SOME PHOTOCHEMISTRY OF MALEIC ANHYDRIDE;
THE ADDITION TO BENZENE AND THE DIMERIZATION

Thesis by

William Morgan Hardham

In Partial Fulfillment of the Requirements

For the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

1965

(Submitted August 27, 1964)

ACKNOWLEDGEMENTS

To Professor George S. Hammond, whose infectious enthusiasm and wise council were invaluable during the course of this work, goes my sincere appreciation.

Stimulating discussions with and cooperation of all members of the Hammond group on this project are gratefully acknowledged.

Also acknowledged are Graduate Teaching Assistantships, Graduate Tuition Scholarships and a Graduate Research Assistantship from the California Institute of Technology; a summer fellowship from the National Science Foundation, and a summer fellowship from the Shell Oil Company.

Finally, the love and encouragement of my parents, grandparents and especially of my wife are most highly acknowledged.

ABSTRACT

The detailed mechanism of the sensitized and unsensitized addition of maleic anhydride (MA) to benzene has been determined. By suitable quenching studies on both additions and use of a variety of sensitizers a triplet mechanism has been established. Studies of the variation of initial quantum yield with concentration of reactants showed the benzene and MA effects to be independent. This information, together with the fact that the benzene-MA charge transfer complex is a better quencher of benzophenone triplets than free MA by a factor of 13 led by elimination to the following mechanism. Energy transfer or direct absorption leads to the triplet state of the complex which can decay to a cyclohexadiene-like intermediate or dissociate to triplet MA and benzene. The major energy loss in the sequence comes from decay of MA triplets before they recombine with benzene. Competition between Diels-Alder addition of MA and dissociation of the intermediate provides the other energy loss and the MA concentration effect.

By comparison of the rates of energy transfer from three ketones to MA or the complex determined by photoreduction or flash photolytic techniques and from the phosphorescence spectrum of MA we calculate that the triplet state of the complex is $\sim$ 2 kcal./mole lower than that of MA.

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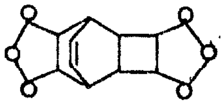
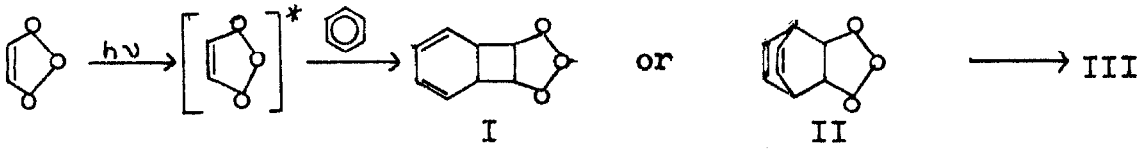
INTRODUCTION

Since the nearly simultaneous discovery by three groups that irradiation of solutions of maleic anhydride (MA) in benzene with (1) or without (2,3) a sensitizer leads to the formation of the diadduct III, a comprehensive study of the detailed reaction mechanism has not appeared. In their first paper on the subject, Angus and Bryce-Smith (2) proposed a mechanism involving primary excitation of benzene followed by 1-2 addition of maleic anhydride. They favored a 1-2 rather than a 1-4 addition as the first step because II would be a higher energy intermediate than I. If I were an intermediate in the diaddition, III would have to be formed by a Diels-Alder addition; however, formation of III via II would have to be a photo-process at room temperature. Shortly afterwards (4), the same authors proposed that MA absorbs the light which initiates the reaction. Initial excitation of benzene was eliminated when it was found that the presence of acetone in the benzene solution of MA did not depress the yield of diadduct, whereas acetone does quench the photoisomerization of benzene to fulvene (5). Implicit in this reasoning was the assumption that the same excited



III

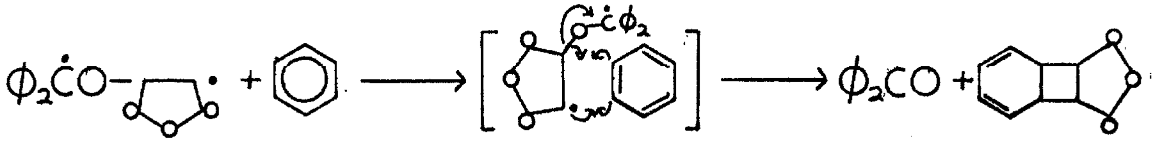


state of benzene would be responsible for both reactions. In the next paper of the series (6) it is concluded that the unsensitized reaction proceeds via the excited singlet state of the benzene-maleic anhydride charge transfer complex (7,8) on the basis of three experiments. First, oxygen did not quench the reaction; second, filtering out 57% of the light absorbed by the charge transfer band with a Pyrex filter reduced the yield of diadduct by 55%. In the third experiment it was found that irradiation of a solution in which 32% of the maleic anhydride present was complexed resulted in product formation within four hours whereas from a solution in which 3% of the anhydride was complexed no adduct was formed. The interpretation of all three of these experiments is ambiguous because in the first case it is quite probable that a very fast intra-molecular decay to I by the excited complex could not be quenched regardless of the multiplicity of the excited state. While in the interpretation of the second experiment no consideration is given to the amount of light absorbed by free MA that may have been cut out by the pyrex filter. Consideration of the concentrations of reactants involved in the third experiment shows that the concentration of complex in the solution which did not yield product was approximately 3.7 times that in the solution which did yield the diadduct. This experiment merely shows that varying the initial concentration of reactants changes the yield of diadduct.

Concerning the sensitized reaction, Bryce-Smith and Lodge (6) proposed that benzophenone can transfer triplet energy to the complex to initiate the reaction and at the same time can inhibit the "normal direct photoactivation route". Evidence for this supposition was that with enough benzophenone present to absorb only 30% of the light, no diadduct was formed with light of $\lambda > 2800\text{Å}$. However, when light of $\lambda < 2800\text{Å}$ was used diadduct was formed in the presence of benzophenone. The fact that passage of pure oxygen through a solution of MA in benzene containing 0.1M benzophenone using light of $\lambda < 2800\text{Å}$ totally inhibited the reaction, was taken as proof that the sensitized reaction went through the triplet state of donor and acceptor. When benzil (0.1M) was present in a benzene solution of MA, no diadduct was formed. From this experiment it was concluded that "the use of photosensitizers for this class of aromatic addition is a present largely a matter of trial and error".

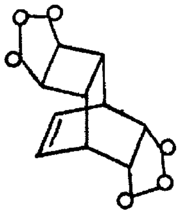
In a later note Bryce-Smith, et al. (9) state that the diadduct is formed in the presence of benzophenone when light of $\lambda > 2800\text{Å}$ is used and that their earlier report was incorrect.

Another mechanism has been proposed by Schenck and Steinmetz (1) which involves addition of excited sensitizer to MA to form a diradical which can attack benzene. The Schenck mechanism is depicted below using benzophenone as the sensitizer. Finally, it has been shown recently (10) that



both MA and the complex can accept triplet excitation energy from appropriate sensitizers.

Chemical and spectral studies led Grovenstein, et al. (3) to conclude that the stereochemistry of the diadduct is that shown in IV. Angus and Bryce-Smith (4) had correctly

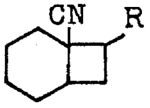


IV

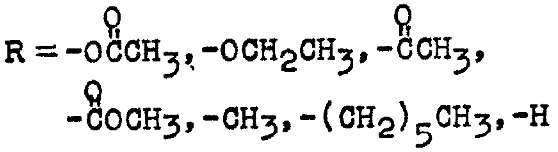
assigned the stereochemistry of the endo-anhydride unit on the basis of the cis-endo stereospecificity of Diels-Alder reactions, but incorrectly assigned the anti-anhydride unit affixed to the four membered ring. Although this study was only made on the product of the unsensitized reaction, the sensitized photolysis probably yields the same stereoisomer for the decomposition points of the two are identical and a mixed melting point of the tetramethylesters prepared from the adducts shows no depression (11).

Other benzene derivatives which undergo the diaddition are toluene, o-xylene and chlorobenzene (1). Nothing has been published on the structure of the products of the latter three photolyses. Of the other attempts to add MA to aromatics, irradiation of MA in nitrobenzene or o-dichlorobenzene gave nothing (12) and a polymer containing mostly MA was isolated from photolyses in p-xylene and ethereal solutions of durene, biphenyl, naphthalene and phenol (12).

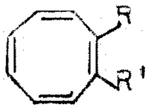
In a closely related study Atkinson, Ayer and Büchi (13) found that various olefins (both activated and unactivated) photoadded to benzonitrile to produce monoadducts such as V. Surprisingly, maleic anhydride could not be added to benzonitrile. (12,13).



V

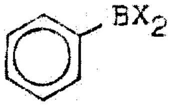

$R = -O\overset{O}{\overset{\|}{C}}CH_3, -OCH_2CH_3, -\overset{O}{\overset{\|}{C}}CH_3, -\overset{O}{\overset{\|}{C}}OCH_3, -CH_3, -(CH_2)_5CH_3, -H$

It has been supposed that an intermediate formed by 1-2 addition is present during the photoaddition of various acetylenic compounds (13,14,15,16) and boron trihalides (17) to benzene, but their existence has not been demonstrated. In the former case the products isolated are substituted cyclooctatetraenes such as VI. and in the latter case they are phenylboron dihalides (VII).



VI

$R = R' = -CO_2CH_3$
$R = CH_3, R' = CO_2CH_3$
$R = \phi, R' = H$



VII

$X = Br, I$

Other photoreactions of MA which have been reported recently include dimerization (18,19), and 1-2 addition to cyclohexene (20), various chloro-olefins (21) and to phenanthrene.

These papers are primarily descriptive with the exception of the cyclohexene work. From a direct irradiation of MA in cyclohexene, Robson, et al. (20) isolated three stereoisomeric cyclobutane type adducts. Their rationalization of these results involved absorption of light by a one to one charge transfer complex followed by a two step bond formation sequence. Although the complex is reported to absorb 98% of the light, in the absence of a quantum yield measurement or other data participation of the complex is not proven.

EXPERIMENTAL

MATERIALS

All melting points were taken on a hot stage.

2-Acetonaphthone

2-Acetonaphthone (Matheson Coleman and Bell, Reagent Grade) was recrystallized from acetic acid/water m.p. 54.0-54.0°C.

Acetonitrile

Acetonitrile (Eastman, Anhydrous Grade) was distilled from phosphorous pentoxide until no discoloration was observed - generally three to five times - and then distilled from potassium carbonate. This procedure typically reduced the initial volume of acetonitrile by 60%.

Acetophenone

Acetophenone (Matheson Coleman and Bell, Reagent Grade) was distilled at about 0.5 mm. pressure. The fraction boiling at 72° was collected and then recrystallized twice from ligroin/Ethanol at -5°C.

2-Acetylfluorene

2-Acetylfluorene (Aldrich, Research Grade) had been dissolved in benzene and chromatographed on alumina, treated with norit (carbon black), and finally recrystallized twice from methanol by Dr. A. A. Lamola.

Anisole

Anisole (Matheson Coleman and Bell, Reagent Grade) was distilled at ambient pressure. The fraction boiling at 152°C. was collected.

Anthracene

Anthracene (Matheson Coleman and Bell, Reagent Grade) m.p. 213-214° was used without further purification.

Anthraquinone

Anthraquinone (Matheson Coleman and Bell, Reagent Grade) was recrystallized from acetic acid, m.p. 284-285°C (sublimes 272°C).

Azulene

Azulene (Calbiochem) was sublimed twice by Dr. A. A. Lamola.

Benzene

Benzene (Matheson Coleman and Bell, Spectroquality Reagent) was generally used without further purification. This product rarely darkened sulfuric acid and less than 0.1% of cyclohexane and/or toluene was observed by vapor phase chromatography.

Benzaldehyde

Benzaldehyde (Matheson Coleman and Bell, Reagent Grade) was distilled twice, the second time a spinning band column was employed. The fraction boiling at 65°C (25mm.) was collected.

Benzhydrol

Benzhydrol (Matheson Coleman and Bell, Reagent Grade) was recrystallized first from ethanol/water and then from ligroin.

Benzil

Benzil (Matheson Coleman and Bell, Reagent Grade) was recrystallized from ethanol, m.p. 96.5-96.8°C.

Benzophenone

Benzophenone (Matheson Coleman and Bell, Reagent Grade) was recrystallized twice from ligroin, m.p. 50°C.

Carbon Tetrachloride

Carbon Tetrachloride (Eastman, Spectro Grade) was used without further purification.

Chelates:Ferric Dipivaloylmethide and Ferric Dibenzoylmethide

Ferric dipivaloylmethide and ferric dibenzoylmethide were obtained pure from Dr. R.P. Foss. The preparation and physical properties of these chelates have been reported. (23)

Chloroform

(Matheson Coleman and Bell, Spectroquality Reagent) was used without further purification.

Chrysene

Chrysene was obtained from Dr. J.R. Fox. It had been recrystallized and sublimed.

Cyclohexane

Cyclohexane (Matheson Coleman and Bell, Reagent Grade) was purified by the method of Vinogradov (24). First, 300 ml. was shaken twice with 100 ml. portions of a 1 to 1 mixture of concentrated sulfuric and nitric acids, then twice with 100 ml. portions of concentrated sulfuric acid. The cyclohexane was then washed three times with water, dryed over $CaSO_4$, and finally passed through a silica gel column.

p-Cyanobenzophenone

p-Cyanobenzophenone was obtained from Dr. Chin-Hua Wu. It was recrystallized from Ligroin/benzene m.p. 115.5-116°C.

p-Diacetylbenzene

p-Diacetylbenzene (Aldrich, Research Grade) had been dissolved in benzene, chromatographed on alumina, and then recrystallized twice from methanol by Dr. A. A. Lamola.

4,4-Dichlorobenzophenone

4,4-Dichlorobenzophenone (K & K Laboratories) was used without further purification, its phosphorescence spectrum taken by Dr. A. A. Lamola showed no trace of benzophenone.

1,2-Dimethoxyethane

1,2-Dimethoxyethane (Matheson Coleman and Bell, Reagent Grade) was distilled from sodium at room pressure. The fraction boiling at 81-82°C was collected for use.

Dimethylaniline

Dimethylaniline (Matheson Coleman and Bell, Mono-free Grade) was refluxed with one-half its volume of acetic anhydride for four hours and then distilled. The fraction which boiled at 191-92°C (ambient pressure) was collected for use.

Dioxane

Dioxane (Baker and Adamson, Technical Grade or Eastman, White Label) was refluxed over sodium for 9-12 hours and then distilled from sodium at room pressure. The fraction boiling at 101°C was collected for use.

Ethyl Iodide

Ethyl Iodide (Mallinckrodt, Analytical Reagent Grade) was chromatographed on alumina and distilled immediately before use, b.p. 71.0°C at room pressure.

9-Fluorenone

9-Fluorenone (Matheson Coleman and Bell, Reagent Grade) was recrystallized once from ligroin and once from ethanol, m.p. 83.8-84.5°C.

Isopropyl Alcohol

Isopropyl Alcohol (Matheson Coleman and Bell, Reagent Grade) was distilled through a vigreaux column at ambient pressure and the fraction boiling at 81°C was collected.

Maleic Anhydride

Maleic Anhydride (Matheson Coleman and Bell, Reagent Grade) was sublimed at 45°C (about 0.5mm) immediately before use.

Mesitylene

Mesitylene (Matheson Coleman and Bell, Reagent Grade) was distilled at atmospheric pressure through a vigreaux column. The fraction boiling at 162-163° was collected.

Naphthalene

Naphthalene (Matheson Coleman and Bell, Reagent Grade) was recrystallized twice from ethanol.

Nitromethane

Nitromethane (Matheson Coleman and Bell, Practical Grade) was dried over drierite, distilled and then redistilled over phosphorous pentoxide at atmospheric pressure, b.p. 101°C.

2,3-Pentanedione

2,3-Pentanedione (Eastman, White Label) was distilled through a spinning band column at atmospheric pressure. The fraction boiling at 105-106°C was collected.

Propiophenone

Propiophenone (Matheson Coleman and Bell, Reagent Grade) was recrystallized from ligroin at -5°C and then distilled at about 0.5mm. through a vigreaux column. The fraction boiling at 63-64°C was collected.

Tetracyanoethylene

Tetracyanoethylene (Aldrich, Research Grade) was recrystallized from Ethyl acetate/chloroform.

Tetrahydrofuran

Tetrahydrofuran (Eastman, White Label) was refluxed over lithium aluminum hydride for twenty-four hours and then collected from a take off on the reflux condenser.

Thioxanthone

Thioxanthone (Aldrich, Research Grade) was treated with norit (carbon black) and then recrystallized twice from methanol by Dr. A. A. Lamola, m.p.209°.

Toluene

Toluene (Matheson Coleman and Bell, Reagent Grade) was shaken three times with concentrated sulfuric acid, dryed over $CaCl_2$ and finally distilled from sodium through a vigreaux column. The fraction boiling at 110°C (atmospheric pressure) was collected.

Triphenylene

Triphenylene (Aldrich, Research Grade) was sublimed by Dr. J. R. Fox, m.p. 193.6-98°C.

Tetralin

Tetralin (DuPont, Technical Grade) was passed through a dry packed alumina column twice to remove yellow colored impurities.

Xanthone

Xanthone (Aldrich, Research Grade) was passed through a dry packed alumina column using benzene as the eluent and then recrystallized twice from methanol.

GENERAL PROCEDURE FOR IRRADIATIONS

The procedure described below was used for all irradiations carried out on the "merry-go-round" apparatus including concentration effects, most of the quenching studies, and evaluation of the various sensitizers. In all cases the pyrex culture tubes (13 x 100mm.) used were washed with Orvus soap, rinsed with distilled water five times and once with methanol, dried at 125°, and finally constricted about 20mm. from the open end.

Solutions were prepared in 10 or 25ml. volumetric flasks and 3 or 4ml. portions were added to the aniseptic culture tubes. The samples were then degassed, using three freeze-degas-thaw cycles at pressures of 5×10^{-4}mm. and sealed at the constriction.

Simultaneous irradiations of as many as 24 tubes could be carried out on the "merry-go-round" apparatus designed by Mr. F. G. Moses. This equipment has been described by Saltiel (25), but briefly it consists of a rotating turntable which is fitted with 18 holes in an inner ring and 24 in an outer ring surrounding the inner jacket of a quartz Hanovia immersion reactor. For all irradiations described in this work a Hanovia 450 watt medium pressure lamp was used. Its output characteristics are listed below together with the transmittance of a typical pyrex culture tube employed throughout this work.

Table 1. Properties of Hanovia 450 Watt Lamps

Wavelength (Å)	Lamp Output watts /100mμ	Transmittance of one side of Pyrex tubes
2753	0.7	20%
2804	2.4	30
2894	1.6	50
2967	4.3	63
3025	7.2	70
3130	13.2	78
3341	2.4	84
3660	25.6	87
4045	11.0	90

Without any added filters, it is evident that very little light of $\lambda < 2800$Å is passed by the pyrex tubes. Most sensitized reactions were run with $\lambda > 3300$Å provided by a filter consisting of a cylindrical glass tube of uranium glass. In the presence of sensitizers, essentially no light of $\lambda > 3300$Å was absorbed by either the complex or free MA.

In cases where the yield of diadduct or dimer was measured, the tubes were cracked open and the product collected by suction filtration, washed with the solvent used in the reaction, dried (20 min. at 115°C after which no weight loss occured) and weighed on a Mettler balance.

QUANTUM YIELD DETERMINATIONS

The quantum yield of the diaddition was determined by two similar methods which differed in the source of the light and in the filter used.

Method (a) employed the apparatus described by Moore (26) which consists of a Westinghouse (SAH 800-C) 800 watt short arc, medium pressure, mercury lamp mounted on an optical bench. The light from this lamp was collected and collimated by mirrors so that a parallel beam of light passed through a filter holder and fell on a Beckmann D.U. ultraviolet spectrophotometer cell holder. This cell holder held four 15mm. pyrex culture tubes which were rotated during irradiations to insure equal exposure. The 3660Å lines of mercury were isolated with a filter system consisting of a Corning 0-52 and a Corning 751 glass filter in series. These filters transmitted a band with a broad maximum at 3800Å (transmittance = 55%), half-heights at 3600 and 3950Å, and zero intensity at 3400 and 4200Å.

For method (b), the merry-go-round apparatus was used with a Hanovia (L-679A) 450 watt medium pressure mercury lamp surrounded by a uranium glass filter which transmits $\lambda > 3300$Å. Since neither a 0.100M benzophenone nor a 1.00M acetophenone solution absorbs beyond 4200Å, the distribution of light that the ketones see in the two methods is very similar with the exception that some of the low intensity

3341Å line is passed by the uranium glass filter. Method (b) however, has an intensity advantage of approximately a factor of ten, probably resulting mainly from the fact that the tubes are closer to the light source in method (b).

In both kinds of experiment yields were on the order of 10mg. corresponding to $< 2\%$ conversion of the MA, benzophenone-benzhydrol actinometry was employed, and samples were degassed by the freeze-degas-thaw method described earlier.

ACTINOMETRY

Actinometry for all quantum yield and benzophenone quenching experiments was provided by monitoring the extent of photoreduction of benzophenone by benzhydrol. This system is suitable for intensity measurements for wavelengths up to 3800Å, where it ceases to absorb. After preliminary experiments using two or three actinometer tubes per irradiation, precision was developed sufficiently to permit the use of only one tube per run in the procedure described below.

Stock actinometer solutions, generally 0.100M in ketone and alcohol, were prepared in 25ml. volumetric flasks with benzene as the solvent. For certain runs with 1.00M acetophenone as a sensitizer, 0.046M benzophenone solutions were used in the actinometer so that the absorbance of benzophenone and acetophenone at 3660Å would be equal. In this way we attempted to insure that the tail absorption by both ketones would be the same. However, it was found that benzophenone absorbed the same amount of light within experimental error at the two concentrations.

Degassed actinometer tubes were usually irradiated for no longer than two hours. If an irradiation took longer, the actinometer was employed at the mid-point of the period. After irradiation, the tubes were opened, diluted by a factor of 14 (when concentration of ketone was 0.100M) with methanol, and analyzed for residual benzophenone on a

Beckmann D.U. spectrophotometer at 345,350,355 and 360mμ. Then the amount of ketone consumed and the average concentration of alcohol were calculated and plugged into equations 1 and 2 below. Typical intensities measured on the "merry-go-round" with the uranium glass filter in place

$$\Phi = \frac{1}{1 + \frac{0.033}{[BH_2]_{ave.}}} \qquad (1)$$

$$I = \frac{(\Delta[B])(V)(6.023 \times 10^{23})}{\Phi t} \qquad (2)$$

$\Delta[B]$ = change in concentration of benzophenone
V = volume of sample
t = time of irradiation

ranged between 5 x 10^{15} quanta/sec. and 7 x 10^{16} quanta/sec. whereas the optical bench produced about 7 x 10^{15} quanta/sec. through the two Corning filters.

A different approach, namely one described by Foss (23), was utilized for some of the acetophenone and benzophenone quenching experiments. Manipulation of the integrated rate expression for production of acetone or consumption of benzophenone in the absence of quencher yields equation 3. Thus, a plot of Y vs. X yields the intensity as the ordinate intercept and the ratio k_d/k_r as the slope. Of course, the samples containing MA were irradiated simultaneously with tubes containing varying concentrations of alcohol so that the values of intensity and k_d/k_r determined as above were used in the calculation of the quenching rate constant.

$$Y = \left(\frac{kd}{k_r}\right) X - I \qquad (3)$$

where $Y = \frac{1}{t}\left([IH_2]_f - [IH_2]_o \right)$

$X = \frac{1}{t} \ln \frac{[IH_2]_o}{[IH_2]_f}$

t = time

I = light intensity

k_r=rate of H abstraction by ketone

k_d=rate constant for radiation-less deactivation of ketone triplet state

ACETOPHENONE REDUCTION

All solutions were prepared in 25ml. volumetric flasks using calibrated syringes to measure the quantities of acetophenone and isopropanol. Samples were then added to clean, constricted culture tubes, degassed and sealed in vacuo. Irradiations were on the "merry-go-round" apparatus using the uranium glass filter for approximately 48 hours. Analysis for acetone and isopropyl alcohol was made by vapor phase chromatography using a 10' x 1/4" aluminum column packed with 35% carbowax 20M on firebrick at 95°C. The area ratios (R) of isopropyl alcohol to acetone were converted to concentration of acetone produced using the relation below.

$$\frac{1 - x}{x} = AR \qquad (4)$$

A = conversion factor, area ratio to mol ratio 0.985

$x = [\text{acetone}]$ formed

Vapor phase chromatography was also used for the product analysis. The 10' column was used for acetone analysis as above and a 16" x 1/4" column packed with 10% carbowax on firebrick was employed for the acetophenone pinacol and acetophenone. Using anisole as an internal standard the decrease in the amount of ketone was measured with the short column at 100°C on a Loe Model 70 temperture programed chromatograph. Then the temperature was raised to 210° and the acetophenone pinacol was eluted. The retention time of the latter was identical with a sample of acetophenone pinacol prepared by a preparative size photolysis of acetophenone in isopropyl alcohol and recrystallized from 85-100° ligroin (m.p. 122°C). It was shown that the latter did not decompose on the column under the conditions of the analysis. Pinacol was shown to be absent by comparison of chromatography traces from the photolyses solutions with one obtained from pure pinacol. The acetone-isopropyl alcohol analyses were performed on a Loe Model 15B chromatograph. Both of the Loe chromatographs were equipped with a thermal conductivity detector. When available, a Texas Instrument recorder equipped with their disc integrator was used to measure peak areas, otherwise the peaks were carefully cut out and weighed. Area ratios obtained by the two methods agreed to within 0.5%.

DIMER - DIADDUCT

The samples were prepared by adding 8.9ml. benzene and 9.8g.MA and the appropriate sensitizer to 50ml. volumetric flasks and diluting with freshly purified dioxane. By joining 13mm. tubing to 25 x 200mm. pyrex culture tubes sample tubes large enough to hold 50ml. were constructed. After degassing, the samples were sealed off at a constriction in the small diameter tubes. Besides the solutions listed in Table 19 a 2.00M solution of MA in dioxane was prepared to provide samples of the MA dimer.

The samples were suspended about the quartz inner jacket of a Hanovia immersion reactor which held a 450 watt Hanovia mercury lamp. A 5000ml. beaker filled with water was used as a cooling bath and this together with circulating water through the jacket kept the temperature of the samples at 35-40°C. After five days the four samples were opened, and the product was filtered off and weighed. Yields from samples 1,2,3 and the dimerization sample were 1.24, 0.95, 0.82 and 0.39g. respectively. The solutions in all of the tubes had turned yellow.

The anhydrides were easily converted to the tetracarboxylic acids by refluxing for one-half hour in 40ml. of a 2:1 mixture of tetrahydrofuran and water. After filtration, the solutions were carefully evaporated to dryness and the solid acids esterified by refluxing eight hours with (20) x (weight of anhydride)ml. of methanol and (0.20) x (weight of anhydride)ml. concentrated H_2SO_4. The resulting solutions were concentrated and cooled to produce crystals which were filtered and washed with benzene prior to analysis. Second crops of crystals were obtained from samples 2 and 3.

Because of the very high boiling point of the tetramethylester of the diadduct, long (2 hours) retention times and smeared out peaks had to be accepted. The 16" x ¼" carbowax column which was used for the acetophenone pinacol analysis was employed in this analysis at a temperature of 205°C. Under these conditions the tetramethylester of the MA dimer was retained for approximately 6 minutes. Order of magnitude estimates of the relative concentrations of the two tetraesters were made from peak areas.

LOW TEMPERATURE IRRADIATION OF MA IN TOLUENE

Three of the large tubes used in the dimer-diadduct experiment were filled with a solution of 0.5M MA and 0.05M benzophenone in toluene. After degassing, the tubes were hung about the pyrex inner jacket of a Hanovia immersion apparatus through which cold methanol was circulated. The circulating methanol was cooled by passage through a coil of copper tubing in a large dewar filled with dry ice - methanol. Cooling of the samples was achieved by immersing the jacket and tubes in a n'icer ice bucket filled with dry ice - methanol. The heat generated by the 450 watt mercury lamp was such that the dry ice in the dewar and bucket had to be changed every one-half to three-quarters of an hour. Furthermore, after approximately six hours the circulating methanol had become yellow and had to be changed. These requirements placed a fifteen hour practical limit on the duration of the experiment which further refinement of the experimental apparatus should overcome.

Immediately after the lamp was switched off, the tubes were opened and poured into a stirred solution of 6M tetracyanoethylene in 50ml. of acetone. Acetone was required as a cosolvent to dissolve TCNE in toluene. After reaching room temperature and stirring for 24 hours, no precipitate had appeared so the volume of the solution was reduced by one-half and it was seeded with diadduct. Since this did not produce a precipitate in two days the solution was evaporated to dryness. During this evaporation most of the TCNE precipitated and was filtered off. The residue was sublimed to give 90% recovery of MA, but, no high melting material was left in the sublimator. It is likely that the rest of the MA was lost to the dry ice traps during the vacuum sublimation or appeared in the polymeric material in the sublimator residue.

RESULTS

BENZOPHENONE REDUCTION

The benzophenone-benzhydrol photoreduction system as described by Moore, Hammond and Foss (27) was employed in an effort to determine the efficiency of energy transfer to MA in various solvents. Analysis of the extent of photoreduction of ketone in the presence of small amounts of MA was carried out with equation 5. A plot of $1/\Phi - 1 - k_d/k_r\ [\phi_2CHOH]_{ave.}$ vs. $[MA]\ /\ [\phi_2CHOH]_{ave.}$ yields the rate

$$\frac{1}{\Phi} = \frac{1}{a} + \frac{k_d}{ak_r\ [\phi_2CHOH]_{ave.}} + \frac{k_q\ [MA]}{ak_r\ [\phi_2CHOH]_{ave.}} \qquad (5)$$

where k_q = second order rate constant for energy transfer
k_r = " " " " " hydrogen abstraction
k_d = first " " " " decay of ϕ_2CO triplets
a = quantum yield of ϕ_2CO triplet state
Φ = " " " " disappearance

constant ratio k_q/k_r as the slope, or the relation may be solved directly. In either case we use the value $k_d/k_r = 0.033$ determined by Foss (23) in the calculation of the data presented in Table 2. All of the values of $(k_q/k_r)_o$ tabulated here were calculated using the initial concentration of MA in the numerator of the last term of equation 5.

Table 2 - Maleic Anhydride Quenching the Photoreduction of 0.100M Benzophenone in Benzene

Run	$[\phi_2\text{CHOH}]_o$	$[\text{MA}]_o \times 10^3$	Φ	$(k_q/k_r)_o$	(k_q/k_r)corrected
1 A	0.100M	2.0M	0.341	75	79
1 B	"	1.0	0.517	53	56
1 C	0.050	1.0	0.314	56	59
1 D	0.200	2.0	0.536	67	70
1 E	0.100	0	0.731	-	-
					ave.=65

When the photoreduction is run in benzene, one might expect some MA to be consumed via the diaddition. We therefore attempted a calculation of the consumption of MA as a function of length of irradiation. Equations 6 to 10 illustrate this calculation for the ϕ_2CHOH system

$$-\frac{dx}{dt} = \left(\begin{array}{l}\text{fraction of light absorbed by}\\ \phi_2\text{CO which is transferred to MA}\end{array}\right)\left(\begin{array}{l}\text{quantum yield}\\ \text{of diaddition}\end{array}\right)\left(\text{intensity}\right) \qquad (6)$$

$$-\frac{dx}{dt} = \left(\frac{k_q\ X}{k_d + k_r\ [\phi_2\text{CHOH}] + k_q\ X}\right)\left(\frac{8.01X}{1 + 7.9X}\right)\left(\ I\ \right) \qquad (7)$$

$$\left(-dx\right)\left(\frac{k_d + k_r\ [\phi_2\text{CHOH}] + 7.9X(k_d + k_r[\phi_2\text{CHOH}]) + k_qX + 7.9k_qX^2}{k_qX^2}\right) \qquad (8)$$

$$= 8.01\ I\ dt$$

$$-\int_{x_o}^{x_t} \frac{k_d + k_r[\phi_2CHOH]}{k_q X^2}dx \quad -\int_{x_o}^{x_t} \frac{7.9(k_d + k_r[\phi_2CHOH]) + k_q}{k_q X}dx \qquad (9)$$

$$-\int_{x_o}^{x_t} 7.9\, dx = \int_o^t 8.01\ I\ dt$$

$$\left(\frac{k_d + k_r\ [\phi_2CHOH]}{k_q}\right)\left(\frac{1}{X_t} - \frac{1}{X_o}\right) + \left(\frac{7.9(k_d + k_r[\phi_2CHOH]\ ) + k_q}{k_q}\right) \qquad (10)$$

$$\left(\ln \frac{X_o}{X_t}\right) + 7.9\ (X_o - X_t) = 8.01\ I\ t$$

where $I =$ intensity, einsteins $l.^{-1}$
$X = $[Maleic Anhydride]

The first term of equation 6 is simply given by the ratio of the pseudo first order quenching rate constant to the sum of all pseudo zero and first order processes which can lead to deactivation of benzophenone triplets, while the second term is taken from the experimentally determined variation of Φ with the concentration of MA. In the latter determination all of the energy absorbed by the sensitizer is transferred to MA or the complex even if k_q is as low as 1 x 10^8 $l.mole^{-1}$ $sec.^{-1}$. In order to evaluate the rate constants k_q and k_r for the case of benzophenone and MA we take Bell and Linschitz's (29) value of k_d 1 x $10^5 \pm 50\%$ (obtained by flash spectroscopy), multiply it by $k_r/k_d = 1/0.033$ to give $k_r = 3 \times 10^6$ and then find $k_q = (3 \times 10^6)\ (k_q/k_r) = 1.8 \times 10^8$. Using these numbers and $[\phi_2CHOH]_o = 0.10$, equation 10 becomes 11 upon integration.

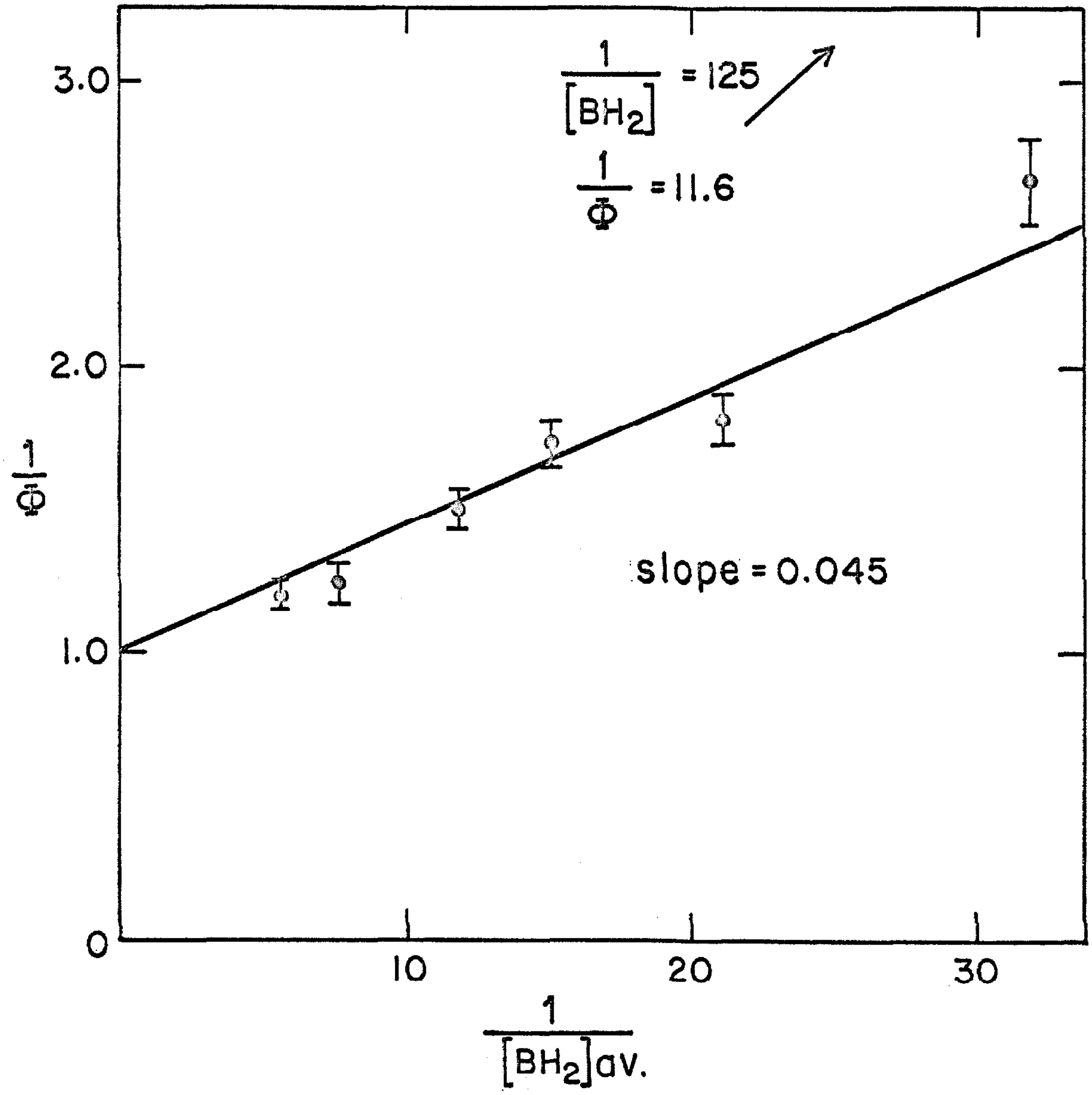
$$2.2 \times 10^{-3}\left(\frac{1}{\bar{X}_t} - \frac{1}{\bar{X}_o}\right) + 1.02 \ln X_o/X_t + 7.9\ (X_o - X_t) = 8.01\ I\ t \qquad (11)$$

Now, we substitute the intensity measured using run 1E of Table 2, $I = 1.45 \times 10^{15}$ quanta/sec. $= 7.76 \times 10^{-7}$ einsteins $l.^{-1}$ and calculate the time required to consume one-half of the maleic anhydride when $[MA]_o = 1 \times 10^{-3}$M. Equation 11 predicts that this will take 470,000 seconds or 5.4 days. For comparison we shall make a similar calculation using a modified form of equation 7 obtained by replacing dx by x and dt by t. Using $X = 1 \times 10^{-3}$M in the first two terms of the right hand side we find that it would take 7.2 days to consume one-half of the MA. Thus we see the importance of using the integrated form of the expression. By trial and error methods using equation 11 it can be shown that 10% of the maleic anhydride was consumed in all quenching runs in benzene listed in Table 2. Thus, the column headed $k_q/k_r)_{corrected}$ was obtained by employing an average concentration of MA which was less than $[MA]_o$ by 5%.

Since two species are present in solutions of MA in benzene - the complex and free MA - we attempted to measure the quenching rate constant for free MA. Two solvents, carbon tetrachloride and cyclohexane, with which MA does not complex were chosen. Before collecting quenching data in either solvent, it was necessary to determine whether or not there was a solvent effect on the ratio of triplet decay to the rate of hydrogen abstraction (k_d/k_r). Accordingly, a series of photolyses in both solvents in which the concentration of benzhydrol was varied between 0.010M and 0.200M were carried out. The results of the carbon tetrachloride determinations will be discussed first.

In Figure 1 are displayed the results of a determination of k_d/k_r in carbon tetrachloride as calculated using the unintegrated form of the rate equation (27). The slope is k_d/k_r=0.045 and the intensity of the light was 1.18 x 10^{16} quanta/sec. by benzophenone - benzhydrol actinometry. Since some of the points of Figure 1 represent 40% conversion it was deemed advisable to employ the integrated form of the rate equation as described in the experimental section of this work. A least squares analysis of the data obtained in this way gave k_d/k_r= 0.0526 and I = 1.20 x 10^{16} quanta/sec. In the calculation of the sets of quenching data presented in Table 2, the latter value of k_d/k_r was used. It is interesting to speculate on the reason for the apparent increase in this rate constant ratio by a factor of 1.6 over the corresponding ratio in benzene. Of course it could result from an increase

Fig. 1. Determination of k_d/k_r for ϕ_2CO-ϕ_2CHOH in CCl_4



in k_d and/or a decrease in k_r. A reasonable rationalization for the former cause is enhancement of the rate of intersystem crossing to the ground state because of the operation of the heavy atom effect (30,31).

Table 3 - MA Quenching the Photoreduction of Benzophenone

Sample[a,b,c]	[MA]	Solvent	Φ	k_q/k_r	I^d
A-1	5×10^{-4}M	CCl_4	0.6527	1 ± 1	9.86×10^{15}
A-2	1×10^{-3}M	CCl_4	0.6364	1 ± 1	"
A-3	-	Benzene	0.724	-	"
B-1	5×10^{-4}	CCl_4	0.6199	9.6	4.82×10^{15}
B-2	1×10^{-3}	CCl_4	0.6022	9.5	"
B-3	-	Benzene	0.674	-	"
				ave.= 5 ± 5	

(a) $[\phi_2CO] = [\phi_2CHOH] = 0.100M$

(b) A-1,2,3 and B-3 are averages of two samples.

(c) $\lambda > 3300 \mathring{A}$, irradiations done on merry-go-round

(d) Benzophenone-benzhydrol actinometry was used.

Admittedly the agreement between the two experiments listed in Table 3 is not good on a relative basis. However, in the case of low quenching rate constants this is not surprising for the ratio k_q/k_r becomes a small difference between two large numbers. By assuming that k_r in carbon tetrachloride is equal to the previously cited value, $3 \times 11^6 \pm 50\%$ l. mole^{-1} sec.$^{-1}$ found in benzene, we calculate $k_q = 1.5 \times 10^7 \pm 100\%$.

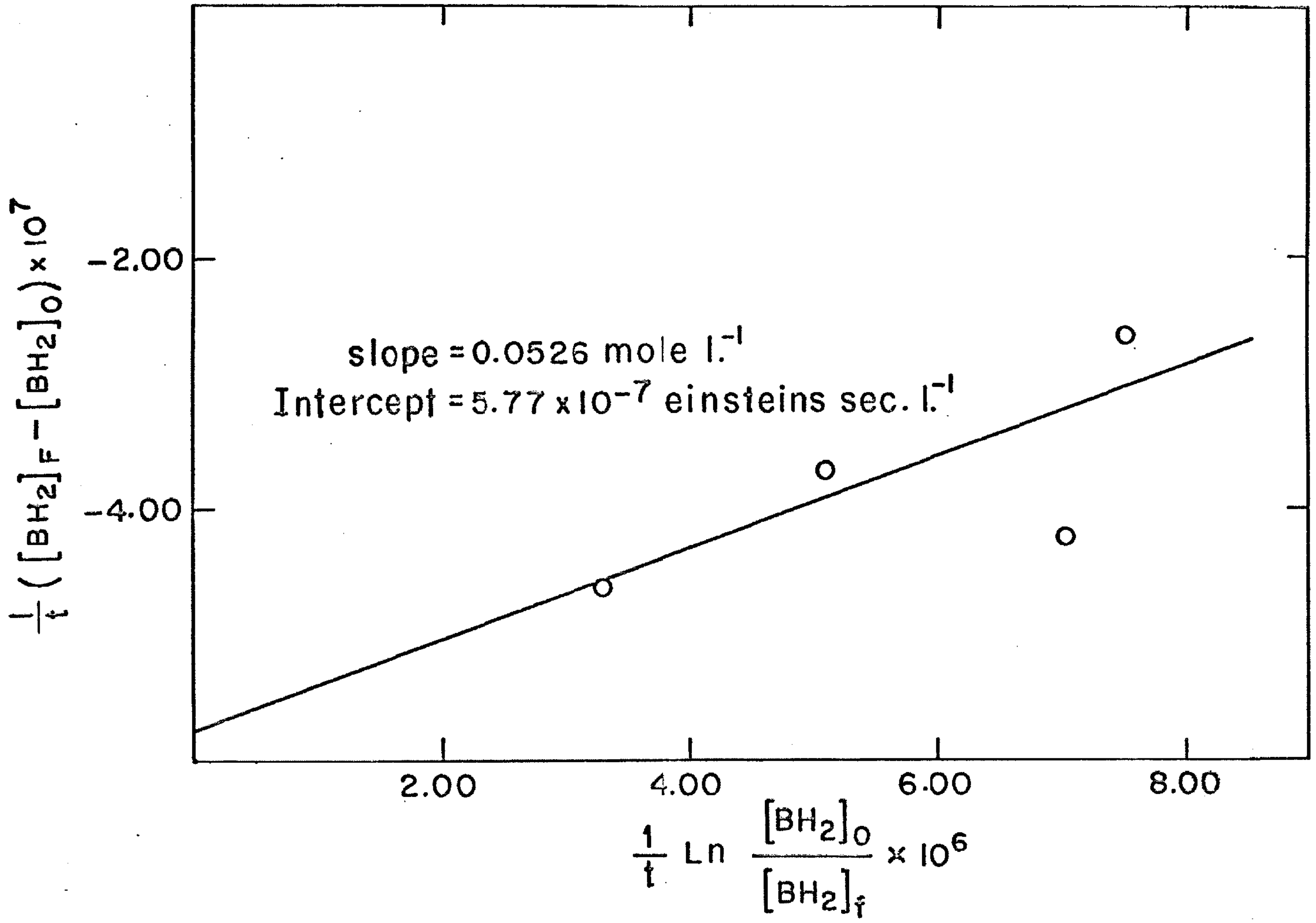
The ratios k_q/k_r and k_d/k_r together with the light intensity were found in a single experiment using a solvent mixture composed of 95% cyclohexane - 5% acetone. A small amount of acetone was necessary to dissolve all the MA in the quenching samples. It seems safe to assume that this amount of acetone did not participate in either energy transfer or hydrogen abstraction reactions for its triplet state energy is undoubtedly higher than that of benzophenone by 5 - 7 kcal./mole and it did not absorb any light. Table 4 contains the data pertinent to this experiment. Application of the integrated rate equation to the data from the first four entries of Table 4 as previously described gave the least squares line displayed on Figure 2. The value of the ratio $k_d/k_r = 0.0364$ is very close to that determined by Foss in benzene (0.033) and tends to corroborate the previous assumption that the higher value in carbon tetrachloride is

Table 4 - Maleic Anhydride Quenching the Photoreduction of 0.100M Benzophenone in Cyclohexane

Sample [a]	$[\phi_2CHOH]$	$\Delta[\phi_2CO]$	$[MA]$	k_q/k_r
2	0.04M	0.00935M		
3	0.06	0.01325		
4	0.08	0.01315		
6	0.15	0.01640		
8	0.10	0.01728	1×10^{-3}M	1 ± 1
9	"	0.01375	2×10^{-3}	4.2
10	"	0.01124	3×10^{-3}	13.4
11	"	0.01034	4×10^{-3}	13.9
				ave. = 8

(a) $3400\text{Å} < \lambda > 4200\text{Å}$, irradiations done on quantum yield merry-go-round.

Fig. 2. Determination of k_d/k_r and Light Intensity for ϕ_2CO-ϕ_2CHOH in C_6H_{12}



due only to an increase in k_d. Furthermore, the value of the quenching rate constant obtained in this experiment $2.4 \times 10^7 \pm 100\%$ is in substantial agreement with that obtained in carbon tetrachloride.

We are now in a position to calculate the rate constant for quenching by the complex assuming that the MA quenching rate constant is not effected by the change in solvent from cyclohexane or carbon tetrachloride to benzene. The contributions to the measured k_q/k_r in benzene by free MA and the complex are then given by equation 12. In order to evaluate

$$\left(\frac{k_q}{k_r}\right)_{total} = X\left(\frac{k_q}{k_r}\right)_{MA} + (1 - X)\left(\frac{k_q}{k_r}\right)_{complex} \qquad (12)$$

X, the fraction of MA which is not complexed, the ultraviolet spectrum of a 1×10^{-3}M and a 2×10^{-3}M solution of MA in benzene were taken with benzene in the reference beam of a Cary Model 14. Then, using $\epsilon_{270} = 3140$ given by Andrews and Keefer (7) for the complex it was found that 42.5% and 51.0% respectively of the MA in the two solutions was complexed. Use of the value of 0.66 for the equilibrium constant found by Andrews and Keefer for the complex using cyclohexane as the cosolvent leads to a calculated 88% of the MA complexed in both solutions. Since it is not clear whether the extinction coefficient or the equilibrium constant method can best be extrapolated to neat benzene, the values of k_q/k_r in Table 5 were calculated from both values. Thus, we find that the quenching rate constant for the complex is between 4×10^8 l. mole^{-1} sec.$^{-1}$ and 2×10^8 l. mole^{-1}sec.$^{-1}$.

Table 5 - Quenching the Photoreduction of Benzophenone by the Complex

Run	$[MA]_o$	Fraction MA Complexed	(k_q/k_r) complex
1 A	2×10^{-3}M	0.510 - 0.88	149 - 89
1 B	1×10^{-3}	0.425 - 0.88	121 - 63
1 C	1×10^{-3}	0.425 - 0.88	130 - 66
1 D	2×10^{-3}	0.510 - 0.88	130 - 79
		ave. =	133 - 72

ACETOPHENONE REDUCTION

Preliminary experiments with the photoreduction employed α-methylbenzyl alcohol in carbon tetrachloride as the reducing agent so that only one kind of radical and thus one pinacol would be formed (d,l-α-methylbenzyl alcohol was used so that the pinacol would be a mixture of optical isomers). These experiments showed that analysis for acetophenone by ultraviolet spectroscopy was not reliable, that some side reactions leading to yellow compounds were taking place, and that the reaction was about ten times slower than the reduction of benzophenone by benzhydrol. Therefore, we turned to another alcohol, isopropyl alcohol, and another solvent, cyclohexane. Since this particular system has only been cursorily (32) examined heretofore, it was necessary to make a product study, and determine the limiting quantum yields. This was especially desirable in light of the results of Testa (33) on the variation of Φ_{ketone} with light intensity and of Beckett and Porter (34) on the variation of Φ_{ketone} with concentration of ketone; both studies having been made on the benzophenone - isopropyl alcohol system. Testa found that the quantum yield for disappearance of benzophenone depended linearly on $(\text{intensity})^{-\frac{1}{2}}$, varying between 1.2 at 3.3×10^{15} quanta/sec. and 1.6 at 3.4×10^{13} quanta/sec. These experiments were performed in neat isopropyl alcohol. The data of Beckett and Porter was gathered in neat isopropyl alcohol using a flash photolytic technique; they found identical quantum yields using 3660Å or 2537Å light. In the latter work Φ_{ketone} varied between 0.84 ± 0.06 and 1.90 ± 0.08 while the concentration of benzophenone changed from 8×10^{-6} to 1×10^{-1}M. Neither of the above studies included product analyses so that statements concerning the mechanism of photoreduction by isopropyl alcohol contained in both papers are actually educated guesses.

We found that quantitative vapor phase chromatography provided a suitable method for product analysis. The results shown in Table 6, make it evident that the reduction is relatively clean and susceptible to kinetic analysis. Following a modified Moore, Hammond and Foss (27) procedure the ratio k_d/k_r and the limiting quantum yield of acetone production were determined in cyclohexane. Equations 13 to 20 provide the basis for the treatment of data. As in the

Table 6 - Products of the Photoreduction of 1.00M Acetophenone by Isopropyl Alcohol

Product or reactant[a,b]	$10M=[IH_2]_o$	$5.0M=[IH_2]_o$
$\phi COCH_3$ reduced	0.32M	0.22M
acetophenone pinacol formed	0.16	0.14
acetone formed	0.16	0.12
pinacol formed	0	0
mixed pinacol formed	0.5%	0.5%

(a) both samples degassed, $\lambda > 3300$Å
(b) cosolvent was cyclohexane

case of the reduction of benzophenone, the reaction is characterized by the ratios k_d/k_r and k_q/k_r.

$$A \xrightarrow{I} {}^1A^* \xrightarrow{aI} {}^3A^* \qquad (13)$$

$$ {}^3A^* \xrightarrow{kd} A \qquad (14)$$

$$ {}^3A^* + IH_2 \xrightarrow{k_r} IH\cdot + AH\cdot \qquad (15)$$

$$2AH\cdot \xrightarrow{k_1} AH\text{-}AH \qquad (16)$$

$$IH\cdot + A \xrightarrow{k_2} BH\cdot + C \qquad (17)$$

where $A =$ acetophenone, ground state

${}^1A^* =$ " , first excited singlet state

${}^3A^* =$ " , " " triplet state

$IH_2 =$ isopropanol

$C =$ acetone

$a =$ fraction of excited singlets which intersystem cross to triplet state $= 1$(28)

Using the steady state hypothesis for excited states and radicals we have:

$$\left[{}^3A^*\right] = \frac{I}{k_d + k_r\left[IH_2\right]} \quad \text{and} \quad \left[IH\cdot\right] = \frac{k_r\left[IH_2\right]\left[{}^3A^*\right]}{k_2\left[A\right]}$$

and, the quantum yield of appearance of acetone becomes:

$$\Phi = \frac{k_2\left[IH\cdot\right]\left[A\right]}{I} = \frac{k_r\left[IH_2\right]_{ave.}}{k_d + k_r\left[IH_2\right]_{ave.}} \qquad (18)$$

or

$$\frac{1}{\Phi} = 1 + \frac{k_d}{k_r [IH_2]_{ave.}} \qquad (19)$$

Similarly, if a quencher is present:

$$\frac{1}{\Phi} = 1 + \frac{k_d}{k_r [IH_2]_{ave.}} + \frac{k_q [Q]}{k_r [IH_2]_{ave.}} \qquad (20)$$

From Figure 3 we see that at infinite alcohol concentration the quantum yield of acetone can be taken as one and k_d/k_r is 9.55. This implies that the quantum yield of ketone disappearance is nearly two and that a combination of faster decay and slower k_r compared with the benzophenone-benzhydrol system operates to give k_d/k_r ratios different by a factor of 9.5/0.033 = 290. In order to separate these two effects, k_d/k_r was determined for the photoreduction of benzophenone by isopropyl alcohol in benzene. Analysis for the depletion of benzophenone by UV spectroscopy yielded data which fitted equations 13 to 20 deduced for the acetophenone reduction. Using the steady state hypothesis for all radicals and excited states yields (21) as the expression for the quantum yield of benzophenone depletion. When the experimental data

$$\frac{1}{\Phi} = \frac{1}{2} + \frac{1}{2} \quad \frac{k_d}{k_r [IH_2]_{ave.}} \qquad (21)$$

are put into this equation, Figure 4 results. Twice the

Fig. 3. Determination of k_d/k_r for $\phi COCH_3$-$CH_3CH(OH)CH_3$ in C_6H_{12}

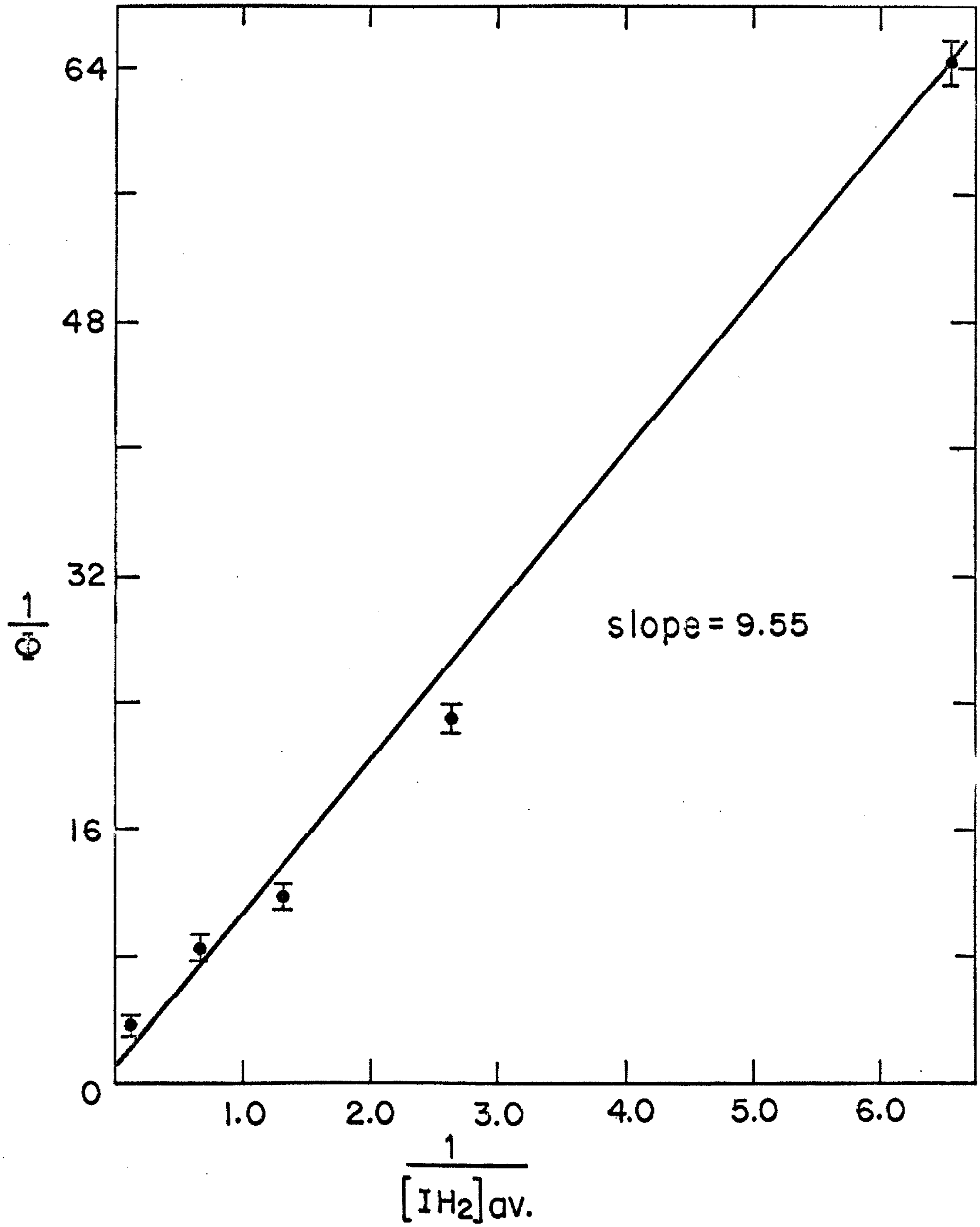
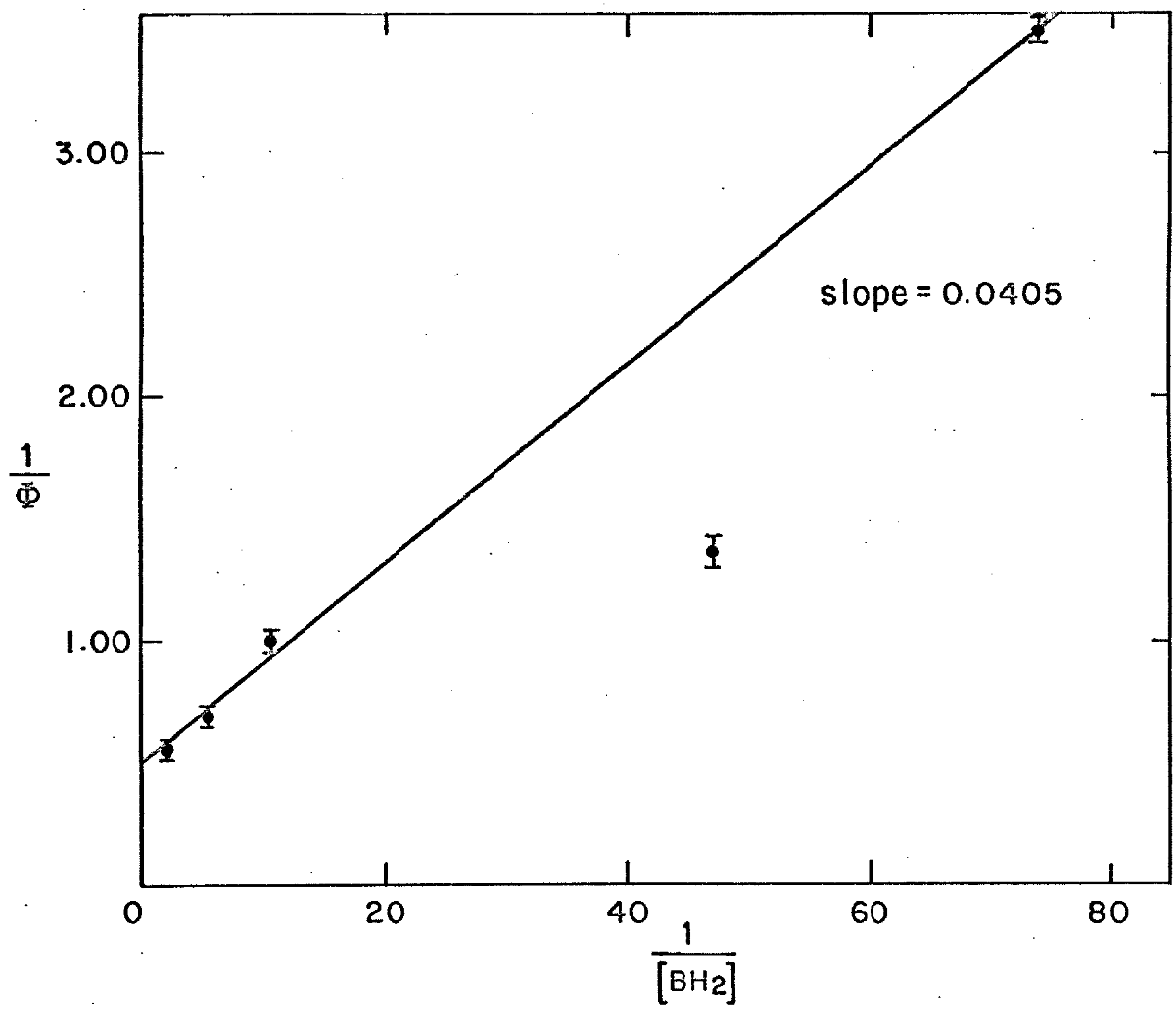


Fig. 4. Determination of k_d/k_r for ϕ_2CO-$CH_3CH(OH)CH_3$ in C_6H_6



slope of the plot of $1/\Phi$ vs. $1/[IH_2]_{ave.}$ is $k_q/k_r = 0.081$ for the benzophenone reduction by isopropyl alcohol, so this H - abstraction is slower by a factor of 2.5 than the H - abstraction from benzhydrol. As a check on the assumed stoichiometry of the benzophenone reduction by isopropyl alcohol, the yield of acetone was examined by VPC. Unfortunately this analysis took place several days after the reaction tubes had been opened and although they were stoppered, it is likely that some acetone evaporated. Inasmuch as all the yields of acetone are low by about 0.0015M evaporation seems to be an adequate explanation for the low values. When the yields of acetone are adjusted accordingly, the correspondence between the yields of acetone and benzophenone are consistent with the assumed stoichiometry.

Table 7 - Comparison of $[\phi_2CO]$ consumed with [Acetone] Formed

Sample[a, b]	$[IH_2]_0$	[Acetone][a]	2([acetone] + 0.0015)	$[\phi_2CO]$ consumed
1	0.015M	0.00124M	0.0055M	0.00581M
4	0.10	0.0086	0.020	0.0205
5	0.20	0.0128	0.029	0.0295
6	0.50	0.0171	0.037	0.0366

(a) all samples degassed
(b) solvent was benzene

Now, if we assume that acetophenone and benzophenone abstract hydrogen at approximately the same rate we conclude that the acetophenone triplet state has a 1st order decay rate larger than that of benzophenone by a factor of ~ 100.

If this is the correct order of magnitude, the acetophenone triplet has the shortest lifetime ($\sim 10^{-7}$ sec.) of any ketone yet measured in solution. There is a possibility, however, that the large value of k_d/k_r is due in part to a quencher present in the acetophenone. While it was carefully purified by low temperature recrystallization and distillation, small amounts of impurities on the order of 0.01% could be important when the solution is 1.00M in acetophenone. That this possibility has no effect on the value of k_q/k_r determined for added quenchers can be seen by considering the quantum yield expression for photoreduction of

$$\frac{1}{\Phi} = 1 + \frac{k_d}{k_r[IH_2]} + \frac{k_q[Q]}{k_r[IH_2]} + \frac{k_q[Q']}{k_r[IH_2]} \qquad (22)$$

if $k_q[Q]$ is constant,

$$\frac{1}{\Phi} = 1 + \frac{(k_d - k_q[Q])}{k_r[IH_2]} + \frac{k_q[Q']}{k_r[IH_2]} \qquad (23)$$

let $(k_d + k_q[Q]) = k_d'$

$$\frac{1}{\Phi} = 1 + \frac{k_d'}{k_r[IH_2]} + \frac{k_q[Q']}{k_r[IH_2]} \qquad (24)$$

acetophenone in the presence of two quenchers, Q and Q'. If Q is present in the acetophenone, we can expect its concentration to be constant during the course of all photolyses and therefore $k_q[Q]$ can be combined with k_d to produce k_d'.

Thus, the presence of a constant amount of quencher only effects the absolute value of k_d/k_r, not the ratio k_q/k_r for added quenchers.

As a means of checking the validity of the high value of k_d/k_r obtained from this particular batch of acetophenone, quenching studies were made using naphthalene. In this case transfer of triplet energy is exothermic by 12.7 kcal./mole and is surely a diffusion controlled process. The slope of the plot of $1/\Phi - 1 - k_d/k_r \left[IH_2\right]_{ave.}$ vs. $\left[\text{naphthalene}\right]/\left[IH_2\right]_{ave.}$ is 4.3×10^3 (Figure 5). Taking k_r for this system as $3 \times 10^6/2.5 = 1.2 \times 10^6$ l.mole^{-1}sec.$^{-1}$, we calculate $k_q = 5.2 \times 10^9$ l.mole^{-1}sec.$^{-1}$. This rate is close to the center of the range of numbers reported in the literature as being characteristic of diffusion controlled processes in benzene and cyclohexane, i.e. 1×10^9 to 8×10^9 l.mole^{-1} sec.$^{-1}$. We can conclude that our value of k_r for the abstraction of hydrogen by acetophenone is correct to within a factor of two.

Two sets of quenching data are presented in Table 8 for the MA - acetophenone-isopropyl alcohol system. Since the two sets of experiments were done with different batches of purified acetophenone, it is not surprising that the two values of k_d/k_r differ by a factor of two. In the C series, carried out in conjunction with Mr. Ping Scheng, the light intensity and ratio k_d/k_r were determined from the first four

Fig. 5. Naphthalene Quenching the Photoreduction of $\phi COCH_3$ by $CH_3CH(OH)CH_3$

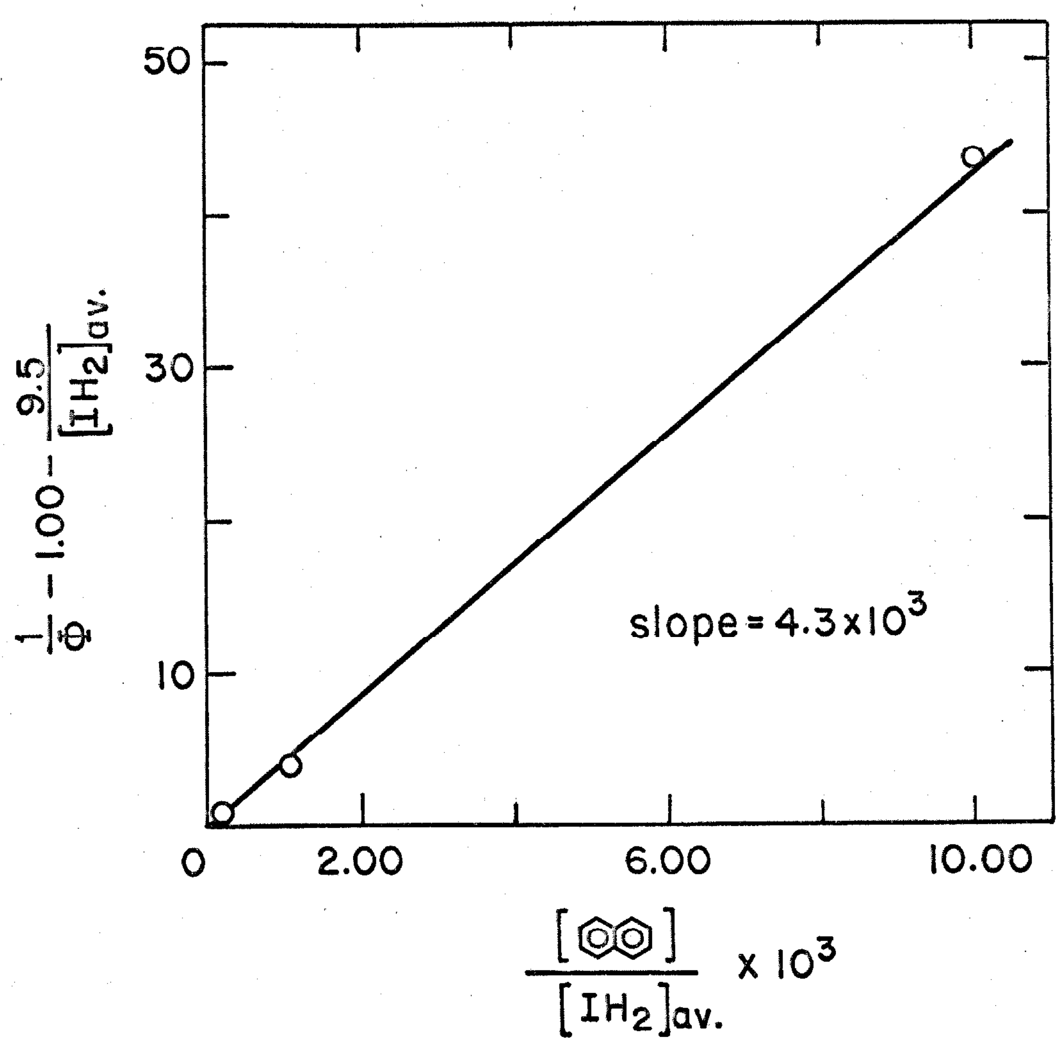


Table 8 - Maleic Anhydride Quenching the Photoreduction of 1.00M Acetophenone in Cyclohexane

Run[a,b]	$[IH_2]$	[acetone] formed	[MA]	k_q/k_r
C-1	0.157M	0.0137M	0	-
C-2	0.392	0.0317	0	-
C-3	0.784	0.0564	0	-
C-4	2.00	0.1324	0	-
C-6	"	0.1201	1×10^{-3}M	312
C-7	"	0.1193	2×10^{-3}	181
C-9	"	0.1170	4×10^{-3}	126
D-1	3.00	0.0679	5×10^{-3}	251
D-2	"	0.0649	1×10^{-2}	183
D-3	"	0.0638	2×10^{-2}	103
				ave.=193 ± 78

(a) Intensity and k_d/k_r for C series were 4.52×10^{15} quanta/sec. and 4.761./mole respectively and 7.68×10^{15} quanta/sec. and 9.55 1./mole resprctively for the D series.

(b) Irradiations carried out on merry-go-round with $\lambda > 3300\mathring{A}$.

samples using the integrated rate equation as discussed in the benzophenone section. As before, the method of least squares was employed to extract the slope and intercept of the line obtained in this treatment. The D series samples were irradiated at the same time as the experiment which determined k_d/k_r as shown in Figure 3. Within each series the values of k_q/k_r seem to decrease with increasing concentrations of MA although the trend is not clear when the experiments are considered together. The best that we can do is average the six results and note that the relative standard deviation of the measurements is 0.40. Assuming that the rate of hydrogen abstraction from isopropyl alcohol by acetophenone and benzophenone are equal, we calculate that

$k_q = 2.3 \times 10^8 \pm 100\%$.

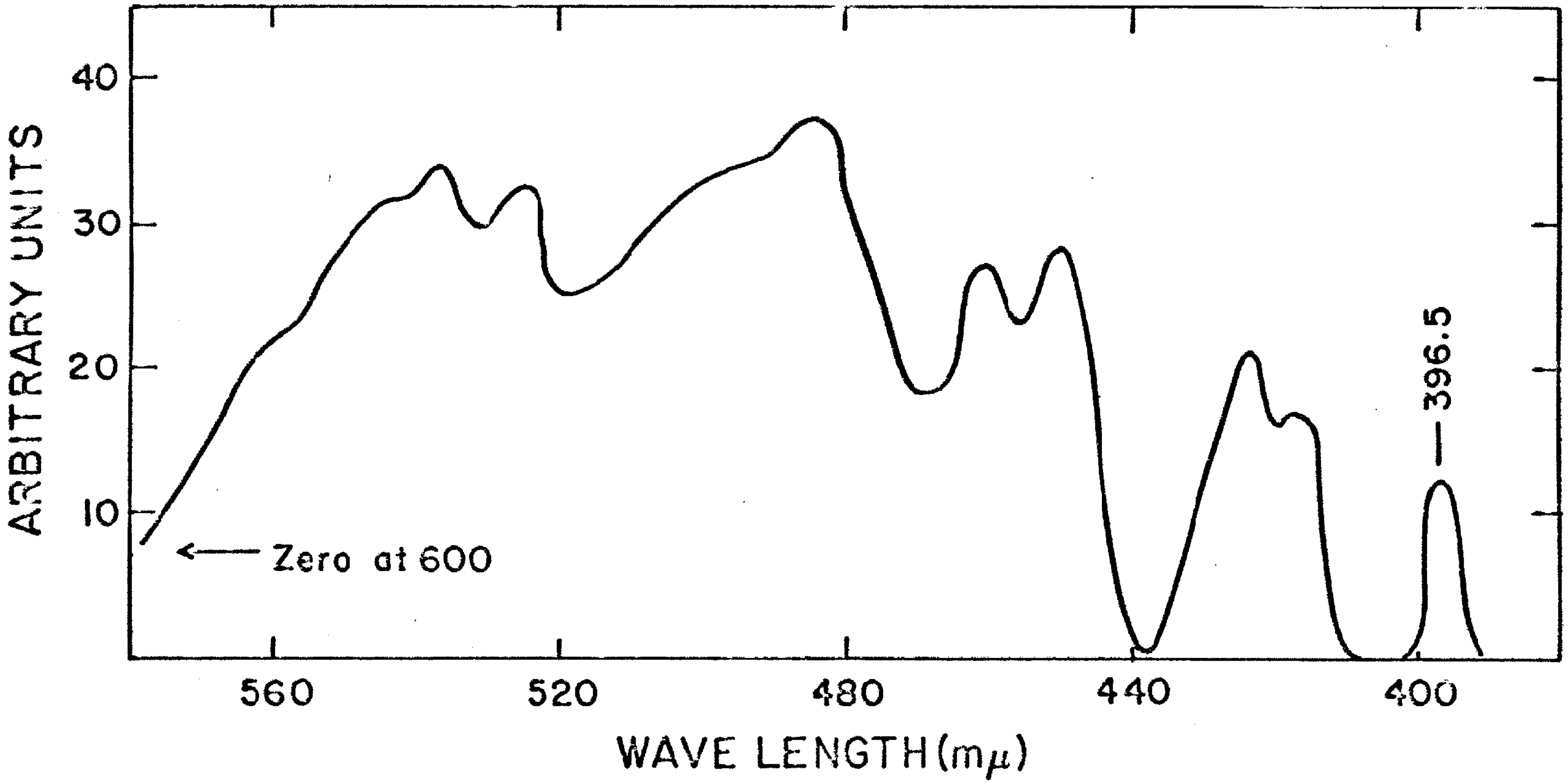
PHOSPHORESCENCE OF MALEIC ANHYDRIDE

From a methyl cyclohexane-isopentane (MCIP) glass at 77°K containing approximately 10^{-3}M MA, a very weak emission was detected. The spectrum obtained after careful subtraction of a solvent background emission is reproduced in Figure 6. If we assume that the shortest wavelength band is that corresponding to the 0-0 transition, the triplet state of MA lies 72.1 Kcal/mole above the ground state. While the rest of the spectrum was obtained by subtraction, this peak at 3965Å was not present in the solvent and is considered more reliable than the rest of the spectrum.

A second spectrum is shown in Figure 7. In this case the intensity of the emission was approximately ten times as great and there was virtually no background. The difference between the two spectra can be reasonably explained by three factors: (1) higher purity of the constituents of the glass, (2) variations in the properties of the glass - such as cracking, or crystallization and (3) use of a better phototube. Most importantly the position of the 0-0 band is unchanged at 3965Å.

When a slight excess of benzene was added to an MCIP solution of MA, no emission was detected under the same conditions as above.

Fig. 6. Phosphorescence from MA



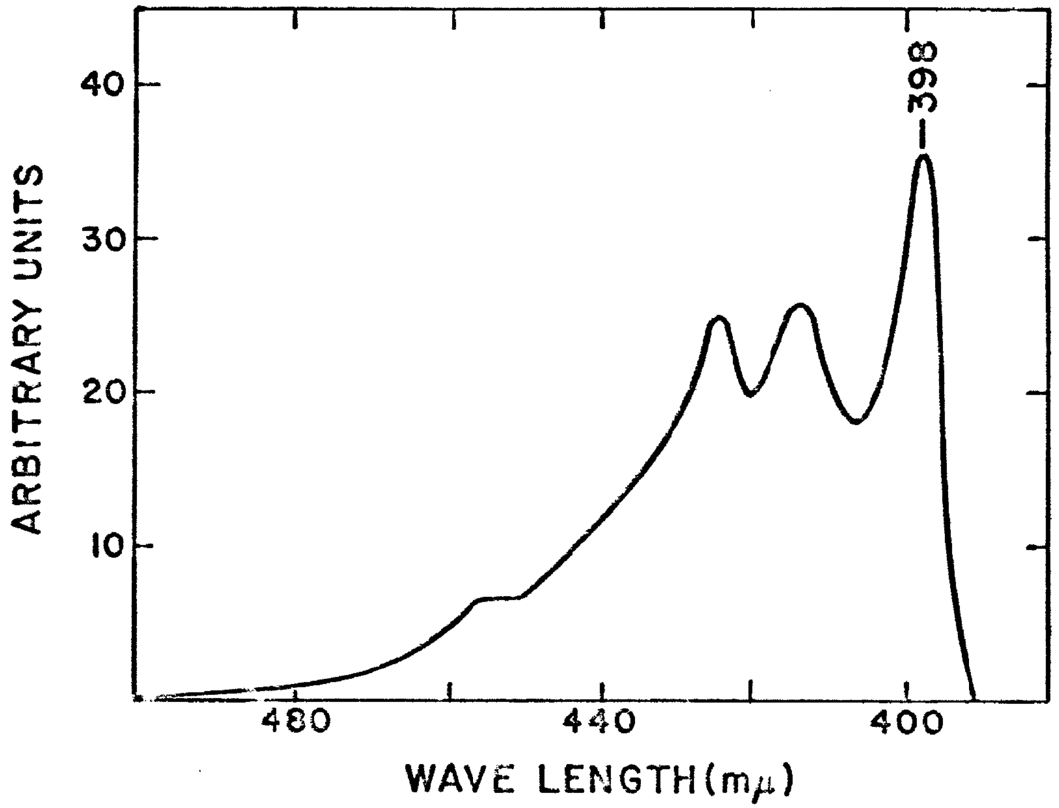


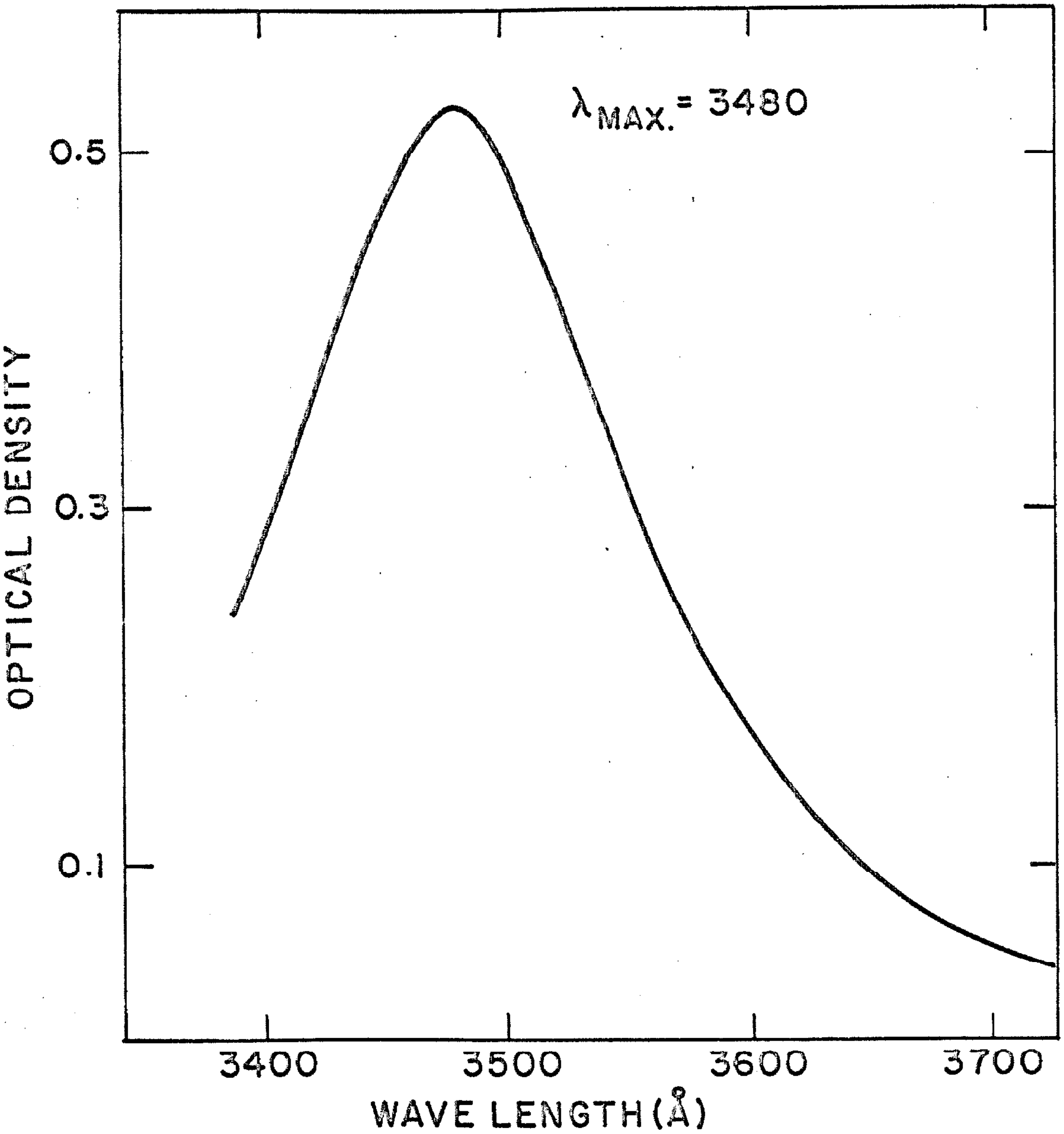
Fig. 7. Phosphorescence from MA

ETHYL IODIDE SPECTRUM OF MA

An attempt to substantiate the triplet state energy of MA obtained from the phosphorescence study was made using the external heavy atom effect (35) to enhance the probability of singlet-triplet absorption.

Solution of MA in purified ethyl iodide gave rise to the single absorption band (λ max $= 348 m\mu$), shown in Figure 8, proper to neither MA nor ethyl iodide. Unfortunately, there is no sign of any vibrational progression in the peak and no assignment of the 0-0 band could be made. It is possible that the absorption corresponds to a charge transfer transition of MA-ethyl iodide complex rather than the enhanced singlet-triplet absorption of MA. This seems reasonable in view of the assertion by McGlynn, et al. (36) that charge transfer is part of the process by which the external heavy atom effect operates. According to Katzin and McBeth (37) the iodine-ethyl iodide complex absorbs at $275 m\mu$ so this is not the cause of the maximum at $348 m\mu$.

Fig. 8. Absorption Spectrum of 0.067M MA in Ethyl Iodide



FLASH PHOTOLYSIS OF XANTHONE

As a physical check on the quenching rate constants derived from the photoreduction technique, the flash spectroscopy of benzophenone, acetophenone and xanthone was investigated. Of the three, only xanthone gave a triplet with a lifetime long enough to permit reliable quenching studies. Rate constants were obtained by computer analysis of data taken from photographs of the decay of triplet-triplet absorption displayed on an oscilloscope. The computer was programmed(35) to separate processes that are first order in triplet state from those that are second order according to equation 25. When MA is present in known concentration α is increased by the addition of the term $k_q [MA]$. Thus, the

$$\frac{d}{dt} \ln \frac{A_0}{A} = \alpha + \beta A \qquad (25)$$

where A = Absorbance due to the triplet-triplet absorption at any time

A_0 = Absorbance due to the triplet absorption at time zero

α = Sum of first and pseudo first order triplet decay rate constants

β = A second order rate constant for triplet decay

analysis of two xanthone solutions, one with and one without MA yields the desired k_q. In Table 9 the pertinent data are gathered from the flash photolysis experiment. From these results we calculate that $k_q = 6.1 \times 10^7$ l.mole^{-1}sec.$^{-1}$. This number represents quenching by uncomplexed MA, for the solvent in this experiment was cyclohexane. When we attempted the same experiment in benzene no T-T absorption was detected and formation of an unknown yellow compound occured.

Table 9 - k_q for MA Quenching Xanthone by Flash Photolysis

Run[a, b]	[xanthone]	[MA]	α	β
A - 3	1.0×10^{-3}M	0	1.08×10^4	4.18×10^4
D - 11	"	2.0×10^{-4}M	2.30×10^4	1.39×10^4
D - 12	"	"	2.30×10^4	9.35×10^4

(a) wavelength monitored was 5500Å
(b) Power delivered to flash lamps was 90 joules

QUANTUM YIELDS AND CONCENTRATION EFFECTS

Quantum yields for the diaddition were determined using both benzophenone and acetophenone as sensitizers. The fact that intersystem crossing is 100% ± 2% efficient in both sensitizers (28) permitted the use of benzophenone-benzhydrol actinometry (27) in the two determinations. In order to insure that the same amount of light was absorbed in the actinometer and the acetophenone solutions, the concentration of benzophenone was adjusted so that the absorbance of both solutions at 3660Å was equal. As reported earlier (10) the quantum yield of diadduct was approximately 0.09 for both sensitizers in the MA concentration range 1.500M to 0.500M. This data is collected in Table 10. Simultaneous irradiation

Table 10 - Quantum Yields in the Photosensitized Diaddition of MA to Benzene

Series[a]	$[MA]^b$	Φ
with ϕ_2CO		
A	0.500	0.088 ± 0.005
A	1.000	0.092 ± 0.001
A	1.500	0.096 ± 0.007
B	1.000	0.096
B	1.500	0.106
C	0.500	0.064
C	1.000	0.075
C	1.500	0.082
with $\phi COCH_3$		
D	1.500	0.10
D	1.500	0.090

(a) series A irradiations carried out on our optical bench, the others on our merry-go-round.

(b) Benzophenone 0.10M and acetophenone 1.00M of two benzene solutions containing 1.00M MA, one with 0.100M benzophenone and one without, through pyrex gave 1.50 and 0.55g. of diadduct respectively. Since a calculation shows that benzophenone absorbed 10% of the light in the first solution, we conclude that the quantum yield of the unsensitized reaction was $\sim$1/18 that of the sensitized reaction. This calculation considered the extinction coefficients of the complex and of benzophenone at all the mercury lines between 2804 and 3660Å.

The 10% decrease in quantum yield with concentration over the range reported in Table 10 prompted the further studies of concentration effects which are displayed in Tables 11 to 16. All of the irradiations reported in these tables were carried out with a Hanovia 450 watt mercury arc lamp filtered with a uranium glass filter which permitted only light of $\lambda > 3300$Å to pass. Yields are reported as the results from three degassed 4 ml. samples sealed in pyrex tubes.

Table 11 - MA Concentration Effect, Benzophenone Sensitized

$[\mathrm{MA}]^a$ \ Yield from run no.	1	2	3
0.050M	8.59 ± 0.2mg	9.56 ± 0.1mg	7.45 ± 0.5mg
0.100	17.58 ± 1.0	19.48 ± 0.2	15.67 ± 0.5
0.250			28.43 ± 1.5
0.500	25.26 ± 4.0	41.58 ± 1.0	31.87 ± 1.0
1.00	24.94 ± 4.0	47.71 ± 1.5	35.39 ± 1.0
1.500		49.12 ± 3.0	33.84 ± 3.0

(a) Concentration of benzophenone was 0.100M

Table 12 - MA Concentration Effect, Acetophenone Sensitized

$[MA]^a$ \ Yield from run no.	1	2
0.050M	12.29 ± 0.8mg	11.48 ± 1.0mg
0.100	21.78 ± 0.5	37.00 ± 2.0
0.250	25.78 ± 2.0	42.10 ± 1.5
0.500	21.99 ± 1.5	45.60 ± 3
1.000	28.29 ± 0.5	45.45 ± 3
1.5000	25.17 ± 3.0	39.47 ± 2

(a) Concentration of acetophenone = 1.00M

Table 13 - MA Concentration Effect, Xanthone Sensitized

$[MA]^a$ \ Yield from run no.	1	2
0.050M	9.97 ± 1.0mg	14.04 ± 1.0mg
0.100	15.68 ± 1.0	25.40 ± 0.5
0.250	17.37 ± 2.0	31.61 ± 1.0
0.500	18.13 ± 1.5	33.02 ± 1.5
1.000	13.34 ± 1.0[b]	30.04 ± 2.0
1.500	11.41 ± 1.0[b]	25.85 ± 1.0[c]

(a) Concentration of Xanthone = 0.050M

(b) Different cyrstalline form isolated from these samples which had the same decomposition point

(c) solution turned yellow

Table 14 - Benzene Concentration Effect, [MA] = 1.00M

$[Benzene]^a$ \ Yield when Diluent was	Dioxane	Chloroform	Acetonitrile
1.1M	0		
2.26		9.10 ± 0.4mg	15.04 ± 1.9mg
3.4	0		
4.52		15.27 ± 0.2	42.11 ± 1.9
5.6	23.20 ± 3mg		
6.75		18.98 ± 0.5	65.85 ± 1.0
7.9	65.16 ± 4		82.71 3.0
9.0		27.06 ± 1.0	94.28 ± 3.0
10.7	81.82 ± 5	33.45 ± 1.5	98.90 ± 1.0

(a) Concentration of benzophenone was 0.100M

Table 15 - Benzene Concentration Effect, Benzophenone Sensitized

[Benzene]^a \ Yield	$[MA]^b = 0.500M$	$[MA]^b \simeq 0.075M$
2.26M	6.8 ±0.4mg.	5.24 ± 0.2mg.
4.52	10.95±0.5	8.87 ± 1.0
6.78	13.29±0.5	11.03 ± 0.7
9.04	15.63±0.6	13.67 ± 0.5
10.4	16.03±1.0	14.78 ± 0.7

(a) Concentration of benzophenone = 0.10M

(b) Chloroform was the diluent

Table 16 - Benzene Concentration Effect, Unsensitized Reaction

Benzene^{a,b} \ Yield from run no.	1	2
2.26M	36.3mg.	17.9mg.
4.52	28.2	13.4
6.78	29.6	14.0
9.04	29.8	12.8
10.4	30.4	13.3

(a) Concentration of MA was 1.00M

(b) Chloroform was diluent

When the yields in Tables 11,12 and 13 are normalized at MA = 0.500M and averaged, Figures 9,10 and 11 result. From the yields of the benzophenone experiments one can calculate the dependence of yield on MA to be

$$\text{Yield} = \frac{236\,[MA]}{1 + 7.3\,[MA]} \qquad (26)$$

Fig. 9. MA Concentration Effect in Benzene, ϕ_2CO Sensitized

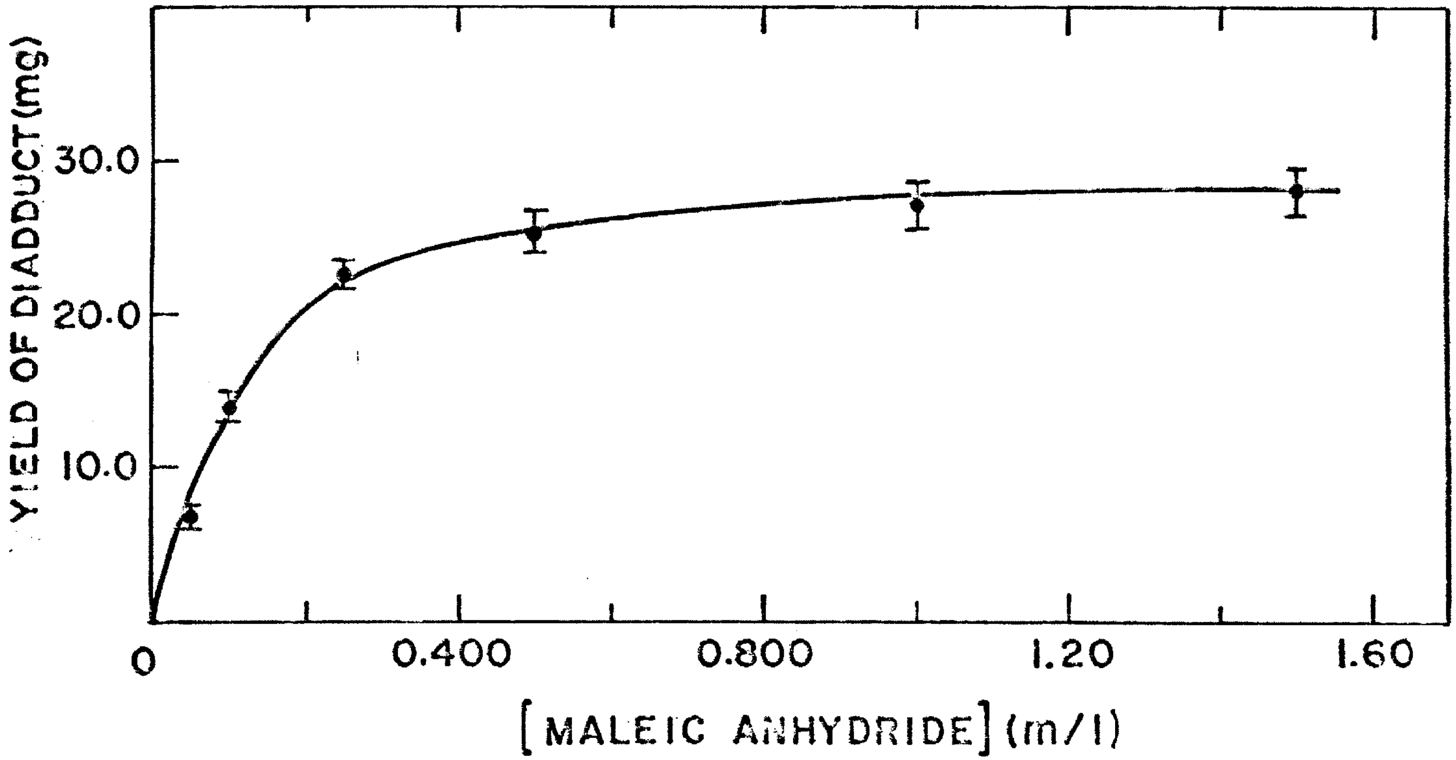


Fig. 10. MA Concentration Effect in Benzene, $\phi COCH_3$ Sensitized

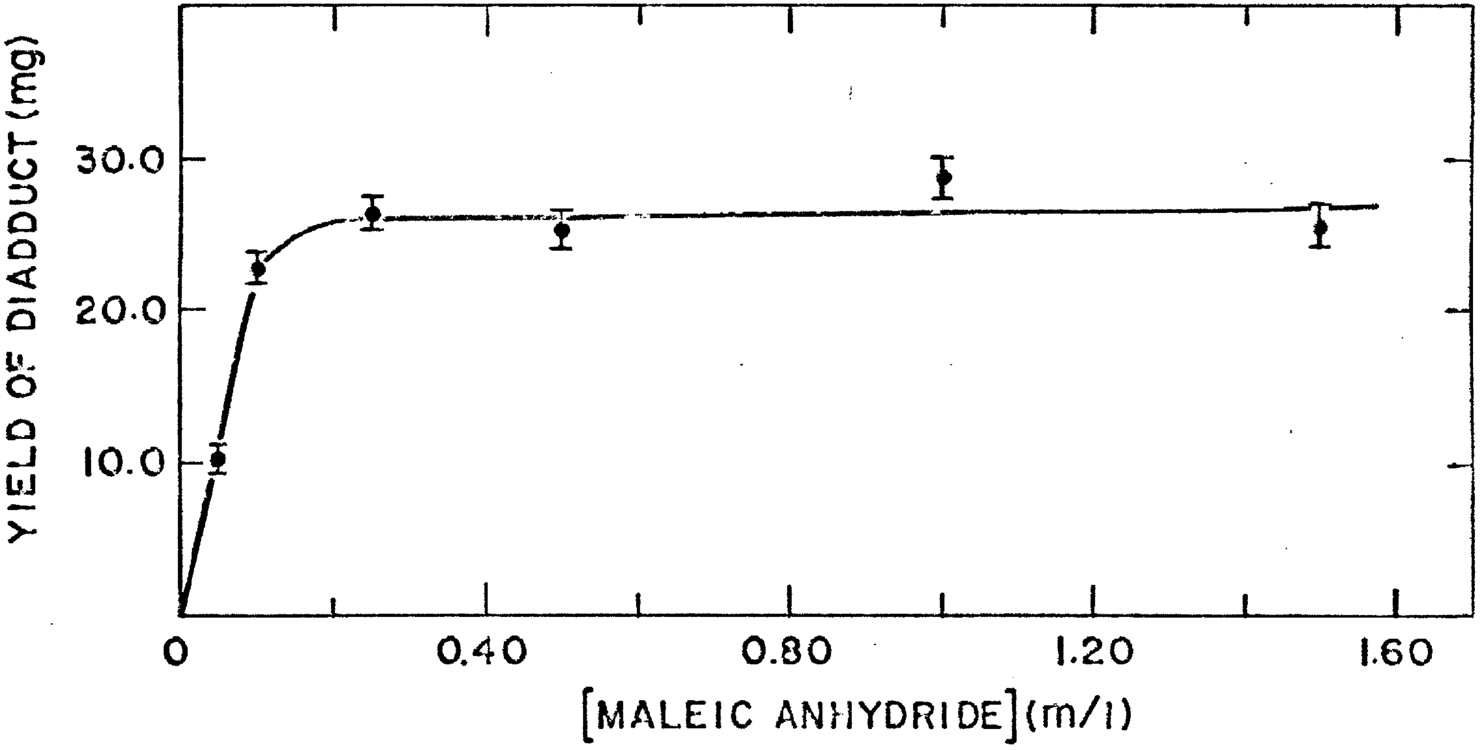
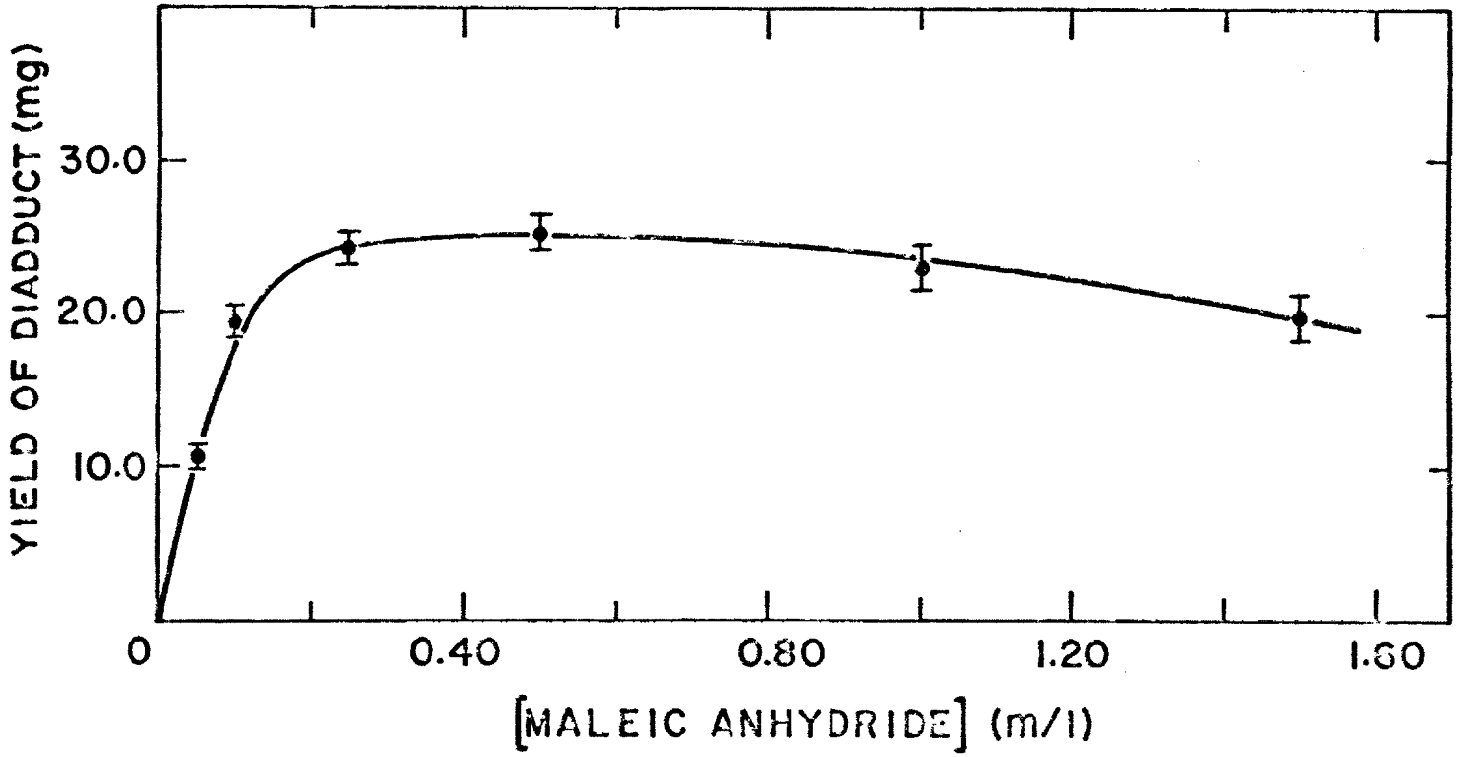


Fig. 11. MA Concentration Effect in Benzene, Xanthone Sensitized



to an accuracy of 10% which is close to experimental error, or

$$\text{Yield} = 36 \; [\text{MA}]^{\frac{1}{2}} \qquad (27)$$

with an accuracy of 22% which is outside of experimental error.

In Tables 14 and 15 are collected data on the benzene concentration effect at different concentrations of MA and in the presence of different diluents. These results are shown graphically in Figures 12, 13 and 14. The discrepancy evident in Figure 14 is probably not real, for the experiment at 0.075M MA contains yields which represent from 13 to 36% conversion of the MA. These yields were corrected with the help of the MA concentration effect curve of Figure 9. The ratio of the yield of diadduct from Figure 9 corresponding to the initial MA concentrations of Table 15 to the yield corresponding to the average concentration of MA during the run was taken as a correction factor. This tends to convert all the yields of Table 15 to higher values indicative of the situation at very low conversion. Figure 15 indicates the results of this treatment on the benzene concentration effect data taken at $[\text{MA}] = 0.075\text{M}$. The effect of this type of correction on the 0.500M MA curve of Figure 14 is not so large; but in the same direction, while the change in the 1.00M MA curve is negligible. We conclude that the dependence of yield of diadduct is of the following

Fig. 12. Benzene Concentration Effect at [MA] = 1.00M, ϕ_2CO Sensitized, Dioxane Diluent

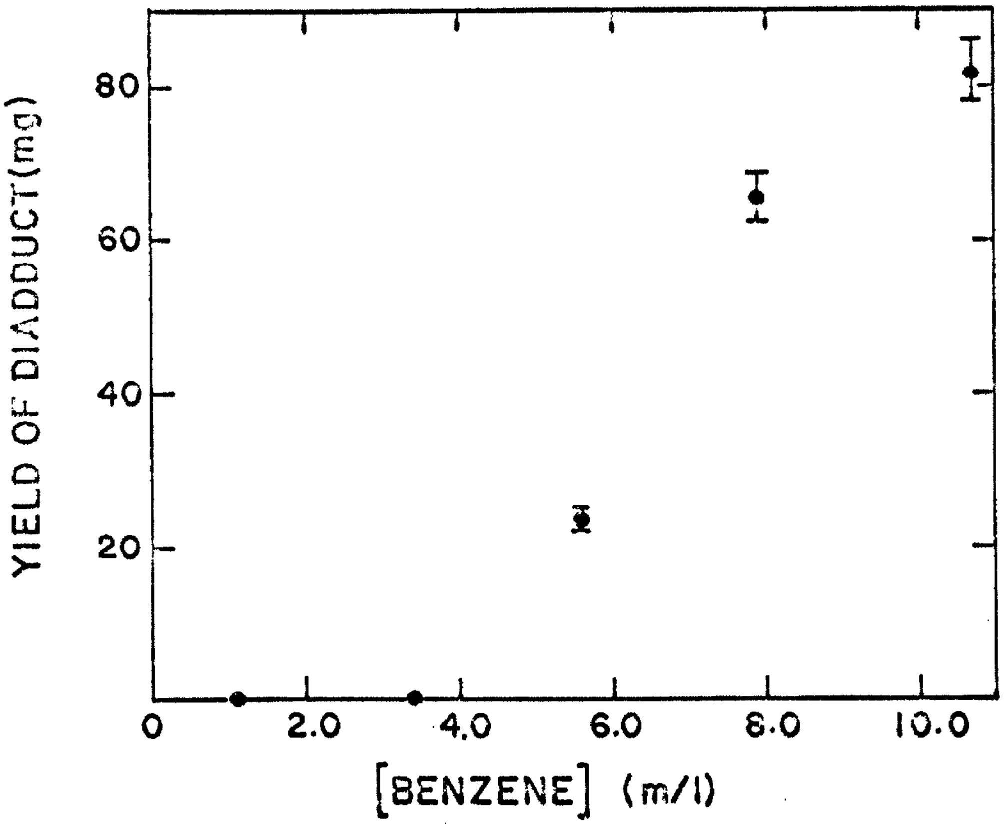


Fig. 13. Benzene Concentration Effect at [MA] = 1.00M, ϕ_2CO Sensitized, CH_3CN Diluent

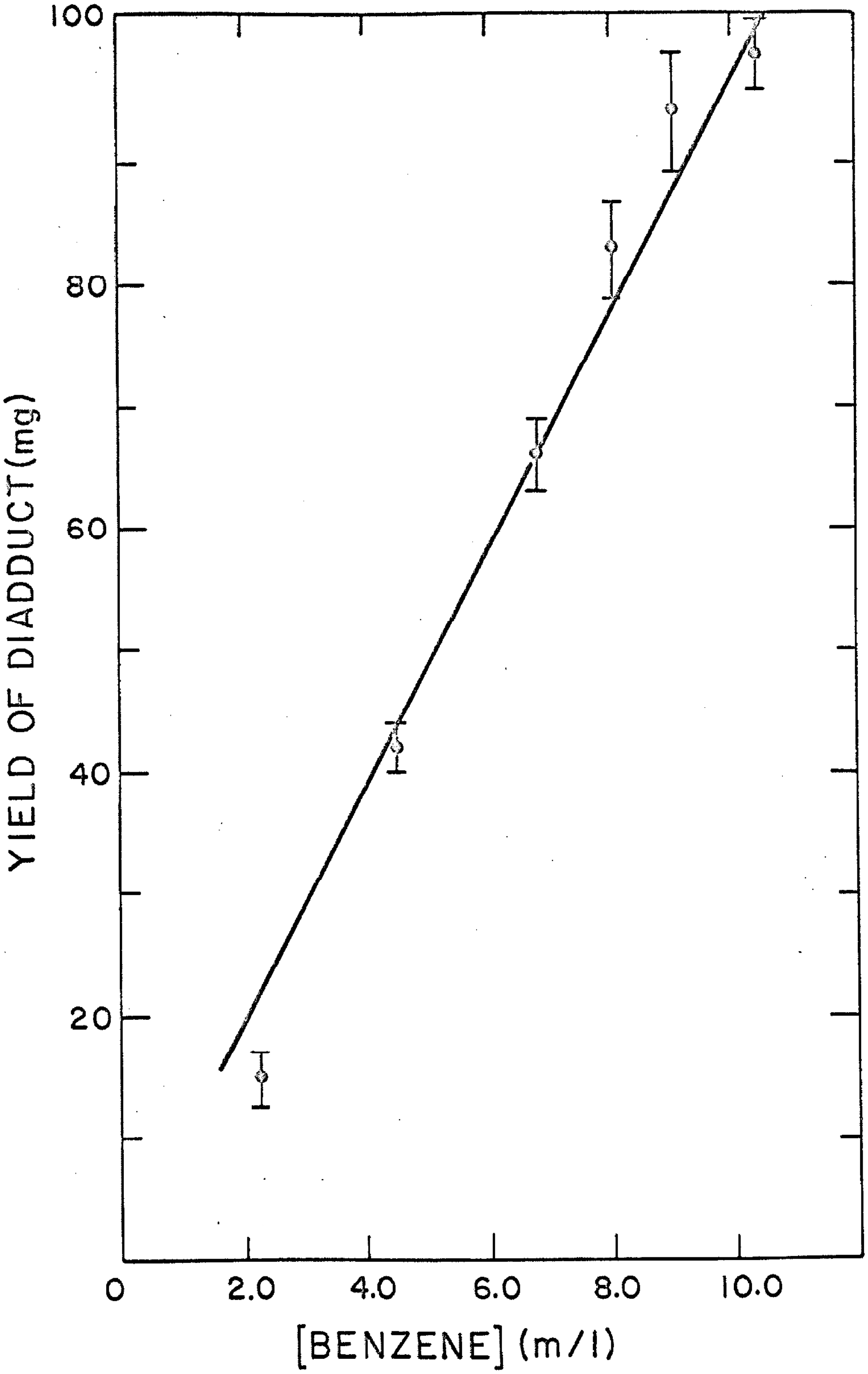


Fig. 14. Benzene Concentration Effect at Various Concentrations of MA, $CHCl_3$ Diluent

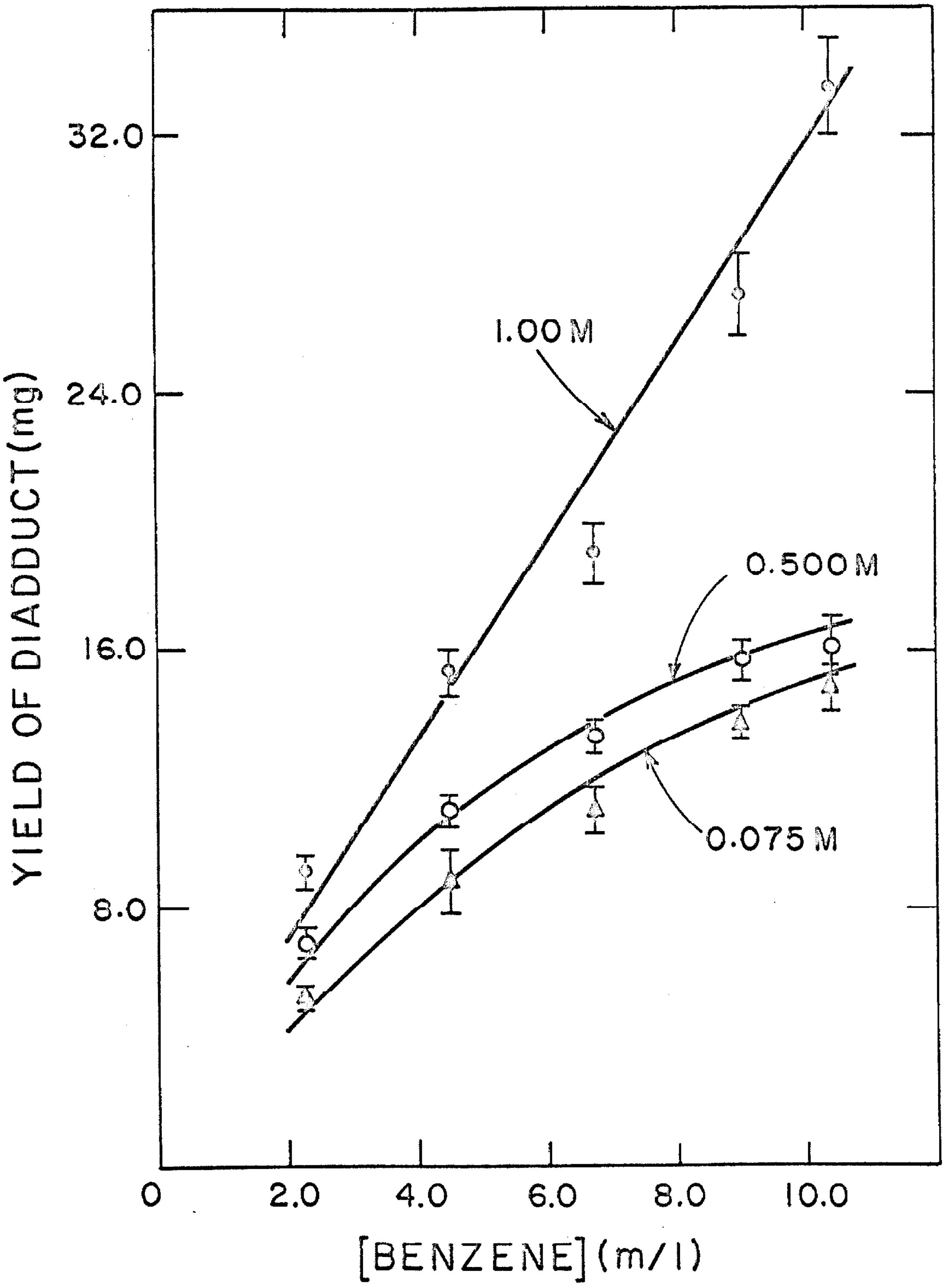
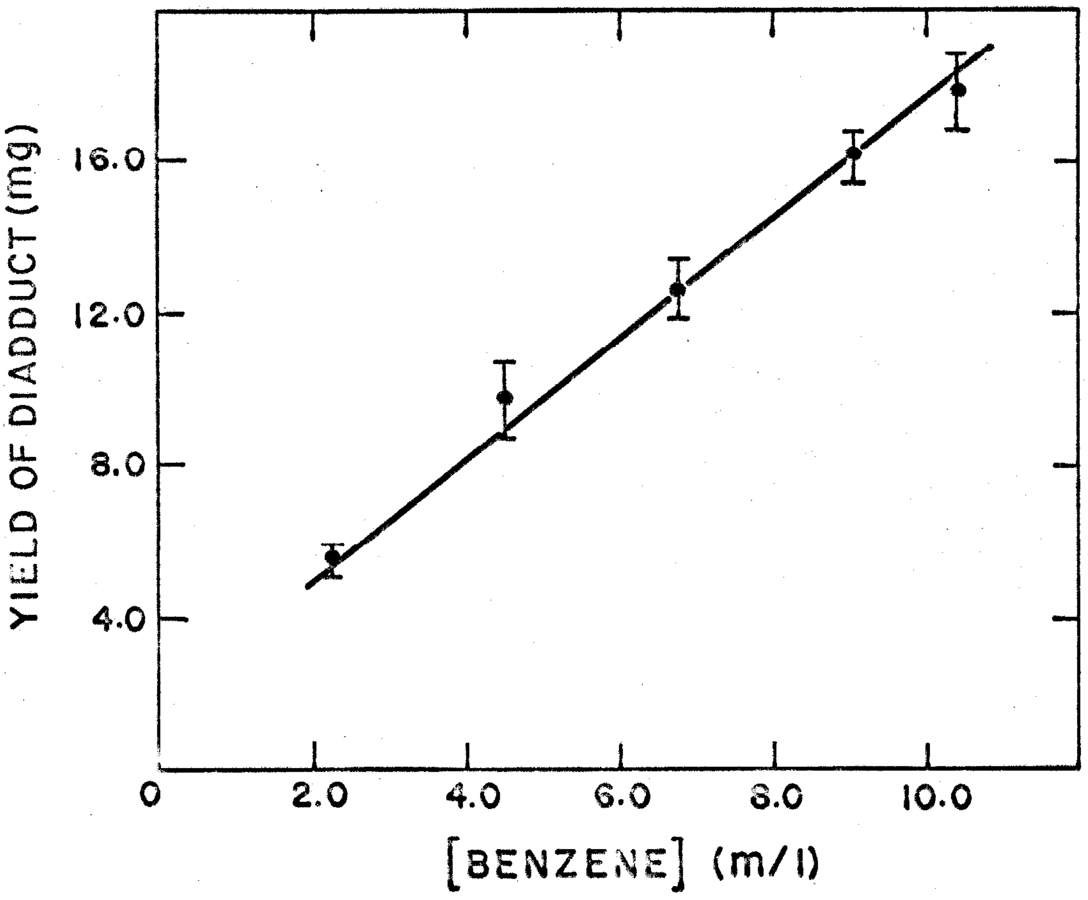


Fig. 15. Corrected Benzene Concentration Effect at $[MA] = 0.075M$, $CHCl_3$ Diluent



form, and that the 0.500M MA experiment is erroneous due to

$$\text{Yield} = K\,[\text{Benzene}]\;;\;K = \text{a constant} \qquad (28)$$

incomplete crystallization or other unknown factors. The anomalous behavior of dioxane as a diluent is associated with the fact that the solutions turn yellow and polymerization occurs at low concentrations of benzene.

In Table 16 may be found the results of two experiments on the effect of benzene concentration on the yield from the unsensitized reaction. There is no significant difference in the amount of light absorbed in these solutions; either all of the light is absorbed (at mercury lines below 3130Å) or an insignificant amount (at 3341 and 3660Å).

SENSITIZER CONCENTRATION EFFECT ON THE DIADDITION

Table 17 shows the results of an experiment in which the concentration of benzophenone was varied by a factor of ten. The amount of benzophenone present in all of the samples was sufficient to absorb all of light emitted near 3660Å by the mercury arc. However, the difference in the amount of light absorbed between the principal emission lines between 3700 and 4100Å is probably enough to account for the rise of 16% in yield.

Table 17 - Effect of Varying [Benzophenone] on Yield of Diadduct

sample	$[\phi_2CO]$	Yield of Diadduct
1	0.03M	24.9 ± 1.2mg
2	0.06	24.2 ± 1.2
3	0.10	25.4 ± 1.2
4	0.15	26.1 ± 1.3
5	0.20	28.3 ± 1.3
6	0.30	29.1 ± 1.3

EFFICACY OF VARIOUS SENSITIZERS

By the use of a graded series of compounds which have been observed to be effective as sensitizers, and others which should be effective because they are known to cross to the triplet state efficiently, it is often possible to gain some knowledge of the triplet energy of the energy acceptor of an energy transfer process. Accordingly some 18 different hydrocarbons and ketones have been evaluated as sensitizers for the diaddition. In all of the cases listed in Table 18 the sensitizer or inhibitor was the only species in solution which absorbed an appreciable amount of light. The yields reported here are those from simultaneous irradiation of two samples of each type on our "merry-go-round" appara-

Table 18 - Sensitizers and Inhibitors of the Diaddition

Sensitizers[a,b]	Triplet Energy[e] Kcal/mole	Yield of Diadduct	Inhibitors[c,d]	Triplet Energy[e]
Propiophenone	74.7	26mg	Triphenylene	66.6
Xanthone	74.2	14	Thioxanthone	65.5
acetophenone	73.6	41	Anthraquinone	62.4
benzaldehyde	71.9	36	2-acetylfluorene	62.6
benzophenone	68.5	46	naphthalene	60.9
4,4-dichlorobenzene	68.1	59	2-acetonaphthone	59.3
			Chrysene	56.6
p-diacetylbenzene	67.6	35	Benzil	53.7
			Fluorenone	53.0
p-cyanobenzophenone	66.4	40		

(a) all samples carefully degassed
(b) $\lambda > 3300$Å was used
(c) $\lambda > 2900$Å " "
(d) yields of 0.001g can easily be detected
(e) These values determined by Lamola, Herkstroeter and Hammond (39)

tus. They do not necessarily reflect differences in quantum yields or in efficiencies of energy transfer, for the sensitizers do not all intersystem cross to the same extent and they did not all absorb the same amount of light. None of the sensitizers used absorb beyond 4000Å so that the wavelength range of interest lies between 3300Å and 4000Å. Since the group of mercury emission lines about 3660Å are the major source of light in the experiment and since the concentrations of sensitizers were such that all 3660Å light was absorbed, differences in yields due to variations in light absorbed should be no greater than 10%.

Compounds which are listed as inhibitors do not necessarily quench the reaction, their essential characteristic is that energy transfer from them (if occuring) must be at least 25-50 times slower than from the sensitizers since this is the minimum ratio of yield from sensitizer to yield from inhibitor. Thus, the inhibition of the diaddition could be a result of internal filtering and/or quenching.

A sample of 1.00M MA in benzene when irradiated with light of $\lambda > 3300$Å gives no product within a period twice as long as that used for the sensitized reactions of Table 18.

EFFECT OF LIGHT INTENSITY ON THE DIADDITION

The effect of light intensity of the diaddition was tested by comparing the yield of diadduct from two experiments. In the first, degassed 1.00M solutions of MA in benzene were irradiated through pyrex glass ($\lambda > 2800\text{Å}$) for 32.5 hours; while in the second, the same 450 watt lamp was surrounded by a piece of 80 mesh stainless steel screening which allowed 32.5% transmission between 2700 and 3700Å. Under the latter conditions, a yield which was 33% ± 3% of the yield obtained without the filter was found after an identical irradiation period.

COMPETITION BETWFEN FORMATION OF THE DIADDUCT AND THE MA DIMER

Although the sensitized and unsensitized dimerization of MA and 2,3-dimethylmaleic anhydride in dioxane and benzene respectively have been reported by Schenck et al. (19), no attempt to detect the MA dimer in irradiated solutions of MA in benzene have been made. By irradiation of equimolar solutions of benzene and MA in dioxane, competition between addition of MA to benzene and to another molecule of MA should be observed. In fact, as shown by vapor phase chromatography of the methyl esters of the products (Table 19) only small amounts of dimer are formed whether or not the reaction is sensitized.

Table 19 - Dimer Formation From Eqimolar Benzene-MA Solutions

Sample	[MA] = [Benzene]	Sensitizer	[Sensitizer]	Amount of Dimer
1	2.00M	acetophenone	1.00M	3% ± 2%
2	"	benzophenone	0.10M	1% ± 0.5%
3	"	none	0	1% ± 0.5%

DIMERIZATION OF MA

In order to evaluate the results of the dimer-diadduct experiment and to obtain a stock of pure dimer, we performed some orienting dimerization in dioxane. These results may be found in Table 20. Although the dioxane used in these experiments was carefully purified, large amounts of polymer formed in all of the reactions. In an effort to circumvent polymer formation the same experiments were run in acetonitrile with the results shown in Table 21. Again, there was polymer formation in both the sensitized and unsensitized reactions. Addition of 10^{-3}M chloranil or hydroquinone to inhibit polymerization was without success - higher concentrations were not practical for internal filtering would become important.

Table 20 - Yields of Dimer with Dioxane as Solvent;
$[MA] = 2.00M$

Sensitizer	$\lambda > 2800$ Å			$\lambda > 3300$ Å	
	run #1	#2	#3	#4	#5
acetone-0.50M		21.9 ± 1mg			
propiophenone-1.0M		17.8 ± 1	7.6mg	10.5 ± 2mg	10.7mg
acetophenone-1.0M		16.2 ± 1	10.4	14.9	9.8 ± 0.5
benzophenone-0.10M	0.292g	29.0 ± 1	18.7	18.8	19.4 ± 0.3
none	0.254	22.7 ± 2		0	

Table 21 - Yields of Dimer with Acetonitrile as Solvent; [MA] = 2.00M

	$\lambda > 2800 \mathring{A}$			$\lambda > 3300 \mathring{A}$	
Sensitizer	run #6	#7	#8	#9	#10
acetone-0.50M	51.6 ± 1mg	33.0 ± 3mg	86 ± 10mg		
propiophenone-1.0M			3.5	0	
acetophenone-1.0M			trace		0
benzophenone-0.10M	18.2 ± 0.7	20.5 ± 1	43 ± 5	0	0
none	55.2 ± 0.6	42.0 ± 1	116	0	0

Examination of the spectra of Figure 16 shows that MA forms a charge transfer complex in dioxane. When the Ketelaar (40) treatment was applied to the data of Table 22 to determine the equilibrium constant of the complex the results were unsatisfactory. From Figure 17 it can be seen that the points describe a curve rather than a straight line.

Table 22 - Equilibrium Constant Determination; MA-Dioxane Complex at 2800Å.

Sample[a]	[MA]	$[\text{dioxane}]^{-1}$	ϵ_a [b]	$(\epsilon_a - \epsilon_d)^{-1}$ [c]
1	0.010M	$4.0M^{-1}$	32.7	0.0709
2	"	2.0	39.7	0.0474
3	"	1.0	59.9	0.0319
4	"	0.50	84.7	0.0151
5	"	0.33	104.7	0.0112
6	"	-	18.6	-

(a) solvent was chloroform

(b) ϵ_a = Absorbance of solution/[MA]

(c) ϵ_d = extinction coefficient of MA

For order of magnitude purposes, the slope and intercept of the straight line give $K = 0.72$ and $\epsilon_{280} = 106$ for the complex. Behavior of this kind is expected if the complex is not en-

Fig. 16. Ultraviolet Spectra of MA

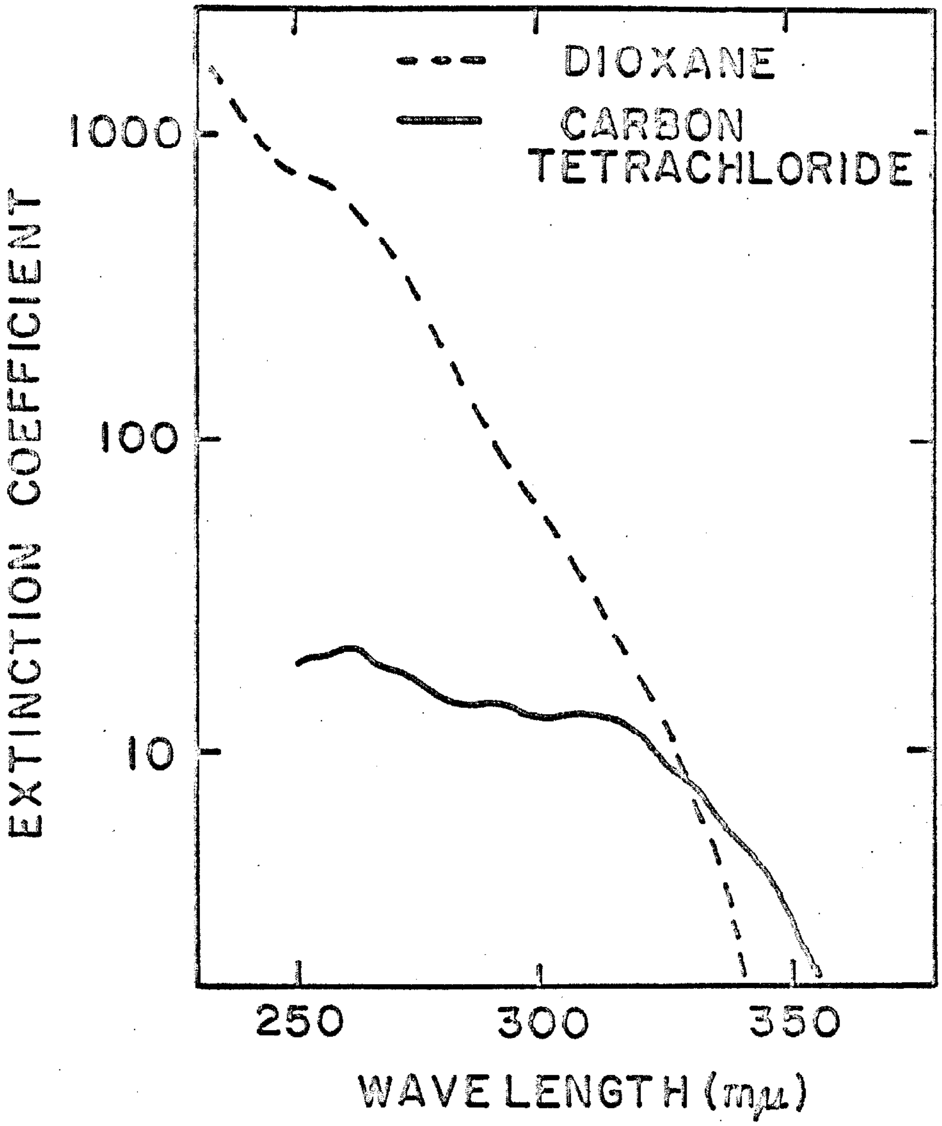
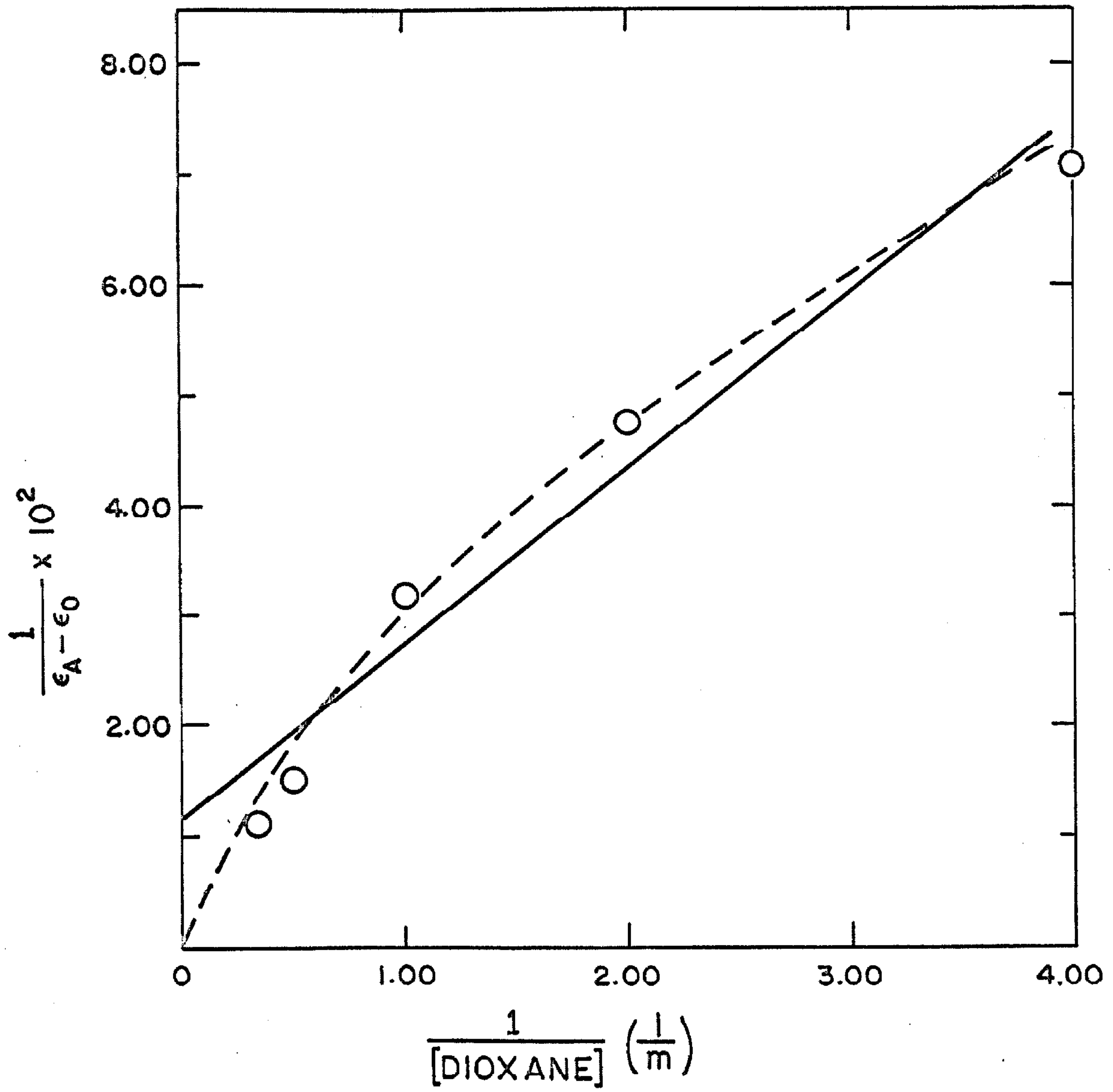


Fig. 17. Equilibrium Constant Determination, MA-Dioxane Complex



tirely 1 to 1. In this case 2 to 1 complexes involving both oxygen atoms of a single dioxane molecule are certainly reasonable. If we assume that the equilibrium constants for both complexes are the same, there should be a large excess of 1 to 1 complexes in neat dioxane when [MA] = 1M. Thus, the treatment of Moore and Anderson (42) when applied to the data of Table 23 gives 0.9 as the slope of a plot of log A vs. log [MA]. With substantial amounts of 2:1 complex present the number of molecules of MA per complex would be between 1 and 2, i.e. the slope would fall between these limits. There is no evidence for complex formation in acetonitrile; the spectrum of MA in this solvent is identical with the spectrum in carbon tetrachloride in Figure 16. Solution of MA in tetrahydrofuran produces a UV spectrum similar to the dioxane spectrum and a yellow charge-transfer band is obvious in veratrole. Fruitless attempts were made to prepare the MA dimer from benzophenone sensitized irradiations in chloroform, tetrahydrofuran, and 1,2-dimethoxyethane as well as by direct irradiations of 1.50M solutions of MA in 1,2-dimethoxyethane, veratrole (1,2-dimethoxybenzene),

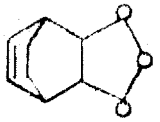
Table 23 - Stoichiometry of the MA-Dioxane Complex at 2800Å

Sample	[Dioxane]	[MA]	Absorbance	log A	log [MA]
1	2.50M	0.002	0.302	-0.520	-2.699
2	"	0.004	0.527	-0.278	-2.398
3	"	0.008	0.994	-0.0026	-2.097
4	"	0.012	1.453	0.162	-1.921

methanol, tetrahydrofuran and tetralin. The dimer is formed in the direct reaction, though.

ADDITION OF MA TO BICYCLO [2,2,2] -5-OCTENE-2,3-DICARBOXILIC ANHYDRIDE

As a test of the ability of MA to add to the possible intermediate II we attempted the photochemical addition of MA to VIII, the product of the Diels-Alder reaction of MA with cyclohexadiene. Degassed acetonitrile solutions approximately 0.5M in MA and 0.5M in VIII both with and without benzophenone were irradiated for 10 days with a 450 watt lamp. Small amounts (4mg. per 4ml. sample) of white crystals precipitated after this time and were found to be fumaric acid in the unsensitized case and fumaric acid plus an unknown compound which melted at 318°C in the tubes containing benzophenone. Although the compound was not isolated we estimate that it comprised no more than 1/3 of the yield. No high melting compounds were isolated from the filtrate from either reaction. Assuming that this material is an adduct of MA with VIII, we estimate that the maximum quantum yield for the addition is 0.007.



VIII

ATTEMPTS TO TRAP THE INTERMEDIATE

In order to trap the supposed cyclohexadiene-like intermediate formed during the diaddition, it was necessary to find an active dienophile which would not inhibit the reaction when employed in high concentrations. Ethyl acrylate was found to be suitable for this purpose, and accordingly a benzene solution 1.00M in MA, 2.50M in ethyl acrylate and 0.10M in benzophenone was prepared, degassed and irradiated. After 22% conversion of the MA, the diadduct precipitate was collected and its IR spectrum taken. It proved to be identical to that of diadduct. From the filtrate 52% of the MA was recovered, the remaining yellow goo was probably a mixture of MA and ethyl acrylate polymers and copolymers.

This approach was abandoned and a preliminary low temperature experiment using the addition to toluene was attempted. It was hoped that at -77°C a large enough concentration of intermediate could be built up so that it could be trapped by a dienophile added after halting the irradiation. Tubes containing 0.5M MA and 0.05M benzophenone were irradiated for 15 hours at dry ice temperature. Then, while still cold, the contents of the tubes were mixed with a concentrated solution of tetracyanoethylene. After reaching room temperature and standing for one day, no diadduct or cross adduct was isolated. Failure to observe any product probably reflects the low quantum yield for the addition to toluene.

QUENCHING THE UNSENSITIZED DIADDITION

Although Bryce-Smith and Lodge (6) had reported that oxygen did not quench the unsensitized reaction, it was deemed advisable to check this work in view of the previously noted discrepancy in their results. Indeed, our results contradict the above observation in that oxygen at its equilibrium concentration at atmospheric pressure did quench the unsensitized reaction. If we assume that the solubility of oxygen in toluene and benzene is the same, the concentration of oxygen in these experiments was 5×10^{-3}M (41). The numbers given in Table 24 as the fraction quenched represent ratios of the average yields of ten sample tubes; five sealed at room pressure and five degassed. Quenching experiments with several other good triplet quenchers (one of which-Fe(DBM)- is a good singlet quencher also (23)) were carried out as shown in Table 25. Little or no quenching was observed in these experiments, probably this was a result of the low concentrations of quenchers employed to obviate internal filtering.

Table 24 - Oxygen Quenching of the Diaddition

Run^{a,b}	[MA]	Fraction Quenched
1	2.00	0.23 ± 0.05
2	1.50	0.20 ± 0.07
3	0.200	0.31 ± 0.07

(a) benzene was the solvent
(b) $\lambda > 2800\text{Å}$ used

Table 25 - Quenching the Diaddition

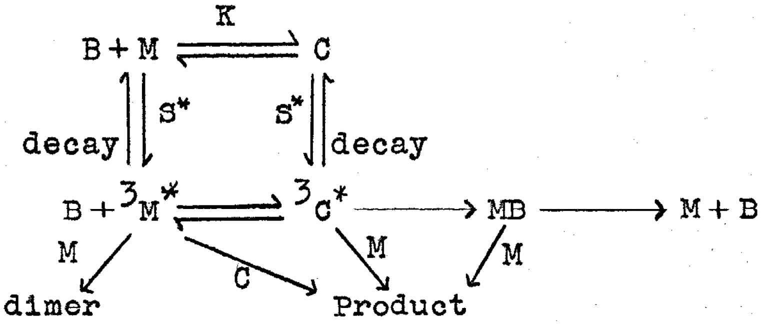
Run[a]	Quencher	Yield of Diadduct(mg.)
1[b]	none	2.3 ± 0.5
	1×10^{-4}M $Fe(DBM)_3$[d]	2.1 ± 0.7
2[b]	none	2.3
	1×10^{-3}M azulene	3.2
	1×10^{-4}M $Fe(DPM)_3$[d]	3.5
3[b]	none	2.5
	5×10^{-4}M azulene	2.3
4[c]	none	21.9 ± 0.3
	5×10^{-4}M naphthalene	22.2 ± 0.8
	" 2-acetonaphthone	22.4 ± 1.0
	" anthracene	19.0 ± 2.0
	" azulene	16.6 ± 0.8

(a) Benzene was the solvent, all samples degassed
(b) filter system on optical bench isolated the mercury 3130Å line, yields are average of two samples
(c) λ>2800Å used, yields are average of three samples
(d) $Fe(DBM)_3$ is ferric dibenzoylmethide and $Fe(DPM)_3$ is ferric dipivaloylmethide

In an oxygen quenching experiment run simultaneously with Run 2 which contained 0.10M benzophenone and 1.50M MA, 24% ± 7% quenching was observed. Assuming a diffusion controlled rate for oxygen quenching benzophenone triplets and using the k_q for MA in benzene we find that less than 10% quenching comes from direct quenching of sensitizer.

DISCUSSION

The mechanisms which have been proposed for the sensitized diaddition fall into two broad categories based on the mechanism assumed for the sensitization process. These processes are addition of excited sensitizer to MA (1) or transfer of triplet energy from excited sensitizer to MA or the complex (6,10). By considering the diagram below which just shows possible steps in the second category of mechanisms the complexity of the problem can be visualized. It is possible that all of the processes shown here occur: none can be ruled out _a priori_, but hopefully one of the routes will predominate to such an extent that the problem is tractable. As a beginning, we shall examine the kinetic consequences of some of the routes by deriving the way in which the quantum yield should vary with concentration of reactants and compare the answers with the empirical results. For this pur-



where B = benzene
M = maleic anhydride
C = complex
S = benzophenone
MB = an intermediate consisting of a benzene-maleic anhydride adduct

pose, the benzophenone data will be used because the benzene concentration effect was not studied with acetophenone or xanthone. As collected, the concentration effect data are not in terms of quantum yields as are the kinetic expressions. However, all of the tubes of a particular run were irradiated simultaneously with light absorbed only by the sensitizer. Under these conditions the relative yields correspond to relative quantum yields. Furthermore, the yields in most experiments involving variation of concentrations were low enough so that the initial concentration can be used in the rate expressions with no more than 10% error.

The features which the data demand from any mechanism are: (1) a relation between the quantum yield and MA concentration of the following type where R is a constant, and (2)

$$\bar{\Phi} = \frac{R\,[M]}{1+7.3\,[M]} \qquad (29)$$

a straight line dependence of quantum yield on concentration of benzene between 2M and 10M which could extrapolate to a low, non zero intercept. Actually an expression of the form

$$\bar{\Phi} = \frac{S\,[B]}{T + [B]} \qquad (30)$$

where S is a constant and T $\geqq$ 20 would be indistinguishable within the limits of error. Thus it is clear that the benzene and MA concentration effects are independent.

KINETICS - SCHENCK MECHANISM

Let us first consider the Schenck mechanism. In this discussion as well as in those kinetic analyses of other categories to follow one model derivation will be presented. Only the quantum yield expression, or a description of it, will be presented for the rest of the mechanisms.

Mechanism 1

The mechanism discussed in the introduction is shown below along with the equation which describes the quantum yield obtained by making the steady state approximation for radicals, excited states and intermediates. The excited sensitizer in the Schenck mechanism is treated as a biradical without specifying its multiplicity. Addition of the excited sensitizer to MA gives an adduct biradical which is denoted by $\cdot MS\cdot$. This mechanism is eliminated because it predicts no benzene concentration effect.

Reaction	Rate
$S \longrightarrow S^*$	I
$S^* \longrightarrow S$	$k_d [S^*]$
$S^* + M \longrightarrow \cdot MS\cdot$	$k_1 [S^*][M]$
$\cdot MS\cdot + B \longrightarrow MB + S$	$k_2 [\cdot MS\cdot] [B]$
$MB + M \longrightarrow$ Product	$k_3 [MB] [M]$

$$[S^*] = \frac{I}{k_{d_1} + k_1[M]} \quad ; \quad [\cdot MS \cdot] = \frac{k_1[M]\,[S^*]}{k_2[B]} \quad ; \quad [MB] = \frac{k_2\,[B]\,[\cdot MS\cdot]}{k_3[M]}$$

$$\Phi_1 = \frac{k_3[M]\,[MB]}{I} = \frac{k_1[M]}{k_{d_1} + k_1[M]}$$

Mechanism 2

If reversion of the intermediate MB to benzene and MA is added to the above sequence as shown, the quantum yield becomes

Reaction	Rate
$MB \longrightarrow M + B$	$k_9[MB]$

$$\Phi_2 = \frac{k_3[M]^2}{(k_9 + k_3[M])(k_d + k_1[M])}$$

This is eliminated for the same reason.

Mechanism 3

A benzene effect can be built into these mechanisms by allowing the diradical, $\cdot MS \cdot$, to revert to $S^* + M$ or to $S + M$. Since the former possibility is unreasonable, and requires similar M and B concentration effects, it need not be considered. However, the second alternative produces Φ_3 which can explain the data if $k_1[M] \gg k_d$, $k_3/k_9 = 7.3$ and $k_4 \geq 20k_2$.

Reaction	Rate
$\cdot MS \cdot \longrightarrow M + S$	$k_4[\cdot MS \cdot]$

$$\Phi_3 \quad \frac{k_1k_2k_3[M]^2[B]}{(k_d + k_1[M])\;(k_9 + k_3[M])\;(k_4 + k_2[B])}$$

Mechanism 4

Mechanism 4 is identical with the previous one except that there is no dissociation of the intermediate. With $k_1/k_d = 7.3$ and $k_2 \geqq 20k_4$, this is acceptable.

$$\Phi_4 = \frac{k_1 k_2 [M] [B]}{(k_d + k_1 [M])(k_4 + k_2 [B])}$$

KINETICS: ENERGY TRANSFER TO FREE MA

Next we shall treat mechanisms which have as their first step energy transfer to free MA. Since it was shown that only small amounts of the MA dimer are formed during the irradiation of solutions of MA in benzene, the dimerization path was not included in any of the kinetic analyses. It will be shown later that the concentration of the intermediate MB is too low to compete in energy transfer or light absorption so these steps are left out. Also reversible energy transfer as discovered by Sandros and Bäckstrom (43) is not included because its operation requires a decrease in quantum yield with increasing concentration of sensitizer. We found that there actually was little or no effect.

In all of the following an asterisk indicates a molecule in its first excited triplet state. It should be recognized, however, that excitation of the sensitizer leads first to excited singlet states. Intersystem crossing follows with high efficiency and is omitted in the derivations.

Mechanism 5

What is probably the most straightforward mechanism in this class is derived below. Since the benzophenone quenching studies show $k_{t_2}/k_{d_1} = 200$, this mechanism is inconsistent with the empirical ratio of 7.3 obtained from the MA concentration effect curve.

Reaction	Rate
$S \longrightarrow S^*$	I
$S^* \longrightarrow S$	$k_{d_1}[S^*]$
$S^* + M \longrightarrow M^* + S$	$k_{t_2}[S^*][M]$
$M^* \longrightarrow M$	$k_{d_3}[M^*]$
$M^* + B \rightarrow MB$	$k_6[M^*][B]$
$MB + M \longrightarrow$ Product	$k_5[MB][M]$

$$[S^*] = \frac{I}{k_{d_1} + k_{t_2}[M]} \qquad [M^*] = \frac{k_{t_2}[M][S^*]}{k_{d_3} + k_6[B]}$$

$$[MB] = \frac{k_6[B][M]}{k_5[M]}$$

$$\Phi_5 = \frac{k_6 k_{t_2}[M][B]}{(k_{d_3} + k_6[B])(k_{d_1} + k_{t_2}[M])}$$

Mechanism 6

When reversion of the intermediate is added as before (first order rate constant k_9) Φ_5 becomes

$$\Phi_6 = \frac{k_5 k_6 k_{t_2}[M]^2[B]}{(k_{d_3} + k_6[B])(k_{d_1} + k_{t_2}[M])(k_9 + k_5[M])}$$

Since $k_{t_2}[M] \gg k_{d_1}$ throughout the concentration range studied Φ_6 is reduced to Φ_6'. With the restrictions that

$$\Phi_6' = \frac{k_5 k_6[M][B]}{(k_{d_3} + k_6[B])(k_9 + k_5[M])}$$

$k_5/k_9 = 7.3$ and $k_{d_3}/k_6 \geq 20$, the mechanism is in accord with the results of the concentration effect work.

Mechanism 7

If instead of adding to benzene, excited MA can react directly with the complex to form the diadduct as indicated below, Φ_7 can be derived. Since Φ_7 demands that the MA and benzene concentration effects have similar form it is not a valid mechanism.

Reaction	Rate
$M^* + C \longrightarrow \text{Product}$	$k_8[M^*][C]$

$$K = \frac{[C]}{[M]\,[B]}$$

$$\Phi_7 = \frac{k_8 k_{t_2} K [M]^2 [B]}{(k_{d_3} + k_8 K [M]\,[B])(k_{d_1} + k_{t_2}[M])}$$

Mechanism 8

By allowing formation of the intermediate by decay of excited complex formed from excited MA and benzene as shown below another family of mechanisms is generated.

Reaction	Rate
$M^* + B \rightleftharpoons C^*$	$k_{-2}[M^*]\ [B], k_2[C^*]$
$C^* \longrightarrow MB$	$k_3[C^*]$

$$\Phi_8 = \frac{k_3 k_{-2} k_{t_2} [M]\ [B]}{(k_{d_1} + k_{t_2}[M])\left[k_3(k_{d_3} + k_{-2}[B]) + k_2 k_{d_3}\right]}$$

The quantum yield expression Φ_8 for the first member of this family predicts a very small MA concentration effect (recall $k_{t_2}[M] \gg k_{d_1}$) so it is not considered farther.

Mechanism 9

In mechanism 8 the dissociation and reformation of the excited triplet state of the complex was not considered as an equilibrium. If the rate constants k_2 and k_{-2} are much greater than k_3 and k_{d_3} respectively we can use the equilibrium formulation, as below. For the same reason that mechanisms 5 and 8 were eliminated this must be incorrect.

$$K' = \frac{[C^*]}{[M^*]\ [B]}$$

$$\Phi_9 = \frac{k_3 k_{t_2} K' [M]\ [B]}{k_{d_3}(k_{d_1} + k_{t_2}[M])}$$

Mechanisms 10 and 11

Again when the thermal reversion of the intermediate is put into either of the two previous mechanisms the concentration effect data can be accomodated. Mechanism 8 becomes 10, and mechanism 9 becomes 11. In the case of Φ_{10} we need $k_5/k_9 = 7.3$ and $(k_3 k_{d_3} + k_2 k_{d_3})/k_3 k_{-2} \gtrsim 20$ but Φ_{11} only requires the former relationship.

$$\Phi_{10} = \frac{k_5 k_3 k_{-2} k_{t_2} [M]^2 [B]}{(k_{d_1} + k_{t_2}[M])(k_9 + k_5[M])\left[k_3(k_{d_3} + k_{-2}[B]) + k_2 k_{d_3}\right]}$$

$$\Phi_{11} = \frac{K' k_5 k_{t_2} [M]^2 [B]}{k_{d_3}(k_{d_1} + k_{t_2}[M])(k_9 + k_5[M])}$$

Mechanism 12

Instead of product formation by thermal reaction of an intermediate, a mechanism can be envisioned which forms product by direct reaction of the excited complex with MA. The quantum yield for this mechanism together with the two new reactions is written out below. By requiring that $k_{d_3}/k_{-2} \geqq 20$ and $k_4/(k_2 + k_{d_2}) = 7.3$ the concentration effect data are satisfied.

Reaction	Rate
$C^* \longrightarrow C$	$k_{d_2}[C^*]$
$C^* + M \longrightarrow \text{Product}$	$k_4[C^*][M]$

$$\Phi_{12} = \frac{k_4 k_{-2} k_{t_2} [M]^2 [B]}{(k_{d_1} + k_{t_2}[M])\left[(k_{d_2} + k_4[M])(k_{d_3} + k_{-2}[B]) + k_2 k_{d_3}\right]}$$

Mechanism 13

Equilibration of the excited complex in the previous scheme produces a mechanism which does not predict the correct MA concentration effect (Φ_{13}). It should be noted that

$$\Phi_{13} = \frac{k_4 kt_2 K' [M]^2 [B]}{k_{d_3}(k_{d_1} + k_{t_2}[M])}$$

in the schemes which led to Φ_8 through Φ_{11} the first order decay $C^* \longrightarrow C$ is surplanted by decay to the intermediate. Since there are no competing second order processes, its inclusion could not alter the dependence of the quantum yield on concentration of reactants.

KINETICS: ENERGY TRANSFER TO THE COMPLEX

Now, we shall examine mechanisms which have as their first step energy transfer to the complex. Inasmuch as energy transfer to the complex is highly efficient ($k_{t_1}/k_{d_1}=$ 3000, the term $k_{t_1}[C]/(k_{d_1}+k_{t_1}[C])$ which appears in all of the following mechanisms is equal to unity. Obviously, no concentration effects can arise from this step. The mechanism which Bryce-Smith and coworkers seem to favor is presented first.

Mechanism 14

The mechanism derived here does not have any possible concentration dependent inefficiencies except the energy transfer step at MA concentrations below 10^{-3}M. It is therefore eliminated.

Reaction	Rate
$S \longrightarrow S^*$	I
$S^* \longrightarrow S$	$k_{d_1}[S^*]$
$S^* + C \longrightarrow C^* + S$	$k_{t_1}[S^*][C]$
$C^* \longrightarrow MB$	$k_3[C^*]$
$MB + M \longrightarrow$ Product	$k_5[MB][M]$

$$[S^*] = \frac{I}{k_{d_1}+k_{t_1}[C]} \qquad [C^*] = \frac{k_{t_1}[S^*][C]}{k_3}$$

$$[\mathrm{MB}] = \frac{k_3[\mathrm{C}]}{k_5[\mathrm{M}]}$$

$$\Phi_{14} = \frac{k_{t_1}[\mathrm{C}]}{k_{d_1} + k_{t_1}[\mathrm{C}]}$$

Mechanism 15

In order to produce the necessary concentration dependence we must incorporate both dissociation-recombination of the complex and reversion of the intermediate. The quantum yield expression in this case, Φ_{15}, will reproduce the concentration effect data if $k_{-2} \geq k_{d_3}$, $k_5/k_9 = 7.3$ and $k_{d_3}(k_3 + k_2)/k_3k_{-2} \geq 20$.

$$\Phi_{15} = \frac{k_3k_5k_{t_1}[\mathrm{C}][\mathrm{M}](k_{d_3} + k_{-2}[\mathrm{B}])}{(k_9 + k_5[\mathrm{M}])(k_{d_1} + k_{t_1}[\mathrm{C}])[(k_{d_3} + k_{-2}[\mathrm{B}])k_3 + k_{d_3}k_2]}$$

Mechanism 16

Considerable simplification of Φ_{15} is achieved if the excited complex is considered to be in equilibrium with excited MA and benzene. However the quantum yield in this case should not be effected by the concentration of benzene (Φ_{16}).

$$\Phi_{16} = \frac{k_{t_1}k_5[\mathrm{M}][\mathrm{C}]}{(k_{d_1} + k_{t_1}[\mathrm{C}])(k_9 + k_5[\mathrm{M}])}$$

Mechanism 17

Now we shall look at several mechanisms which do not involve the formation of any intermediates. Thus, decay from the excited complex leads to the ground state of the complex in the following. As we have seen, dissociation of the excited complex in this type of mechanism is essential if the concentration of benzene is to effect the quantum yield. The most straightforward of these (Φ_{17}) is nearly identical with mechanism 12 except that sensitizer transfers its energy to the complex rather than to MA. Accordingly the quantum yield expression is similar, but has an important difference. With $k_{d_3} > k_{-2}$ as needed to submerge the benzene term in the denominator, the benzene concentration effect line would be expected to extrapolate to a large, non-zero ordinate intercept. From Figures 13, 14, and 15 it is evident that the intercept is small compared with the yield obtained in neat benzene.

$$\Phi_{17} = \frac{k_4 k_{t_1} [C][M](k_{d_3} + k_{-2}[B])}{(k_{d_1} + k_{t_1}[C])[(k_{d_2} + k_4[M])(k_{d_3} + k_{-2}[B]) + k_{d_3}k_2]}$$

Mechanism 18

Formulating the dissociation and reformation of the excited complex as an equilibrium gives Φ_{18} which wouldn't provide a benzene concentration effect.

$$\Phi_{18} = \frac{k_4 k_{t_1} [C]\,[M]}{(k_{d_1} + k_{t_1}[C])(k_{d_2} + k_4[M])}$$

Mechanisms 19 and 20

Finally, two mechanisms can be devised which form product by attack of excited MA on the ground state of the complex as in mechanism 7. The quantum yields for these mechanisms with and without equilibrium formulation of the excited complex dissociation are Φ_{19} and Φ_{20} respectively. Neither one of the mechanisms can be valid for in the first case there would be little effect of benzene concentration and in the second case the benzene and MA effects must have the same form.

$$\Phi_{19} = \frac{k_8 k_{t_1} [C]^2}{K k_{d_2} [B] (k_{d_1} + k_{t_1} [C])}$$

$$\Phi_{20} = \frac{k_8 k_2 k_{t_1} [C]^2}{(k_{d_1} + k_{t_1} [C]) \left[(k_{d_2} + k_2)(k_{d_3} + k_8 [C]) + k_{d_2} k_{-2} [B] \right]}$$

After having reduced the number of mechanisms deserving further consideration by comparison of their prediction of the dependence of quantum yield on inital concentration of reactants, the absolute value of the quantum yield will be used as a further criterion. Using the value given by Andrews and Keefer for the equilibrium constant of the complex the ratio of the pseudo first order quenching rate constants in a 1.00M solution of MA in benzene is $\frac{k_{t_1} [M]}{k_{t_2} [C]} = 0.012$. This ratio becomes 0.067 if $[M] = [C]$, certainly an upper limit at these concentrations. Thus, even if only energy accepted by MA were utilized in the reaction, the maximum quantum yield if all subsequent processes were 100% efficient would be between 0.012 and 0.067. Since the quantum yield in a 1.00M solution of MA in benzene is in fact 0.092, the hypothesis is untenable and we conclude that the energy accepted by the complex begins the sequence of chemical events which lead to a diaddition. In this way all but mechanism 15 of those involving energy transfer can be eliminated.

The basis for the Schenck mechanism is the proposal by Schönberg (44) that dye photosensitized autoxidations involve addition of the sensitizer to oxygen to form a diradical which can transfer oxygen to substrate. Recently, however, Foote (45) has shown that in several instances hydrogen peroxide-sodium hypochlorite-olefin systems in which excited singlet oxygen is formed give rise to the same products as the corresponding dye sensitized reaction. Thus it is becoming clear that the first step of the dye sensitized oxidation is not addition, but energy transfer as shown. Since there appears now to be no precedent for Schenck-type

$$^{3}\mathrm{dye} + {}^{3}O_2 \longrightarrow {}^{1}\mathrm{dye} + {}^{1}O_2$$

mechanisms and because of the generality of the energy transfer concept as applied to photochemistry and emission spectroscopy, we prefer to discuss this reaction in terms of energy transfer. It must be emphasized that there is no direct experimental evidence which can exclude the Schenck mechanism for the reaction; only the above considerations.

It will now be necessary to examine mechanism 15 in the light of the other available evidence. First we shall examine the magnitude of the rate constants, then treat the involvement of the complex and finally consider the intermediate.

MAGNITUDE OF THE RATE CONSTANTS

Rather than evaluate the rate constants using Φ'_{15} obtained from Φ_{15} by canceling the $k_{t_1}[C]$ term we shall

$$\Phi'_{15} = \frac{k_5 k_3 [M] (k_{d_3} + k_{-2}[B])}{(k_9 + k_5[M])\left[k_3(k_{d_3} + k_{-2}[B]) + k_2 k_{d_3}\right]}$$

formulate the quantum yield as a product of efficiencies. For ease of calculation we shall choose the concentration of MA to be 1.00M, take that of benzene as 10M and use 0.092 as the quantum yield (Table 10). Efficiencies of the following steps will be considered: (1) energy transfer to the complex, (2) partition of energy delivered to the complex and (3) competition between reaction with MA and dissociation of the intermediate. At the concentrations covered by the concentration effect studies, process (1) is >99% efficient. The efficiency of step (3) calculated from the expression $k_5[M]/(k_9 + k_5[M])$ using $k_5/k_9 = 7.3$ is 88%. Thus, the leaking of energy through the decay of MA triplets arising from the dissociation of the triplet state of the complex accounts for the major loss in the sequence. An expression for fraction of energy (f) received by the complex which goes on toward product is given below. The summation expresses the fact that a constant fraction of the excited

$$f = x\left[1 + (1-x)y + (1-x)^2y^2 + \text{-----}\right] = \frac{x}{1-(1-x)\ y} \qquad (29)$$

$$x = \frac{k_3}{k_2 + k_3} \qquad y = \frac{k_{-2}[B]}{k_{d_3} + k_{-2}[B]}$$

MA which dissociates (1-x) recombines (y) rather than decaying and is partitioned again and again. Since the dissociation of the intermediate is responsible for merely 12% of the energy loss we have

$$f = \frac{0.092}{0.88} = 0.105 \qquad (30)$$

If the ratio k_2/k_3 is arbitrarily set at 200 so that the term containing benzene in the denominator of Φ'_{15} is completely damped out, k_{-2}/k_3 becomes 2.2. Note that the rate constant ratio k_{-2}/k_{d_3} determines the intercept of the benzene concentration effect line and that use of 2.2 would lead to a predicted intercept of 1.4mg. for the 1.00M MA line of Figure 14. This could easily be accommodated. These relationships between rate constants can reproduce the quantum yield at any concentration of MA or benzene to within 10%.

With the relationships between k_{d_3}, k_{-2}, k_3 and k_2 established we can now calculate their magnitudes using the oxygen quenching result and an assumed value for the first order decay of triplet MA. Since the phosphorescope used could see triplets with decay rates as fast as 5×10^4 sec^{-1}

and the intensity from MA was small we shall take k_{d_3} as 5×10^5 sec^{-1}. This number is probably a lower limit for oxygen or small amounts of impurities in solvent or solute quenching at diffusion controlled rates could effectively increase k_d. Other numbers we shall need are 0.25 as the fraction of energy quenched by oxygen (Table 24), 5×10^9 as the second order diffusion controlled quenching rate constant and 5×10^{-3}M as the concentration of O_2 (41). The rates in Table 26 were calculated with equation 29 by assuming that quenching C* led to MB and that the energy loss came from quenching M*. It will be of interest later to estimate the rate at which the intermediate is formed.

Table 26 - Rate Constants for the Diaddition

Reaction	Rate
Decay of excited MA	$k_{d_3} = 5 \times 10^5$ sec^{-1}
Dissociation of the excited complex	$k_2 = 4.6 \times 10^8$ sec^{-1}
Formation of excited complex (M*+B)	$k_{-2} = 1.1 \times 10^6$ l. mole^{-1} sec^{-1}
Decay of excited complex	$k_3 = 2.3 \times 10^6$ sec^{-1}

This rate is

$$\frac{d\,[MB]}{dt} = k_3\,[C^*] \tag{31}$$

A reasonable estimation of $[C^*]$ can readily be deduced by employing the steady state approximation as shown. Of course, the $k_{t_1}[C]$ terms in the numerator and denominator have been cancelled out. Solution of equation 32 using 2.95×10^{-6} einsteins l.$^{-1}$ sec.$^{-1}$ as a typical intensity yields $[C^*] = 1.33 \times 10^{-13}$M. This means that the rate of formation of intermediate is approximately 3.1×10^{-7} mole l.$^{-1}$sec.$^{-1}$.

$$[C^*] = \frac{(k_{-2}[B] + k_{d_3})\ I}{k_3(k_{d_3} + k_{-2}[B]) + k_{d_3}k_2} \tag{32}$$

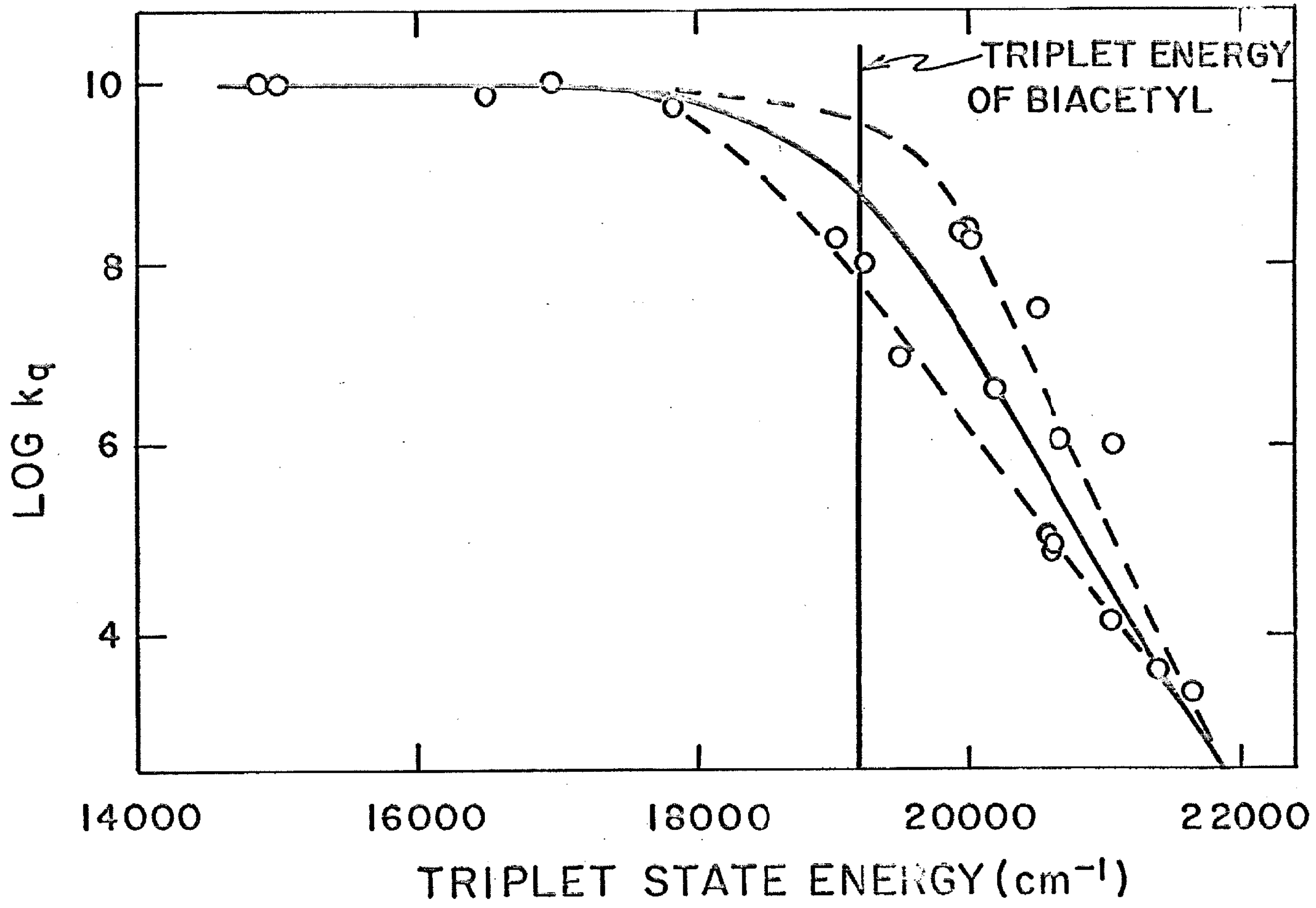
THE TRIPLET STATE OF THE COMPLEX

Next the details of the part played by the complex will be considered. In the sensitized diaddition spin conservation requires that the energy acceptor (the complex) must find itself in a triplet state immediately after the energy transfer. According to mechanism 15, the complex can then dissociate to yield MA in a triplet state and ground state benzene, or collapse (decay) to a state which resembles one of the two feasible intermediates. The dissociation path is assumed to yield triplet MA because of the energetics of the situation.

Since the triplet state energies of MA and benzene are at 72.1 and 84.4 kcal./mole, the lowest triplet state of the complex must be at or lower than 72.1 kcal./mole. Using the latter value, we can estimate that dissociation from the triplet state of the complex to give triplet benzene is at least 12.3 kcal./mole endothermic. On the other hand, if the binding energy of the triplet state of the complex is comparable to that of the ground state, the corresponding energy gap to triplet MA and benzene is probably less than 4 kcal./mole. The possibility of singlet energy transfer can be similarly ruled out, for the 0-0 bands of the MA, benzene, complex and benzophenone singlet-singlet long wavelength absorption are ~ 100, 108, 104, and 86 kcal/mole respectively.

The relationships between the various rate constants which we must postulate in order to make mechanism 15 fit the quantum yield and concentration effect data tell us that in the case of benzophenone, dissociation is the more important of the two paths which depopulate the complex triplet state. However, they also tell us that over 90% of the excited (triplet) MA formed in this way recombines to reform the complex triplet state. It is appropriate at this time to inquire as to the energy of the triplet state of the complex. In the absence of any phosphorescence from the complex this can be little more than a rough estimate based on the difference in quenching rate constants between free and complexed MA. For this purpose we introduce some results of Sandros and Bäckström (43) in Figure 18. This data on the quenching of the biacetyl phosphorescence by hydrocarbons with widely differing triplet energies is the only study of its kind in the literature. It shows the dramatic effect of the difference in triplet energy level between donor and acceptor in a triplet energy transfer process. The solid curve and the outer limiting dotted lines were not on the graph presented by Sandros and Bäckström, nor was the vertical line denoting the triplet energy of the donor (biacetyl). If we make the reasonable assumption that variations in quenching rate constants caused by varying the size and sign of the energy difference between donor and acceptor in the

Fig. 18. Rate Constants for Hydrocarbons Quenching Biacetyl Phosphorescence



biacetyl system can be applied to our system we can estimate the gap between the triplet states of MA and the complex. From the MA quenching rate constant 2 x 10^7 l.mole^{-1}sec^{-1}, we estimate that its triplet energy is from 2.0 to 4.1 kcal/mole higher than that of benzophenone. The complex quenching rate constant 3.0 x 10^8 liter mole^{-1}sec^{-1} tells us that the complex triplet state is between 1.2 kcal./mole below or 2.1 kcal./mole above the triplet energy level of benzophenone. Since the triplet state of benzophenone is 68.5 kcal./mole we have 70.5 to 72.6 and 67.3 to 70.6 kcal./mole as the limits of the triplet states of MA and the complex respectively. When the acetophenone and xanthone quenching data are transformed in the same way, similar results for the triplet energy of MA were obtained. From the quenching rate constant for acetophenone we find limits of 72.6 to 75.9 kcal./mole and from xanthone, 74.3 to 77 kcal./mole. The ranges for the triplet state energy of MA fixed by quenching the triplet states of these three ketones seem to bracket the value of 72.1 kcal./mole obtained from the phosphorescence spectrum. It should be realized that the latter value can be considered a lower limit, for the true 0-0 band might not have been detected in the emission experiments.

Even though the limits set by the benzophenone quenching results for the triplet state energies of the complex and of MA overlap slightly it seems safe to say that there is an energy gap between them. Since the triplet state energy of MA is placed close to the upper limit set by the MA quenching data the gap can be estimated as 2 kcal./mole. This is probably close to the depth of the energy minimum of the ground state of the complex. This latter value is not known but the MA-styrene complex which has a slightly lower free energy has an enthalphy of 1.0 to 1.5 kcal./mole (8). Further substantiation for our estimation of the triplet energy of the complex comes from consideration of the efficacy of various compounds as sensitizers in light of Figure 18.

From Figure 18 we can estimate that energy transfer rates will fall to 1 x 10^5 l.mole^{-1} sec.$^{-1}$ when the transfer is 4.5 kcal./mole endothermic and to 1 x 10^4 l.mole^{-1} sec.$^{-1}$ when it is 5.5 kcal./mole endothermic. Taking the triplet energy of the complex as 70 kcal./mole we would expect the psuedo first order rate of energy transfer in 1.00M MA solutions to become competitive with decay of sensitizer triplets for sensitizers having $E_t < 65$ kcal./mole. This expectation is born out in Table 18. The fact that triphenylene with $E_t = 66.6$ kcal./mole does not sensitize the reaction merely reflects the fact (obvious from Figure 18) that factors other than the energy gap between donor and acceptor are important in triplet energy transfer.

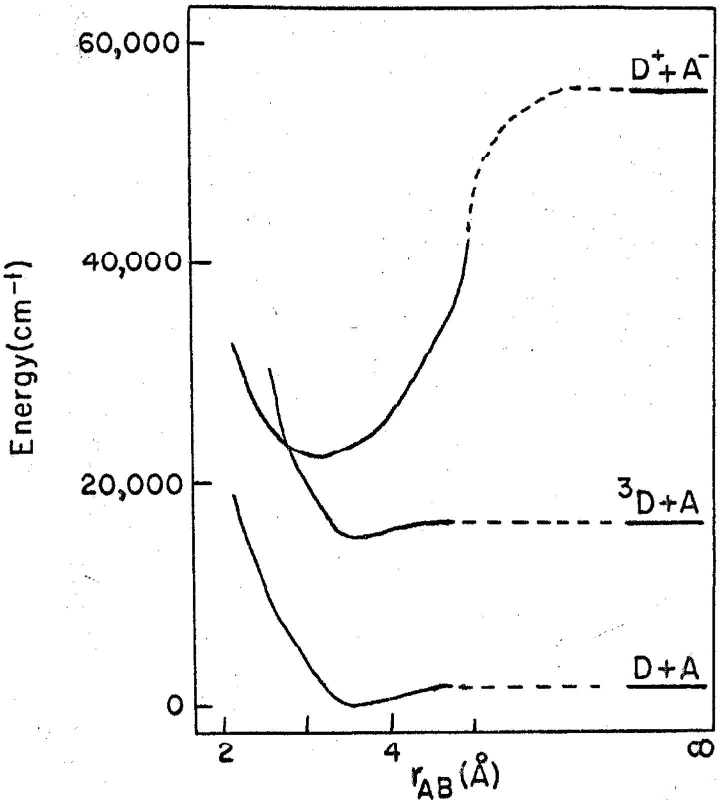
It seems to be a well entrenched idea that absorption of light by a complex often leads in part to intersystem crossing to a dissociative triplet state (46,47). This concept seems to be based on the usual observation that excitation of hydrocarbon-trinitrobenzene (TNB) complexes (47, 48,49) and hydrocarbon-tetrachlorophthalic anhydride (TCPA) complexes (50,51) in glasses at 77°K results in phosphorescence from the hydrocarbon. It is important to note, however, that nearly always the emission has less vibrational structure and is red-shifted with respect to free hydrocarbon emission. The wave function of this triplet state is envisioned as being formed from a linear combination of the wave functions of triplet donor and ground state acceptor. McGlynn (47) has come to the theoretical conclusion that the triplet state which has the same space part as the excited singlet (charge transfer) state of the complex probably lies above the later.

Not until the work of McGlynn, Boggus and Elder (52) has a complete vibrational analysis been carried out on the phosphorescence from a glass in which a complex was present They found that certain skeletal bending, breathing, and C-C stretching vibrations had decreased in frequency by 2.5 to 4% in the anthracene - TNB complex compared with free anthracene. This decrease correlated well with the calculated decrease in electron density in anthracene when complexed.

Their explanation was that while dissociation of the triplet state of the complex occurs, the components recombine in a time which is short compared with the lifetime of the phosphorescence of the donor. Since there is no evidence that dissociation occurs at all, the former explanation must be based on the theoretical expectation (47) that the lowest triplet state of the complex is dissociative. Needless to say, such a treatment would lead to very interesting results if applied to the numerous other similar cases in the literature. Briegleb and Czekalla (46) have reached what could be called a compromise conclusion i.e. that partial dissociation can occur during the lifetime of the triplet state of a complex. Their conclusions were based on the observation of increasing red shifts, loss of fine structure, and intensity, and shorter phosphorescence lifetimes at 77°K as they went from free donors in a glass to complexes in a glass, to the crystalline complexes of TCPA with various aromatic hydrocarbons. All of the above parameters showed the larger change upon going from the complex in a glass to the crystalline complex and the authors felt that the properties of the system in the latter state were those of the complex. On this basis the smaller changes in the emission of the donor in the glass when aceptor was added indicated partial dissociation of the complex. On the contrary, these effects may be merely associated with the change in the state i.e. triplet-triplet annihilation in the crystal can account for large decreases in intensity and lifetime, and loss of vibrational structure could be a result of anisotropic crystal structure or blurring of the donor levels due to closer packing and stronger interaction in the crystal. Furthermore the few red shifts in vibrational frequencies which Czekalla, et al. (53) do report for donor emission in the presence of acceptor are of the same order of magnitude as those reported by McGlynn (52) which were consistent with emission from a complex of comparable stability. It is therefore not clear that even a partial dissociation of the triplet state of the complexes has to be invoked to rationalize the phosphorescence data.

It is important to note that in all of the above cases the triplet state of the complex was reached by intersystem crossing from the first excited singlet state of the complex. From Figure 19 which is part of the potential energy diagram for the TNB-anthracene complex drawn by McGlynn and Boggus (47), it is obvious that intersystem crossing will lead to a triplet state with vibrational energy greater than its dissociation energy. Although McGlynn and Boggus did exclude one triplet state as stated previously, they did not consider the possibility that other triplet states may intervene between the lowest one and the singlet charge transfer state. Such states might correlate with free acceptor plus

Fig. 19. Energy Levels for TNB - Anthracene Complex

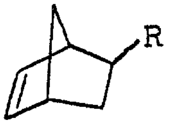


higher triplet states of the donor or free donor plus acceptor triplet states. Such states could provide a means of relaxing the extra vibrational energy without dissociation. In our system we have a case where the same product results from the attainment of the triplet case both by intersystem crossing and by energy transfer. Thus it appears that vibrational relaxation and/or internal conversion in either the triplet states of MA or the complex occur before any photochemistry occurs. Otherwise, we could expect that products differing in stereochemistry, at least, would appear when the triplet state of the complex is formed with an excess of energy amounting to 34 (unsensitized), 5 (propiophenone sensitized), or with little or no excess. It is true that the quantum yield of the unsensitized reaction is less by a factor of 18 than the sensitized reaction. This can be accommodated in one of or a combination of any of three ways. One is that intersystem crossing is much less efficient in the complex than it is in benzophenone. The other two are an increase in the ratio k_2/k_3 or a decrease in the ratio k_{-2}/k_{d_3}. Assigning most of the decrease to the latter cause is consistent with the lack of a benzene concentration effect in the unsensitized reaction. Since the decay rate of the MA triplet (k_{d_3}) is unlikely to change, this decrease must come from k_{-2}. This change could be rationalized by considering that k_{-2} derived from concentration effects on the sensitized reaction is abnormally high due to a cage effect (54). When excited MA is produced by intersystem crossing in the complex it must aquire sufficient energy to escape the "cage" and this lowers the apparent recombination rate.

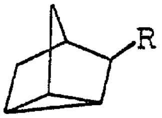
The calculated magnitudes of k_2 and k_3 deserve special comment in connection with our phosphorescence results. Failure to observe emission from MA in the presence of slightly more than an equal amount of benzene can be attributed to either or both of two reasons; (1) the extent of intersystem crossing in the complex is less than in MA, or (2) the rate of radiationless decay is relatively faster than the rate of radiative decay in the complex than in free MA. These reasons are based on the reasonable assumption that more than 90% of the light was absorbed by the complex in the experiment. In a recent article Christodouleas and McGlynn (55) reported that complexing with TNB or tetrahalophthalic anhydrides increased the ratio of phosphorescence to fluorescence quantum yields by factors of ~50 and ~5000 respectively in each of three hydrocarbon donors. While they did not determine whether emission emanated from free or complexed donor, it was shown that the increases resulted from increased intersystem crossing to the triplet state. However it seems clear that at least the phthalic anhydride results are a special case which can be explained by the heavy atom effect which McGlynn, et al. (56) have shown operates in the same fashion. If we take the TNB result as indicative of the effect complexing has on the phosphorescence to fluorescence ratio, we must conclude that something different operates in the MA-benzene complex. This factor could be the emergence of the very fast radiationless transition k_3 as the dominant mode of deactivation of the complex triplet state due to a decrease in the rate of dissociation at $77^{\circ}K$ in a glass. That k_3 is so high is not surprising when it is realized that intersystem crossing to states of the intermediate could well be compared with the often very fast (10^7 sec^{-1}) rates of intersystem crossing between excited singlets and triplets of the same molecule rather than decay from a high energy triplet state.

THE INTERMEDIATE

The kinetic schemes of the previous section excluded the participation of the intermediate II by not including a second photoactivated step in any mechanisms. Since the quantum yield of the diaddition is certainly not too high for a two quanta process, justification for the choice in two ways will be given. First, the intensity experiment indicates that the quantum yield does not vary with intensity as expected for a two quanta process. Second, the quantum yield of the addition of MA to VIII at $[MA]=[VIII]=0.5M$ is at least six times lower than that of the addition at a benzene concentration of 0.50M. This is a lower limit because not only is it not certain that an addition to VIII occured, but it is unlikely that the concentration of the intermediate ever approaches the initial concentration of benzene during a diaddition photolysis where $[MA] = [\text{Benzene}] = 0.50M$. We must consider the possibility that the second double bond in II could raise the quantum yield for MA addition enough to make it compatible with the quantum yield for the diaddition. It has been shown theoretically (57) that there is no interaction between the similarly placed double bonds of bicycloheptadiene in the ground state. However from the work of several groups (58,59,60,61) it is clear that some interaction develops upon radical addition because products with both norbornene (IX) and nortricyclene (X) skeletons are formed. We therefore expect that there might be some anchimeric assistance to the rate of addition of triplet MA to II. This probably does not occur for Trecker and Henry (62) have shown that the rate of addition of trichloromethyl radical to norbornene and norbornadiene is the same when corrected for the statistical difference. Thus, it seems unlikely that addition of MA to II could have a quantum yield comparable to that of the diaddition. By a process



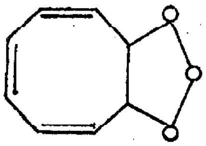
IX



X

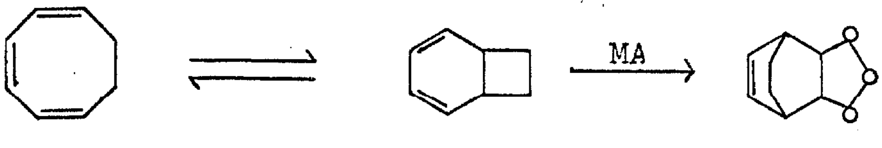
of elimination we can settle upon I as the intermediate in the diaddition.

It is appropriate to ask why the valence tautomer XI of the intermediate or products derived from addition to it



XI

are not isolated. At 100°C Cope, et al. (63) found that the equilibrium mixture of XII and XIII contained 85% XII.



XII XIII XIV

However, these authors found that pure XIII gave a 100%

yield of adduct XIV with MA at 10°C whereas XII gave none under identical conditions. When the temperature of the reaction was raised to 60-80°C so that the XII → XIII isomerization could take place, XIV was formed. It appears then that I reacts with MA faster than it isomerizes to XI at room temperature. The former rate can be estimated as $k_5 = 1.53 \times 10^{-4}$ l.mole^{-1} sec.$^{-1}$ if we assume that the rate measured by Craig, et al. (64) for the addition of MA to 1,3-cyclohexadiene applies here. This assumption also gives us $k_9 = 2.1 \times 10^{-5}$ sec^{-1}.

Now we shall calculate the concentration of the intermediate from the intensity and quantum yield of a diaddition experiment and see how it compares with the value obtained by making the steady state approximation on MB. From one of the quantum yield experiments in which the light intensity was 2.95×10^{-6} einsteins l.$^{-1}$ sec.$^{-1}$, the quantum yield was 0.092, and the total concentration of MA was 1.00M, the yield was 8.7mg. in 4 ml. Using equation 33 and 0.15M as the concentration of free MA we calculate that the steady

$$\frac{k_5 [M] [MB]}{I} = 0.092 \qquad (33)$$

state concentration of MB was 0.012M. This concentration can be compared with the value of 0.0071M obtained by employing equation 34 with the value of $k_3 [C^*]$ calculated in the previous section. The agreement between the two methods

$$\frac{d[MB]}{dt} = k_3[C*] - (k_5[M] + k_9)[MB] = 0 \qquad (34)$$

of calculation is excellent considering the assumptions as to the oxygen concentration, the quenching rate constant, the value of the equilibrium constant for the complex and the magnitude of k_5 which were made.

Our failure to form any cross adduct in either the ethyl acrylate or tetracyanoethylene experiments reflect the lower activity of ethyl acrylate compared with MA as a dieneophile and the low quantum yield of the addition of MA to toluene respectively. According to Sauer (65) the rate of addition of MA to cyclopentadiene is faster than the rate of methyl acrylate addition by a factor of 5×10^3 at 20°C. From Sauer's compilation of rate data we can estimate that reactivity ratios are reduced by a factor of 5 to 10 relative to cyclopentadiene when rates of addition to cyclohexadiene are compared. Thus the rate of addition of ethyl acrylate to II is probably 500 times slower than the addition of MA and therefore cannot compete with thermal reversion. If longer irradiation times at low temperature become practical, the tetracyanoethylene technique holds the best promise of success.

THE UNSENSITIZED REACTION

Up to this point it has been tacitly assumed that the mechanisms of the sensitized and direct diaddition were identical after the light energy reached MA in solution. In this section the evidence for this assertion will be presented.

As stated in the introduction Bryce-Smith and Lodge (6) dismissed the possibility that absorption of light by MA could initiate the direct reaction. However, a calculation based on the intensity of the mercury emission lines from 2900 to 3341Å shows that the complex absorbs ~120 times as much light as MA in a 1.00M solution of MA in benzene. Assuming all other processes to be completely efficient, a maximum quantum yield of 0.0083 is indicated if only light absorbed by MA is effective. Because this is very close to the quantum yield of 0.0051 calculated before for the direct diaddition we cannot eliminate the possibility that light absorbed by MA is responsible for the reaction.

The kinetic expressions of first section can be transformed to show the form of the concentration effects expected in the unsensitized reaction by leaving out the k_{d_1} and $k_{t_1}[C]$ or $k_{t_2}[M]$ terms. For example where energy was transferred from sensitizer to free MA, the expression becomes that for the direct diaddition with MA absorbing the "effective light". It is clear that by making the proper assumptions about rate constant relationships most of the mechanisms can explain the absence of a benzene concentration effect. One of these is 15' as mentioned earlier. Given the fact that the unsensitized reaction involves the triplet state(s) of the excited species and the magnitudes of k_2 and k_{-2} compared with k_{d_3} and k_3, it is reasonable to assume that both $^3M^*$ and $^3C^*$ will exist in solution no matter which entity absorbs the "effective light". For this reason and because of the high probability that the same product is formed in both reactions, it is logical to assume that a mechanism anologous to either mechanism 10 or 15 of the first section operates. The pertinent quantum yield expression for the former is given below, and Φ'_{15} can be found in the first section. Since the condition under which Φ'_{15}

$$\Phi'_{10} = \frac{k_5 k_3 k_{-2} [M] [B]}{(k_9 + k_5 [M]) \left[k_3 (k_{d_3} + k_{-2} [B]) + k_2 k_{d_3} \right]}$$

predicts a negligible benzene concentration effect ($k_{d_3} > k_{-2}$) has been discussed, mechanism 10' will be now examined. In order to damp out a benzene effect we need $k_{-2}k_3 \geqq 20\ k_{d_3}(k_2 + k_3)$. Using values from Table 26 for k_{d_3}, k_2 and k_3 which should remain invariant, we see that k_{-2} must be increased to 1 x 10^9 in the unsensitized reaction. There is no reasonable way of explaining a rise in k_{-2} by a factor of ~1000 so we conclude that mechanism 15' describes the course of the unsensitized diaddition.

The argument concerning the Schenck - type mechanism holds in this situation also, for the kinetics do not eliminate mechanism 3'. It is, however, necessary to assume that the attack of the diradical $\cdot M \cdot$ formed by absorption of light by M gives rise to the same intermediate as the attack of $\cdot MS \cdot$.

THE DIMERIZATION

As in the addition of MA to benzene, we find that the dimerization of MA is strongly influenced by charge transfer interactions. It appears from our study of the dimerization in seven solvents that dioxane occupies a unique position as the only solvent in which the dimerization can be accomplished both directly and by sensitization. Since we only have results for both direct and sensitized reactions in chloroform, acetonitrile and dioxane; the discussion to follow is somewhat limited, and could be modified in the light of more extensive data.

Our results in these three solvents can be rationalized by assuming that dimerization in both sensitized and unsensitized cases involves triplet states. The lack of a sensitized reaction in acetonitrile or chloroform can be explained in terms of quenching mechanisms other than energy transfer. Two possibilities are shown below which illustrate deactivation of triplet state sensitizer(S^*) by formation of excited dimers (equation 35) or adduct biradicals after the Schenck mechanism (equation 36). Failure of either of these

$$S^* + M \longrightarrow (SM)^* \longrightarrow S + M \qquad (35)$$

$$S^* + M \longrightarrow \cdot S - M \cdot \longrightarrow S + M \qquad (36)$$

intermediates to dimerize would not be surprising. It is instructive to make an approximate calculation of the amount of internal filtering to be expected from acetone and benzophenone. For this purpose we added the product of the individual ketone absorbance and the power of the mercury emission lines between 2804 and 3341Å and compared the sums with the corresponding sum of products for MA. We found that 8 and 43% of the light should be absorbed in solutions containing acetone and benzophenone respectively. From Table 21 we see that in acetonitrile the yields of dimer are reduced by 17 and 37% by these two ketones. This is agreement within the experimental error and the uncertainty of the calculation.

In dioxane we conclude that the dimer is formed after ejection of dioxane from a dissociative triplet state of a 2:1 complex leaves adjacent molecules of MA in close proximity. Polymerization in dioxane could be initiated by excited MA produced directly (light absorption or energy transfer) or by dissociation of the 1 to 1 complex.

As for the failure of the unsensitized dimerization in the rest of the solvents there is only speculation. Two of these (veratrole, 1,2-dimethoxyethane) are difunctional and might be expected to form some 2:1 complex with MA. However it is well known that the cyclic structure of dioxane allows its nonbonding electrons unusual freedom from steric hindrance. Thus we expect larger concentration of all types of complexes in dioxane than in either veratrole or 1,2-dimethoxyethane. Lack of any dimerization, sensitized or unsensitized, in tetrahydrofuran - a monofunctional analog of dioxane - suggests that a 2:1 complex is required for the sensitized reaction, but tells us little about the unsensitized.

When the various results of irradiations of MA in different aromatic solvents are collected in Table 27 an interesting pattern is apparent. Although MA forms complexes of varying stability with all of them, the addition reaction only occurs with the less perturbed benzene systems. Polymerization occurs in the more strongly perturbed solvents which have available hydrogens and no photoreactions of MA occur in the two most strongly perturbed systems. As a

Table 27 - Irradiation of MA in Various Solvents

Solvent	$\lambda_{max.}^{a}$	Triplet Energy	Diadduct	Polymer	Nothing	Reference
Benzene	254mμ	84.0Kcal/	x			1,2,3
Toluene	261	82.3mole	x			1
Chlorobenzene	263.5	81.9	x			1
Phenol	270	82.0		x		12
O-Xylene		81.9	x			1
Anisole	269	80.7		x		this work
P-Xylene		80.1		x		12
Durene		79.8		x		12
Hexamethylbenzene		79.0		x		66
Benzonitrile	271	77.0			x	12
Nitrobenzene	---^{b}	59.9			x	12

(a) λmax. for secondary band ('L_b) of benzene (67)
(b) The primary band is shifted more than that of benzonitrile

standard of electronic interaction of substituents with the benzene nucleus we have used the singlet and triplet excitation energies listed in Table 27. From the differing results among the sterically similar mono-substituted benzenes we conclude that steric effects are not as important as electronic effects. This trend with increasing electronic perturbation suggests that no diaddition or dimerization occurs via the triplet state of MA complexes (if formed) with the last six compounds because decay from these states gives ground state complex rather than an intermediate. Polymerization could easily be initiated by energy transfer to free MA, if hydrogen abstraction or radical-like additions are faster than formation of the excited triplet states of the complexes.

There is some evidence in the work of Schenck et al. (19) on the dimerization of analogs of MA. While they are somewhat confusing, the quantum yields in Table 28 emphasize that the addition of MA to benzene is an exceptional case. The sensitized dimerization in dioxane of methylmaleic anhydride and N-phenylmaleimide follow the pattern, but unlike MA no dimer is formed without sensitizer. In the absence of further data no meaningful explanation for the latter anomaly or for the successful dimerization of maleimide and 1,2-dimethylmaleic anhydride in benzene can be given. We can, however, present reasons for the fact that no addi-

Table 28 - Quantum Yields For Dimerization of MA and Derivatives

Compound	Φ sens.	Φ direct	Solvent
MA	0.26	0.14	dioxane
Methyl MA	0.23	0.000032	dioxane
1,2-dimethyl MA	0.18	0	benzene
Maleimide	0.39	0	benzene
N-phenylmaleimide	0.13	0	dioxane

tion to benzene by 1,2-dimethyl MA or maleimide occurs. In the case of maleimide the final Diels-Alder reaction with an intermediate can not be the source of inefficiency for MA and maleimide have very similar reactivities in these reactions (65). It is likely that either decay from the complex does not occur to an intermediate and/or k_{-2} is a factor of ten lower than is the case for MA. To explain the reaction of 1,2-dimethylmaleic anhydride the same reasons plus its lower reactivity in the Diels-Alder reaction serve. It is likely that close scrutiny would show that some diadduct is formed at least in the maleimide solutions.

THE POLYMERIZATION OF MA

The homopolymerization of MA initiated by light or radical initiators has only recently been observed (67,68) although MA is easily copolymerized. It now appears that polymerization is an integral part of the photochemistry of MA.

In the presence of sensitizers, one can always invoke hydrogen abstraction from solvent or addition to MA as chain initiators, however the direct photopolymerization of MA in chloroform or acetonitrile, for instance, is another question. One of the four likely mechanisms for this reaction is shown below. In the unusual circumstance that

$$M \longrightarrow M^{*} \xrightarrow{M} \cdot M - M \cdot \begin{cases} \longrightarrow \text{dimer} \\ \xrightarrow[M]{} \cdot M - M - M \cdot \end{cases} \tag{37}$$

addition of another MA is faster than ring closure, the high yields of polymer from dimerization in acetonitrile could be rationalized. The two other possibilities involve H-abstraction either from acetonitrile or from MA itself. This type of mechanism is unlikely, for no polymer is isolated from irradiations of MA in isopropyl alcohol (69). It appears that H-abstraction leads to an as yet unidentified monomeric compound. A final possibility is direct ejection of a vinyl hydrogen atom from MA, for which there is barely enough energy in light passed by pyrex.

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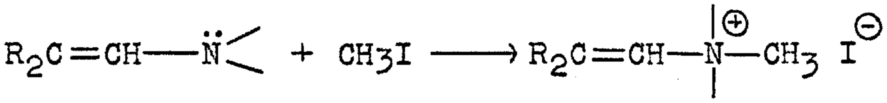
PROPOSITIONS

Proposition I

A study of solvent effects on the alkylation of enamines is proposed.

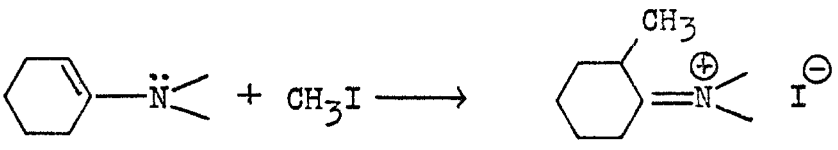
* * * * * * *

Enamines (α,β-unsaturated amines) are known to undergo both carbon and nitrogen alkylations giving iminium salts or normal ammonium salts respectively (1,2,3,4). The mechanisms of these reactions are not known, but it is reasonable to assume both products are formed via an S_n2 path when methyl or ethyl iodide is the substrate. The limited amount of data available indicate that enamines derived from the condensation of aldehydes with secondary amines are N alkylated by methyl and ethyl iodide while those formed from cyclic ketones are C alkylated (5). Typical reactions are shown in equations 1 and 2. No results of the alkylation of



$$R_2C{=}CH{-}\ddot{N}\!< \;+\; CH_3I \longrightarrow R_2C{=}CH{-}\overset{|\oplus}{\underset{|}{N}}{-}CH_3\;\; I^{\ominus} \qquad (1)$$

I III.



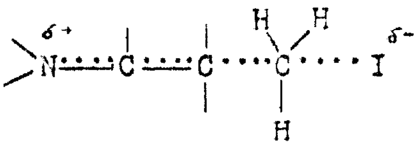
(2)

II. IV.

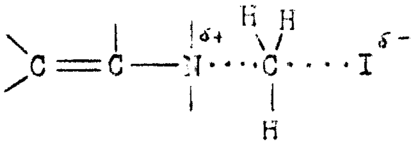
enamines derived from straight chain ketones have been reported. There is no apparent relation between structure and reaction path based on an S_n2 mechanism although substitution of the carbon α to nitrogen could stabilize a transition state similar to IV relative to the transition state for the C alkylation of I. This effect would not be expected to account for complete reversal of the N to C alkylation ratio as is observed. However, failure of a clear pattern to energy may be a result of differences in transition state (T.S.) energies which arise from solvent effects.

Generally, the alkylations of aldehyde derived enamines have been carried out in hexane or ether whereas the reactions of cyclic ketone derived enamines have been performed in dioxane or methanol. The implication being that poorly solvating solvents tend to produce N alkylation while strongly solvating media give C alkylation.

We expect little difference in solvation energy between III and IV (T.S. like products) or between V and VI (T.S. intermediate between products and reactants). However, if



V

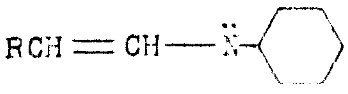


VI

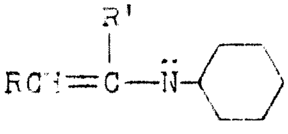
VII VIII

we examine the two canonical forms VII and VIII of an enamine, we would predict that increasing solvation would favor increased contribution to the hybrid from the polar form VI. Thus, with steric effects held reasonably constant, transition states like VIII (T.S. like reactants) and thus C alkylation should be favored as solvent solvating power is increased. This is the sort of behavior observed although there are surely other factors acting.

To test this hypothesis, a series of alkylations of aldehyde- and ketone -derived enamines with similar substitution patterns should be carried out in solvents of varying solvating ability. Suitable enamines would be IX and X, and methyl iodide would be a good substrate. An adequate range of solvating power would be covered by using hexane, diethyl ether, dioxane and acetonitrile. Alcohols are avoided because of the possibility that hydrogen bonding to nitrogen would reduce the extent of N alkylation.



IX



$R = CH_3, C_2H_5$

$R' = CH_3, C_2H_5$

X

The results of these solvent studies should indicate the direction for future probes into the mechanism of the enamine alkylation reaction.

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Proposition II

It is suggested that low-lying triplet states are available in 1,2-dihalocyclopropanes which can be populated by energy transfer from suitable sensitizers. Further, it is proposed that such transfer of excitation energy will cause cis-trans isomerization.

* * * * * * * *

The recent work of Hammond, Turro and Leermakers (1) on the sensitized isomerization of 1,2-dichloroethylene produced evidence for a significant barrier to rotation and hence considerable $n-\pi^*$ character in the lowest triplet state of the olefin. This barrier would be associated with stabilization of the planar configuration relative to the perpendicular form. If the same reasoning were applied to a 1,2-dihalocyclopropane, one would conclude that $n-\pi^*$ like character in the lowest triplet state would lead to facile cis-trans isomerization. By $n-\pi^*$ like is meant a state derived from the excitation of a halogen n electron to an antibonding molecular orbital centered on the carbon atoms.

Ample evidence has accumulated during the last fifteen years to support the assertion that there is electron delocalization in cyclopropane (2). Several molecular orbital calculations which allow for delocalization have been made and good correlations with various physical properties have resulted (3). Furthermore, the vacuum UV specta of cyclopropane and ethylene are similar; both have weak absorption near 1950Å and strong absorption from 1650Å to shorter wavelength (4). No other saturated hydrocarbon has comparable low energy transitions. Evidence for the location of the lowest-lying cyclopropane triplet state at or below 113 kcal./mole comes from the Hg ($^3P_1$) sensitized isomerization of sym-cyclopropane-d_2 in the gas phase (5). This can be compared with ethylene's lowest ("vertical") triplet at 106 kcal./mole. (6)

The n-π^* like character of the lowest chlorocyclopropane optical transition is suggested by the work of Eberlin and Pickett (7). They found a bathochromic shift of 13 kcal./mole when comparing the vacuum UV spectrum of the chloro derivative with that of cyclopropane, whereas chlorocyclohexane displayed a negligible shift from the parent compound.

There seem to be grounds, then, for supposing that a n-π^* like triplet state can be formed from 1,2-dihalocyclopropanes by energy transfer. The triplet energy transfer process can be envisioned as a non-vertical process (8) in which halogen atoms achieve coplanarity with the ring coincident with energy transfer. Decay of this triplet state could produce either cis or trans isomer. By analogy with the dichloroethylenes the triplet should be accessible through the use of high energy sensitizers of $E_t > 70$ kcal./mole.

The dihalocyclopropanes can be easily prepared by halogenation of cyclopropene.

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Proposition III

Experiments are suggested to differentiate between homolytic, nucleophilic and electrophilic mechanisms for the addition of 2,4-dinitrobenzenesulfenyl chloride to acetylenes.

* * * * * * * *

The report by Kharasch and Yiannios (1) on the addition of 2,4-dinitrobenzenesulfenyl chloride (ArSCl) to phenylacetylene and 3-hexyne serves to underline a paucity of mechanistic information on additions to acetylenes. Beyond the facts that the additions were _trans_ and were first order in each reactant in glacial acetic acid, only analogy with the corresponding additions to olefins dictated their assumption of electrophilic attack by ArSCl. In view of the ambiguous evidence on halogen additions to acetylenes and the lack of further information on the ArSCl additions, this assignment can be questioned.

That addition by homolytic or nucleophilic mechanisms are possible and compatible with the above observations can be seen by considering the data of Truce and coworkers published during the last eight years on the additions of thiols and thiolates to acetylenes. They have found that nucleophilic addition of _p_-toluene sodium thiolate proceeds in stereospecific _trans_ fashion to a number of neutral acetylenes in ethanol (2). Furthermore, one kinetic analysis on the addition of p-toluene sodium thiolate to phenylacetylene (3) showed that in ethanol the reaction probably involves a concerted mechanism ($\Delta S = -30$cal./deg.-mole), but that in dimethylformamide + ethanol the entropy of activation is substantially lower and consistent with a stepwise mechanism. In the latter case the product is also formed by trans addition, so the vinyl anion has a preferred configuration. Although documentation is slim, it is likely that radical additions to acetylenes can be stereospecific for Truce, et al. (4) report that mesitylthiol adds trans to mesitylacetylene in what is surely a radical reaction. There is also a report of a stereospecific radical addition of bromine to dinitrotolane, (5), but Robertson et al. (6) find an electrophilic order of rates for addition of bromine to substituted acetylenes in glacial acetic acid.

In order to resolve the question in the case of the addition of ArSCl to acetylenes, several experiments should be carried out in the classical organic chemical manner. First, radical mechanisms can be tested by noting the effect of light, the decomposition of initiators such as azo-bis-isobutyronitrile and inhibitors such as sulfur, NO or hydroquinone on the reaction. In the absence of any effect by these agents, a comparison of the rates (or better enthalpy of activation) of addition to a series of suitably substituted acetylenes should be made. For instance p-substituted phenylacetylenes from nitro to N,N-dimethylamino would be satisfactory for this purpose. Should electrophilic order be observed, N,N-dimethylanimo > nitro we must decide whether or not ArS^+ or more properly the ion pair $ArS^+ Cl^-$ is involved. Since the addition to phenylacetylene is first order in the acetylene the equilibrium $ArSCl \rightleftharpoons ArS^+ + Cl^-$ must be fast and addition of LiCl should depress the rate if these ionic species are responsible for the addition.

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Proposition IV

A reinterpretation of published work on the photoreduction of eosin is offered.

* * * * * * * *

Uchida, Kato and Koizumi (1) studied the effect of certain added compounds on the photoreduction of eosin in degassed ethyl alcohol. They found that isopentane, n-hexane, benzene and cyclooctatetraene inhibited the reaction whereas cyclohexene and n-hexene-2 accelerated it. In Table 1 can be found three sets of their data.

Table 1 - Effect of Added Substances on the Rate of Photoreduction of Eosin in Ethyl Alcohol

n-Hexane		Benzene		n-Hexene-2	
mole fraction	$k \times 10^4$	mole fraction	$k \times 10^4$	mole fraction	$k \times 10^4$
0.334	1.18	0.220	1.23	0.0181	7.25
0.143	2.53	0.141	1.27	0.0119	5.34
0.0814	4.86	0.0681	1.38	0.00593	3.98
0.0529	4.94	0.0334	1.41	0.00296	3.48
0.0254	5.66	0.0167	1.67	0	2.18
0	5.82	0.000269	2.10		

The rate constant k found in the table come from the expression for the rate of bleaching below, where c is the

$$-\frac{dc}{dt} = \frac{t}{d} I_0 (1 - e^{-\alpha cd}) \times 10^3 \qquad (1)$$

concentration of dye, I_0 the intensity of illuminating light, α the effective molar absorption coefficient and d the thickness of the solution in cm. It was necessary to include the exponential because not all of the light was absorbed by the eosin. Integration of equation 1 gave the relation from which k was extracted.

To rationalize the quenching ability of the three relatively inert compounds and cyclooctatetraene it was suggested that they deprived the eosin triplet state of excess energy. This loss of energy would then decrease the rate of H-abstraction from ethyl alcohol. Formulation of this explanation in terms of k gave equation 2 where k_r is the rate

$$k = \phi_{s \rightarrow t} \frac{k_r [EH]}{k_r [EH] + k_q [Q]} \qquad (2)$$

of H-abstraction, k_q the rate of quenching $\phi_{s \rightarrow t}$ the fraction of singlets which intersystem cross, Q the added compound and EH denotes ethyl alcohol. Surprisingly, this equation does not contain what is probably the fastest mode of deactivating eosin triplets - radiationless decay. Analysis of the data gave values of k_q/k_r between 1.9 and 6.3 for the four inhibitors.

As an explanation for the increase in rate in the presence of the two mono-olefins, it was suggested that hydrogen abstraction was speeded by collision of the olefin with a complex made up of either triplet eosin + alcohol or the semiquinone radical derived from eosin + the hydroxyethyl radical. From this mechanism a rate relation was generated which predicted a linear relation between rate and concentration of "promoter", if it was assumed that deactivation of the complex was faster than attack of the olefin. Hydrogen abstraction from the olefins was eliminated because cyclooctatetraene did not also promote the bleaching. A revaluation of the retarding effect based on the commonly accepted mechanism of photoreduction of ketones (2) and a more reasonable mechanism for the promoting effect will now be given.

Since in solution internal conversion and vibronic relaxation to the lowest excited triplet state is faster than almost any second order chemical reaction imaginable, it is unlikely that deactivation can explain the quenching observed. By formulating the rate constant as below (equation 3) analogous to the expressions derived by Moore, Hammond and Foss (2) a more reasonable explanation is obvious. In equation 3, k_d is the rate of radiationless

$$k = \phi_{s \rightarrow t} \frac{I \; k_r [EH]}{k_d + k_r [EH]} \qquad (3)$$

decay of the eosin triplet. The reason for the inhibiting effect now becomes reduction of alcohol concentration. While the data was not collected with this treatment in mind, we can determine the ratio k_d/k_r. Due to the large extrapolation this is very uncertain, but a least squares analysis of the results with benzene in terms of equation 3 gives $k_d/k_r = 9 \times 10^4 \pm 3 \times 10^4$ and an intercept of 828 ± 900. The unusually large value of k_d/k_r is easily rationalized as a result of a combination of high k_d and low k_r. It is likely the lowest triplet state of eosin has a π-π^* configuration and thus has a relatively low rate of H-abstraction. Since eosin has a long phosphorescence lifetime but does not emit in solution at room temperature, psuedo first order quenching probably dominates k_d, making it quite high ($> 10^5$). This treatment requires an intercept close to 1 ($1/\phi_{s \rightarrow t}$), which is obtained within the huge experimental error involved in the extrapolation.

To explain the increase in rate in the presence of olefins it is proposed that either allylic H-abstraction or addition of eosin to olefin is faster than H-abstraction from ethyl alcohol. The former reason is slightly favored because allylic abstraction is clearly not possible from cycooctatetraene and accordingly it is an inhibitor. Equation 4 shows the expected dependence of k on the concentration of promoter, P. The rate constant k_1 corresponds to either H-abstraction or addition. Since $k_d \gg k_r$ and the rate

$$k = \frac{k_r[EH]}{k_d + k_r[EH]} + \frac{k_1[P]}{k_d + k_1[P]} \qquad (4)$$

increases are small (Table 1) so that $k_d \gg k_1$, equation 4 can be simplified as shown below. From the ratio of the

$$k = \frac{k_r[EH] + k_1[P]}{k_d} \qquad (5)$$

slope and intercept of the authors' line we calculate that k_1/k_r is 10 and 6 for cyclohexene and hexene-2 respectively. If the above proposal is correct, the reduction of eosin should proceed faster in cyclohexene than in ethyl alcohol.

If this alternate explanation is correct, then the recent explanation offered by Toppet, Delzanne and Smets for the way in which acrylamide accelerates the reduction of eosin by water must similarly be modified. These authors, following Vchida, et al. (1) invoked a fast reaction of acrylamide with a triplet eosin-water complex to give the eosin derived semiquinone radical + acyrlamide with a hydroxy radical attached to it in an unspecified manner. The radicals produced in this way initiated the polymerization of acyrlamide. Of course the preferred explanation is that acrylamide can reduce eosin directly faster than water.

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Proposition V

The existence of a photostationary state in the photoreduction of certain ketones is proposed.

* * * * * * * *

Irradiation of benzophenone in isopropyl alcohol is a common way of preparing benzopinacol (1). This reaction is quite general with various aromatic ketones and is clean; the pinacol usually precipitates in pure form. One aspect of photopinacolization which has lacked attention since its discovery in 1944 by Schönberg and Mustafa (2) is the reverse process. These authors found that irradiation of benzopinacol, several substituted benzopinacols, the acetophenone pinacol, and several other pinacols in the presence of quinone yielded the corresponding ketones and hydroquinone. Also, acetone was found to be capable of converting the pinacols of xanthone and fluorenone to the respective ketones. This study was primarily qualitative and no further work on this problem seems to have appeared.

Recently, work in these laboratories has commenced with the aim of discovering the mechanism of the reversion (3). We have found some evidence that nonvertical energy transfer (4) to some pinacols can occur giving two hydroxy radicals directly.

These bits of evidence suggest the possibility of an intriguing solvent effect and a novel type of photostationary state. If, for example, the irradiation of benzophenone (B) is run in a solvent in which benzopinacol (BH-BH) is highly soluble we can expect the reactions shown below to occur. In this formulation benzhydrol (BH_2) is used as the

Reaction	Rate
$B \longrightarrow B^*$	I
$B^* \longrightarrow B$	$k_d [B^*]$
$B^* + BH_2 \longrightarrow 2BH\cdot$	$k_r [B^*] \; [BH_2]$
$B^* + BH\text{-}BH \longrightarrow 2BH\cdot + B$	$k_1 [B^*] \; [BH\text{-}BH]$
$2BH\cdot \longrightarrow BH\text{-}BH$	$k_2 [BH\cdot]^2$
$2BH\cdot \longrightarrow B + BH_2$	$k_3 [BH\cdot]^2$

alcohol. As the alcohol is consumed and the concentration of the pinacol builds up in solution a point will be reached where energy transfer to the pinacol (equation 4) becomes competitive with hydrogen abstraction (equation 3). From the preliminary work of De Boer (5) we know that non-vertical energy transfer with sigma bond breaking in the case of 1,2-diphenylcyclopropane has a second order rate constant of 5×10^4. Comparing this with $k_r = 3 \times 10^6$ (6) for this system we see that high conversions will be necessary to reach this point. Franzen (7) showed that disproportionation occurs in the case of benzophenone with C^{14} experiments, but no estimation of the rate is available. At the steady state we predict that the ratio of pinacol to alcohol concentration will reach a constant value as shown below. Other ketones with various substituents should, when photo-

$$\frac{[BH - BH]}{[BH_2]} = \frac{k_1}{k_2} \cdot \frac{k_3}{k_4} \qquad (7)$$

reduced by the corresponding alcohol, show widely varying photostationary states. The rate constants k_d and $k_3 + k_4$ can usually be determined by flash spectroscopy; and the ratios k_d/k_1 and k_d/k_2 can be found by irradiation of ketone in the presence of varying concentrations of alcohol or pinacol. Thus, measurement of the photostationary state as described above provides the relation needed to fix k_3 and k_4.

In the case of reduction of ketones by isopropyl alcohol the same photostationary state could be realized in a cosolvent which dissolves the pinacol. However, it would require that k_2k_4 be greater than k_3 times the rate of H-abstraction from isopropyl alcohol.

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