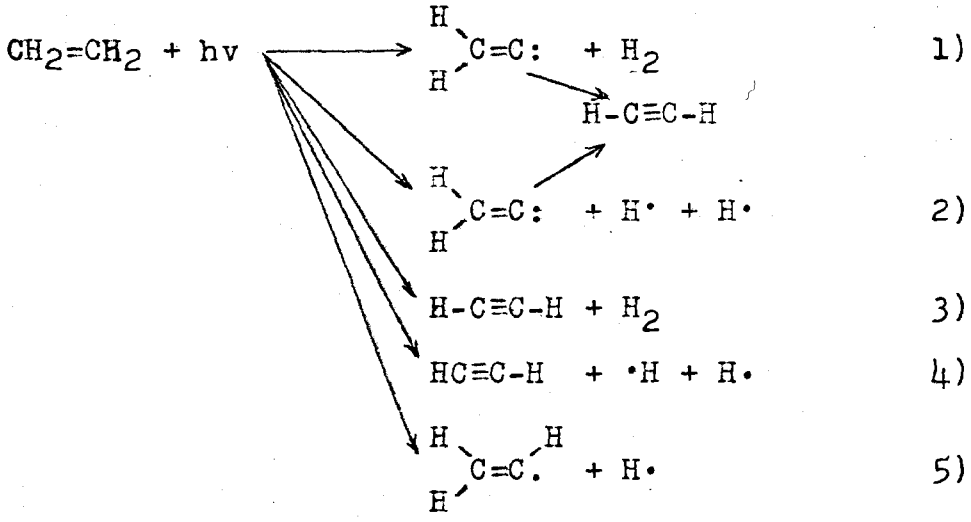
INTRODUCTION

Photochemistry of Unsaturated Compounds.

Over the past few decades the photochemistry of simple alkenes has been extensively researched but only recently have the major primary processes been well understood. In the case of ethylene[1,2] five modes of decomposition have been identified.



Process 5 is not very important compared to the others.

The vacuum ultraviolet photolysis of propylene[3] produces methyl and vibrationally excited vinyl radicals by the following reactions:

$$CH_3\text{-}CH{=}CH_2 + h\nu \longrightarrow {\bullet}CH_3 + {\bullet}CH{=}CH_2^{*} \qquad 6)$$

$${\bullet}CH{=}CH_2^{*} \longrightarrow H\text{-}C{\equiv}CH + H{\bullet} \qquad 7)$$

Molecular elimination of hydrogen by reaction (8) is also relatively important.

$$CH_3\text{-}CH{=}CH_2 + h\nu \longrightarrow H_2 + CH_2{=}C{=}CH_2 \qquad 8)$$

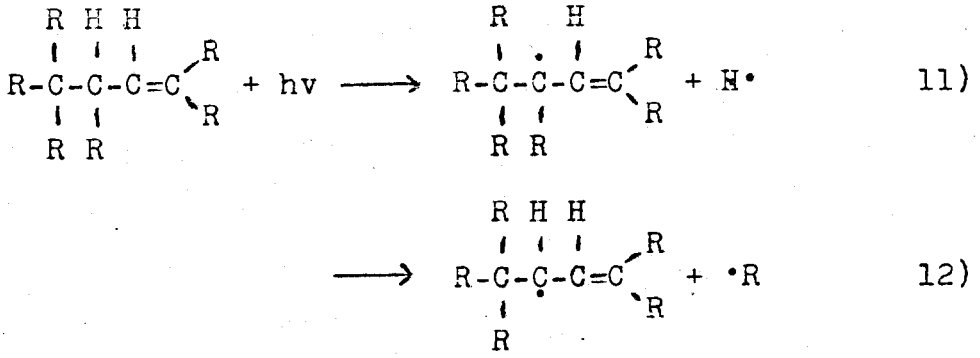
Other less important processes also occur.

An early study of the photolysis of isobutene[4] gave evidence for two modes of decomposition:

$$(CH_3)_2C{=}CH_2 + h\nu \longrightarrow \dot{C}H_2C(CH_3){=}CH_2 + H\cdot \qquad 9)$$

$$\longrightarrow \cdot CH_3 + CH_3{-}\dot{C}{=}CH_2 \qquad 10)$$

Other alkenes have been photolyzed by Poole and Anderson[5] with the radical products identified in situ by electron spin resonance. These studies were performed in the solid phase at 77°K and the reactions may or may not be valid for gas phase processes. It was found that most of the alkenes studied exhibit C-H and C-R bond breakage only at the carbon atoms one removed from the double bond, where R is an alkyl group.



$$\longrightarrow \quad + \cdot R \qquad 12)$$

In comparison to the alkenes, little photochemical research has been done on the alkynes and in the case of

acetylene, the little that has been reported proves to be contradictory at best.

Le Roy and Steacie[6] studied the mercury photosensitization of acetylene and from their results it was postulated that the primary process was free radical in nature. Later work by Zelikoff[7] appeared to indicate that both a free radical mechanism and an excited molecule reaction were operative in the photolysis of acetylene with 1849 Å radiation.

$$H\text{-}C{\equiv}C\text{-}H + h\nu(1849\ \text{Å}) \longrightarrow \cdot C_2H + H\cdot \qquad 13)$$

$$\longrightarrow C_2H_2^* \qquad 14)$$

Reaction (14) was thought to lead to polymerization.

$$C_2H_2^* + C_2H_2 \longrightarrow C_4H_4^* \text{ etc} \qquad 15)$$

Chain termination could occur by reactions similar to the following:

$$C_4H_4^* + C_2H_2 \longrightarrow C_6H_6 \qquad 16)$$

Such a mechanism could account for the benzene observed as a product.

It was further postulated that the ethynyl radicals produced in reaction (13) combined to form butadiyne.

$$2\cdot C_2H \longrightarrow C_4H_2 \qquad 17)$$

The need for a third body in reaction (17) was not considered.

Further evidence for the free radical mechanism in the mercury photosensitized reaction of acetylene was found by Sherwood and Gunning[8]. It was felt that most of the results could be explained [illegible] collision of a [illegible]

could be explained by collision of a triplet mercury atom with an acetylene molecule to form a hydrogen atom and an ethynyl radical.

$$Hg6(^3P_1) + C_2H_2 \longrightarrow Hg6(^1S_0) + H\cdot + \cdot C_2H \qquad 18)$$

S. Shida et al.[9] attempted to resolve the mechanism of acetylene decomposition by photosensitizing deuterated acetylene and studying the deuterium distribution of the benzene products. Both an excited state and a free radical mechanism were again proposed. The free radical mechanism was that proposed by Mains.[10]

$$H\cdot + C_2H_2 \longrightarrow \cdot C_2H_3 \qquad 19)$$

$$\cdot C_2H_3 + C_2H_2 \longrightarrow \cdot C_4H_5 \qquad 20)$$

$$\cdot C_4H_5 + C_2H_2 \longrightarrow \cdot C_6H_7 \qquad 21)$$

$$\cdot C_6H_7 \longrightarrow C_6H_6 + H\cdot \qquad 22)$$

The above mechanism is analogous to the formation of benzene in the methyl radical[11] and the chlorine atom[12] initiated polymerization of acetylene.

Shida's attempt at distinguishing between the free radical processes and the excited molecule reactions was shown to be invalid. Le Roy[13] demonstrated that all the results obtained by Shida could be explained solely on the basis of a free radical mechanism. In a subsequent paper by Shida[14] it was conceded that the original data could not distinguish between a free radical and an excited molecule process and that both were possible.

At the present time there remain unanswered questions as to the primary process of acetylene photolysis and photosensitization. Much of the confusion probably derives from the fact that the various studies often utilize different light sources and the photochemical processes observed may in fact not be the same.

The only other alkyne of any significance to be studied photochemically is propyne. Two studies have been done, both employing E.S.R. techniques to identify the radical products in the frozen state. Volman et al.[15] photosensitizing 2537 Å light and Poole[5] irradiation with light in the range 2500 - 3800 Å identified the propargyl radical. It was found to have two resonance structures:

$$\cdot CH_2\text{-}C{\equiv}C\text{-}H \longleftrightarrow CH_2{=}C{=}\dot{C}H \qquad 23)$$

Evidently the primary process in the photolysis of propyne is cleavage of the β C-H bond, similar to most alkenes. By replacing the β hydrogens with less labile fluorine atoms it is hoped that breakage of the β C-F bonds will be restricted and that other modes of decomposition can be observed. Accordingly the photochemical characteristics of 3,3,3,-trifluoropropyne were studied. .

Reactions of Unsaturated Free Radicals:

Since the primary products from the photochemical reactions of unsaturated compounds are often unsaturated radicals, a short description of vinyl and ethynyl radical reactions is presented below.

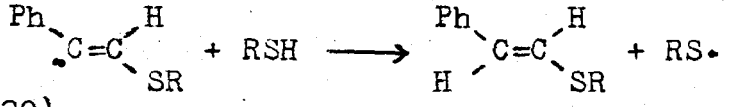
In comparison to the amount of quantitative data available concerning the reactions of alkyl radicals, very little is known about the reactions of vinyl and ethynyl radicals. The problems that arise in the investigation of unsaturated radical reactions can generally be attributed to the difficulty in obtaining clean radical sources and also to the problems associated with separating the alkene-alkyne product mixtures. However, development of compounds with more efficient separating qualities for gas-liquid chromatography[16] has eased the latter problem somewhat. From the few studies performed on the reactions of vinyl and ethynyl radicals, it appears that these radicals undergo essentially the same reactions as alkyl radicals; namely disproportionation, abstraction, and addition. In the case of unsubstituted vinyl radicals the following reactions have been observed.[17,18]

$$2\cdot C_2H_3 \longrightarrow C_4H_6 \text{ combination} \qquad 24)$$

$$\longrightarrow C_2H_2 + C_2H_4 \text{ disproportionation} \qquad 25)$$

$$\cdot C_2H_3 + C_2H_4 \longrightarrow \cdot C_4H_7 \text{ addition} \qquad 26)$$

Oswald et al.[19] observed that substituted vinyl radicals abstracted hydrogen from thiols.



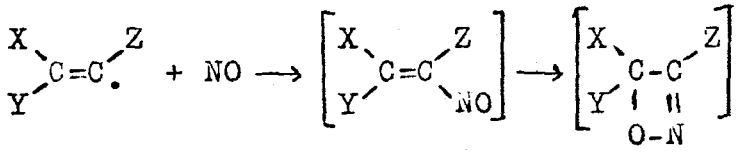
27)

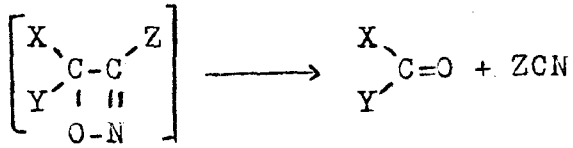
Sherwood[20] reacted vinyl radicals, produced from the photolysis of divinylmercury, with hydrocarbons and obtained ethylene.

$$H_2C=\dot{C}H + RH \longrightarrow C_2H_4 + R\cdot \qquad 28)$$

At the same time, the yield of C_4H_6 decreased as the combination reactions were suppressed.

Reactions of various vinyl radicals with nitric oxide have been studied by Sherwood and Gunning[21] and it was postulated that the following mechanism could account for the results.





29)

X,Y,Z, are the substituents of the vinyl radical.

Gunning's group[22,23] has extensively studied the reactions of ethynyl radicals and it appears it undergoes many of the same radical reactions as alkyl radicals as well as a number of characteristic ones. For instance the ethynyl radical abstracts primary, secondary and tertiary hydrogen from alkanes much like alkyl radicals do but with generally less selectivity. Apparently the activation energy for hydrogen abstraction by ethynyl radicals is lower than for alkyl radicals.

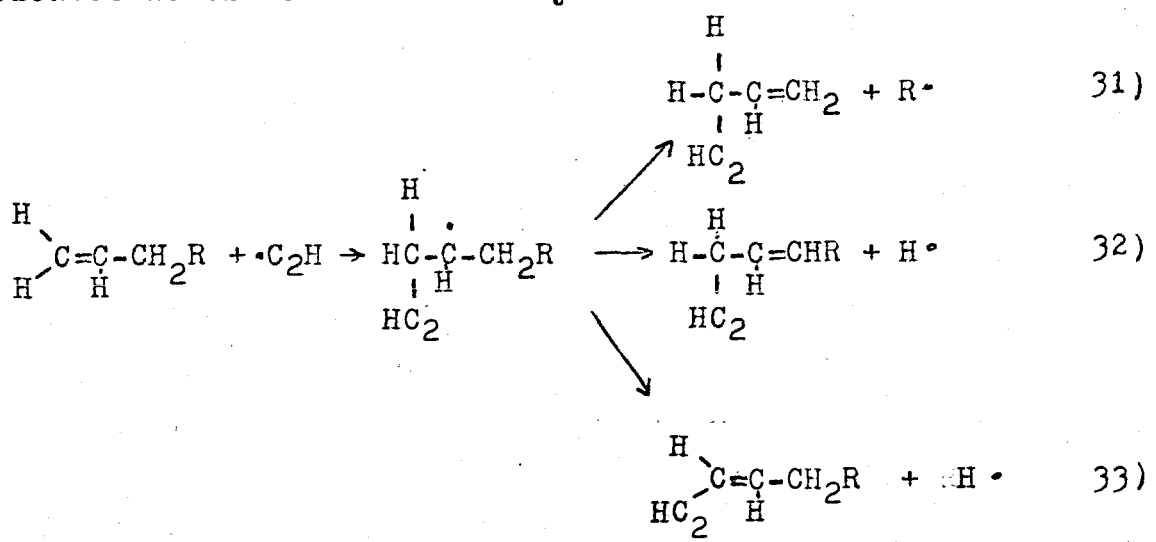
Whereas alkyl radicals tend to combine relatively easily, combination of ethynyl radicals does not appear to be a very important process except at high radical concentrations.

Unlike many other radicals, ethynyl radicals were found to be non reactive towards nitric oxide.

A characteristic reaction of ethynyl radicals is the displacement of substituents from acetylene compounds[20]. For example

$$\cdot C_2H + C_2HBr \longrightarrow C_4H_2 + Br\cdot \qquad 30)$$

Additions of ethynyl radical to various alkenes[23] have shown that the ethynyl radical attacks the olefinic bond to give an ethynyl-substituted alkyl radical, which cleaves at the carbon atom adjacent to the radical site.



$$\xrightarrow{} \quad H\text{-}\overset{H}{\underset{HC_2}{C}}\text{-}C\equiv CH_2 + R\cdot \qquad 31)$$

$$\xrightarrow{} \quad H\text{-}\overset{H}{\underset{HC_2}{C}}\text{-}C\equiv CHR + H\cdot \qquad 32)$$

$$\xrightarrow{} \quad \begin{matrix} H \\ \diagdown \\ HC_2 \end{matrix}\!\!>\!C\equiv C\text{-}CH_2R + H\cdot \qquad 33)$$

With a knowledge of the types of photochemical reactions characteristic of unsaturated compounds, the reaction mechanisms operative in the photolysis of 3,3,3,-trifluoropropyne were more easily understood.

EXPERIMENTAL METHOD.

Apparatus and Procedure:

The apparatus used in all experiments was a vacuum line entirely constructed of Pyrex except for the reaction system which was quartz. This apparatus had facilities for gas storage, reactant measurement, vapor phase photolysis, product distillation, product measurement, gas chromatographic analysis, and product collection. These specialized facilities were interconnected to allow quantitative and efficient handling of the volatile materials.

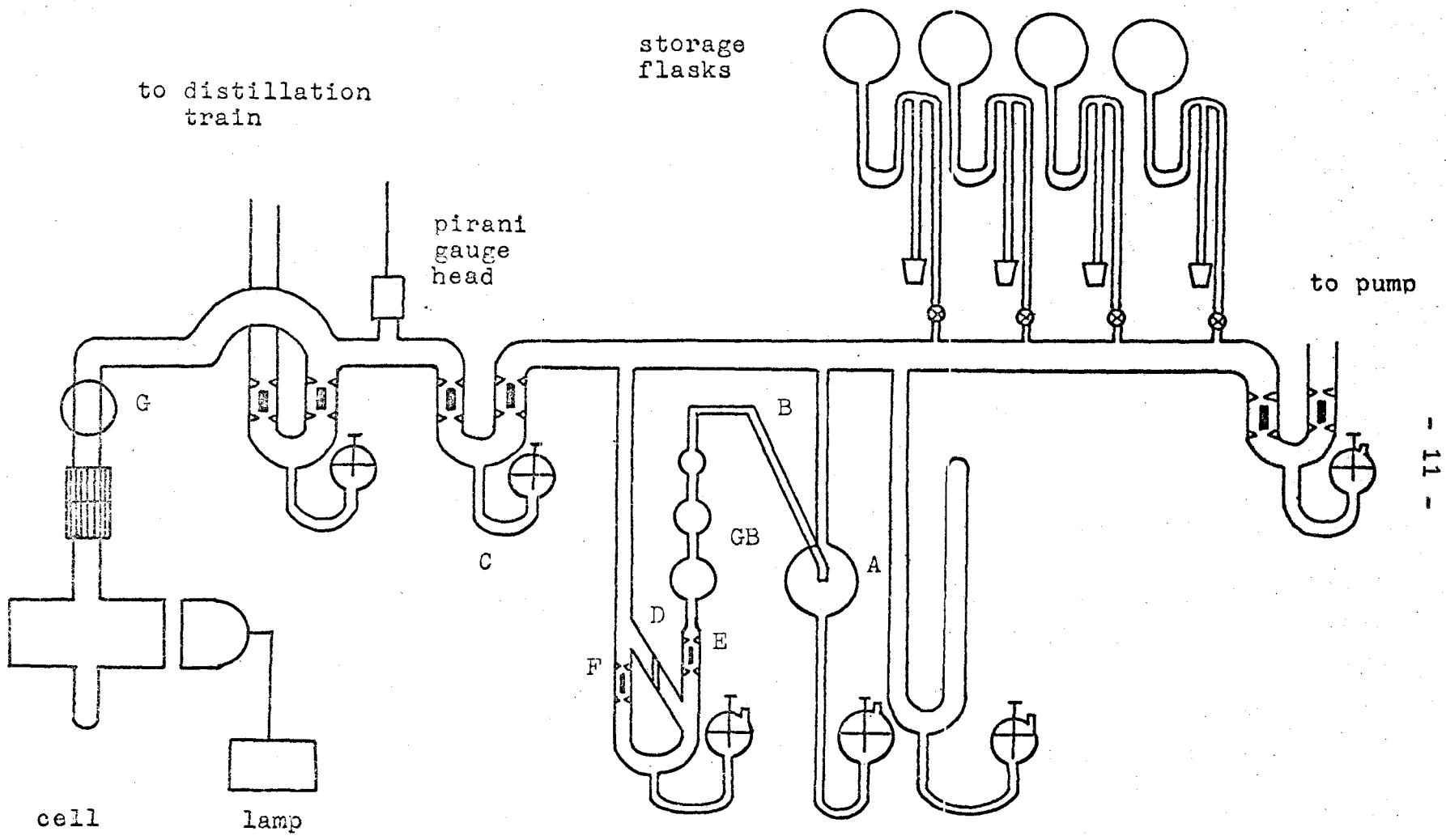
Evacuation of the apparatus to a pressure of about 10^{-5} torr was achieved by a large single-stage mercury diffusion pump backed by a mechanical oil pump (Precision Scientific Co., Model Number 25). Situated between the diffusion pump and the mechanical pump was a removable trap immersed in liquid nitrogen to protect the latter pump from evacuated contaminants. In addition another mechanical pump (Precision Scientific Co., Model Number S-35) was connected to selected parts of the apparatus, including a portable hose attachment, so that various operations requiring only partial evacuation could be performed.

A four-stage pirani vacuum gauge (Edwards, Model Number 9) was used to monitor the pressure at various points in the apparatus.

Four gas storage flasks were connected to the main vacuum line by Veeco metal valves. The valve input and

output ports were connected to the pyrex line with glass-Kovar joints. Each flask was equipped with a mercury manometer and a cold trap.

To keep to a minimum the amount of reactant required, the reactant measurement facilites were situated adjacent to the storage flasks and consisted of a manometer and a modified gas buret (G.B). A typical measuring procedure was as follows. The vacuum line connecting the storage flasks, gas buret, manometer, and reaction cell was evacuated, float valves were closed, mercury was raised to level (A) just below the right port of the buret and the mercury level was raised in the left side of the buret to the desired volume mark. The telescope of the cathetometer (Precision Optical Co.) was situated at a position for the desired pressure reading. The storage flask valve was slowly opened until the gas filled the buret to the desired pressure, as seen through the telescope, at which time the valve was closed. The pressure was then recorded along with the volume of the buret. The right port of the buret was then sealed by allowing the mercury level to rise in this side to the horizontal section (B). At this stage of the operation a known volume and pressure of reactant has been isolated from the original stored sample. The reactant left in the line was condensed back into the storage flask. The valve on the flask was then closed and valve (C) was opened. The mercury on the left side of the gas buret was pulled down by the roughing pump, allowing the measured reactant to


storage
flasks
to distillation
train
pirani
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to pump
G
B
GB
A
C
D
E
F
cell
lamp

Fig. 1(a)

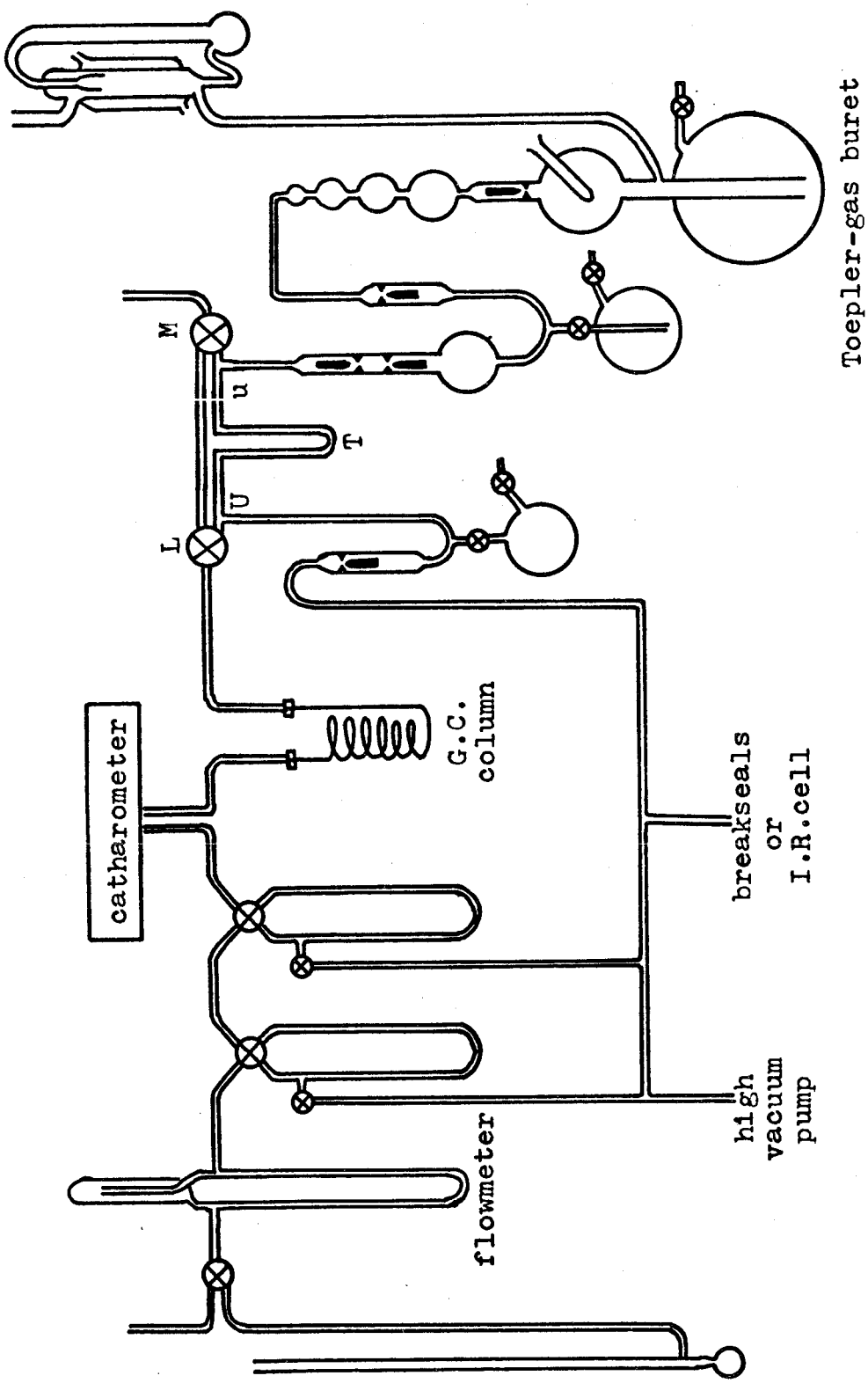

Toepler-gas buret
M
u
T
U
L
catharometer
G.C.
column
breakseals
or
I.R.cell
high
vacuum
pump
flowmeter

Fig. 1(b)

diffuse through the Corning medium grade glass sinter (D). This sinter readily allowed gas to diffuse through it but prevented passage of mercury. The arrangement of the float valves E and F along with the sinter was necessary to remove the gas from the buret without having mercury forced into the main line. The reactant was then condensed in the reaction cell and valve G closed. Other reactants could be measured and added to the reaction cell by the same method making possible any desired combination of gas mixtures.

The procedure for measuring nitric oxide was slightly different than that described above because of its vapor pressure of 70μ at liquid nitrogen temperatures. After isolation of the NO in the gas buret the remaining NO could not be completely condensed into the storage flask. Hence the residual 70μ was allowed to remain in the line as the measured NO was being transferred to the cell. A small error in the amount of NO actually entering the cell could be produced by this procedure but it was not measureable.

For quantitative transfer all other reactants had to be introduced into the cell before the nitric oxide.

Mixtures of reactants were allowed to stand in the cell for approximately 20 minutes before irradiation was started to ensure complete gas mixing.

Two quartz reaction cells were employed in these experiments. Each cell was 10cm in length, 5cm in diameter, and

respective volumes of 163.9ml and 173.2ml. The volumes of the reaction chamber included the reaction cell as well as the space in the line to valve G.

A $\frac{1}{2}$ inch "O" ring Cajon fitting was used to attach the cells to the vacuum line. The transmission properties of each cell were tested by comparing the yields obtained from both cells under identical conditions. There was no noticeable difference in the yields.

Irradiations were performed with an unfiltered Hanovia Utility Ultraviolet Quartz Lamp 30620 connected to a Sola Constant Transformer CVS. The lamp was allowed to stabilize for approximately 20 minutes before irradiation of the sample. The temperature in the reaction chamber was $25 \pm 2^{o}C$ for all irradiations. A series of three U-shaped cold traps for low temperature distillation were situated between the reaction cell and the analytical system. These traps could be isolated from each other by closing the mercury float valves placed between the traps.

The analytical system consisted of a gas buret and Toepler pump apparatus, and injection system and a gas chromatograph as shown in Fig. 1 (b). After the product mixture had been measured in the gas buret it was condensed in the injection tube (T) ready for analysis. Prior to injection the mercury levels were raised to the positions marked (u) and (U) in the diagram. Vaporizing the gas and reversing the 3-way stopcocks L and M, the helium carrier gas guantitat-

ively flushed the contents of the tube into the separating column.

A 6' by 3/16" pyrex column packed with 50-80 mesh Porapak Q was used for all separations. Temperature programming the column from 0°C to 200°C proved to be very effective for achieving separation of all the products. The retention times and the elution temperature of the products are listed in Table (1).

An ice-water bath was used for the separations at 0°C and a furnace connected to an Armaco Voltage Regulator was used in raising the column temperature to 200°C.

Upon elution from the column the products were directed through a Gow Mac Model 24 catharometer connected to a Gow Mac Model 9999 DI power supply. The catharometer was maintained at 50°C and the current output of the power supply at 7.5 m amps. Signals from the catharometer were fed into a Texas Instrument Co. Servo/riter II Model FS01 6D chart recorder equipped with an attenuator to reduce the signal by factors of 1 to 1000.

Helium used as the carrier gas was dried by passing it through a molecular sieve column. The divided flow was maintained at 50 ml per minute through the reference side of the detector.

Collection of samples for mass spectroscopic or spectrophotometric identification was achieved by the three traps

TABLE 1

Temperature Programmed Gas Chromatography

Temperature	Product	Elution Time min.	System
	CO_2	6.4	
0° C	N_2O	9.0	
	C_2HF	11.2	
	CF_3NO	12.5	
	C_2H_2	16.5	CF_3C_2H + NO
25°	CF_3CN	21.5	
50°	CF_3C_2H	36.0	
85°	PA	54.0	
125°	C_4H_2	61.0	
200°	$C_9F_9H_3$	90.0	
	C_2HF	11.2	
	CF_3H	13.0	
0° C	C_2H_2	16.5	CF_3C_2H + C_3H_8
50°	CF_3C_2H	36.0	
80°	$(CF_3)_2C_2H_2$	48.0	
200°	$C_9F_9H_3$	90.0	

connected to the helium flow downstream from the detector. The products could then be transferred from the traps to breakseal tubes or spectrophotometer cells.

The GC was calibrated by determining the peak areas of measured samples of the compound over a range roughly corresponding to the range of yields obtained in these experiments. Over this range the molar response values were found to be independent of sample size. Areas were measured with a Gelman 39321 planimeter. Relative response values were calculated using carbon dioxide as a reference so that corrections could be made for day to day deviations in the catharometer sensitivity. By measuring the daily molar response value of carbon dioxide the response values of the other compounds could be calculated from their relative response values. The daily variation in the response value was less than 5%.

Examination of the ultraviolet absorption spectrum of 3,3,3,-trifluoropropyne showed appreciable absorption at wavelengths shorter than 1950 Å. The only emission produced by the medium pressure mercury arc lamp in this region is the 1849 Å line.

Since nitric oxide has quite a large absorption in the ultraviolet there is a possibility that photolysis of NO by the 1849 Å line was initiating a significant part of the reaction for the systems with NO added. To eliminate or greatly reduce any nitric oxide absorption in the reaction

TABLE 2

Effect of nitric oxide filter on yields in the photolysis of 3,3,3,-trifluoropropyne in the presence of nitric oxide.

Compound	Yields (moles x 10^{-7})	
	filter with NO	filter without NO
CO_2	5.8	6.6
N_2O	4.6	6.3
C_2HF	4.4	4.6
C_2H_2	2.5	2.8
CF_3CN	7.6	8.5
C_4H_2	22.8	24.7
PA	18.3	15.3

The filter cell had a path length of 2.0 cm. The NO pressure was 20 torr.

cell an auxilliary cell containing NO at 2.0 torr was placed between the lamp and the reaction cell. 60 minute irradiations were performed on identical mixtures of nitric oxide and 3,3,3,-trifluoropropyne when the NO in the filter was condensed and when it was vaporized. The yields of the products of the filtered reaction were slightly lower as can be seen in Table (2). This effect could be a result of a reduction in light intensity as well as to a decrease in NO photosensitization.

Materials:

3,3,3,-trifluoropropyne was obtained from the Peninsular Chemresearch Co. The major impurity, carbon dioxide, was reduced to about 0.1% by gas chromatographic separation. Another small impurity (about 0.5%) could not be easily removed by the GC or by distillation.

Nitric oxide obtained from Matheson of Canada Ltd. was distilled through a 2-methyl butane slush to remove some of the higher oxides of nitrogen. Besides the above distillation, care was taken in removing the NO from the storage flask by the following method. Prior to use the NO was condensed in the flask and the valve opened. The NO was then allowed to partially vaporize until the desired pressure in the gas buret was reached. In this way the higher oxides of nitrogen remained condensed in the storage flask.

Carbon dioxide and propane were obtained from Matheson

of Canada Ltd. and were used without further purification.

Butadiyne was prepared according to the method of Georgieff and Richard[24]. A concentrated sodium hydroxide solution was reacted with a solution of 1,4-dichloro-2-butyne and ethyl alcohol under a flow of helium. The product was swept out of the reaction vessel and condensed in a liquid nitrogen trap. The 1,4-dichloro-2-butyne was obtained from K and K Laboratories Inc.

The other materials required for calibration of the GC were obtained from commercial suppliers.

Data Presentation:

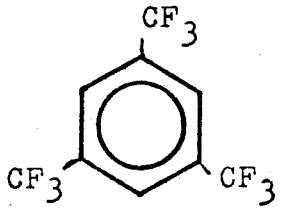
All the spectra used for product identifications have been grouped together at the end of the Results section. The mass spectra have been presented in tabular form indicating the relative abundance of the m/e peaks along with their ion assignments.

Yield data for each system of reactions have in most cases been presented in tabular as well as in graphical form.

RESULTS

A. Photolysis of 3,3,3,-Trifluoropropyne.

The only volatile product formed in the photolysis of 3,3,3,-trifluoropropyne has been indentified by its mass, spectra and its nuclear magnetic resonance spectra as 1,3,5,-tris (trifluoromethyl) benzene



(Table 10, fig. 19). Besides the benzene derivative a non-volatile brown deposit is observed in the reaction cell after irradiation.

The yield of 1,3,5,-tris (trifluoromethyl) benzene as a function of irradiation time is presented in Table (3). The values are only proportional to the molar yield because the response value for the substituted benzene could not be determined. Its low vapor pressure restricted the molar quantities that could be measured in the gas buret.

Deposition of the brown substance seemed to be more severe at longer irradiation times indicating polymer formation. This material could not be removed with water and only partially with organic solvents. The cell had

TABLE 3

Effect of exposure time on the yield of 1,3,5,-tris (trifluoromethyl) benzene in the photolysis of 3,3,3,-trifluoropropyne.

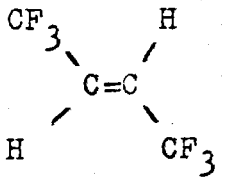
Exposure time (mins.)	Relative Yield	Approximate Molar Yields
15.0	280	1.4×10^{-5}
30.0	375	1.9×10^{-5}
45.0	538	2.7×10^{-5}
61.0	660	3.3×10^{-5}

The yields are only proportional to molar values because the relative response value was not obtained. From consideration of relative response values as a function of molecular weight the molar quantities are approximately as shown.

to be cleaned after every reaction by washing with a hot mixture of concentrated sulphuric and nitric acid.

B. Photolysis of 3,3,3,-Trifluoropropyne in the Presence of Propane.

Propane was added to the reaction system as a source of abstractable hydrogen atoms in order to elucidate the reaction mechanism. The main products of the photolysis of CF_3C_2H in the presence of propane are fluoroform, acetylene, trans-1,1,1,4,4,4,-hexafluoro-2-butene, and 1,3,5,-tris (trifluoromethyl) benzene.



A trace amount of fluoroacetylene is also formed.

Yields of the products as a function of propane pressure at a constant substrate pressure and a constant irradiation time are displayed graphically in Figs. 2 to 5 as well as in tabular form (Table 4).

The non-volatile deposit was considerably reduced in the reactions done with added propane but was still in evidence after long exposure times.

C. Photolysis of 3,3,3,-Trifluoropropyne in the Presence of Nitric Oxide.

Nitric oxide was added to the substrate to act as a free radical scavenger during the photolysis of CF_3C_2H. The main products of this reaction are carbon dioxide,

nitrous oxide, trifluoronitrosomethane, trifluoroacetonitrile, butadiyne, 1,3,5,-tris (trifluoromethyl) benzene, and an unidentified product designated as PA. A discussion on the identification of PA is presented on page 56. Trace amounts of fluoroacetylene and acetylene are also formed.

Yields of these products as a function of exposure time are given in Table 5. The same results are also shown graphically in Figs. 6 to 9 and clearly show a linear dependence at shorter times with a gradual levelling at longer exposures.

Table 6 and Figs. 10 and 11 show the effect of nitric oxide concentration on the yield of products for runs of thirty minutes except where indicated. In cases where the exposure time was not thirty minutes the yields were multiplied by the appropriate factor. Such a correction is only feasible for times of less than forty minutes because the yields as a function of exposure time are linear only in this range.

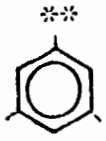
D. Photolysis of 3,3,3,-Trifluoropropyne in the Presence of CO_2 and NO.

In order to determine the effect of an inert gas on the product yields in the propyne-nitric oxide reaction, irradiations were performed with varying carbon dioxide

Table 4

Photolysis of 3,3,3,-trifluoropropyne with added propane.

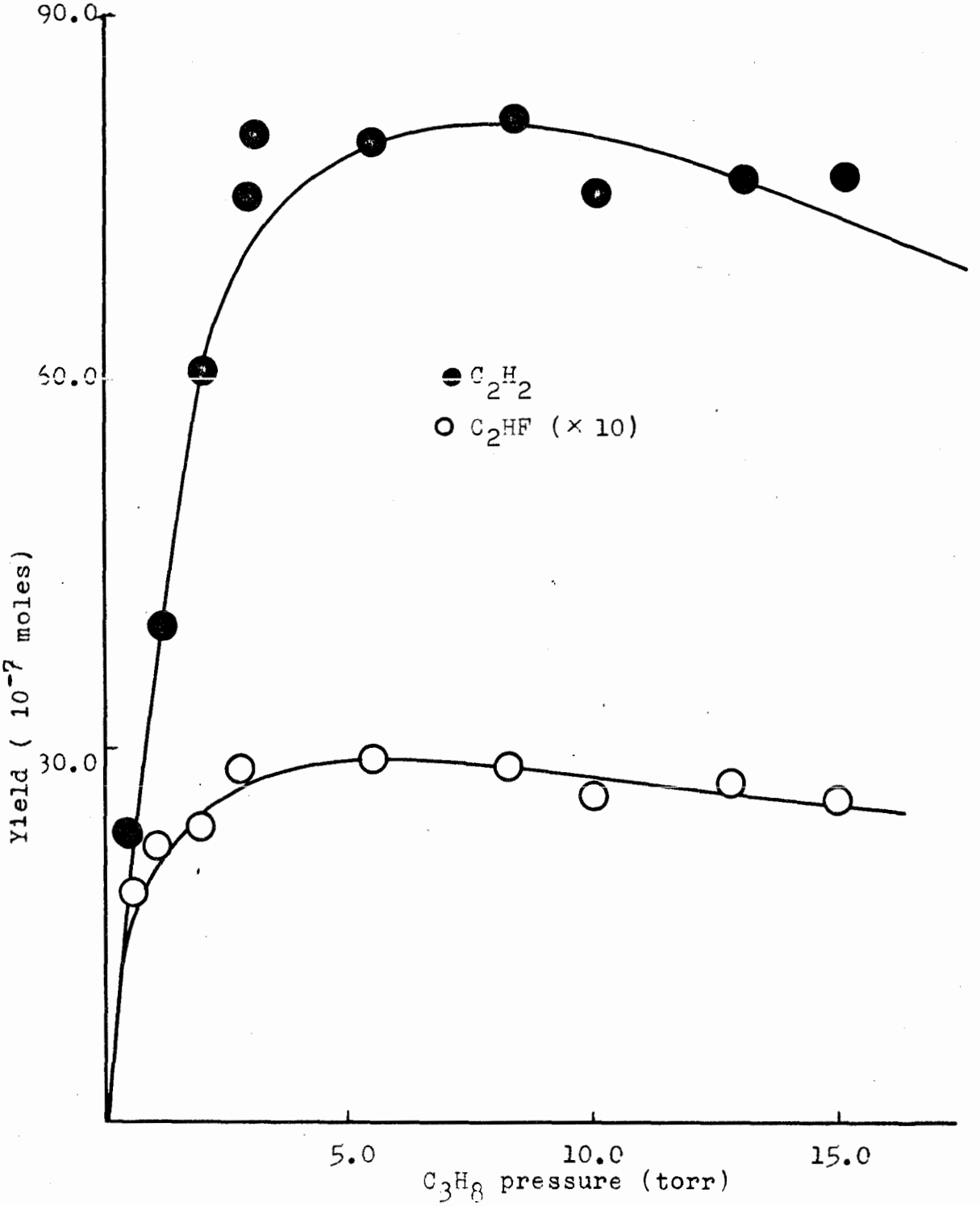
Product yields as a function of propane pressure.

C_3H_8 pressure (torr)	Product Yields (moles × 10^{-7}) C_2HF*	CF_3H	C_2H_2	$(CF_3)_2C_2H_2$	 **
0.51	1.9	1.7	22.8	63.9	232.0
1.01	2.2	2.9	40.1	82.5	
1.98	2.4	3.8	60.3	81.2	53.0
3.03	2.9	5.6	79.9	89.7	33.2
3.06	2.9	5.8	74.9	100.9	
5.37	2.9	7.3	79.3	85.5	18.5
7.95	2.9	10.3	81.5	84.5	
10.0	2.7	8.8	75.5	79.5	
13.0	2.8	12.0	76.7	75.3	
15.0	2.6	13.0	76.7	66.1	

** yields are proportional to 10^{-7} moles and are approximately twice the molar values.

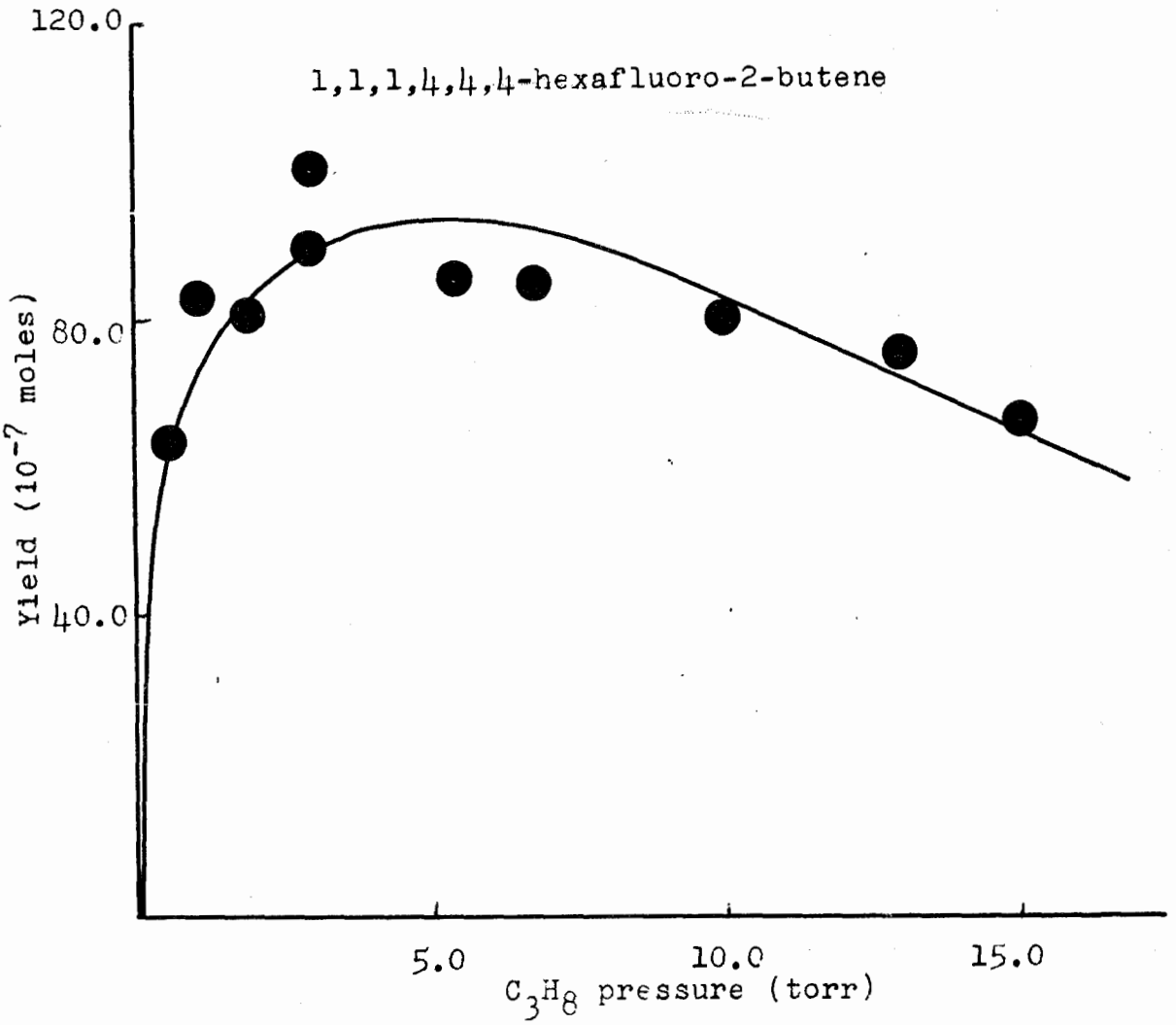
*yields are approximate to the actual yields.

Starting pressure of CF_3C_2H, 2.61 torr; irradiation time, 60 min.



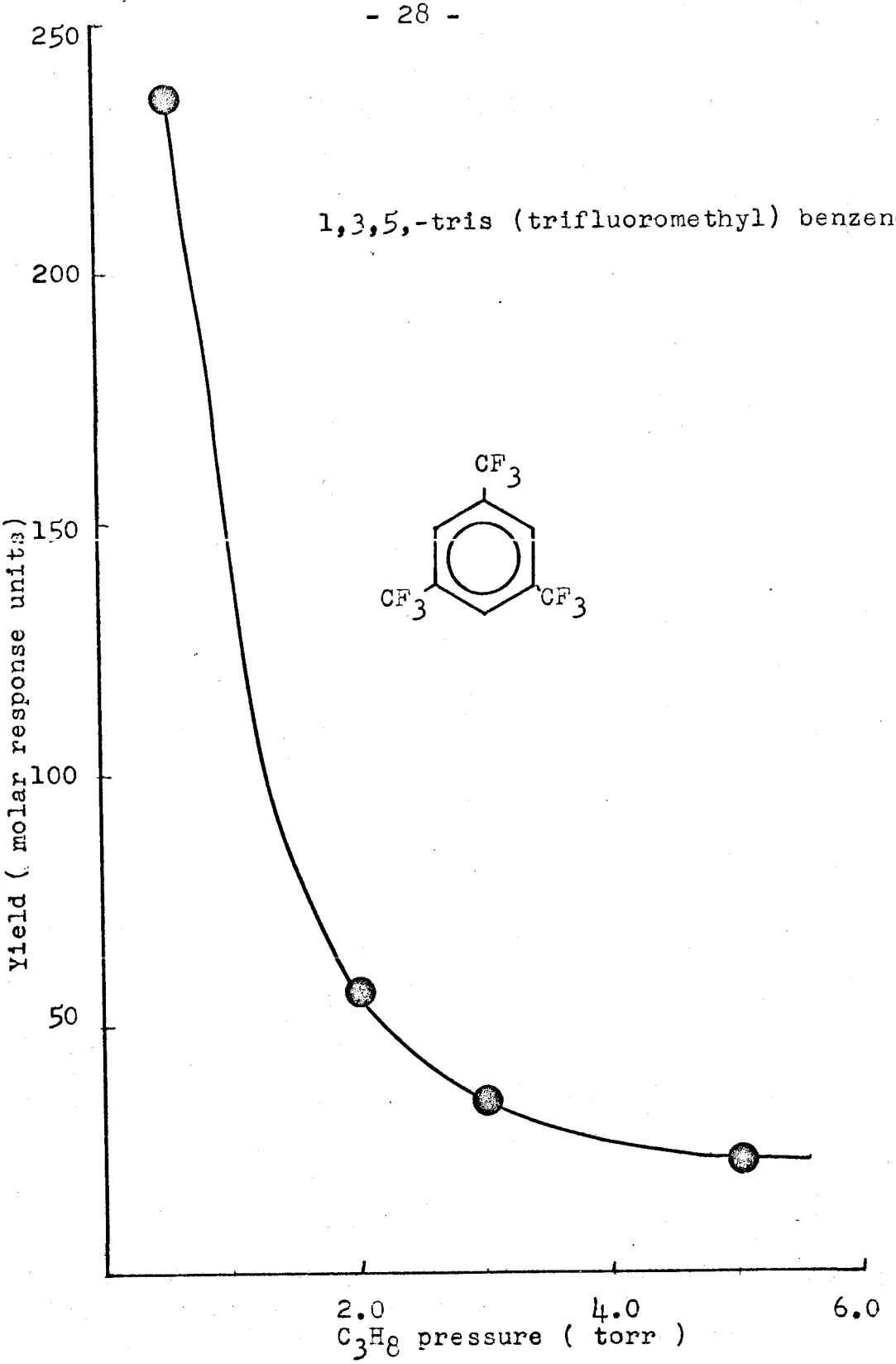
Starting pressure of CF_3C_2H, 2.61 torr; irradiation time, 60 min.

Fig. 2



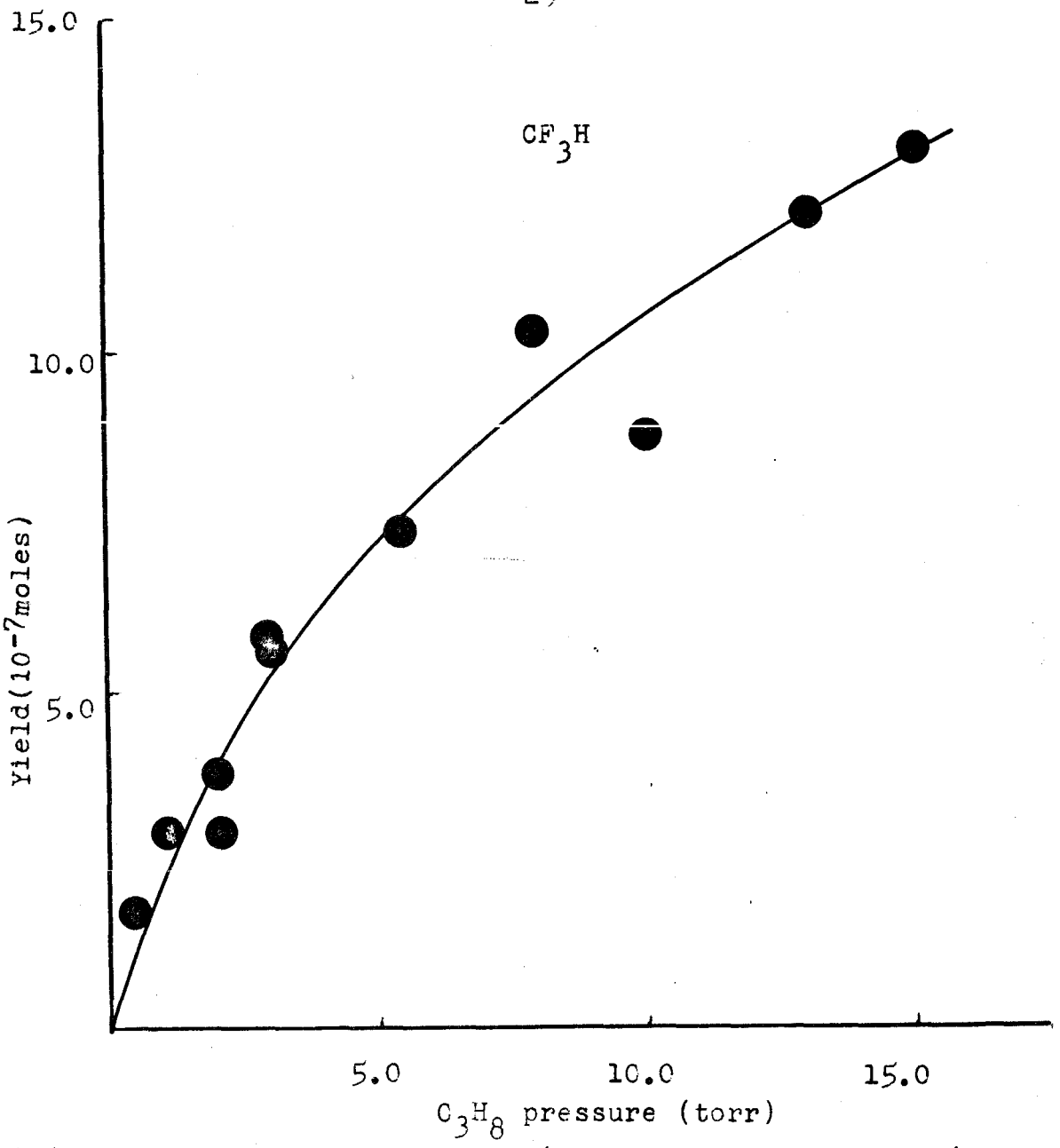
Starting pressure of CF_3C_2H, 2.61 torr; irradiation time, 60 min.

Fig. 3



Starting pressure of CF_3C_2H, 2.61 torr; irradiation time of 60 minutes.

Fig. 4



Starting pressure of CF_3C_2H, 2.61 torr; irration time, 60 min.

Fig.5

Table 5

Photolysis of 3,3,3-trifluoropropyne with added nitric oxide

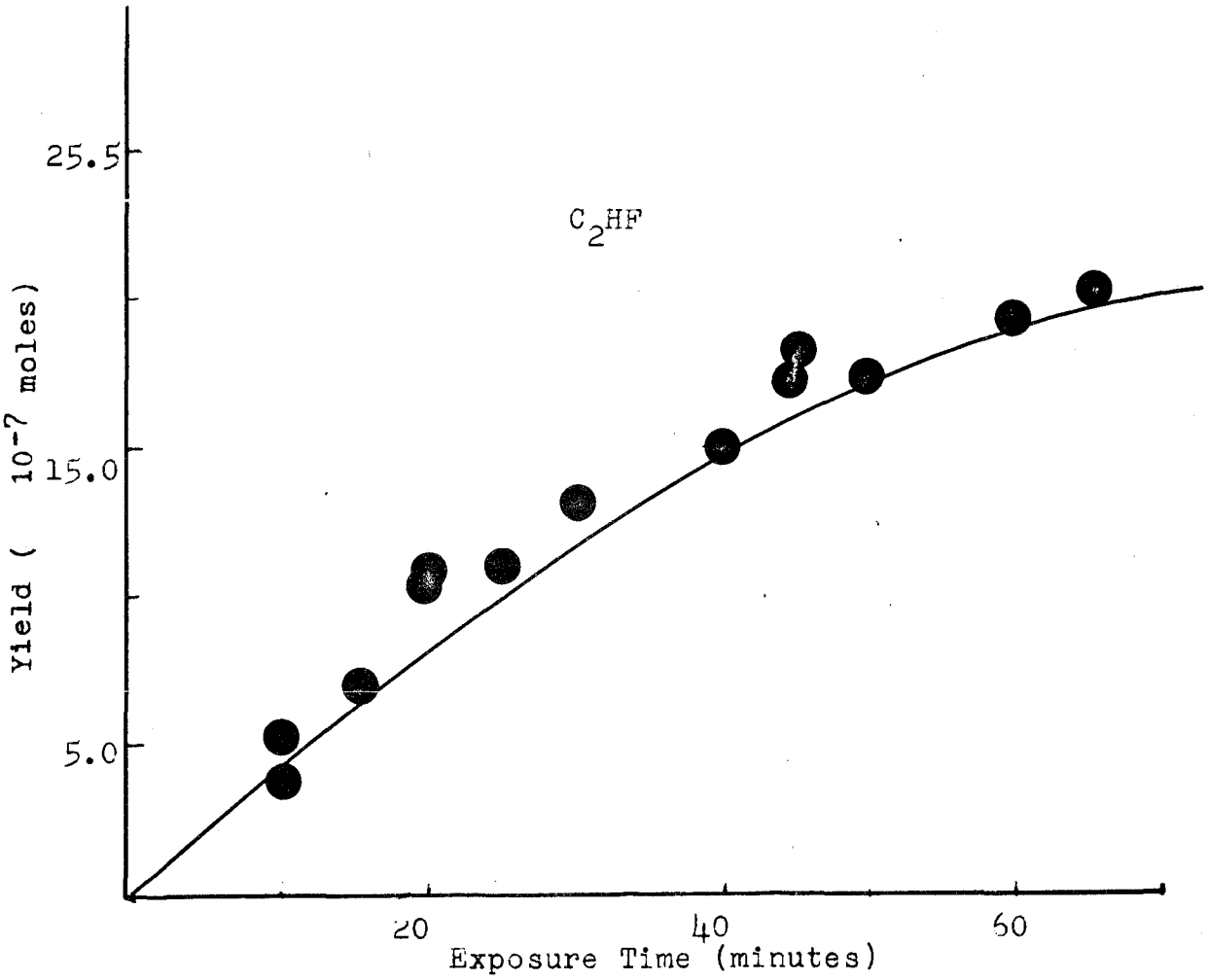
Product yields as function of exposure-time.

Exposure time (mins.)	Product Yields (moles × 10^{-7})								
	CO_2	N_2O	C_2H_2	C_2HF*	CF_3CN	C_4H_2	PA	$P_{C_4H_2}$	P_{N_2O}
10	5.9	4.9	3.6	3.7		20.0		2.0	0.49
10	7.3	8.4	4.0	5.3	10.0	28.3	3.9	2.83	0.84
15	11.2	8.9	5.0	6.9		34.5	8.8	2.30	0.59
20	15.1	13.7	8.3	11.1		51.4		2.57	0.69
20	13.5	8.0	9.3	10.6	20.6	52.0	7.4	2.60	0.40
25	20.4	12.0	13.2	10.9	23.8	52.8	5.9	2.11	0.42
30	20.9	10.8	13.3	13.2	29.3	60.5	13.9	2.02	0.36
40	28.9	15.3	21.5	14.9	36.9	72.3	6.0	1.81	0.37
45	35.9	17.9	13.5	18.3	38.0	83.1	9.8	1.85	0.40
45	31.8	19.2	16.6	17.2		77.3	9.2	1.72	0.43
50	35.4	16.3	24.8	17.3	39.8	79.0	8.2	1.58	0.33
60	53.6	21.0	26.4	19.6	51.2	73.9		1.23	0.35
65	47.3	23.2	31.7	20.3	48.4	92.2	12.3	1.42	0.36

* Yeilds are approximate to molar quantities.

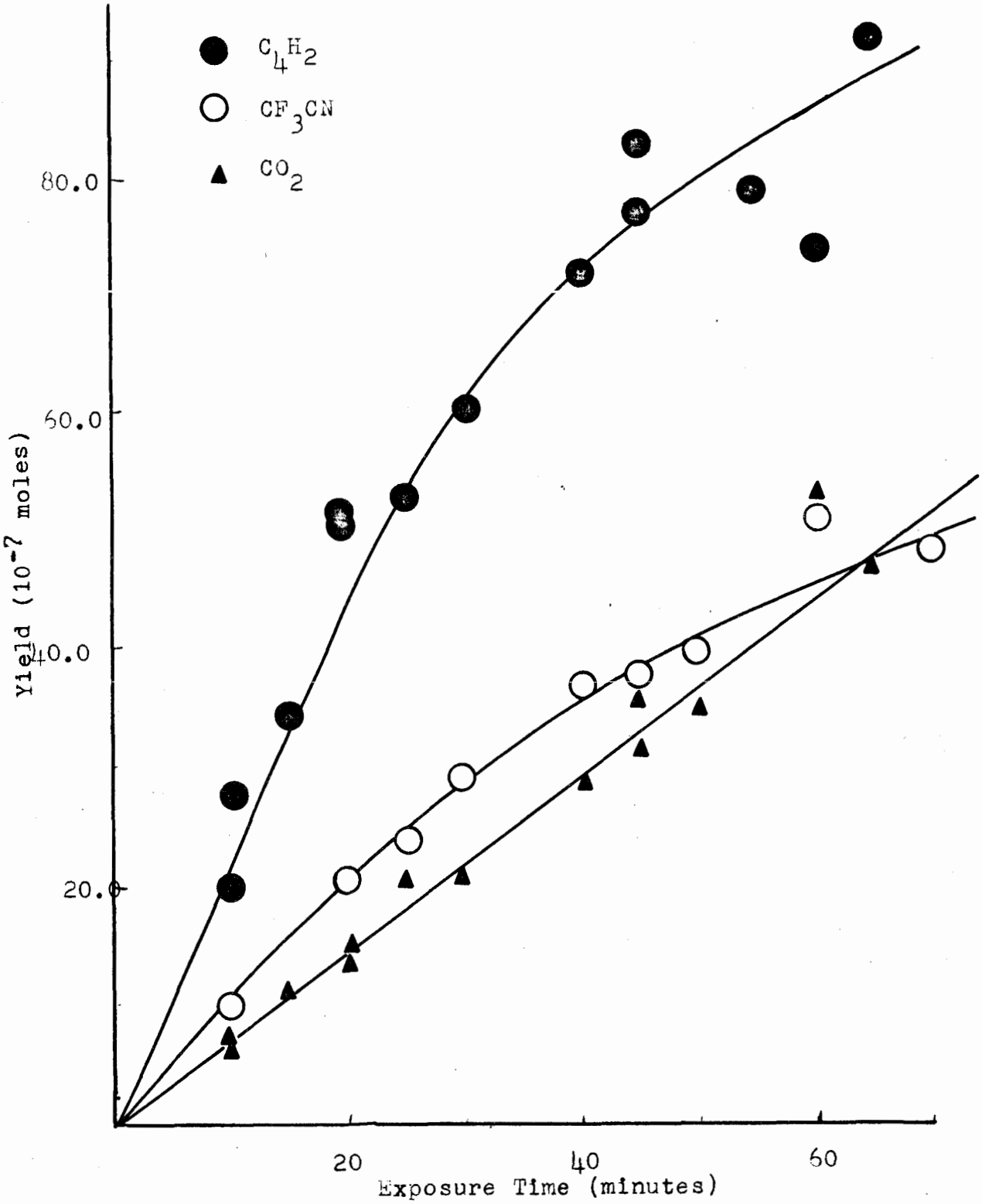
Starting pressure of CF_3C_2H, 5.22 torr;

Starting pressure of NO, 1.05 torr.

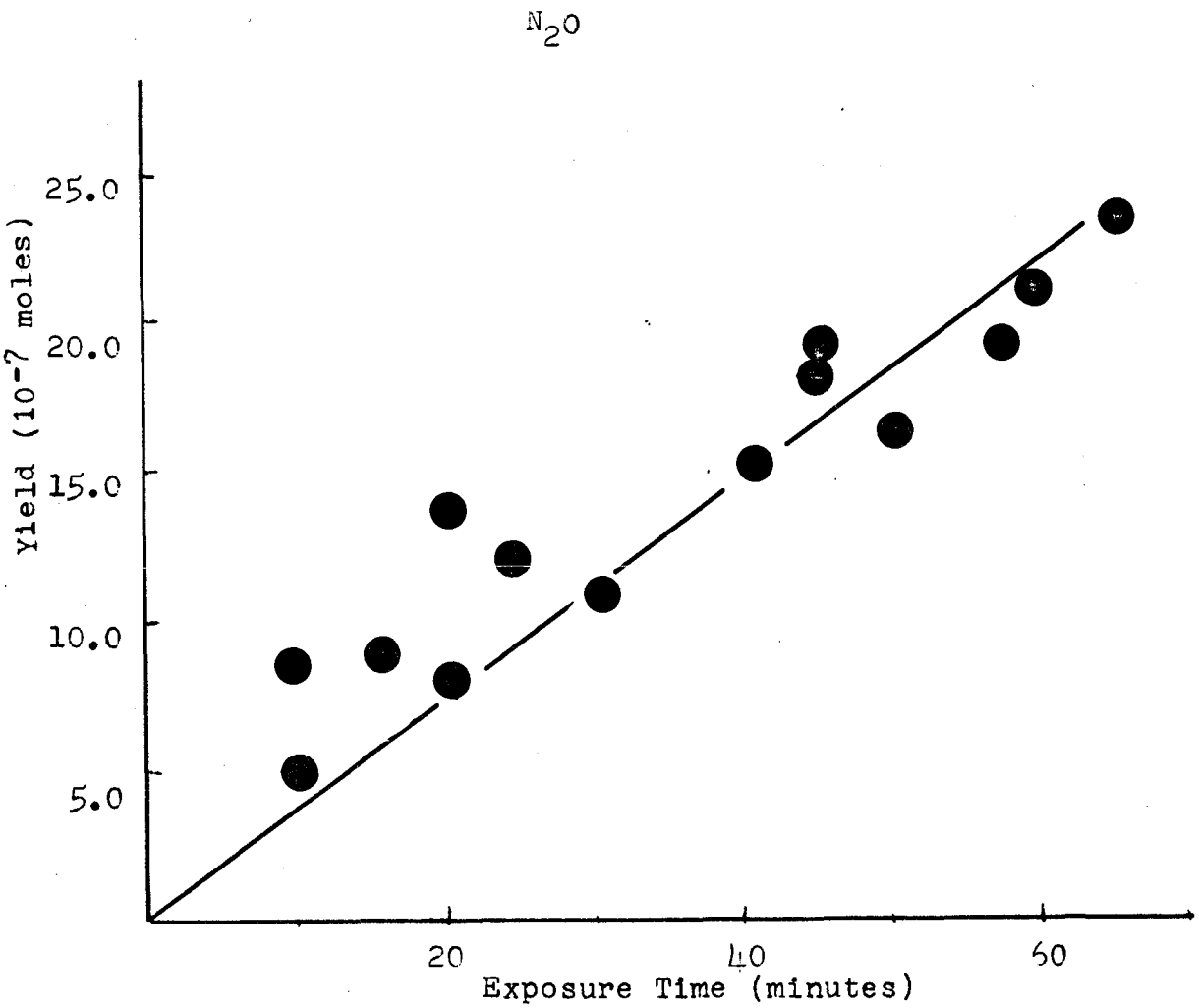


Starting pressure of CF_3C_2H, 5.22 torr; starting oressure of NO, 1.05 torr.

Fig. 6

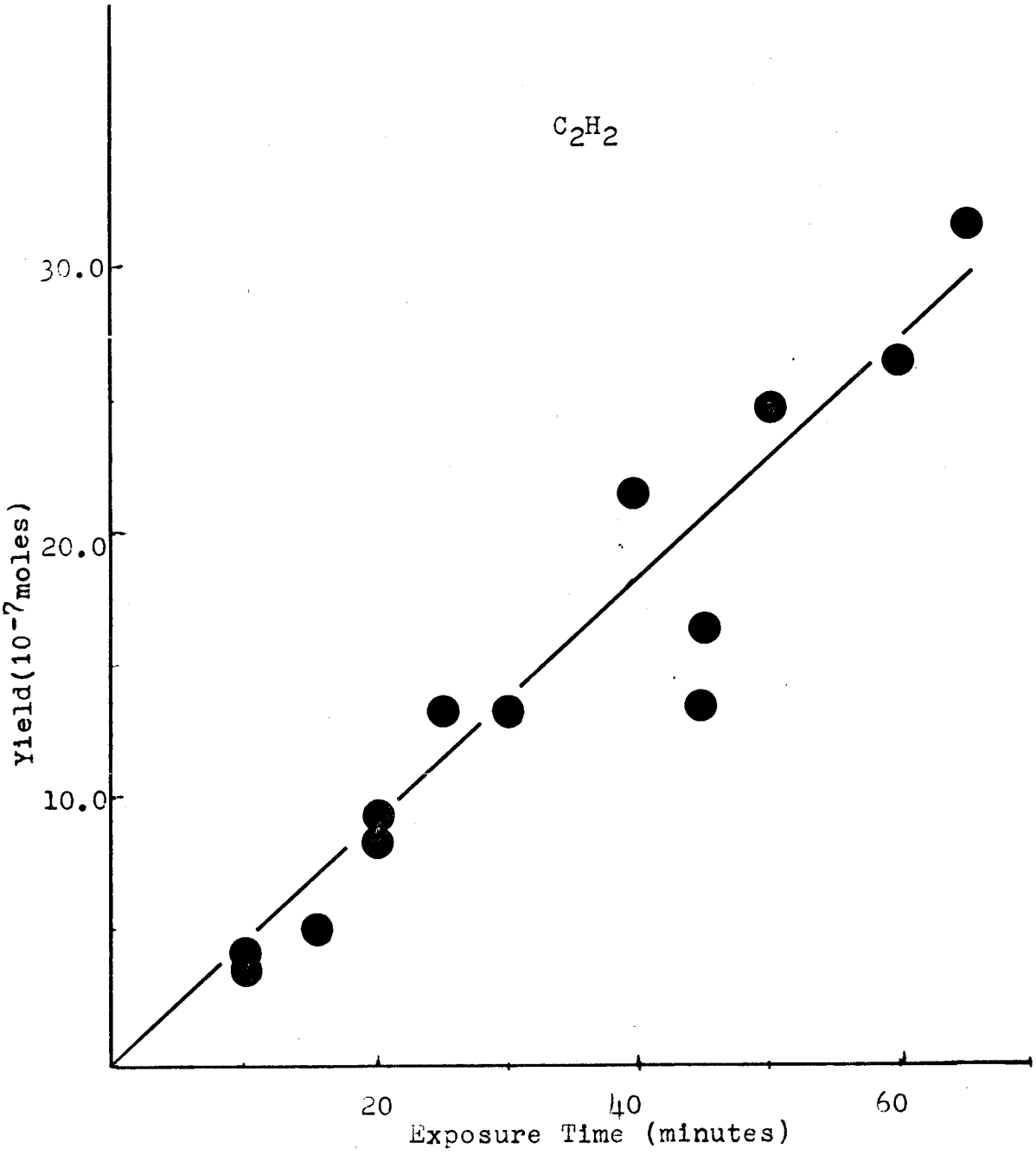


Starting pressure of CF_3C_2H, 5.22 torr; starting pressure of NO, 1.05 torr. Fig. 7



Starting pressure of CF_3C_2H, 5.22 torr; starting pressure of NO, 1.05 torr.

Fig. 8



Starting pressure of CF_3C_2H, 5.22 torr; starting pressure of NO, 1.05 torr.

Fig. 9

pressure. The yields presented in Table 7 do not depend on CO_2 pressure.

E. Photolysis of CF_3C_2H in Presence of NO and Propane.

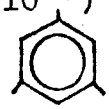
Propane was added to the nitric oxide-propyne system to demonstrate competition between the propane and nitric oxide for the free radicals. To this end, the yields of the products as a function of propane pressure at constant nitric oxide and propyne pressure and at constant irradiation times were determined. The results are presented in Table 8 and in Figs. 12 to 15.

Table 9 summarizes the reaction systems studied and tabulates the presentation of data. Table 10 lists the relative abundances of the ion peaks obtained from the mass spectra of the identified products. Fig. 16 (a) and (b) shows the infrared spectra of 1,1,1,4,4,4,-hexafluoro-2-butene and the unidentified product PA. These spectra were obtained from gaseous samples in a 5cm cell using Beckman IR 12 spectrometer. Figs. 17, 18, and 20 represent the nuclear magnetic resonance spectra of 1,1,1,4,4,4,-hexafluoro-2-butene, compound PA, and 1,3,5,-tris (trifluoromethyl) benzene. The proton signals from the first two compounds were not observed because of the small sample quantities.

Table 6

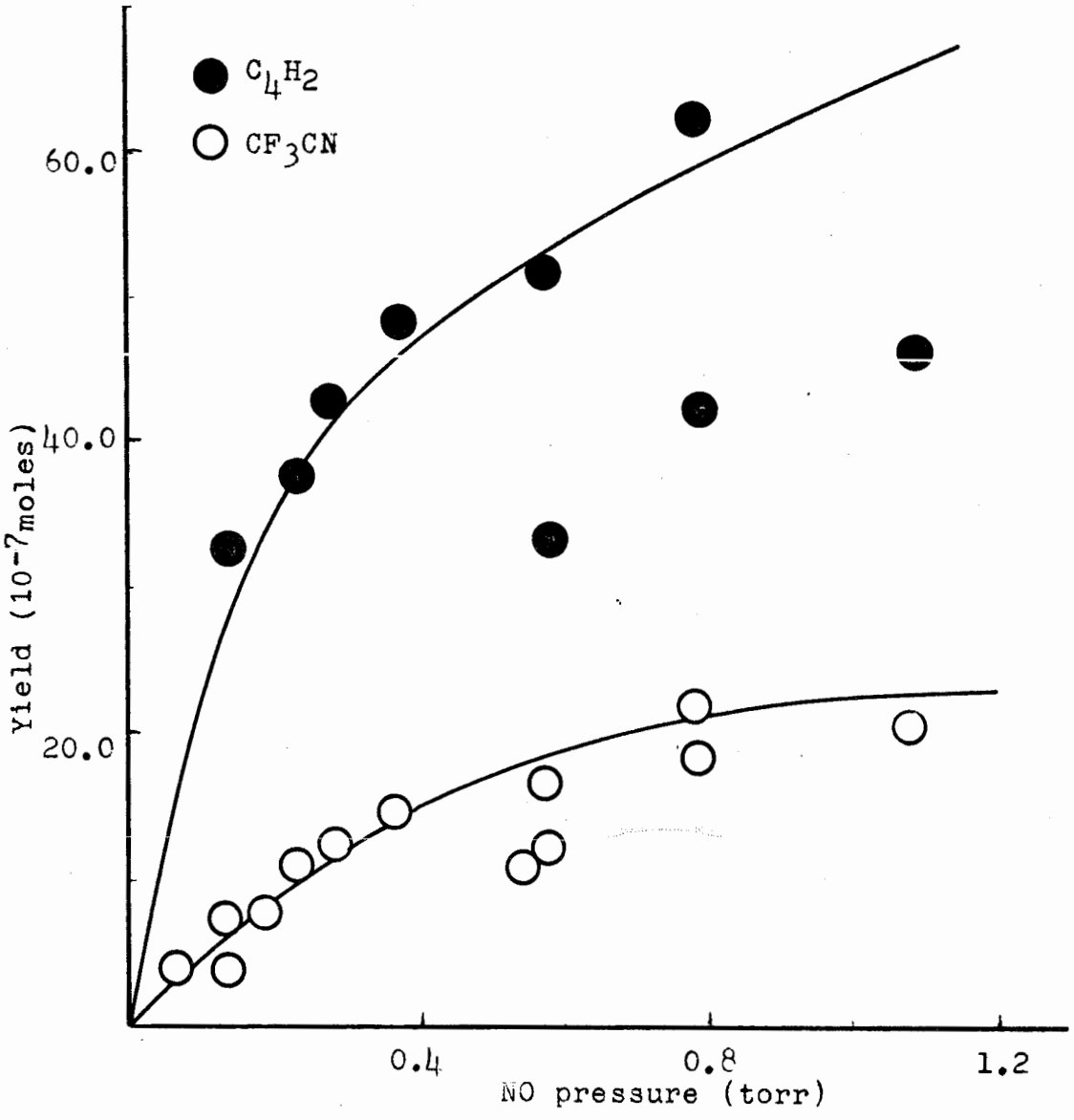
Photolysis of 3,3,3,-trifluoropropyne with added nitric oxide.

Product yields as a function of nitric oxide pressure.

NO pressure	Product Yields (moles x 10^{-7})							
(torr)	CO_2	N_2O	C_2HF	C_2H_2	CF_3CN	C_4H_2		PA
0.00	0.0	0.0	0.0	0.0	0.0	0.0	375	0.0
0.06	4.9	0.7	1.4	0.9	4.0		146	
0.13	9.0	2.0	3.3	2.9	7.5	32.4		
* 0.14	5.0	1.5	0.6	1.1	4.0			5.0
0.19	9.1	2.8	4.5	5.1	8.1			13.3
0.23	12.3	4.0	5.8	6.4	11.2	37.5		21.1
0.27	10.9	3.7	5.9	8.4	12.4	42.9		16.5
0.37	12.3	5.6	7.3	6.3	14.5	47.9		8.2
* 0.54	14.3	5.0	4.3	5.7	11.0			5.1
0.57	12.4	7.6	6.4	5.6	16.4	51.5		6.3
* 0.58	15.2	6.2	4.5	5.7	11.7	33.0		6.6
0.78	14.7	10.4	6.4	5.8	21.4	62.0	78	10.3
* 0.79	15.3	8.9	6.2	10.2	18.4	42.0		6.7
1.08	14.6	12.1	8.0	6.4	20.3	45.8		8.3

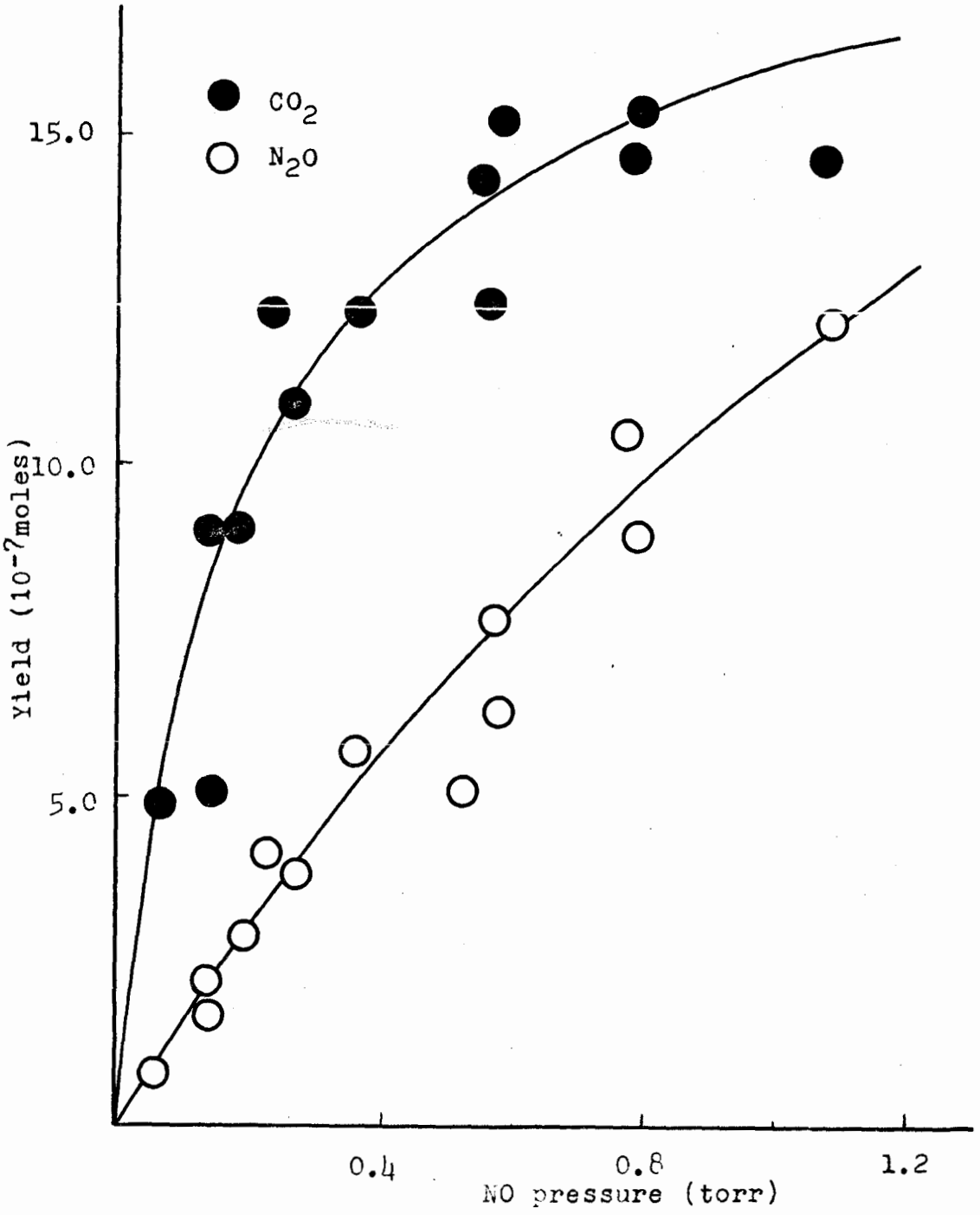
* Exposure time not 30 min. for these runs: the yields have been corrected accordingly.

Yields cited for the benzene derivative are proportional to the molar values.



Starting pressure of CF_3C_2H, 2.61 torr; irradiation time, 30 min.

Fig. 10



Starting pressure of CF_3C_2H, 2.61 torr; irradiation time, 30 min.

Fig. 11

Table 7

Photolysis of 3,3,3,-trifluoropropyne with added nitric oxide and carbon dioxide.

Product yields as a function of carbon dioxide pressure.

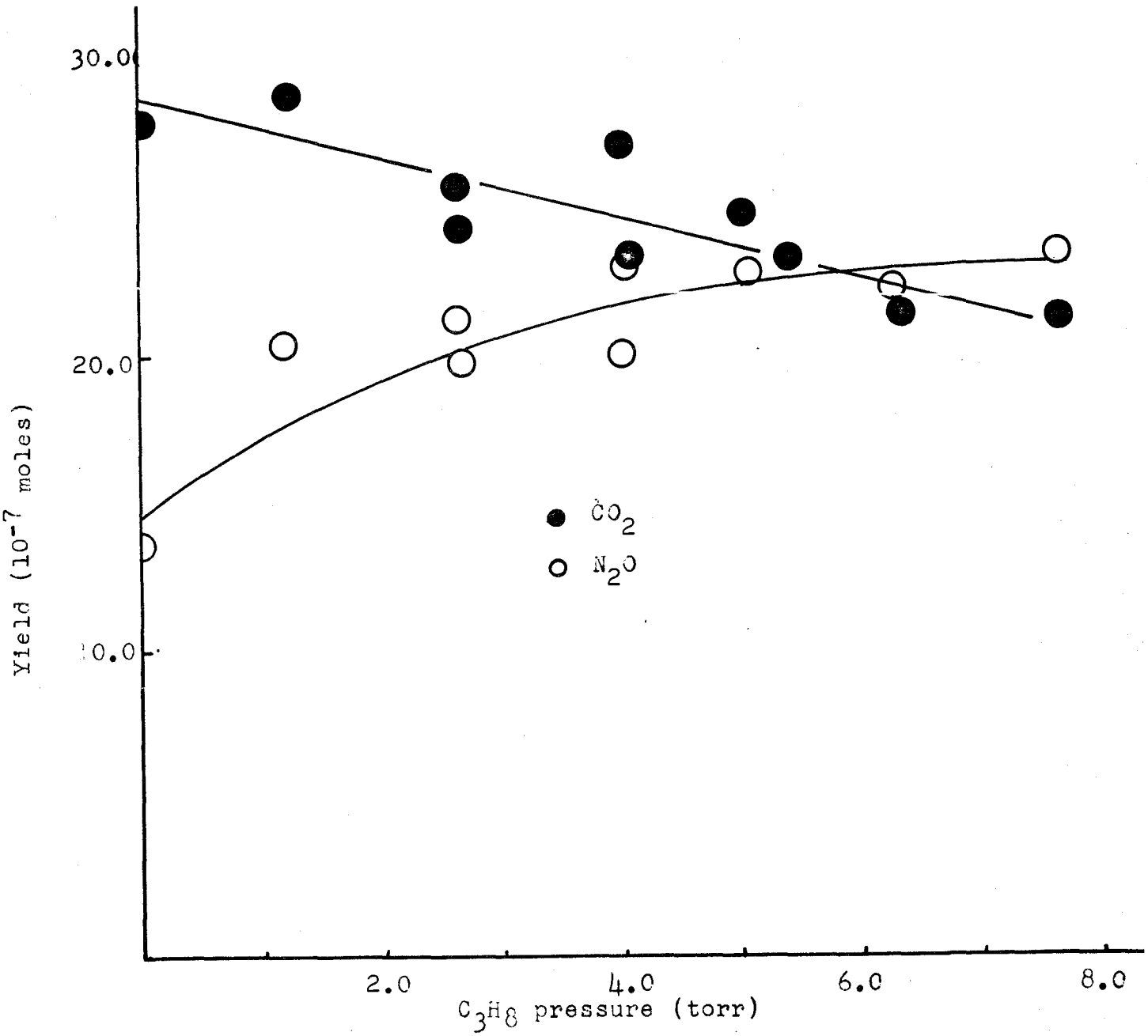
CO_2 pressure	Product Yields (moles $\times 10^{-7}$)					
(torr)	N_2O	C_2HF	C_2H_2	CF_3CN	C_4H_2	PA
0.0	14.1	3.8	6.1	24.6	60.7	
1.36	10.7	6.4	7.7	16.3	34.6	135
1.27	10.9	5.9	6.7	23.7	72.2	45
2.50	14.1	5.2	7.9	26.1	55.5	62
2.66	18.6			31.3	65.9	11
5.31	12.9	6.2	8.1	30.5	50.2	18
5.34	13.0		8.8	28.3	47.9	31
6.63	15.5		9.8	33.2	59.2	14

Table 8

Photolysis of 3,3,3-trifluoropropyne in the presence of nitric oxide and propane.

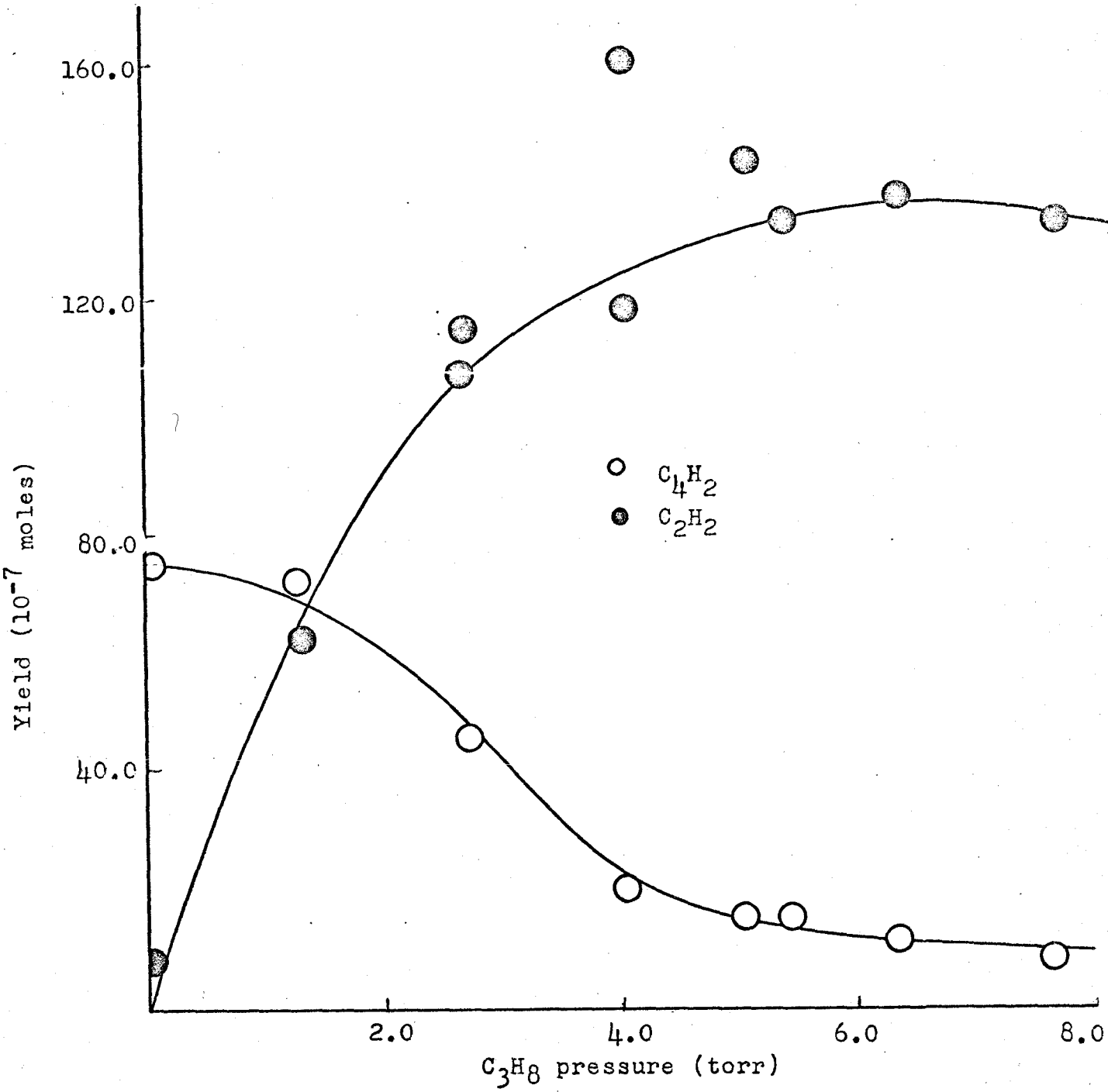
Product yields as a function of propane pressure.

C_3H_8 pressure (torr)	Product Yields (moles × 10^{-7})							
	CO_2	N_2O	C_2HF	C_2H_2	CF_3CN	C_4H_2	CF_3H	PA
0.00	27.6	15.6	11.4	7.5	27.8	75.5	0.0	29.1
1.26	28.8	20.3	5.8	61.9	13.8	72.7		70.8
2.63	25.6	21.4	5.3	115.4	9.6	19.6		58.7
2.65	24.1	19.7	5.3	106.5	11.1	45.8		26.9
3.97	27.1	23.1	4.8	160.1	9.6	20.1		57.5
4.01	22.8	19.9	4.8	119.0	9.1	21.1		30.8
5.06	25.2	22.8	4.4	142.6	10.3	16.3		51.2
5.35	22.8	18.6	4.2	132.7	8.7	14.8		40.8
6.30	21.4	22.2	4.4	137.1	9.2	12.5	9.0	41.9
7.65	20.6	23.4	4.0	132.8	10.1	8.8	10.9	45.8



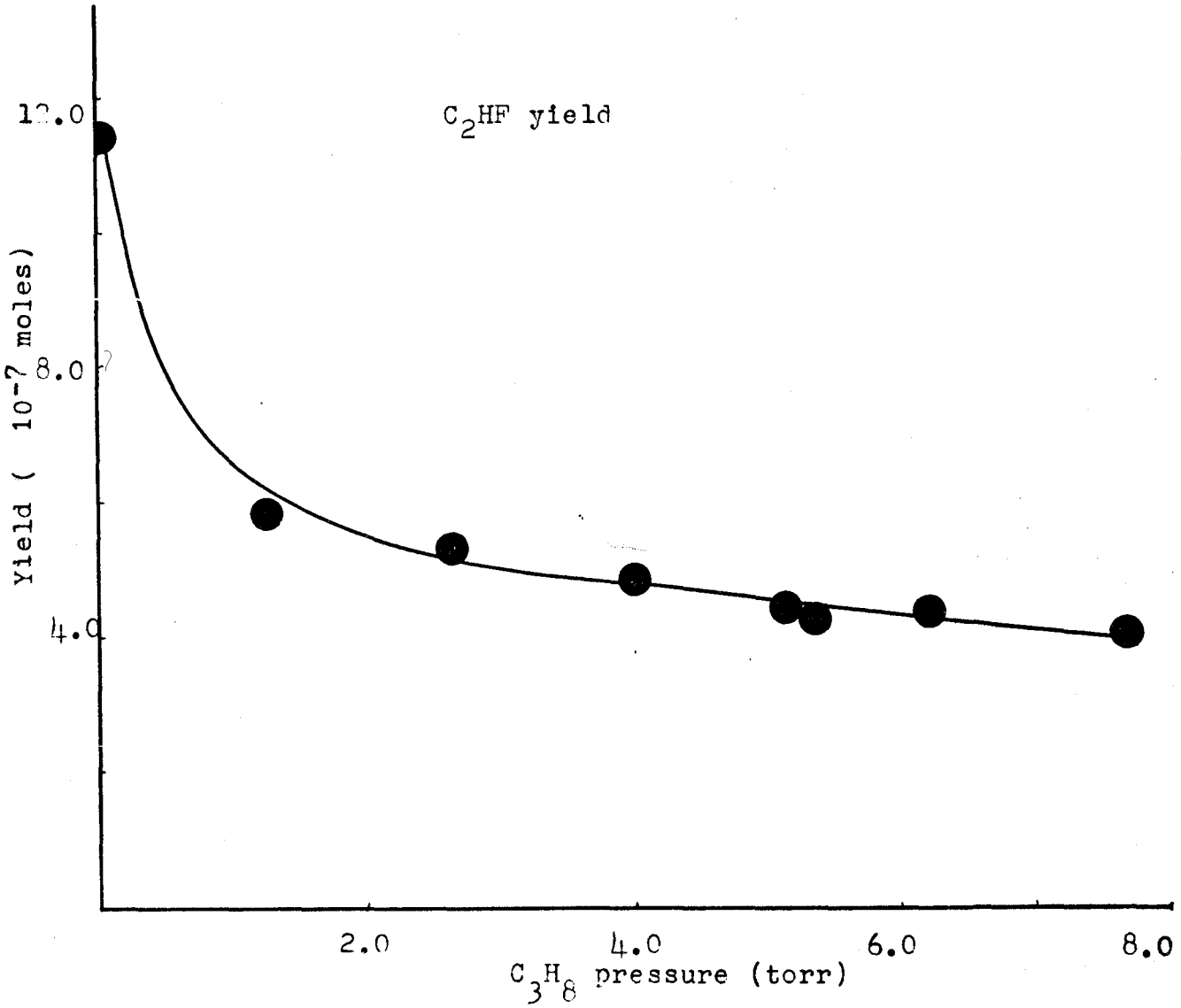
Starting pressure of CF_3C_2H, 2.61 torr; starting pressure of NO, 0.52 torr; irradiation time of 60 minutes.

Fig. 12



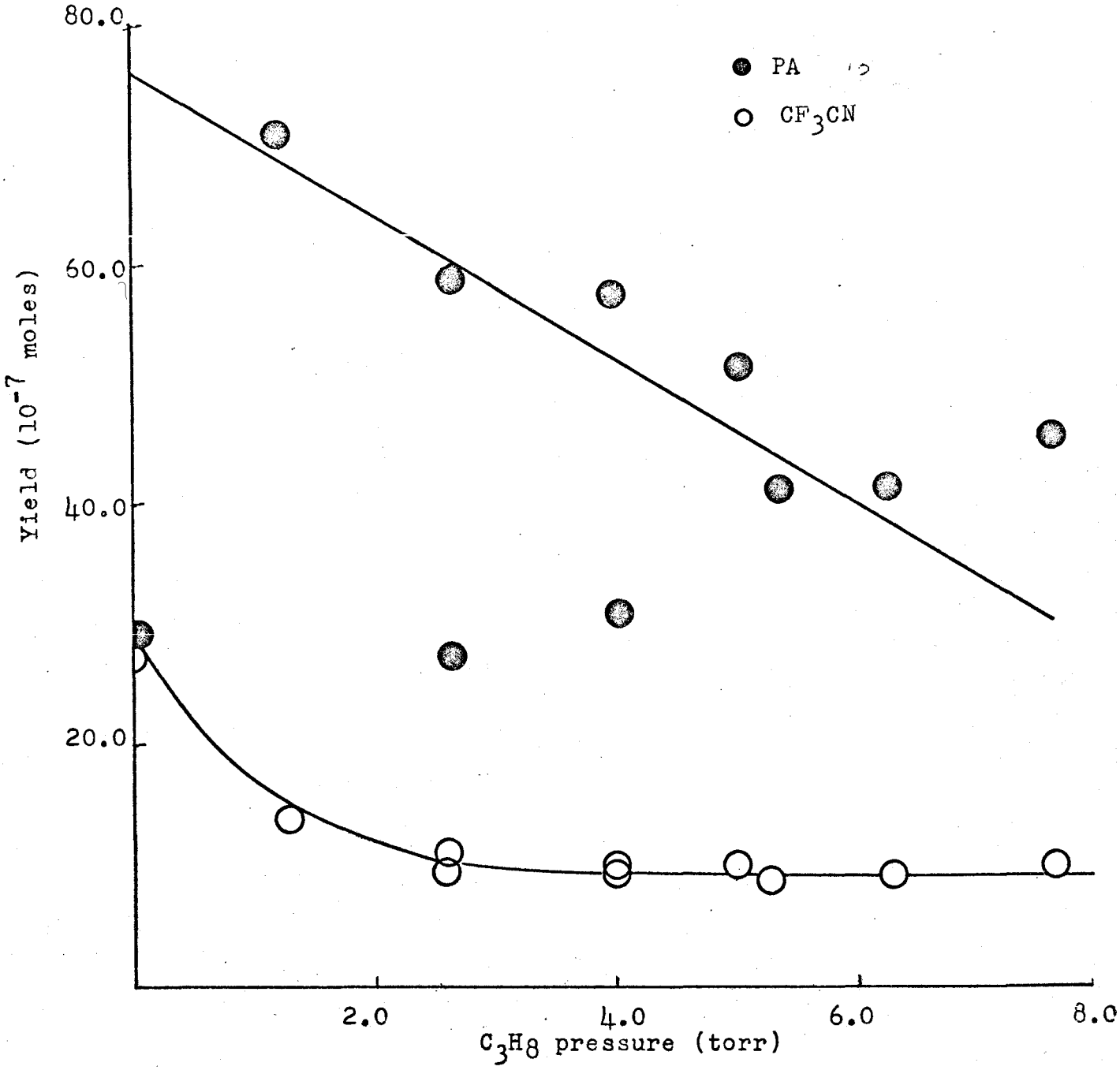
Starting pressure of CF_3C_2H, 2.61 torr; starting pressure of NO, 0.52 torr; irradiation time of 60 minutes.

Fig. 13



Starting pressure of CF_3C_2H, 2.61 torr; starting pressure of NO, 0.52 torr; irradiation time 60 mins.

Fig. 14



Starting pressure of CF_3C_2H, 2.61 torr; starting pressure of NO, 0.52 torr; irradiation time of 60 minutes.

Fig. 15

Table 9

Reaction conditions for the various systems studied.

Reaction system	Reactant pressure (torr)	Exposure time (min.)	Data presentation
CF_3C_2H neat	2.61	0 - 61	Table 3,
CF_3C_2H + C_3H_8	2.61 0 - 15	60	Table 4, Fig.2 to55
CF_3C_2H + NO	5.22 1.05	0 - 65	Table 5, Fig.6 to 9
CF_3C_2H + NO	2.61 0 - 1.1	30	Table 6, Fig. 10 and 11
CF_3C_2H + NO + CO_2	2.61 0.52 0 - 6.63	60	Table 7
CF_3C_2H + NO + C_3H_8	2.61 0.52 0 - 7.65	60	Table 8, Fig.12 to 15

Table 10

Product analysis by mass spectroscopy

Compound	m/e	Relative Abundance Electron Voltage 80ev	20ev	15ev	Assignment
1,3,5,-tris (trifluoromethyl) benzene ($cC_9H_3F_9$)					
	283	9.5	10.7	12.2	
	282	86.8	100.0	100.0	$C_9H_3F_9^+$
	281	4.5			$C_9H_2F_9^+$
	264	10.8	1.1		
	263	100.0	9.6		$C_9H_3F_8^+$
	262	2.4			$C_9H_2F_8^+$
	233	4.2	1.5		
	232	44.7	14.1		$C_8H_3F_7^+$
	231	3.7			$C_8H_2F_7^+$
	214	7.1	1.1		
	213	71.1	11.9		$C_8H_3F_6^+$
	212	4.2			$C_8H_2F_6^+$
	194	6.3			$C_8H_3F_5^+$
	193	3.7			$C_8H_2F_5^+$
	182	7.4			$C_7H_3F_5^+$
	181	1.8			$C_7H_2F_5^+$

Table 10 cont.

1,3,5,-tris (trifluoromethyl) benzene

163	21.8	$C_7H_3F_4^+$
162	4.7	$C_7H_2F_4^+$
144	11.3	$C_7H_3F_3^+$
143	11.1	$C_7H_2F_3^+$
125	5.8	$C_7H_3F_2^+$
99	6.3	
75	15.8	$C_6H_3^+$
74	6.1	$C_6H_2^+$
69	18.2	CF_3^+
51	2.9	CHF^+
50	3.7	CF_2^+
44	3.2	C_2HF
31	4.2	CF^+

Table 10 Cont.

Compound	m/e	Relative Abundance Electron Voltage 80ev	20ev	15ev	Assignment
PA					
	163	1.1	3.4		$C_4HF_6^+$
	69	100.0	70.7	9.6	CF_3^+
	50	4.6			CF_2^+
	46	9.7	43.3	100.0	
	45	17.8	79.1	98.0	
	43	10.5	23.9	11.5	C_2F^+
	31	31.5	100.0	28.8	CF^+
	30	22.2	18.6		NO^+
acetylene	(C_2H_2)				
	26	100.0	100.0		$C_2H_2^+$
	25	24.0			C_2H^+
	24	11.5			C_2^+
butadiyne	(C_4H_2)				
	51	28.0	14.0		$C_4H_3^+$
	50	100.0	100.0		$C_4H_2^+$
	49	42.0			C_4H^+
	48	11.0			C_4^+
	25	11.0			C_2H^+

Table 10 Cont.

Compound	m/e	Relative Abundance Electron Voltage 80ev	20ev	15ev	Assignment
fluoroacetylene (C_2HF)					
	44	100.0	100.0		C_2HF^+
	43	20.7			C_2F^+
	31	14.6			CF^+
trifluoroacetonitrile (C_2F_3N)					
	95	2.1			$C_2F_3N^+$
	76	15.7			$C_2F_2N^+$
	69	100.0			CF_3^+
	50	10.5			CF_2^+
	38	3.1			C_2N,F_2^+
	31	3.6			CF^+
	26	1.6			CN^+
carbon dioxide (CO_2)					
	44	100.0			CO_2^+
	28	7.0			CO^+
nitrous oxide (N_2O)					
	44	100.0			N_2O^+
	30	13.6			NO^+
	28	5.9			N_2^+

Table 10 cont.

Compound	m/e	Relative Abundance Electron Voltage 80ev	25ev	20ev	Assignment
trans 1,1,1,4,4,4, hexafluoro-2-butene ($C_4H_2F_6$)					
	165	1.3			
	164	22.2	100.0	51.9	$C_4H_2F_6^+$
	146	1.9			
	145	30.5	18.7		$C_4H_2F_5^+$
	114	1.6			$C_3H_2F_4^+$
	113	7.1			$C_3HF_4^+$
	96	3.4	2.7		
	95	100.0	61.5	100.0	$C_3H_2F_3^+$
	76	6.8			$C_3H_2F_2^+$
	75	18.8			$C_3HF_2^+$
	69	59.4	12.0		CF_3^+
	51	6.5			CHF_2^+
	43	6.5			C_2F^+
	31	8.8			CF^+

Table 10 cont.

Compound	m/e	Relative Abundance Electron Voltage 80 ev	Assignment
trifluoronitrosomethane (CF_3NO)			
	69	100	CF_3^+
	50	22	CF_2^+
	30	55	NO^+
trifluoromethane (CF_3H)			
	70	1.3	CF_3H^+
	69	100.0	CF_3^+
	51	86.4	CF_2H^+
	50	13.6	CF_2^+
	31	45.3	CF^+

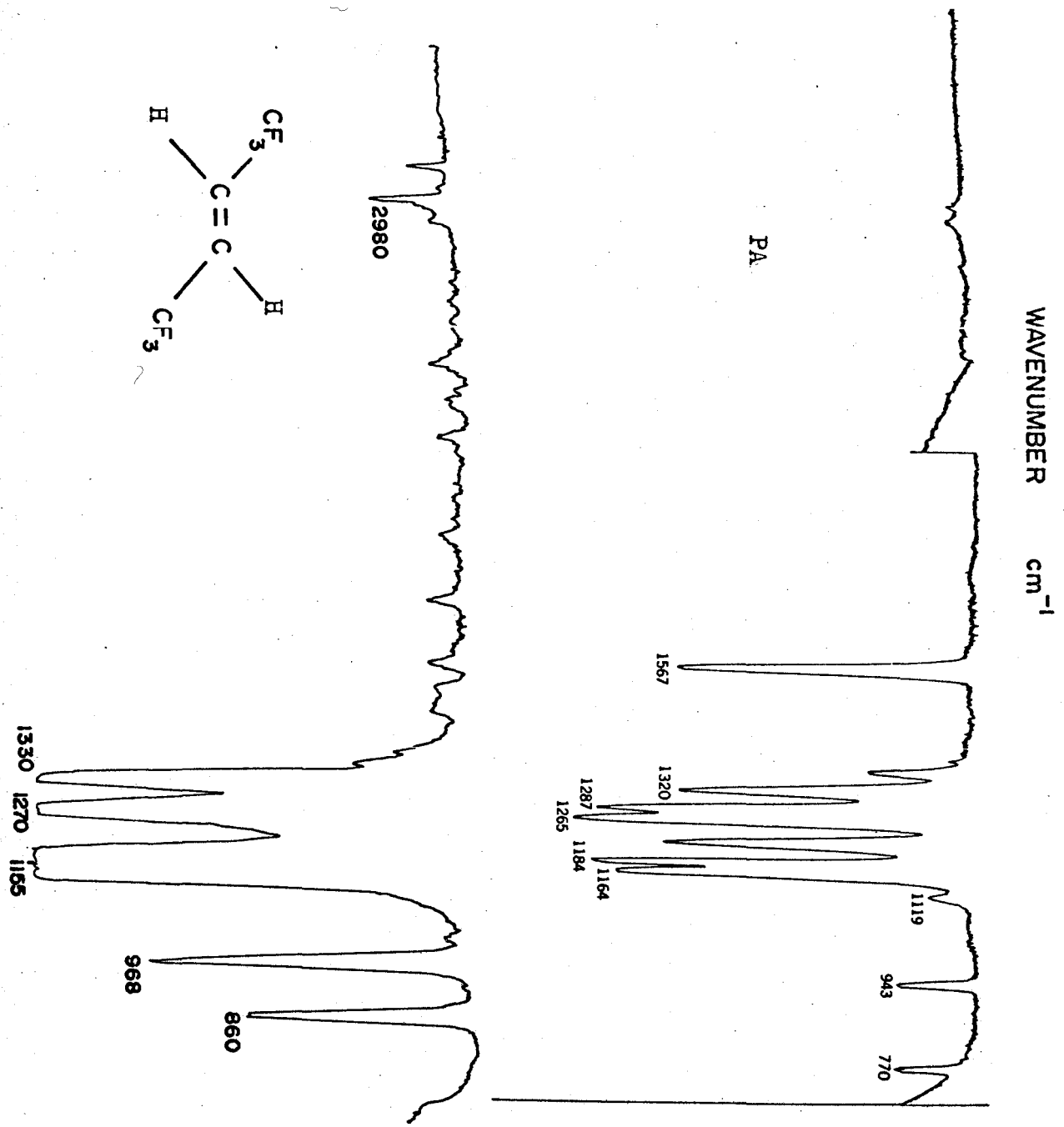


Fig. 16

(a) Infrared spectrum of 1,1,1,4,4,4,-hexafluoro-2-butene

(b) PA

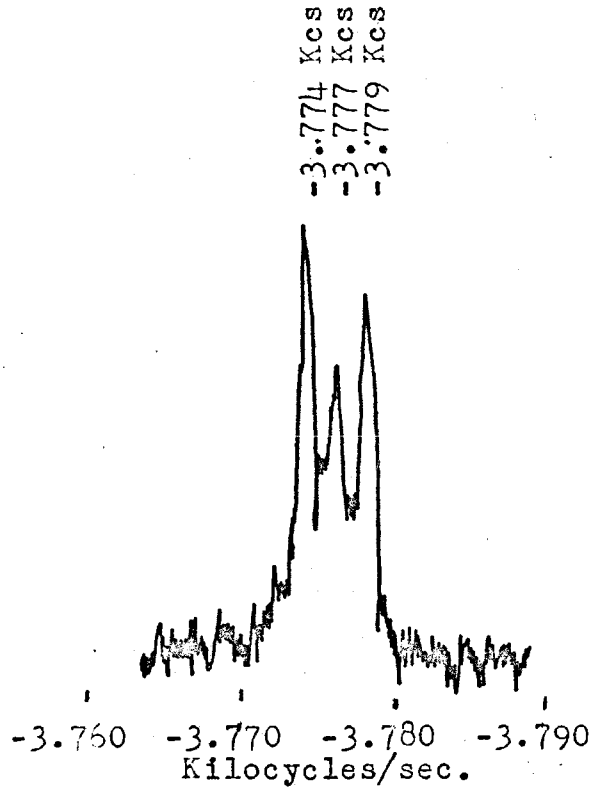


Fig. 17

1,1,1,4,4,4,-hexafluoro-2-butene; F^{19} NMR spectrum, 56.4 Mc, $CFCl_3$ as solvent and reference.

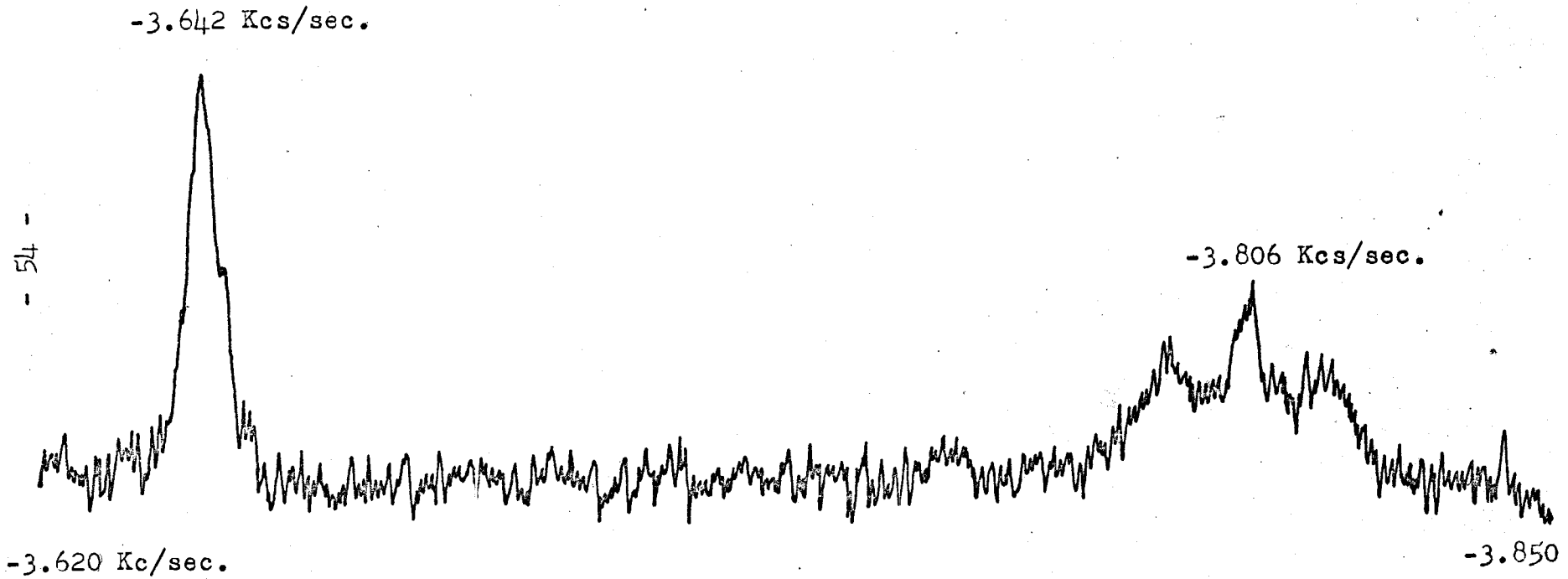
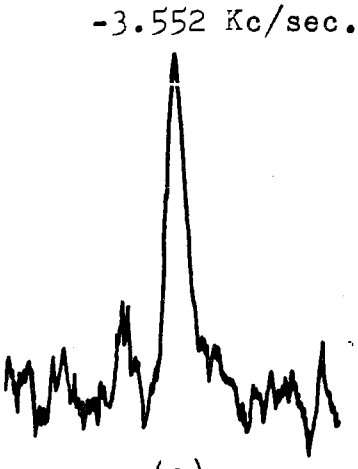
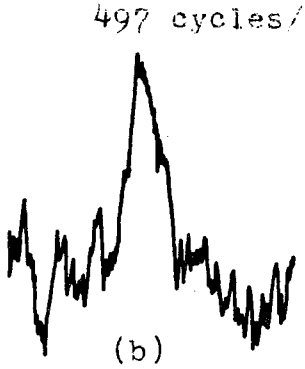


Fig. 18

Unidentified product PA. F^{19} NMR spectrum,
56.4 Mc, $CDCl_3$ as a solvent, $CFCl_3$ external reference.



(a)



(b)

Fig. 19

(a) F^{19} NMR spectrum of 1,3,5,- tris (trifluoromethyl) benzene, 56.4 Mc, $CFCl_3$ as a solvent and a reference.

(b) H^1 NMR spectrum, 60.0 Mc, TMS as a reference.

Discussion of the identification of a product formed in the CF_3C_2H photolysis with added NO.

Attempts at identifying the product designated as PA have not resulted in a conclusive assignment, even though an excellent infrared spectrum has been obtained. The mass spectrum and the F^{19} NMR spectrum did not yield a great deal of information.

A peak at 69 m/e in the mass spectrum has been assigned to CF_3^+ . The ion with the highest m/e value (163) has been assigned to the ion $(CF_3)_2C_3H^+$. Often the highest mass of nitroso compounds is not the parent ion but rather a fragment ion resulting from loss of the NO group during the spectroscopic analysis. It is possible that a similar fragmentation occurred in this case with the parent ion of $(CF_3)_2C_3HNO$ (193) not being observed.[25]

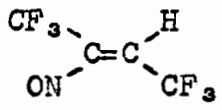
The strong absorption band at 1564 cm^{-1} in the infrared spectrum (Fig. 16 a) has been assigned to a nitroso group. The effect of the electron withdrawing CF_3 groups may be weakening the N=O stretching mode , shifting its absorption to lower energy than that observed for trifluoronitrosoethylene (1590 cm^{-1})[26].

The F^{19} NMR spectrum of the unidentified product displays an unsplit absorption at -3.642 Kc and a triply split absorption centered at -3.806 Kc which have been assigned to two isolated CF_3 groups. Since only one peak is strongly split it is evident that the CF_3 groups are not strongly coupled to one another. Therefore, the splitting must be caused by some add-

itional nucleus such as hydrogen. The triplet nature of -3.806 Kc absorption is unexpected, as one coupled hydrogen would be expected to produce a doublet and not a triplet on a first-order basis.

However, coupling to a single hydrogen can produce a triplet like splitting in certain cases. When the molecule contains magnetic non-equivalent groups that are structurally equivalent, certain characteristic absorption patterns can arise, a triplet being one[27]. The F^{19} NMR spectrum of trans 1,1,1,4,4,4,-hexafluoro-2-butene (type $X_3AA'X'_3$) displays a triplet absorption which may be an example of such an effect. On the other hand the triplet displayed by PA is difficult to rationalize as arising from magnetic non-equivalence because only one CF_3 group is strongly split.

From a mechanistic standpoint a reasonable compound would be some isomeric form of this nitrosobutene.



However, attempts at rationalizing the F^{19} NMR spectrum, on a first-order basis, to this compound are not convincing.

CONCLUSIONS

A. Absorption Process:

To elucidate the primary chemical process two main questions had to be answered: is there a long-lived excited intermediate, and do free radicals exist in the system?

To determine whether a long-lived excited intermediate state of the substrate was produced in the absorption process carbon dioxide was added to act as a quencher. As can be seen from Table 6 no appreciable effect on the yield is observed. It was concluded that an excited substrate molecule or an excited radical species with lifetimes longer than 10^{-8} sec. were not intermediates in the reaction.

Evidence for free radical formation was obtained from the photolysis of the propyne-propane and propyne-nitric oxide reaction systems. Identification of CF_3H and C_2H_2 as products in the first mixture indicated presence of CF_3 and C_2H radicals. Similar conclusions were drawn from the formation of CF_3NO and C_4H_2 in the nitric oxide system. The following reactions account for these products:

$$\cdot CF_3 + C_3H_8 \longrightarrow CF_3H + \cdot C_3H_7 \qquad 34$$

$$\cdot C_2H + C_3H_8 \longrightarrow C_2H_2 + \cdot C_3H_7 \qquad 35$$

$$\cdot CF_3 + NO \longrightarrow CF_3NO \qquad 36$$

$$\cdot C_2H + CF_3C{\equiv}CH \longrightarrow \begin{matrix} CF_3 \\ \diagdown \\ C{=}C \\ \diagup \\ HC_2 \end{matrix}\!\!\begin{matrix} \diagup H \\ \\ \diagdown \end{matrix} \longrightarrow C_4H_2 + \cdot CF_3 \qquad 37$$

Reactions 34 and 35 are hydrogen abstraction reactions. Reaction 36 is a typical reaction of nitric oxide with free radicals.

A more detailed mechanism for reaction 37 is presented below in reactions 50 and 51. Sherwood[20] has observed that the characteristic reaction of ethynyl radicals with substituted alkynes was similar to reaction 37.

It therefore appears from the evidence discussed above that the primary photolytic reaction of 3,3,3,-trifluoropropyne is direct breakdown into the trifluoromethyl and ethynyl radicals.

$$CF_3C_2H + h\nu(1849\ \text{Å}) \longrightarrow \cdot CF_3 + \cdot C_2H \qquad 38$$

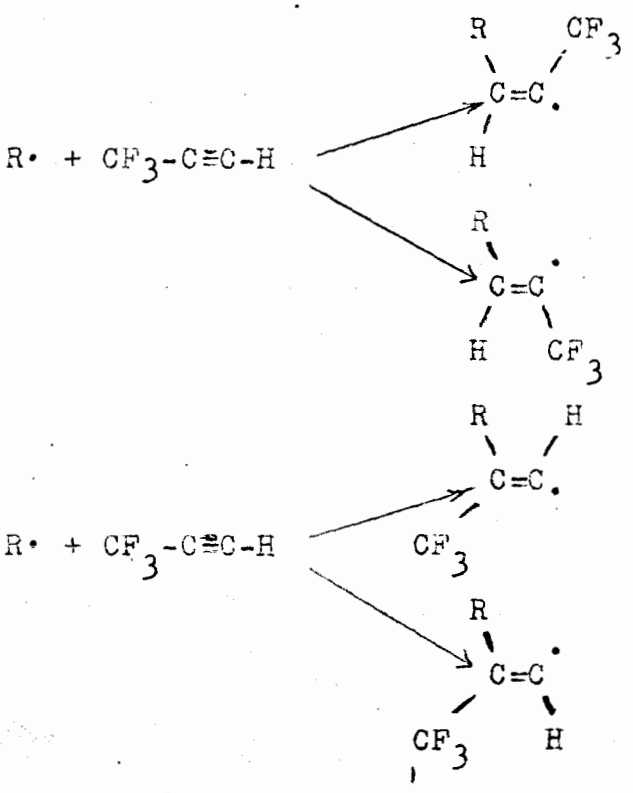
B. Secondary Reactions of Trifluoromethyl and Ethynyl Radicals.

The reaction mechanism of a photochemical process must include reactions that explain the fate of the radicals and other intermediates and that also account for all the products observed. The secondary reactions of each system studied above will be discussed separately.

Photolysis of CF_3C_2H:

In the photolysis of neat 3,3,3,-trifluoropropyne

the only volatile product identified was 1,3,5,-tris (trifluoromethyl) benzene. This product and the non-volatile deposit in the cell have been postulated to be formed by a chain mechanism initiated by the trifluoromethyl and ethynyl radicals. The possible initiating reactions are:



and in general by:

$$R\bullet + S \longrightarrow RS\bullet \qquad 41$$

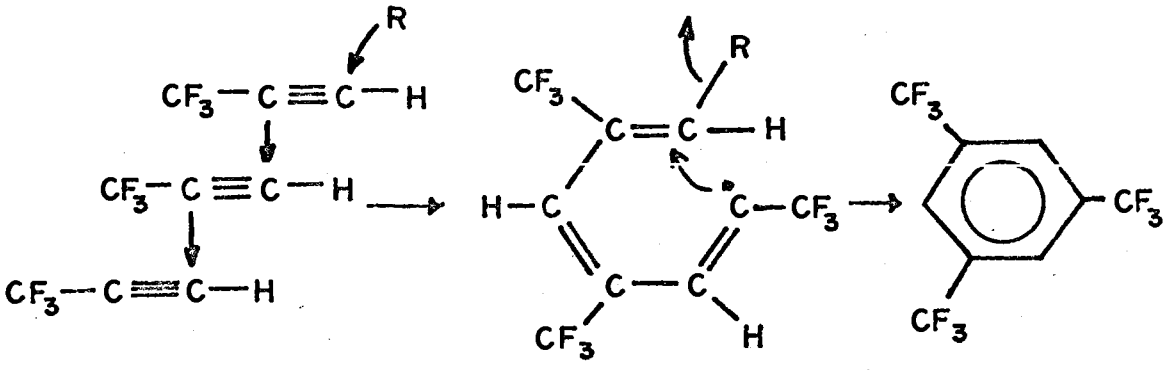
where R• is either $\bullet CF_3$ or $\bullet C_2H$ and S is CF_3-C≡C-H. Chain propagation steps then occur by

$$RS\bullet + S \longrightarrow RSS\bullet \qquad 42$$

$$RSS\bullet + S \longrightarrow RSSS\bullet \qquad 43$$

leading to a polymeric product which could be the deposit observed in the reaction cell.

A cyclization reaction was postulated to account for 1,3,5,-tris (trifluoromethyl) benzene formation and is represented as follows:



A similar free radical process has been considered to occur for the formation of benzene during the photolysis of acetylene.[6,8]

Attack on the triple bond will produce the 1,3,5 isomer regardless of the site of initial attack, provided that subsequent attacks in the polymerization steps are identical.

Photolysis of CF_3C_2H with added C_3H_8.

In the presence of added propane the primary radicals may still add to the substrate as depicted by reactions 39 and 40, but hydrogen abstraction reactions can also occur.

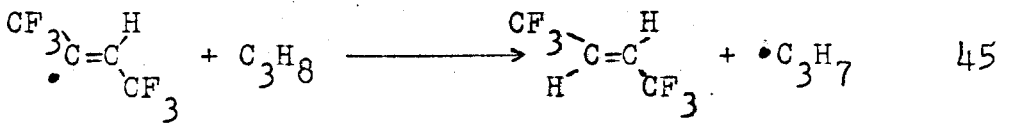
$$\cdot CF_3 + C_3H_8 \longrightarrow CF_3H + \cdot C_3H_7 \qquad 34$$

$$\cdot C_2H + C_3H_8 \longrightarrow C_2H_2 + \cdot C_3H_7 \qquad 35$$

With reference to the addition $\cdot CF_3$ to trifluoropropyne, it appears that reaction 39(a) is the only one of importance.

$$\cdot CF_3 + CF_3\text{-}C{\equiv}C\text{-}H \longrightarrow \underset{(I)}{\overset{CF_3}{\overset{\diagdown}{}}\!\!\cdot C{=}C\!\!\overset{H}{\overset{\diagup}{}}\atop{\diagdown\ CF_3}} \qquad 39(a)$$

Abstraction of hydrogen by I would produce trans 1,1,1,-4,4,4,-hexafluoro-2-butene, the only one of the four possible isomers which is actually observed.



45

Presumably attack at the hydrogen substituted carbon allows the free electron to be stabilized by the electronegative CF_3 group. The trans isomer produces less steric interaction between the CF_3 groups than does the cis form. The fact that no ethynyl addition products analogous to the butene formed in reaction (45) are observed suggests that hydrogen abstraction by ethynyl radicals is more favorable than addition to substrate.

Such competition between abstraction and addition is reflected in the yields of CF_3H, C_2H_2, and 1,3,5,-tris (trifluoromethyl) benzene as a function of increasing propane concentration. CF_3H and C_2H_2 increase in yield in accordance with the increased abstraction rates. At the same time the benzene yield drops because of the fewer radicals available for the chain initiation reaction. The yield of the trans 1,1,1.4,4,4,-hexafluoro-2-butene is low for low propane concentrations because reaction (45) cannot occur. After rising quickly the yield decreases for the same reason that the benzene yield drops. The yields have been displayed graphically in Figs. (2) to (5) and in tabular form in Table (3).

Table 11

Photolysis of 3,3,3-trifluoropropyne with added propane.

Product balance for CF_3 and C_2H radicals.

C_3H_8 pressure (torr)	Sum of CF_3H and $(CF_3)_2C_2H_2$ yields	C_2H_2 yield
0.51	65.6	22.8
1.01	85.4	40.1
1.98	85.0	60.3
3.03	95.3	79.9
3.06	106.7	74.9
5.37	92.8	79.3
7.95	94.8	81.5
10.0	88.3	75.5
13.0	87.3	76.7
15.0	79.1	76.7

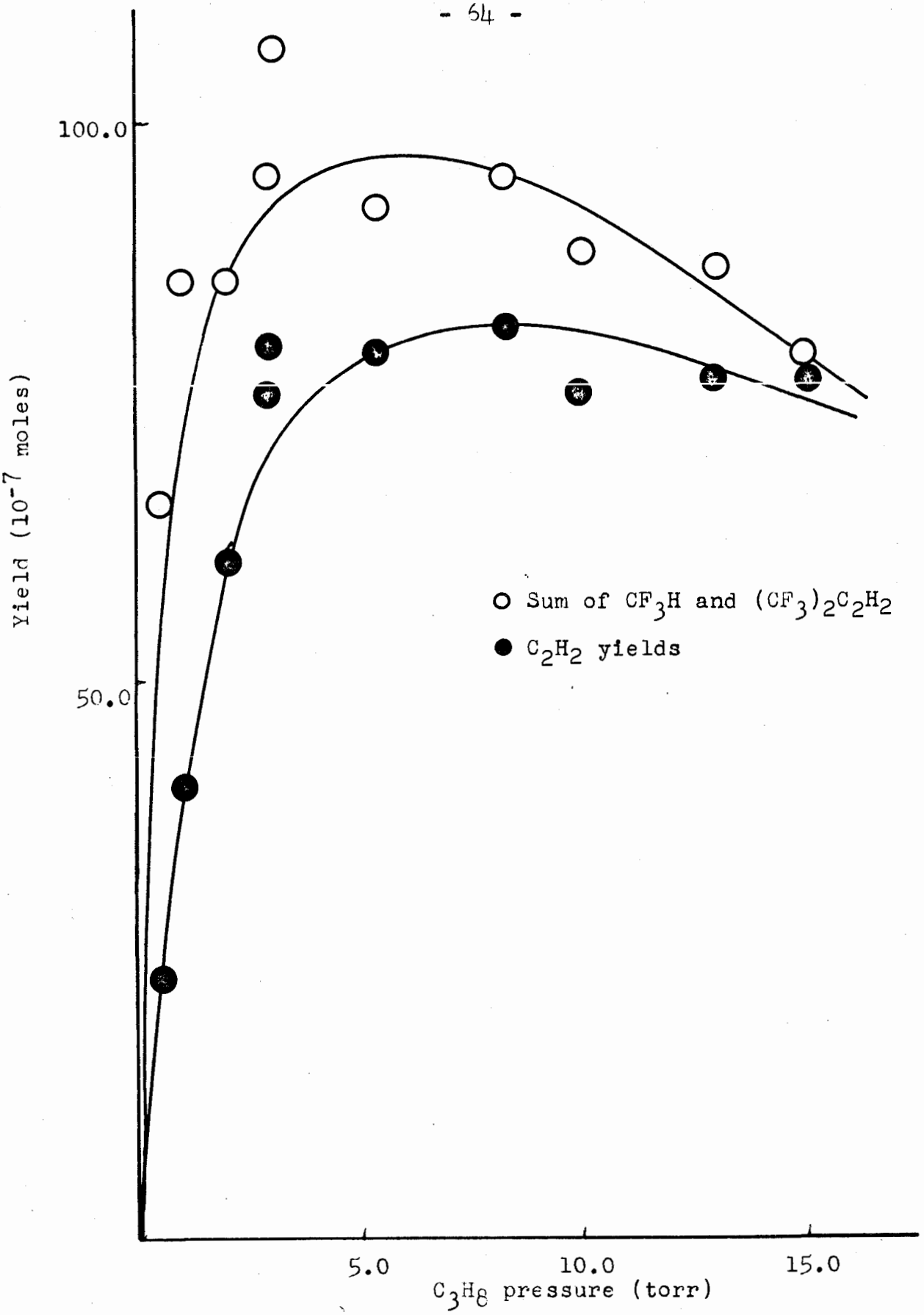

100.0
50.0
Yield (10^{-7} moles)
○ Sum of CF_3H and $(CF_3)_2C_2H_2$
● C_2H_2 yields
5.0
10.0
15.0
C_3H_8 pressure (torr)

Fig. 20

Since the CF_3 and C_2H radicals are produced in a one to one ratio in the photolytic process the yield of CF_3 initiated products should equal the yield of the C_2H initiated products. Calculation of the sum of yields of fluoroform and trans 1,1,1,4,4,4,-hexafluoro-2-butene for all propane concentrations studied reveals that this value does not agree with the yield of C_2H_2 but the two values do converge at high propane concentrations. This calculation is presented graphically in Fig. (20) and in tabular form in Table (11). An explanation of the lower C_2H yields may be that ethynyl radicals initiate more polymerization reactions than do CF_3 radicals.

The trace amount of fluoroacetylene in these reactions is thought to arise from two possible reactions; abstraction of fluorine by C_2H, and production of C_2HF in a primary process.

Fluorine abstraction may occur as follows;

$$CF_3\text{-}C{\equiv}C\text{-}H + \cdot C_2H \longrightarrow \cdot CF_2C{\equiv}C\text{-}H + C_2HF \qquad 46$$

Since the C-F bond energy of the substrate is about 109 kcal/mole[28] this process would be expected to have a high activation energy which may account for the small yield. Evidence against such a mechanism comes from the relatively slight effect of added propane on the yields of fluoroacetylene. A pronounced decrease with increasing propane concentration would be expected for the free radical reaction. The following primary process was considered:

$$CF_3C_2H + h\nu \longrightarrow :CF_2 + F\text{-}C{\equiv}C\text{-}H \qquad 47$$

However no evidence for the presence of difluoromethylene

was found when ethylene was added as a trapping agent. No other attempt was made to determine the mechanism for fluoroacetylene formation. Whatever mechanism is operative it would only represent about 5% of the total reaction.

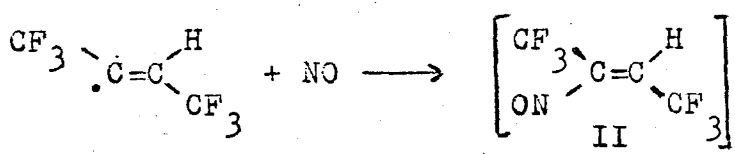
<u>Photolysis of CF_3C_2H with added NO:</u>

When nitric oxide is added to the substrate the fates of the CF_3 and C_2H radicals are somewhat similar to their fates in the reactions with added propane.

CF_3 radicals are scavenged by nitric oxide.[29]

$$\cdot CF_3 + NO \longrightarrow CF_3NO \qquad 36$$

As well as being scavenged by NO, the trifluoromethyl radicals can react with substrate by reaction 39(a) as has already been suggested. The radical intermediate I can either continue the chain reaction to form the benzene derivative or it can react with nitric oxide to form trans 1,1,1,4,4,4,-hexafluoro-2-nitroso-2-butene



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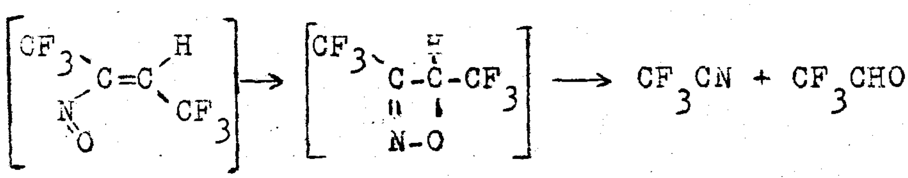
A discussion of the identification of II has been presented above.

Decomposition of II can occur via a cyclic intermediate to form trifluoroacetonitrile.[21]

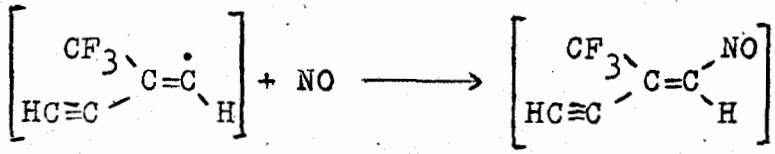


49

Reaction 49 has been postulated to account for the presence of CF_3CN in the product mixture. However CF_3CHO has not been observed under the same conditions. An authentic sample of fluoral was introduced into the vacuum line and injected into the gas chromatograph. Quantitative recovery of the sample was not achieved, although a small amount did elute from the column with a retention time similar to that of the substrate. A film was observed on the inner surfaces of the vacuum line at the points where fluoral was condensed during the normal transferring operations. It is possible that hydration of the fluoral was occurring upon contact with trace amounts of water adsorbed on the surface of the vacuum line.[30] Another explanation could be the polymerization of fluoral.

Ethynyl radicals can also react with the substrate as previously postulated by reactions 39 and 40. Subsequent reactions of the radical formed in this addition process have been postulated to account for the production of butadiyne. The proposed reaction mechanism is as follows:

40



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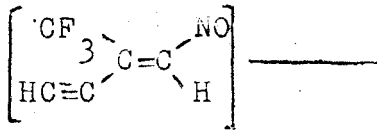
III



$$\cdot CF_3 + NO\cdot + H\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}H \qquad 51$$

The above reaction sequence produces the same overall effect as reaction 37 except that C_4H_2 formation is now not possible in the absence of NO in agreement with the experimental evidence.

The possibility that C_4H_2 is being photolyzed as it is formed has not been eliminated. A small sample of butadiyne was introduced to the reaction flask along with 3,3,3,-trifluoropropyne and was irradiated in the usual manner. Gas analysis of the products revealed that all the C_4H_2 had been consumed. Photolysis of butadiyne is evidently an important process.

$$C_4H_2 + h\nu(3000 - 2500\ \mathring{A}) \longrightarrow 2\cdot C_2H \qquad 52$$

Reaction 52 has been proposed by Pitts[31]. In the presence of NO, photolysis of butadiyne still occurs but the ethynyl radical produced reacts with the substrate and NO by reaction 40 and 50 to regenerate the butadiyne.

The small yield of acetylene formed in the nitric oxide system may be the result of a hydrogen abstraction reaction of ethynyl radicals.

$$\cdot C_2H + CF_3C_2H \longrightarrow C_2H_2 + CF_3C_2\cdot \qquad 53$$

Ethynyl radicals have been observed to abstract other acetylenic hydrogens.[22]

The trace amounts of fluoroacetylene may again be the result of fluorine abstraction or of a primary photolysis reaction as discussed previously.

The yields of all the products from the propyne-nitric oxide system are linearly dependent on the exposure time as shown in Fig. 6 to 9. This indicates that all the products are produced from photolysis of the substrate and not from photolysis of products. The slight levelling occurring for exposure times greater than about 45 minutes has been attributed to the reduction of the transmitted light intensity by the polymeric deposit.

The yield of CF_3NO was not determined because a linear response value could not be obtained. Inconsistency in the yield of the unidentified product designated as PA was attributed to its partial decomposition on the GC column.

For all products except 1,3,5,-tris (trifluoromethyl) benzene an increase in yield with increasing nitric oxide concentration is observed. The increase in CO_2 and N_2O yields is explained by the increased scavenging of CF_3 radicals and the subsequent increase in the amount of CF_3NO decomposition. Similarly the increase in yield of the decomposition product CF_3CN is accounted for by the enhancement of reaction 49 at higher nitric oxide concentrations. Butadiyne increased in yield because of the increased rate of reactions 50 and 51.

Trifluoronitrosomethane is known to undergo reaction

with nitric oxide[32] to produce nitrogen, nitrogen dioxide, and trifluoromethyl radicals.

$$CF_3NO + 2NO \longrightarrow CF_3 + N_2 + NO_3 \qquad 54$$

$$NO + NO_3 \longrightarrow 2NO_2 \qquad 55$$

Heicklen also observed carbon dioxide and nitrous oxide which he attributed to the decomposition of CF_3NO during the gas chromatographic analysis. Production of CO_2 and N_2O in the present system may be due to the same type of decomposition. Although CO_2 and N_2O are not observed when neat CF_3NO is injected through the GC, quantitative recovery of CF_3NO is not achieved.

Another mechanism of CO_2 and N_2O production could be formation of the trifluoronitrosomethane dimer as observed by Haszeldine[33] and its subsequent decomposition.[34] Formation of the dimer results from attack of $\cdot CF_3$ on the nitrogen of the nitroso group followed by reaction with NO.

$$\cdot CF_3 + CF_3N{:}O \longrightarrow (CF_3)_2N\cdot O\cdot \qquad 56$$

$$(CF_3)_2N\cdot O\cdot + NO \longrightarrow (CF_3)_2N\cdot O\cdot NO \qquad 57$$

Although the mechanism is not understood, Mason has attributed production of carbon dioxide and nitrous oxide as well as other side products to the decomposition of trifluoronitrosomethane dimer.

$$(CF_3)_2N\cdot O\cdot NO \longrightarrow CO_2,\ N_2O,\ CF_3NO_2,\ \text{other products} \qquad 58$$

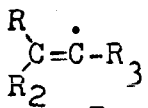
The nitro compound has not been observed in the present study. At the present time, no final conclusion can be drawn concerning

the source of carbon dioxide and nitrous oxide.

Free radical additions to acetylenes:

To explain the stereospecific production of trans 1,1,1,4,4,4,-hexafluoro-2-butene in the attack of trifluoromethyl radicals on 3,3,3,-trifluropropyne, a short review of the current schools of thought about such additions, the stability of the resulting vinyl radicals, as well as the stereochemisty of the products from vinyl radical reactions is presented. In an attempt to clarify some of the above areas of concern, L.A. Singer[35] has classified vinyl radicals into three groups according to their electronic configuration and to their relative stabilities.

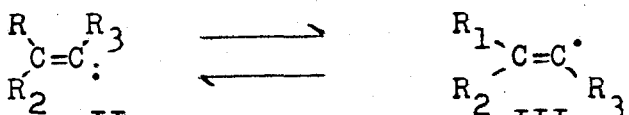
Case I



I

sp hybridization

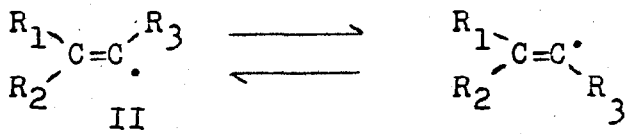
Case II



II III

sp^2 hybridization, fast inversion

Case III



II III

sp^2 hybridization, slow inversion

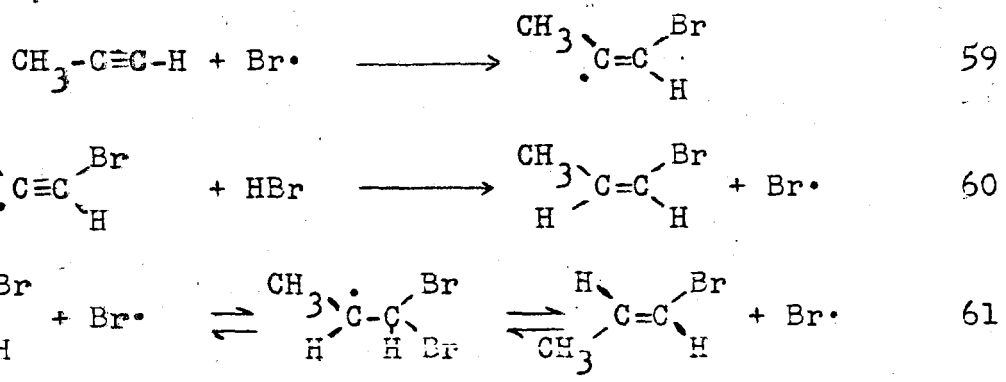
Both cis- and trans-olefins can be formed from the

linear vinyl radical with the cis/trans ratio determined by stereochemical interactions between the incoming scavenger and the substituent groups R_1, R_2, R_3

When the vinyl radical is sp^2-hybridized and undergoes fast inversion between the cis and trans structures the ratio of the products is determined by the relative stability of II and III as well as by the stereochemical interactions of the scavenger. When the inversion is slow, however, the product ratio is determined solely by the stereochemical aspects of the addition process.

In most of the studies on radical additions to acetylenes the products observed are predominately the cis isomer with small amounts of trans product. Although these results can be explained with appropriate arguments by either Case I or Case II, conclusions as to the stereochemical aspects of the addition process is not possible.

For instance Skell and Allen[36] have studied the addition of bromine atoms to propyne and have postulated that addition is stereospecifically trans with little or no inversion to the cis radical. The presence of both cis- and trans-1-bromo-1-propene is attributed to secondary reaction of Br with cis-1-bromo-propene.



59

60

61

Although the results obtained can be accounted for by the above mechanism, no discussion as to the importance of cis addition in the primary step was presented. It appears possible that both cis and trans addition can occur, followed by hydrogen abstraction as in reaction 60 and then subsequent secondary reactions with bromine radical. Such a process would be similar to Case III as described by Singer.

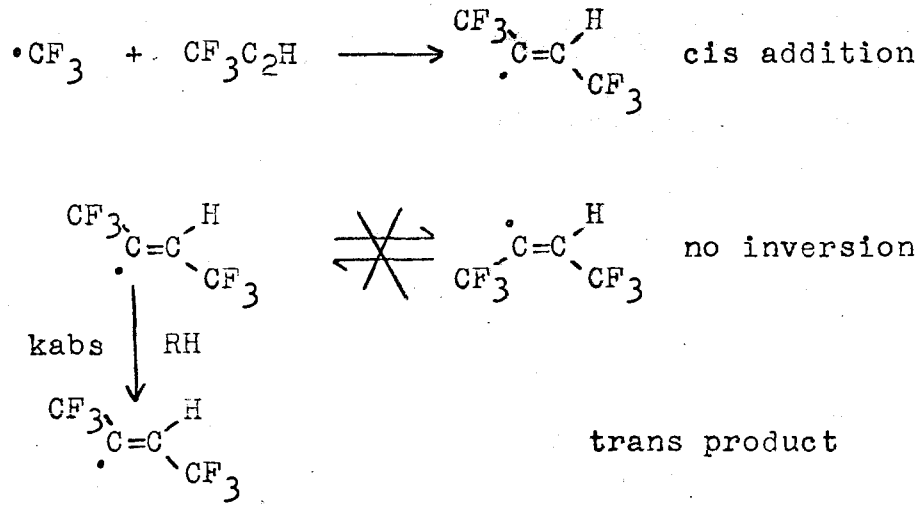
Free radical addition of chloroform to alkylacetylenes[37] appears to be non-stereospecific in the primary process with the cis/trans ratio being determined by the relative stability of the two vinyl radicals and by the stereo-selectivity of the scavenging reactions. The reaction can be categorized as Case II.

Similar results are obtained for other free radical additions to acetylenes[19,38] with the cis/trans ratios being explained in terms of vinyl radical stability and the relative rates of inversion and scavenging reactions.

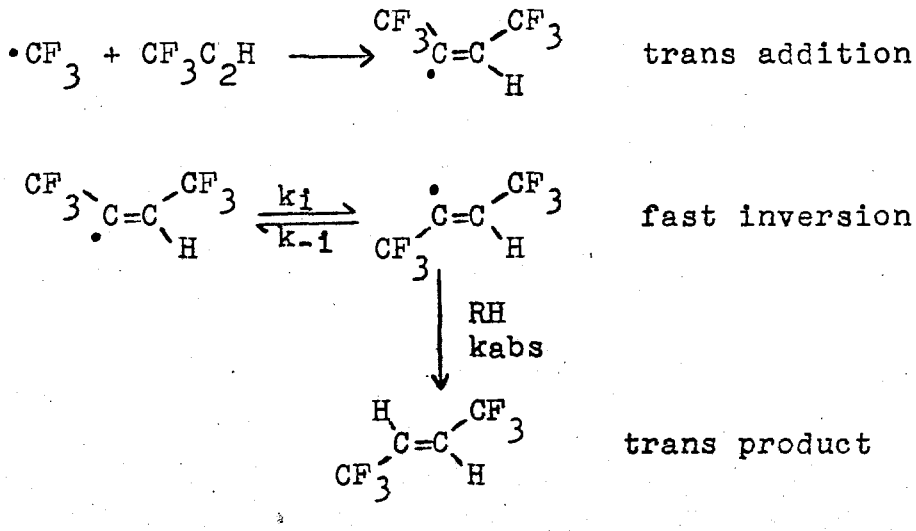
The main result of the above studies has been to

demonstrate that although plausible explanations can be advanced for the observed distribution of cis and trans isomers arising from radical additions to carbon triple bonds, the stereospecificity of the primary radical attack is not known. With this in mind there are a number of possible mechanisms that can be proposed for the exclusive formation of trans 1,1,1,4,4,4,-hexafluoro-2-butene.

(A) Cis addition of CF_3

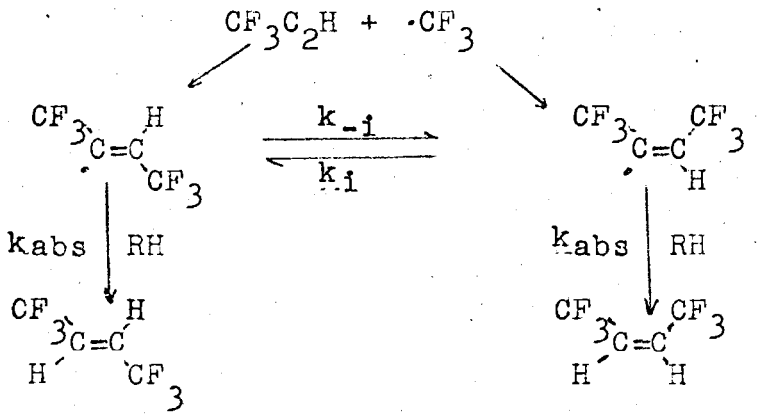


(B) Trans addition of CF_3



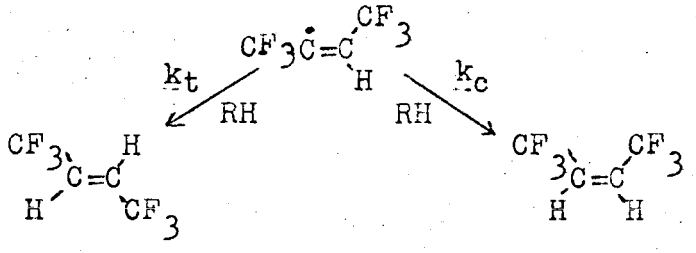
ki $\gg$ k-i, kabs

(C) Cis and trans addition



$k_i \gg k_{-i}$, k_{abs}

(D) Linear vinyl radical intermediate

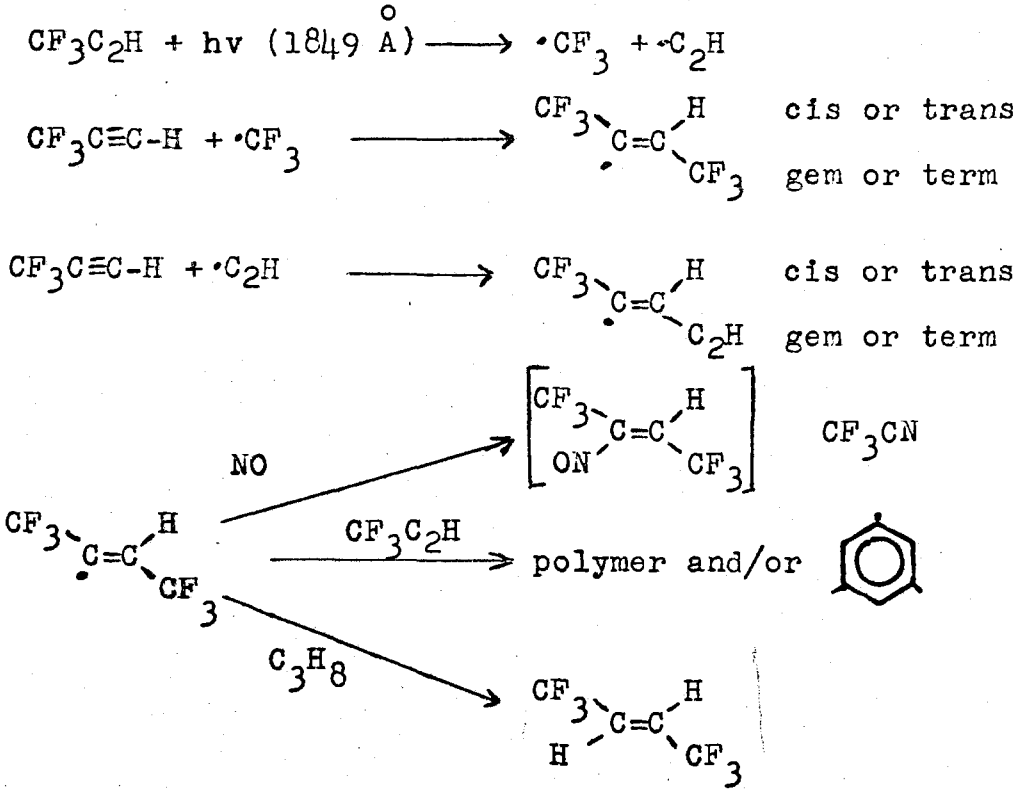


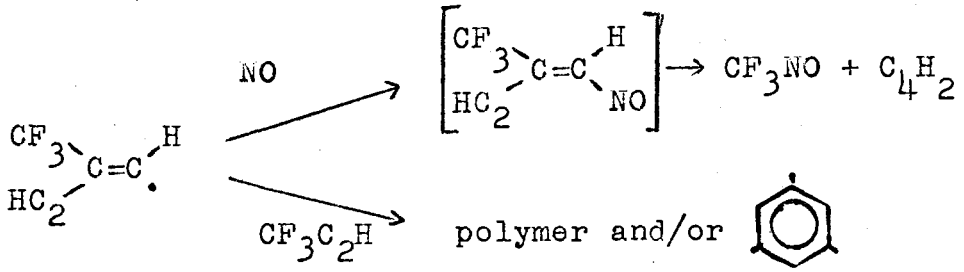
$k_t \gg k_c$

In the present study no attempt was made to distinguish which of the above mechanisms was operative in the formation of 1,1,1,4,4,4,-hexafluoro-2-butene.

Summary:

The 1849 Å line from a medium pressure mercury arc lamp has been assumed to be the active radiation in the photolytic decomposition of 3,3,3,-trifluoropropyne. The primary process involves formation of trifluoromethyl and ethynyl radicals. Subsequent reactions of the radicals with the substrate lead to formation of a polymeric material and 1,3,5,-tris (trifluoromethyl) benzene. Studies with added propane and nitric oxide have revealed the nature of the radical attack and subsequent reactions of the vinyl radicals with both propane and nitric oxide.





In addition photolysis of C_4H_2 probably occurs by

$$C_4H_2 + h\nu \longrightarrow 2 \cdot C_2H$$

Reactions of $\cdot CF_3$ and $\cdot C_2H$ with propane have also been observed.

$$\cdot CF_3 + C_3H_8 \longrightarrow CF_3H + \cdot C_3H_7$$
$$\cdot C_2H + C_3H_8 \longrightarrow C_2H_2 + \cdot C_3H_7$$

$\cdot CF_3$ radicals also react with nitric oxide to form CF_3NO, which has been postulated to decompose by an unknown mechanism to produce CO_2 and N_2O.

$$CF_3 + NO \longrightarrow CF_3NO \longrightarrow CO_2 + N_2O$$

BIBLIOGRAPHY

1. M.C. Sauer, Jr., and L.M. Dorfman, J. Chem. Phys., 35, 497 (1961).
2. H. Okabe and J.R. McNesby, J. Chem. Phys., 36, 601 (1962).
3. D.A. Becker, H. Okabe, and J.R. McNesby, J. Phys. Chem., 69, 538 (1966).
4. W.F. Kieffer and J.P. Howe, J. Am. Chem. Soc., 64, 1 (1942).
5. C.P. Poole, Jr., and R.S. Anderson, J. Chem. Phys., 31, 346 (1959).
6. D.J. Le Roy and E.W.R. Steacie, J. Chem. Phys., 12, 117 (1944).
7. M. Zelikoff and L.M. Aschenbrand, J. Chem. Phys., 24, 1034 (1956).
8. A.G. Sherwood and H.F. Gunning, J. Phys. Chem., 69, 1732 (1965).
9. M. Tsukado and S. Shida, J. Chem. Phys., 44, 3133 (1966).
10. G.J. Mains, H. Niki, and M.H.J. Wijnen, J. Phys. Chem., 67, 11 (1963).
11. C.M. Drew and A.S. Gordon, J. Chem. Phys., 31, 1417 (1959).
12. M.H.J. Wijnen, J. Chem. Phys., 36, 1672 (1962).
13. D.J. Le Roy, J. Chem. Phys., 45, 3482 (1966).
14. S. Shida, M. Tsukado and T. Oka, J. Chem. Phys., 45, 3483 (1966).
15. D.H. Volman, K.A. Maas, and J. Wolstenholme, J. Am. Chem. Soc., 87, 3041 (1965).
16. T.R. Lynn, Guide to Stationary Phases for Gas Chromatography, 4th ed. (1967).
17. N.A. Weir, J. Chem. Soc., 6870 (1965).
18. R.A. Holroyd and R.W. Fessenden, J. Phys. Chem., 67, 2743 (1963).

19. A.A. Oswald, K. Griesbaum, B.E. Hudson, and J.M. Bregman, J. Am. Chem. Soc., 86, 2877 (1964).

20. A.G. Sherwood, Phd. Thesis, Edmonton, Alberta (1963).

21. A.G. Sherwood and H.E. Gunning, J. Am. Chem. Soc., 85, 3506 (1963).

22. A.M. Tarr, O.P. Strauz, and H.E. Gunning, Trans. Faraday Soc., 61, 1946 (1965).

23. A.M. Tarr, O.P. Strauz, and H.E. Gunning, Trans. Faraday Soc., 62, 1221 (1965).

24. K.K. Georgieff and Y. Richard, Can. J. Chem., 36, 1280 (1958).

25. K.Y. Chang, Org. Mass Spectr., 3, 1055 (1970).

26. C.E. Griffin and R.N. Haszeldine, J. Chem. Soc., 1398 (1960).

27. R.K. Harris, Can. J. Chem., 42, 2275 (1964).

28. J.G. Clavert and J.N. Pitts, Jr., Photochemistry, John Wiley and Sons, Inc., New York, page 824 (1966).

29. J. Banus, J. Chem. Soc., 3755 (1953).

30. D.E. McGreer, R. Stewart, and M.M. Mocek, Can. J. Chem., 41, 1024 (1963).

31. J.G. Calvert and J.N. Pitts, Jr., Photochemisty, John Wiley and Sons, Inc., New York, page 515 (1966).

32. J. Heuklen, J. Phys. Chem., 70, 112 (1966).

33. R.N. Haszeldine and B.S.H. Mattinson, J. Chem. Soc., 1741 (1957).

34. J. Mason, J. Chem. Soc., 4537 (1963).

35. L.A. Singer, Intra-Science Chem. Reports, 4, 139 (1970).

36. P.S. Skell and R.G. Allen, J. Am. Chem. Soc., 86, 1559 (1964).

37. R.M. Kopchik and J.A. Kampmeier, J. Am. Chem. Soc., 90, 6733 (1968).

38. J.A. Kampmeier and G. Chen, J. Am. Chem. Soc., 87, 2608 (1965).