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**THE PHOTOLYSIS OF BIACETYL SOLUTIONS**

by

**Stanley A. <sup>Arthur</sup> Greenberg**

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**A Dissertation**

**Submitted to the Faculty of the**

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**DOCTOR OF PHILOSOPHY**

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**1960**

THE UNIVERSITY OF ARIZONA

GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my  
direction by Stanley A. Greenberg  
entitled THE PHOTOLYSIS OF BIACETYL SOLUTIONS

be accepted as fulfilling the dissertation requirement of the  
degree of DOCTOR OF PHILOSOPHY

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In Nature's infinite book of secrecy

A little can I read.

SHAKESPEARE, Antony and Cleopatra

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## INTRODUCTION

One of the main objectives of photochemical research is to increase the understanding of the processes which occur between the absorption of a photon by a molecule and the decomposition or reversion of that entity to its original state. The energy absorbed may be degraded as fluorescence or phosphorescence, thermal energy of the surroundings or kinetic and vibrational energy of the fragments of dissociation.

The two most useful approaches to the study of primary processes are investigations of luminescence and photo-decomposition as a function of concentration, temperature and other parameters affecting the environment of the molecule in question.

Biacetyl (2,3-butanedione) is rather unique in that fluorescence, phosphorescence and photo-decomposition are all observable in the vapor phase as well as in solution. The luminescence and photolysis of biacetyl vapor have been quite thoroughly investigated, and a mechanism proposed to correlate the luminescence and decomposition data<sup>1</sup>.

Only recently has any information concerning the luminescence behavior of biacetyl solutions become available<sup>2</sup>, while there has been virtually no comprehensive attempt to investigate the photolysis of these systems.

It is not unreasonable to expect that solution studies may differ from vapor phase photolysis due to the effect of solvent. Aside from specific solvent interactions, it might be expected that excess vibrational energy in excited biacetyl molecules would be efficiently removed by

collisions with the solvent<sup>3</sup>, thereby inhibiting dissociation. In addition, "cage" effects<sup>4</sup> may play an important role in reducing interaction between two biacetyl molecules or fragments from the dissociation process.

On the other hand, through the use of inert solvents it may be possible to approximate the vapor phase behavior and gain some information about the rates of primary recombination and the probability that the fragments from the photolysis of a biacetyl molecule escape the "cage".

The overall objective is to correlate the luminescence, photo-decomposition and spectroscopy of biacetyl in the vapor and liquid phases, and to determine the effect of changing the environment on the primary photochemical process. This investigation has been undertaken in an attempt to study the effects of solvents upon the photo-decomposition of biacetyl, and to thereby fill some of the gaps in the current knowledge of the photochemistry of biacetyl.

## EXPERIMENTAL

### Purification of Materials

#### Biacetyl

The biacetyl, a Lucidol product, was dried for two weeks over calcium sulfate and distilled in a Todd column under reduced pressure. The material was then further purified by bulb-to-bulb distillation on a vacuum line. The triplet state lifetime of the purified biacetyl vapor was found to be  $1.8 \times 10^{-3}$  seconds, in excellent agreement with previously published values<sup>5</sup>, indicating the absence of quenching impurities. The purified biacetyl was stored in the dark at  $-78^{\circ}\text{C}$  under reduced pressure. No changes in spectroscopic properties were observed over a twelve month period, indicating the stability of this material under the storage conditions.

#### Solvents

The solvents employed in this study were n-heptane, FC-75, perfluoro-n-octane and mineral oil.

The n-heptane was shaken three times for six hours with concentrated sulfuric acid to remove unsaturated contaminants. It was then washed eight times with distilled water, shaking the last two washings for two hours each. The solvent was then dried over solid potassium hydroxide followed by shaking over anhydrous calcium sulfate for twelve hours. After decanting, it was refluxed for twelve hours over metallic sodium and distilled.

FC-75, an eight carbon fluorinated cyclic ether, was supplied by

Minnesota Mining and Manufacturing Company. It was refluxed for twenty-four hours with saturated acid permanganate, neutralized, distilled, dried with  $P_2O_5$  and passed through a three foot column of silica gel. Absorbance measurements with a Cary Spectrophotometer showed that the material was optically transparent in the region 8000-2200  $\text{\AA}$ , indicating that essentially all unsaturated impurities were removed.

A sample of highly purified perfluoro-n-octane was generously supplied by Minnesota Mining and Manufacturing Company and was used without further purification.

The mineral oil, (N. F., viscosity 100-110), was supplied by the Rabin Company. This material showed considerable absorbance in the region 4000-2200  $\text{\AA}$ , indicating the presence of unsaturated contaminants in considerable quantity. Attempts to purify this material by shaking with portions of silica gel were unsatisfactory, so that the mineral oil was used as supplied.

#### Sample Preparation

Phosphorescence studies have indicated that oxygen reacts with biacetyl in the presence of light<sup>6</sup>. In order to eliminate the effects of photo-oxidation, it was necessary to rigorously remove all traces of oxygen from the samples subjected to photolysis.

The degassing cell, as pictured in figure 1, was constructed entirely of glass. Solvent was introduced into the bulb, and the stopcock lubricated with Apiezon M grease. A trap in the stem of the cell prevented solvent from becoming contaminated with stopcock grease. A 1 cm. Pyrex cuvette fitted with a break-seal was connected to the stem by means of capillary tubing.

With the stopcock closed, the degassing cell was connected to a

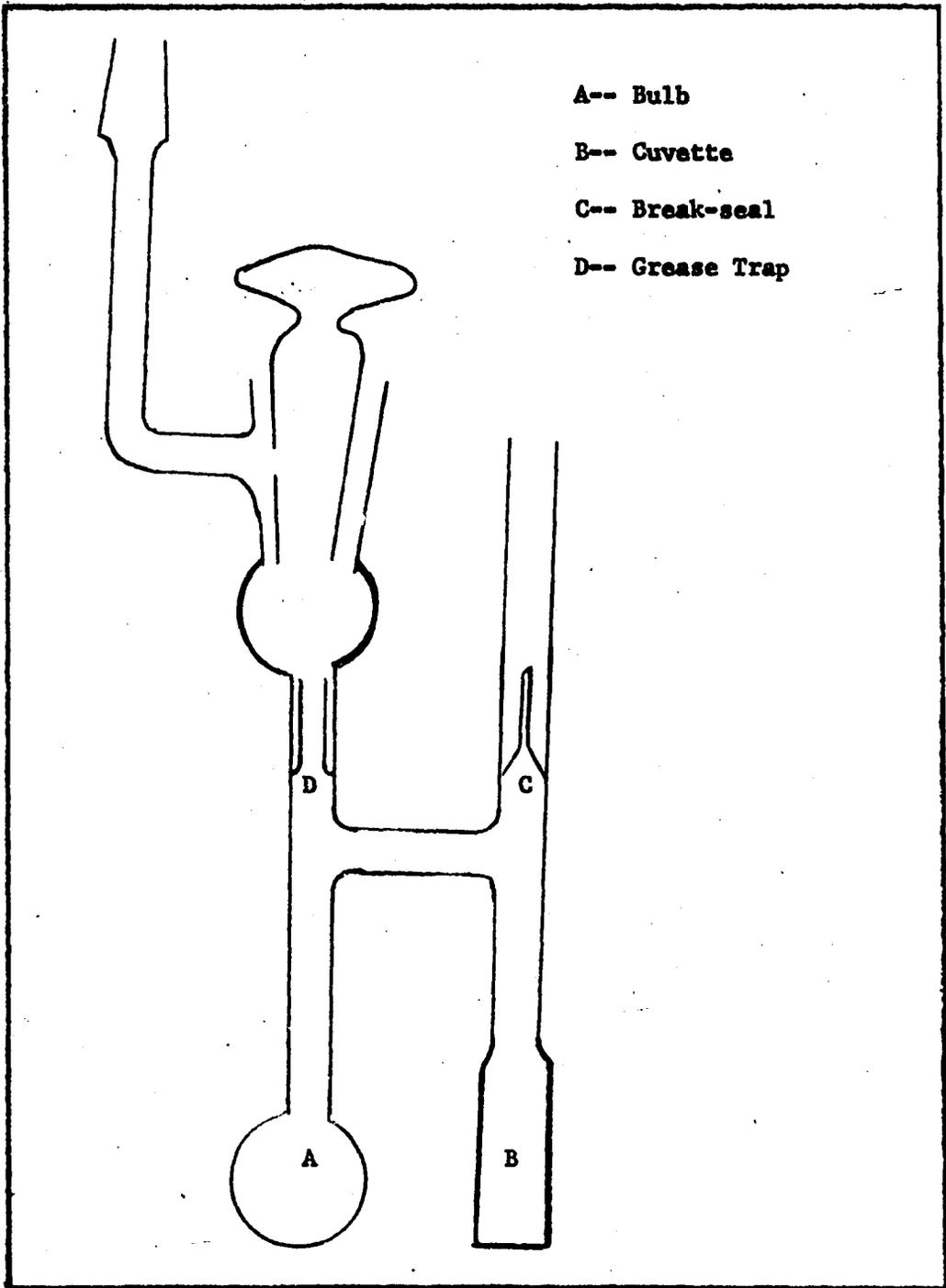


Figure 1 - Degassing Cell

standard vacuum line by means of a 14/35 standard taper ground glass joint. The bulb containing the solvent was then immersed in a dry ice-acetone bath, the stopcock opened and the air pumped out. Alternate cycles of warming, cooling and pumping served to rid the solvent of dissolved gases. When the residual pressure above the solvent was less than 0.1 micron, as determined by measurement with a McLeod gauge, it was assumed that degassing was essentially complete. As a final check, several bulb-to-bulb distillations of the solvent were performed. In the cases in which the residual pressure rose after the bulb-to-bulb distillations, due to escape of small amounts of dissolved gases, the degassing procedure was repeated until the residual pressure was constant.

Concurrently with the solvent degassing process, the biacetyl supply was also freed of any traces of air which might have leaked into the storage bulb. Several cycles of warming, cooling and pumping sufficed to rid the biacetyl of dissolved gases.

The solvent having been degassed, 5 c.c. were distilled over from the bulb (A) to the Pyrex cuvette (B), and the excess solvent pumped off and condensed in a trap cooled with liquid nitrogen. In order to introduce biacetyl into the solvent, the biacetyl supply was warmed and its stopcock opened momentarily. Thus biacetyl vapor was able to diffuse into the cell and condense on the surface of the cooled solvent. With the cell still connected to the vacuum line, the capillary tubing was heated with a hand torch so as to seal off the cuvette containing the biacetyl and solvent. A sample prepared in the manner described above, could then be kept indefinitely without the complications arising from leakage of air into the sample.

As an additional check of the extend of oxygen removal from the

biacetyl solution, the lifetime of the phosphorescence of each sample was determined by a flash technique<sup>2b</sup>. Since oxygen quenches the phosphorescence, and the quenching constant has been determined<sup>2b</sup>, it was possible to accurately estimate the residual oxygen concentration in any prepared sample. In no case did this quantity exceed  $10^{-5}$  M. The limits of the detection of changes in the biacetyl concentration, as described below, were of the order of  $4 \times 10^{-5}$  M., so that the extent of any reaction of biacetyl due to a photo-oxidation process was negligible.

#### Determination of Concentration

Since the degassed sample was sealed in a 1 cm. square cuvette, it was possible to determine the optical density of biacetyl in a Beckman D. U. spectrophotometer. Extinction coefficients of biacetyl in a number of solvents have been accurately determined<sup>7</sup>. In this work it was found that the extinction coefficients of biacetyl, in all of the solvents used, were identical with those previously determined in n-heptane. In all cases the biacetyl concentration was below 0.2 M. and Beer's Law has been shown to be valid in this concentration range. Therefore, the concentration could be calculated from the expression

$$(B) = \frac{\log \frac{I_0}{I}}{(\epsilon)(l)} \quad (I)$$

where (B) = biacetyl concentration, moles/liter

$\log \frac{I_0}{I}$  = experimental optical density

$\epsilon$  = maximum molar extinction coefficient

l = path length, 1.0 centimeter

Since the volume of the solution was known, it was also possible to determine the total number of moles of biacetyl initially present.

### Irradiation Procedure

The light sources employed in this work were AH-6 and AH-4 mercury arcs. The AH-4 arc was air cooled while the high pressure, more intense AH-6 was water jacketed.

Monochromatic 3660 Å radiation was produced by passing the incident light through a Corning glass filter number 5860. Similarly, 4358 Å light was produced by employing the combination of Corning glass filters numbers 3389 and 5113. Spectrophotometric measurements indicated that these filters transmitted less than 0.5% of any mercury lines other than those specified.

The excitation intensity was monitored with a Photovolt photometer, model number 514M. The galvanometer deflection was found to be proportional to the intensity of light incident upon the phototube. Through the use of uranyl oxalate actinometry<sup>8</sup> it was possible to directly relate the galvanometer deflection to the number of incident quanta (see Appendix A).

Mounted between the light source and the phototube was a brass block furnace, into which the sample to be irradiated was placed. The temperature maintained by this furnace was found to be constant to within ±1 degree over a period of 100 hours.

With this apparatus, a nearly parallel beam of suitably filtered light was incident upon the cell, the transmitted light impinging upon the phototube. Since only light transmitted by the sample was detectable by the phototube, the photometer system served the additional purpose of determining the fraction of incident light absorbed by the sample. With no sample in the light beam, the deflection of the galvanometer was directly proportional to the intensity of light incident upon the phototube. When a cuvette containing a biacetyl solution was placed in the light beam,

absorption by the biacetyl resulted in a decreased galvanometer deflection. The galvanometer deflection corresponding to a cuvette containing pure solvent was also recorded. The fraction of light absorbed by the biacetyl solution was then calculated from the difference between the deflections measured with a sample and a solvent blank respectively, divided by the deflection observed with the solvent blank in the beam. The number of quanta absorbed by the sample could then be calculated from the expression

$$I_a = (K)(G)(\Delta t)(I/I_0) \quad (II)$$

where  $I_a$  = quanta absorbed

$G$  = galvanometer deflection with no sample

$K$  = actinometric constant, quanta/second-unit deflection

$\Delta t$  = irradiation period, seconds

$I/I_0$  = fraction of light absorbed by sample

In most cases the fraction of biacetyl decomposed was less than 5% so that the rate at which energy was absorbed remained essentially constant throughout the irradiation period. Furthermore, since the biacetyl concentration was kept low, the illumination was assumed to be homogeneous throughout the body of the solution. For a given sample, the fraction of light transmitted, as measured with the Photovolt photometer, was identical to the same quantity as measured with the Beckman D. U. spectrophotometer. This agreement verified that the filter systems employed were efficient in producing highly monochromatic illumination. No corrections were made for reflection effects. Solutions of biacetyl at identical concentrations in different solvents were found to transmit the same fraction of incident light, so that refractive index corrections have not been deemed necessary.

#### Determination of the Quantum Yield of Biacetyl Decomposition

At the conclusion of the irradiation period, the absorbance of

the biacetyl solution was determined and the residual concentration of biacetyl calculated from expression I. The difference between the concentrations determined before and after irradiation is equal to the concentration of biacetyl reacted. Since the volume of solution is known, the number of molecules of biacetyl reacted may be calculated.

$$n_B = \frac{(B)_i - (B)_f}{6.02 \times 10^{23}} V \quad (\text{III})$$

$n_B$  = number of biacetyl molecules reacted

$(B)_i$  = initial biacetyl concentration, moles/lit̄er

$(B)_f$  = final biacetyl concentration, moles/liter

$V$  = volume of solution:  $5.0 \times 10^{-3}$  liters

No changes in the position or shape of the biacetyl spectra in irradiated samples relative to freshly prepared solutions were observed, indicating that products of the photolysis do not absorb in the region 350-500 millimicrons. Thus, the quantity of biacetyl reacted, as calculated from equation III, should be accurate and independent of the extent to which photolysis proceeds.

The quantum yield of biacetyl decomposition ( $\phi_B$ ) is a measure of the efficiency with which biacetyl utilizes light energy to rupture its chemical bonds. This quantity may be defined as

$$\phi_B = \frac{\text{number of biacetyl molecules decomposed}}{\text{number of quanta absorbed}} \quad (\text{IV})$$

The numerator in expression IV is given by equation III, while the denominator is calculated from equation II.

#### Analysis of Gaseous Products

After irradiation, a glass enclosed iron rod was placed above the breakseal on the sample cuvette, this assembly then being sealed into the analytical system. By means of a mercury diffusion pump, the pressure

in the system could be reduced to less than 0.1 micron, as determined by measurement with a McLeod gauge. The analytical system was constructed without stopcocks, mercury cutoffs being used to isolate various portions of the system. The construction of the gas analysis system is schematically represented in figure 2.

With the irradiated sample (S) in place, and the pressure (as determined by McLeod gauges (A) and (B)) reduced below 0.1 micron, the mercury cutoffs (C-L) were raised. Trap (M) was immersed in a dry ice-acetone bath, and cutoff (D) lowered. Using a small magnet to manipulate the iron rod, the seal isolating the sample from the analytical system could be broken. Gentle warming of the sample cell hastened the transfer of material to (M). In this manner the unreacted biacetyl and the bulk of the solvent were condensed in trap (M). By packing the well of (M) with dry ice, and removing the cold bath from the exterior, it was possible to allow the solvent to continuously reflux. Thus any gaseous products which were dissolved were freed from the solvent.

Spiral trap (N) in figure 2 was wrapped with asbestos, wound with fine resistance wire and equipped with two copper-constantan thermocouples. This trap was placed in a glass tube immersed in liquid nitrogen. Adjustment of a Variac regulated the voltage supplied to the heating coil, making it possible to maintain trap (N) at  $-150^{\circ}\text{C}$ .

With trap (N) equilibrated at the appropriate temperature, cutoff (E) was lowered, and the vapors allowed to pass into (N) where any traces of solvent not removed in (M) were condensed.

Cutoff (F) was lowered, and the gases were allowed to diffuse into a LeRoy still (P)<sup>9</sup> kept at liquid nitrogen temperature. Any ethane produced in the photolysis was found to condense in (P). Several cycles

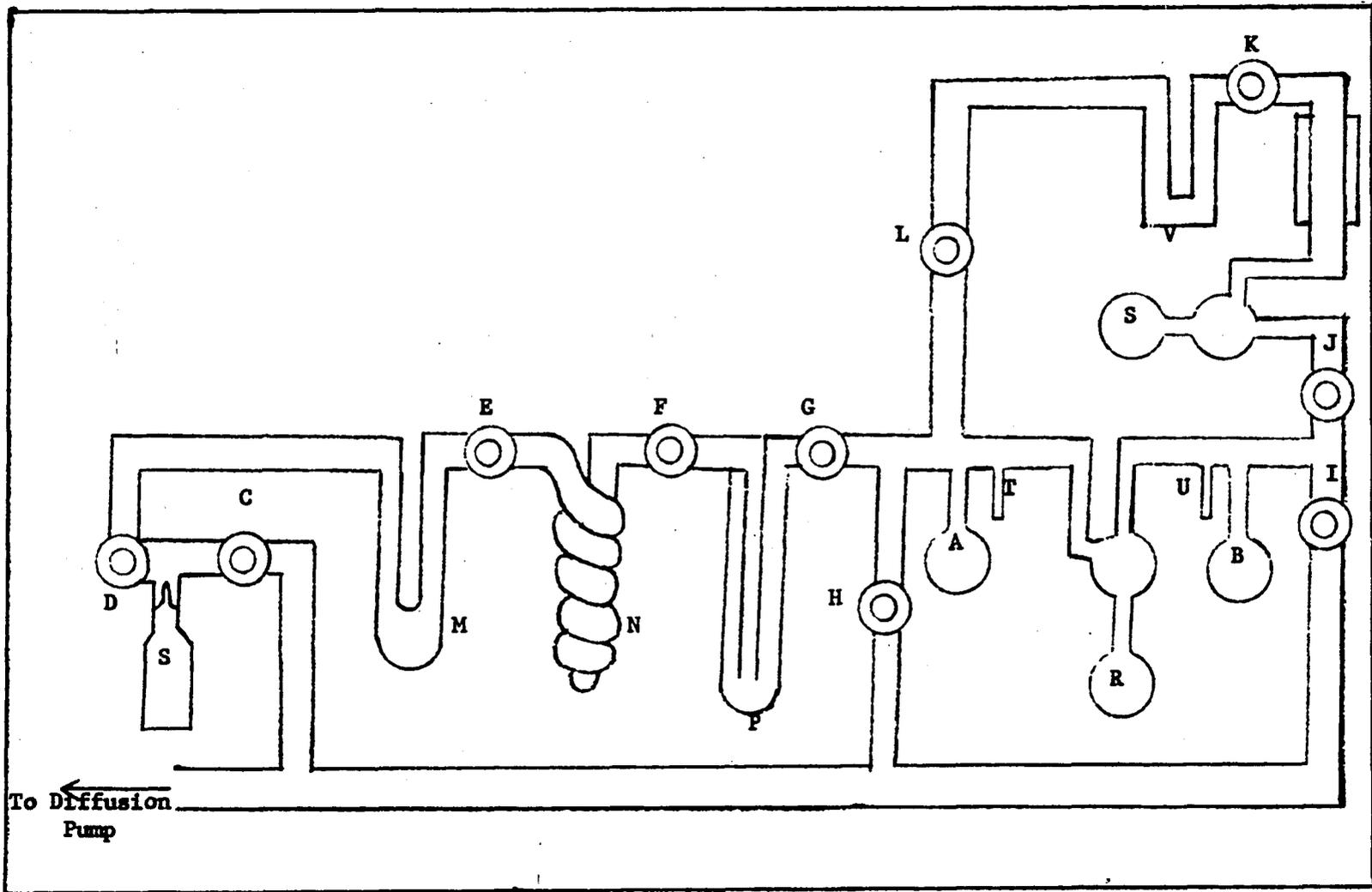


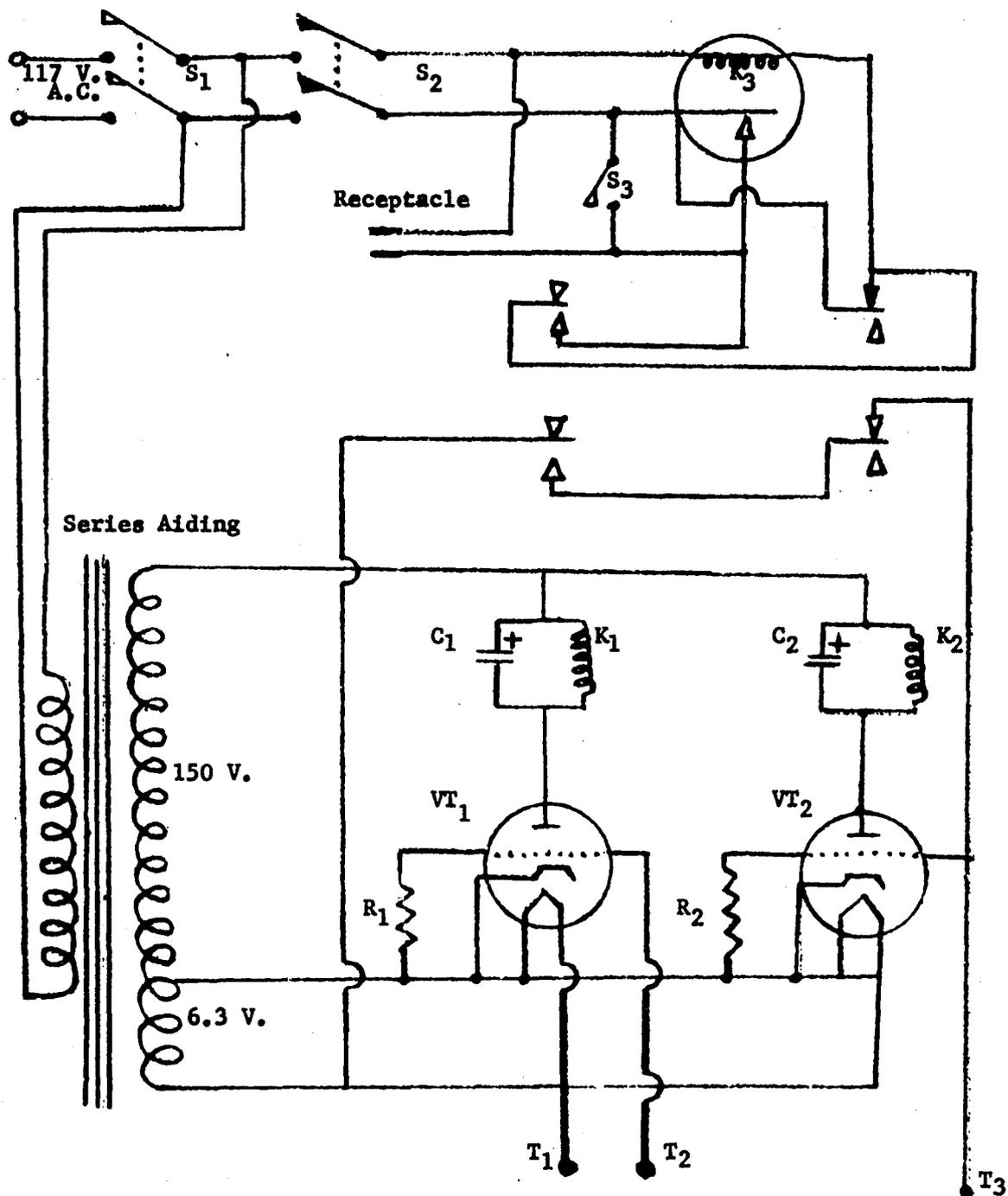
Figure 2 - Schematic Representation of the Gas Analysis System

of warming to  $-130^{\circ}\text{C}$  and recooling to  $-195^{\circ}\text{C}$  served to insure that other products volatile at  $-195^{\circ}\text{C}$  were not mechanically trapped by the condensed ethane.

The residual gases not condensable at  $-195^{\circ}\text{C}$  were characterized by their properties. When this material was allowed to remain in contact with hot copper oxide, as described below, a portion was converted to a material condensable at liquid nitrogen temperature. This behavior is characteristic of CO, which is oxidized to  $\text{CO}_2$  under these conditions. The portion of the gas not oxidized was assumed to be methane. The presence of nitrogen would interfere with the methane analysis, since nitrogen behaves similarly to methane under these conditions. However, since dissolved oxygen was found to be efficiently removed from the solutions, it is assumed that the degassing procedure was equally as effective in removing dissolved nitrogen. Therefore, it may be safely assumed that the products volatile at  $-195^{\circ}\text{C}$  consisted exclusively of methane and carbon monoxide. No other volatile products are observed in the vapor phase photolysis of biacetyl<sup>10</sup>.

With cutoff (G) lowered, these gases were allowed to diffuse into the next stage of the analytical system, and their combined pressure measured with McLeod gauge (A). Immersion of cold finger (I) in liquid nitrogen was necessary to determine the extent of ethane removal by the LeRoy still. A decrease in pressure at this point was indicative of the fact that some ethane came over with the other gases. In most cases, however, ethane retention in the LeRoy still was complete.

By means of an automatic Toepler pump (R)<sup>11</sup> (figure 2a) the CO and  $\text{CH}_4$  could be quantitatively transferred to a previously calibrated volume, and the total pressure measured with McLeod gauge (B). In order to improve



S<sub>1</sub>, S<sub>2</sub> - DPDT  
 S<sub>3</sub> - SPST  
 K<sub>1</sub>, K<sub>2</sub> - 5000 Ohm LM11 DPDT  
           Potter and Brumfield Relays  
 K<sub>3</sub> - 115 NO 15T Amperite Delay  
       Relay

Tr - Transformer  
 VT<sub>1</sub>, VT<sub>2</sub> - 6C4 Vacuum Tubes  
 R<sub>1</sub>, R<sub>2</sub> - 470 K Ohms  
 C<sub>1</sub>, C<sub>2</sub> - 1 MFD, 450 V.  
 T<sub>1</sub>, T<sub>2</sub>, T<sub>3</sub> - Binding Posts

Figure 2a - Automatic Toepler Pump Control Unit

the efficiency of the automatic toepling operation, it was necessary to replace the mercury-filled float valve suggested by Urry with a smaller one containing a two cm. iron rod. A small horseshoe magnet perpendicular to the axis of the rod enhanced the proper seating of the float valve throughout the toepling cycle.

When the input pressure was reduced to two microns, it was found that the gas bubble could not pass through the mercury seal on the float valve. By manipulation of the magnet on the upstroke of the Toepler pump, the float valve could be lifted, the gas bubble allowed to pass, and the valve reseated. In this manner, the input pressure could be sufficiently reduced. It was found that at least 50 cycles of the Toepler pump were required to reduce the input pressure to below 0.1 micron. Cutoffs (F) and (G) were then raised to isolate the ethane in (P).

After the pressure of the gases in the calibrated volume was recorded, Toepler pump (S) was used to draw the gases into a Cu-CuO furnace maintained at 210°C. With cutoff (K) lowered, U-tube (V) was immersed in liquid nitrogen. Thus, any CO oxidized to CO<sub>2</sub> in the furnace would be condensed in (V). Methane was found to be stable and completely recoverable at the temperature and contact time employed. The gases were allowed to remain in contact with the furnace for three hours, a period of time which is sufficient to allow for the quantitative oxidation of carbon monoxide to carbon dioxide.

At this point the CO<sub>2</sub> was frozen in (V), so that by lowering cutoff (L) and toepling the residual gas with pump (R), the methane could be again transferred to the calibrated volume and its pressure recorded. Cold finger (U) at liquid nitrogen temperature served as a check on the efficiency of (V) for condensing all the CO<sub>2</sub>. Replacing the

liquid nitrogen bath on (V) with one of dry ice-acetone, and repeating the toepling process enabled the  $\text{CO}_2$  to be transferred to the calibrated volume, and the sum of the pressures of  $\text{CH}_4$  and  $\text{CO}_2$  to be determined. This method not only served to measure the absolute quantities of  $\text{CH}_4$  and  $\text{CO}_2$ , but also indicated the extent of recovery of gases from the furnace. The methane and carbon dioxide could then be pumped away, after their pressures were recorded.

At this point in the analysis, the LeRoy still was warmed to  $-175^\circ\text{C}$  at which temperature ethane exhibits a vapor pressure of several microns<sup>12</sup>. Opening cutoff (G) and toepling the gas permitted the ethane to be pumped to the calibrated volume and its pressure recorded.

The volumetric calibration was performed in the following manner. A large glass bulb fitted with a vacuum stopcock was attached to a vacuum line equipped with a McLeod gauge. This system was evacuated, and a small quantity of air introduced. After a 2 hour equilibration period, the pressure recorded on the McLeod gauge was found to be constant indicating that the pressure in the bulb was equal to that in the rest of the vacuum line. The stopcock was then closed and the bulb removed and sealed onto the analytical system. With the stopcock still closed, the system was evacuated to less than 0.1 micron and isolated from the pump by mercury cutoffs.

The stopcock on the bulb was then opened, allowing the air to diffuse into the analytical system. With all the traps at room temperature, the air was quantitatively transferred to the volume to be calibrated by means of Toepler pump (R). The pressure in this volume was then measured by McLeod gauge (B). The ratio of the pressure in this volume to the initial pressure in the bulb was equal to the ratio of the volumes. With

initial bulb pressures of 31.2 and 48.4 microns, the ratios determined were 1.39 and 1.41 respectively. The volume of the bulb was determined by first weighing the bulb evacuated then weighing it filled with water at 27°C. Taking the density of water at this temperature as 0.9965 grams/c.c., the volume of the bulb was calculated to be 1026 ± 2 c.c. The calculated volume of the analytical system was then equal to 1.45 ± 0.02 liters.

Analysis was not performed for gaseous products other than methane, ethane and carbon monoxide, and there was little indication that significant amounts of other gases were produced during the photolysis of biacetyl solutions.

Some preliminary attempts were made to develop a system for the determination of the gaseous products using vapor phase chromatography. The details are presented in Appendix B.

#### Quantum Yields of Gaseous Products

The determination of pressure, temperature and volume of each gaseous product permits the calculation of the number of moles of each gas produced. Since pressures never exceeded 60 microns, it may be assumed that the gases obey the ideal gas law. The quantity of gas produced is given by the expression

$$n_g = \frac{PV(6.02 \times 10^{23})}{RT} \quad (V)$$

$n_g$  = number of molecules of gas produced

$V$  = volume in which gas is contained

$P$  = pressure of gas

$R$  = universal gas constant

$T$  = absolute temperature

The quantum yield of gas formation is defined by

$$\phi_{\text{gas}} = \frac{\text{number of molecules of gas produced}}{\text{number of quanta absorbed}}$$

The quantities contained in this expression are calculated by equations V and II. In this manner  $\phi_{\text{CO}}$ ,  $\phi_{\text{CH}_4}$  and  $\phi_{\text{C}_2\text{H}_6}$  may be experimentally determined.

### Liquid Products

No attempt was made to completely characterize the liquid products resulting from the photolysis. In many runs, especially at the higher initial biacetyl concentrations, small amounts of a brown oil, insoluble in the solvent were formed. This material was soluble in ether, and ultraviolet absorption spectra of these solutions were recorded (figure 3). While the positions of its absorption maxima are quite similar to those exhibited by  $\alpha, \beta$ -unsaturated ketones it would be premature to attempt to specify its constitution. This product was produced in quantities too small to allow any chemical tests to be performed. However, irradiation of pure biacetyl at 100°C gives rise to a considerable amount of brown product similar to that produced in solution photolysis. It may be possible to prepare sufficient amounts of this product for characterization in this manner.

### Luminescence Measurements

The effect of temperature and concentration upon the fluorescence and phosphorescence yields of biacetyl in perfluoro-n-octane was investigated. Details of the instrumentation and techniques involved in the fluorescence measurements have been described elsewhere<sup>23</sup>. The phosphorescence measurements were made by modifying the irradiation procedure previously described. A 4050 Å interference filter was used to provide monochromatic excitation. A sharp cutoff Corning glass filter 3384 was placed in front

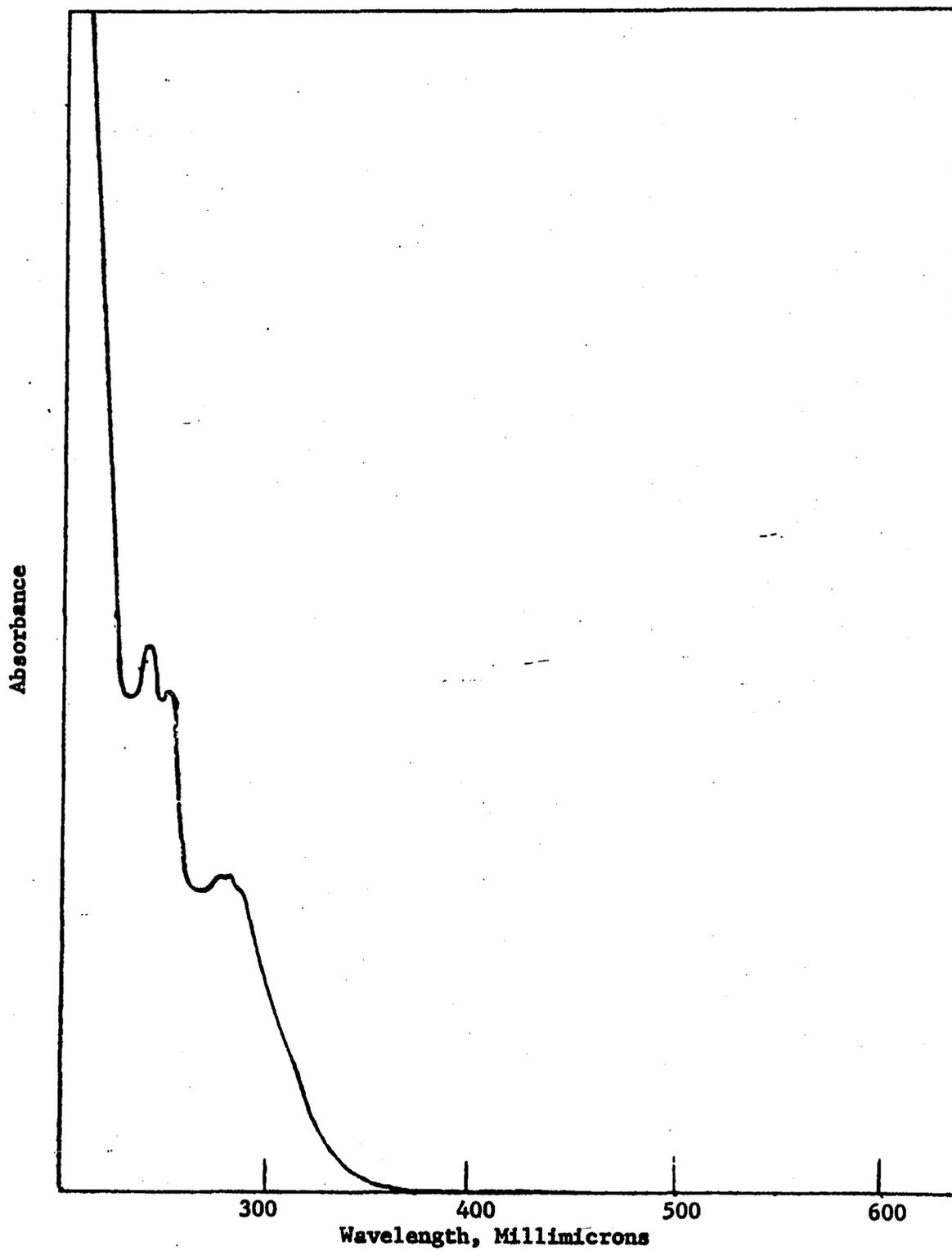


Figure 3 - Absorption Spectrum of Non-volatile Residue

of the phototube. With no sample in the light beam, no deflection of the galvanometer was observed since this filter only transmitted wavelengths above 5200 Å. With a biacetyl solution in the light beam, the only light incident upon the phototube came from the phosphorescence emission of biacetyl above 5200 Å. Since the major portion of the biacetyl fluorescence is restricted to wavelengths shorter than 5200 Å, this emission could not be detected by the phototube. The deflection of the galvanometer was then assumed to be proportional to the phosphorescence intensity. By adjusting the thermostat, the temperature of the furnace was controlled and the phosphorescence of the biacetyl solution was measured as a function of temperature. Since the fraction of incident light absorbed was measured in the manner previously described, the galvanometer deflection divided by the fraction of light absorbed at a given temperature was set equal to the relative phosphorescence yield.

#### Viscosity Determinations

The variation of viscosity of FC-75 with temperature has been previously investigated, and these data were supplied by the Minnesota Mining and Manufacturing Company<sup>13</sup>.

The kinematic viscosity of  $C_8F_{18}$  at 100°C was determined by using a Cannon-Fenske-Ostwald type viscometer<sup>14</sup>. The viscometer constant was determined using distilled water as the calibrating fluid. The viscosity in centistokes of  $C_8F_{18}$  was determined by multiplying the efflux time in seconds by the viscometer constant. The product of the density and kinematic viscosity yields a value for the viscosity in centipoise.

The viscosities of mineral oil at 25°C and 100°C were determined in a previously calibrated viscometer of the Cannon-Fenske-Ostwald type, number 350 J53. Densities at the two temperatures were obtained

experimentally by determining the weight of 25.0 ml. of the material at the desired temperature. It was assumed in this work that the small amounts of dissolved biacetyl did not significantly change the viscosity of the solvent.

### Special Precautions

#### Sample Cell

In order to assure that changes in biacetyl concentrations during irradiation could be accurately determined, it was necessary to ascertain that the cell and cuvette were scrupulously clean. After each run, the cell was washed with petroleum ether to remove traces of stopcock grease. It was then filled with hot concentrated nitric acid and allowed to stand for 1 hour. It was then thoroughly rinsed with distilled water, until the rinse water showed no further traces of acid. Three rinses with acetone followed by heating for 8 hours at 150°C concluded the cleansing operation. The cell was periodically checked for deposits on the optical surfaces, which would give rise to spurious absorbance measurements.

#### Analytical System

Great care was taken to prevent air from leaking into the system. Continuous evacuation prevented the build-up of absorbed air on the glass walls, which might tend to desorb during the course of an analysis.

Many times the development of pin-holes or cracks in the vacuum line resulted in the contamination of the system. After each repair, the system was pumped out for several days until desorption from the walls was minimized.

Especially serious were the occasions in which air entered the portion of the system containing the Cu-CuO furnace. It was found that increasing the temperature to 350°C and pumping for 2 weeks was necessary

to completely outgas the furnace. Following this treatment CO was placed in contact with the Cu-CuO at 210<sup>o</sup>C for 12 hours in order to recondition the furnace.

At the termination of each analysis the sample cuvette was removed from the vacuum line and a glass tube sealed on in its place. After evacuation, the biacetyl and solvent in the system were frozen back into this tube, and the tube sealed off. In this manner it was possible to remove all the solvent and unreacted biacetyl and prevent contamination of the analytical system.

## RESULTS

The results of the photolyses of various biacetyl solutions as a function of solvent, concentration, wavelength and temperature are presented in tables I-VII. The quantity  $\phi_B$  represents the quantum yield of biacetyl disappearance, while  $\phi_{CO}$ ,  $\phi_{CH_4}$  and  $\phi_{C_2H_6}$  represent the quantum yields of carbon monoxide, methane and ethane respectively. The significance of the tabulated values of the term  $\phi_D$  will be elucidated during the course of the discussion of the experimental results and the development of the reaction mechanism.

In several cases, analyses were not made for gaseous products due to malfunction of the analytical system or cracking of the sample cell before analysis.

Because of difficulties inherent in the determination of small changes in the biacetyl concentrations as a result of photolysis, the tabulated values of  $\phi_B$  are probably correct to only two significant figures. The quantities of gaseous products produced were measured more accurately, so that  $\phi_{CO}$ ,  $\phi_{CH_4}$  and  $\phi_{C_2H_6}$  are assumed to be valid to three significant figures.

Although the absolute magnitudes of the tabulated quantum yields may be uncertain due to errors in the calibration of the light sources, the relative values retain their significance. However, it is estimated that the actinometric error was probably less than 10%. Since the results will be discussed primarily on the basis of observed trends and orders of magnitude, small errors will, in general, not be significant.

TABLE I

FC-75 - 100°C - 4358 Å

Biacetyl Conc. (M/l) $\times 10^2$	$\phi_B$ $\times 10^3$	$\phi_{CO}$ $\times 10^4$	$\phi_{CH_4}$ $\times 10^4$	$\phi_{C_2H_6}$ $\times 10^5$	$\phi_D$ $\times 10^3$	$I_a$ Quanta/sec $\times 10^{-15}$	% Decomposed	Triplet State Lifetime Microseconds
0.98	4.13	4.6	1.38	4.8	2.6	3.20	12.5	---
2.00	5.97	---	---	---	---	5.83	6.19	870 (159*)
2.32	6.33	6.2	1.87	6.2	4.0	7.65	3.63	75 (83*)
2.46	6.38	---	---	---	---	7.86	13.4	---
4.24	8.71	9.2	2.73	7.9	5.5	10.08	8.95	10
8.48	3.28	3.38	1.03	3.27	2.07	11.42	4.09	704

\*Refers to lifetime after irradiation.

TABLE II

FC-75 - 100°C - 3660 Å

Biacetyl Conc. (M/l) $\times 10^2$	$\phi_B$ $\times 10^3$	$\phi_{CO}$ $\times 10^4$	$\phi_{CH_4}$ $\times 10^4$	$\phi_{C_2H_6}$ $\times 10^5$	$\phi_D$ $\times 10^3$	$I_a$ Quanta/sec $\times 10^{-15}$	% Decomposed	Triplet State Lifetime Microseconds
0.196	10.9	205	214	0	0.5	0.153	11.8	---
0.330	9.92	161	154	4	1.2	0.227	7.76	---
1.82	11.5	34.5	6.44	144	6.5	1.99	6.95	250
2.74	9.02	14.6	8.88	20	5.5	2.44	6.92	975 (70*)
3.78	10.8	---	---	---	---	5.00	9.45	683
4.03	10.0	10.2	6.02	23	6.3	21.6	4.03	---
4.73	10.5	11.1	5.43	26	6.6	1.82	2.23	335
14.3	14.3	2.04	4.20	7	9.2	1.44	7.95	220
20.5	164	5.7	0	34	109	6.85	29.5	680

\*Refers to lifetime after irradiation.

TABLE III

Perfluorooctane - 100°C - 4358 Å

Biacetyl Conc. (M/l) $\times 10^2$	$\phi_B$ $\times 10^3$	$\phi_{CO}$ $\times 10^4$	$\phi_{CH_4}$ $\times 10^4$	$\phi_{C_2H_6}$ $\times 10^5$	$\phi_D$ $\times 10^3$	$I_a$ Quanta/sec $\times 10^{-15}$	% Decomposed
0.467	0.635	3.7	0	14	0.33	0.889	14.4
1.07	0.950	4.4	0	22	0.49	2.23	5.51
2.44	1.36	3.4	0	17	0.78	2.90	4.85
6.92	2.08	5.8	0	28	1.20	392	1.77

TABLE IV

Perfluorooctane - 100°C - 3660 Å

Biacetyl Conc. (M/l) $\times 10^2$	$\phi_B$ $\times 10^3$	$\phi_{CO}$ $\times 10^4$	$\phi_{CH_4}$ $\times 10^4$	$\phi_{C_2H_6}$ $\times 10^5$	$\phi_D$ $\times 10^3$	$I_a$ Quanta/sec $\times 10^{-15}$	% Decomposed
0.773	2.40	36.8	0	184	0.37	2.64	7.11
2.51	2.63	27.7	0	139	0.83	9.26	3.37
3.89	2.26	14.5	0	73	1.02	27.8	3.04
7.19	2.47	12.6	0	63	1.23	69.5	5.99
18.0	2.60	6.1	0.2	30	1.53	66.4	4.85

TABLE V

Mineral Oil - 25°C - 3660 Å

Biacetyl Conc. (M/l) $\times 10^2$	$\phi_B$ $\times 10^3$	$\phi_{CO}$ $\times 10^4$	$\phi_{CH_4}$ $\times 10^4$	$\phi_{C_2H_6}$ $\times 10^5$	$\phi_D$ $\times 10^3$	$I_a$ Quanta/sec $\times 10^{-15}$	% Decomposed	Triplet State Lifetime Microseconds
0.916	1.53	23.0	0	114	0.23	6.20	11.5	133
0.97	1.51	---	---	---	---	10.4	5.65	161
1.26	1.51	21.1	13.2	39	0.30	8.50	3.02	175
6.72	1.56	15.9	0	80	0.51	33.7	2.20	---
11.0	1.62	15.6	0	78	0.56	44.5	1.98	103

TABLE VI

Mineral Oil - 100°C - 3660 Å

Biacetyl Conc. (M/l) $\times 10^2$	$\phi_B$ $\times 10^3$	$\phi_{CO}$ $\times 10^4$	$\phi_{CH_4}$ $\times 10^4$	$\phi_{C_2H_6}$ $\times 10^5$	$\phi_D$ $\times 10^3$	$I_a$ Quanta/sec $\times 10^{-15}$	% Decomposed
0.528	5.58	87.7	9.9	380	0.80	3.28	4.86
0.929	5.70	73.8	0.9	370	1.00	5.64	20.0
1.87	5.65	40.8	0	200	4.3	11.7	10.1
3.28	5.28	27.7	0	140	4.7	19.5	9.50

TABLE VII

n-heptane - 100°C - 4358 Å

Biacetyl Conc. (M/l) $\times 10^2$	$\phi_B$ $\times 10^3$	$\phi_{CO}$ $\times 10^4$	$\phi_{CH_4}$ $\times 10^4$	$\phi_{C_2H_6}$ $\times 10^5$	$\phi_D$ $\times 10^3$	$I_a$ Quanta/sec $\times 10^{-15}$	% Decomposed	Triplet State Lifetime Microseconds
1.88	6.70	27.7	19.1	68	3.55	339	10.7	---
2.01	5.52	21.9	16.0	57	2.95	348	4.41	---
4.43	18.2	40.8	51.3	35	10.8	6.95	4.75	385 (38*)
18.6	33.2	27.9	18.2	49	21.2	1380	17.6	410

\*Refers to lifetime after irradiation.

### Temperature Dependence

In the gas phase, photolysis of biacetyl has been found to proceed at 25°C, with both 4358 Å and 3660 Å excitation. The data in Table V indicate that biacetyl undergoes decomposition at 25°C when dissolved in mineral oil and irradiated at 3660 Å. However, in neither the FC-75 nor the perfluorooctane systems did prolonged irradiation result in significant decomposition at 25°C. It is estimated that  $\phi_B$  is less than one-hundredth as large at 25°C than at 100°C.

In order to estimate the temperature dependence one run was made at 75°C in FC-75 solution with 3660 Å excitation. In this run the initial biacetyl concentration was 0.0825M and the observed  $\phi_B$  was 0.0083. An Arrhenius plot of the results at 75° and 100° yielded an apparent activation energy of 3 kcal/mole, which coincides with the activation energy for diffusion of FC-75. Similarly, in mineral oil, the temperature dependence observed in photolysis parallels the effect of temperature on the viscosity of the solvent.

### Intensity Dependence

A ten-fold intensity variation did not result in significant changes in either the magnitudes or trends of the observed quantum yields. In the majority of runs, the incident intensity was adjusted to correspond to the maximum value that could be produced by the light source and still be accurately monitored by the phototube.

### Luminescence Effects

It has been postulated that decomposition proceeds from a high vibrational level of the first excited singlet state as well as by interaction between long-lived triplet state biacetyl molecules<sup>1</sup>. Since emission from the singlet state (fluorescence), as well as from the

triplet state (phosphorescence) are observable in solution, luminescence measurements were made in an attempt to gain insight about the competition between emission and photo-decomposition.

An intensity effect has been observed in the phosphorescence of biacetyl vapor, using a flash technique<sup>5</sup>. The observed decrease in the triplet state lifetime was ascribed to the formation of quenching products. In the present work, using steady illumination, both the fluorescence and phosphorescence yields were found to be independent of the incident intensity, as indicated by the linearity of the plots in figure 4 over a hundred-fold variation in intensity. The failure to observe an intensity dependence under these conditions, might possibly be due to the lower intensities compared to those generated by a flash tube, resulting in lower concentrations of quenching products. That quenching products are formed is verified by the observation that in a typical case the lifetime of the triplet state decreased from about 1000 microseconds to the neighborhood of 70 microseconds during the course of photolysis.

The effect of temperature upon the fluorescence yield is shown in Table VIII. In solution at 25°C, it has been shown that the fluorescence yield of biacetyl from low lying vibrational levels of the first excited singlet state is determined entirely by the relative rates of light emission and internal conversion to the lowest triplet state<sup>2c</sup>. The observed fluorescence yield of 0.002 corresponds to 99.8% of the biacetyl molecules in low lying vibrational levels of the first excited singlet state undergoing internal conversion to the lowest triplet state. It is possible that various vibrational levels in the ground state or the first excited singlet state are thermally activated at 100°C, leading to dissociation at this temperature. Since only a small fraction

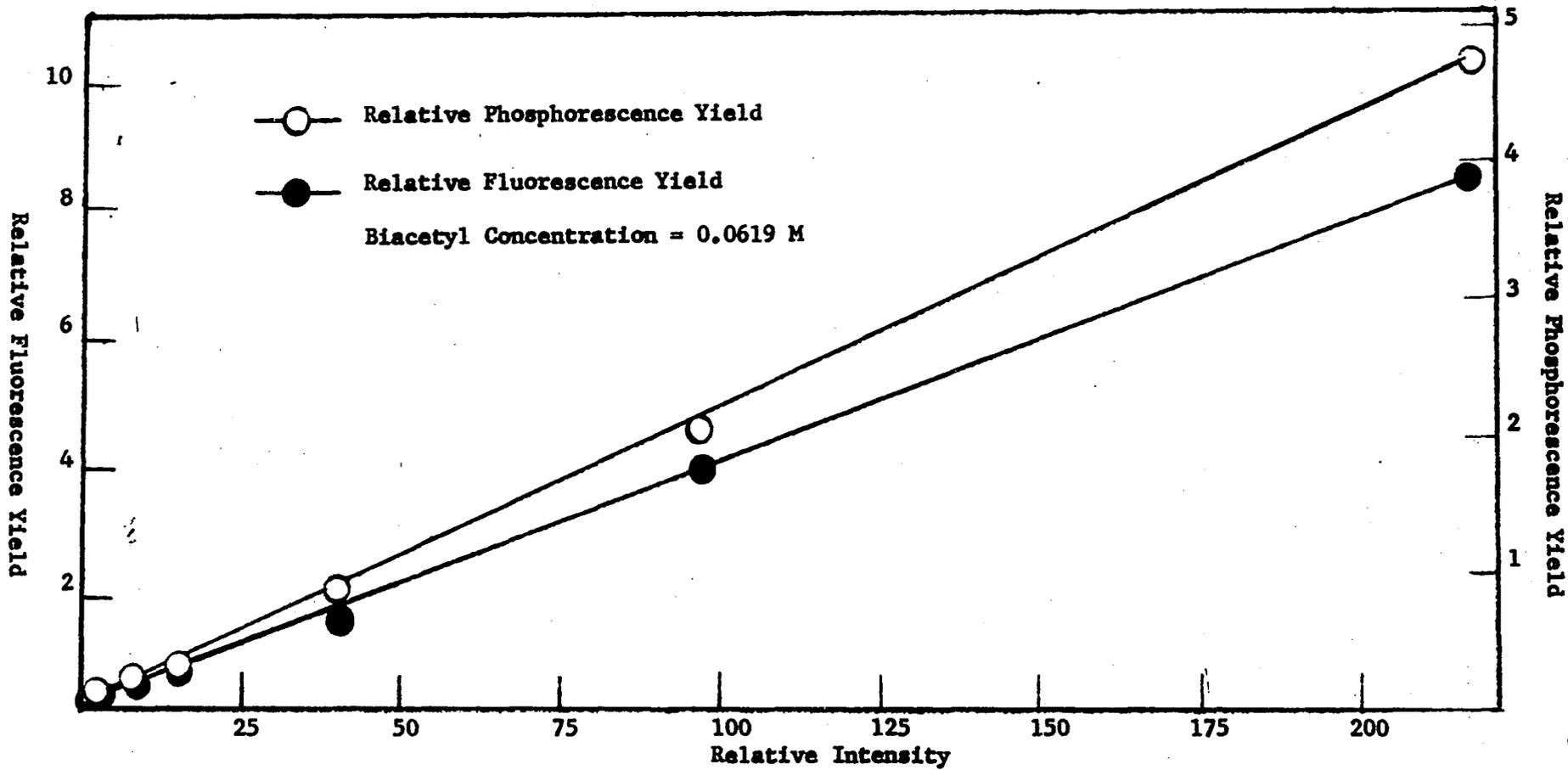
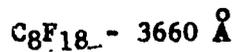


Figure 4 - Effect of Intensity on the Relative Quantum Yields of Fluorescence and Phosphorescence in FC-75

TABLE VIII

## Temperature Dependence of Fluorescence



Biacetyl Concentration = 0.0619 M/l

Temperature	Relative Fluorescence Yield
10°C	10.8
30	10.2
35	10.8
55	10.3
75	10.3
90	10.2
115	10.0

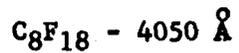
of the excited molecules undergo a radiative transition to the ground singlet state, the observed increase in  $\phi_B$  of 0.01 might not result in a significant decrease in the fluorescence yield. Similarly, since the phosphorescence yield is always much greater than the decomposition yield (ca. 0.15), the necessary increase in  $\phi_B$  would not result in a drastic diminution of the phosphorescence yield. The effect of temperature upon the relative phosphorescence yields is shown in Table IX. These results are in good agreement with those reported for the effect of temperature upon the triplet state lifetime of biacetyl vapor<sup>5</sup>, in which the lifetimes were  $1.80 \times 10^{-3}$  and  $1.27 \times 10^{-3}$  seconds at 25°C and 79°C respectively.

The possibility also exists that decomposition proceeds at 100°C from thermally excited vibrational levels of the lowest triplet state. If this mode of dissociation is important, it would be expected that a decrease in the triplet state lifetime would reduce the thermal population of upper vibrational levels. However, this effect would probably be small enough to be obscured by the temperature effect of non-radiative transitions from the triplet state to the ground state. The increased importance of these non-radiative transitions as the temperature is raised probably accounts for the major portion of the temperature dependence of the phosphorescence.

The importance of the participation of the lowest triplet state in the photo-decomposition of biacetyl solutions can be evaluated in another way. The measured lifetime of the lowest triplet state was found to decrease as photolysis progressed. In any given solvent, the initial and final lifetimes varied considerably from run to run, independent of the concentration of biacetyl. Traces of oxygen or solvent impurities probably accounted for this irregularity. However, despite this

TABLE IX

## Temperature Dependence of Phosphorescence



Biacetyl Concentration = 0.0619 M/l

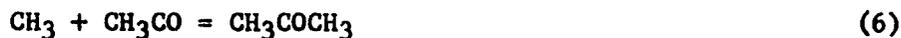
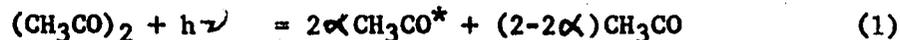
Temperature	Relative Phosphorescence Yield
24°C	100.0
32	96.0
40	91.6
55	86.8
60	82.2
70	79.6
87	74.8
97	71.2

apparently random fluctuation of the lifetime, the trends described in the next section persist. It must, therefore, be concluded that the lowest triplet state cannot be responsible for a significant portion of the photolysis of biacetyl solutions.

Because of the complexity of the system and the large number of competing processes, a good deal of caution is necessary in attempting to draw conclusions about the photolysis from the limited luminescence data available.

## DISCUSSION

Several of the steps generally accepted in the vapor phase photolysis of biacetyl are<sup>10</sup>

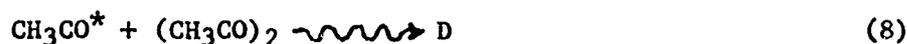


where  $\text{CH}_3\text{CO}^*$  represents an acetyl radical with sufficient vibrational energy to dissociate before collisional deactivation, while  $\text{CH}_3\text{CO}$  represents a thermally equilibrated radical. The quantity  $\alpha$  is the fraction of biacetyl molecules which dissociate into vibrationally excited acetyl radicals.

Except in FC-75 solutions at 4358 Å excitation, the ratio  $(\phi_{\text{CH}_4} + \frac{1}{2}\phi_{\text{C}_2\text{H}_6})/\phi_{\text{CO}}$  is very close to unity. On this basis it must be concluded that the formation of acetone by step (6) is unimportant, since a significant amount of acetone production would tend to lower the ratio. The absence of acetone from the reaction products may indicate that many of the acetyl radicals formed in the primary process have sufficient kinetic energy to escape the solvent "cage" before dissociation. This conclusion is in accord with many of the observed trends.

According to steps (1)-(5) and (7), the fate of an acetyl radical is either to recombine to reform biacetyl or to decompose into  $\text{CH}_3$  and  $\text{CO}$ . On this basis, each biacetyl molecule which disappears should give rise to two molecules of  $\text{CO}$ . This is equivalent to the prediction that  $\phi_{\text{CO}}/\phi_{\text{B}} = 2$ . The results in all solvents at  $3660 \text{ \AA}$  are not at all in accord with this relation. In figure 5 it can be seen that  $\phi_{\text{CO}}/\phi_{\text{B}} = 2$  is obtained as a limiting value only as the biacetyl concentration approaches zero. As the biacetyl concentration increases, this ratio decreases rapidly.

Whereas steps (1)-(7) account for most of the trends observed in the vapor phase photolysis, they obviously do not constitute a complete mechanism for biacetyl solution photolysis. The striking decrease in the yields of gaseous products with increasing biacetyl concentration suggests the inclusion of steps whereby biacetyl is consumed without gaseous products being formed. It is likely that these steps involve reaction of an acetyl radical with a biacetyl molecule according to



The reaction product D has not been characterized nor has its exact mode of formation been specified. However, this does not invalidate the conclusion that a secondary reaction involving unexcited biacetyl molecules is important.

If biacetyl disappears only by steps (1)-(5) and (7)-(9) an expression may be obtained for the quantum yield of the species D. From steps (8) and (9) it can be seen that  $3/2$  biacetyl molecules are required to form one molecule of D. At very low concentrations where all of the biacetyl which decomposes gives rise to gaseous products  $\phi_{\text{B}}$  is equal to

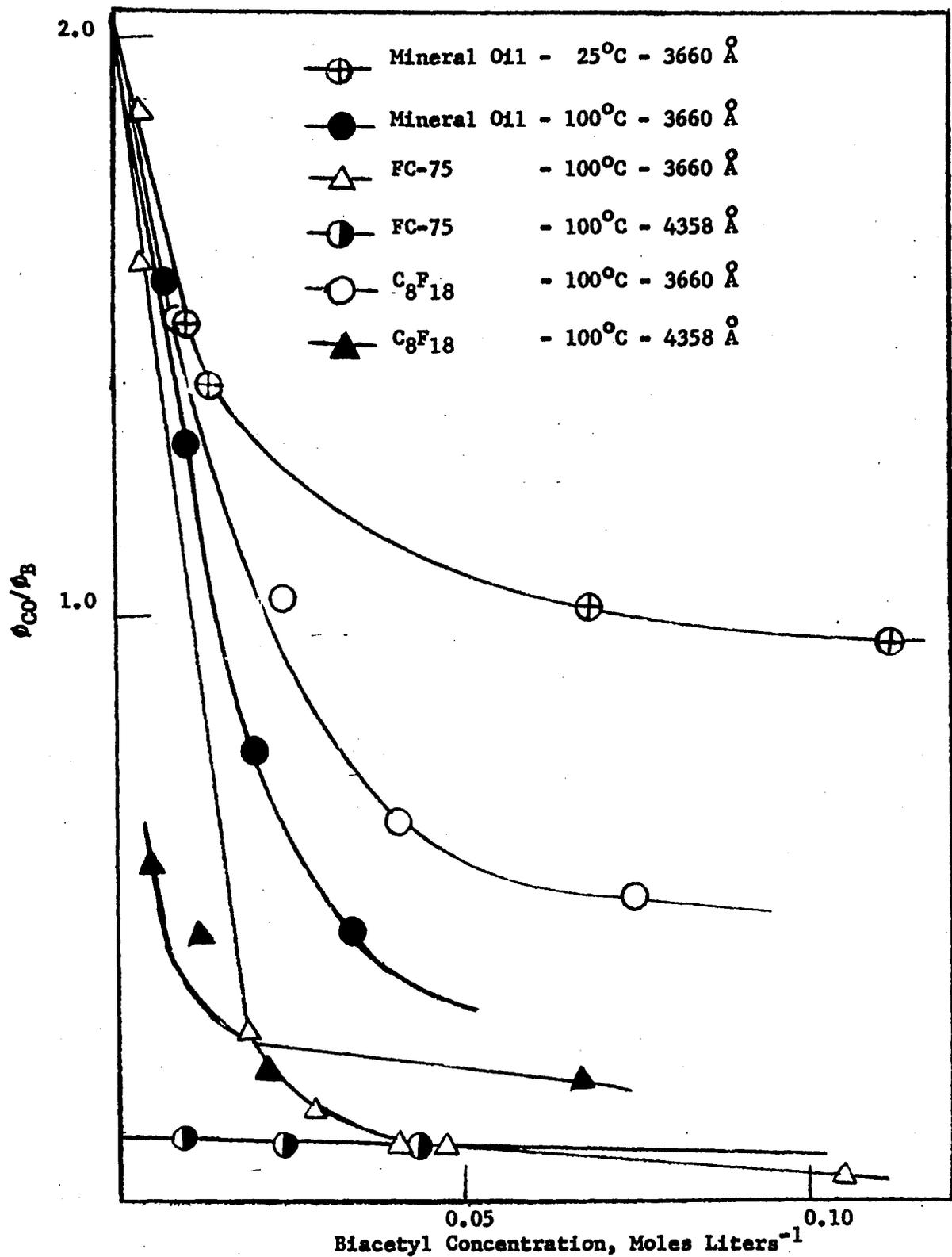


Figure 5 - Effect of Biacetyl Concentration Upon The Ratio of Quantum Yields of Carbon Monoxide Production and Biacetyl Disappearance

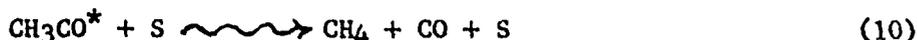
$\frac{1}{2}\phi_{CO}$ . It is therefore evident that

$$\phi_D = 2/3(\phi_B - 1/2\phi_{CO}) \quad (VI)$$

where  $\phi_D$  represents the quantum yield of formation of product D. The values of  $\phi_D$  computed from VI are included in Tables I-VII.

At very low biacetyl concentration, interactions between solute molecules will be minimized and the photolysis will approximate the vapor phase behavior. If this assumption is correct  $\frac{1}{2}\phi_{CO}$  should be a good measure of the primary yield less the geminate ("cage") recombination. The limiting values of  $\phi_{CO}$  in solution and in the high pressure vapor phase photolysis are listed in Table X.

The generally low quantum yields in solution compared to the vapor are not surprising in view of the high probability of geminate recombination<sup>3,15,16</sup>. Although in all cases  $\phi_{CO}$  is less in solution than in the vapor, the yield in FC-75 at 3660 Å is significantly higher than in the other solvents investigated. This anomalously high yield can be tentatively ascribed to reaction of a vibrationally excited acetyl radical with the solvent.



It has been quite conclusively demonstrated that FC-75 contains a considerable amount of very reactive hydrogen<sup>3</sup>. The abstraction of hydrogen atoms from FC-75 by methyl radicals is so efficient at 25°C that the photolysis of acetone in this solvent produces no ethane. In contrast to this, photolysis of acetone under the same conditions in a completely fluorinated solvent results in a predominance of ethane over methane. These results lend credence to the validity of step (10) as a mode of production of carbon monoxide in FC-75 at 3660 Å. The assumption that it is the species  $CH_3CO^*$  rather than  $CH_3CO$  which participates in the

TABLE X

 $\phi_{CO}$  at 100°C

Excitation Wave-length	Vapor <sup>10</sup>	C <sub>8</sub> F <sub>18</sub>	FC-75	Mineral Oil
3660 Å	0.21	0.005	0.10	0.016
4358 Å	0.06	0.0002	0.0003	

reaction with this solvent is based on the observation that  $\phi_{CO}$  is very low at 4358 Å where thermally equilibrated radicals predominate.

The comparable magnitude of  $\phi_{CO}$  at 3660 Å in the vapor phase and in FC-75 suggests that solvent deactivation cannot compete efficiently with dissociation. The high CO yield indicates that the reaction of acetyl radicals with the solvent competes favorably with geminate recombination. Thus FC-75 acts as a radical sink with high efficiency.

If attention is directed to the value of  $\phi_{CO}$  at 4358 Å in FC-75, it can be seen that there is a 300-fold decrease in this quantity relative to that at 3660 Å. This drastic reduction in  $\phi_{CO}$  cannot be ascribed to the reduction of the primary yield. The vapor phase data indicate that the primary yield is reduced by only a factor of about 4 as excitation is shifted from 3660 Å to 4358 Å. The much larger effect observed in solution may be attributed to the increased efficiency of (10) compared to the abstraction from the solvent by thermally equilibrated acetyl radicals. A more likely explanation is that the higher kinetic energy of the acetyl radicals formed at 3660 Å permits a large fraction to escape from the cage and to avoid geminate recombination<sup>16</sup>. Since the energy available at 4358 Å does not provide much margin above that necessary to dissociate a biacetyl molecule, it is reasonable to expect that radicals formed at this wavelength have small kinetic energies. Therefore, it is to be expected that a larger fraction of the acetyl radicals formed at 4358 Å are confined to the "cage" and undergo recombination to regenerate biacetyl than at 3660 Å. The larger CO yields at 3660 Å than at 4358 Å in both C<sub>8</sub>F<sub>18</sub> and FC-75 tend to support this argument.

The results of the photolysis of biacetyl in C<sub>8</sub>F<sub>18</sub> solutions

indicate that the quantum yields are lower in this system than in FC-75. There is some evidence that completely fluorinated hydrocarbons are more efficient quenchers of electronic excitation than FC-75<sup>3</sup>. A more efficient degradation of excited biacetyl molecules would correspond to a reduction of the primary yield. The lower yields in C<sub>8</sub>F<sub>18</sub> may, therefore, be due in part to a lower primary yield than occurs in FC-75.

The difficulties involved in the establishment of an unambiguous mechanism are so great that it would seem premature to propose a definitive mechanism on the basis of the somewhat limited study of the character reported herein. It should be emphasized that the mechanism postulated for the liquid phase photolysis of biacetyl is offered primarily as an aid in the discussion of the results and as a guide to further study in this area.

The trends observed in the data shown in Tables I-VII and figure 5 differ considerably at the two wavelengths employed. Due to the character of the wavelength dependence of the photolysis, the results will be considered separately at each wavelength.

#### 4358 Å Excitation

The principal facts to be explained are:

1.  $\phi_B$  and  $\phi_{CO}$  increase slightly with increasing biacetyl concentration.
2.  $\phi_B$  is about six times larger in FC-75 than in C<sub>8</sub>F<sub>18</sub>.

The first point can be accounted for partially on the basis of energetics of the reaction. The energy available per photon at 4358 Å is insufficient to produce acetyl radicals at 25°C in the vapor phase<sup>10</sup>, and it is not to be expected that solvents alter this result. As the temperature is raised to 100°C the extra thermal energy enables dissociation

to proceed, but the primary act probably produces  $\text{CH}_3\text{CO}$  rather than  $\text{CH}_3\text{CO}^*$ . If the thermally equilibrated acetyl radicals react with biacetyl according to step (9), the increase in  $\phi_{\text{CO}}$  with increasing biacetyl concentration can then be ascribed to the greater efficiency of



relative to (3). The inclusion of step (11) implies that the species D is less stable than  $\text{CH}_3\text{CO}$ . The reaction sequence of step (9) followed by (11) is tantamount to the formation of some sort of short-lived complex, in which a redistribution of vibrational energy results in the production of CO and  $\text{CH}_3$  and the regeneration of an unexcited biacetyl molecule. Increasing the biacetyl concentration would result in an increase in the rate of formation of D and therefore an increase in the quantities  $\phi_{\text{CO}}$  and  $\phi_{\text{B}}$ .

The second point concerning the relative magnitudes of  $\phi_{\text{B}}$  in FC-75 and C8F18 can be explained on the basis of the reactivity of FC-75. The larger quantum yield for biacetyl disappearance in the fluorinated ether is probably due to a reaction of the type



From figure 5, it can be seen that  $\phi_{\text{CO}}/\phi_{\text{B}}$  is essentially constant in FC-75, and equal to 0.1. The constancy of  $\phi_{\text{CO}}/\phi_{\text{B}}$  in this system is somewhat puzzling in view of the increase in  $\phi_{\text{B}}$  with increasing biacetyl concentration. This trend indicates that reaction (9) is more efficient than (12) in removing acetyl radicals. It might be expected that the rate of (12) would be greater than (9) due to the very high concentration of solvent relative to biacetyl. However, it is quite probable that the species S represents not the bulk solvent molecule, but rather a reactive solvent molecule. The high methane yields indicate the presence of

residual hydrogen in FC-75, so that S may be an incompletely fluorinated molecule. In this case, step (12) might be more accurately described as an abstraction rather than an addition reaction. In  $C_8F_{18}$  the chemical inertness of the solvent prohibits reactions of this type, making it possible for acetyl radicals to diffuse together and recombine. This process would then result in a lower  $\phi_B$  than in FC-75. Although  $\phi_{CO}/\phi_B$  remains essentially independent of the biacetyl concentration in FC-75, this ratio increases markedly in  $C_8F_{18}$  as the biacetyl concentration decreases. Although there is insufficient data at extremely low biacetyl concentrations to perform an accurate extrapolation,  $\phi_{CO}/\phi_B$  appears to approach a value near 2. This behavior is to be expected if  $C_8F_{18}$  does not participate in a reaction analogous to (12), and  $CH_3CO$  only reacts according to steps (3), (9) and (7).

#### 3660 Å Excitation

The principal trends to be explained at this wavelength are:

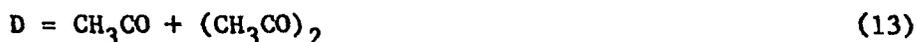
1.  $\phi_{CO}$  decreases markedly with increasing biacetyl concentration.
2.  $\phi_B$  is nearly independent of the biacetyl concentration over a wide range.

The very much larger  $\phi_{CO}$  at 3660 Å than at 4358 Å can be attributed to the greater efficiency of step (2) compared to (3). It is certainly reasonable to expect that the probability of decomposition of vibrationally excited acetyl radicals will exceed that of the thermally equilibrated species. The magnitude of  $\phi_{CO}$  indicates that a significant fraction of the excited radicals decompose prior to collisional deactivation at 3660 Å.

It is conceivable that the increasing importance of step (8) with increasing biacetyl concentration could explain the diminution of

$\phi_{CO}$ , since this reaction involves the disappearance of biacetyl without the production of carbon monoxide. However, it should be noted that step (8) uses  $3/2$  biacetyl molecules for every potential CO molecule lost. This sequence would then predict an increase in  $\phi_B$  accompanying the decrease in  $\phi_{CO}$ . Since this prediction is clearly inconsistent with the experimental data, the effect of biacetyl concentration upon  $\phi_{CO}$  cannot be attributed exclusively to a reaction between excited acetyl radicals and biacetyl molecules.

However, if reaction (8) was followed by another step of the form



the result would be the deactivation of  $CH_3CO^*$  and the formation of much more stable acetyl radicals which could then recombine to regenerate biacetyl according to step (7). The postulation of steps (11) and (13) as parallel reactions is equivalent to the assumption that only the fraction  $\beta$  of species D produced are sufficiently long lived to react by (11) or an analogous process and that  $(1 - \beta)$  form  $CH_3CO$  and regenerate biacetyl.

The quantity  $\beta$  can be estimated from the experimental results. Since only the fraction  $\beta$  of D gives rise to carbon monoxide, any observed variation in  $\phi_D$  would be reflected in a change in  $\phi_{CO}$  multiplied by  $\beta$ .

$$- \beta \Delta \phi_{CO} = \Delta \phi_D \quad (VII)$$

From equation (VI) the relation is obtained whereby

$$\Delta \phi_D = 2/3(\Delta \phi_B - 1/2 \Delta \phi_{CO}) \quad (VIII)$$

Combining these two equations, it follows that

$$- \beta \Delta \phi_{CO} = 2/3 \Delta \phi_B - 1/3 \Delta \phi_{CO} \quad (IX)$$

In order to account for the near constancy of  $\phi_B$  ( $\Delta \phi_B = 0$ ) a value of  $\beta = 1/3$  is required. This value of  $\beta$  is a lower limit based on the mechanism herein developed. Additional steps for the reaction of D could result in a higher calculated value of  $\beta$ .

On the basis of the postulated mechanism for the photolysis of biacetyl solutions it is possible to calculate expressions for the various quantum yields in terms of the rate constants for the pertinent steps. If it is assumed that the rate of formation of  $\text{CH}_3\text{CO}^*$  is  $2\alpha\phi_P I_a$ , where  $\phi_P$  = (primary dissociation yield - geminate recombination yield) and  $\text{CH}_3\text{CO}^*$  refers to vibrationally excited acetyl radicals which have escaped cage recombination, the concentration of  $\text{CH}_3\text{CO}^*$  can be calculated by means of the usual steady state approximations.

$$2\alpha\phi_P I_a = k_2(\text{CH}_3\text{CO}^*) + k_8(\text{CH}_3\text{CO}^*)(B) \quad (\text{X})$$

where (B) = biacetyl concentration

$I_a$  = rate of absorption of quanta

$\alpha$  = the fraction of biacetyl molecules which dissociate into vibrationally excited acetyl radicals

Solution of this equation for  $(\text{CH}_3\text{CO}^*)$  gives

$$(\text{CH}_3\text{CO}^*) = \frac{2\alpha\phi_P I_a}{k_2 + k_8(B)} \quad (\text{XI})$$

The rate of formation of carbon monoxide is given by

$$\frac{d}{dt}(\text{CO}) = k_2(\text{CH}_3\text{CO}^*) \quad (\text{XII})$$

Substitution of  $(\text{CH}_3\text{CO}^*)$  into the rate expression for CO yields

$$\frac{d}{dt}(\text{CO}) = \frac{2\alpha\phi_P I_a k_2}{k_2 + k_8(B)} \quad (\text{XIII})$$

Since the ratio of the rate of formation of carbon monoxide and the rate at which quanta are absorbed is equal to the quantum yield of

formation of CO, rearrangement of equation (XIII) gives

$$\phi_{\text{CO}} = \frac{2\alpha \phi_p k_2}{k_2 + k_8(B)} \quad (\text{XIV})$$

or the equivalent expression

$$\frac{1}{\phi_{\text{CO}}} = \frac{1}{2\alpha \phi_p} + \frac{k_8(B)}{2k_2\alpha \phi_p} \quad (\text{XV})$$

Similarly, the expression for the rate of formation of the product D is given by

$$\frac{d-(D)}{dt} = \beta k_8(\text{CH}_3\text{CO}^*)(B) \quad (\text{XVI})$$

where, as before,  $\beta$  refers to the fraction of the reaction which does not result in acetyl radical stabilization. Substitution of  $(\text{CH}_3\text{CO}^*)$  into this expression and rearrangement leads to the result

$$\frac{1}{\phi_D} = \frac{1}{2\alpha \beta \phi_p} + \frac{k_2}{2k_8\alpha \beta \phi_p} \quad (\text{XVII})$$

Equations (XV) and (XVII) predict that  $1/\phi_{\text{CO}}$  and  $1/\phi_D$  should be linear functions of  $(B)$  and  $1/(B)$  respectively. It can be seen from figure 6 that a plot of  $1/\phi_{\text{CO}}$  vs.  $(B)$  is quite linear, which is consistent with the mechanism.

In figure 6 it can be seen that the slopes obtained for  $\text{C}_8\text{F}_{18}$  and mineral oil are nearly identical. This means that  $k_8/2k_2\alpha \phi_p$  is the same for the two systems. If (8) is a diffusion controlled reaction, then  $k_8$  would be much smaller in the more viscous solvent [Table (XI)]. Since  $k_2$ ,  $\alpha$  and  $\phi_p$  cannot be very viscosity dependent,  $k_8$  appears to be constant. The lack of viscosity dependence for the bimolecular rate constant could be attributed to the requirement of an activation energy for reaction (8). The activation energy of 13,300 cal/mole found in the vapor phase photolysis of biacetyl<sup>17</sup> may correspond to the activation energy for (8).

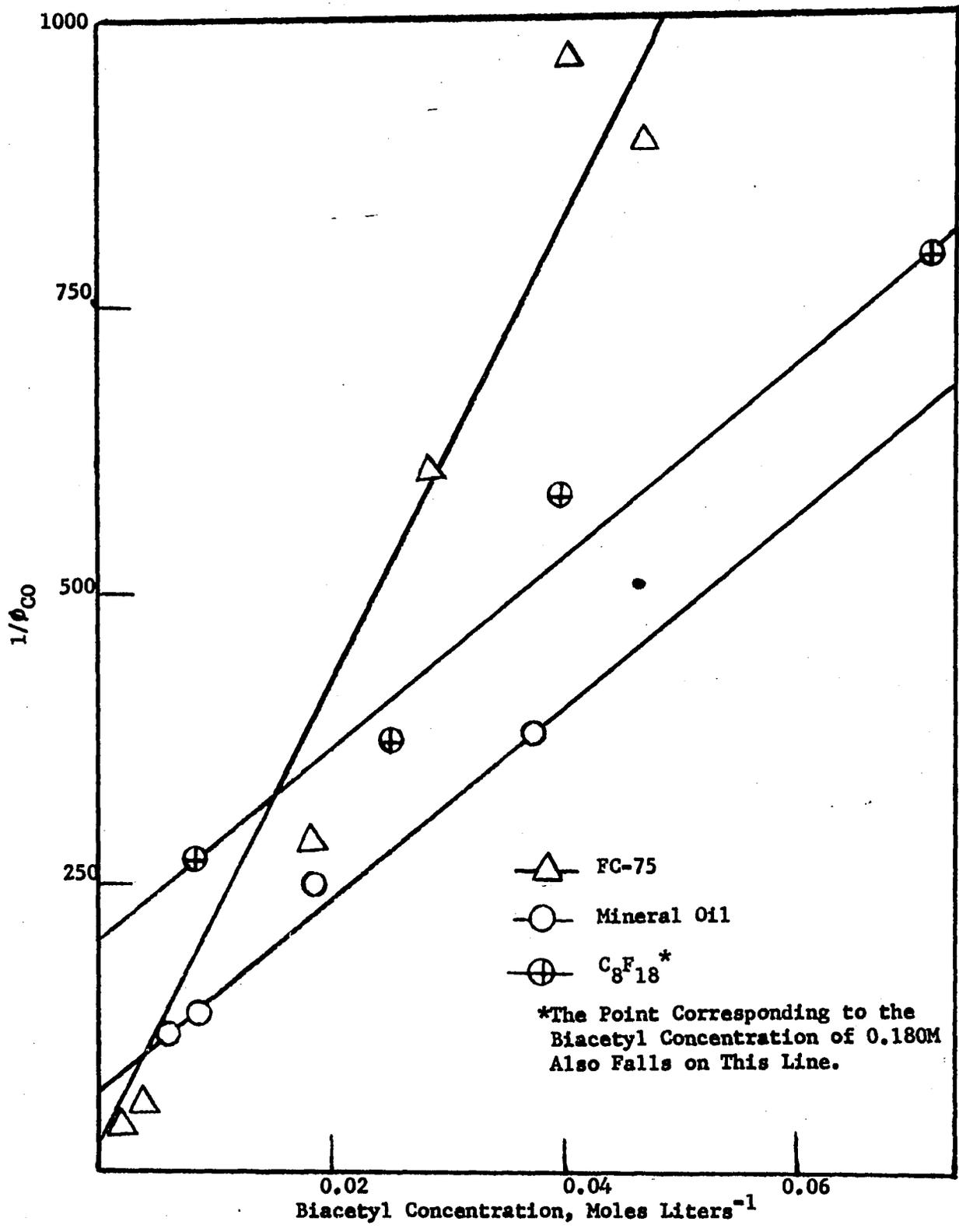


Figure 6 - Effect of Concentration Upon the Quantum Yield of Carbon Monoxide Production at 100°C and 3660 Å Excitation

TABLE XI

## Viscosity of Solvents

Solvent	Temperature	Viscosity Centipoise
FC-75	100°C	0.52
C <sub>8</sub> F <sub>18</sub>	100°C	0.63
Mineral Oil	100°C	4.27
Mineral Oil	25°C	34.1

The calculation of  $1/\phi_{CO}$  is applied to the most general case, so that reaction (10) is neglected. However, in FC-75 the importance of reactions with the solvent has been mentioned. Inclusion of step (10) leads to

$$\frac{1}{\phi_{CO}} = \frac{1}{2\alpha\phi_P} + \frac{k_8(B)}{2[k_2 + k_{10}(S)]\alpha\phi_P} \quad (\text{XVIII})$$

The very small intercept of FC-75 in figure 6 can be interpreted in terms of a larger primary yield in the perfluoro-ether than in  $C_8F_{18}$  or mineral oil.

In figure 7 are shown the plots of  $1/\phi_D$  vs.  $1/\phi_B$ . The striking linearity in accord with prediction again tends to support the proposed mechanism. From the intercepts of the plots in figures 6 and 7 it is possible to calculate  $\beta$ . The ratio of the intercepts of figures 6 and 7 for any solvent is equal to  $\beta$ . The values calculated for FC-75 and  $C_8F_{18}$  are 0.22 and 0.36 respectively, in good agreement with the predicted value of 0.33.

If attention is directed to the expressions derived for  $1/\phi_{CO}$  and  $1/\phi_B$  it will be noted that the ratio  $k_8/k_2$  appears in both equations. By inserting the value of  $1/2\alpha\phi_P$  obtained from the intercept of figure 6 into the slope obtained from the same plot, a value may be obtained for  $k_8/k_2$ , and compared to this ratio calculated from the results of figure 7. For  $C_8F_{18}$  solutions the values of  $k_8/k_2$  calculated from figures 6 and 7 are 41 l/m and 36 l/m respectively. This agreement is striking in view of the fact that the intercepts are obtained by extrapolation to zero biacetyl concentration in one case and high concentration in the other. Due to the scatter in the mineral oil results in figure 6 the slope and intercept are subject to considerable uncertainty. If, however, only

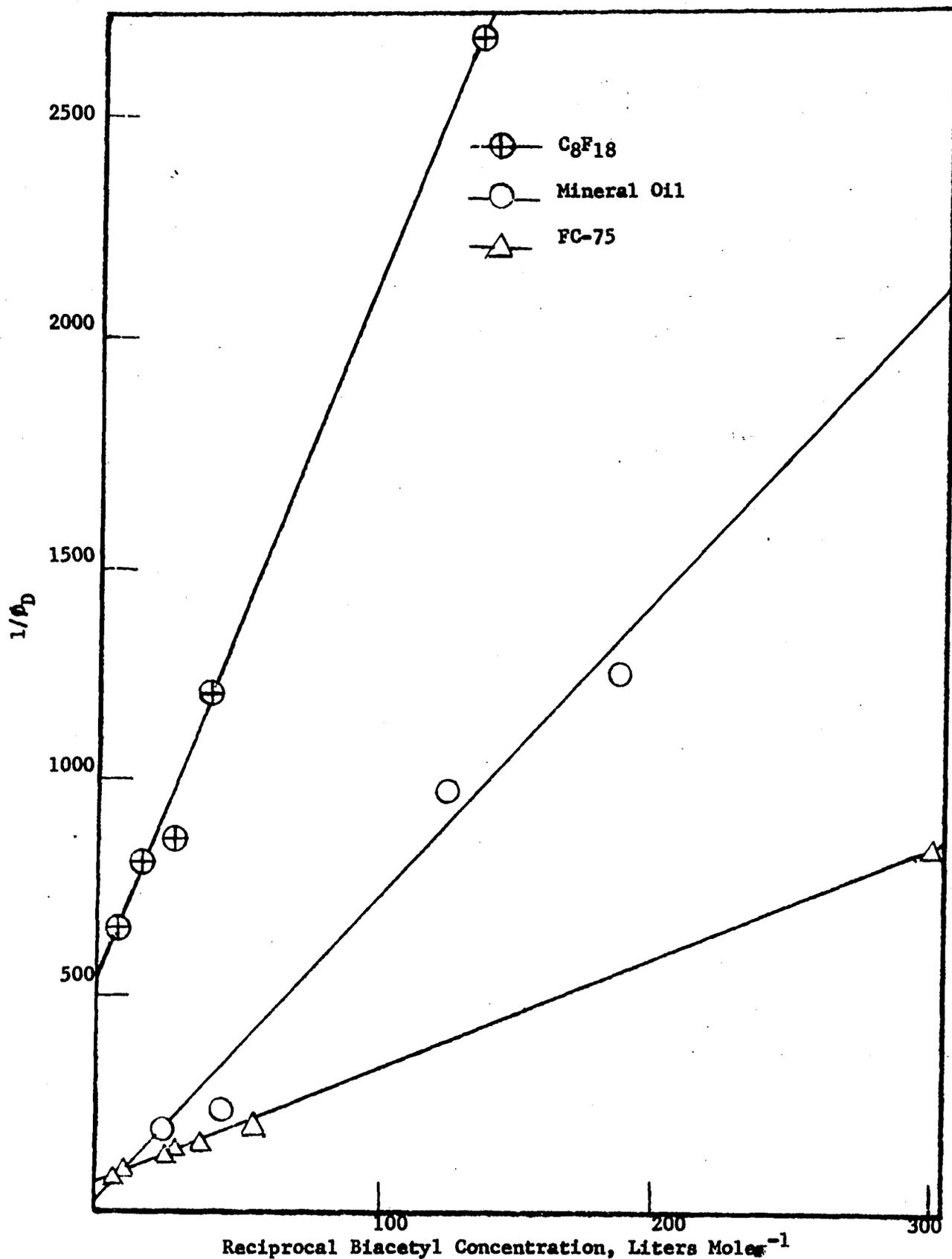


Figure 7 - Effect of Biacetyl Concentration Upon The Quantum Yield of Product D at 100°C and 3660 Å Excitation

points corresponding to low biacetyl concentrations are considered, agreement comparable to that obtained for  $C_8F_{18}$  is obtained. For FC-75 solutions, the expression for  $\phi_{CO}$  involves step (10), a bimolecular reaction with the solvent. Since, at this time, it is impossible to evaluate the quantity  $k_{10}(S)$ , this type of treatment cannot be meaningfully applied to the FC-75 data.

The observation of photo-decomposition of biacetyl in mineral oil at  $25^\circ$  poses a problem in relation to the mechanism at  $3660 \text{ \AA}$ . As previously mentioned, mineral oil was the only solvent employed in which photolysis was found to proceed to measurable extent at this temperature. It is possible that the very high viscosity of this system would strongly inhibit the diffusion of biacetyl and thereby reduce the importance of reaction (8). If the  $CH_3CO^*$  is not deactivated by reaction with biacetyl it may then decompose. In the other solvents, the viscosity remains low enough for considerable diffusion to occur, allowing deactivation of excited acetyl radicals to occur.

The limiting  $\phi_{CO}$  is of the order of 0.003 at  $25^\circ$  compared to 0.016 at  $100^\circ$ . This reduction closely parallels the temperature dependence of the primary yield in the vapor phase. From figure 5 it can be seen that the biacetyl concentration has little effect upon  $\phi_{CO}$  at  $25^\circ$  compared to  $100^\circ$ . This result tends to verify the assumption that the high viscosity severely reduces the rate of step (8). Although the mineral oil is much more viscous than  $C_8F_{18}$  at  $100^\circ$ , the values of  $\phi_D$  are larger in mineral oil than in the perfluorooctane. This result appears to be inconsistent with the explanation of the low temperature photolysis. However, the mineral oil used contained a considerable amount of unsaturated impurities. It is possible that these impurities

might alter the course of reaction to an appreciable extent.

As previously mentioned, failure to observe decomposition at 25° in the other solvents might be due to the importance of step (8) in the mechanism. It would then be expected that at sufficiently low biacetyl concentrations the rate of reaction (8) would be suitably diminished so that some reaction would occur at 25°. Failure to observe this effect leads to the conclusion that the mineral oil results are anomalous in respect to the 25° photolysis. However, the possibility remains that the biacetyl concentration was not sufficiently reduced to effectively eliminate the effects of reaction (8). Under the experimental conditions employed, it was not possible to utilize concentrations below 0.002 M and still obtain meaningful results.

#### The Mechanism of Ethane Formation

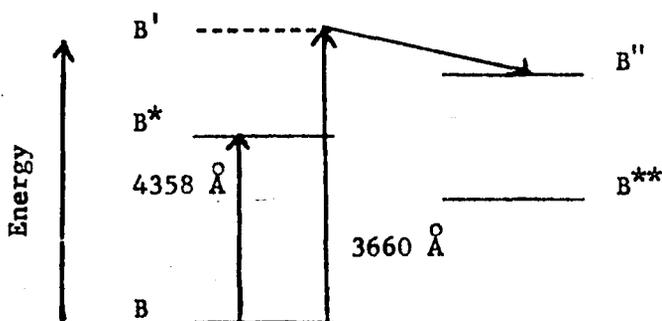
Only at very high concentrations is methane produced in C<sub>8</sub>F<sub>18</sub> solutions. When the incident intensities and concentrations are comparable to those employed in the vapor phase photolysis, no methane is produced, although in the vapor phase methane and ethane are produced in approximately equivalent amounts. This is surprising since it is to be expected that biacetyl in C<sub>8</sub>F<sub>18</sub> would exhibit gas-like behavior. In the gas phase, methane is produced by the methyl radical abstraction of a hydrogen atom from biacetyl. In perfluoro<sup>18</sup>octane, where the solvent does not contain hydrogen, CH<sub>4</sub> must be produced by the same mode as in the vapor phase photolysis. If the ethane is produced by step (4), the only explanation for the absence of methane would be a smaller steric factor for methyl abstraction of hydrogen from biacetyl in solution than in the gas phase. Some evidence exists that this indeed may be the case<sup>18</sup>.

The possibility that "cage" recombination is responsible for ethane

formation cannot be excluded. The predominance of  $C_2H_6$  over  $CH_4$  in mineral oil at both  $100^\circ$  and  $25^\circ$  lends support to a "cage" process for ethane production. Photolysis of mixtures of biacetyl and completely deuterated biacetyl, followed by an isotopic analysis of the resulting ethanes might help to resolve this point.

### An Alternative Mechanism

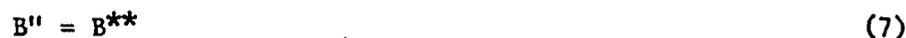
The preceding mechanism was developed on the assumption of the existence of a relatively long-lived (ca.  $10^{-9}$  sec) vibrationally excited acetyl radical. Undoubtedly the non-gas producing part of the reaction can be attributed to a reaction of a comparatively long-lived species with unexcited biacetyl. It might be useful to consider a mechanism in which the intermediate is a biacetyl molecule in an excited electronic state,  $B''$ . The lack of effect of varied triplet state lifetime upon the observed trends, as previously discussed, probably excludes the lowest triplet state from participating in the bimolecular reaction. However, the possibility remains that another higher triplet level might be involved. The postulated relationship of this level to the first excited singlet and triplet states is shown below.



In this scheme B,  $B^*$ ,  $B'$ ,  $B^{**}$  and  $B''$  refer to the ground state, first excited singlet, upper vibrational levels of the first excited singlet, lowest triplet and the higher triplet level respectively.

On the basis of this energy relationship, the mechanism for 4358 Å excitation would be identical to that previously discussed. However, at 3660 Å the absorbed energy may be great enough to raise the biacetyl molecule to a high vibrational level of the excited singlet state. If B'' lies just below B' a radiationless intersystem crossing may occur between B'' and B'. Dissociation may then occur from the B'' level. This does not occur at 4358 Å since B'' is of higher energy than the level reached with this excitation.

The nature of the product which is formed in the process of biacetyl disappearance has not been determined. Some evidence exists that in the vapor phase photolysis, a dimer may be formed. On the basis of these assumptions the mechanism for 3660 Å excitation would be



The steady state treatment gives the result

$$2k_4(B'') = k_5(\text{CH}_3\text{CO}) + k_9(\text{CH}_3\text{CO})^2 \quad (\text{XIX})$$

Solution of this expression for (CH<sub>3</sub>CO) yields

$$(\text{CH}_3\text{CO}) = \frac{-k_5 \pm k_5 \left[ 1 + \frac{8k_9k_4(B'')}{k_5^2} \right]^{\frac{1}{2}}}{2k_9} \quad (\text{XX})$$

The choice of the plus sign in this expression is dictated by the requirement that  $(\text{CH}_3\text{CO})$  vanishes as  $(B'')$  goes to zero. Hence

$$(\text{CH}_3\text{CO}) = \frac{-k_5 + k_5 \left[ 1 + \frac{8k_9k_4(B'')}{k_5^2} \right]^{\frac{1}{2}}}{2k_9} \quad (\text{XXI})$$

Since  $\frac{2k_4k_9(B'')}{k_5^2}$  is much less than 1 the quantity in brackets can be expanded according to the approximation

$$(1 + x)^{\frac{1}{2}} = 1 + \frac{1}{2}x$$

which leads to

$$(\text{CH}_3\text{CO}) = \frac{-k_5 + k_5 \left[ 1 + \frac{4k_9k_4(B'')}{k_5^2} \right]}{2k_9} \quad (\text{XXII})$$

and finally to

$$(\text{CH}_3\text{CO}) = \frac{2k_4(B'')}{k_5} \quad (\text{XXIII})$$

In a similar manner the expression

$$(B'') = \frac{k_3 I_a}{(k_2 + k_3) [(k_4 + k_7) + (k_6 + k_8)(B)]} \quad (\text{XXIV})$$

can be obtained using the steady-state treatment. Substitution of this result into the expression for  $(\text{CH}_3\text{CO})$  gives

$$(\text{CH}_3\text{CO}) = \frac{2k_4k_3I_a}{k_5(k_2 + k_3) [(k_4 + k_7) + (k_6 + k_8)(B)]} \quad (\text{XXV})$$

From step (6)

$$\frac{d}{dt}(B_2) = k_6(B'')(B) \quad (\text{XXVI})$$

Using the above expression for (B'') leads to

$$\phi_{B_2} = \frac{k_3 k_6 (B)}{(k_2 + k_3) [(k_4 + k_7) + (k_6 + k_8) (B)]} \quad (\text{XXVII})$$

$$\text{or } \frac{1}{\phi_{B_2}} = \frac{(k_2 + k_3)(k_4 + k_7)}{k_6 k_3} + \frac{(k_2 + k_3)(k_4 + k_7)}{k_6 k_3 (B)} \quad (\text{XXVIII})$$

From step (5)

$$\frac{d}{dt}(\text{CO}) = k_5(\text{CH}_3\text{CO}) \quad (\text{XXIX})$$

Using the expression derived for (CH<sub>3</sub>CO) leads to

$$\phi_{\text{CO}} = \frac{2k_4 k_3}{(k_2 + k_3) [(k_4 + k_7) + (k_6 + k_8) (B)]} \quad (\text{XXX})$$

$$\text{or } \frac{1}{\phi_{\text{CO}}} = \frac{(k_2 + k_3)(k_4 + k_7)}{2k_4 k_3} + \frac{(k_2 + k_3)(k_6 + k_8) (B)}{2k_4 k_3} \quad (\text{XXXI})$$

Since 2 molecules of biacetyl are consumed for each dimer formed, and 2 molecules of CO are produced for each biacetyl dissociated, numerical evaluations of  $\phi_{B_2}$  may be performed by inserting the experimental values of  $\phi_B$  and  $\phi_{\text{CO}}$  into the expression

$$\phi_{B_2} = \frac{1}{2}(\phi_B - \frac{1}{2}\phi_{\text{CO}}) \quad (\text{XXXII})$$

This relation is similar to equation VI from which the values of  $\phi_D$  were calculated,

$$\phi_D = \frac{2}{3}(\phi_B - \frac{1}{2}\phi_{\text{CO}}) \quad (\text{VI})$$

It is evident, therefore, that values of  $\phi_B$  may be obtained by multiplying the values of  $\phi_D$  in Tables I-VII by 3/4.

These equations not only lead to the same linear dependence as the previous set, but also the evaluation of  $(k_6 + k_8)/(k_4 + k_7)$  from figures 6 and 7 gives precisely the same numerical agreement: 41 l/m and 38 l/m in C<sub>8</sub>F<sub>18</sub>. This is not surprising because the mathematical formalism is the same for both mechanisms. The ratio of the intercepts

in  $C_8F_{18}$  of figures 6 and 7 (corrected to  $\phi_{B_2}$ ) can be evaluated to give

$$\frac{k_6}{2k_4} \frac{(k_6 + k_8)}{(k_4 + k_7)} = 0.28 \quad (\text{XXXIII})$$

Insertion of the calculated value of  $(k_6 + k_8)/(k_4 + k_7)$  into this equation leads to a value of approximately 30 l/m for the ratio  $k_6/k_4$ .

If reaction (6) is diffusion controlled,  $k_6$  would be of the order of  $10^{10} \text{ l m}^{-1} \text{ sec}^{-1}$  and  $k_4$  would be equal to approximately  $3 \times 10^8 \text{ sec}^{-1}$ .

A value of  $k_4$  of this order of magnitude would enable the dissociation of  $B''$  to compete favorably with internal conversion to the lowest triplet state, which is consistent with this mechanism.

## CONCLUSIONS

The difficulties inherent in the establishment of an unambiguous mechanism are demonstrated in the previous section. Although two mechanisms have been proposed to account for the results of this study, neither has been conclusively demonstrated to be correct.

Physically the second mechanism is perhaps more satisfactory, since it is more plausible to postulate a long-lived electronically excited species than a long lived-vibrationally excited species in solution.

Unfortunately, a spectroscopic verification of a higher triplet level of the type proposed would be difficult. Due to the rather narrow energy gap between this level and the lowest triplet, transitions would occur in the infra-red region of the spectrum where detection is difficult.

The only real way that a verification of either mechanism could be obtained would be through a complete product analysis. Although the quantities of products formed are small, recent advances in such techniques as vapor phase chromatography and mass spectrometry indicate that such analyses could be performed.

In the future, particular emphasis should be placed on studies at very low concentrations, since the ratio  $\phi_{CO}/\phi_B$  shows the most marked concentration dependence below biacetyl concentrations of 0.02 M. The use of 10 cm. cells would permit accurate measurement of changes in the concentration in more dilute solutions than was possible in this study.

Quartz cells would also permit absorption measurements in the ultraviolet region where the products absorb.

Liquid phase photolytic studies of acetone<sup>20,21</sup> and other ketones<sup>22</sup> have indicated the difficulties to be expected as well as the potentialities of these systems for useful information. This work bears out the fruitfulness of solution photolyses. Further work in this area coupled with further vapor phase studies may lead to a complete understanding of the photochemical behavior of biacetyl and other simple ketones in the near future.

Although this work is by no means conclusive it is hoped that the trends observed and the mechanisms proposed will serve as a guide to further study in this area.

## APPENDIX A

The calibration of the light sources was performed by uranyl oxalate actinometry. The details of the procedure are described elsewhere<sup>8</sup>. Into an identical cuvette as that used in the biacetyl photolysis, was placed a carefully measured volume of uranyl oxalate solution. With no sample in the light beam, the galvanometer deflection was recorded. The sample was then placed in the light beam. At ten minute intervals the cuvette was removed and the photometer reading again recorded. No change in the deflection throughout the irradiation was noted. The irradiation period was varied between 100 and 120 minutes for various runs.

The irradiated solution was then titrated with 0.2408N  $\text{KMnO}_4$  to a near end-point, followed by titration with 0.0366N  $\text{KMnO}_4$  to a permanent end-point. The end-point was assumed to be reached when the first pink coloration lasting 30 seconds was observed in the solution. An unirradiated sample was also titrated as a blank.

The data and calculations for a typical determination are shown below.

Volume of solution	= 8.00 ml.
Irradiation period	= 100 minutes
Galvanometer deflection	= 18.0
Volume 0.2408N $\text{KMnO}_4$ consumed	= 3.13 ml.
Volume 0.0366N $\text{KMnO}_4$ consumed	= 1.23 ml.

Moles oxalate initial	= 4.1368 x10 <sup>-4</sup>
Moles oxalate final	= 3.9936 x10 <sup>-4</sup>
Moles oxalate decomposed	= 1.43 x10 <sup>-5</sup>
Molecules oxalate decomposed	= 8.60 x10 <sup>18</sup>
Quantum yield of decomposition <sup>8</sup>	= 0.49
Quanta absorbed	= 1.76 x10 <sup>19</sup>
Quanta absorbed/minute	= 1.76 x10 <sup>17</sup>
Quanta incident/minute	= 6.77 x10 <sup>17</sup>

Since the galvanometer deflection is proportional to the incident intensity, the ratio of quanta incident/minute to the deflection gives a value for the number of incident quanta/minute per unit deflection. Values of this ratio (K) at 3660 Å with the AH-6 lamp were found to be 3.82 x10<sup>16</sup>, 3.73 x10<sup>16</sup>, 3.71 x10<sup>16</sup>, 3.75 x10<sup>16</sup> and 3.76 x10<sup>16</sup> for five determinations.

Similarly values of K determined using 4358 Å incident radiation were 5.30 x10<sup>16</sup>, 5.34 x10<sup>16</sup> and 5.32 x10<sup>16</sup>. For quantum yield determinations an average value of K was taken as the photometer constant.

Using the appropriate value of K, the product of the galvanometer deflection and K yielded a value for the rate at which light was incident upon the sample in the light beam.

## APPENDIX B

Preliminary attempts to develop a vapor phase chromatographic technique for the quantitative analysis of methane, ethane and carbon monoxide were made using a six foot column constructed of 3 mm. copper tubing packed with silica gel (Burrell Corp. catalog no. 341-25), a Gow-Mac power supply and thermal conductivity cell, and a Leeds and Northrup Model S type G single point E. M. F. recorder of 1.0 millivolt sensitivity. Poor resolution and extensive tailing were observed with the column at room temperature.

When the column was activated at 200°C for 2 hours, then cooled to -195°C by immersion in liquid nitrogen good resolution of the peaks corresponding to CO, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> was obtained. Although a qualitative separation was obtained with a column temperature of -195°C, quantitative reproducibility was not observed. No correlation between the amount of gas introduced and either peak heights or areas was found.

It is quite probable that a more thorough investigation of this procedure would indicate that this method of analysis could be effectively applied to the determination of the gaseous products of biacetyl photolysis. Certainly this method is more rapid than the manometric technique, and can differentiate between products that could not be separated on the basis of their vapor pressures.

## APPENDIX C

The temperature dependence of the photo-decomposition of biacetyl solutions poses some problems which have not been resolved by the proposed mechanism. Thermal population of high vibrational levels of the ground state leading to increased population of high vibrational levels of the first excited singlet state cannot account for the hundred-fold increase in the measured quantum yields as the temperature is raised from 25°C to 100°C in FC-75 and C<sub>8</sub>F<sub>18</sub>.

In relation to the alternative mechanism, the absence of decomposition at 25°C can be interpreted as meaning that the removal of vibrational energy from B' by solvent molecules at 100°C is so efficient that internal conversion to B'' does not occur to an appreciable extent. At 100°C this deactivation is apparently less efficient. The vapor phase results do show that the primary yield is diminished with increasing pressure, and that this pressure effect is more pronounced as the temperature is decreased. This implies that vibrational deactivation is much more efficient at 25°C than at 100°C.

The mineral oil results may be considered in terms of this deactivation hypothesis. The very high viscosity at 25°C may so inhibit the removal of vibrational energy that internal conversion to the B'' state can occur. Further work with highly purified solvents of different viscosities might be useful in testing this suggestion.

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