MERCURY 6($^3P_1$) SENSITIZED PHOTODECOMPOSITION OF 2,5-DIHYDROFURAN IN VAPOUR PHASE

by

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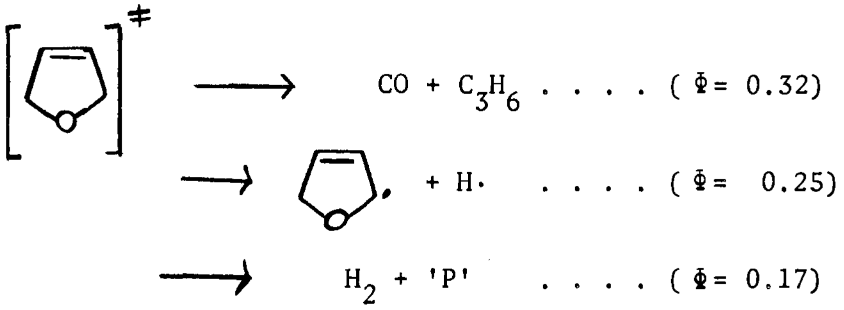
This thesis is dedicated to my late
beloved mother.

ABSTRACT

The mercury photosensitized decomposition of 2,5-dihydrofuran was studied in the vapour phase at room temperature and in a pressure range of 5 to 130 mm of Hg. Carbon monoxide, propene and hydrogen are the major products. The minor products of the reaction are biallyl, allene, methylacetylene, furan, 2,3-dihydrofuran, tetrahydrofuran and three unidentified compounds.

Runs with increasing substrate pressure or added foreign quenchers indicate the formation of an excited 2,5-dihydrofuran molecule in the primary energy transfer act. Decomposition of this excited molecule in the following three ways explains all the products formed in the reaction.



Identity and fate of the product 'P' is unknown at this time. Nitric oxide added runs were done to test the suggested mechanism.

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INTRODUCTION

It has been known for a long time that light could bring about chemical changes.[1,2] The subject of photochemistry deals with such reactions. The range of electromagnetic radiation of importance in photochemistry lies generally from about 1800 to 7000A.

Absorption of radiation above 7000A, i.e. in the infra red and microwave region, imparts too little energy to a molecule to cause a chemical change. On the other hand, absorption of radiation below 1800A, i.e. X-rays and γ-rays, leads to ionization of molecules and this is conventionally treated as Radiation Chemistry. In the spectral region of 1800 to 7000A, the energies imparted to molecules range from 40 to 160 kcal/mole and so are of the right magnitude to rupture chemical bonds to cause chemical reactions.

Reactions of many types may be brought about by exposure to suitable light, e.g. decomposition, isomerization, polymerization, synthesis, oxidation, reduction, etc.[3] Although studies of such reactions started as early as 1800, systematic progress in photochemistry had to await the development of quantum theory and molecular spectoscopy. Today photochemistry is important not only because of its intrinsic interest but for the important contributions it has made to the general understanding of reaction kinetics.

Laws of Photochemical Reactions

As light causes chemical reaction, it seems obvious that there is a correlation between them. The correlation was first stated by

Grotthus and Draper in 1818 as "Only radiations which are absorbed by the reacting system are effective in producing chemical change." The quantitative relation between the amount of radiation absorbed and the extent to which reaction has occured in the system was stated by Einstein in 1912. It is known as Einstein's law of photochemical equivalence, "In the primary photochemical process each molecule is activated by the absorption of one photon."

The experimental yields in photochemistry are usually expressed in terms of quantum yields (Φ) or quantum efficiency. Quantum yield is defined as the number of molecules of reactant decomposed by each photon of radiation absorbed.

$$\Phi = \frac{\text{number of molecules decomposed}}{\text{number of photons absorbed}} \quad . \ . \ . \ . \ (1)$$

$$= \frac{\text{number of moles of reactant decomposed}}{\text{number of einsteins absorbed}} \quad . \ . \ . \ . \ (2)$$

An einstein is Avogadro number of photons. The quantum yield of a reaction may vary from almost zero to about 10^6. No matter how large or small the quantum yield may be, it is generally accepted the law of photochemical equivalence is always applicable to the primary light absorbing process. The deviations of the overall quantum yields are due to secondary processes. The secondary chain reactions produce high quantum yields and the low values are due to collision deactivation or recombination of the products of the primary process.

Excited States

A molecule or an atom can exist in a number of electronic states, and the change from one particular state to another results in absorption or emission of radiation of a definite wave length. There are important selection rules that help us to understand the nature of electronic transitions. The spin conservation rule states that only transitions involving no change in spin or multiplicity are allowed, others are strongly forbidden. The parity rule applies to all molecules with centre of symmetry. The rule can be stated by saying that only $u \leftarrow g$ and $g \leftarrow u$ transitions are allowed. When a wave function of a molecule changes sign on reflection through a centre of symmetry, it is called ungerade (u), while those not changing sign on reflection are called gerade (g). The Frank-Condon principle[4] states that electronic transitions will take place only when the internuclear distances are not significantly different in the two electronic states and where the nuclei have no velocity. In addition to the above rules there are other types of forbidden transitions, a detail discussion of which is given by Pitts.[5]

Dissipation of Excitation Energy

The excitation energy acquired by a molecule "A" on absorption of light may be dissipated by any one of the four general processes.[6]

A^* (excited) $\longrightarrow A + h\nu$ . . . . light emission . . . . (3)

$A^* \rightsquigarrow A +$ heat . . . . radiationless conversion . . . . (4)

$A^* \longrightarrow$ products . . . . chemical reaction . . . . (5)

$A^* + B \longrightarrow A + B^*$ . . . . energy transfer . . . . (6)

Emission is observed either as fluorescence or phosphorescence. Fluorescence is the phenomenon of emission from the excited state to the ground state of same spin multiplicity and phosphorescence from the excited state to ground state of different multiplicity. If the ground state of a species is singlet, the average lifetime of an excited singlet state is generally 10^{-9} to 10^{-15} secs and that of an excited triplet state is 10^{-5} to 10 secs.

A radiationless process converts one electronic state to another without absorption or emission of radiation. There are two such important processes:-

(i) Internal conversion:- This involves intramolecular radiationless interconversions between electronic states of same multiplicity i.e., singlet $\rightsquigarrow$ singlet or triplet $\rightsquigarrow$ triplet conversions.

(ii) Intersystem crossing:- This involves intramolecular radiationless interconversions between electronic states with different multiplicity i.e., singlet $\rightsquigarrow$ tripet or triplet $\rightsquigarrow$ singlet conversions. These radiationless processes involve some type of transfer of energy from the excited molecule to its environment.

The third process by which the excited molecule dissipates its energy leads to chemical reaction. An excellent summary of the primary photochemical processes that generally occur is given by Pitts and Calvert.[7]

Sensitized Photoreactions

We see from this general discussion that for a photochemical reaction to occur, the system in question should absorb radiation in the convenient region of spectrum and the energy of the quanta absorbed should be large enough to break chemical bonds. A large class of compounds have dissociation energies corresponding to wave lengths in the convenient region of the spectrum but they are transparent down to Schumann region where photochemical experiments are very difficult to carry out.

Photodecomposition of such non-absorbing compounds may be studied in the convenient region of the spectrum by adding foreign substances which absorb in that region and then transfer their excitation energy by collisions to the non-absorbing substrate molecules. Such processes are called photosensitizations[8] and the added foreign substances are photosensitizers. A variety of sensitizers have been used, Hg,[9] Xe,[10] Cd,[11] NH_3,[12] etc.

Mercury has been widely used, as it has a comparatively high vapour pressure of about 10^{-3} mm at room temperature, it is rather chemically inert in its ground state and it has a high extinction coefficient for its resonance radiation, ensuring complete absorption of its radiation in an experimentally convenient path length. It is also possible to get very intense and convenient sources of resonance radiation.

Spectroscopy of Mercury Atom

The spectroscopy of the mercury atom has received widespread attention. The principal optical lines of the mercury spectrum are at 1849 and 2537A. These correspond to the transitions $Hg(6^1S_0) + h\nu \rightarrow Hg(6^1P_1)$ and $Hg(6^1S_0) + h\nu' \rightarrow Hg(6^3P_1)$ respectively. The selection rules allow just one optical transition, i.e. 6^1S_0 to 6^1P_1. The presence of the resonance radiation at 2537A suggests that the spin selection rule ($\Delta S = 0$) does not hold very rigorously for heavy atoms. The forbidden nature of this singlet → triplet transition is reflected in the relatively long life[13] of the Hg(6^3P_1) state ($\tau = 1.1 \times 10^{-7}$ secs). The lifetime of an isolated Hg(6^1P_1) atom is 1.3×10^{-9} secs.

Quenching of Hg(6^3P_1) Atoms

An excited mercury atom by collision with a molecule of a foreign gas may lose its excitation energy in four fundamentally different ways.[14]

(i) The mercury atom is transferred to the metastable $6(^3P_0)$ state. The excitation energies of the two states are

$$6^3P_1 = 112.20 \text{ Kcal/mole}$$

$$6^3P_0 = 107.17 \text{ Kcal/mole}$$

Hence in dropping to the (6^3P_0) state the amount of energy transferred to the quencher molecule is only 5 Kcal/mole. This is too small to cause any chemical reaction and the energy ultimately appears as heat. N_2 - gas and water vapour are good quenchers of this type.

(ii) In this type of process the quenching is done by an electronic transition.

$$Hg(6^3P_1) + AB \longrightarrow Hg(6^1S_0) + AB^* \quad . \; . \; . \; . \; (7)$$

here AB* represents an electronically excited molecule of the quencher. In this case the energy transferred is 112 Kcal/mole and this is sufficient to break most chemical bonds. The excited molecule AB* in general either decomposes or is deactivated.

$$AB^* \longrightarrow \text{Products} \quad . \; . \; . \; . \; (8) \text{ decomposition}$$

$$AB^* + AB \longrightarrow 2AB \quad . \; . \; . \; . \; (9) \text{ deactivation}$$

(iii) In this process the quenching involves direct dissociation of the quencher molecule.

$$Hg(6^3P_1) + AB \longrightarrow Hg(6^1S_0) + A + B \; . \; . \; . \; . \; . \; . \quad (10)$$

A and B are the fragments of the parent molecule.

(iv) In this case the quenching involves compound formation with $Hg(6^3P_1)$ atom.

$$Hg(6^3P_1) + AB \longrightarrow HgA + B \; . \; . \; . \; . \quad (11)$$

If the bond in HgA is very weak, it is followed by dissociation

$$HgA \longrightarrow Hg(6^1S_0) + A \; . \; . \; . \; . \quad (12)$$

To rationalize the experimental results on the metal-photosensitized reactions of hydrocarbons, Laidler[15] in 1947 applied the Wigner spin conservation rule to these energy transfer processes. This approach is found successful even today in all mercury sensitized reactions. It states that "in the transfer of electronic energy between an excited atom or molecule and a molecule in its ground or excited states the overall spin angular momentum of the system should not change."

Quenching Cross Sections

An isolated $Hg(6^3P_1)$ atom will emit the resonance radiation 2537A° and come back to its ground state. But in the presence of foreign gas molecules, it will suffer collisions and transfer its energy to the colliding molecules. The extent of this quenching of resonance radiation will depend on the pressure of the foreign gas and on the efficiency of such collisions. This efficiency varies widely from gas to gas and it is generally expressed in terms of the quenching cross sections (σ_q^2).

Quenching cross section is most easily defined by considering the effective number of collisions as derived from a simple collision theory formalism.

$$Z = 2n_{Hg}n_{AB}\sigma_q^2 \{2\pi RT (\frac{1}{M_{Hg}} + \frac{1}{M_{AB}})\}^{\frac{1}{2}} \ . \ . \ . \ . \ (13)$$

here Z is the number of collisions, M_{Hg}, M_{AB} and n_{Hg}, n_{AB} are the molecular weights and concentrations respectively of mercury and the colliding species. T is the absolute temperature and R the universal gas constant.

The rate equation for the disappearance of $Hg(6^3P_1)$ atoms can be given as

$$\frac{d\{Hg^*\}}{dt} = K_q \ (n_{Hg^*}) \ (n_{AB}) \ . \ . \ . \ . \ (14)$$

where K_q is the rate constant for the quenching process. If we assume every collision to be effective in quenching, then the rate of disappearance of Hg* should be equal to the number of effective collisions per sec. Therefore

$$K_q = \sigma_q^2 \{8\pi RT (\frac{1}{M_{Hg}} + \frac{1}{M_{AB}})\}^{\frac{1}{2}} \ . \ . \ . \ . \ (15)$$

σ_q^2, expressed in A^2, can be determined by two different experimental methods using the above relation.

(i) Physical Method:- This method is based upon the measurements of the intensity of fluorescence in the presence and absence of the quenching gas. The ratio of these two intensities is defined as the Quenching, "Q".

If we apply a steady state treatment for the formation and disappearance of $Hg(6^3P_1)$ atoms in a system in which these following processes are at equlibrium,

$$Hg(6^1S_0) + h\nu \longrightarrow Hg(6^3P_1) \ . \ . \ . \ . \ (16)$$

$$Hg(6^3P_1) \longrightarrow Hg(6^1S_0) + h\nu \ . \ . \ . \ . \ (17)$$

$$Hg(6^3P_1) + AB \longrightarrow Hg(6^1S_0) + AB^* \; . \; . \; . \; . \; (18)$$

$$Hg(6^3P_1) + AB \longrightarrow Hg(6^3P_0) + AB^{**} \; . \; . \; . \; . \; (19)$$

we may derive a linear relationship between 1/Q and P, where P is the pressure of the quenching gas.

$$Q = \frac{1}{1 + \tau K_q(n_{AB})} \; . \; . \; . \; . \; (20)$$

$$Q \equiv \frac{I_P \leftarrow \text{absence of quencher}}{I_P^{Q} \leftarrow \text{presence of quencher}}$$

This is known as the Stern-Volmer equation. τ here represents the life time of $Hg(6^3P_1)$ atoms. A complete list of the quenching cross section values which have been determined by this method can be found in the data of references 13, 14, 7, 16. The absolute values of σ_q^2 so obtained have a great deal of uncertainity because of the difficulty in treating quantitatively the effect of "imprisonment of resonance radiation" and Lorentz broadening. The later effect can be made effectively negligible by choosing proper experimental conditions.

(ii) Chemical Method:- Cvetanović developed a chemical method[17,18] for obtaining relative quenching cross sections that is highly successful and free of such effects as pressure broadening and radiation imprisonment. This method is based on competetive rates of mercury photosensitized reactions between the quencher AB and the added nitrous oxide.

$$Hg(6^3P_1) + N_2O \longrightarrow Hg(6^1S_0) + N_2 + O \; . \; . \; . \; . \; (21)$$

$$Hg(6^3P_1) + AB \longrightarrow Hg(6^1S_0) + \text{products} \; . \; . \; . \; . \; (22)$$

The experiments should be performed under conditions where there is sufficient amount of AB to scavenge the oxygen atoms formed in reaction (21), otherwise oxygen atoms react with mercury vapour forming solid deposits of HgO on cell walls. Also the oxygen atoms react with N_2O to give more nitrogen which upsets the determination of nitrogen quantum yield for reaction (21).

$$O + N_2O \longrightarrow O_2 + N_2 \; . \; . \; . \; . \; (23)$$

Focusing attention on nitrogen production in mixtures of AB and nitrous oxide as a function of the ratio of their concentrations, it can be found that the following expression is obeyed,

$$1/\Phi_{N_2} = 1 + \beta\,(n_{AB})\,/\,(n_{N_2O}) \quad . \; . \; . \; . \quad (24)$$

The ratio of the effective quenching cross sections is related to β by the expression,

$$\frac{\sigma^2_{AB}}{\sigma^2_{N_2O}} = \beta\,\frac{(1 + M_{Hg}/M_{N_2O})^{\frac{1}{2}}}{(1 + M_{Hg}/M_{AB}\,)^{\frac{1}{2}}} \quad . \; . \; . \; . \quad (25)$$

A plot of $1/\Phi_{N_2}$ against n_{AB}/n_{N_2O} gives β as slope. Hence accurate values for the ratio $\sigma^2_{AB}/\sigma^2_{N_2O}$ can be obtained. If an accurate absolute value for a cross section of any compound is determined, all other values could be normalized to that result. Gunning[19] et al.have recently determined accurate absolute quenching cross sections for a number of compounds. They eliminated the Lorentz broadening by using an improved Zemansky's apparatus.[20] To compensate the radiation imprisonment effect, a correction factor, obtained by the application of Milne's theory, was included.[21]

Mercury Photosensitized Reactions

No general principle has yet been found which correlates the efficiency of the energy transfer process to the physico-chemical properties of the substrate. However, a survey of the various photosensitized reactions and the quenching cross section data, suggest that the primary interaction between excited mercury atoms and substrate molecules takes place in some definite pattern. To make the last point clear a brief resume of various investigations, which are related to the present investigation, is given here.

The quenching cross sections of alkanes have been found to be comparatively small, e.g. CH_4 - 0.085A^2, C_2H_6 - 0.16A^2, C_3H_8 - 2.3A^2. The primary process seems to be always a C-H bond split to give an hydrogen atom and an alkyl radical.

$$Hg(6^3P_1) + RH \longrightarrow R\cdot + H\cdot + Hg(6^1S_0) \quad . \; . \; . \; . \; (26)$$

R· here represents the alkyl radical and H· the hydrogen atom. The alkyl radical undergoes secondary recombination and disproportionation reactions to give the observed products.

$$H\cdot + RH \longrightarrow H_2 + R\cdot \quad . \; . \; . \; . \; (27)$$

$$R\cdot + R\cdot \longrightarrow R_2 \quad . \; . \; . \; . \; (28)$$

$$R\cdot + R\cdot \longrightarrow RH + R^* \quad . \; . \; . \; . \; (29)$$

R* is the corresponding olefin. The question of whether the quenching occurs by direct dissociation or by formation of HgH as an intermediate is unsolved even today. However there is no direct evidence for HgH formation[22] in reactions studied so far. Early works on alkanes reported low quantum yields for hydrogen. This was explained later on as due to the self scavenging process taking place in the system.[23] Hydrogen atoms formed in the primary process add rapidly to the olefins formed by secondary disproportionation reactions, thus lowering the primary quantum yields for hydrogen (Φ_{H_2}).

But at very low conversions and high pressures of alkanes the quantum yield for hydrogen levels off to a value greater than 0.9,[24] indicating that at zero conversion the quantum yield is actually unity.

Darwent pointed out in 1950 that the quenching cross sections of paraffinic hydrocarbons can be reasonably well estimated by assigning quenching diameters to CH_3, CH_2 and CH groups. The overall quenching diameter of the alkane molecule is the sum of all such increments.[25]

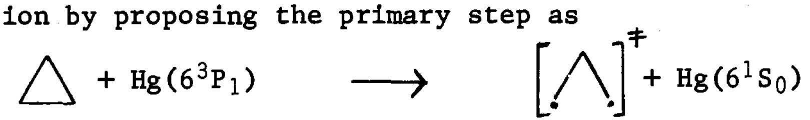
Cycloalkanes appear to follow the same primary act of quenching as the alkanes do, i.e. scission of a C-H bond.

$$Hg(6^3P_1) + \text{cycloalkane} \longrightarrow \text{cycloalkyl radical} + H\cdot + Hg(6^1S_0) \quad \ldots . (30)$$

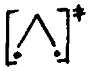
The cycloalkyl radical then undergoes the usual recombination and disproportionation reactions. Gunning et al.[26] have shown that the reaction of cyclopentane vapour with $Hg(6^3P_1)$ atoms leads to the formation of cyclopentyl radicals and hydrogen atoms with a primary quantum efficiency of 80%. Cyclopentyl radical undergoes secondary reactions to give bicyclopentyl and cyclopentene as products. The complete free radical nature of the reaction was demonstrated by showing that 0.7 mole % of added nitric oxide leads to a complete inhibition of bicyclopentyl and cyclopentene formation. Cyclobutane[27] and cyclohexane[28] also seem to follow the same mechanism.

The cyclopropane - $Hg(6^3P_1)$ reaction is of particular interest because a low molecular weight polymer has been reported as the major product.[29] Cyclopropane itself is not polymerized by free radicals. Rabinovitch et al.[30] observed cis-trans isomerization in the mercury sensitized reaction of trans-dideuterocyclopropane. The relative importance of the two basic products, i.e. cis-cyclopropane-d_2 and the polymer, was found to be pressure dependent. Hence the polymerization was suggested to proceed via an excited triplet state of cyclopropane. It was found that oxygen up to 15% had only a slight effect on the isomerization, although only a small amount of it was enough to completely inhibit the polymerization.

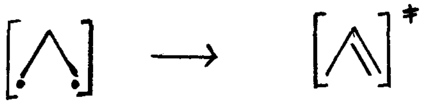
Gunning et al.[31] observed that the inhibition of polymerization by free radical scavengers, such as nitric oxide and oxygen, was followed by a simultaneous large increase in propylene yields. They summed up the situation by proposing the primary step as



. . . . (31)

 here represents the excited triplet state of cyclopropane (i.e. triplet trimethylene diradical). The excited species may be deactivated by collisions to give the isomeric product or undergo rearrangement to give propylene molecules with excess energy.


. . . . (32)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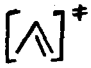
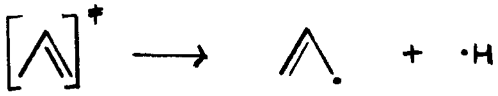
 here represents the propylene molecule with excess energy. The hot propylene molecule dissociates to give allyl radicals.


. . . . (34)

They were able to account for most of the products by the self scavenging of H-atoms by propylene.

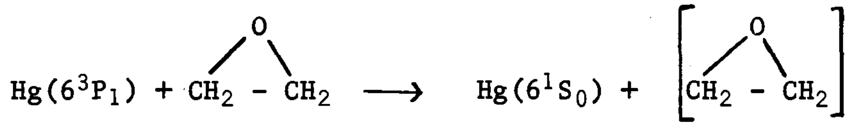
In contrast to the alkanes the quenching cross sections of olefins are large. The rate of the sensitized reactions decrease as the pressure of the substrate is increased, suggesting the presence of an excited molecule which can be deactivated by collisions. It is now generally agreed that the primary act[32] is triplet energy transfer to produce a relatively long lived vibrationally excited triplet state of the olefin.

$$Hg(6^3P_1) + RCH = CHR \longrightarrow (R\dot{C}H - \dot{C}HR)^{\ddagger} + Hg(6^1S_0) \quad . \ . \ . \ . \ (35)$$

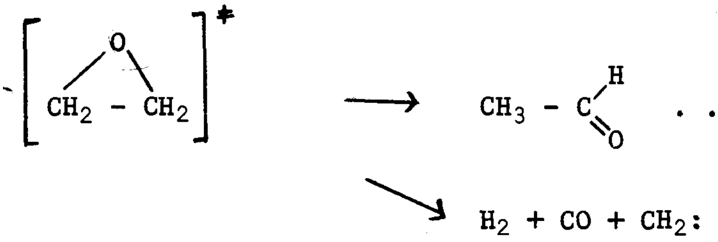
The work of Lossing et al.[33] has helped in understanding the mechanisms of decomposition of these excited molecules. They observed the primary reaction products directly with a mass spectrometer coupled to the reaction system. They found that the decomposition involves cleavage of the weak bonds C-H or C-C in β-position to the double bond with the formation of resonance stabilized allylic radicals.

Formation of an excited state was also proposed in the case of cycloolefins. $Hg(6^3P_1)$ sensitized decomposition of cyclooctatetraene has been studied by Yamazaki and Shida.[34] Evidence was obtained for initial formation of an excited C_8H_8 molecule, which then decomposes into acetylene and benzene. Similar examples of ring contraction were observed by Gunning et al. in the mercury sensitized reaction of cyclopentene[35] and cyclohexene.[36]

A limited amount of work has been done on the sensitized reactions of ethers and epoxides. The mercury sensitized decomposition of ethylene oxide was first studied by Steacie et al.[37] They found CO, H_2, CH_3CHO and a polymer as major products. Initial formation of an excited ethylene oxide molecule was postulated which was capable of isomerising to acetaldehyde or decomposing into H_2, CO and CH_2:



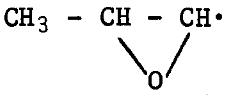
. . . . (36)



. . . . (37)

. . . . (38)

Later work of Cvetanović[38] showed that small amounts of ethylene or butene added to the system brought a remarkable decline in the quantum yield of hydrogen, indicating that most of the hydrogen came from reactions of H-atoms. Using 1:1, C_2D_4O-C_2H_4O mixtures he showed that only a small fraction of the hydrogen came by molecular elimination. Careful analysis indicated the products as CO, H_2, C_2H_6, little of C_2H_4 and large amounts of aldehydes. Some of the aldehydes were higher than acetaldehyde. $CH_3\cdot$, $CHO\cdot$, $\dot{C}H_2CHO$ and $C_2H_5\cdot$ radicals are assumed to be participating in this reaction. No complete and unambiguous explanation for this complex process has yet been obtained.

Cvetanović and Doyle[39] studied the sensitized decomposition of trans-2,3.-epoxybutane. This system also proved to be a very complex one. The main products formed were, $(CH_3)_2$ CHCHO, C_2H_6, CO, C_2H_4, C_3H_8, CH_3CHO, C_2H_5CHO, $CH_3COC_2H_5$, CH_4 and H_2. The yields of most of the products decrease with increasing pressure of the substrate, indicating the formation of an excited substrate molecule, which then undergoes decomposition. $CH_3\cdot$ and  $CH_3-\underbrace{CH-CH}_{O}\cdot$ radicals seem to play important roles in this process. The complexity of the system precluded quantitative treatment of the process.

In contrast to the epoxides, the ethers seem to have simple and straight forward mechanisms in $Hg(6^3P_1)$ sensitized reactions. The sensitized decomposition of dimethylether was studied by Steacie et al[40] in 1948. At 25°C the products consisted entirely of hydrogen and 1,2-dimethoxyethane, suggesting the primary act to be

$$Hg(6^3P_1) + CH_3OCH_3 \longrightarrow CH_3OCH_2\cdot + H\cdot + Hg(6^1S_0) \quad . \ . \ . \ . \ (39)$$

Lossing et al[41] studied the reaction at 55°C and at very low substrate pressure in a reactor coupled to a mass spectrometer. They observed that along with the above primary process there also takes place a primary C-O split.

$$Hg(6^3P_1) + CH_3OCH_3 \longrightarrow CH_3O\cdot + CH_3\cdot + Hg(6^1S_0) \quad . \ . \ . \ . \ (40)$$

The absence of the second primary process of C-O split in the expriments of Steacie et al was interpreted by Lossing as suggesting that this reaction might proceed via an excited molecule formation,

$$Hg(6^3P_1) + CH_3OCH_3 \longrightarrow [CH_3OCH_3]^{*} + Hg(6^1S_0) \quad . \ . \ . \ . \ (41)$$

and that at the higher pressures used by Steacie et al, $[CH_3OCH_3]^{*}$ were completely deactivated by collisions.

Laidler and coworkers[42] took up the study of this reaction in 1967. They investigated the decomposition from 30° to 300°C and over a wide range of pressure from 3 to 600 mm Hg. They concluded that the only primary process taking place in the system in the whole range of study was C-H split. At temperatures lower than 30°C the radicals combined to give the products observed by Steacie et al. But at temperatures above 30°C the methoxymethyl radical decomposed to give the methyl radicals observed by Lossing et al.

$$CH_3OCH_2\cdot \longrightarrow CH_3\cdot + CH_2O \quad . . . . (42)$$

Role of the Present Investigation

Mercury photosensitized reactions of cyclic compounds are of intrinsic interest because of the possibility of ring cleavage in the primary process to yield a triplet biradical. In the case of cycloparaffins larger than cyclopropane, the important primary process is the cleavage of a C-H bond to give a hydrogen atom and a cycloalkyl radical. The reaction of cycloolefins produce ring contracted compounds which suggest that the primary processes produce biradicals with free electrons separated by several carbon atoms. The presence of heteroatoms in the ring would also be expected to change the nature of the primary process. The reactions of the epoxides of ethylene and butene-2 produce excited molecules which at lower pressures can decompose with cleavage of the ring. Little work has been done on heterocyclic compounds with larger rings. Srinivasan has studied the mercury photosensitized reaction of furan[43,44]. The main reaction products were cyclopropene, methylacetylene and carbon monoxide. The quantum yields of the products decreased continuously with increasing pressures, suggesting the intermediacy of an electronically excited state of furan. A study of the minor products formed in this system indicated that the substrate molecule also underwent Diels-Alder

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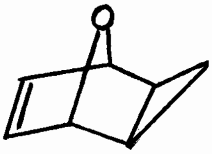
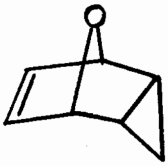
additions to monoolefins to give the following adducts:

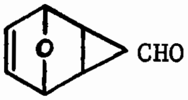


(I)



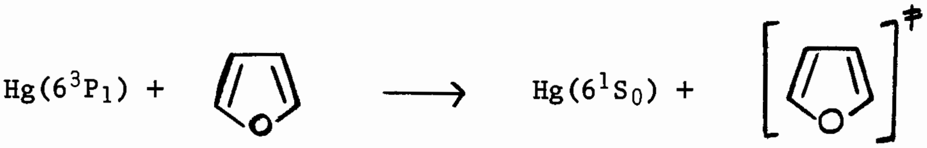
(II)

and

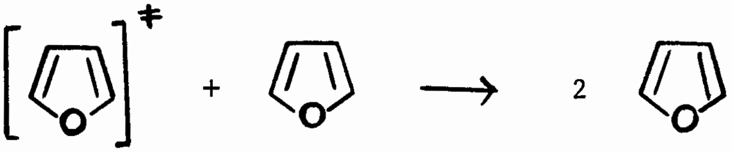


(III)

(I) and (II) are the adducts of furan molecules to cyclopropene and (III) is of furan to 2-cyclopropenecarboxaldehyde. The presence of (III) strongly suggests that the excited furan molecule first rearranges to give 2-cyclopropenecarboxaldehyde and this then undergoes decarbonylation to give carbon monoxide and cyclopropene.



. . . . (43)



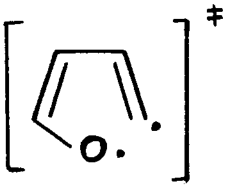
. . . . (44)

. . . . (45)

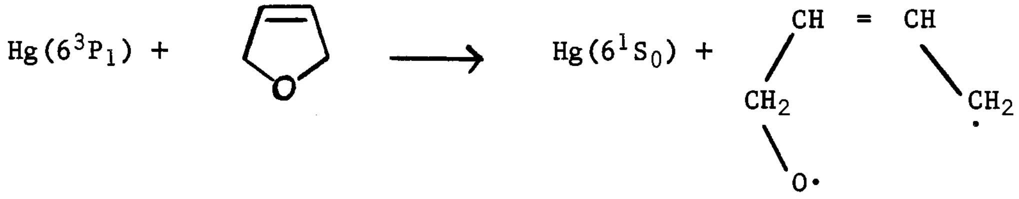
. . . . (46)

. . . . (47)

According to the spin conservation rule the excited furan molecule should be in a triplet state. There is no information in the literature on the triplet levels of furan. Srinivasan presumed that the primary process was the C-O split to give the excited triplet biradical.



We have undertaken a study of the mercury photosensitized decomposition of 2,5-dihydrofuran. The C-O bond, in a position allyl to the double bond represents a likely site for bond cleavage i.e.



. . . . (48)

The resulting biradical should be compared to that suggested by Cvetanović and Doyle[45] as the intermediate formed by the addition of ground state oxygen atoms to butadiene.

$$O\ (^3P) + CH_2 = CH - CH = CH_2 \longrightarrow \dot{O} - CH_2 - \dot{C}H - CH = CH_2$$

. . . . (49)

This biradical differs from that produced in reaction (48) only in the position of the double bond and the free electrons. These structures may be regarded, in valence bond terminology, as representing contributions to a resonance hybrid structure which may be written as

$$\dot{O} - CH_2 - \overset{\cdots\cdots\cdots\cdots}{CH - CH - CH_2}.$$

The products of the O-atom-butadiene reaction were butadiene monoxide, formed by pairing of the unpaired electrons of the biradical represented in equation (49), 3-butenal, formed by a hydrogen shift in this biradical and carbon monoxide, formed by its decomposition. Because the major emphasis of these authors was on the higher molecular weight products, some of their work was repeated. Propylene and CO in roughly equimolecular amounts were found to be the major products.

In relation to the present work, the most interesting observation of Cvetanović and Doyle was that no 2,5-dihydrofuran was produced. The intermediate formed in reaction (49) does not cyclize to any extent to give a five membered ring. It is tempting to interpret this observation as indicating that the structure $\dot{O} - CH_2 - CH = CH - \dot{C}H_2$ does not contribute significantly to the structure of the biradical intermediate. On the other hand, the exclusive formation of the three membered ring may be the result of an interaction between the unpaired electrons which controls the direction of the reaction from the moment of addition of the oxygen atom.

It was considered likely that a study of the 2,5-dihydrofuran photosensitization would contribute to the understanding of this question.

EXPERIMENTAL METHODS

Apparatus

In this study the apparatus was constructed of Pyrex glass except for the reaction cell, which was made of quartz. It consisted of a pumping system, a distillation system, a reaction system, an analytical system, a gas chromatograph and a storage system, all interconnected to permit any desired manipulation involving volatile materials.

The entire apparatus was evacuated with a large mercury diffusion pump backed by a mechanical pump (Precision Scientific Co., Model #75). A removable trap was connected immediately before the mechanical pump and was kept immersed in liquid nitrogen, whenever the system was in operation to prevent the contamination of the pump oil by condensable vapours. The system could be evacuated to $1\overline{0}^6$ mm Hg with this arrangement. Pressures were read on a four station L. K. B. pirani vacuum guage. The pirani guage was calibrated from time to time with a McLead guage, connected to the high vacuum manifold by a grease-free mercury float valve.

Low temperature distillations were carried out in a train of several 'U'-traps interconnected by Delmar mercury float valves. The distillation unit (A), shown in figure #1, connected the reaction cell to the analytical system.

The cylindrical reaction cell (B) was 10cm. long, 5cm. in diameter and was made of fused quartz. It was connected to one end of the distillation train by a grease free "Cajon" fitting (C). A metal valve (D) (Hoke incorporated, Type 440) separated the reaction cell from

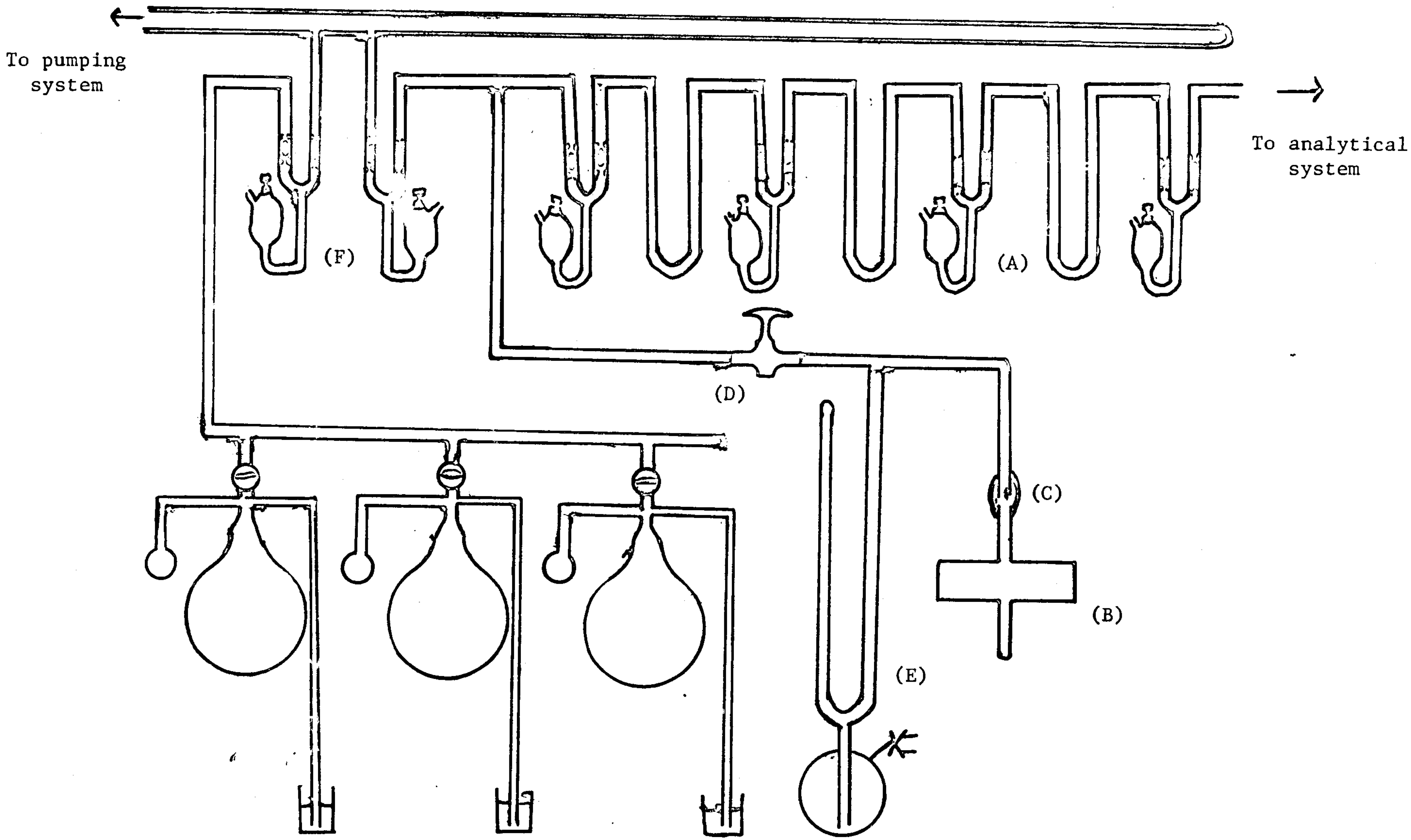


Figure 1. Reaction System

the distillation unit. A mercury manometer (E), connected directly to the reaction system, was read with a cathetometer. The reaction cell was provided with a cold finger to transfer condensable substances into it.

The storage unit was joined to the main vacuum system by a mercury float valve (F). This manifold consisted of three, one-liter storage bulbs separated from one another by Pyrex stopcocks. Each bulb was provided with a cold finger and a manometer. Nitric oxide, butane, nitrous oxide and carbon-tetrafluoride were generally stored in these bulbs.

The analytical system is shown in figure #2. The system was of conventional design and used principally for the manipulation of volatile materials in the course of their analysis. The components were a solid nitrogen trap (not shown in figure), a small diffusion pump (G), a large Toepler-gas burette (I), a small Toepler pump (J), a mercury float valve (K) and two two-way Pyrex stop cocks (L & M). Substances non-volatile at -196°C were condensed into the Toepler gas burette (I), by pouring liquid nitrogen into the cold finger (N). Non-condensables were pumped in by the small diffusion pump (G), backed by the large Toepler. The gas burette had five calibrated volumes ranging in size from 0.4947 to 91.9337mls. at room temperature. The calibrated volumes are between the point marked (O) and the points marked by arrows. The small Toepler pump (J) was used as a float valve and to pump non-condensables into the gas chromatography sampler (P). The sampler (P) was evacuated through the float valve (K). By using the two-way stop cocks (L & M), it was possible to direct the flow of the carrier gas, either through the sampler (P), or directly to the gas chromatography (G.C) column (Q).

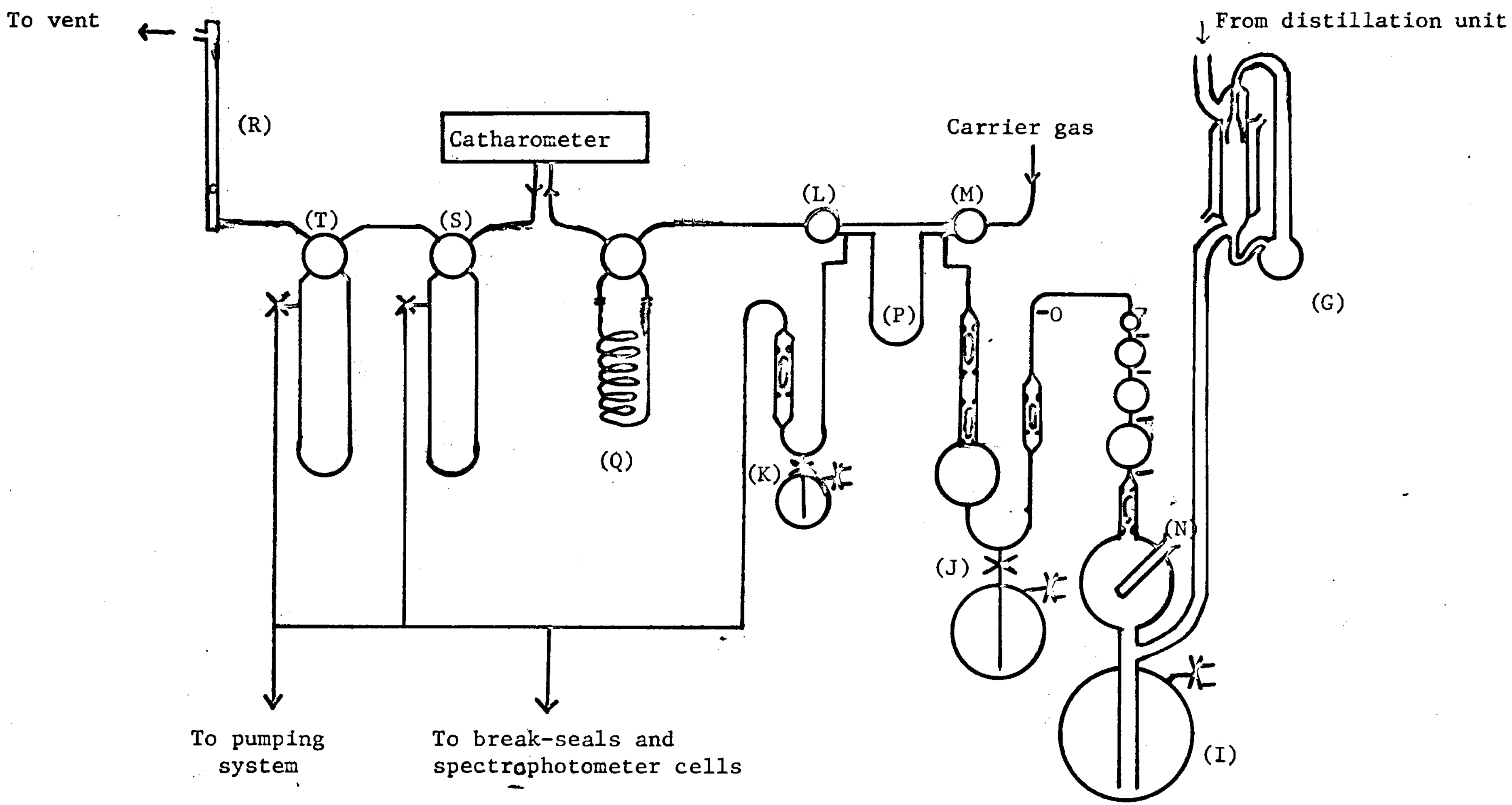


Figure 2. Analytical System

The gas chromatograph consisted of a Gow-Mac (Model TR-III A) temperature regulated thermistor catharometer, coupled to a Gow-Mac (Model 40-05 D) power supply. The catharometer was maintained at 50°C and the bridge current at 7 mamps. The signal from the detector was fed into a Texas Instrument (Model PS01-W6A) recording potentiometer. The recorder was equipped with an attenuator, which allowed the signal to be reduced by factors of from 1 to 512.

The columns were made of 6mm. Pyrex tubing wound into a spiral and connected to the system by "Cajon" joints. Column temperatures were controlled with a cylindrical brass furnace, insulated with asbestos and wound with Nichrome resistance wire. The temperature of the furnace was controlled with a Variac transformer. The flow-rate of the carrier gas, Helium, was read on a rotameter (R). The rotameter was calibrated with a soap bubble flow-meter. A flow of 50 mls. per min. was usually used in the experiments.

The G. C. was calibrated for all the substances used and the products obtained. Various amounts of pure substances were measured by means of the gas burette, transferred to the sampler and introduced into the G. C. using the appropriate columns. (See Table #1). The peak (signal) areas were measured with a planimeter. A plot of the peak areas against the amount of substance introduced, was always linear in the range of yields obtained in the present investigations.

Downstream from the detector, and attached to two 4-way stop cocks (S) and (T) were two traps, immersed in liquid nitrogen, to trap the compounds as they were eluted from the column. Samples collected this way

Table 1. Gas Chromatography Columns

Packing and Lengths	Operating Temp. in °C	Operating flow mls/min	Compounds Measured and Retention time (mins. from N_2).
Molecular Sieves 5A 40-60 mesh 6 ft.	25	50	Nitrogen - 0 Nitric oxide - 2.5 Carbon monoxide - 4.5
Porapak - P 50-80 mesh 6 ft.	60	60	Nitrous oxide - 1 Propene - 7 Allene - 11 Methyl acetylene - 13
6%, Carbowax-600 on 30-80 mesh celite 6 ft.	35	50	Biallyl - 1.5 Furan - 2.5 2,3-dihydrofuran - 3.5 Tetrahydrofuran - 5 2,5-dihydrofuran - 6.5 Crotonaldehyde - 15 A - 20 B - 26 C - 33 Acrylonitrile - 22

A, B and C have not been identified.

could be distilled into breakseals for mass-spectrometric identification or distilled into spectrophotometer cell for the determination of spectra. This arrangement was also useful for G. C. purifications.

A low pressure mercury resonance lamp was used for illumination. The discharge tube 5mm. in diameter and 30cm. long was of quartz and coiled into a helix. It was supplied with 50 m amps. of current at a potential of 3,000 volts by a transformer. Two Vycor 7910 filters were used to remove the 1849A resonance line. The lamp was warmed up for at least 30 mins. before every experiment.

15 is enough

Materials Used

2,5-Dihydrofuran (2,5-DHF) used in these experiments was obtained from the Aldrich Chemical Co.. The main impurities were furan, 2,3-dihdrofuran (2,3-DHF) and tetrahydrofuran (THF). Pure 2,5-DHF was obtained by preparative G. C. using a 6 ft., 6% carbowax-600 on celite column at 25°C. The purified substrate was degassed before introducing into the reaction cell.

Furan, THF, crotonaldehyde and biallyl were obtained from Matheson, Coleman and Bell, Inc.. Each was purified by preparative G. C. and then used for calibrating the gas chromatograph.

2,3-DHF was prepared by the method of Paul et al.[46] 2,5-DHF was heated in the presence of potassium tert-butoxide for 6 hours at 170°C in a sealed tube. The resultant mixture was distilled and the fraction at 55-6°C collected. 2,3-DHF was separated from this fraction by preparative G. C..

Nitric oxide obtained from Matheson of Canada Ltd., contained trace amounts of CO_2, N_2 and higher oxides of nitrogen. It was purified by distillation through a trap cooled with liquid oxygen. The distillate was condensed at $-196^{\circ}C$ and contained no detectable impurities. CF_4 also obtained from Matheson, was purified in a similar way.

Propene, methyl acetylene and nitrous oxide were also obtained from Matheson. Each was purified by preparative G. C. before being used for calibration.

Reagent grade hydrogen, nitrogen and butane were obtained from Matheson and were used without futher purification.

Actinometry

The lamp intensity was determined using the nitrous oxide-n-butane actinometer. Cvetanovic´[17,18] has shown that in the mercury sensitized photodecomposition of a mixture of N_2O and a hydrocarbon, the following processes take place:-

$$Hg^* + N_2O \longrightarrow Hg + N_2 + O \qquad \ldots . (21)$$

$$Hg^* + RH \longrightarrow Hg + \text{Products} \qquad \ldots . (22)$$

Hg^* here represents the excited $Hg(6^3P_1)$ atoms and RH the hydrocarbon molecules. In the absence of RH, the quantum yield of O from reaction (21) is unity. In the presence of excess RH, the oxygen atom formed is completely removed and the only source of N_2 is reaction (21).

In the pressure region of complete quenching.

Light intensity (I_a) = Rate of reaction (21) + Rate of reaction (22)
(einsteins/secs) (moles/sec) (moles/sec)

i.e.,

$$I_a = k_1\ (Hg^*)\ (N_2O) + k_2\ (Hg^*)\ (RH) \qquad \ldots . (50)$$

k_1 and k_2 are the specific rate constants for the two quenching processes respectively.

and Rate of N_2 production $(R_{N_2}) = k_1 \ (Hg^*) \ (N_2O)$ . . . . (51)

$$I_a/R_{N_2} = 1 + \frac{k_2}{k_1} \ \frac{(RH)}{(N_2O)} \qquad \text{. . . . (52)}$$

or

$$1/R_{N_2} = \frac{1}{I_a} + \frac{k_2}{k_1 \ (I_a)} \cdot \frac{(RH)}{(N_2O)} \qquad \text{. . . . (53)}$$

Hence the plot of $1/R_{N_2}$ vs (RH) / (N_2O) would be linear and the intercept value at (RH) / (N_2O) = 0 should yield the value of $1/I_a$.

Various mixtures of n-C_4H_{10} and N_2O were illuminated for 15 mins. N_2 was separated from the other products by passing the reaction products through traps cooled to liquid nitrogen temperature. Quantitative determination of N_2 was done gas chromatographically using the molecular sieves column. The plot of $1/R_{N_2}$ vs (n-C_4H_{10}) / (N_2O) is given in figure #3. The value of I_a obtained was 0.81±.02 µEin/min.

Procedures

(i) 2,5-DHF was freshly purified by preparative G. C., degassed and introduced into the reaction cell containing a small droplet of mercury. By means of the needle valve (D in figure #1) and the cathetometer the desirable pressure of 10mm Hg was obtained. The shutter between the reaction cell and the prewarmed lamp was then removed rapidly and the stop watch started. At the end of the desired irradiation period, the lamp

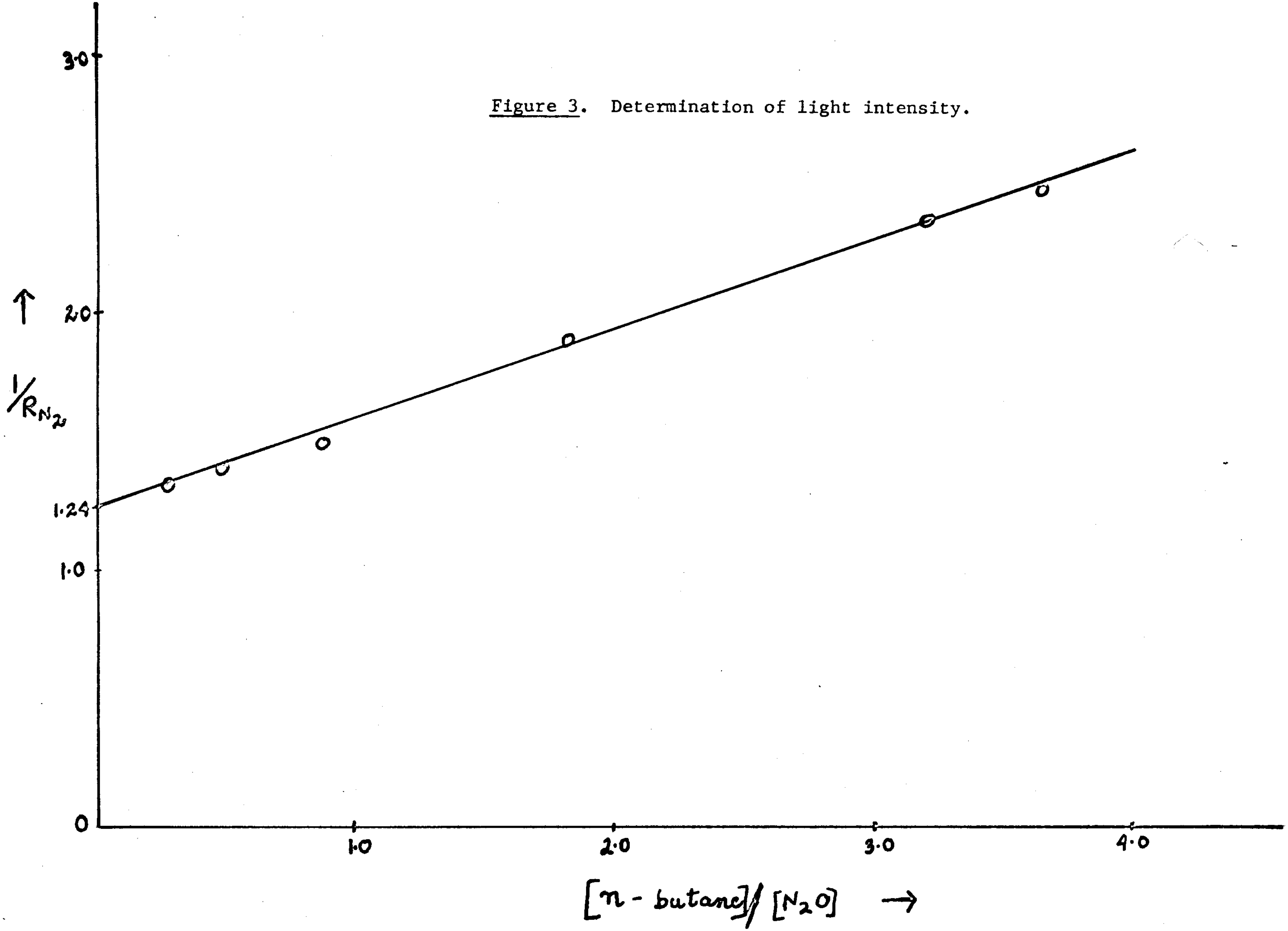


Figure 3. Determination of light intensity.

was turned off and the reaction products analysed.

The contents of the reaction cell were passed through traps cooled to -196°C and the non-condensable (N.C) fraction was measured in the gas-burette, transferred to the sampler and analysed on the molecular sieves column.

The fraction that was nonvolatile at liquid nitrogen temperature, was passed through traps maintained at -112°C with carbon disulphide slush baths. The distillate was condensed in a liquid nitrogen trap. This fraction contained the C_3- products and was called the "Liquid nitrogen fraction". The Porapak-P column was used to analyse this fraction.

The fraction nonvolatile at -112°C was called the "CS_2-fraction". It was analysed on the carbowax-600 on celite column. It was observed that after prolonged runs the reaction cell was coated with a nonvolatile material. Hence the cell was removed, cleaned, dried at 120°, and pumped overnight between runs.

(ii) Runs with added CF_4

In these runs the substrate pressure was maintained at 10mm Hg, but the total pressure in the reaction cell was altered by adding various amounts of CF_4. The mixture was allowed to stand for 6 hours to ensure complete mixing. The illumination was kept constant at 20 mins. Due to the presence of large amounts of added CF_4, the non-condensable fraction of the product could not be analysed. The cell contents were condensed at -196°C, the material volatile at this temperature was pumped away and the condensed fraction was analysed in the usual way.

Table 2. Determination of light intensity using the n- butane- nitrous oxide Actinometer.

Φ_{N_2}	$1/\Phi_{N_2}$	Run No.	$\frac{(n\text{-}C_4H_{10})}{(N_2O)}$	Pressure mm. Hg	P_{N_2O}	Reaction time in mins	R_{N_2} µ moles/min	$\frac{1}{R_{N_2}}$
0.8857	1.129	1	0.478	101.0	68.3	15	0.721	1.388
0.9247	1.081	2	0.267	88.1	69.5	15	0.749	1.335
0.8284	1.207	3	0.872	98.4	52.3	15	0.671	1.490
0.6531	1.531	4	1.824	111.0	39.3	15	0.529	1.890
0.5259	1.901	5	3.196	124.0	29.6	15	0.426	2.347
0.5012	1.995	6	3.655	107.0	23.0	15	0.406	2.463

I_{abs} = 0.814 µmoles/min

b = 1.228

m = 0.344

corr : 0.998

$1/\Phi_{N_2}$ = 1.273 $\left(\frac{n\text{-}C_4H_{10}}{N_2O}\right)$ + 0.980

lit gives 0.255

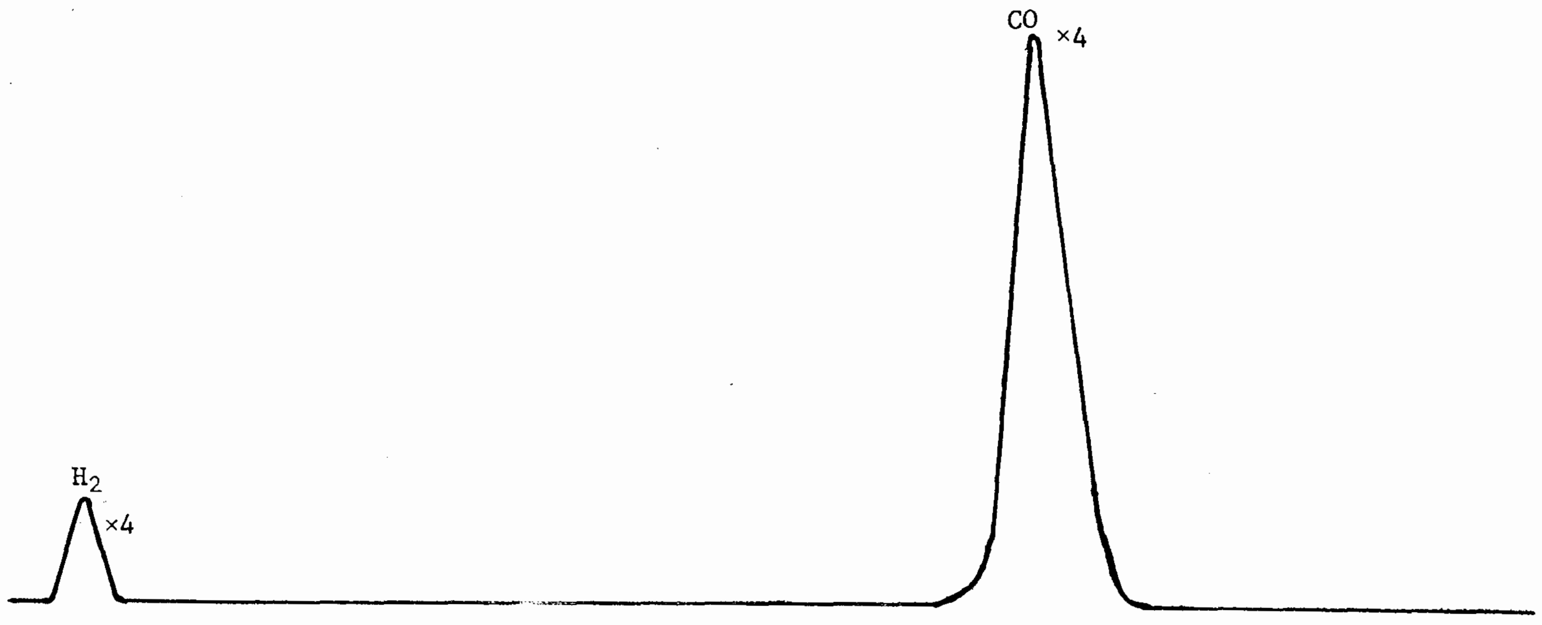
should have been kept constant !

(iii) Runs with added NO

A substrate pressure of 10mm. was used and various percentages of nitric oxide were added. The mixture was allowed to equilibrate for 6 hours and was then irradiated for 20 mins. The significant vapour pressure of NO at $-196^{\circ}C$ ($\simeq$ 70 microns) necessitated a change in the analytical procedure. By using a solid nitrogen trap most of the NO was separated from the N.C. fraction. The little that distilled through the trap did not interfere with the chromatographic analysis of CO.

Quantitative estimation of H_2 was done by difference in all these experiments. The total volume, pressure and temperature of the N.C. fraction was determined in the gas burette. Hence the total number of moles of the non-condensable gas was obtained. The number of moles of CO (CO and NO in the NO - added runs) was obtained by G. C. analysis. The values for H_2 calculated by this method for several runs, were checked by gas chromatographic analysis using argon as the carrier gas. The 6 ft. molecular sieves column was used at $25^{\circ}C$ and a flow rate of 50 mls/min. Bridge current was kept constant at 4.0 m amps. Values obtained by these different methods agreed to within 1%.

Mass spectrometric and I R analysis of the isolated peaks as well as the retention times from G. C. analysis, were used for product identification. Mass spectrometric analyses were done on a Hitachi Perkin-Elmer RMU-6E mass spectrometer. I. R spectra were obtained by a Perkin-Elmer 457 grating infra red spectrometer. Figures #4 to 7 illustrate the chromatograms obtained.



<u>Figure 4</u>. G. C. Analysis of the N. C. Fraction

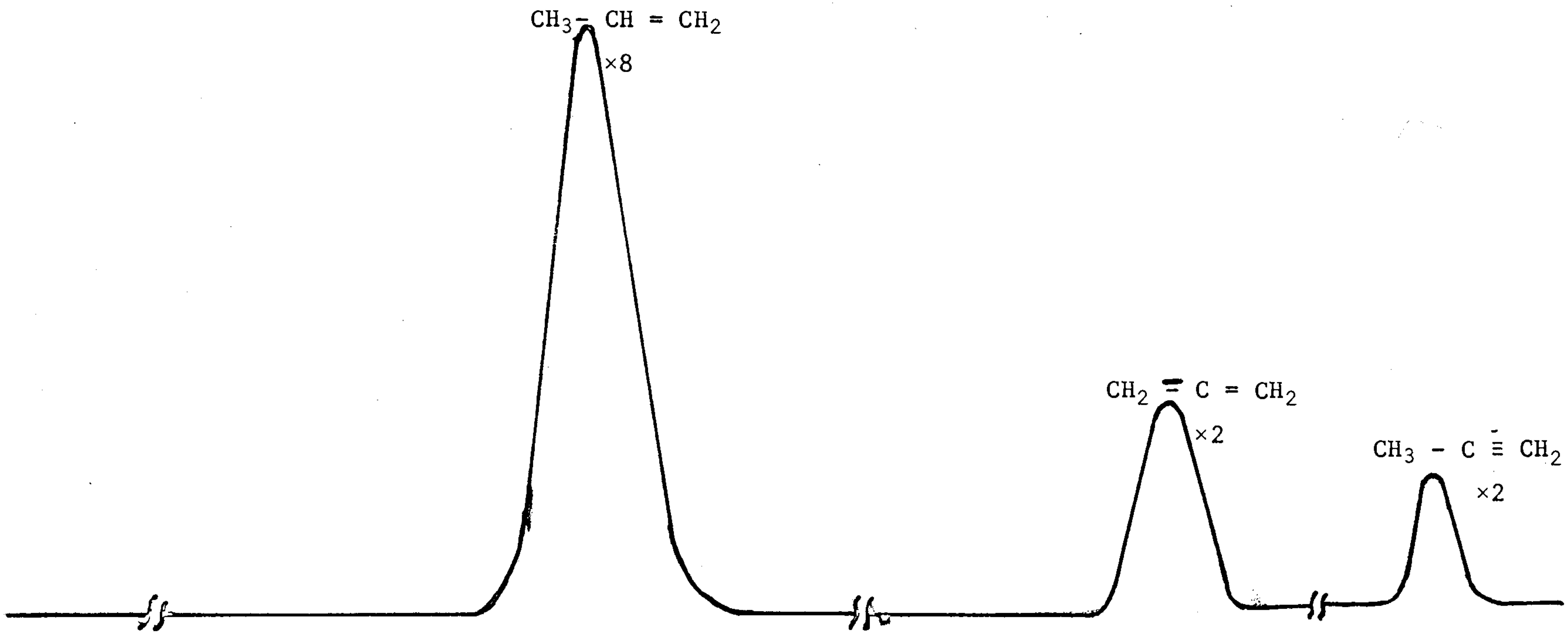


Figure 5. G. C. Analysis of "Liq.-N_2 fraction"

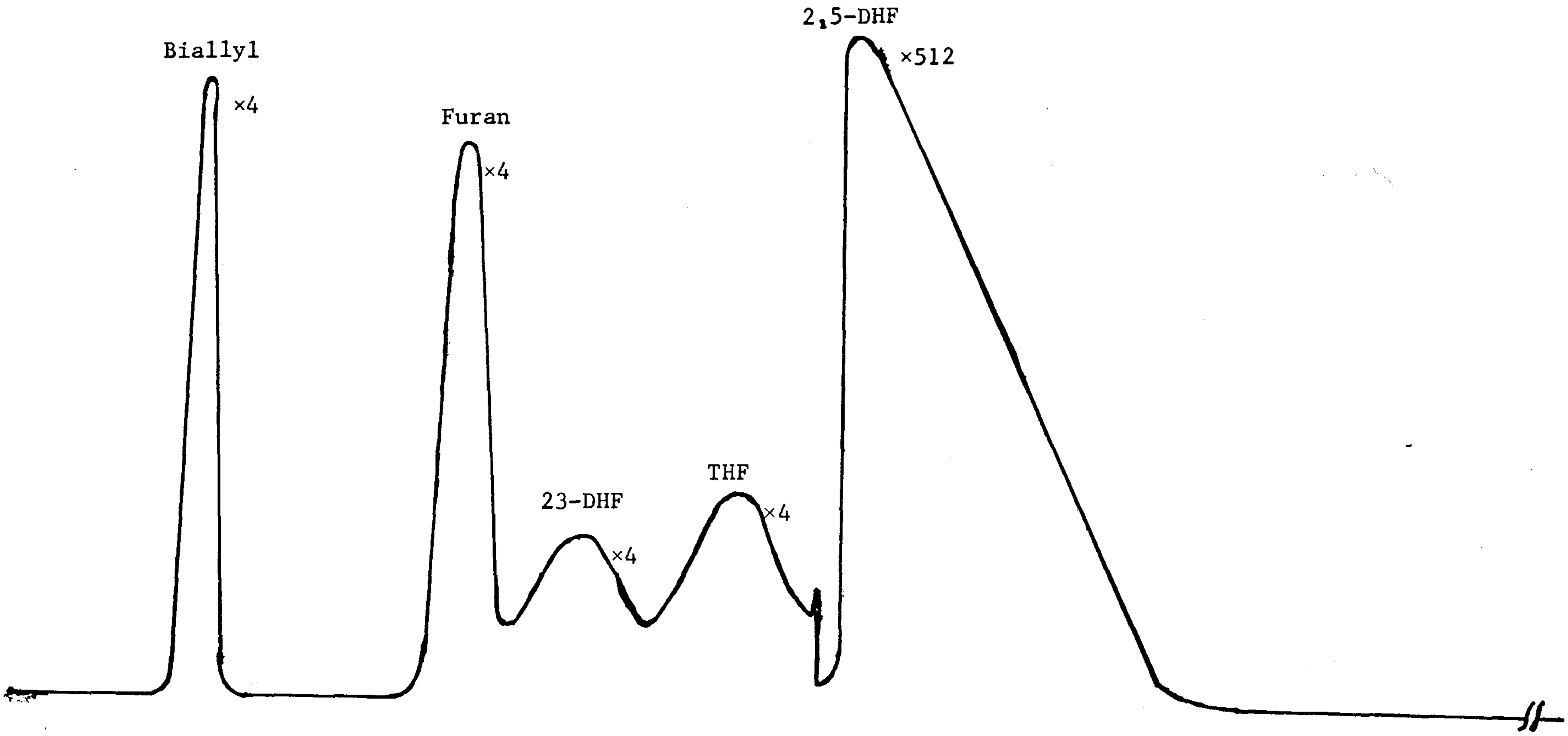
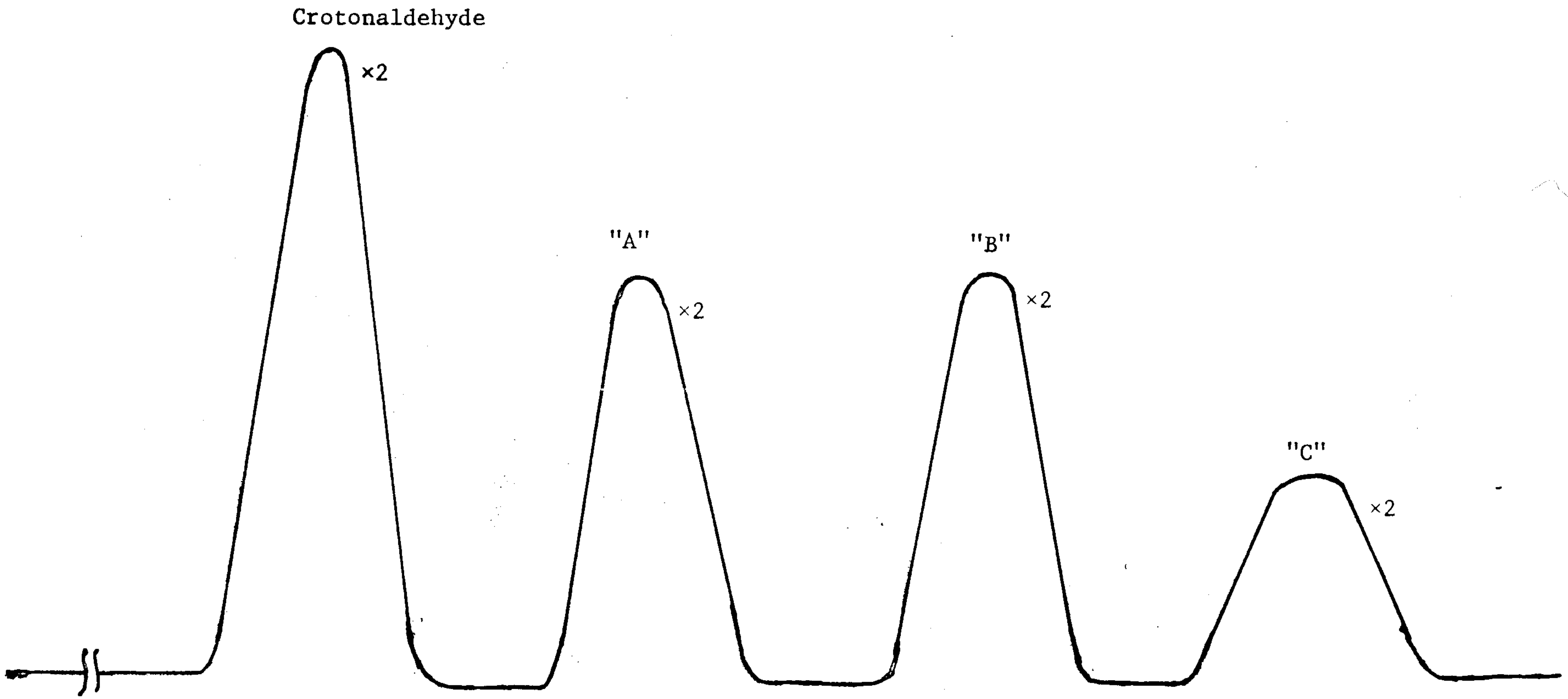


Figure 6. G. C. Analysis of "CS_2-fraction"



<u>Figure 7</u>. G. C. Analysis of the "CS_2-fraction" continued

Determination of the Quenching Cross-section for 2,5-DHF

It has been shown earlier that in the sensitized photodecomposition of a mixture of hydrocarbon and N_2O, the following relation applies,

$$I_a/R_{N_2} = 1 + \frac{k_2}{k_1} \cdot \frac{(RH)}{(N_2O)} \qquad \ldots\ldots (52)$$

For the mercury photosensitization of a mixture of 2,5-DHF and N_2O, we would get

$$I_a/R_{N_2} = 1 + \frac{k_3}{k_1} \frac{(2,5\text{-DHF})}{(N_2O)} \qquad \ldots\ldots (54)$$

Where k_3 is the rate constant for the quenching process

$$Hg(6^3P_1) + 2,5\text{-DHF} \qquad \text{Products} \qquad \ldots\ldots (55)$$

As I_a/R_{N_2} is $1/\Phi N_2$, a plot of $1/\Phi N_2$ vs (2,5-DHF) / (N_2O) would be linear with an intercept of unity at (2,5-DHF) / (N_2O) = 0. The slope of this line would yield the value of k_3 / k_1. Plots of the 2,5-DHF-N_2O and n-butane-N_2O mixtures are given in figure #8. The ratio of the two slopes gives k_3 / k_2.

From equation (15) we get

$$k_3 = \sigma^2_{2,5DHF} \left\{8\pi RT \left(\frac{1}{M_{Hg}} + \frac{1}{M_{2,5DHF}}\right)\right\}^{\frac{1}{2}} \qquad \ldots\ldots (56)$$

and

$$k_2 = \sigma^2_{n\text{-}C_4H_{10}} \left\{8\pi RT \left(\frac{1}{M_{Hg}} + \frac{1}{M_{C_4H_{10}}}\right)\right\}^{\frac{1}{2}} \qquad \ldots\ldots (57)$$

$$\therefore \quad \frac{\sigma^2_{2,5DHF}}{\sigma^2_{n\text{-}C_4H_{10}}} = \frac{k_3}{k_2} \quad \frac{(1 + M_{Hg}/M_{n\text{-}C_4H_{10}})^{\frac{1}{2}}}{(1 + M_{Hg}/M_{2,5DHF})^{\frac{1}{2}}} \qquad \ldots\ldots (58)$$

M's are the molecular weights of the respective substances.

Figure 8. Determination of the Quenching Cross Section for 2,5.DHF

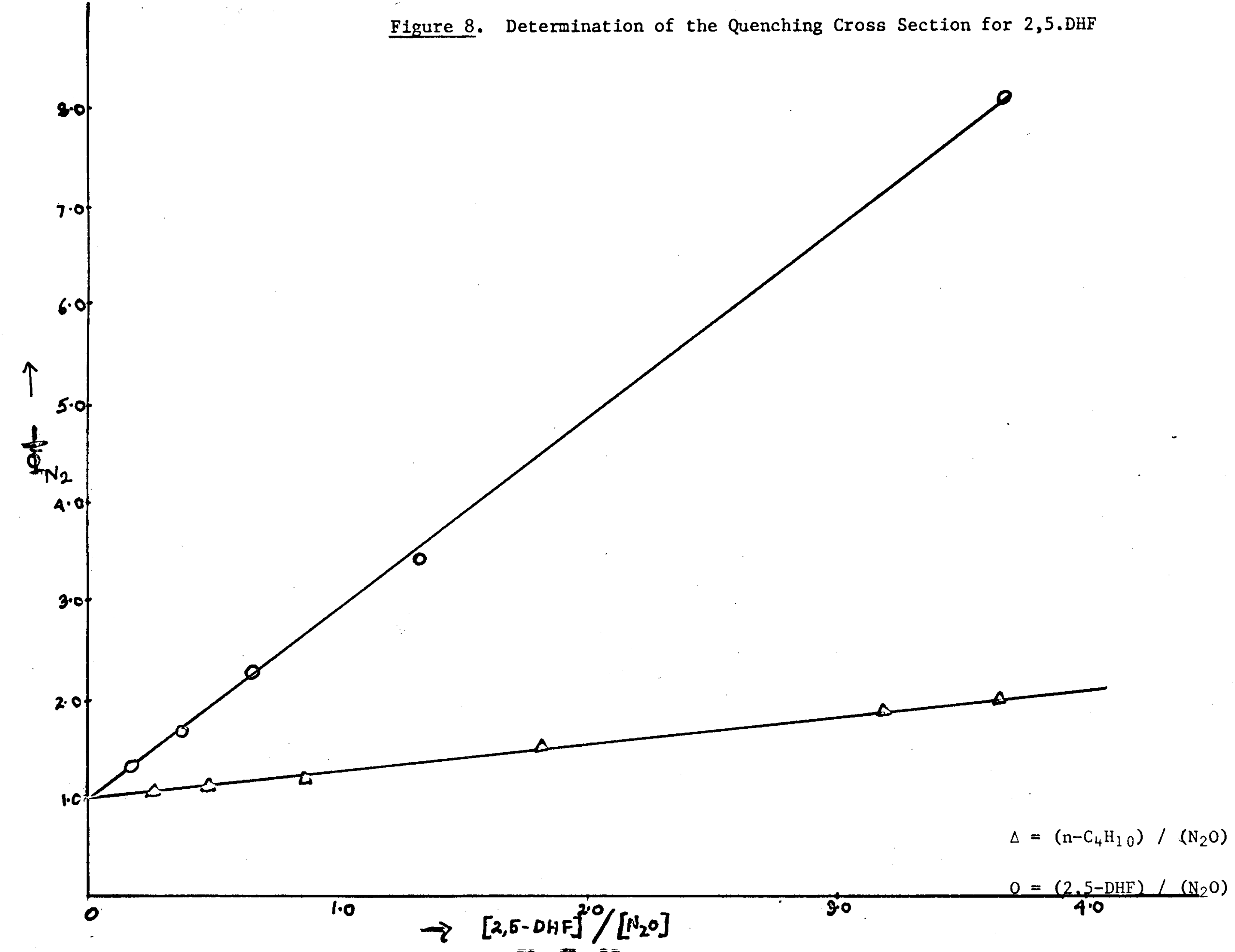


Table 3

Determination of the Quenching Cross Section for 2,5.DHF

Run NO	$\frac{(2,5\text{-DHF})}{(N_2O)}$	Pressure in mm Hg	Reaction time in mins.	Φ_{N_2}	$1/\phi_{N_2}$
1	3.6850	96.34	10	0.124	8.086
2	0.6598	106.62	10	0.439	2.276
3	1.3350	107.69	10	0.292	3.421
4	0.3864	103.47	10	0.593	1.686
5	0.1760	106.58	10	0.738	1.355

The value of k_3 / k_2 was obtained as 7.33±0.37 Hence

$$\frac{\sigma^2_{2,5\text{-DHF}}}{\sigma^2_{n\text{-}C_4H_{10}}} = 7.9 \pm .4$$

Taking the value of $\sigma^2_{n\text{-}C_4H_{10}} = 3.6A^2$ we get $\sigma^2_{2,5DHF} = 28.4 \pm 1.4$

Calculation for Competitive Quenching

In the experiments performed in the presence of nitric oxide and carbontetrafluoride, the reported yields have been corrected for competitive quenching of $Hg(6^3P_1)$ by those addends. The fraction of the total quenching processes involving nitric oxide and 2,5-DHF can be represented as

$Hg(6^3P_1)$ + 2,5-DHF fraction = π

$Hg(6^3P_1)$ + NO fraction = $1 - \pi$

Thus the factor, Q.C.F. by which the observed yields must be corrected, to allow for the net decrease in the concentration of excited mercury atoms, is given by $1/\pi$.

The ratio of $(1-\pi)/\pi$ can be obtained from the relative number of collisions between Hg* and NO and between Hg* and 2,5-DHF. Hg* here represents the excited $Hg(6^3P_1)$ atoms.

$$\frac{1-\pi}{\pi} = \frac{(NO)}{(2,5.DHF)} \cdot \frac{\sigma^2_{NO}}{\sigma^2_{2,5DHF}} \cdot \frac{\left(\frac{1}{M_{Hg}} + \frac{1}{M_{NO}}\right)^{\frac{1}{2}}}{\left(\frac{1}{M_{Hg}} + \frac{1}{M_{2,5\text{-}DHF}}\right)^{\frac{1}{2}}} \quad \ldots\ldots (59)$$

Letting

$$\Sigma = \frac{\left(\frac{1}{M_{Hg}} + \frac{1}{M_{NO}}\right)^{\frac{1}{2}}}{\left(\frac{1}{M_{Hg}} + \frac{1}{M_{2,5\text{-}DHF}}\right)^{\frac{1}{2}}} \quad \ldots . (60)$$

We get

$$Q.C.F = \frac{1}{\pi} = 1 + \left(\frac{1-\pi}{\pi}\right) \quad \ldots . (61)$$

$$\therefore \quad Q.C.F = 1 + \frac{(NO)}{(2,5\text{-}DHF)} \cdot \frac{\sigma^2_{NO}}{\sigma^2_{2,5\text{-}DHF}} \cdot \Sigma \quad \ldots . (62)$$

The values of the factor, Q.C.F., as calculated from the above equation are indicated in the tables of results for each nitric oxide-2,5-DHF, CF_4-2,5-DHF, and CO_2-2,5-DHF mixtures investigated.

$\sigma^2_{(NO)}{}^7 = 23.0A^2$, $\sigma^2_{(CF_4)}{}^7$ = less than $0.001A^2$, $\sigma^2_{(CO_2)}{}^7 = 2.5A^2$ and $\sigma^2_{2,5\text{-}DHF} = 28.4A^2$ are the values used in these calculations.

Method of Presentation of Data

For each series of experiments performed the results are presented in both tabular and graphic form. In few cases, where data are not amenable to graphic representation, they are presented in tables only. In the tabular form, the following data are routinely given:- conditions of the experiment, run number, value of the varied parameter and quantum yield. Where a particular datum is absent from the table, the explanation is indicated as "n.d" (not determined) or "t.m" (too minute to allow accurate estimation).

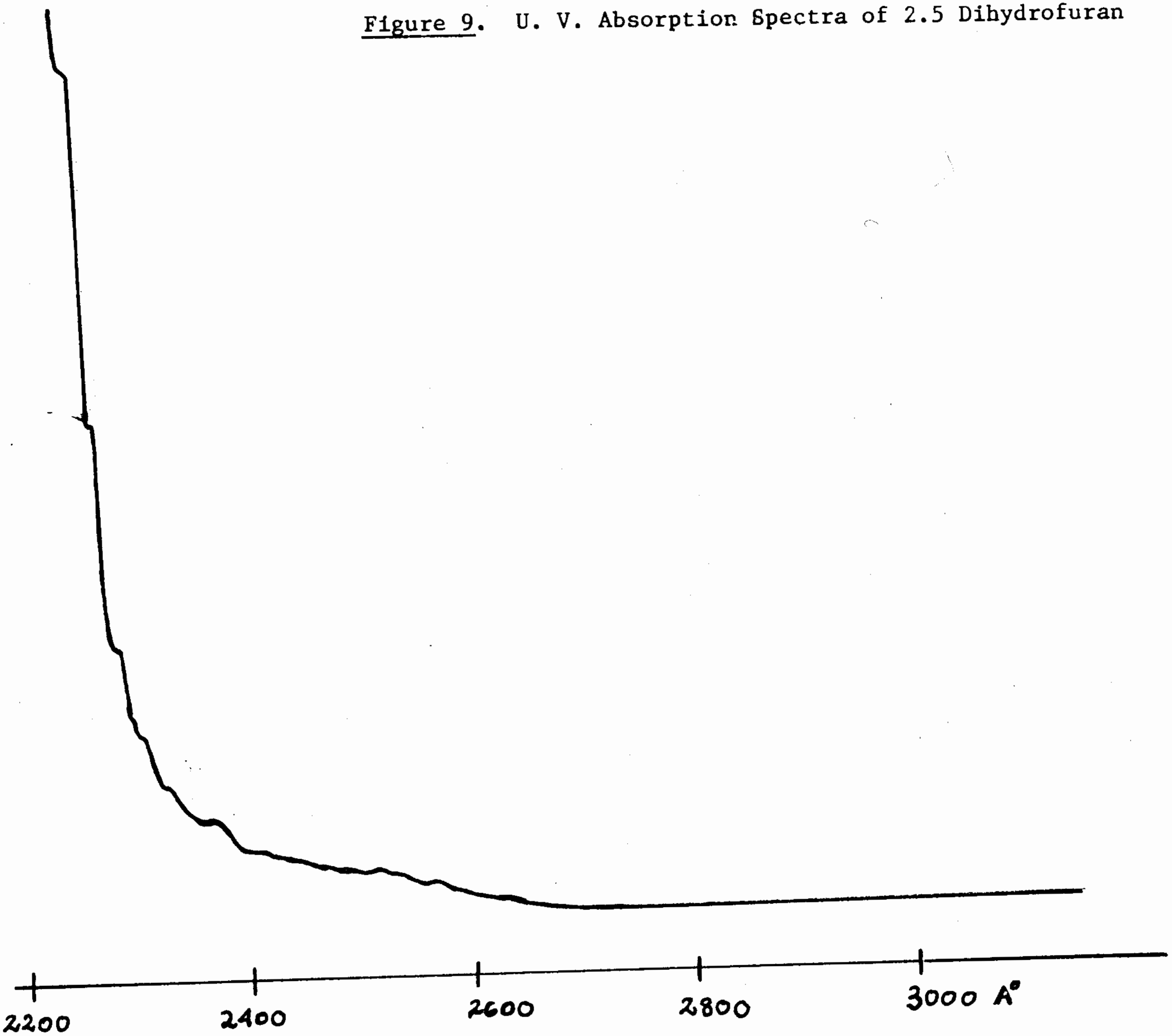
RESULTS AND DISCUSSIONS

U. V. absorption spectrum of 2,5-DHF is presented in figure 9. The spectrum was recorded at 25°C and 10mm. Hg of substrate pressure, using a 10cm long quartz cell. As 2,5-DHF shows practically no absorption in the region 2400 to 2600A , a study of the mercury photosensitized reaction is possible.

The main products of the sensitized reaction are hydrogen, carbon monoxide and propene. The minor products are allene, methyl acetylene, biallyl, crotonaldehyde, furan, 2,3-dihydrofuran, (2,3-DHF), tetrahydrofuran (THF) and three unidentified compounds "A", "B" and "C" (See figure 7). The quantum yields of these products as a function of reaction time is given in table 4 and 5. Figure (10 to 14) show plots of product yields as a function of time (in the case of the unidentified compounds "A", "B" and "C", areas of the G. C. peaks are used instead).

Taking into account the large experimental uncertainty in the analysis of very short runs, the quantum yields of all products are essentially independent of time, indicating that none of these products are the result of secondary reactions. A small amount of nonvolatile material was observed in very long runs. Addition of nitric oxide to the system did not prevent its formation and moreover the summation of the carbon content of the products of the reaction in the presence of NO is, within experimental error, equal to the value in the absence of NO. This suggests that a chain mechanism consuming substrate molecules is not important.

Figure 9. U. V. Absorption Spectra of 2.5 Dihydrofuran



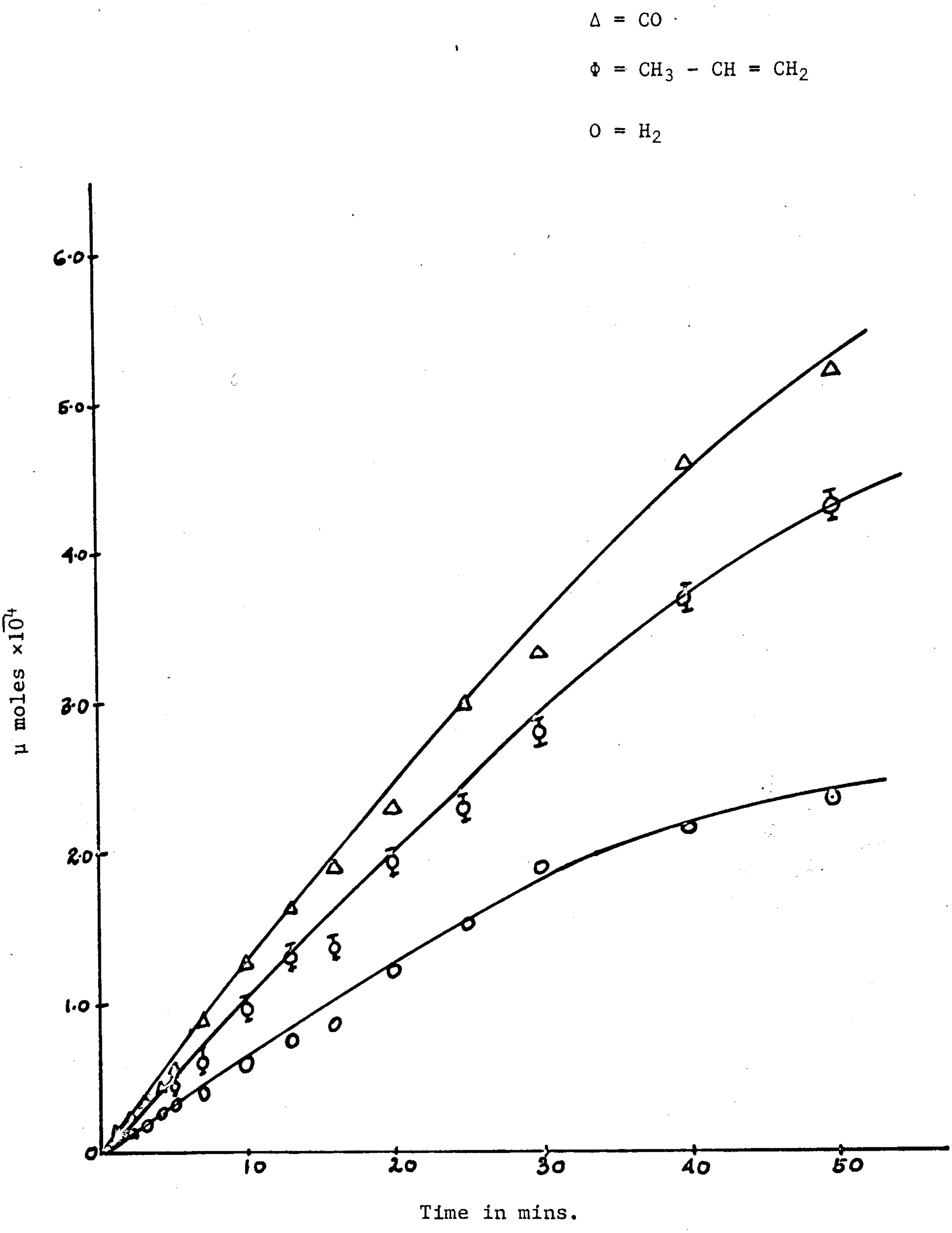


Figure 10. Time Dependence.

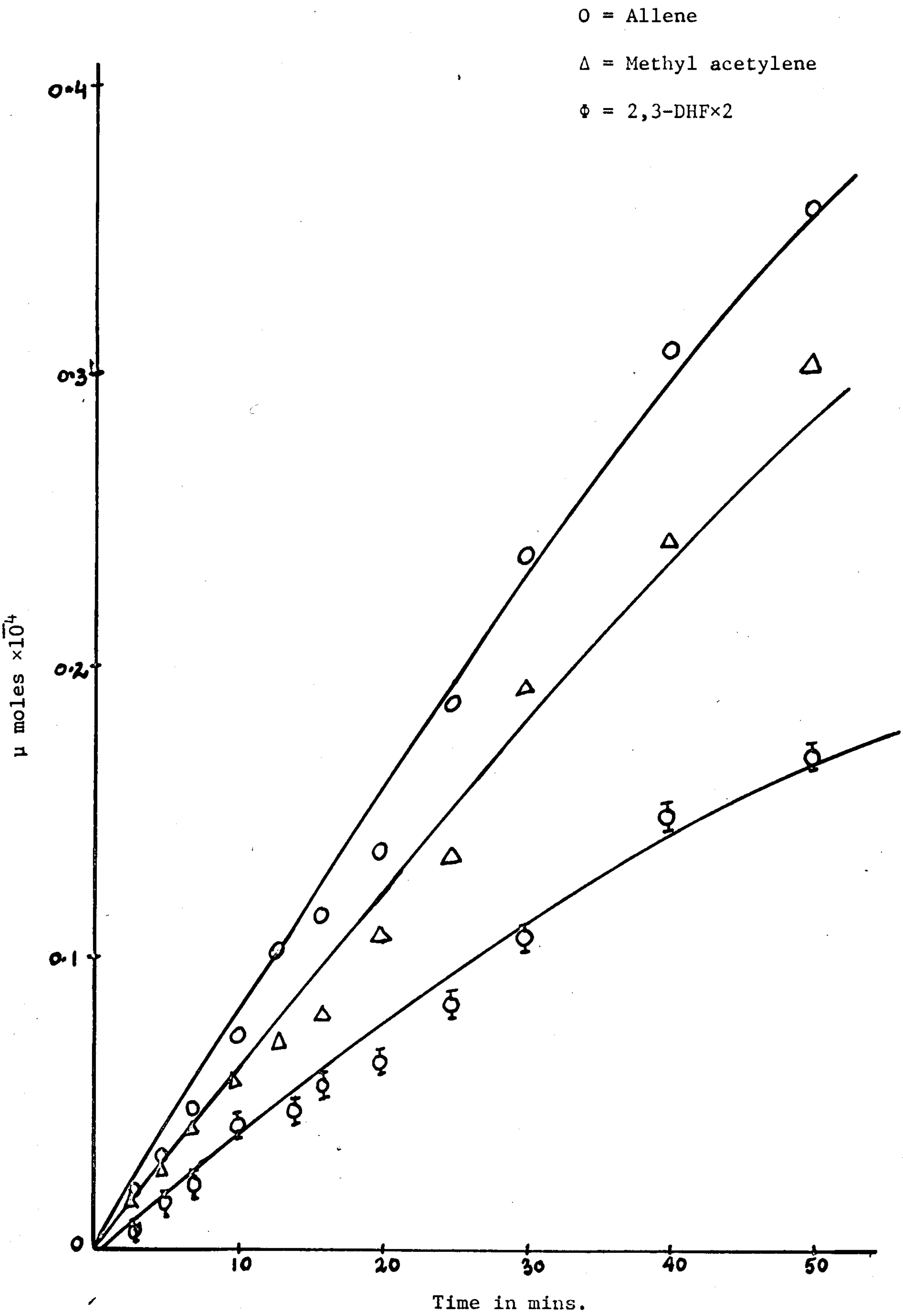


Figure 11. Time Dependence.

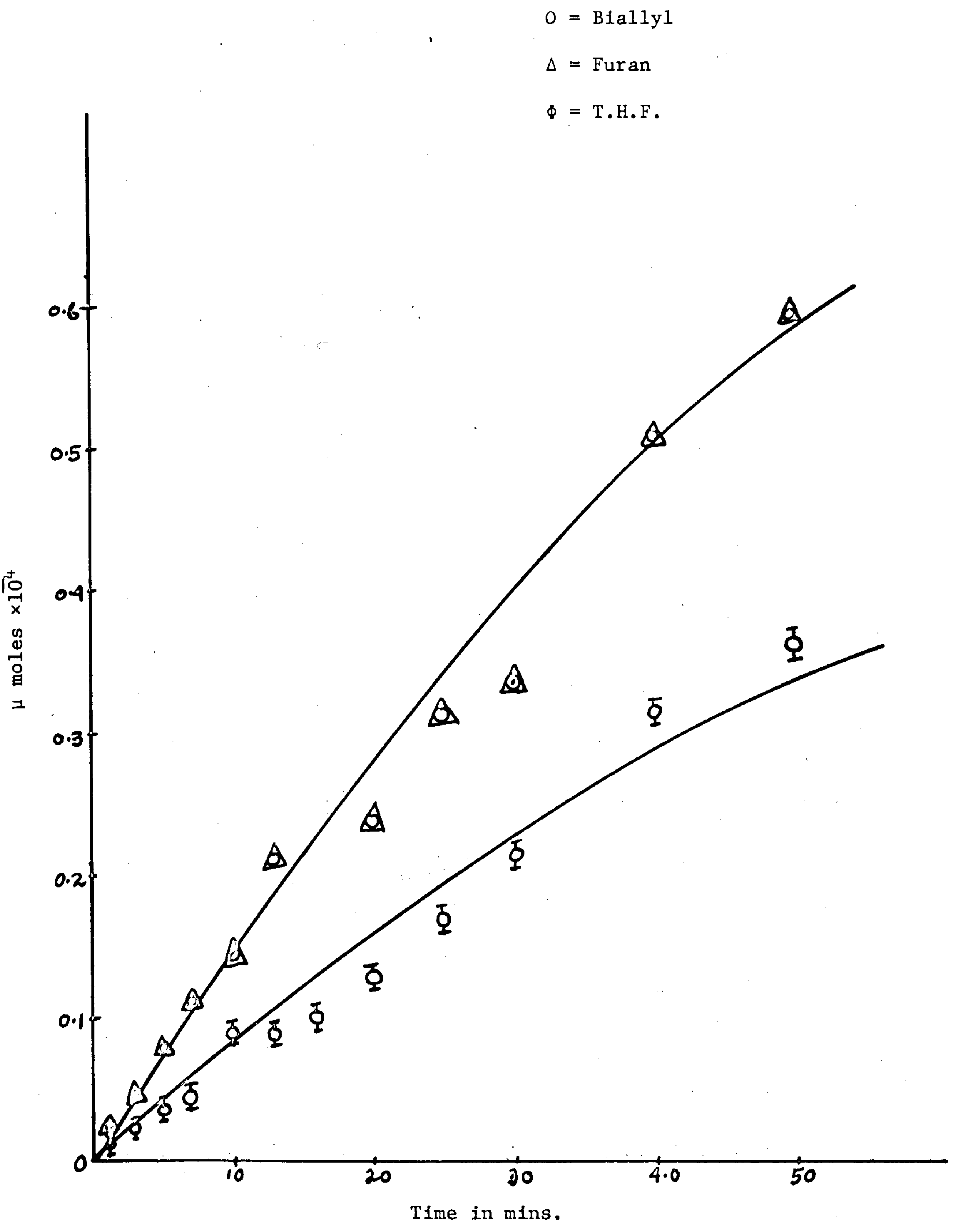


Figure 12. Time Dependence.

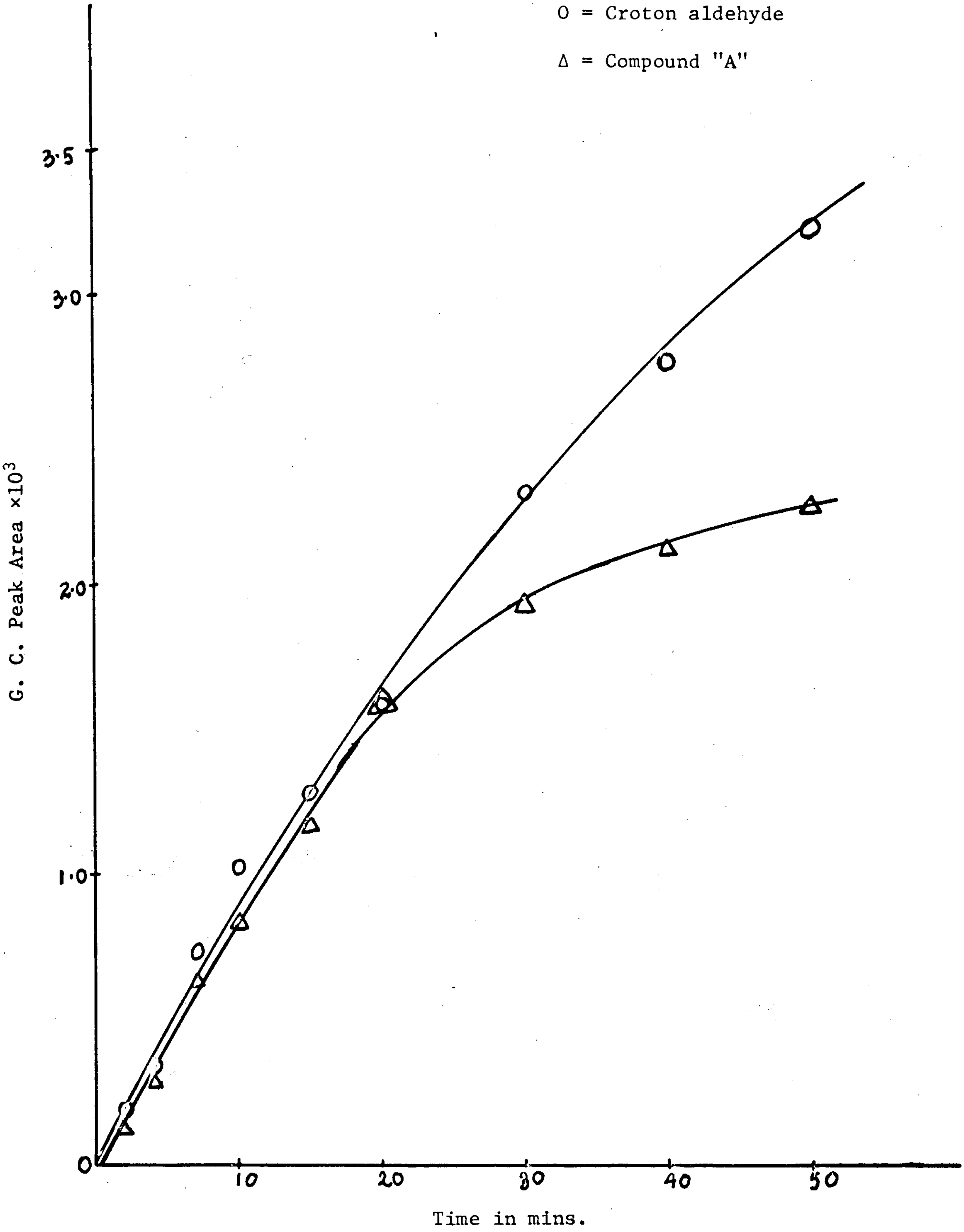


Figure 13. Time Dependence.

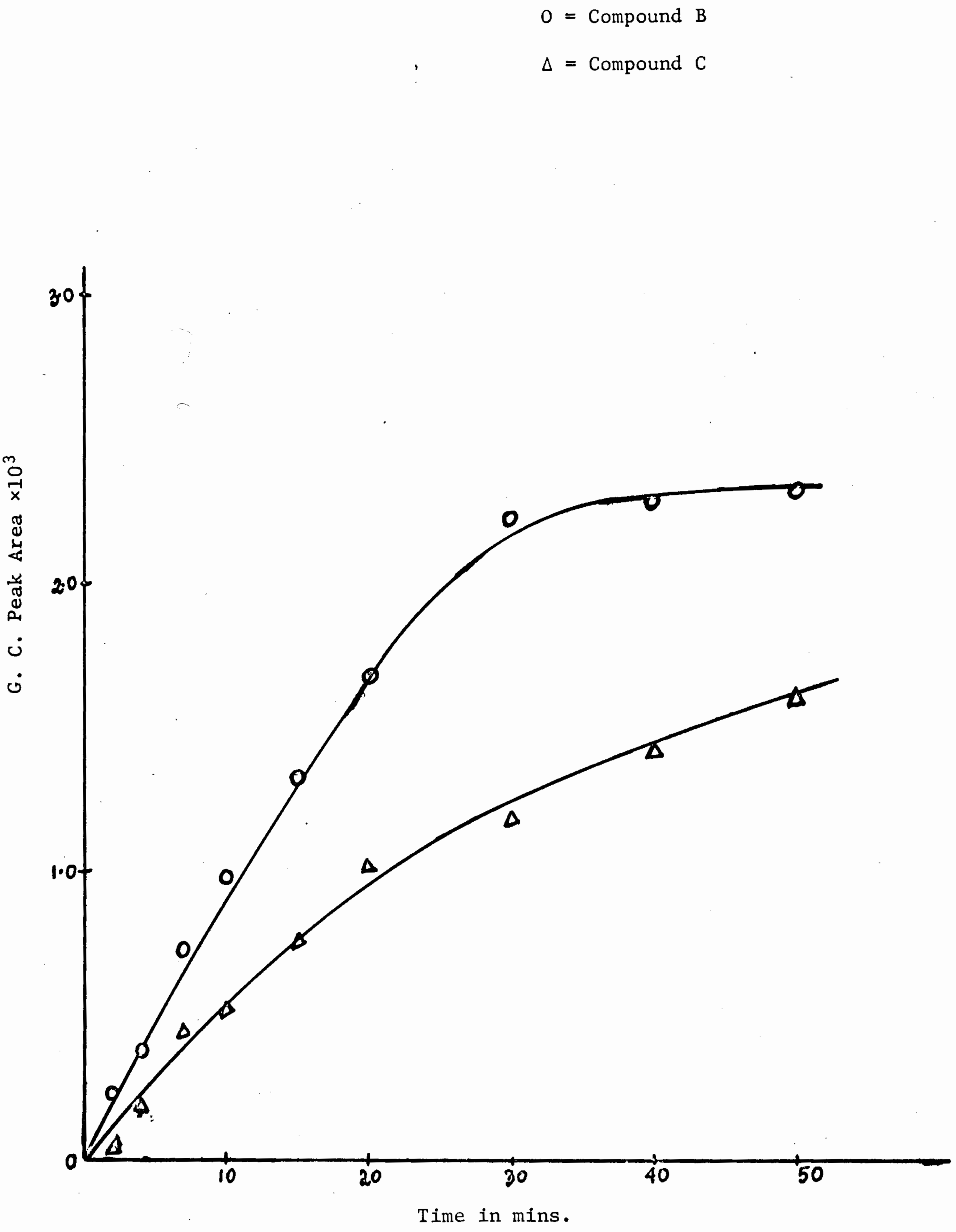


Figure 14. Time Dependence.

Table 4. Quantum Yield of Products at Different Irradition Period.

Run NO.	Substrate Pressure in mm. Hg	Irradiation Time in mins.	Quantum Yields				
			H_2	CO	propene	Allene	Methylacetylene
1	10	1	0.29	0.27	0.28	0.013	0.010
2	10	2	0.17	0.32	0.29	0.012	0.014
3	10	3	0.18	0.37	0.30	0.021	0.014
4	10	4	0.20	0.31	0.29	0.018	0.016
5	10	5	0.19	0.33	0.26	0.017	0.015
6	10	7	0.18	0.36	0.26	0.019	0.017
7	10	10	0.17	0.36	0.27	0.020	0.014
8	10	13	0.16	0.35	0.28	0.022	0.015
9	10	16	0.15	0.33	0.24	0.018	0.014
10	10	20	0.13	0.32	0.27	0.019	0.015
11	10	25	0.17	0.34	0.26	0.021	0.015
12	10	30	0.19	0.31	0.26	0.023	0.018
13	10	40	0.15	0.32	0.26	0.022	0.017
14	10	50	0.17	0.29	0.24	0.020	0.017

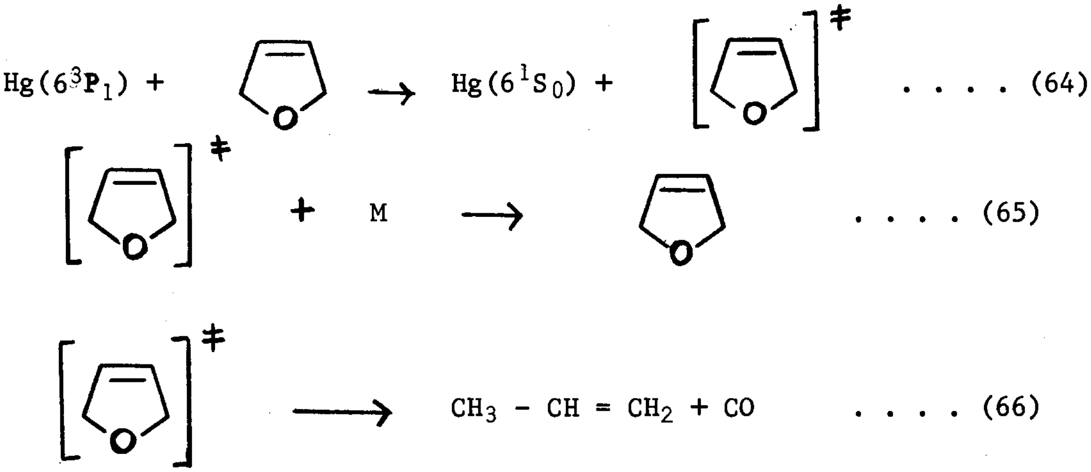
Table 5. Quantum Yield of Products at Different Irradiation Period.

Run NO.	Substrate Pressure in mm. Hg	Irradiation Time in mins.	Quantum Yields Croton-aldehyde	Furan	Biallyl	2,3-DHF	T.H.F.
1	10	1	n.d.	0.067	0.067	0.048	0.057
2	10	2	0.042	0.046	0.046	0.014	0.020
3	10	3	n.d.	0.045	0.045	0.023	0.026
4	10	4	0.040	0.047	0.047	0.029	0.025
5	10	5	n.d.	0.046	0.046	0.026	0.024
6	10	7	0.049	0.046	0.046	0.016	0.018
7	10	10	0.048	0.041	0.041	0.025	0.025
8	10	13	n.d.	0.046	0.046	0.021	0.020
9	10	16	n.d.	0.033	0.033	0.020	0.018
10	10	20	0.037	0.033	0.033	0.018	0.019
11	10	25	n.d.	0.035	0.035	0.019	0.019
12	10	30	0.036	0.031	0.031	0.020	0.020
13	10	40	0.032	0.036	0.036	0.021	0.022
14	10	50	n.d.	0.033	0.033	0.019	0.020

The variation of quantum yields of products with substrate pressure is indicated in figures (15) to (18). Analysis of 2,3-DHF and THF was impossible at higher substrate pressures due to inadequate resolution of G. C. peaks. All products show a behaviour characteristic of the decomposition of an excited molecule subject to collisional deactivation, hydrogen and furan are less affected than the other products, suggesting that they arise from a different mechanistic path. Runs with added CF_4 and CO_2 were done in an attempt to verify this difference in behaviour. See figures (19) to (22). The results are corrected for the competitive quenching of CO_2 for triplet mercury. When CF_4 was used as an inert gas, its very low quenching cross-section eliminated the problem of competitive quenching of triplet mercury. In these cases again quantum yields were decreased, although CO_2 increased the quantum yield of furan to small extent. (See figure 22).

The following mechanism is suggested for the sensitized reaction

$$Hg(6^1S_0) + h\nu \longrightarrow Hg(6^3P_1) \quad .\ .\ .\ .\ (63)$$



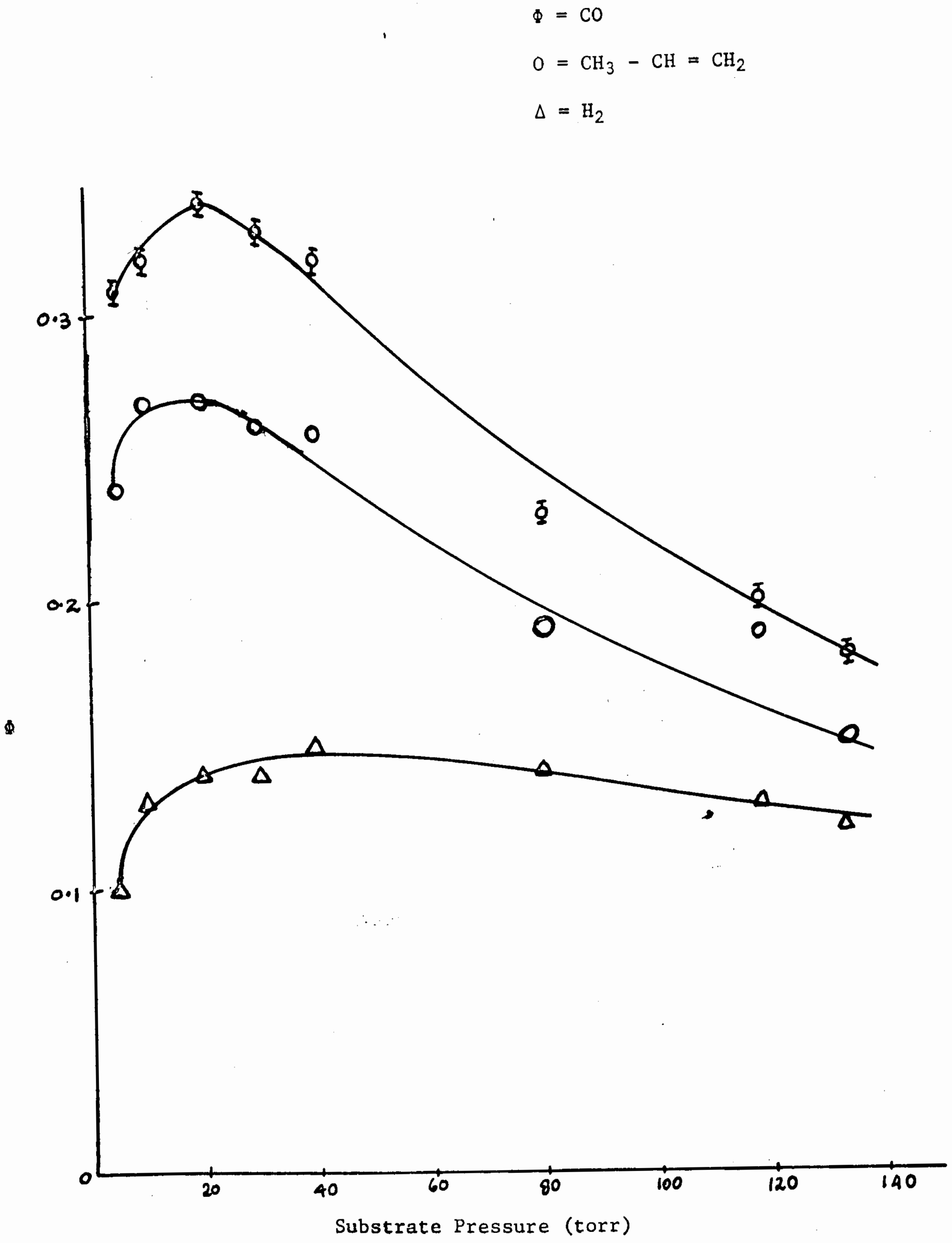


Figure 15. Pressure Dependence Runs.

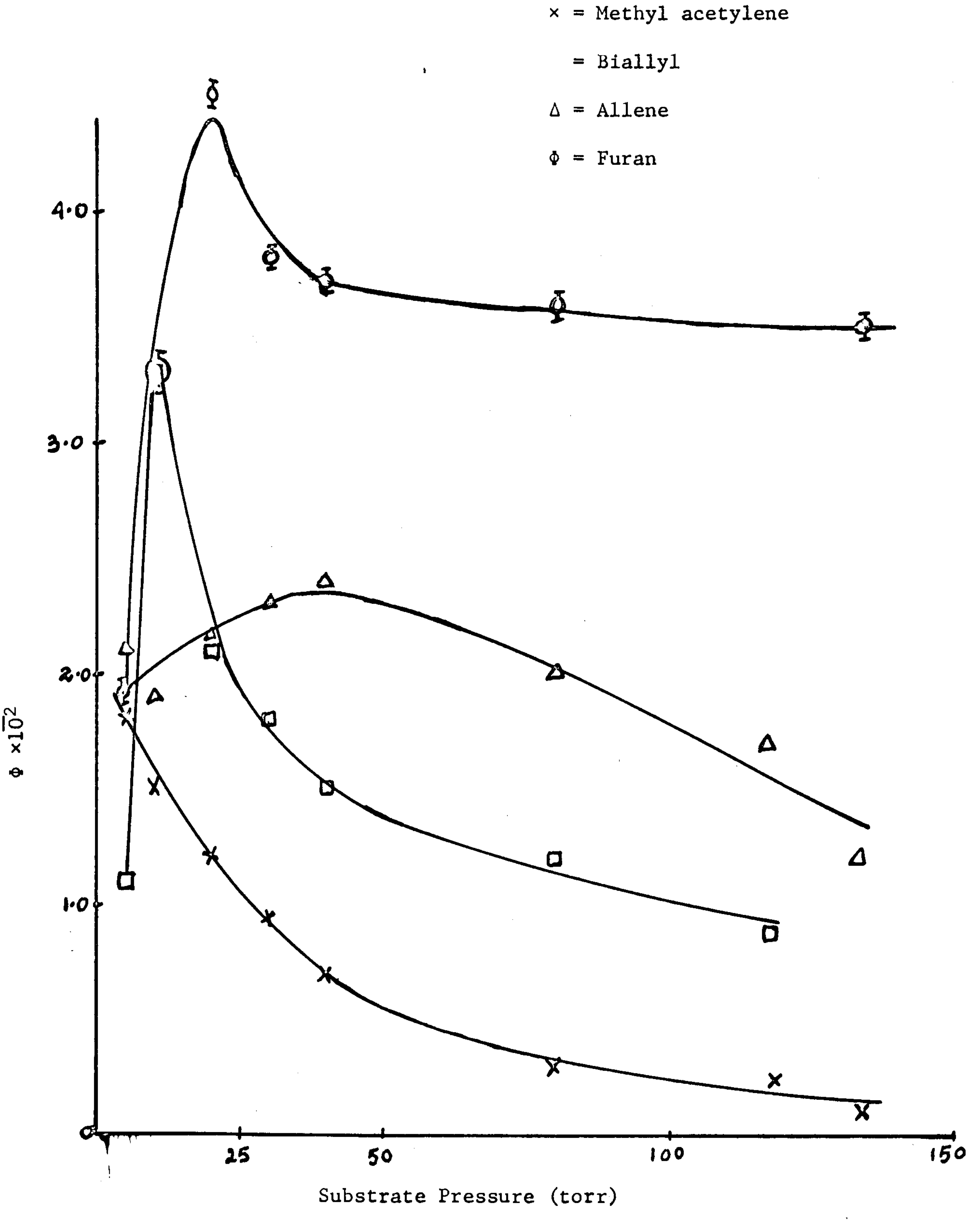


Figure 16. Pressure Dependence Runs.

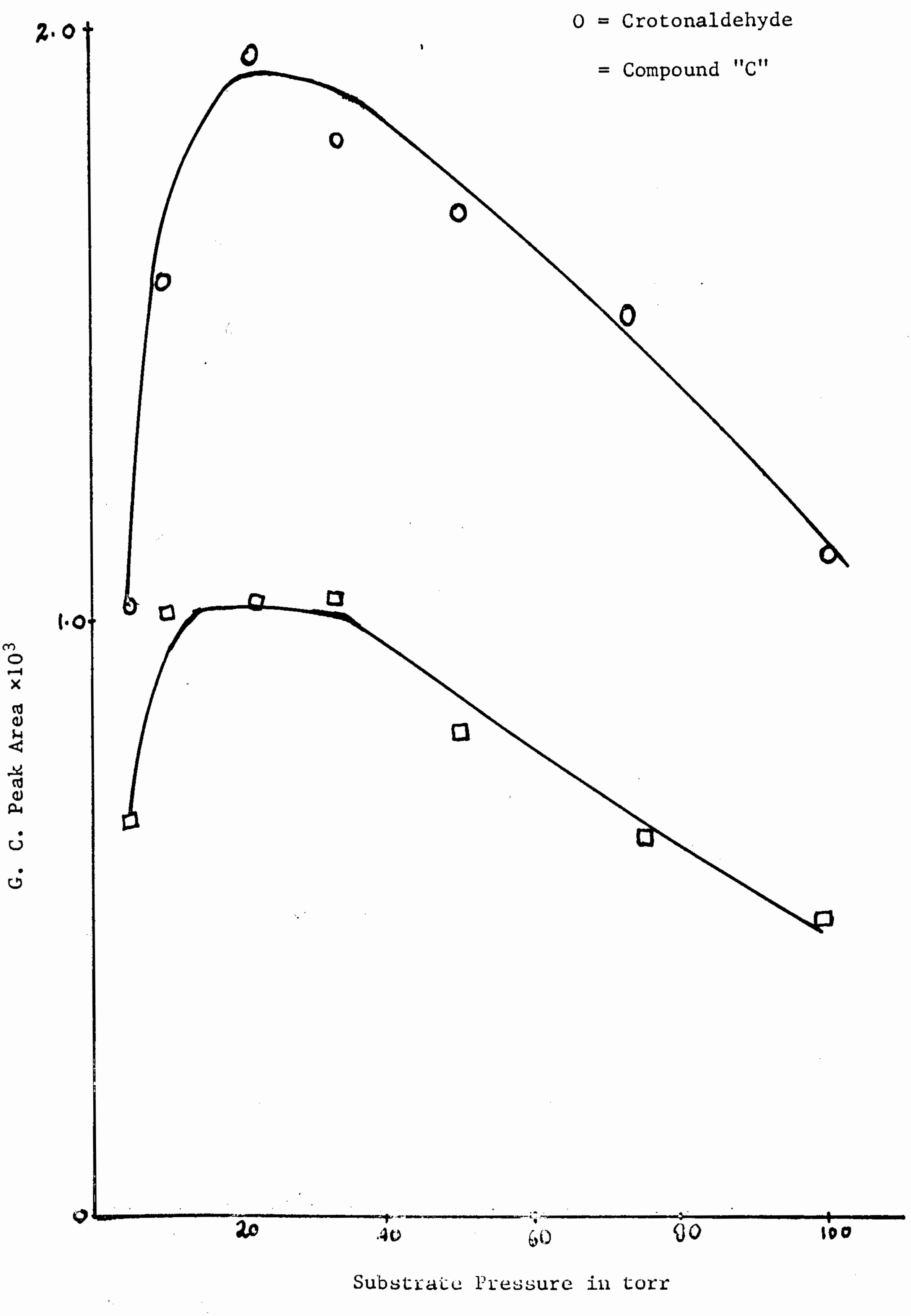

O = Crotonaldehyde
= Compound "C"
2.0
1.0
0
G. C. Peak Area ×10³
20
40
60
80
100
Substrate Pressure in torr

Figure 17.

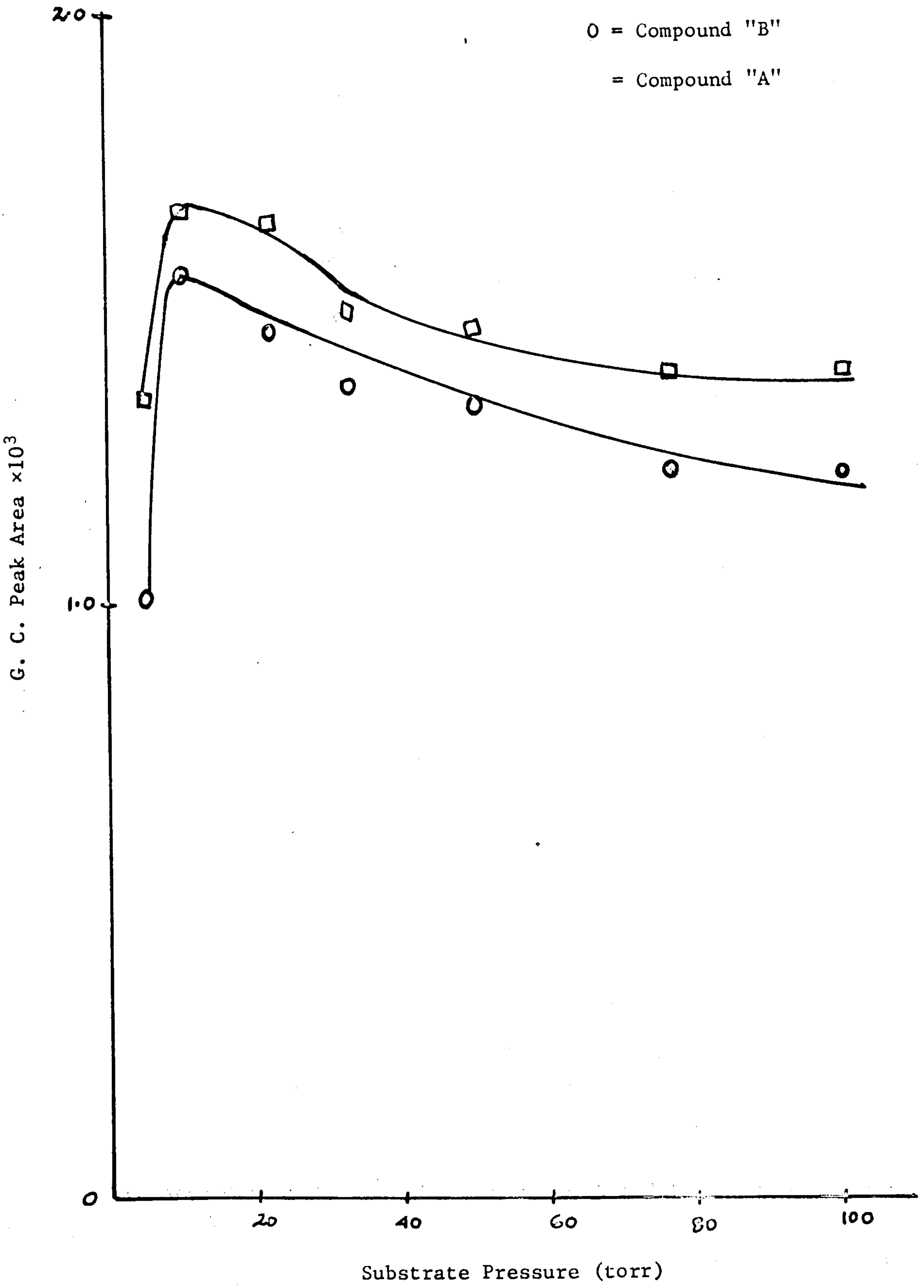

O = Compound "B"
= Compound "A"
2·0
1·0
0
G. C. Peak Area ×10^3
20
40
60
80
100
Substrate Pressure (torr)

Figure 18.

Table 6. Quantum Yield of Products at Various Substrate Pressures

Run NO.	Substrate Pressure in mm. Hg	Time of Irradiation in mins.	Quantum Yields H_2	CO	propene	Methyl acetylene	Allene	Biallyl	Furan,	2,3-DHF,	THF	Croton-aldehyde
1	5	20	0.10	0.31	0.24	0.0180	0.021	0.011	0.018	n.d.	n.d.	0.024
2	10	20	0.13	0.32	0.27	0.0150	0.019	0.033	0.033	n.d.	n.d.	0.037
3	20	20	0.14	0.34	0.27	0.0120	0.021	0.021	0.060	n.d.	n.d.	0.046
4	30	20	0.14	0.33	0.26	0.009	0.030	0.018	0.038	n.d.	n.d.	0.042
5	40	20	0.15	0.32	0.26	0.007	0.040	0.015	0.037	n.d.	n.d.	n.d.
6	80	20	0.14	0.23	0.19	0.003	0.020	0.012	0.036	n.d.	n.d.	0.035
7	118	20	0.13	0.20	0.19	0.0025	0.017	0.009	n.d.	n.d.	n.d.	0.025
8	133	20	0.12	0.18	0.15	0.001	0.012	n.d.	0.035	n.d.	n.d.	n.d.

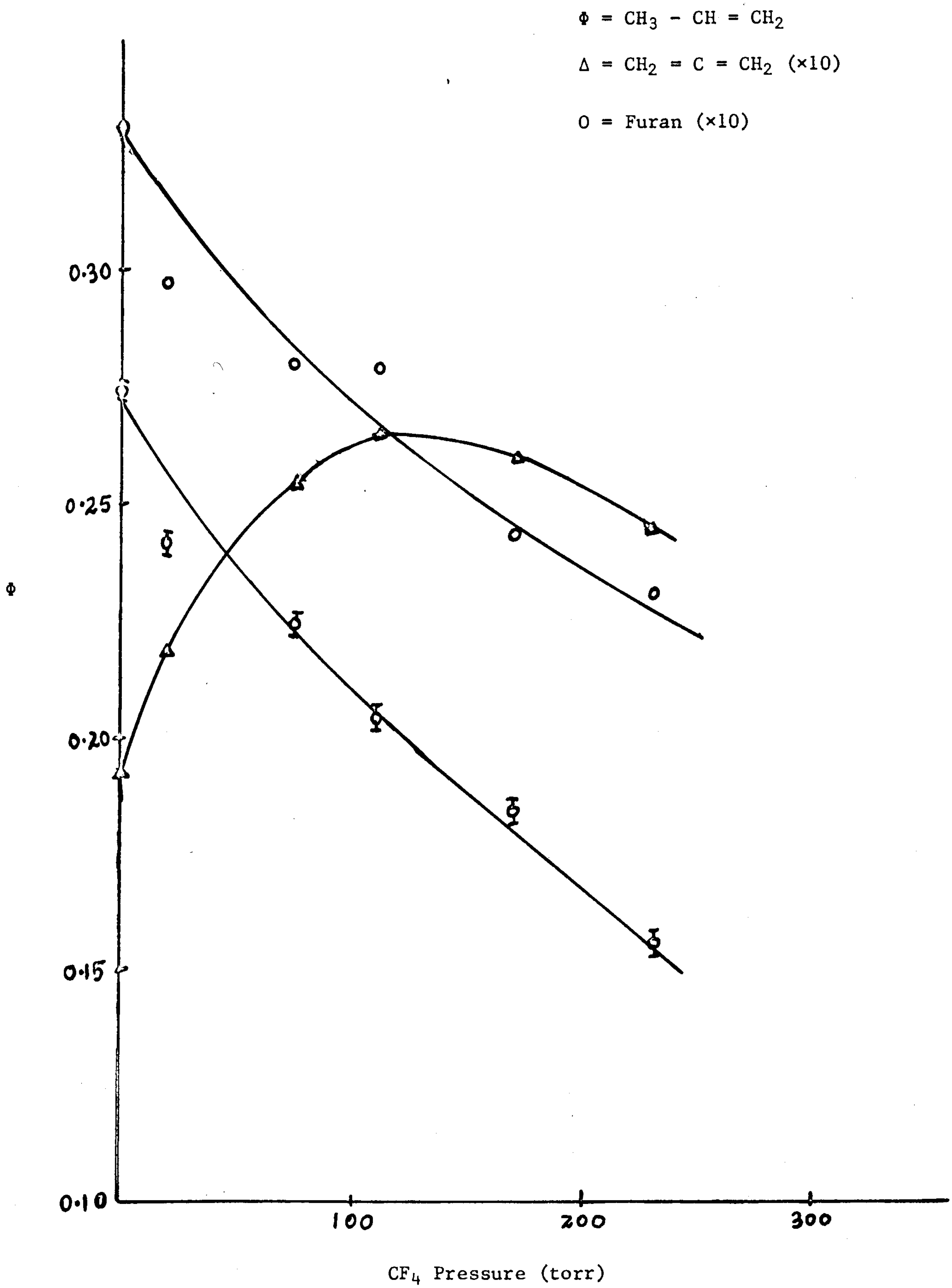

$\Phi = CH_3 - CH = CH_2$
$\Delta = CH_2 = C = CH_2$ (×10)
O = Furan (×10)
Φ
0·30
0·25
0·20
0·15
0·10
100
200
300
CF_4 Pressure (torr)

Figure 19.

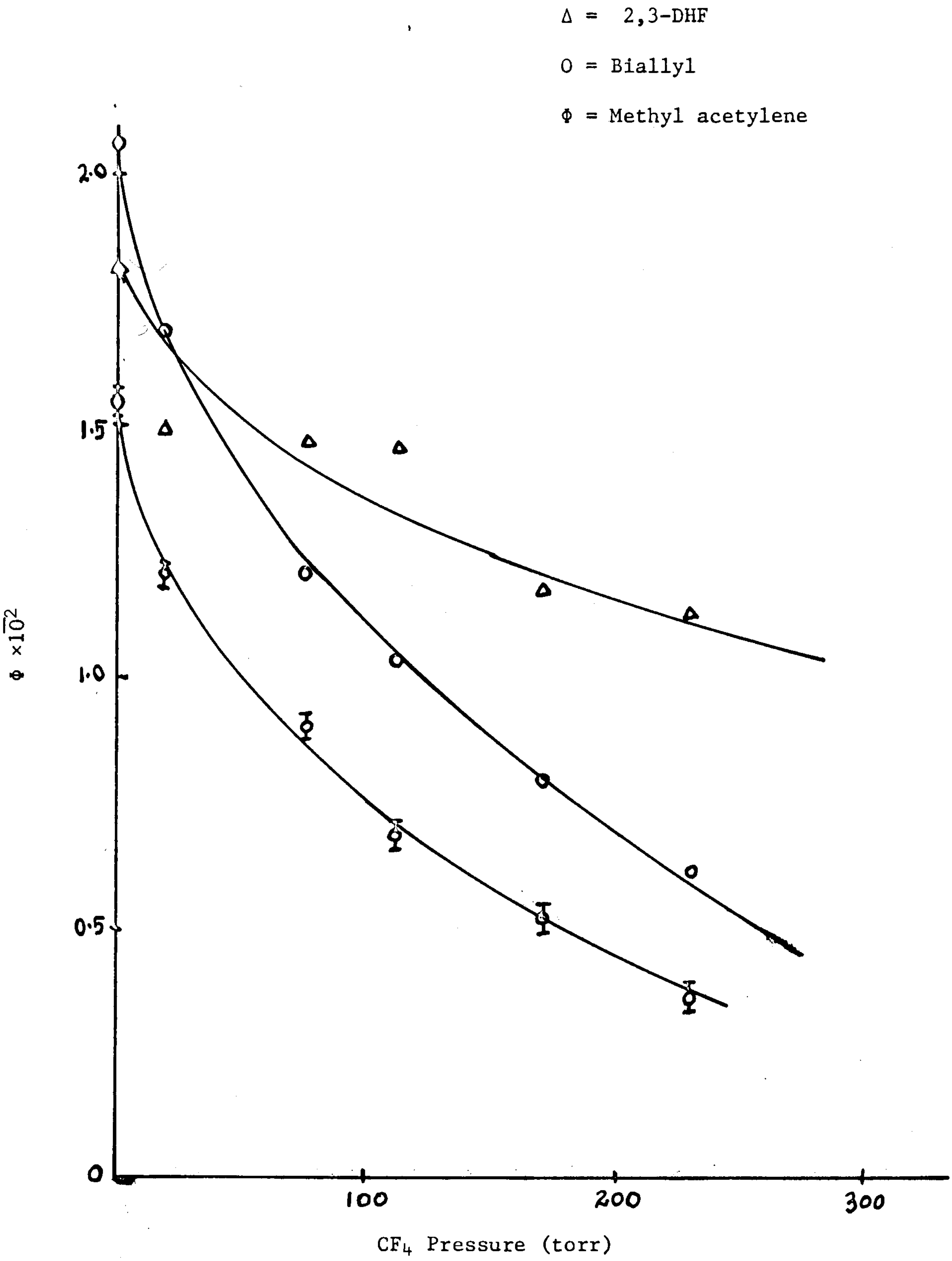

Δ = 2,3-DHF
O = Biallyl
Φ = Methyl acetylene
Φ ×10^-2
2.0
1.5
1.0
0.5
0
100
200
300
CF₄ Pressure (torr)

Figure 20.

Table 7. Effect of Added CF_4

Substrate Pressure = 10mm.

Reaction Time = 20 mins.

		Quantum Yields						
Run NO.	Pressure of CF_4 in mm.	propene	Allene	Methyl acetylene	Biallyl	Furan	2,3-DHF	T.H.F.
1	0	0.27	0.019	0.015	0.02	0.033	0.018	n.d.
2	19	0.24	0.022	0.012	0.017	0.029	0.015	n.d.
3	75	0.22	0.025	0.009	0.012	0.028	0.015	n.d.
4	111	0.20	0.026	0.007	0.010	0.028	0.014	n.d.
5	170	0.18	0.026	0.005	0.008	0.024	0.012	n.d.
6	230	0.16	0.024	0.004	0.007	0.023	0.011	n.d.

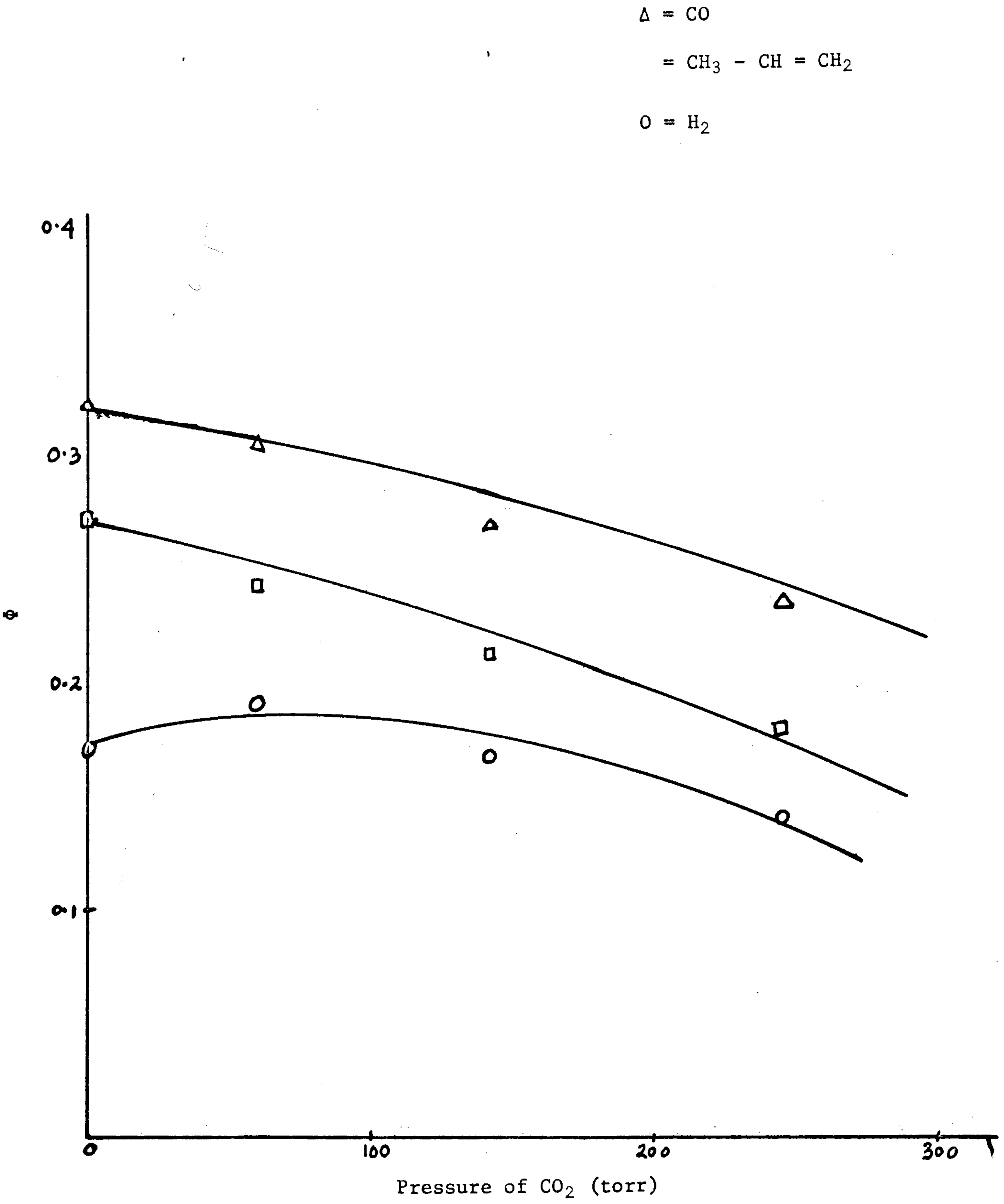


Figure 21. Effect of added CO , after correcting for competitive quenching

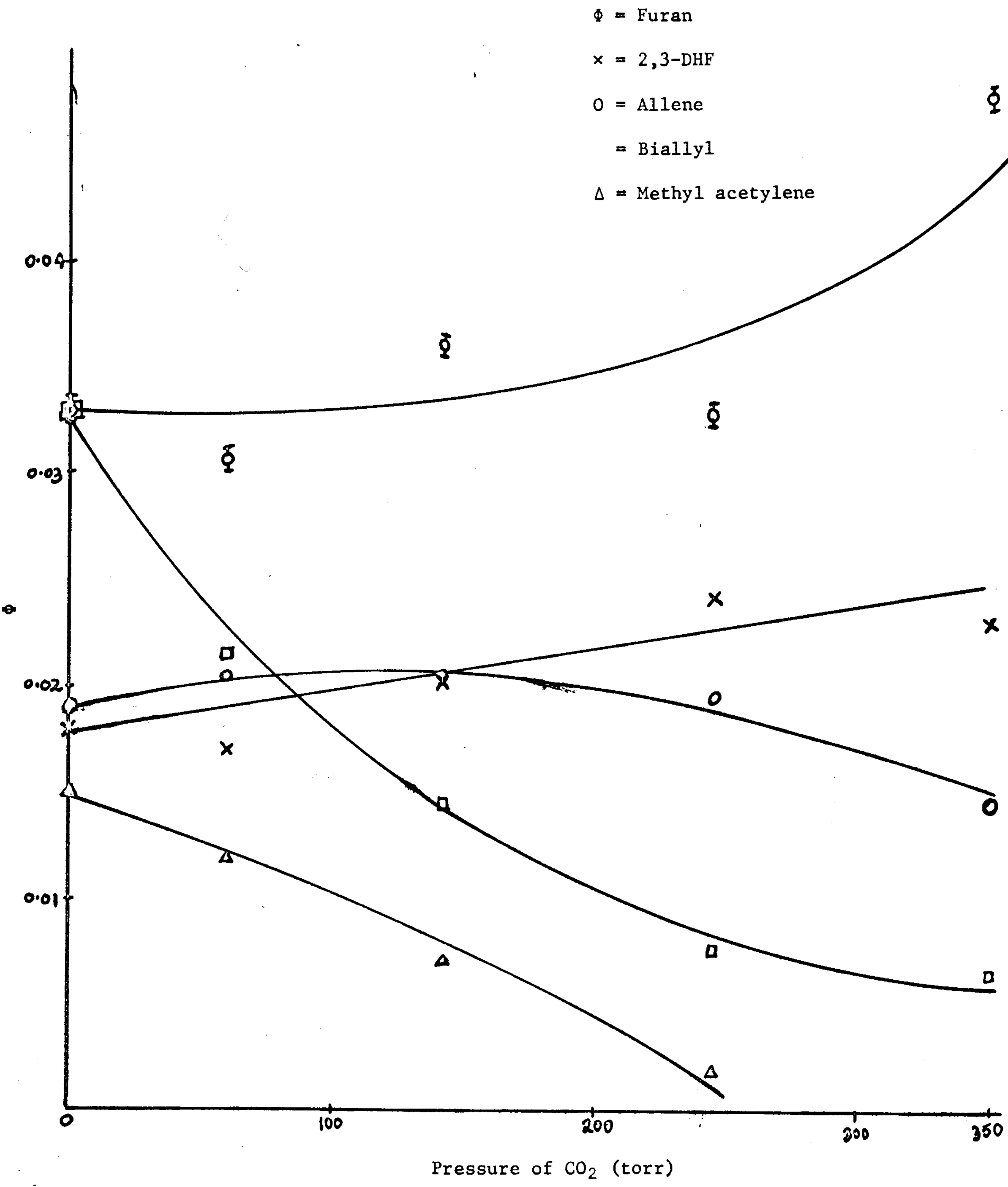


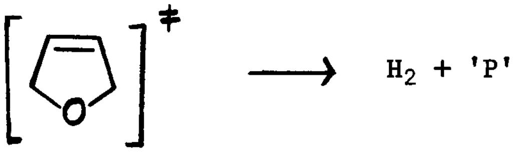
Figure 22. Effect of added CO after correcting for competitive quenching

Table 8. Effect of added CO_2 (data corrected for competitive quenching).

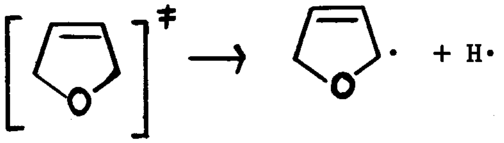
Pressure of 2,5-DHF = 10mm.

Reaction time = 20 min.

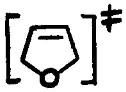
Run NO	CO_2 Pressure in mm. Hg	Q.C.F.	Quantum Yields								
			H_2	CO	propene	Allene	Methyl acetylene	Biallyl	Furan	2,3-DHF
1	0	1.00	0.17	0.32	0.27	0.019	0.015	0.033	0.033	0.018
2	60	1.47	0.18	0.29	0.24	0.019	0.010	0.021	0.030	0.017
3	142	2.12	0.16	0.26	0.20	0.019	0.007	0.014	0.034	0.020
4	245	2.93	0.13	0.22	0.17	0.018	0.002	0.007	0.031	0.023
5	350	3.76	0.13	0.19	0.14	0.014	t.m.	0.006	0.044	0.021



. . . . (67)

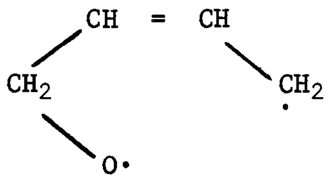


. . . . (68)

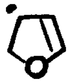
It is postulated that the primary energy transfer process produces an electronically excited molecule of 2,5-DHF. The excited molecules represented by , may either be deactivated by collisions (equn (65)), or decompose according to the equation (66) to (68).

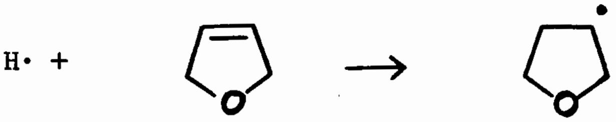
The spin conservation rule suggests that the excited molecules are in triplet state. No detailed spectroscopic study of 2,5-DHF has been reported in the past to help confirm the existence of an excited triplet state for this molecule.

Ring opened biradicals were proposed as intermediates in the mercury sensitized reactions of cycloölefins[35,36] and furan[43,44]. It is likely that here also the excited molecule formed in reaction (64) is a ring opened biradical.



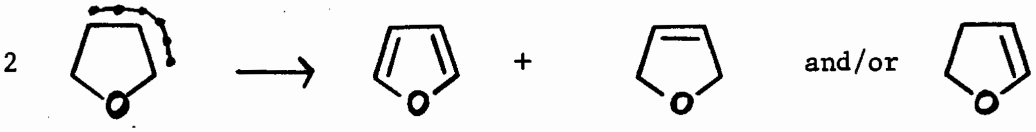
. . . . (69)

The dihydrofuranyl radicals  formed in (68) may also be written as . To represent the delocalization of the free electron, we may represent its structure as . The hydrogen atom formed in (68) presumably adds to a substrate molecule to give a tetrahydrofuranyl radical

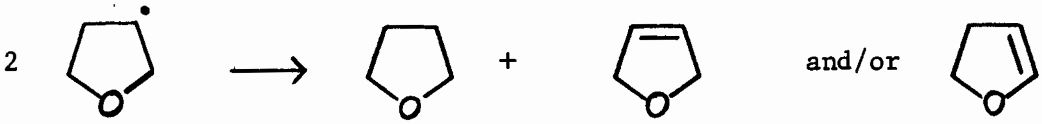


. . . . . (70)

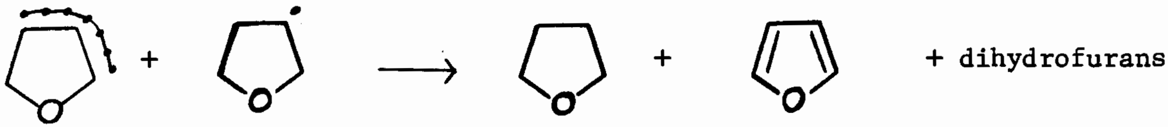
The two radicals may undergo disproportionation and combination reactions to give the following products.



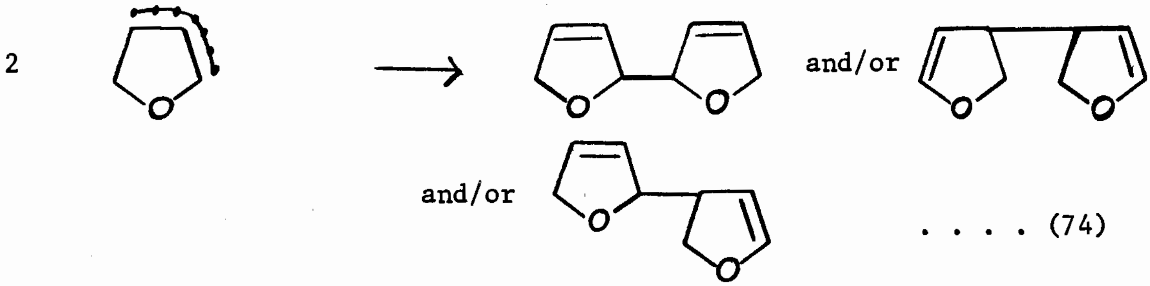
. . . . . (71)



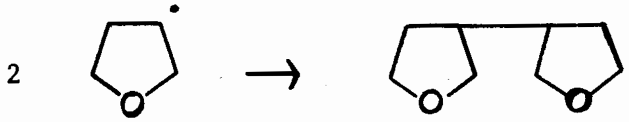
. . . . . (72)



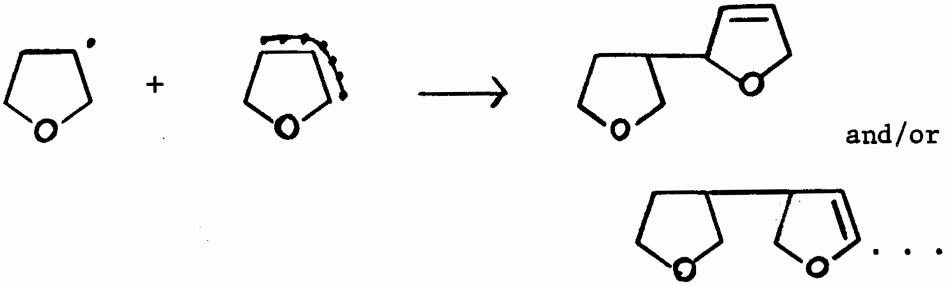
. . . . . (73)



. . . . . (74)



. . . . . (75)



. . . . . (76)

No higher molecular weight compounds other than "A", "B" and "C" were found, suggesting that combination reactions (74) to (76) are less important in this system.

To test the proposed mechanism, 2,5-DHF was mercury photosensitized in the presence of a radical scavenger, nitric oxide. Results of the NO- added reactions are given in table 9 to 10. The data have been corrected for competitive quenching of triplet mercury atom by added NO molecules. It was observed that the presence of NO completely inhibits the formation of biallyl, allene, 2,3-DHF, THF, compound 'A' and compound "B", suggesting that these products have free radical precursors. The yield of crotonaldehyde went down by 50%, suggesting this fraction to arise from free radical reaction. Yields of furan increased eightfold and two new products, nitrous oxide and acrylonitrile were isolated and identified. Quantitative analysis of acrylonitrile was not possible due to the overlapping of its G. C. peak with that of crotonaldehyde.

It was noted that the addition of NO decreased the yield of propene by about 28%, indicating that this fraction of propene was formed by free radical reaction. The ring opened biradical, suggested as the intermediate excited state in this reaction, is most probably the source of propene.

Table 9. Effect of Nitric oxide.

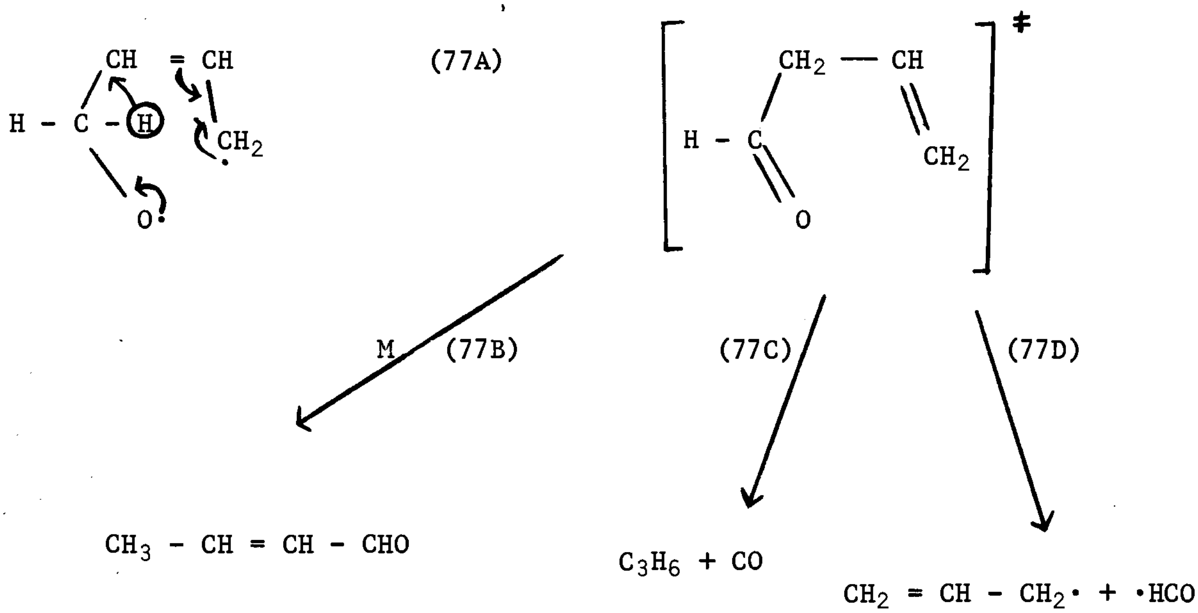
Substrate Pressure = 10 mm of Hg.

Run NO	% of NO	Reaction Time in mins.	Q.C.F.	Quantum Yields							
				H_2	CO	propene	N_2O	Methyl acetylene	Allene	Biallyl	2,3-DHF
1	0	10	1.00	0.17	0.32	0.27	0.0	0.014	0.02	0.041	0.025
2	3.7	5	1.03	0.17	0.42	0.19	0.17	0.010	0.0	0.0	0.0
3	10.2	5	1.08	0.17	0.42	0.20	0.18	0.014	0.0	0.0	0.0
4	11.4	30	1.09	0.165	0.38	0.18	0.12	0.012	0.0	0.0	0.0
5	15.5	30	1.12	0.17	0.416	0.17	0.12	0.011	0.0	0.0	0.0

Table 10. Effect of NO

Substrate Pressure = 10mm of Hg

				Quantum Yields			G.C. peak areas		
							Compounds		
Run NO	% of NO	Reaction Time in mins.	Q.C.F.	Furan	T.H.F.	Crotonaldehyde	"A"	B	"C"
1	0	10	1.00	0.041	0.025	0.048	838	980	511
2	3.7	5	1.03	0.27	0.0	n.d.	0.0	0.0	241
3	10.2	5	1.08	0.25	0.0	0.025	0.0	0.0	253
4	11.4	30	1.09	0.24	0.0	0.024	0.0	0.0	1178
5	15.5	30	1.12	0.25	0.0	0.023	0.0	0.0	1201



The 3-butenal formed in (77A) would be excited to the extent of approximately 112 kcal/mole and would react in three ways. Reaction (77C) would yield directly CO and propene, whose formation would not be inhibited by NO. Reaction (77D) produces formyl and allyl radicals. Allyl radicals may yield propene by disproportionating with formyl radicals.

$$\overset{\cdots\cdots\cdots\cdots}{CH_2 - CH - CH_2} + \cdot HCO \longrightarrow CH_3 - CH = CH_2 + CO \quad . \ . \ . \ . \ (78)$$

Formation of propene by this route would be inhibited by NO. The presence of allyl radicals in this system is further supported by the formation of acrylonitrile^{47A} in the presence of NO and biallyl and allene in the absence of NO.

$$\begin{tikzcd} \overset{\cdots\cdots\cdots\cdots}{CH_2 - CH - CH_2} + NO \arrow[r] & CH_2 = CH - CH_2NO \arrow[d, "- H_2O"] \\ & CH_2 = CH - CN \quad . \ . \ . \ . \ (79) \end{tikzcd}$$

$$2\ \overset{\cdots\cdots\cdots\cdots}{CH_2 - CH - CH_2} \longrightarrow CH_2 = CH - CH_2 - CH_2 - CH = CH_2 \quad \ldots . (80)$$

$$2\ \overset{\cdots\cdots\cdots\cdots}{CH_2 - CH - CH_2} \longrightarrow CH_3 - CH = CH_2 + CH_2 = C = CH_2 \quad \ldots . (81)$$

Disproportionation reactions of formyl radical with other radicals have been reported.[47] In the presence of allyl radicals it seems most likely that reaction (78) takes place to give propene and CO.

The formyl radicals in the presence of NO give[48]

$$NO + \cdot HCO \longrightarrow \cdot HNO + CO \quad \ldots . (82)$$

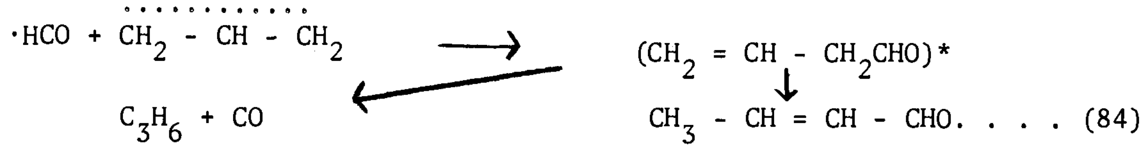
This is consistent with the small increase in the yields of CO (about 29%) in the NO added runs. The ·HNO radicals react to give nitrous oxide and water.[49]

$$2\ \cdot HNO \longrightarrow N_2O + H_2O \quad \ldots . (83)$$

N_2O and H_2O have been isolated and identified in the products of the runs with added NO.

In the absence of NO, the formyl radicals seem to undergo the usual combination and disproportionation reactions.[47]

$$\cdot HCO + \overset{\cdots\cdots\cdots\cdots}{CH_2 - CH - CH_2} \longrightarrow CH_3 - CH = CH_2 + CO \quad \ldots . (78)$$



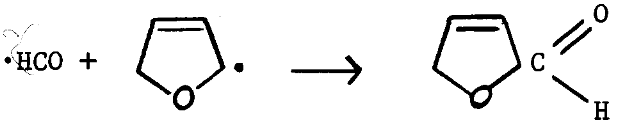
$$\cdot HCO + \overset{\cdots\cdots\cdots\cdots}{CH_2 - CH - CH_2} \longrightarrow (CH_2 = CH - CH_2CHO)^*$$

$$(CH_2 = CH - CH_2CHO)^* \longrightarrow C_3H_6 + CO$$

$$(CH_2 = CH - CH_2CHO)^* \longrightarrow CH_3 - CH = CH - CHO \quad \ldots . (84)$$

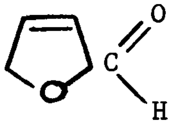
$$\cdot HCO + \cdot HCO \longrightarrow (CHO)_2 \quad \ldots . (85)$$

$$\cdot HCO + \cdot HCO \longrightarrow H_2CO + CO \quad \ldots . (86)$$

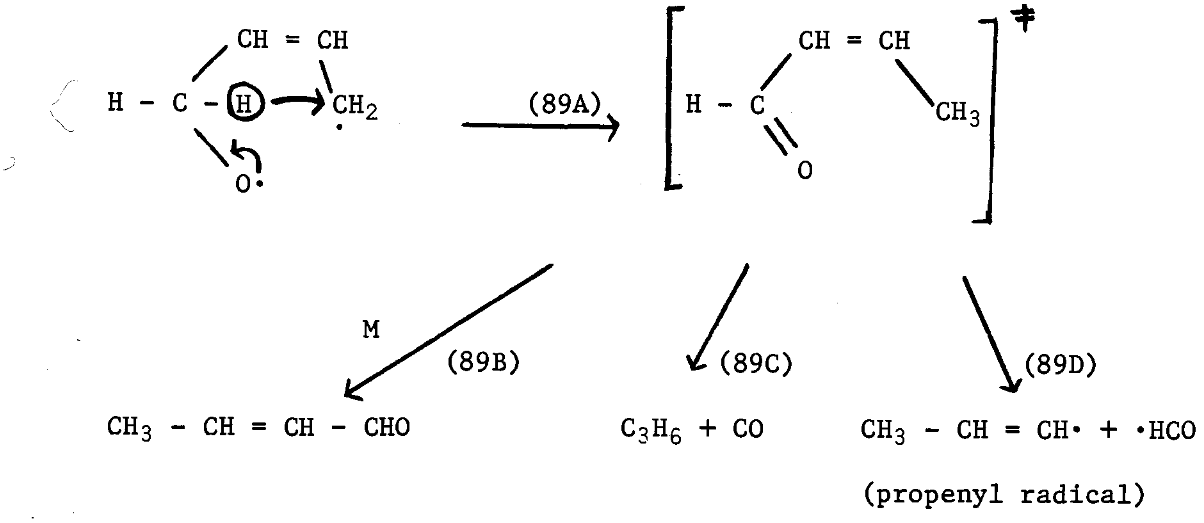


. . . . (87)

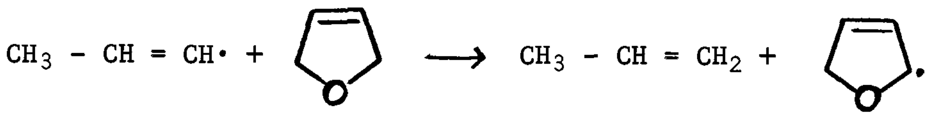
. . . . (88)

The 50% decrease in the quantum yield of crotonaldehyde produced in the presence of NO, suggests that the reaction of formyl with allyl produces crotonaldelyde, presumably by way of vibrationally hot 3-butenal. The absence of H_2CO suggests that reaction (86) is less important in this system. $(CHO)_2$ was also not found in the reaction products. Under the conditions in which the experiments were performed, $(CHO)_2$ if formed, would polymerize to give involatile materials[47B].  was unavailable and so we were unable to measure its G. C. retention time and check its presence in the reaction products.

An alternative mechanism may be considered for the formation of propene. The ring opened biradical may rearrange to $CH_3 - CH = CH - CHO$ directly and the decomposition of excited crotonaldehyde would give propene and CO. Lossing and Harrison[50] have shown that the excited crotonaldehyde molecule, formed by the primary process in the mercury sensitized reaction of crotonaldehyde, decomposed in two different ways. It either rearranges to give C_3H_6 and CO or splits to give propenyl and formyl radicals. Propenyl radicals would then react with the formyl radical to give propene, and this fraction of propene formed could be completely inhibited by addition of NO.



$$CH_3 - CH = CH\cdot + \cdot HCO \longrightarrow CH_3 - CH = CH_2 + CO \quad . \; . \; . \; . \; (90)$$



. . . . (91)

The best evidence against such a mechanism is the absence of propenyl radicals in the system. If propenyl radicals were present, they would have reacted with NO in the NO inhibited runs to give acetaldehyde and HCN[51].

$$CH_3 - CH = CH\cdot + NO \longrightarrow CH_3 - CH = CH\;NO$$

$$\downarrow$$

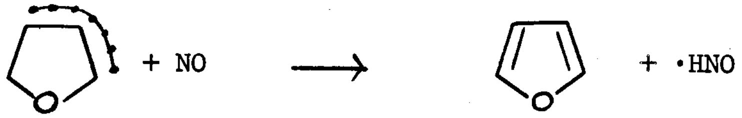
$$CH_3CHO + HCN \quad . \; . \; . \; . \; (92)$$

The absence of CH_3CHO and HCN support the formation of propene by reactions (77A) to (78).

Further support for the formation of 3-butenal, as an intermediate, arises from the work of McDowell and Sifniades[52]. They deduced that in the photolysis of crotonaldehyde, an excited molecule of

3-butenal was formed as an intermediate, which could decompose to give C_3H_6 and CO or allyl and formyl radicals.

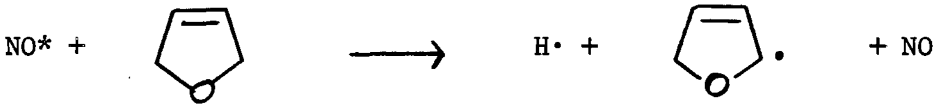
It has been observed that the yield of furan increases eightfold in the NO added runs. This is probably due to two reactions. One is the reaction between the dihydrofuranyl radicals and NO.



. . . . (93)

Such disproportionations of free radicals with NO occur to some extent in the case of ethyl radicals[53], to give ethylene and •HNO, in the case of vinyl radicals[54] to give acetylene and •HNO and in the case of isopropoxy radicals[55] to give acetone and •HNO. The other reaction involves the excited NO molecules produced in the system by the quenching of $Hg(6^3P_1)$ atoms by the added NO.

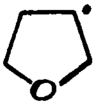
$$NO + Hg(6^3P_1) \longrightarrow Hg + NO^* \quad . . . . (94)$$



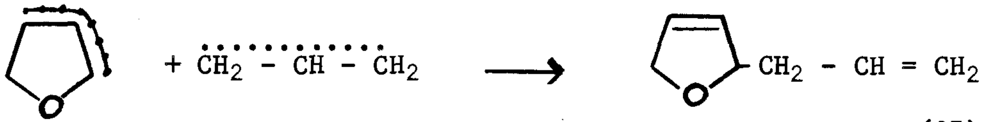
. . . . (95)

. . . . (96)

Decomposition of hydrocarbons initiated by electronically excited NO have been reported[47C]. Since the maximum limiting yield of furan is obtained by the addition of only 3.6% of NO, and since the quenching cross section of NO and substrate are not very different (23.0A and 28.4A respectively), it may be calculated that reaction (95) can be responsible for at most 0·04 of the total quantum yield of furan produced in these runs. Within this limitation the quantum yield of furan in the presence of NO represents the primary quantum yield of dihydrofuranyl radicals

The complete inhibition of THF formation in NO added runs indicates that the precursor radical  also reacts with NO.

Absence of compound "A" and "B" in the products of NO inhibited runs points out that they also have radical precursors. Efforts were made to identify these compounds. Mass spectra of compound 'A' and 'B' are given in table 11 and 12 respectively. Mass spectra obtained at low energy electron beam showed a peak at m/e=110 for compound 'A' and a peak at m/e=69 for compound 'B'. Examination of figures 13, 14, 17 and 18 reveal that these unknown compounds cannot be obtained in large quantities by increasing the irradiation period or the substrate pressures. Samples were therefore collected by repeating runs at low substrate pressures. The amounts collected after several runs were so small that poor I. R. spectra were obtained. I. R. spectra of both the compounds showed absorptions due to basic dihydrofuran ring. It is very tempting thus to assume that compound 'A' with m/e peak at 110, is a combination product of



. . . . (97)

and the compound 'B' with m/e peak at 69, is a combination product of two dihydrofuranyl radicals

Table 11

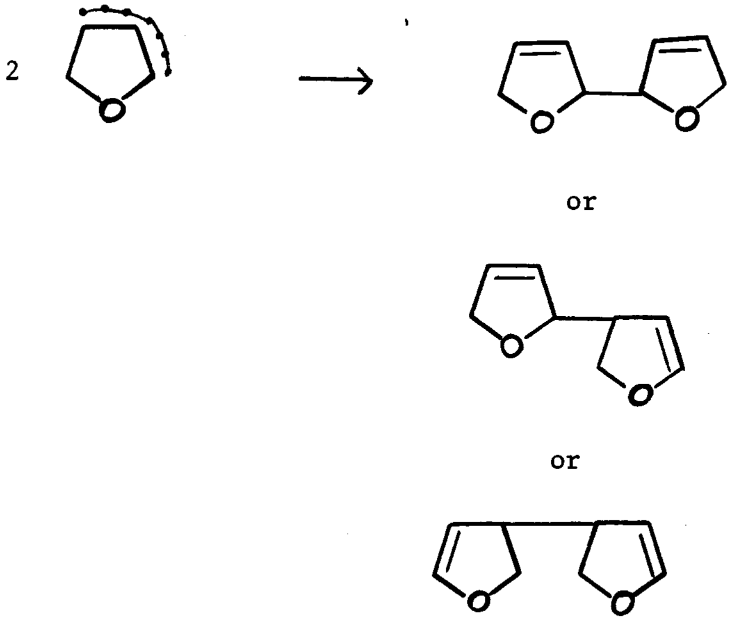
Mass spectrum of Compound A

m/e	10 ev	80 ev
110	100	10.75
81	-	1.07
79	-	1.07
77	-	1.07
71	-	10.75
70	-	6.45
69	-	100.00
68	-	3.22
56	-	2.15
55	-	2.15
52	-	1.07
51	-	2.15
43	-	7.53
42	-	2.15
41	-	37.6
40	-	2.15
39	-	15.05

Table 12.

Mass spectrum of Compound 'B'

m/e	10 ev	80 ev
69	100.00	100.00
70	-	5.2
68	-	1.9
56	-	0.6
55	-	1.3
54	-	0.6
53	-	1.3
42	-	1.3
41	-	32.7
40	-	15.0
38	-	1.3
29	-	2.6
28	-	6.5
27	-	5.2



. . . . (98)

The presence of NO would completely inhibit the formation of such products.

Addition of NO leaves the unknown compound 'C' uneffected, suggesting that it is not formed by radical reaction. The mass spectrum of compound 'C' is given in table 13. I. R. spectrum indicates the presence of the basic 2,5-DHF ring. Nothing definite can be said about its structure until good I. R. and N.M.R. spectra are obtained.

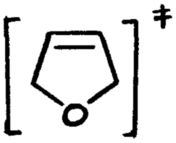
Attempts are now being made to collect these three compounds by carrying out the sensitized reaction in a circulating cell. In this system the substrate is continuously circulated through a cylindrical cell by means of a small mechanical pump. The cell is irradiated with an intense low pressure mercury resonance lamp. The products are pumped out of the cell into a cold trap maintained at -23°C. The substrate has a vapour pressure of 3~4 mm. of Hg at this temperature, hence could be pumped back into the cell. The compounds 'A', 'B' and 'C' which are of higher molecular weight than the substrate would be trapped in the cold trap.

Table 13.

Mass spectrum of Compound C

m/e	10 ev	80 ev
83	100.00	55.5
82	-	2.2
81	-	6.6
79	-	11.1
77	-	7.8
70	-	100.00
69	-	74.4
68	-	8.9
67	-	44.4
66	-	2.2
65	-	3.3
58	-	1.1
56	-	3.3
54	-	37.8
53	-	11.1
51	-	2.2
45	-	3.3
44	-	6.6
43	-	13.3
42	-	26.6
41	-	84.4
39	-	44.4
29	-	8.88

H_2 is produced in the reaction with a quantum yield of 0.17, hence it could be considered as one of the major products. Addition of NO leaves the yield of H_2 uneffected, suggesting that all the hydrogen is formed by a molecular elimination process. If we assume that H_2 is formed by reaction

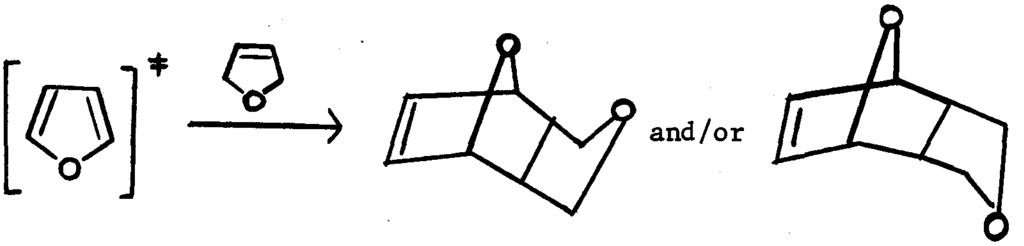


$$\longrightarrow H_2 + 'P' \quad . . . . (67)$$

The product, P, of mass 68, should also be formed with a quantum yield of 0.17. Furan has a mass of 68, but its quantum yield is so low ($\Phi = 0.033$), that we could not consider it be the product 'P' of reaction (67). No other product was observed that had a high quantum yield of 0.17 and a mass of 68.

Pyrolysis of 2,5-DHF was studied by Willington and Walters'[56]. The products are H_2 and  .

The reaction is exothermic with an activation energy of 48 kcal/mole. If  is produced by reaction (67) it will be excited to some extent. Srinivasan[43,44] observed that the excited molecule produced by the mercury photosensitized reaction of furan, decomposed to give CO and cyclopropene but also added to double bonds present in the system to give Diels-Alder addition products. If the same excited state of furan is produced in reaction (67), it may add to a substrate molecule to give Diels-Alder products.



. . (99)

Efforts were made to find such products, by using different G. C. columns at different conditions of temperatures and flow rates, but with no success. The Diels-Alder product of furan and 2,5-DHF may have very low vapour pressure at room temperature. In this case the products will deposite on the cell walls. A deposite on cell walls was observed in long runs. Efforts are now being directed to obtain this deposite in enough quantity to identify by spectroscopic studies.

It appears, in summary, that 2,5-dihydrofuran reacts with triplet mercury to give an excited molecule which decomposes by the following three processes.

(i) Cleavage of a C-H bond to give dihydrofuranyl radical and an H-atom ($\Phi \leq 0.25$).

(ii) Ring cleavage to give a biradical which may decompose to give propene and CO or to give a free radical precursor of propene ($\Phi = 0.32$).

(iii) Molecular decomposition to give hydrogen and an unknown product ($\Phi = 0.17$).

The difference between the products of this reaction and those of the oxygen atom - butadiene reaction indicates that the same biradical intermediate is not involved. Electron delocalization in the intermediate species $\dot{O} - CH_2 - \dot{C}H - CH = CH_2$ and $\dot{O} - CH_2 - CH = CH - \dot{C}H_2$ may not be complete enough to make the two identical. An alternative explanation is that in either or both reactions the formation and isomerization of the initially formed intermediate, represents a single concerted process without involving an identifiable biradical intermediate.

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