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Wilmington, Delaware

January 1965

THE FORMATION AND PROPERTIES OF CERTAIN COMETARY SPECIES

NASA Contract NASw 707

by

G. J. PONTRELLI

ABSTRACT

Continuous- and flash-photolysis techniques have shown that, at wavelengths below 2500 Å., diacetylene decomposes to give C₂, C₃, and CH by radical-radical reactions. The implication of these results is discussed with relation to the mechanism of the radical formation at or near the nucleus of comets. The oscillator strengths for C₂ (Swan), CN (red), CO, CO⁺, CO₂⁺ have been determined.

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THE FORMATION AND PROPERTIES OF CERTAIN COMETARY SPECIES

I. SUMMARY

The work conducted under this contract covered two subjects related to cometary phenomena:

- (1) the mechanism of the photodecomposition of diacetylene to produce the C_2 , C_3 , and CH radicals found in comets, and
- (2) the determination of the oscillator strength of several cometary species: [C_2 (Swan), CN (red), CO (3rd positive), CO^+ (1st negative), and CO_2^+ (${}^2\pi_u \rightarrow X{}^2\pi_g$)].

Under the first subject, diacetylene was chosen as a model compound for several important reasons: it was known to be photolyzed by near-UV radiation (2000-3000 Å.) whose available intensity in the solar spectrum far exceeds that of shorter wavelengths; the cometary species C_2 , C_3 , and CH were known to be photolysis products; diacetylene has the required low vapor pressure at cometary temperature (50°K.). An object of this work was to test whether the observed radicals are formed as primary species or as species derived from secondary radical-radical reactions.

Our results show that for photolysis at wavelengths below 2500 Å., C_2 , C_3 , and CH are formed by radical-radical reactions, while above 2500 Å., C_2 , but not C_3 and CH, may be formed as a primary species. This necessary recourse to radical-radical reactions suggests the need for further study of the vaporization conditions at the surface of the nucleus to ascertain whether the pressure can be high enough for reactions of this type.

Under the second subject, the following values of oscillator strength were measured:

CN red system	3.4×10^{-3}
CO_2^+ (${}^2\pi_u \rightarrow X{}^2\pi_g$)	1.18×10^{-2}
CO^+ (first negative)	7.9×10^{-3}
CO (third positive)	8.9×10^{-3}
C_2 (Swan system)	4.33×10^{-3}

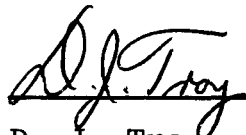
Details of this work are given in the Appendix, Exhibits
F through J, prepared by M. L. Jeunehomme and R. P. Schwenker.

Prepared by:

A handwritten signature in cursive script, reading "G. J. Pontrelli", written over a horizontal line.

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Submitted by:

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D. J. Troy
Research Section Manager
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II. INTRODUCTION

A. GENERAL CHARACTERISTICS OF COMETS

Comets are essentially composed of three parts: nucleus, coma, and tail. The chemical species that constitute the coma and tail have been studied extensively by recording the emission of fluorescing atoms and radicals excited by electromagnetic radiation from the sun. Unique features of the comet emission are the presence of ions (CO^+ , N_2^+ , CO_2^+) in the tail and neutral radicals (CN , CH , C_2 , C_3 , NH_2 , NH , OH , O , Na) in the head*. While knowledge of the nucleus and the mode of radical formation is limited, it is generally agreed that the nucleus is the source of all the species found in the coma and tail of a comet.

B. THEORIES OF COMETARY ACTIVITY

This study begins by assuming that the Whipple¹ "Icy Mass Model" (1950) explains the observed cometary phenomena. The nucleus is essentially an icy conglomerate of a loosely bound solid consisting of H_2O , CH_4 , NH_3 , and meteoric material at 50°K . In the vicinity of the sun, solar heating to temperatures of 150° to 500°K . causes profuse sublimation of the parent molecules into the surrounding vacuum. These vaporized materials absorb solar ultraviolet radiation and dissociate, giving rise to the observed free radicals.

To account for cometary outbursts, Donn and Urey² (1956) suggested that free radicals trapped in the ice are triggered by solar far-ultraviolet radiation to cause highly energetic reactions. However, research to demonstrate the trapping of free radicals in a frozen mass (most notably, the work by the National Bureau of Standards) has shown that, under ideal conditions, 0.1 mole % is the maximum concentration of free radicals that can be trapped. This concentration is two orders of magnitude lower than the concentration required by the Donn-Urey model. These authors have subsequently modified their theory to include stable molecules, such as acetylene and ethylene, which might through minute and violent energy release combine with other molecules and atoms of the nucleus to provide considerable explosive energy.

* The head of a comet refers to the nucleus and the coma combined.

Whipple has subsequently stated³ that cometary outbursts may be explained without the assumption of free energy in the icy mass. If the original deposition of matter in the nucleus is irregular, parent molecules of high vapor pressures will, upon vaporization, carry along parent molecules of lower vapor pressures. This hypothesis suggests the presence of a material such as a hexahydrate of methane that would lower the vapor pressure of methane and prevent its immediate loss because of its high vapor pressure⁴. At best, this seems like an unnecessary ad hoc hypothesis to postulate the presence of methane as a carbon-hydrogen source.

C. MODELS FOR THE PHOTOCHEMICAL PRODUCTION OF COMETARY SPECIES

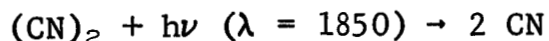
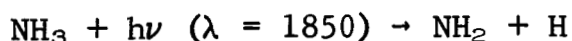
Three models can account for the photochemical production of cometary species by electromagnetic radiation. In each model, we begin with the vaporized parent species at or near the nucleus and assume that the actinic radiation responsible for dissociation lies in the near UV (2000 Å.) where there is three orders of magnitude more energy than in the far UV (1000 Å.).

1. Primary Production of Cometary Species

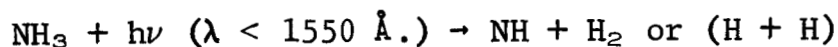
This model assumes that photolysis leads directly to free radicals, which are the cometary species. These radicals are generated in the immediate region around the nucleus (where pressure has been assumed to be on the order of 10^{-3} mm. Hg) and escape so quickly that only a negligible fraction can react further. Steady-state photolysis can demonstrate whether or not it is possible to produce such species in the initial step.

The literature shows that it is possible to produce several cometary species in this manner. For example:

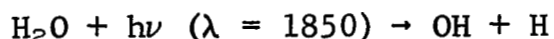
Ramsay²⁹ has shown that:



Groth³⁰ has shown that below 1550 Å.:



Ung and Back³¹ have recently shown that:



Our work has shown that C_2 may be produced as a primary species in the reaction:



2. Production of Cometary Species by Secondary Reactions

This model assumes that photolysis leads to free radicals (not necessarily the cometary radicals) in a relatively high pressure region (> 0.1 mm. Hg) at or near the nucleus. These radicals can react with each other to produce cometary species before escaping into the low-pressure region. Thus, flash photolysis is a realistic experiment to simulate cometary photochemistry. All of the radicals generated by continuous photolysis (NH_2 , CN , NH , OH) have been generated under flash photolysis conditions^{32,33,34}.

3. Production of Cometary Species by Primary and Secondary Reactions

This model is a combination of 1 and 2. Although all the non-carbon-containing radicals can be produced as primary species, our results show that radical-radical reactions are required to produce C_3 , CH , and large concentrations of C_2 . It therefore becomes essential to require higher pressures at or near the nucleus. As previously stated, pressures greater than 0.1 mm. Hg would be sufficient to cause the required radical-radical reaction necessary for the production of C_3 . Thus, a condition may exist on natural comets where several cometary species are produced in the primary step while others result from radical-radical reactions.

D. PROPOSED THEORY FOR C_2 , C_3 , AND CH PRODUCTION ON NATURAL COMETS

There are many literature references showing that methane, acetylene, ethylene, or any of the other suggested parent molecules containing carbon and hydrogen do not produce the C_2 , C_3 , or CH radicals^{5,6,7,8,9} either as a primary species or as a result of radical-radical interaction when subjected to far ultraviolet radiation. It is also known¹⁰ that the

energy available between 2000 and 3000 Å. is three orders of magnitude greater than between 1000 and 2000 Å. It is known, further, that far-ultraviolet radiation produces ionization in many of the possible parent molecules, while the near ultraviolet produces dissociation. Thus, the greater amount of available energy of the near ultraviolet and the dissociation capability needed to produce the desired radicals suggest strongly that the actinic radiation for radical formation is in the 2000-to 3000-Å. region. The only molecule known to give the C₂, C₃, and CH radicals upon irradiation by the near ultraviolet is diacetylene.¹¹ Swings¹² has recently suggested the presence of an organic molecule like diacetylene as a C₃-producing parent molecule. Diacetylene also has a sufficiently low vapor pressure at 50°K. so that no ad hoc hypothesis about hydrated parent molecules is necessary. It is for the above reasons, that diacetylene was chosen as a parent molecule in our studies on the production of C₂, C₃, and CH. The results show that these radicals are not produced as primary species but rather by secondary radical-radical reactions.

Estimates of pressures near the nucleus ($\approx 10^{-3}$ mm.) argue strongly against the possibility of radical-radical reactions. Since the experimental evidence requires radical-radical reactions to produce these cometary species, it suggests that the pressure at or near the nucleus is approximately 0.1-5 mm. Hg. If the pressure then drops by a factor of 10 at a distance of 10 cm. away from the nucleus, there is a sufficient path length for absorption-dissociation and radical-radical reactions. It is hoped that this work will stimulate further study along these lines.

III. EXPERIMENTAL APPARATUS

A. CHEMICALS

The diacetylene used in these studies, prepared from 1,4-dichloro-butyne-2*, was of 99% purity and contained 1% chlorovinylacetylene. A complete description of the preparation and storage of diacetylene is given in Exhibit A.

* Purchased from Columbia Organic Chemical Company, Columbia, South Carolina

Deuterated propylene was obtained from Merck of Canada.

B. VACUUM EQUIPMENT (Figure 1)

The vacuum apparatus used in this study was of conventional design with suitable pumps, gages, liquid nitrogen traps, and gas storage bulbs. A Decker differential pressure gage (0-2 and 0-20 mm. Hg) was used for making kinetic measurements and filling sample cells.

C. CELLS

The sample cells used in the continuous- and flash-photolysis experiments at wavelengths greater than 2000 Å. were constructed of fused quartz, 25 cm. long and 25 mm. o.d. "Suprasil" cells of the same dimensions manufactured by Engelhard Industries, Inc., were used for photolysis studies at 1850 Å.

D. LIGHT SOURCES

1. Continuous Photolysis

(a) Hanovia type 688845 low-pressure mercury lamps were used for experiments requiring 2537 Å. irradiation. The total number of photons at 2537 Å. determined with a thermopile and appropriate filters measured at a distance of 1 cm. is 9.3×10^{15} /cm.²/sec.

(b) For continuous photolysis experiments at 1850 Å., a special helical "Pen Ray" lamp was constructed by Ultra-Violet Products, Inc. The energy output of this lamp is 8% at 1850 Å., 74% at 2537 Å., 6% at 3650 Å., and the remaining 12% at wavelengths greater than 3650 Å. The total output of this lamp is 13.3 mw./cm.² measured at a distance of 1 cm. from the lamp.

E. FLASH PHOTOLYSIS APPARATUS (Figure 2)

These experiments were conducted on a microsecond flash-photolysis apparatus with the following features:

- (1) Reaction cell. Fused quartz tube 40 cm. long by 2.5 cm. o.d., fused quartz windows.

- (2) Photolysis lamp. Quartz tube, 40 cm. long by 1.5 cm. o.d., tungsten electrodes filled with xenon to 30 mm. Hg, fired by a 31- μ f. capacitor charged to 7000 v. Flash duration $\approx$ 35 μ sec.
- (3) Analysis lamp. Quartz capillary tube, $\approx$ 5 cm. long, 3-mm. internal diameter, expanding into two end sections containing tungsten electrodes; filled with xenon to 70 mm. Hg. Fired by a 1- μ f. capacitor charged to 8000 v. Flash duration $\approx$ 30 μ sec.
- (4) Time-delay circuit. Similar to that used by Ramsay,¹¹ modified to permit varying the delay from 10 to $\approx$ 800 μ sec. instead of from 2 to $\approx$ 250 μ sec.
- (5) Spectrographs and spectrometers. Photographic work was performed with a Jarrell-Ash f/6.3 plane grating spectrograph. This instrument was converted into a spectrometer by use of slits and a 1P21 photomultiplier in the focal plane. The signal from the photomultiplier was displayed on an oscilloscope and then photographed.

F. PRODUCT ANALYSIS

All gas-phase product analyses were carried out on a Bendix time-of-flight mass spectrometer.

IV. EXPERIMENTAL RESULTS

A. PHOTODECOMPOSITION OF DIACETYLENE

1. Continuous Photolysis

a. Description of Experiment

The quartz cells were filled with a known amount of gas, as measured by a Decker pressure gage, after the system has been pumped to below 1×10^{-5} mm. Hg. The total sample pressure used in these studies was limited with respect to an upper and lower limit as follows. At pressures above

10 mm. Hg, the decomposition of diacetylene into polymer caused the sample cell walls to become completely coated with polymer within 10 min., thus limiting the amount of radiation reaching the gas sample. A lower pressure limit of 0.1 mm. Hg was set by the sensitivity limits of the mass spectrometer. The polymer coating can be removed from the sample cell walls by heating with a hand torch, thereby permitting reuse of the cell.

After a known pressure of diacetylene (stored in a Ward-LeRoy still) was admitted into the cell, the sample was irradiated with two Hanovia mercury-arc lamps ($\lambda = 2537 \text{ \AA.}$), and the pressure decrease as a function of time was measured with a Decker differential pressure gage. After the photolysis had been terminated, the remaining gas products were analyzed mass spectrometrically.

b. Experimental Observations

The only gaseous products formed by the photo-decomposition of diacetylene with $2537 \text{ \AA.}$ radiation were acetylene (C_2H_2), and triacetylene (C_6H_2). The other product was a brownish-black, almost mirror-like, polymer with a carbon-to-hydrogen ratio of 1.9:1. Table I in the Appendix gives the mole percent of products formed relative to the percent of diacetylene decomposition for a 1-hr. irradiation period. It was also determined that the percent of decomposed diacetylene converted to acetylene remained essentially constant (5%) over a 1-hr. period.

Use of a "Pen Ray"-type helical lamp as a source of both 2537 and $1850 \text{ \AA.}$ radiation and a "Suprasil" sample cell permitted photolysis studies at shorter wavelengths. End-product analysis showed that hydrogen was formed in addition to the products found when $2537 \text{ \AA.}$ was used (Table I).

2. Flash Photolysis

Flash photolysis experiments, with actinic radiation between 2000 to $3000 \text{ \AA.}$, produced C_2H_2 , H_2 , and polymer. However, no H_2 was found when the sample was flashed at wavelengths greater than $2500 \text{ \AA.}$; only C_2H_2 and polymer were produced. In

addition to these end products, the C_2 , C_3 , and CH radicals were observed by their absorption spectra. Table II in the Appendix lists the species and bands observed and their estimated intensities.

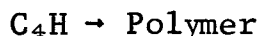
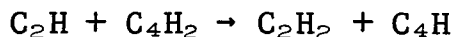
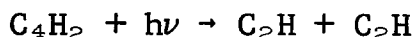
These experiments were conducted with a 650-joule input to fire the photolysis lamp. This energy is sufficient to decompose 60% of the initial diacetylene. Since a considerable polymer deposit formed immediately after the flash, it was necessary to work at sample pressures from 0.5 to 2 mm. Hg.

B. MECHANISM OF DIACETYLENE PHOTODECOMPOSITION

A consideration of the bonds and bond energies involved in the diacetylene molecule, viz., $H - C \equiv C - C \equiv C - H$, indicates that only two bonds are capable of being broken, with the energy available from photons at wavelengths greater than 1850 Å., i.e., C - H and C - C bonds, Table III.

1. Formation of C_2H_2 by the Ethynyl (C_2H) Radical

To account for the formation of acetylene we assume that the C - C bond, which is the weakest, is broken, leading to the formation of two ethynyl radicals (C_2H), which then abstract hydrogen from diacetylene. The postulated mechanism is therefore:



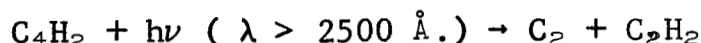
This is the mechanism observed in experiments at wavelengths below 2500 Å., both in continuous and flash photolysis. The technique used to identify the ethynyl radical (C_2H) utilized mixtures of deuterated propylene and diacetylene in ratios ranging from 1:10 to 10:1. Observation of C_2HD verified the proposed reaction by demonstrating that the C_2H abstracts deuterium from propylene to form C_2HD . No evidence for the C_2H radical was found at wavelengths greater than 2500 Å., either in continuous or flash photolysis. Since diacetylene has two electronic states between 1850 and

2970 Å., viz., 1850 — 2500 Å. and 2500 — 2970 Å., the mechanism for acetylene formation is dependent on the excited state involved.

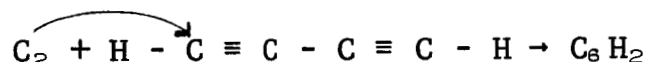
Since the absorption at wavelengths below 2500 Å. occurs at the C ≡ C triple bond, breaking of the C - C bond must be due to a "flow" of the absorbed energy to the C - C single bond, causing the bond to rupture forming two ethynyl radicals (C₂H).

2. Formation of C₂H₂ by Molecular Elimination

The mechanism for acetylene formation at wavelengths greater than 2500 Å. may be based on the molecular elimination of C₂, viz.,



Additional evidence for C₂ formation is the observation of triacetylene (C₆H₂) which is formed by the insertion of C₂ in C₄H₂ at the CH bond, viz.,

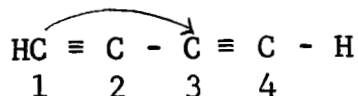


This reaction is similar to the insertion reaction of methylene radicals into C - H bonds^{19,20}. That triacetylene is not formed from the free-radical reaction C₄H + C₂H → C₆H₂ is shown by the absence of C₂HD or C₄HD when mixtures of diacetylene and deuterated propylene are irradiated with 2537 Å. radiation.

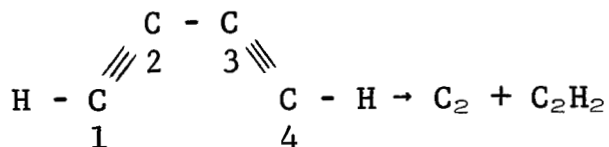
We have also shown that addition of nitric oxide to diacetylene does not alter the acetylene yield, which gives further support to a nonradical mechanism for acetylene formation.

Because of the conjugated nature of diacetylene, we can consider two possible routes for the elimination of C₂:

a. The mobility of a hydrogen from carbon 1 to carbon 3 with the eventual elimination of C₂ (carbon 1 and 2), viz.,



b. Elimination of C_2 via a bent excited state, viz.,



This latter mechanism would form C_2 by elimination of carbon atoms 2 and 3.

Considerable evidence has been obtained to support the existence of a bent excited state; for example, toluene, ethylbenzene, and xylene were produced by irradiating (2537 Å.) mixtures of diacetylene with propylene, butene-1 and cis butene-2, respectively. The details of these studies are given in Exhibit B (to be submitted for publication in J. Chem. Phys.).

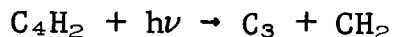
The molecular elimination of C_2 by the mechanism $C_4H_2 \rightarrow C_2H_2 + C_2$ is endothermic by 117 ± 4 kcal./mole. Thus, the energy available at $2537 \text{ \AA}$. (113 kcal./mole) is just sufficient for this reaction to occur. However, this calculation is dependent on the heat of formation of diacetylene. The value used here was calculated via an ionization potential for $C_4H_2 \rightarrow C_4H_2^+$ of 10.2 volts obtained by the direct electron-impact methods of Coats and Anderson.²¹ This leads to a value of 127 ± 4 kcal./mole for the standard heat of formation of diacetylene. The reported values for the standard heat of formation of diacetylene range from 103 to 130 kcal./mole; our results support the upper value.²²

The quantum yield at 28°C. for the formation of acetylene at 2537 Å. has been determined to be 1.8×10^{-1} , while the quantum yield for formation of polymer is 3. This latter value may be compared with a quantum yield of 9 ($\lambda = 2150$ Å.) for photopolymerization²³ and 6.5 for the mercury-photosensitized polymerization of acetylene.²⁴ The polymerization of diacetylene and acetylene, as well as those of methyl acetylene and allene²⁵ all appear to involve short chains in contrast to the polymerization of styrene in which the chain length may reach thousands of molecules per quantum absorbed. A more complete discussion of the photopolymerization of diacetylene and the quantum yield determination is given in Exhibit D.

3. Absence of C₃ as a Primary Species

The C₃ radical is not formed as a primary species when diacetylene is irradiated with 2537 Å. as indicated by the absence of CH₄ or addition reactions to C₃.

The primary reaction to form C₃ is:



Observation of CH₄ derived from CH₂ or addition products to C₃ would verify that this reaction occurs. However, since reactions involving addition to C₃ or CH₂ are exothermic, the absence of addition products does not establish conclusively the absence of C₃ or CH₂. Therefore, we irradiated an icy mass (77°K.) of various mixtures of diacetylene and propylene (ratios from 1:20 to 20:1) but found no evidence of the presence of C₃. We did, however, observe two new compounds which are analogous to the compounds found by Skell and Westcott,²⁶ viz., bis,(2-methylcyclopropyl)acetylene and 1-(2-methylcyclopropyl)-2-(2-ethynylcyclopropenyl-2)acetylene. These experiments are discussed in detail in Exhibit C (paper to be submitted to the J. Am. Chem. Soc. for publication).

4. Formation of C₂, C₃, CH, and H

a. Observations

The mode of decomposition of diacetylene at wavelengths below 2500 Å. to form acetylene (C₂H₂), H₂, C₂, C₃, and CH has been shown to occur by radical-radical reactions. By using argon as a buffer gas, we found that CH, C₂, and C₃ were not formed when the argon-diacetylene ratio was 20:1, 30:1, and 70:1, respectively.

In the case of molecular hydrogen formation, we found that as the argon pressure was increased, the molar ratio of hydrogen formed to diacetylene decreased from 0.21 to a constant value of 0.02. Photolysis of equimolar amounts of deuterated propylene and diacetylene in an excess of argon produced HD. These results show that hydrogen atoms are formed in both a primary and a secondary reaction, which is responsible for most of the hydrogen formed. Table IV in the Appendix lists the radicals, the end products, and the method of detection as a result of flash photolyzing diacetylene.

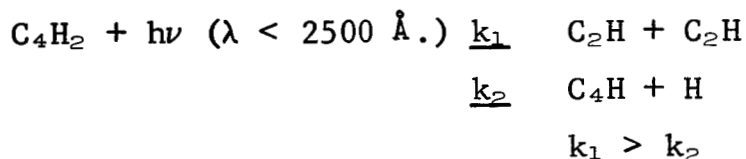
The pressure of diacetylene used was 1.5 mm., with the average percent decomposition being 60 ± 1 . The percent of H_2 and C_2H_2 formed from the decomposed diacetylene was 21 ± 2 and 36 ± 1 , respectively.

Table V in the Appendix lists the radicals, the end products, and the method of detection when diacetylene and deuterated propylene are subjected simultaneously to 1850 Å. and 2537 Å. radiation. The detailed reaction mechanism between diacetylene and propylene is given in Exhibit E.

C. MECHANISM OF RADICAL AND END-PRODUCT FORMATION

Summarized below are the reactions that give rise to the observed radicals and end products consistent with our observations. The discussion is divided into primary and secondary reactions where it is shown that neither C_2 , C_3 , or CH is produced as a primary species.

1. Primary Photochemical Reaction



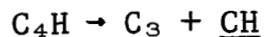
2. Secondary Reactions

- a. Neither an abstraction nor an addition reaction will produce any of the desired radicals.
- b. Only radical-radical reactions produce C_2 , C_3 , and CH.

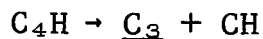
1) Formation of C_2



2) Formation of CH

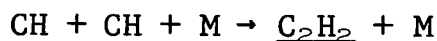
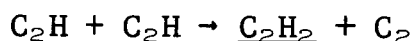


3) Formation of C_3



c. Formation of stable end products. Below are listed the reaction mechanisms that account for the formation of the observed end products. The predominating reactions are listed first.

1) C_2H_2



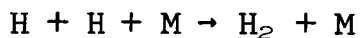
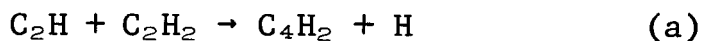
(M represents a third body)

2) C_6H_2



In view of the large concentration of C_4H_2 relative to C_4H and C_2H , reaction (a) would predominate in the formation of acetylene and triacetylene.

3) H_2



Since we have shown that hydrogen atoms are produced mainly by secondary reactions, reaction (a) would predominate.

4) Polymer

The mechanism and rate of polymer formation are discussed in Exhibit D.

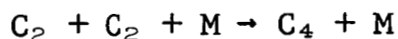
D. THE RATE OF FORMATION AND DISAPPEARANCE OF C_2 AND C_3

The technique used to follow the kinetics of formation of free radicals is essentially that of Porter.²⁷ Since the spectral bandwidth of the measurement instrumentation is finite and the species being measured have a narrow line spectrum, the extinction coefficient changes significantly over this interval. Hence Beer's law will not be valid and measurements of concentration will not be possible. We can, however, obtain from an apparent optical density information on the time required for the maximum concentration to be reached and on the lifetime of the species.

Our observations in the flash photolysis of diacetylene show that both C_2 and C_3 reach their maximum concentrations 180 μ sec. after the photolysis flash and that these radicals have a lifetime of up to 1 min.*

When the reciprocal of the apparent optical density is plotted against time, we find second-order kinetics with respect to the disappearance of C_2 and C_3 . If this apparent optical density is directly proportional to concentration, there would be two possible reaction routes for the disappearance of C_2 and C_3 .

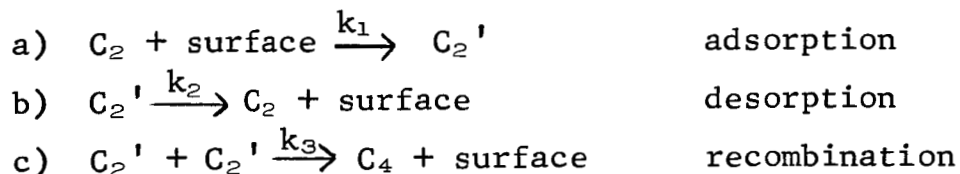
- (1) Gas-phase recombination with a third body, in large excess, viz.,



where M would be C_4H_2 , since only 60% of diacetylene is decomposed.

- (2) Recombination at the walls.

The kinetics of a wall recombination process may be considered in terms of the three reactions:



where C_2' represents the adsorbed species.

* The only other radical reported to have a longer lifetime is CS which was observed for times up to 2 min.²⁸

If a stationary concentration of C_2' is assumed, the rate of disappearance of C_2 is given by

$$\frac{-d[C_2]}{dt} = k_1[C_2] \left(1 - \frac{[C_2']}{[C_2']_s} \right) - k_2 \frac{[C_2']}{[C_2']_s}$$

where $[C_2']_s$ is the concentration of $[C_2']$ at saturation. It follows from this expression that, if there is weak adsorption together with slow recombination, the removal of C_2 is given by

$$\frac{-d[C_2]}{dt} = k_3'[C_2]^2$$

where $k_3' = k_3[C_2']_s \left(\frac{k_1}{k_2} \right)^2$

The rate of C_2 and C_3 removal will therefore be independent of the rate of diffusion or convection.

While the rate of diffusion is inversely proportional to total pressure, further study of the mechanism is difficult because the concentration of radicals produced is dependent on total pressure. We have not been able to determine if process 2 is independent of pressure or diffusion rate. Further detailed studies will require a spectrometer with sufficient resolution to determine a true optical density (concentration) and sensitivity to follow accurately the decay curves as a function of total pressure. This would be a major research project in itself.

V. SUGGESTIONS FOR FUTURE WORK

A. STUDY OF REACTIONS OF C_2 , C_3 , AND CH RADICALS WITH OTHER COMETARY SPECIES

Since our results show that radical-radical reactions are required to produce the C_2 , C_3 , and CH radicals, it becomes important to determine the reaction that these species will undergo in the presence of radicals such as NH, NH_2 , OH, CN. That is, if we require a pressure greater than 0.1 mm. Hg near the head of a comet nucleus to produce the C_2 , C_3 , and CH radical, we must also accept the ensuing reactions that these species may undergo with other radicals.

B. SPECTRUM OF C_2H

The original flash-photolysis work conducted on diacetylene was undertaken to observe the spectrum of C_2H ; observations from 2500 Å. to 9000 Å. yield negative results. Our results have shown the presence of C_2H when diacetylene is photolyzed at wavelengths below 2500 Å. Since the absorption spectrum of a radical occurs at longer wavelengths than the immediate parent from which it can be derived and since the ethynyl radical (C_2H) is derived directly from acetylene which absorbs between 2000 and 2200 Å., the absorption spectrum of C_2H may occur between 2200 and 2500 Å. It is hoped that this region will be investigated to obtain the C_2H spectrum. A high-resolution instrument would be required because absorption by diacetylene will also occur in this region.

C. LIFETIMES OF THE C_2 AND C_3 RADICALS

Further work is required to determine whether the disappearance of the C_2 and C_3 species occurs in the gas phase or at the walls. One way to overcome the aforementioned difficulty in determining whether or not diffusion is important is to use the same total pressure, but different buffer gases. Under these conditions, the same number of species will be produced, but diffusion to the walls will occur more rapidly in helium than in xenon.

D. SPECTRAL STUDIES OF HYDROCARBONS WHEN IRRADIATED WITH WAVELENGTHS BELOW 2000 Å.

Attempts should be made to obtain the absorption spectra of radicals produced when molecules such as acetylene, ethylene, propylene, etc., are irradiated with wavelengths in the far ultraviolet. End-product analysis is not sufficient to determine the reaction mechanism. For example, the production of C_2 and C_3 when diacetylene is photolyzed could not be predicted on the basis of acetylene, hydrogen, and polymer formation.

VI. ACKNOWLEDGMENTS

Appreciation is expressed to R. F. Pottie for his assistance in technical discussions and in developing the experimental program; to A. Mac Lachlan and P. J. McCartin (Radiation Physics Laboratory) for many helpful discussions; to P. S. Bauchwitz (Elastomers Chemicals Research Laboratory) for assistance in synthesizing diacetylene; and finally to my assistant J. A. Handel.

TABLE I
Photodecomposition Products of Diacetylene When
Irradiated with 2537 Å. for 1 Hr.

Initial Pressure <u>C₄H₂ mm. Hg</u>	<u>C₄H₂ Decomposed, %</u>	<u>Decomposed C₄H₂ Converted to C₂H₂, %</u>	<u>Decomposed C₄H₂ Converted to Polymer, %</u>	<u>Decomposed C₄H₂ Converted to C₆H₂, Approx. %</u>
0.2	37	6	94	--
0.4	47	6	94	--
0.6	52	5	95	0.07
0.8	57	5	95	0.08
1.2	62	5	95	0.08
1.6	59	5	95	0.1
4	67	5	95	0.1
8	68	5	95	0.1

emf

TABLE II
Band Systems Observed During the Flash
Photolysis of Diacetylene

<u>Band System</u>	<u>Estimated Relative Intensity</u>	<u>Bands Observed</u>
C ₂ Swan bands		
A ³ π _g - X ³ π _u	100	(0,1), (1,2) (0,0), (1,1), (2,2) (1,0), (2,1), (3,2) (4,3)
C ₃ 4050 Å. bands	15	
CH 3143 Å. bands	10	(0,0)

emf

TABLE III

Bond Energies Involved in the
Diacetylene Molecule

<u>Bond</u>	<u>Bond Energy (Kcal./mole)</u>	<u>Ref.</u>
C $\equiv$ C	228	Brewer ¹³
C - H	114	Knox ¹⁴
C - C	80	Cottrell ¹⁵

emf

TABLE IV

Radicals and End Products Observed in Flash Photolysis of
Diacetylene and Deuterated Propylene

<u>Species</u>	<u>Method of Observation</u>
C_2	Absorption spectra
C_3	Absorption spectra
CH	Absorption spectra
C_2H	Formation of C_2HD (mass spectrometer)
C_4H	Formation of C_4HD (mass spectrometer)
H	Formation of HD (mass spectrometer)
C_2H_2	Mass Spectrometer
H_2	Mass Spectrometer
C_6H_2	Mass Spectrometer

emf

TABLE V

Radicals and End Products Observed in the Continuous
Photolysis of Diacetylene with 1850 Å. and 2537 Å.

<u>Species</u>	<u>Method of Observation</u>
C_2H	C_2HD (mass spectrometer)
C_4H	C_4HD (mass spectrometer)
H	HD (mass spectrometer)
C_2H_2	Mass Spectrometer
H_2	Mass Spectrometer
C_6H_2	Mass Spectrometer

emf

EXHIBIT APREPARATION AND STORAGE OF DIACETYLENE

SAFETY PRECAUTIONS - Diacetylene has the same explosive power as TNT. NEVER OPEN REACTION FLASKS WHILE HOT!

I. PURIFICATION OF NITROGEN TO REMOVE TRACES OF OXYGENA. Preparation of "Silver Salt" Solution

Dissolve 75 g. of sodium hydrosulfite in 875 cc. of water, add 295 cc. of 30% NaOH solution and 1 g. of β - anthroquinone sodium sulfonate. After the solution has been prepared, add it to scrubber for O_2 removal from cylinder N_2 supply. This solution should be protected from the atmosphere (O_2) at all times.

II. PRELIMINARY PREPARATION OF DIACETYLENEA. Apparatus

Set up the apparatus as shown in Figure A-1. Fill the appropriate scrubber, drying towers, and bottles with chemicals shown in Figure A-1 and connect with neoprene or Tygon tubing.

B. Reactants

The chemicals listed below are added to the 500-ml. reaction flask in the following order:

- | | |
|---------------------|-----------|
| 1. Distilled water | 140 cc. |
| 2. KOH | 29.6 g. |
| 3. Dioxane | 10.3 cc. |
| 4. t-butyl catechol | 0.0294 g. |

C. Experimental Procedure

After the reactants have been introduced into the reaction flask, stirring is begun and the system is purged

with N_2 for 30 min. The water-bath temperature is raised to $80^\circ C$. During this period, the condenser temperature should be $10^\circ C$. higher but no more than $15^\circ C$. above the water-bath temperature. Decrease the nitrogen flow from 50 cc./min. to 25 cc./min.

The dropwise addition of 27.6 g. of 1,4-dichlorobutylene-2 is now begun. The addition rate should be kept low so that 2 hr. will be required to make the complete addition. The temperature should be kept between 75° and $80^\circ C$. during the entire reaction time. The quantities used in this procedure will produce approximately 9 g. of diacetylene.

After completion, N_2 should be passed through the system to purge the system of diacetylene. Disconnect the DMF trap and seal off to prevent oxygen from entering. It is then convenient to divide this sample into ten equal parts and dilute to approximately a 1% solution. This must be done either in a dry box or under a nitrogen atmosphere. Store under refrigeration.

III. EXTRACTION OF DIACETYLENE FROM DMF SOLUTION

The apparatus is set up as shown in Figure A-2 with the appropriate solutions and driers, etc. One hundred cc. of $\approx 1\%$ DMF solution is placed in the 500-cc. reaction flask containing 100 g. H_2O , and the system is flushed with N_2 (25 cc./min.) for 30 min., after which stirring is begun and the temperature raised to $75-80^\circ C$. Diacetylene can be detected at the exhaust end of the system with a solution of silver nitrate which will give a distinct yellow precipitate (silver acetylide) if diacetylene is present. As soon as this occurs, collection is begun in the LeRoy still by addition of dry ice and trichloroethylene to the dewar. The presence of diacetylene product may be determined at a silicone tap by using a 2-1/2-cc. gas-sampling syringe. When the rate slows down, the stopcocks on the LeRoy still are closed and the remaining gas is exhausted into a hood by turning stopcock 2. The temperature of the flask is lowered while N_2 is purged through the system for 1 hr.

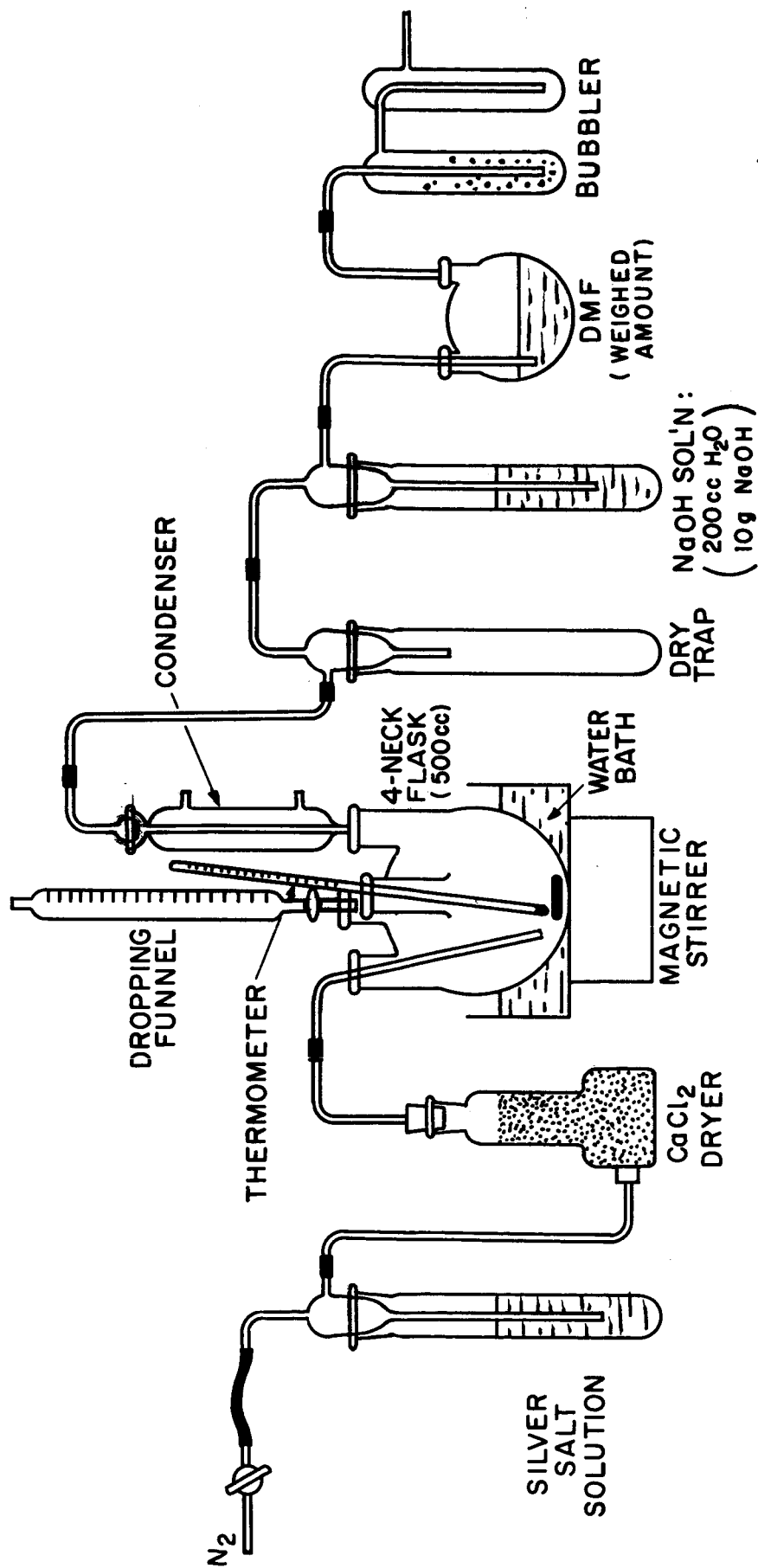
The LeRoy still is placed into a liquid N_2 trap and then connected to a vacuum line via a Mace "Teflon"® TFE-fluorocarbon resin connector. The N_2 atmosphere above the

® Du Pont trademark

frozen diacetylene (≈ 0.4 g.) is then pumped away. Samples of gaseous diacetylene are now available just by heating the LeRoy still.

Once the reaction flask has been cooled to room temperature 20 cc. of xylene and 2 g. of "Neozone"[®] A rubber antioxidant are added to deactivate the remaining diacetylene. NEVER OPEN REACTION FLASKS WHILE HOT! Diacetylene has the same explosive power as TNT.

[®] Du Pont trademark



JOINTS MADE WITH NEOPRENE TUBING

FIGURE A-1 PREPARATION OF DIACETYLENE

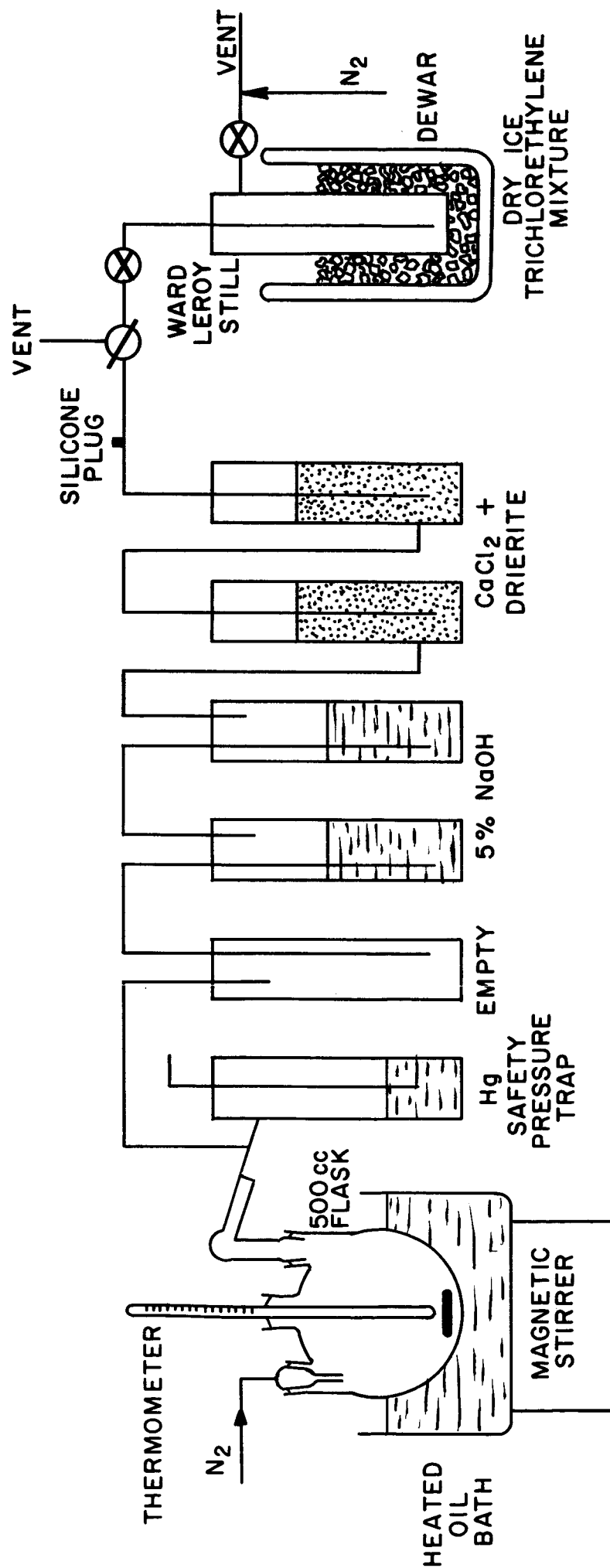


FIGURE A-2 EXTRACTION OF DIACETYLENE FROM DMF SOLUTION

EXHIBIT B

(Proposed Publication)

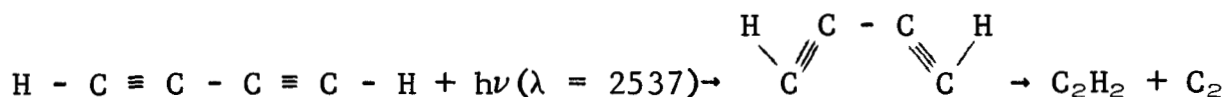
Letter to the Editor
Journal of Chemical PhysicsCHEMICAL EVIDENCE FOR THE BENT
EXCITED STATE OF DIACETYLENE*

Spectroscopic evidence obtained by Woo and Chu^{B1,2} and by Callomon^{B3} indicated that diacetylene has two regions of adsorption below 3000 Å.: "high-pressure bands" ($\lambda > 2500 - 2970$ Å.); and "low-pressure bands" (2000 Å. $\lambda < 2500$ Å.). The complexity of the "high-pressure bands" and the inability to resolve the rotational structure led to the conclusion that diacetylene was predissociated when it absorbed radiation greater than 2500 Å. Woo and Chu suggested further that the excited state produced by absorption at wavelengths greater than 2500 Å. might be bent. I wish to report chemical evidence to support the existence of a bent excited molecule of diacetylene when it absorbs radiation at 2537 Å.

When diacetylene is subjected to 2537 Å. radiation from a Hanovia Type 688845 low-pressure mercury lamp, the only gaseous products observed are acetylene (C_2H_2) and a very small amount of triacetylene (C_6H_2). Analysis of the polymer formed yields a carbon-hydrogen ratio of 1.9:1. This ratio, although somewhat high in hydrogen content, is easily accounted for by the high absorption and reaction of this polymer with water. Experiments using completely deuterated propylene mixed in various ratios with diacetylene (1:10 to 10:1) showed by the absence of any C_2HD that the acetylene formation did not occur through the formation of a C_2H radical. Addition of nitric oxide did not decrease the amount of acetylene formed. This gives additional evidence for the absence of a radical mechanism in the formation of acetylene. In another paper,^{B4} we will show that, at wavelengths below 2500 Å., the formation of acetylene does occur through the formation of a C_2H radical, which then abstracts hydrogen to produce acetylene. On the basis of the above evidence, we suggest that, at wavelengths above 2500 Å., the acetylene is

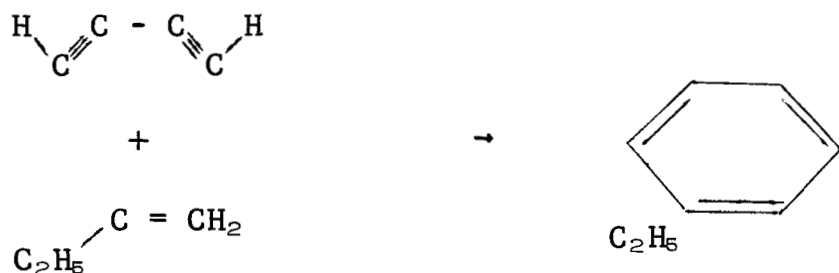
* Work supported by the National Aeronautics and Space Administration. Contract NASw-707.

formed through the molecular elimination of C_2 from the bent excited molecule, leaving acetylene as a gaseous product. The sequence can be visualized as follows:



The actual process of bond breaking and formation must be extremely complicated and cannot be specified with the available data. It would be of interest to determine the molecular orbitals and symmetry of this excited state.

Further evidence for the bent excited state was obtained when mixtures of diacetylene and propylene (at ratios ranging from 1:1 to 1:10, respectively, at total pressures less than 2 mm.) were irradiated with 2537 Å. mercury radiation and produced toluene. The samples were irradiated for times up to 1 hr., and the gas-phase products were analyzed by a Bendix time-of-flight mass spectrometer. A similar reaction occurred when mixtures of diacetylene and butene-1 were irradiated. In this case, the formation of ethylbenzene was observed. The formation of toluene and ethylbenzene can be visualized as follows:



In both cases, a breaking and formation of new bonds with hydrogen atom transfer is required. The reaction between butene-2 and diacetylene yielded xylene. We were not, however, able to determine, mass spectrometrically, whether we formed O, M, or P xylene.

Table BI lists the mole percent of products formed relative to the moles of diacetylene reacted for a 1:1 mixture of diacetylene and propylene.

TABLE BI

<u>Product Formed</u>	<u>Mole % Formed From Reacted Diacetylene</u>
C_7H_8 (toluene)	3
C_6H_2 (triacetylene)	2
C_2H_2 (acetylene)	20
Polymer Formed	75

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- B1. S. C. Woo and T. C. Chu, J. Chem. Phys. 3, 541 (1935).
- B2. S. C. Woo and T. C. Chu, J. Chem. Phys. 5, 786 (1937).
- B3. J. H. Callomon, Can. J. Phys. 35, 129 (1957).
- B4. To be published.

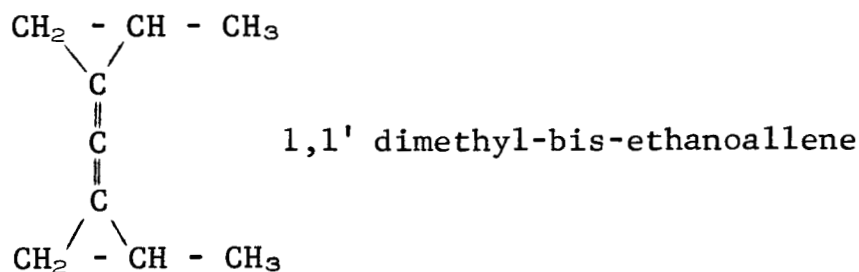
EXHIBIT C

(Proposed Publication)

Letter to the Editor
Journal of the American Chemical Society

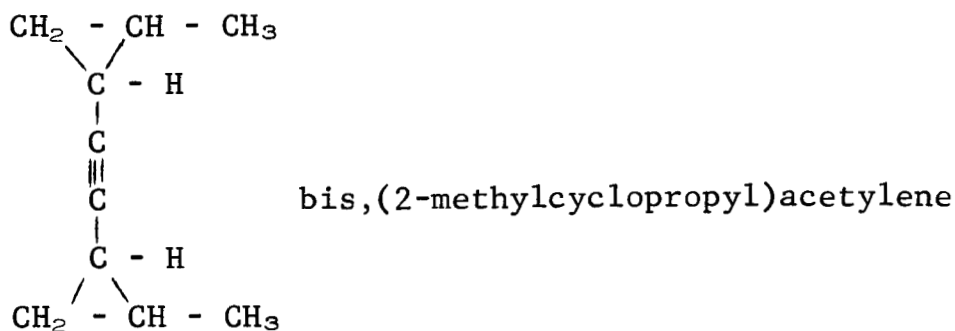
THE PHOTOCHEMICAL REACTION BETWEEN DIACETYLENE
 AND PROPYLENE AT 77°K.*

Recent work by Skell and Westcott^{C1} showed that the carbon species C₃ produced in vacuo (pressure < 10⁻³ mm.) reacted with propylene at 77°K. to form



In an attempt to determine whether C₃ could be formed as a primary species in the photochemical decomposition of diacetylene, mixtures of diacetylene and propylene ranging in ratios of from 20:1 to 1:1, respectively, were trapped on a cold finger at 77°K. and irradiated with 2537 Å. radiation (Hanovia 688845 low-pressure mercury lamp). The products produced by photolysis were then analyzed by warming the cold finger and analyzing the gaseous products with a Bendix T-O-F mass spectrometer.

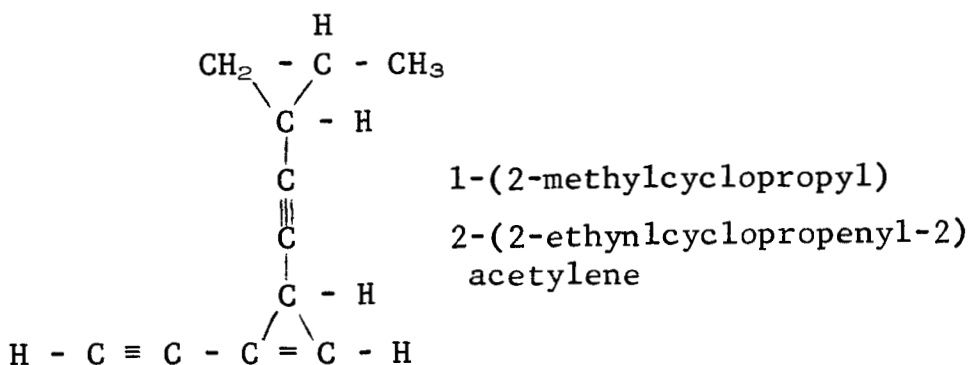
For a 20:1 mixture of propylene to diacetylene, we found a molecule with a parent peak at m/e = 134 and whose mass spectrum suggests that its structure is:



* Work supported by the National Aeronautics and Space Administration. Contract NASw-707.

No evidence was obtained for the formation of the molecule found by Skell and Westcott. In addition to forming bis (2-methylcyclopropyl)acetylene, a small amount of toluene was also formed. It should be noted that toluene was found in the gas-phase photochemical reaction between diacetylene and propylene.^{C2}

When a 1:1 mixture of diacetylene and propylene is photolyzed at liquid nitrogen temperature, no gaseous products were observed above the frozen mass at 77°K. or 183°K. At room temperature, we observed, in addition to a small amount of toluene, a new compound which is composed of two molecules of diacetylene and one molecule of propylene. The mass spectral cracking pattern suggests that we have formed



Irradiation of a pure diacetylene sample at 77°K. did not yield any gaseous products, although a trimer might have been expected. It was also found that these addition reactions do not occur at 142°K. (n-pentane slush). It is felt that while the structures of the compound formed are the most likely ones, additional information is required for confirmation.

Since 1,1'-dimethyl-bis-ethanoallene was not produced, it is concluded that C₃ was not formed as a primary species in the photodecomposition of diacetylene.

REFERENCES

- C1. J. Am. Chem. Soc. 85, 1023 (1963).
 C2. To be published.

EXHIBIT DTHE POLYMERIZATION OF DIACETYLENEI. INTRODUCTION

The excited diacetylene molecule produced by the absorption of 2537 Å. radiation essentially has three fates:

- 1) Polymerization
- 2) Decomposition
- 3) Deactivation

As the pressure increases, we would expect the yield of acetylene to increase linearly, reach a maximum, and then decrease because of collisional deactivation of the excited diacetylene molecule. In our studies, we were not able to reach this maximum at high pressures because of light absorption by the polymer; we did, however, observe a linear increase in acetylene yield as the pressure increased. Consistent with these results is the fact that the observed quantum yield was independent of pressure. Since the purpose of this study was not to study the polymerization of diacetylene, further conclusive experiments to determine unequivocally the actual reaction mechanism were not conducted. It is felt, however, that sufficient information has been obtained to postulate a reaction mechanism consistent with the experimental data.

The study of the photochemical decomposition of diacetylene is complicated by the formation of an opaque polymer on the walls of the reaction vessel. Even in the relatively low pressure range of from 0.2 to 10 mm. Hg, the polymer formed on the walls makes the incident light I_0 irradiating the sample a function of time. To overcome this difficulty and study the rate of decomposition, it was necessary to work over a range of starting pressures, to use a nonoptical method for measuring concentration changes, and to correct data by measuring the decrease in light intensity striking the sample caused by polymer formation on the cell walls.

No structural analysis was carried out on the polymer obtained, although we did determine the carbon-hydrogen ratio to be 1.9. Based on the yield of gaseous products formed, viz., C_2H_2 and C_6H_2 , the ratio should have been 2.1. However, this type of polymer is known to absorb and react readily with water and can thereby account for the excess hydrogen.

II. EXPERIMENTAL PROCEDURE AND RESULTS

A. DETERMINATION OF PRESSURE DECREASE AS A FUNCTION OF TIME

After the sample cell is filled with a known pressure of diacetylene, it is irradiated with 2537 Å. radiation. The cell was kept at $28 \pm 0.5^\circ\text{C}$. by flowing nitrogen between the sample cell and a quartz cylinder surrounding the cell. The decomposition is measured with a Decker differential pressure gage (0-2 mm. Hg). The measured pressure decrease must be corrected since two of the products are gases: acetylene and triacetylene. Hence, the actual decrease in pressure due to the loss of diacetylene is obtained by subtracting the pressure due to the gases formed. Since the amount of triacetylene formed is only 0.1% of the amount of diacetylene decomposed, only the pressure due to acetylene formation (5% of the diacetylene decomposed) need be considered. Thus Δp , the decrease in the partial pressure of diacetylene, is equal to the measured Δp plus 5%. Figure D-1 shows a plot of diacetylene partial pressure vs. photolysis time for four different starting pressures.

B. DETERMINATION OF INITIAL RATE OF REACTION

Since light absorption due to polymer formation becomes troublesome after the reaction has begun, the initial rate for constant light intensity was determined by plotting pressure vs. time and measuring the slope at zero time. Thus, if R_0 represents the rate at zero time, it is equal to $k p_0^n$ where k is the rate constant, p_0 the initial pressure, and n the rate order. Taking the logarithm of both sides of the equation leads to

$$\log R_0 = \log k + n \log p_0$$

A plot of $\log R_0$ vs. $\log p_0$ should yield a straight line with a slope equal to n : Fig. D-2 shows such a plot. Following this procedure, we determined n to be 1.55, which is essentially $3/2$ order over the pressure range from 1 to 10 mm. Hg. From the intercept, we find that $k = 5.26 \times 10^{-4} \text{ mm.}^{-1/2} \text{ sec.}^{-1}$ or $2.2 \times 10^{-1} \text{ liters}^{1/2} \text{ mole}^{-1/2} \text{ sec.}^{-1}$.

The $3/2$ order dependence for the disappearance of diacetylene may be explained in terms of a short chain polymerization of diacetylene brought about by an excited diacetylene molecule. With the procedure of either Flory³⁷ or Laidler³⁸, the following expression is obtained for the photopolymerization of diacetylene:

$$-\frac{d[\text{C}_4\text{H}_2]}{dt} = k_p \left(\frac{I_a}{k_t} \right)^{1/2} [\text{C}_4\text{H}_2]$$

where k_p , k_t , and I_a are the rate constants for polymerization, termination, and light absorption, respectively. Since the extinction coefficient for diacetylene is small and the concentration low, I_a may be written as $I_0 \epsilon M \ell$, where I_0 , ϵ , M , ℓ are the incident intensity, molar extinction coefficient (to base e), concentration, and path length, respectively. Substitution of $I_0 \epsilon M \ell$ into equation D-1 leads to

$$-\frac{d[\text{C}_4\text{H}_2]}{dt} = k_p \sqrt{\frac{I_0 \epsilon \ell}{k_t}} M^{3/2} = KM^{3/2} \quad (\text{D-2})$$

Thus, our data indicates that such a chain mechanism is occurring in the polymerization of diacetylene. Integration of equation D-2 leads to

$$\frac{1}{[\text{C}_4\text{H}_2]^{1/2}} = \frac{k_p}{2} \sqrt{\frac{I_0 \epsilon \ell}{k_t}} t + \text{constant} \quad (\text{D-3})$$

A plot of $1/[\text{C}_4\text{H}_2]^{1/2}$ vs. time should yield a straight line. Fig. D-3 shows such a plot where the slope is constant over the first 10 min. but then decreases because of a decrease in I_0 .

C. REACTION MECHANISM FOR THE DECOMPOSITION OF DIACETYLENE
WHEN IRRADIATED WITH 2537 Å. RADIATION

The following mechanism is postulated to explain the limited experimental results obtained in this particular phase of our study.

<u>Reaction</u>	<u>Rate Constant</u>	
$C_4H_2 + h\nu \rightarrow C_4H_2^*$	I_a	(1)
$C_4H_2^* + C_4H_2 \rightarrow C_4H_2 + C_4H_2$	k_c	(2)
$(C_4H_2)^* + (C_4H_2)_n \rightarrow \text{Polymer}$	k_p	(3)
$C_4H_2^* \rightarrow C_2H_2 + C_2$	k_d	(4)
$C_4H_2 + C_2 \rightarrow C_6H_2$	k_a	(5)

Step (1) is the excitation process where I_a = the absorbed light intensity. Step (2) is the deactivation process, while steps (3), (4), and (5) are the polymerization, decomposition, and addition reactions, respectively. It should be mentioned that n can equal 1 or 2 in the polymerization reaction since the quantum yield for polymerization is approximately 3.

In addition to the above work on the polymerization of diacetylene with 2537 Å. radiation, we have also produced a needle-like crystalline material (length 1-3 mm., diameter < 0.1 mm.). These crystals are formed by photolyzing diacetylene with 1850 Å. radiation, pumping away the remaining gas (C_4H_2 , C_2H_2 , H_2), and adding water to the "Suprasil" tube containing the polymer deposit on the cell walls. Crystals form after the tube is allowed to stand for two days and continue to form for about a week. Infrared spectra of these needles show evidence of C = C, C - H, O - H, Si - O, and Si - H functional groups. These data plus a melting point in excess of 300°C. (limit of melting point block) indicate a reaction between the diacetylene polymer and the silica of the tube to give rise to these crystals. No further work was conducted along these lines.

D. MEASUREMENT OF QUANTUM YIELDS

1. Determination of the Extinction Coefficient for Diacetylene at 2537 Å.

The molar extinction coefficient of diacetylene was determined by measuring the optical density as a function of pressure (1-50 mm. Hg). The transmission through a 20-cm. quartz absorption cell was determined by a 1 P28 photomultiplier connected to a vacuum-tube voltmeter. The same lamp used in the photolysis experiments was used in these measurements with suitable quartz lenses for collimating the light beam. At pressures above 10 mm. Hg, the sample had to be removed and the optical density of the polymer formed on the walls determined and subtracted from the measurement. The value obtained for ϵ , the molar extinction coefficient is (20 ± 4) $\frac{\text{liter}}{\text{mole, cm.}}^*$.

2. Determination of Quantum Yield

a. Determination of Product Yield

The amount of decomposition was determined by measuring the initial and final pressure with a Decker pressure gage. Quantum yield measurements were made for samples which had undergone from 10% to 15% decomposition. The relative amount of gaseous products was determined with a Bendix time-of-flight mass spectrometer.

b. Determination of Quanta Absorbed

The intensity of light absorbed I_a is given by

$$I_a = I_o(1 - e^{-\epsilon Ml})$$

where the symbols have their usual meaning. In our work where the cell length was 20 cm. and the working concentrations on the order of 10^{-5} moles/liter, the exponential is equal to 4×10^{-3} . Thus, the exponential can be expanded and only the first two terms retained, viz., $e^{-\epsilon Ml} = 1 - \epsilon Ml$. With this substitution, $I_a = I_o \epsilon Ml$. The incident intensity I_o was

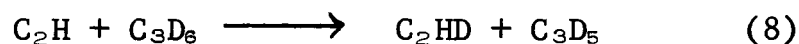
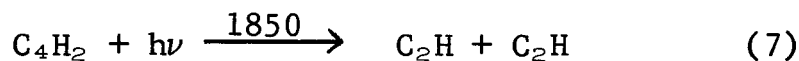
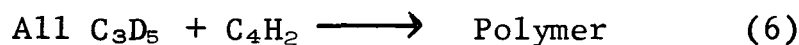
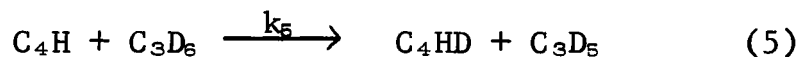
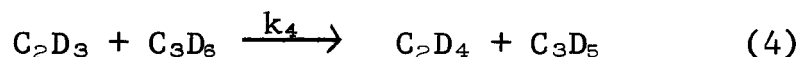
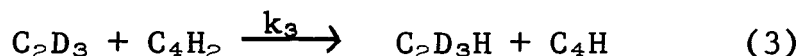
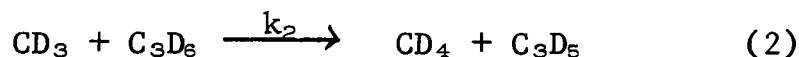
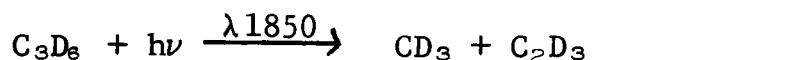
* The value obtained³⁹ in approximately 10^{-3} molar iso-octane is 30 liters/mole-cm.

determined with a thermopile and the concentration M taken as that concentration at completion of one-half of the photolysis. As mentioned previously, I_0 does not remain constant due to absorption by the polymer, and therefore a correction must be made.

The values of quantum yield ϕ for the polymerization of diacetylene and for the formation of acetylene at 1 mm. Hg are 3 ± 1 , and 0.18 ± 0.06 , respectively. The primary source of uncertainty in these measurements is caused by the formation of the opaque polymer on the cell walls; this resulted in a 20% error in the measurement of the extinction coefficient. No dependence of quantum yield on diacetylene pressure could be found between 0.2 to 8 mm. Hg. By taking the ratio of the quantum yield of polymerization to that for decomposition, one arrives at a value of 17 for the ratio of the two rate constants. The quantum yield for disappearance of diacetylene is 3.6 ± 1.2 .

EXHIBIT ETHE REACTION MECHANISM BETWEEN C₄H₂ AND C₃D₆
WHEN IRRADIATED WITH 1850 Å. AND 2537 Å. RADIATION

A gaseous mixture of completely deuterated propylene and diacetylene at a ratio of 1:10 respectively, was placed in a Suprasil tube at a total pressure of 1 mm. The sample was then irradiated for 1 hr. with 1850 Å. and 2537 Å. radiation derived from a special helical-type Pen Ray lamp. Since it has already been demonstrated that no radical reaction can be induced with 2537 Å., only the effect of 1850 Å. will be given. The proposed mechanism is consistent with the experimental results where all of the products listed below have been observed by mass spectrometric analysis of the photolysis products.



Since the bonds broken and formed in reactions 1 and 2 are the same, the ratio of the two rate constants may be calculated from the ratio of the concentrations of CD₃H and CD₄; thus $\frac{k_1}{k_2} = 3.16$. The same reasoning gives $\frac{k_3}{k_4} = 1$.

As mentioned previously, irradiation of diacetylene at 2537 Å. produces acetylene through a molecular elimination reaction. Therefore, when the sample is irradiated with both 2537 Å. and 1850 Å., the ratio of C_2HD to C_2H_2 gives the ratio of rate constants for the production of acetylene by radical-radical reaction as opposed to molecular elimination. We found this ratio to be 15:1 for mixtures of deuterated propylene and diacetylene ranging from 1:10 to 1:1, respectively. It should be noted that the same results were obtained in flash photolysis.

EXHIBIT FTHE OSCILLATOR STRENGTH OF THE CN RED SYSTEM*

BY

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The red system of CN ($A \ ^2\pi \leftrightarrow X \ ^2\Sigma^+$) is one of the prominent spectral features of comets and stars, including the sun.^{F1} The CN radical probably plays a significant role in many chemical reactions yielding important nitrile-substituted industrial products. A determination of the oscillator strength of this transition would permit calculations of the concentration of this radical from the observed intensity in emission (comets and stars) and absorption (chemical reactions). Until very recently, no experimental determination of this number was available.

The present study was undertaken simultaneously and independently of recent work by Wentink, Isaacson, and Morreal^{F2} (WIM). A method similar in principle was used here: the determination of the radiative lifetime of the $A \ ^2\pi$ level. However, the present results are free from two sources of uncertainty which, as pointed out by WIM, could (and do, in fact) affect their number: the dependence on vibration of the electronic transition moment R_e , and collision quenching, which competes with spontaneous radiation to depopulate the excited level.^{F3} The experimental technique has been described elsewhere.^{F3} An electrodeless discharge, which lasts for a time very short in comparison with the lifetime to be measured, is triggered in the gas investigated (acetonitrile in this case). The fluorescence decay is displayed on an oscilloscope screen and photographed.

Individual vibronic bands of the CN red system were separated using a Bausch and Lomb No. 33-86-25 grating monochromator. The band pass was about 20 Å. Photomultipliers

* This work was supported in part by the National Aeronautics and Space Administration, Contract No. NASw-707

having S-1 (RCA C70007) and S-20 (EMI 9558) sensitivities were used with a cathode follower probe attached directly to the anodes.

The CN red spectrum was obtained by scanning the monochromator under the same conditions used in making the lifetime measurements. The relative intensities of the various vibronic bands were similar to those indicated in the literature.^{F4}

The oscillator strength $f_{0,0}$ for the transition $A^2\pi(v' = 0) \leftarrow X^2\Sigma^+(v'' = 0)$ is related to the lifetimes $\tau_{v'}$ of the various vibronic levels of the $A^2\pi$ state by

$$f_{0,0} = \left(\frac{1}{\tau_{v'}}\right) \cdot \frac{G'}{G''} \cdot \left(\frac{mc}{8\pi^2 e^2}\right) \cdot \frac{\nu_{0,0} q_{0,0} R_{0,0}^2}{\sum_{v''} \nu_{v',v''}^3 q_{v',v''} R_{v',v''}^2} \quad (F-1)$$

where G'/G'' is the ratio of the degeneracies of the two states, as defined by Mulliken^{F5}, $\nu_{v',v''}$ are the mean frequencies of the various vibronic transitions, $q_{v',v''}$ are the Franck-Condon factors, and $R_{v',v''}^2$ is the electronic transition moment which is assumed to be slightly vibration-dependent so that

$$R_{v',v''} = R_{0,0} (1 + \alpha[r_{v',v''} - r_{0,0}] + \dots) \quad (F-2)$$

$r_{v',v''}$ being the r-centroid values. Placing (F-2) into (F-1), one obtains a number of relations of the type

$$K = \tau_{v'} (A_{v'} + B_{v'} \alpha + C_{v'} \alpha^2)$$

where $A_{v'}$, $B_{v'}$, and $C_{v'}$ are

$$\sum_{v''} \nu_{v',v''}^3 q_{v',v''}, \quad \sum_{v''} \nu_{v',v''}^3 q_{v',v''} [r_{v',v''} - r_{0,0}],$$

and $\sum_{v''} \nu_{v',v''}^3 q_{v',v''} (r_{v',v''} - r_{0,0})^2$, respectively, and were

calculated with Nicholls'^{F6} Franck-Condon factors and r-centroid values, and $K = \text{const.}/f_{0,0}$. The experimental values of the lifetimes $\tau_{v'}$ are listed in Table F-I and represent extrapolation to zero acetonitrile pressure (measurement range: 5 to 100 microns Hg). Plotting K over α , one obtains a series of

parabolas, one for each τ_v value, which should all intersect at the same point. The abscissa and ordinate of that point then give the actual values of α and K . Figure F-1 shows the intersection of 18 such parabolas, each corresponding to one of the extremes of the uncertainty ranges for each lifetime value. The best fit is obtained for $f_{0,0} = (3.4 \pm 0.3)10^{-3}$ and $\alpha = 1.9 \pm 0.2$ ($r_{v,v}$ are expressed in 0,0 Angstrom units).

This oscillator-strength value is very close to the figure reported by WIM. However, the agreement is misleading because they have defined "f value" as $f_{0,0}(G''/G')$ or $f_{0,0}/2$, which is in contradiction with widely accepted terminology^{F1,5}, or have overlooked the degeneracy factor G' . Our value should be compared with a figure of $7.4 \times 10^{-3} G''$ calculated from WIM's reported lifetime.

Spectroscopic investigations were also made using a pulsed r.-f. discharge (100 Mc.) in acetonitrile with a duty cycle comparable with that used by WIM. It was found that a heavy flow of gas was necessary to obtain a CN spectrum. When the flow is too slow or in a closed system, the acetonitrile polymerizes rapidly giving up hydrogen, and the predominant spectral feature is the H_2 many-line spectrum. It is clear that this r.-f. discharge, whose properties must be comparable to WIM's, decomposes gases much more than the single-shot electrodeless discharge used for the present lifetime measurements. It has been shown previously^{F3} that spectra of benzene and formaldehyde can be observed following a single-shot electrodeless discharge while these compounds are heavily decomposed by the r.-f. discharge. WIM do not present any spectroscopic evidence and are presumably working with a stationary pressure of acetonitrile. It is possible that the production of the H_2 many-line spectrum (which extends with high intensity as far as $11,222 \text{ \AA.}$)^{F7} did affect their results, since quite a heavy gas flow is necessary to avoid it. If WIM's results concern the CN red system, the discrepancy with our results can be explained by collision quenching. WIM's indication of no pressure dependence of the lifetime in the range 0.2 to 2 mm. can be explained by the occurrence of complicated quenching and trapping. It has been observed previously in a number of cases in this Laboratory that, at pressures above about 100 microns, the Stern-Volmer

mechanism ceases to describe the quenching and that the pressure dependence of the decay constant tends to disappear or even to be inverted. R. P. Schwenker^{F8} of this Laboratory has recently studied the CN red system^{F8} at a pressure of about 3 microns of acetonitrile. Using Bennett and Dalby's apparatus^{F9} with a band pass which included the (6,2), (7,3), and (8,4) vibronic bands, he obtained a result of $(1/\tau) = (1.54 \pm 0.05)10^5 \text{ sec.}^{-1}$, which is within 1% of ours (Table F-I). [The (8,4) band is very much weaker than the (6,2) and (7,3) bands and did not contribute significantly.] A value of $f_{0,0} = 3.4 \times 10^{-3}$ is thus recommended for the CN red system. To avoid confusion, it is suggested that the term "oscillator strength" should refer only to the quantity defined in equation (F-1), which is equivalent to Mulliken's formulation.^{F5}

TABLE F-I

Decay Constants ($\equiv 1/\tau_{v'}$) for Various Vibronic Levels of the A $^2\Pi$ State of CN (Units = 10^5 sec.^{-1})

$v' = 1$	$(1.371 \pm 0.029)^*$
$v' = 2$	1.419 ± 0.056
$v' = 3$	1.439 ± 0.064
$v' = 4$	1.519 ± 0.078
$v' = 5$	1.351 ± 0.074
$v' = 6$	1.549 ± 0.091
$v' = 7$	1.542 ± 0.052
$v' = 8$	1.448 ± 0.076
$v' = 9$	1.556 ± 0.056

* The uncertainty ranges were determined from a least-squares computation involving about 30 measurements per level v' . The values are an extrapolation to zero pressure assuming a linear dependence of the decay constant with pressure (Stern-Volmer mechanism).

emf

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EXHIBIT G

*TRANSITION PROBABILITY
OF ${}^2\pi_u \rightarrow X {}^2\pi_g$ SYSTEM OF CO_2^+

By

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A spectrum previously identified as being due to the ${}^2\pi_u \rightarrow X {}^2\pi_g$ transition of CO_2^+ by Mrozowski^{G1} is observed when CO_2^+ is bombarded by 200-v. electrons. The lifetime of the ${}^2\pi_u$ state of CO_2^+ was measured with the experimental method of Bennett and Dalby.^{G2} Using a photomultiplier tube with an S-11 response in conjunction with a Corning C. S. No. 7-54 filter, we measured a mean radiative lifetime of $(13.9 \pm 1.0) \times 10^{-8}$ sec. for the ${}^2\pi_u$ state. The measured lifetimes remained within experimental error for pressures of CO_2 from 0.3 to 30 μ .

Lifetimes were measured at various points in the emission spectrum by means of interference filters and a monochromator. The results of these measurements gave a constant value, within the quoted error limits, for the product of the transition probability ($1/\tau$) and the square of the wavelength. Also, there was no observable deviation from exponential decay for these data. Both of these observations are consistent with the electronic dipole moment, being independent of vibrational level, although this could not be established with certainty because of the high degree of mixing of various transitions in the emission of CO_2^+ .

Using the measured data, we calculated an oscillator strength of $(1.18 \pm 0.1) \times 10^{-2}$ for the system. There are

* This work was supported by the National Aeronautics and Space Administration, Contract No. NASw-707.

no other transitions known that compete with the observed transition for depopulation of the upper electronic state.

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EXHIBIT HEXPERIMENTAL OSCILLATOR STRENGTHS OF CO AND CO⁺ *

By

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ABSTRACT

The radiative lifetimes of the B ²Σ state of CO⁺ and the b ³Σ state of CO have been measured to be $(1.01 \pm .03) \times 10^{-7}$ and $(8.6 \pm 0.9) \times 10^{-8}$ sec., respectively. The oscillator strengths on the first negative system of CO⁺ and third positive system of CO, calculated from these lifetimes, are $(7.9 \pm 0.7) \times 10^{-3}$ and $(8.9 \pm 1.5) \times 10^{-3}$, respectively.

INTRODUCTION

A previous paper from this Laboratory^{H1} reported measurement of the comet-tail system of CO⁺. This paper reports measurements of the oscillator strengths of the first negative system of CO⁺ and the third positive system of CO. The reported oscillator strengths were determined by a direct measurement of the spontaneous radiative lifetime of the upper electronic states of interest. These states were obtained by electron bombardment of CO. The experimental method and relevant theory have[†] been described in an earlier paper on the f-value of the N₂⁺ first negative system.^{H2} An analysis of the calculation of quenching cross sections has been described in another paper^{H3} on the oscillator strength of the violet system of OH.

* This work was supported by the National Aeronautics and Space Administration, Contract No. NASw-707

RESULTS

The emission spectrum resulting from the bombardment of CO at a pressure of 5 μ . by 200-volt electrons is shown in Fig. H-1. The spectroscopic plate of the emission was obtained with a Hilger medium quartz spectrograph. Analysis of the spectrum indicates the presence of three prominent systems: the comet tail and first negative systems of CO⁺ and the third positive system of CO.

For measuring the radiative lifetimes of the latter two systems, a pulse of 200-volt electrons of 0.2- μ sec. duration was used for excitation, and a photomultiplier "gate" of approximately 5×10^{-8} sec. was used for time resolution of the emission. The resolving time of this combination of excitation pulse and photomultiplier gate was determined to be approximately 5×10^{-8} sec. by measuring the apparent lifetime of the 3 'P - 2 'S transition (5016 Å.) of He at a pressure of 1 μ . The actual lifetime of the 3 'P level is less than 10^{-8} sec. at 1- μ pressure.^{H4}

In measuring the radiative lifetime of the B state of CO⁺, a Dumont Type 1688 photomultiplier, with an S-23 spectral response, was used to view the spectral region of 2000-2800 Å. For measuring the b state of CO, a Dumont Type 7664 photomultiplier, with an S-13 spectral response, was used with two Corning filters (C.S. No. 0-53, 7-54) and an aqueous solution of NiSO₄, the combined filters having a maximum transmission at 3200 Å. with a width of 400 Å. at half-maximum transmission.

The apparent radiative lifetimes of both systems were found to be dependent upon the pressure of the CO. Plots of apparent radiative transition probabilities as a function of CO pressure are given in Figures H-2 and H-3. Pressure was measured with an Alphatron gauge.

Using the data of Figures H-2 and H-3, we calculated the oscillator strengths of the B ² Σ $\rightarrow$ X ² Σ transition of CO⁺ and the b ³ Σ $\rightarrow$ a ³ π transition of CO. Also, the quenching cross sections of CO⁺ with respect to electronically excited states of CO and CO⁺ were derived.

The lifetime of the B $^2\Sigma$ levels of CO⁺ extrapolated to zero pressure is $(1.01 \pm 0.03) 10^{-7}$ sec. Using this lifetime and a mean frequency corresponding to 2300 Å., we calculate an oscillator strength of $(7.9 \pm 0.7) 10^{-3}$ where the error limits have been increased to include the uncertainty in λ .

The determined lifetime for the b $^3\Sigma$ ($\nu' = 0$) level of CO at zero pressure is $(8.6 \pm 0.9) 10^{-8}$ sec., corresponding to an oscillator strength of $(8.9 \pm 1.5) \times 10^{-3}$, ($\lambda = 3200$ Å. and $d_n/d_m = 1/2$, where d_n and d_m represent the degeneracy of the upper and lower states, respectively).

The calculated quenching cross sections for CO are:

$$\begin{aligned} Q &= (150 \pm 20) 10^{-15} \text{ cm.}^2 && [\text{B } ^2\Sigma \text{ level of CO}^+] \\ &= (23 \pm 4) 10^{-15} \text{ cm.}^2 && [\text{b } ^3\Sigma \text{ level of CO}] \end{aligned}$$

DISCUSSION

The calculated oscillator strength for the B $^2\Sigma \rightarrow X$ $^2\Sigma$ transition includes contributions of unestablished weights from various vibrational transitions. The Baldet-Johnson system (B $^2\Sigma \rightarrow A$ $^2\Pi$) competes with the first negative system for the depopulation of the B $^2\Sigma$ levels, but the emission of this system is sufficiently weak that the radiative lifetime of the level is assumed to be determined only by the first negative system.

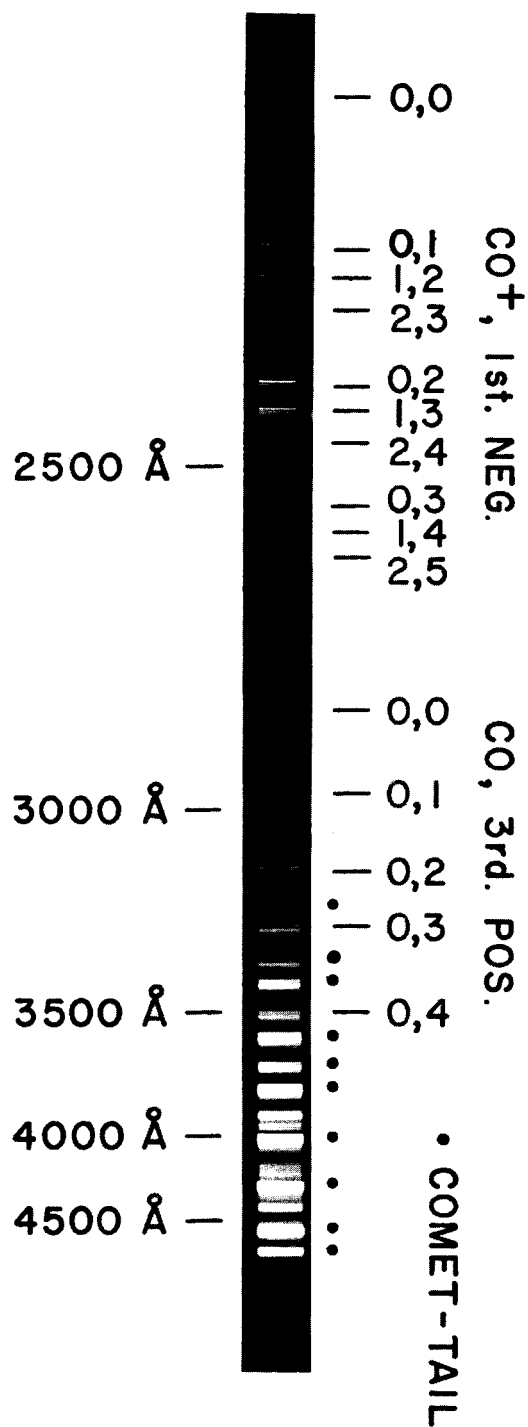
For the b $^3\Sigma \rightarrow a$ $^3\Pi$ transitions, the oscillator strength calculations are based on the combined transition probabilities for the (0,2) and the (0,3) vibrational transitions. There are no known transitions that compete significantly with the third positive system for depopulation of the b $^3\Sigma$ level of CO. Although the b-d transitions might compete, since no emission is observed which corresponds to these transitions, it was concluded that the lifetime of the b $^3\Sigma$ level of CO is dependent only on the transition probability of the b-a transitions.

The uncertainty of the oscillator strength of the CO^+ first negative system is assigned based on an estimate of systematic experimental error, since the standard deviation of the data was less than 2%. The uncertainty in the oscillator strength of the CO third positive system is due to the statistical deviation of the data. The emission of this system was rather weak and difficult to separate from the two CO^+ systems.

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FIGURE H-1



EMISSION SPECTRUM OBSERVED WHEN CO AT 5 μ PRESSURE
IS BOMBARDED WITH 200-v ELECTRONS

EXHIBIT IFOCUSED LASER-BEAM EXPERIMENT AND THE OSCILLATOR
STRENGTH OF THE SWAN SYSTEM*

By

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It has been shown previously by Howe¹¹ that the Swan emission of C_2 can be excited by focusing a laser beam on graphite in air. Chupka and Berkowitz¹² recently analyzed with a mass spectrometer the species formed and showed that their relative concentrations are comparable with what is observed in thermodynamic equilibrium at about $4000^\circ K.$, C_2 being the major constituent.

The present work consists in focusing the beam from a "Q spoiled" ruby laser near a graphite block maintained in a high vacuum and analyzing the light output spectroscopically with time resolution.

The laser apparatus is a Raytheon LHM 6 (11,000-j. pumping energy, $3/4$ in. diam., $6\ 1/4$ in. long ruby rod). "Q spoiling" is provided at various delays from the pumping flash by a rotating prism. The laser output consists of about 6 spikes of comparable intensity and occurring within $2\ \mu sec.$ with a total energy of approximately 5 j. The laser light was filtered (Corning No. 2-59) and focused with a 6-cm. lens on a piece of spectroscopic-quality graphite of $1/2$ in. diam. A Pyrex window perpendicular to the laser beam permits observation of the light emission from the "fireball" at the focus on the graphite surface. This emission was photographed between 3600 and $6000\ \text{\AA}.$ with a medium Hilger spectrograph with glass optics and was time resolved using a Dumont 6292 phototube and a Tektronik 545 oscilloscope after passing

* Work supported in part by the National Aeronautics and Space Administration, Contract No. NASw-707

through a 500-mm. model Bausch and Lomb monochromator (6 Å. band width). Both measurements were done with the laser beam focused at various distances from the carbon surface. When the focus is exactly on the carbon, the spectrum consists entirely of lines of C^+ superimposed on a weak continuum and is very similar to the carbon spark spectrum (Table I-I). When the focus is moved away from the carbon, the first bands detectable are the so-called "high-pressure" bands. At larger distances, the intensity of the high-pressure bands diminishes, whereas the Swan emission increases, goes through a maximum (when the focus is at about 7 mm. from the carbon block), and disappears. Four sequences were observed with intensity distribution close to that of the carbon-arc spectrum.

The light emitted as continuum follows the laser spikes with decays close to 50 nanoseconds. The emission in the Swan region presents the same features followed by a much slower decay. Those results are interpreted as being due to thermal excitation. When the beam is focused on the carbon surface, the temperature of the plasma formed is so high that the only species present are C^+ and C . When the focus is moved off the surface, the temperature diminishes. The high-pressure bands are first produced through inverse predissociation.¹³ At still lower temperature, the concentration of atoms becomes weaker and the intensity of the Swan bands increases. No measurement of the temperature of the vapor has been attempted. A strange result is the absence of the comet head system of C_2 , C_3 being expected to be the predominant species.¹² The slow decay observed for the Swan bands is interpreted as being the fluorescence decay. The decay time constant would be the lifetime of the $A^3\pi_g$ state of C_2 in the absence of competitive first-order processes. Since the pressure at the point of impact is probably quite high, quenching by collision is possible. Our lifetime figures, presented in Table I-II for individual vibrational levels, would in that case be lower limits, the calculated oscillator strength of the transition being an upper limit.

The variation of the transition moment R_e from one vibronic level to the other was investigated in the following way.¹⁴

A dependence

$$R_c(r) = R_e(r_{o,o}) [1 + k(r-r_{o,o})] \quad (1)$$

was postulated, r being the r -centroid of the transition. Four equations relating our lifetime values $\tau(v')$ to the oscillator strength $f(o,o)$ of the (o,o) transition were obtained with k as the parameter. Values of the Franck-Condon factors and r -centroid are from Nicholls.¹⁵ The values of k and $f(o,o)$ which fit our results best are

$$k = 0.8 \pm 0.2 \text{ and } f(o,o) = (4.33 \pm 0.12) 10^{-3}$$

Figures I-1, a and b, are those published by Nicholls on the basis of King's results¹⁶ and on which the lines represent our experimentally determined function $R_e(r)$. It is seen that the agreement is much better with King's original data without rescaling. It is possible that the application Nicholls made of his rescaling procedure¹⁷ might have led to erroneous dependences $R_e(r)$ for other systems.

Table I-IV shows that our value for the oscillator strength compares very well with the only reliable experimental data available, those of L. G. Hagan.¹⁸ Theoretical values are higher by factors from 3 to 50.

Future planned work includes: (1) a thorough study of the variation of the lifetime with the amount of carbon evaporated every shot to determine the influence of collision quenching. (Preliminary results in that respect are negative, no measurable variation of the lifetime.) (2) measurements of the same lifetime under very different conditions - pulsed discharges in noble gases, exploding layer of carbon; and (3) measurements on other transitions of C_2 .

The authors wish to thank Drs. E. Abramson and J. C. Caris of Du Pont's Central Research Department for the use of the laser.

TABLE I-I

<u>λ</u>	<u>Laser*</u>	<u>Spark</u>
6098.62 (II)	w	30
5891.65 (II)	m	30
5889.97 (II)		60
5662.51 (II)	w	50
5648.08 (II)	w	30
5380.24 (I)	-	(300)
5259.62 (II)	vw	30
5151.08 (II)	ms	30
5145.16 (II)		70
5052.12 (I)	?	(100)
5041.66 (I)	-	(30)
4932.00 (I)	vw	40
4618.85 (II)	w	25
4411.52 (II)	m	40
4411.20 (II)		40
4410.06	m	30
4374.28 (II)		40
4372.49 (II)	m	30
4371.33 (I)		30
4348.07	?	30
4317.42 (II)	?	30
4267.27 (II)	vs	500
4267.02 (II)		350
4076.00 (II)	ms	80
4074.89 (II)		40
4074.53 (II)	ms	50
3920.62 (II)		200
3918.98 (II)	ms	80
3876.67 (II)		40
3876.41 (II)		60
3876.19 (II)		125
3876.05 (II)		40

* Intensity Scale = ?, vvw, vw, w, m, ms, s, vs

emf

TABLE I-II

Measured Lifetimes of Individual Vibrational Levels
of the A $^3\pi_g$ State of C₂

$v' = 0$	7.78×10^{-7} sec.
$v' = 1$	6.93×10^{-7} sec.
$v' = 2$	6.41×10^{-7} sec.
$v' = 3$	6.29×10^{-7} sec.

TABLE I-III

Calculated Oscillator Strength $f(o,o)$ Assuming
Various Dependences of $R_e(r)$

	(1)	(2)	(3)
(a)	4.10×10^{-3}	4.12×10^{-3}	4.22×10^{-3}
(b)	4.43×10^{-3}	4.44×10^{-3}	4.41×10^{-3}
(c)	4.67×10^{-3}	4.67×10^{-3}	4.38×10^{-3}
(d)	4.89×10^{-3}	4.86×10^{-3}	4.31×10^{-3}
			<u>(4.33 ± 0.12)</u>

a, b, c, d = Using the lifetime of levels $v' = 0, 1, 2, 3$, respectively.

(1) = Assuming $R_e = \text{Const.}$

(2) = Assuming $R_e = \text{Const.} (1 + 0.056 r)$
r being the r-centroid value in Angstrom
units.

(3) = Assuming $R_e = R_{o,o} [1 + 0.8(r - r_{o,o})]$

emf

TABLE I-IV

Experimental and Theoretical Values for the Oscillator Strength
 $f(o,o)$ of the o-o band of the $A \ ^3\pi_g - X \ ^3\pi_g$ Transition in C_2

Lyddane, et al. ⁹	0.024
Shephenson ¹⁰	0.029
Shull ¹¹	0.13
Coulson, et al. ¹²	0.24
Clementi ¹³	0.0485
Hagan ⁸ *	0.005 ± 0.003
This work*	0.00433 ± 0.00012

* Only the last two values are experimental.

emf

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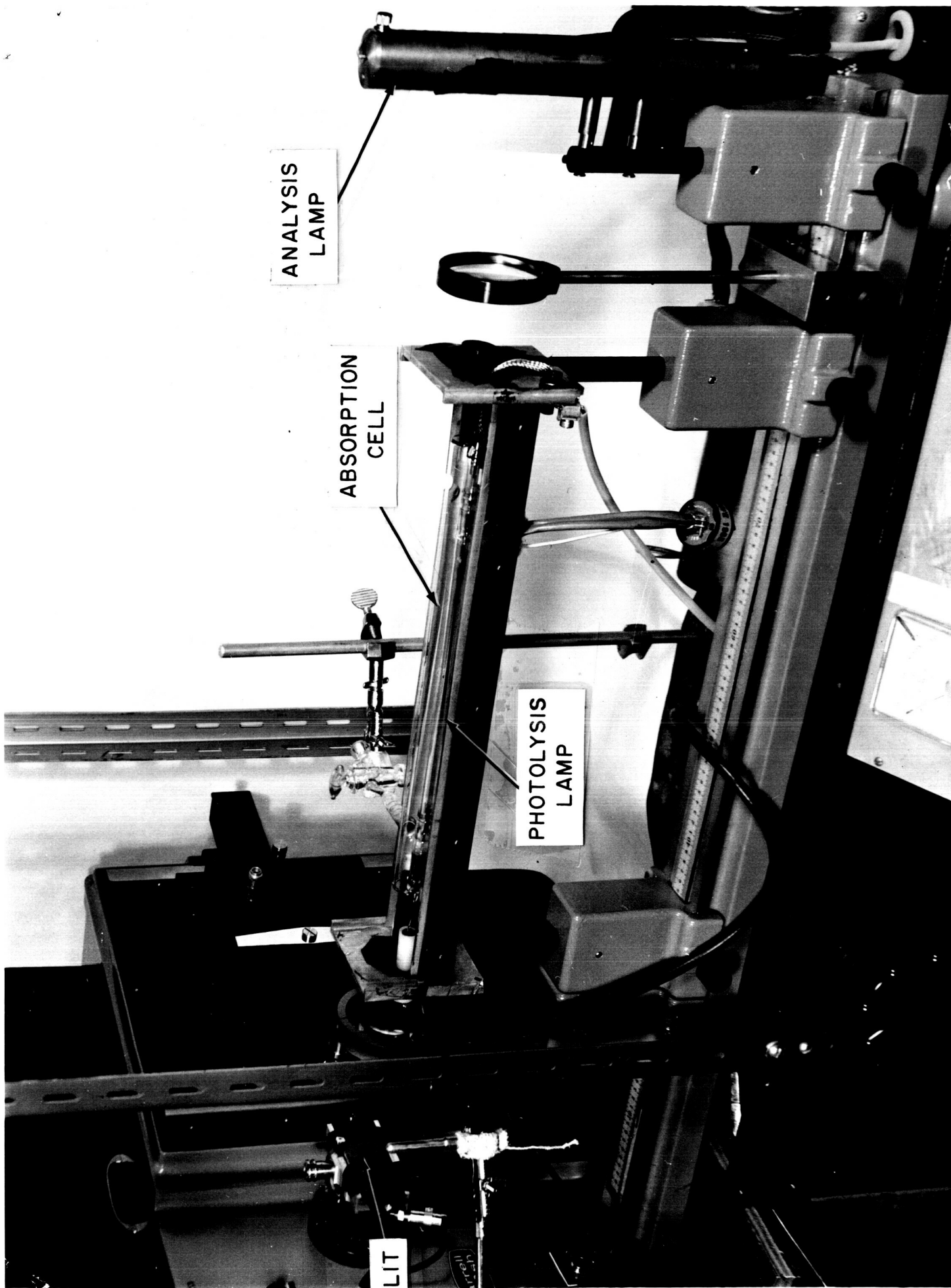
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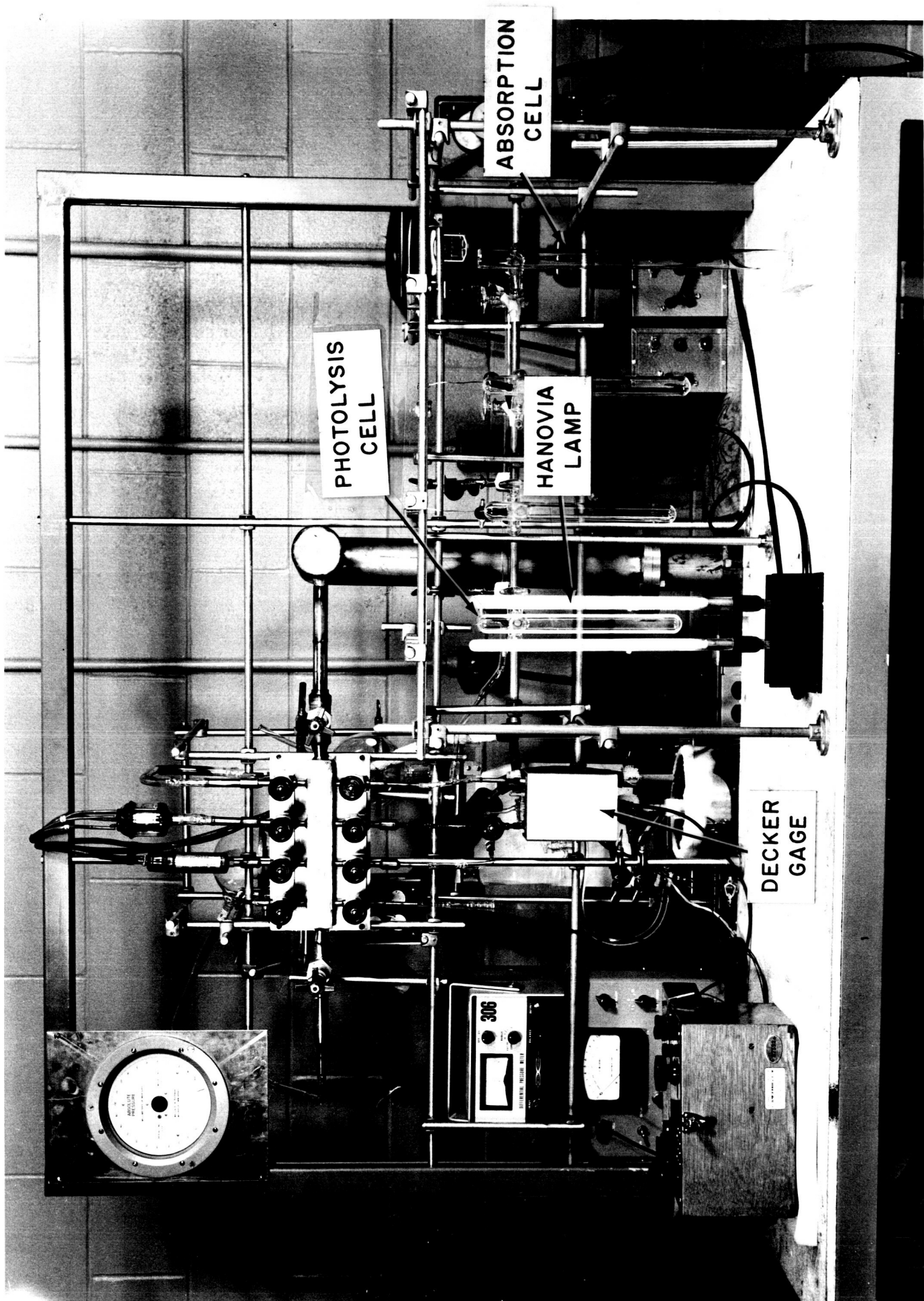


ANALYSIS
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ABSORPTION
CELL

PHOTOLYSIS
LAMP

SLIT



PHOTOLYSIS
CELL

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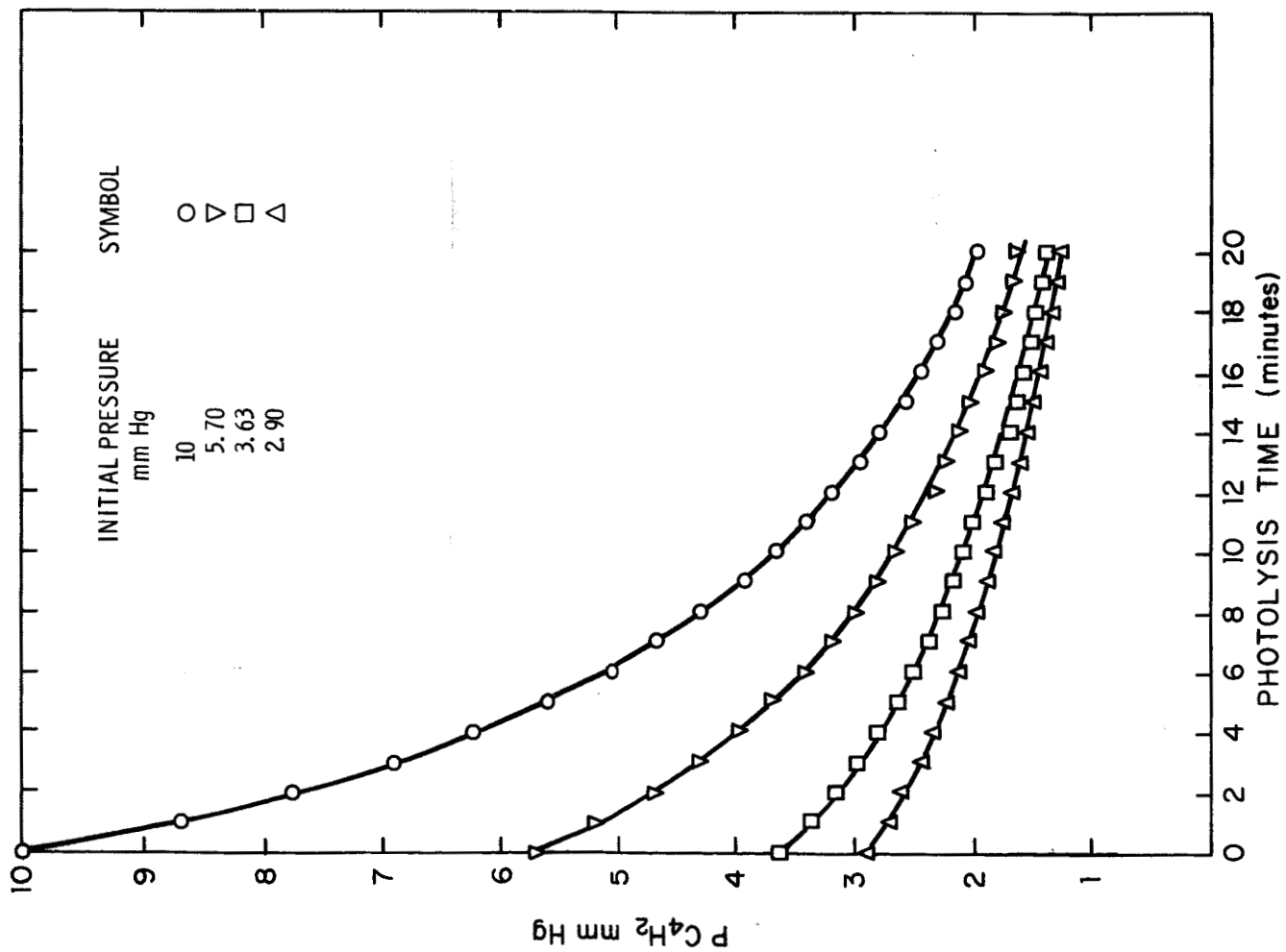
ABSORPTION
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DECKER
GAGE

306
DECKER TUBE METER



FIGURE D-1



DECOMPOSITION OF DIACETYLENE vs. TIME

FIGURE D-2

D-8

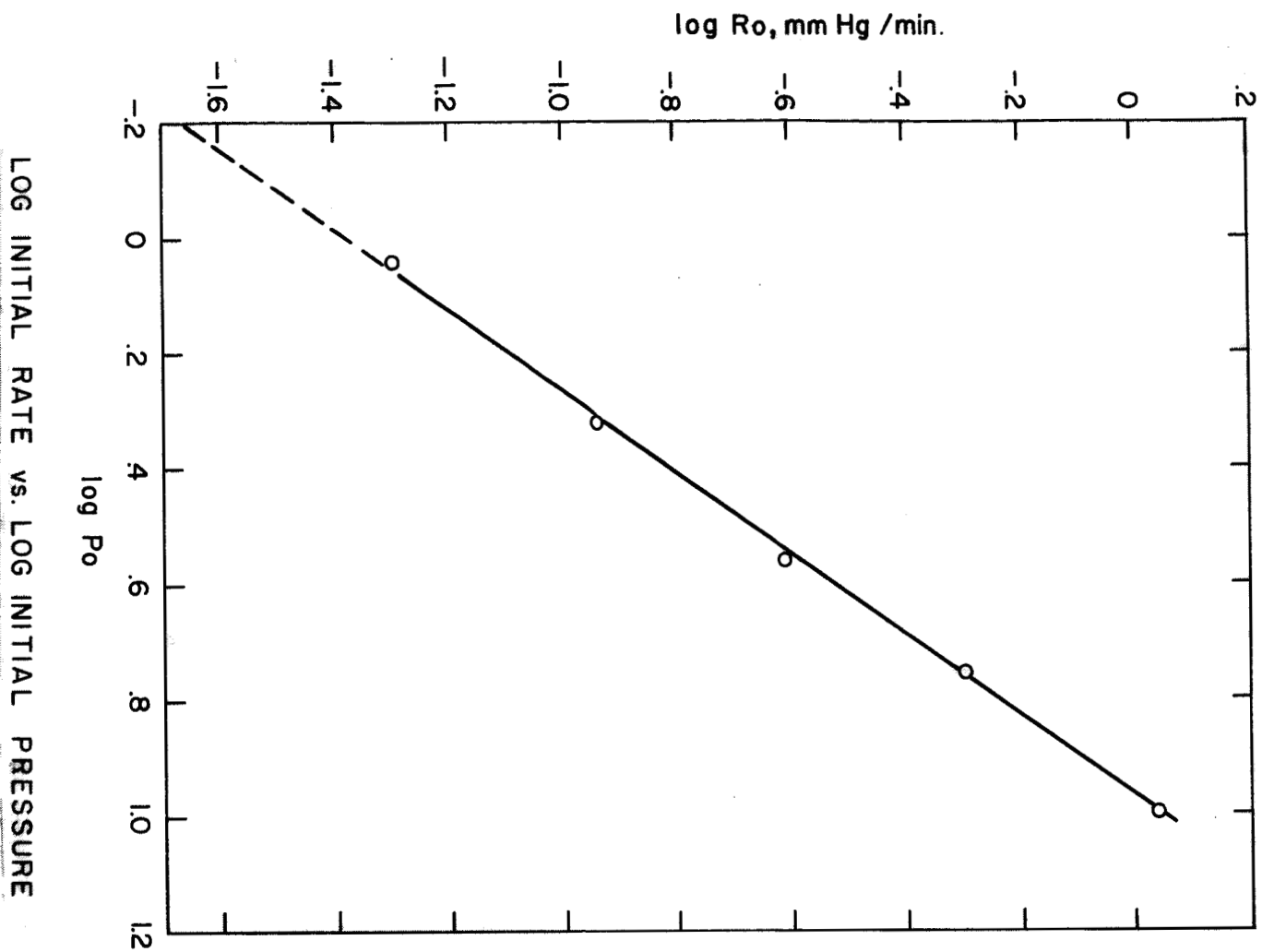
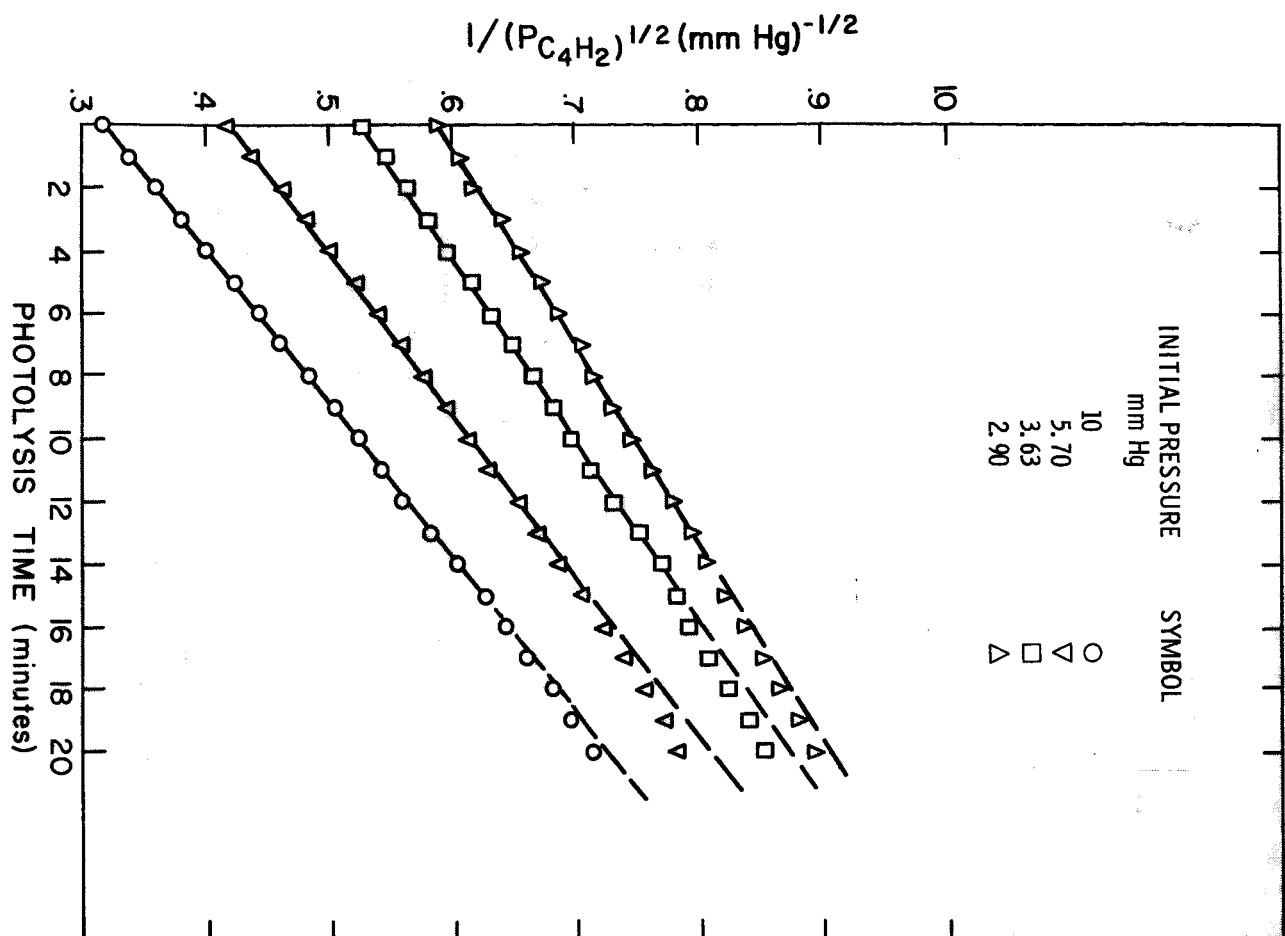
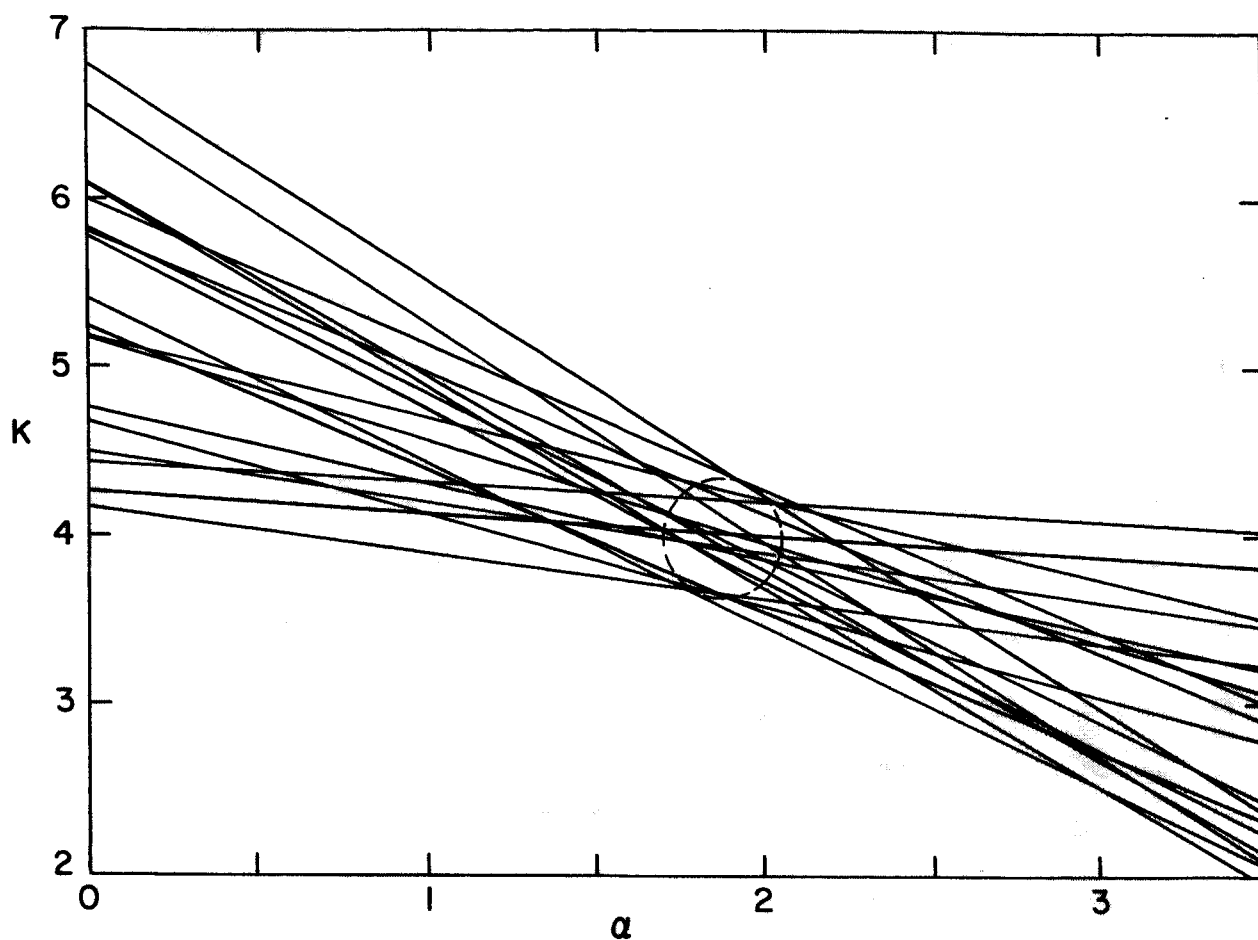


FIGURE D-3

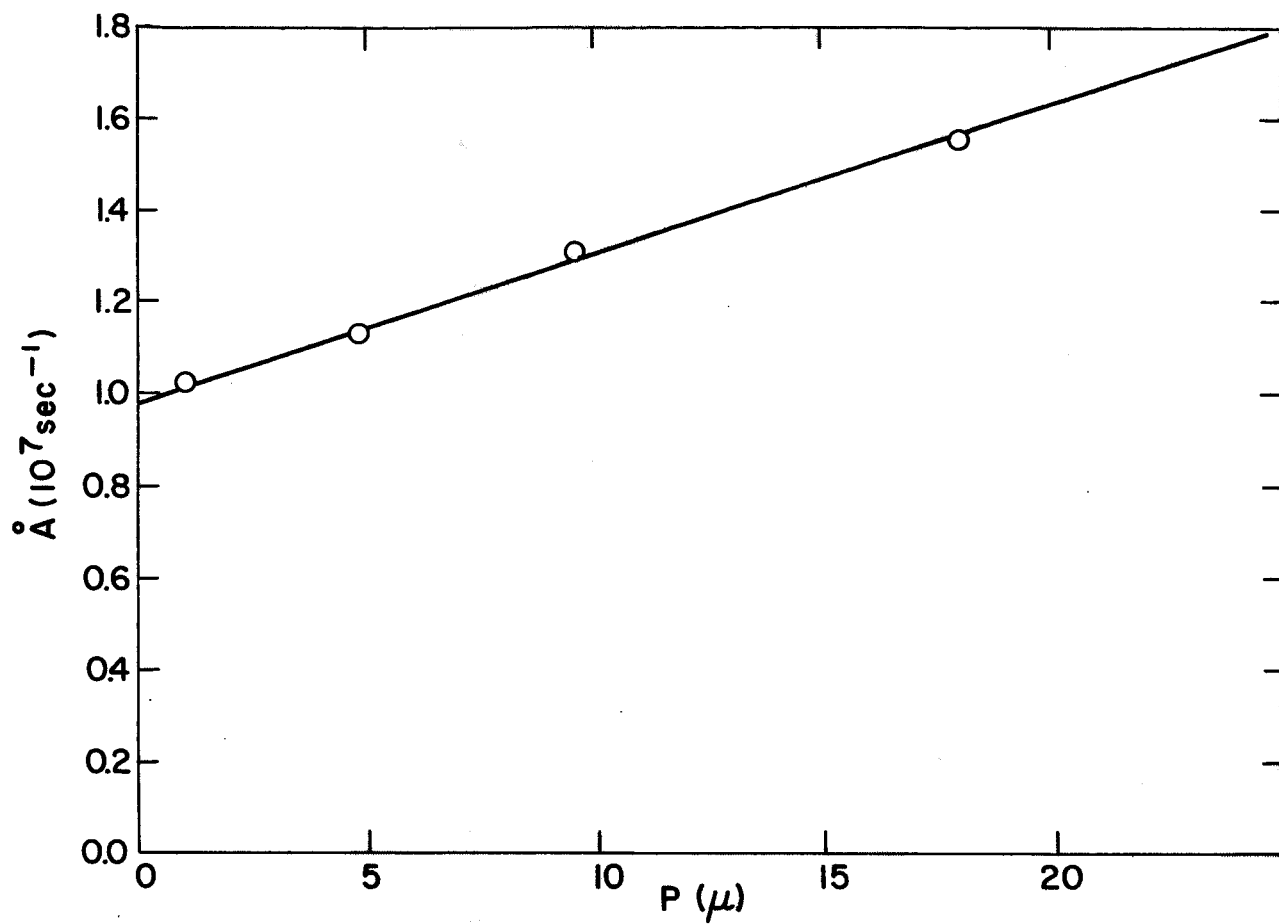


DECOMPOSITION OF DIACETYLENE vs. TIME

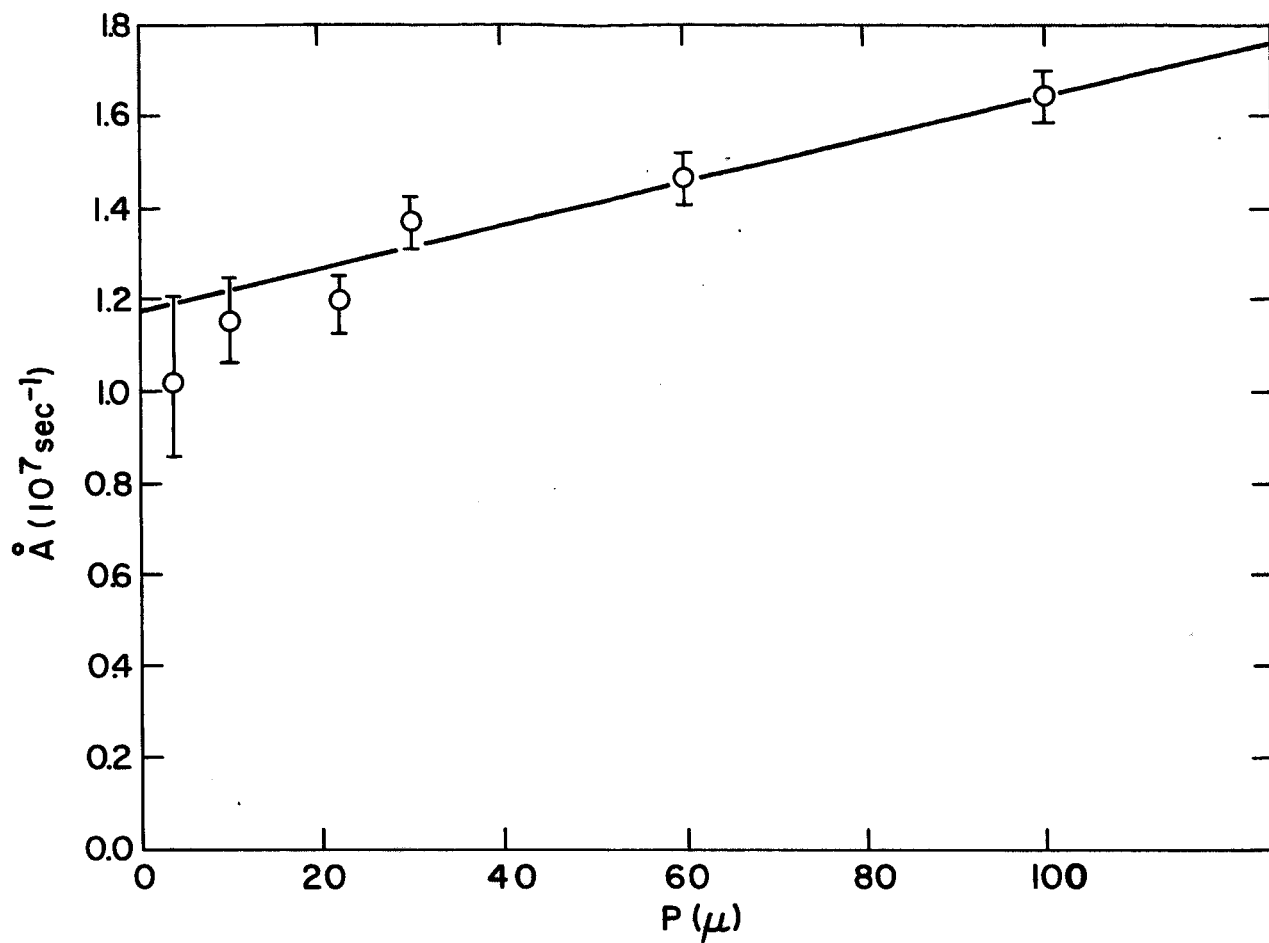
FIGURE F-1



SIMULTANEOUS DETERMINATION OF OSCILLATOR STRENGTH OF THE CN RED SYSTEM AND
COEFFICIENT DESCRIBING VARIATION OF THE TRANSITION MOMENT WITH THE r -CENTROID
VALUE (SEE EQUATION F-2)



APPARENT TRANSITION PROBABILITY OF THE B $\rightarrow$ X SYSTEM OF CO⁺ VS. CO PRESSURE



APPARENT TRANSITION PROBABILITY OF THE $b \rightarrow a$ SYSTEM OF CO VS. CO PRESSURE

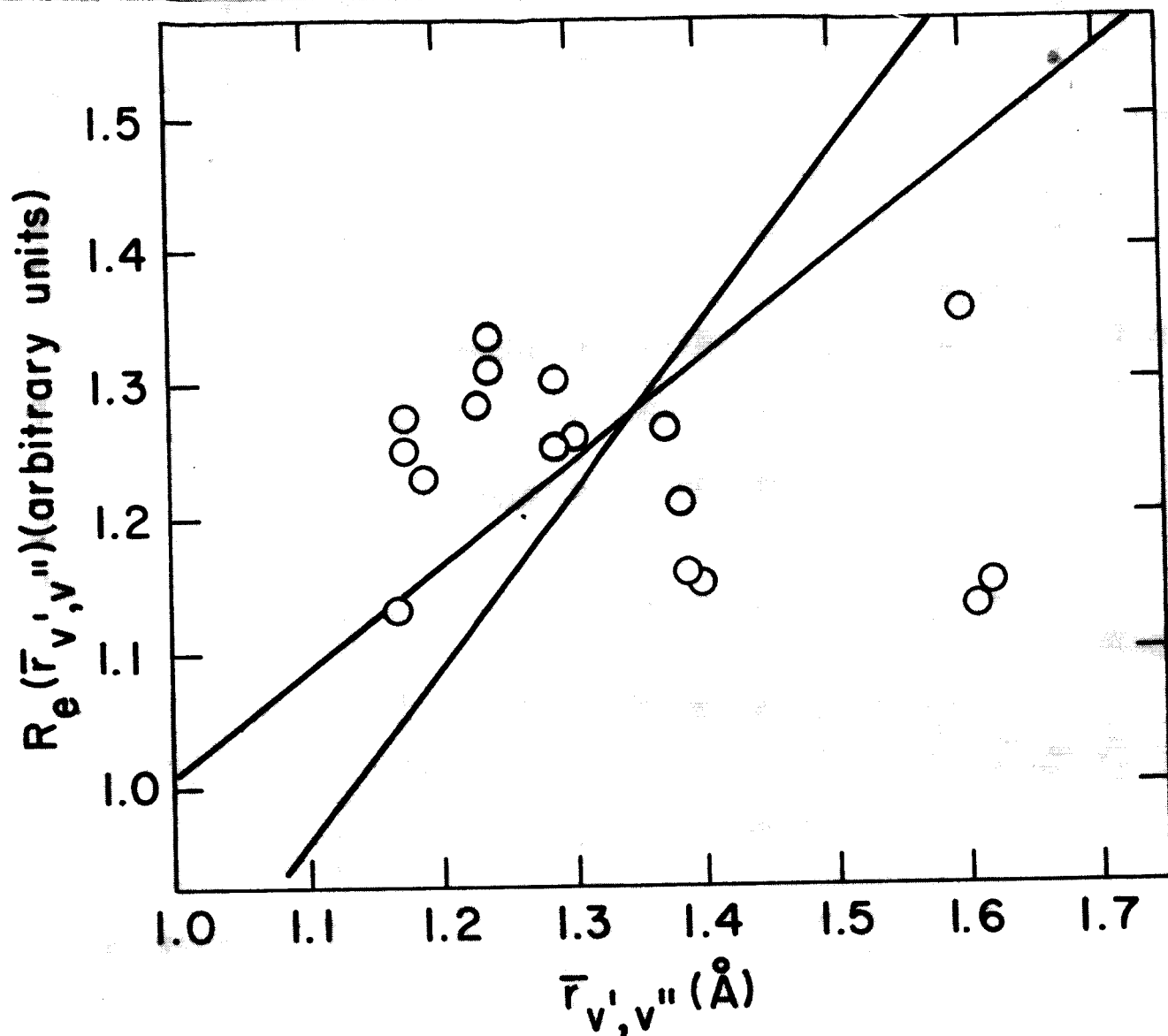


FIGURE I-1 (B)

VARIATION OF THE ELECTRONIC TRANSITION MOMENT
WITH INTERNUCLEAR DISTANCE FOR THE SWAN SYSTEM

(A) From King's original data^{I6}; (B) After rescaling^{I5,7}
The lines represent our experimental dependence
(Eq. I1 and I2).

2

FIGURE I-1

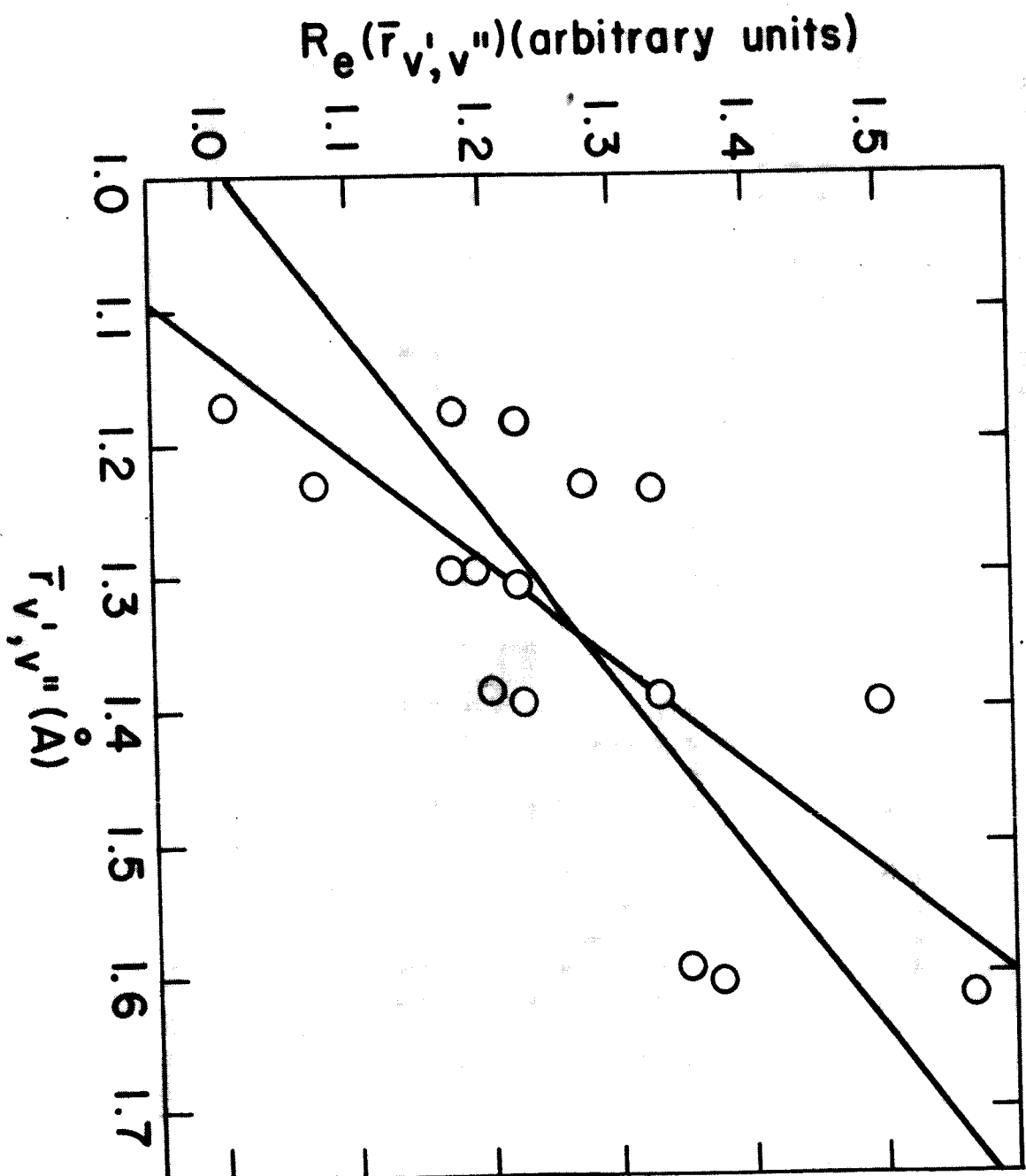


FIGURE I-1 (A)