I. PHOTOCHEMICAL STUDIES OF PHENOXY RADICAL

II. THE PHOTOREACTION OF MICHLER'S KETONE WITH BENZOPHENONE

Thesis by
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In Partial Fulfillment of the Requirements
For the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
1970
(Submitted September 2, 1969)

Dedicated to my father

ACKNOWLEDGMENTS

I am very pleased to have had the opportunity to spend my graduate years in the Hammond group. Professor G. S. Hammond has provided a constant source of inspiration and stimulation. Many members of the Hammond group have contributed towards making my graduate experience both enjoyable and educational. In particular, the techniques of flash photolysis were taught to me by Dr. George F. Vesley, esr experiments were performed with the expert assistance of Mr. Edwin J. Hamilton, and Dr. Jean Kossanyi was very helpful in obtaining and explaining mass spectral data.

Finally, I am deeply indebted to the patience and persistence of my wife, Ruth, who prepared the final draft of this thesis. Throughout, she has offered constant encouragement and understanding, without which my graduate career could hardly have been the successful and gratifying experience that it was.

I am also grateful to the National Science Foundation for three years of sponsorship as an N.S.F. Graduate Fellow.

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Abstract

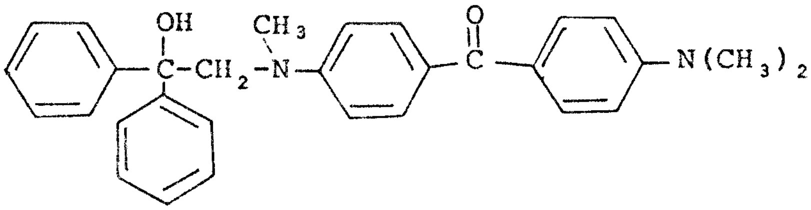
I. PHOTOCHEMICAL STUDIES OF PHENOXY RADICAL

Phenoxy radical was generated by flash photolysis of aqueous phenol. The ultraviolet-visible absorption spectrum of phenoxy radical was obtained. Decay kinetics for the bimolecular disappearance of phenoxy radical led to a second order rate constant of $k_2 = 1.2 \pm 0.1 \times 10^9$ M^{-1} sec^{-1}. In these solution-phase flash photolysis studies, no evidence was obtained for further decomposition of phenoxy radical. Molecular orbital symmetry correlations demonstrate that the conversion of phenoxy radical to cyclopentadienyl radical and carbon monoxide is symmetry-allowed from the ground state and symmetry-forbidden from the excited state of phenoxy radical.

II. THE PHOTOREACTION OF MICHLER'S KETONE WITH BENZOPHENONE

Michler's ketone (4,4'-bis[dimethylamino]benzophenone) undergoes a photoreaction with benzophenone in 2-propanol

to give photoproduct I with moderate quantum efficiency. This product arises from the coupling of benzophenone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ketyl radical with the corresponding radical derived from Michler's ketone. Each of these photointermediates was characterized by the absorption spectra and decay kinetics obtained from flash photolysis studies. The key mechanistic step must be transfer of hydrogen from the triplet state of Michler's ketone to benzophenone, and is without precedent in photochemistry. A triplet "exciplex" is postulated to lead to the hydrogen transfer.

PHOTOCHEMICAL STUDIES OF PHENOXY RADICAL

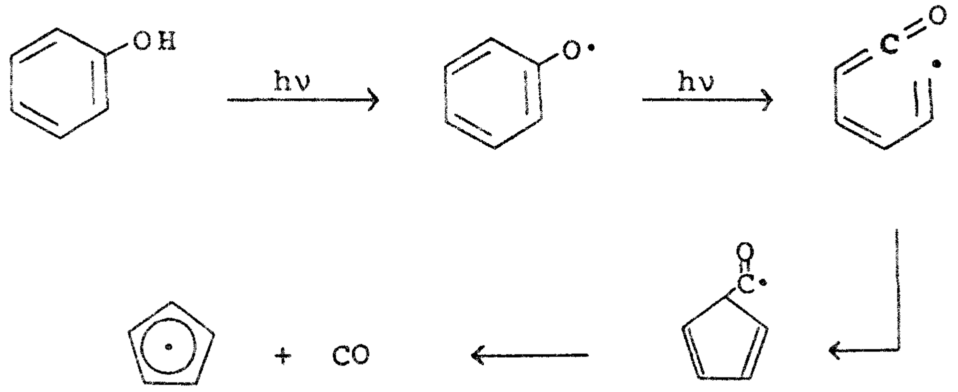
I. INTRODUCTION

Phenoxy radicals comprise an important and interesting class of free radicals.[1,2] Phenoxy radicals substituted in the _ortho_ and _para_ positions are greatly stabilized and provide some classic examples of stable free radicals.[3] Unsubstituted phenoxy radical has been considered to be an intermediate in many reactions[1,2] and has now been observed and characterized in a variety of ways. The electron spin resonance spectrum of phenoxy radical has been observed in flow systems by the oxidation of phenol by acidic ceric sulfate.[4,5] The visible-ultraviolet absorption spectrum of phenoxy radical has been observed by flash photolysis of phenol in the vapor phase,[6,7] in solution,[7-10] and in rigid media,[7,11] and by the pulse radiolysis of phenol.[12]

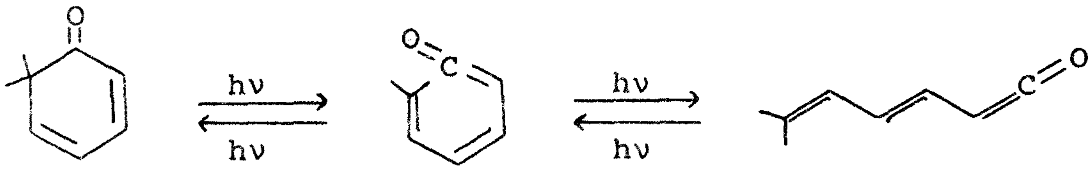
More recently, evidence has been compiled which suggests that photolysis of phenol may proceed with further decomposition of the intermediate phenoxy radical. Irradiation of phenol and alkyl phenyl ethers in a nitrogen matrix at 4° K produces phenoxy radical as a stable species.[13] Under these conditions, phenoxy radical can be irradiated with light not absorbed by the parent compound. Photolysis of phenoxy radical gives rise to a ring-opened ketene radical, as well as some carbon monoxide.[13]

In the vapor phase, flash photolysis of phenol produces not only phenoxy radical, but cyclopentadienyl radical as well.[14,15] Cyclopentadienyl radical was identified as a transient species by the identity of its absorption spectrum with the transient absorption spectrum obtained on flash photolysis of cyclopentadiene (λ_{max} = 3343 A).[16] Furthermore, the same transient absorption spectrum was observed upon vapor phase flash photolysis of a number of other substituted benzenes, including aniline, thiophenol, nitrobenzene, anisole, and phenetole. Carbon monoxide and hydrogen were observed as products of the vapor phase flash photolysis of phenol.[15]

Consideration of these reports suggested a possible mechanistic pathway for the photodecomposition of phenol.



Some support for such a scheme may be found in certain analogous reactions. The mass spectra of anisole and phenol at 1000° show peaks corresponding to C_6H_5O, C_5H_5, and CO.[17] The critical step of ring cleavage is analogous to the photolytic cleavage of 2,4-cyclohexadienones to the corresponding ketenes.[18] Simple Hückel molecular orbital calculations demonstrate that the weakest



bond in phenoxy radical is between C_1 and C_2.[19]

Two physical methods are ideally suited for study of a reaction involving intermediates of this kind. The identification and decay kinetics of photolytically-formed intermediates have been carried out in our laboratories by electron spin resonance techniques[20,21] and by flash photolysis techniques.[22,23] This project was undertaken in hopes of characterizing as many of the proposed intermediates as possible, and in this way elucidating the mechanism of the photodecomposition of phenol.

II. EXPERIMENTAL

Materials

Phenol (Baker and Adamson reagent grade) was sublimed once at 25 mm, m.p. 40-42°, and stored under nitrogen in a freezer until use.

Cyclopentadiene was prepared just prior to use by cracking dicyclopentadiene (Matheson, Coleman, and Bell) at reflux and collecting the monomer by distillation at 42-43° at atmospheric pressure.

2,4,6-Tri-*t*-butylphenol (Aldrich) was recrystallized three times from 95% ethanol, m.p. 129-130°.

2,4,6-Tri-*t*-butylphenoxy radical was prepared by the lead dioxide oxidation of 2,4,6-tri-*t*-butylphenol in hexane solution, according to Cook and Woodworth.[24]

Phenyl *t*-butyl ether was prepared according to Sahyun and Cram,[25] b.p. 72-72.5° at 15 mm.

Solvents

Water was the available tap distilled water, used without further purification.

Hexane and benzene were purified in the same manner, beginning with Baker Analyzed Reagent benzene or Phillips Pure hexane. The solvent was stirred for at least two weeks over concentrated sulfuric acid, replacing the acid when it became brown. The organic layer was then stirred over 10% sodium hydroxide for one day, stirred over distilled water for one day, dried over magnesium sulfate, refluxed over phosphorus pentoxide for one day, and finally distilled at constant boiling point, with removal of at least 200 ml of forerun.

Flash Photolysis Procedures

Flash photolysis cells consisted of cylindrical quartz cells, 21 cm by 15 mm (o.d.), with quartz optical windows at either end. A sidearm connected the cell to a 100 ml round bottom flask and to a 14/35 joint where it could be attached to a vacuum manifold. By syringe, 30-40 ml of solution could be placed directly into the round bottom flask, and there degassed by five freeze-pump-thaw cycles to pressures of 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6}, and 10^{-6} mm.

The flash photolysis apparatus was essentially the same as that built by Herkstroeter.[22,23] Samples were subjected to flashes from two xenon flash lamps situated parallel to the sample cell. Typical flash energies were 200 joules with a flash duration of about 10 μsec. Two types of monitoring sources were used. A continuous source of high-intensity light was provided by a high-pressure mercury-xenon lamp. In this application, the continuum of visible-ultraviolet light is passed down the long axis of the sample cell (21 cm), through a monochromator to a photomultiplier system connected to an oscilloscope. This method thus provides a trace of absorption at a given wavelength as a function of time, and is properly called kinetic spectrophotometry.

A second application of flash photolytic techniques utilizes as a monitoring source a second flash lamp, designed to fire at a prespecified time after the firing of the excitation flash lamps. When this light pulse is passed through the sample cell to a spectrograph,[26] the full visible-ultraviolet spectrum of the contents of the sample cell, at a given time after excitation, is obtained. This method is called flash spectroscopy, or double flash photolysis. Schematic diagrams of these two applications are shown in Figure I.

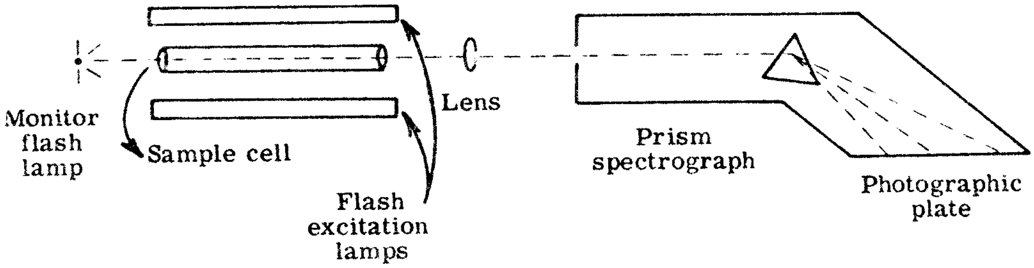
Data from flash spectroscopy studies were obtained on Eastman Kodak Type 103a-F Spectrographic Plates. On each plate seven spectra were taken, each of which was calibrated by an adjacent mercury line spectrum, obtained from a BLE Spectroline Model SCT-1 low-pressure mercury pencil light.

Certain spectra were traced using a Jarrell-Ash High Precision Recording Microphotometer, Model 23-500.[27] Since the dispersion of the prism spectrograph was linear

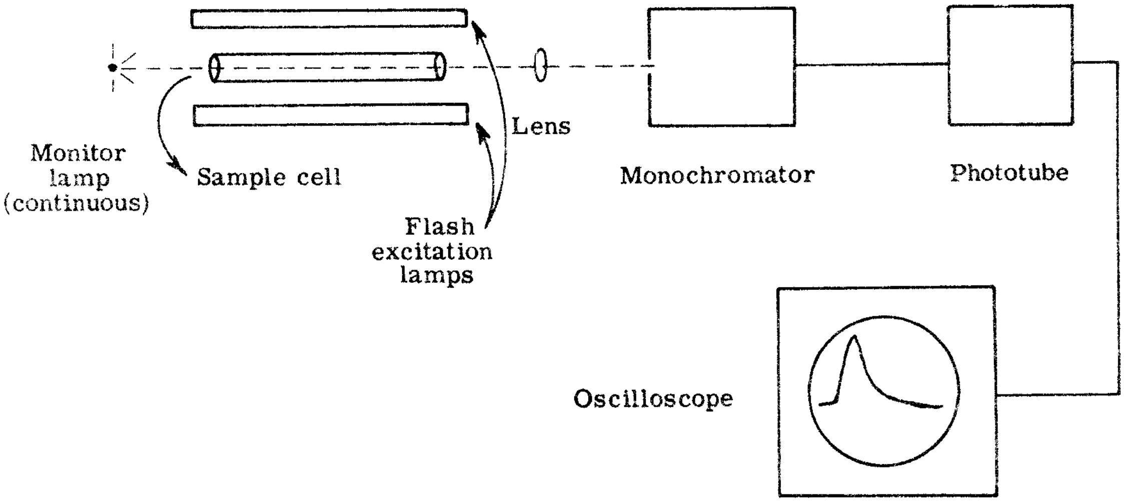
Figure I

Flash Spectroscopy and Kinetic Spectrophotometry

Flash Spectroscopy



Kinetic Spectrophotometry



in neither wavelength nor frequency, it was felt desirable to calibrate the spectra so they could be displayed linear in wavelength. For this purpose, the spacings of the following mercury lines from the BLE Spectroline source were plotted: 3126, 3132, 3341, 3650, 4047, 4358, 5461, 5770, 5790, and 6907 Angstroms. Between these points, a smooth curve was drawn, from which the position of any desired wavelength could be read. Spectra were recreated by plotting the relative densitometer reading at least at every 10 A interval. Blank spectra, obtained by flashing the monitoring pulse through unexcited sample, were subtracted point for point.

Data from kinetic spectrophotometry were obtained as Polaroid Type 46-L negatives of the oscilloscope traces. These pictures were projected to fill an 8-1/2" × 11" sheet of graph paper and the salient features were carefully traced (see Figure II).

From these tracings, simple measurements provided transmittancy as a function of time.

$$T = x/x_0$$

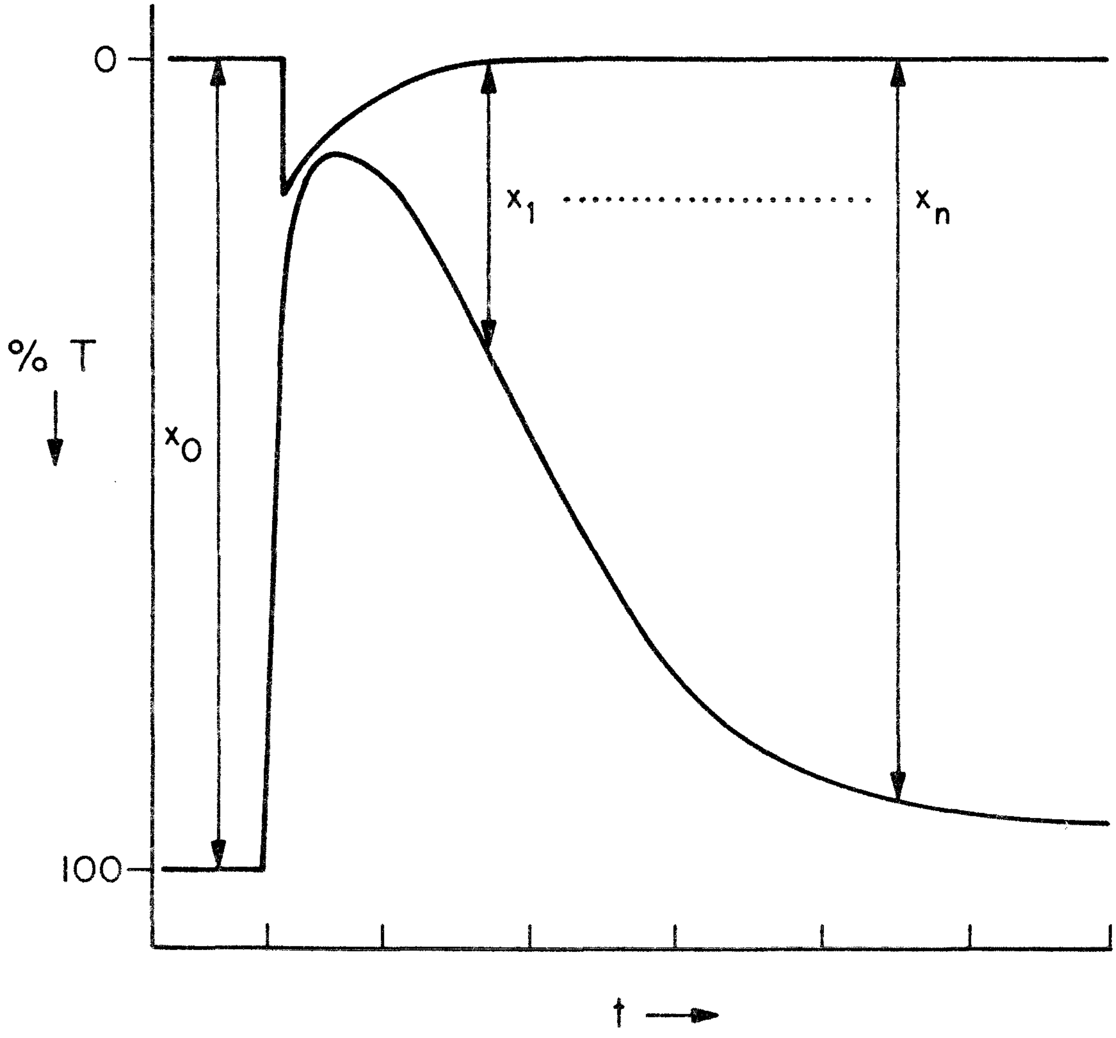
$$A = -\log T$$

For the second-order disappearance of phenoxy radical, these data were fit to the following equations:

Figure II

A Typical Kinetic Spectrophotometric Tracing

A Typical Kinetic Spectrophotometric Tracing



$$-d[C_6H_5O\cdot]/dt = 2k_2[C_6H_5O\cdot]^2$$

$$[C_6H_5O\cdot] = A/\varepsilon\ell$$

$$-dA/dt = (2k_2/\varepsilon\ell)A^2$$

$$A^{-1} = A_0{}^{-1} + (2k_2/\varepsilon\ell)t$$

The length of the flash cell, ℓ, was equal to 21 cm. The extinction coefficient of phenoxy radical at its 400 nm absorption maximum has been recently redetermined to be 2200 ± 200 M^{-1} cm^{-1}.[12] The decay of the 400 nm absorption was followed to at least 70% completion (about 300 μsec under our conditions). Least-squares analysis consistently gave correlation coefficients greater than 0.997.

Electron Spin Resonance Procedures

Esr studies were performed with apparatus previously described.[20] Varian quartz aqueous esr cells were used to contain the samples of aqueous phenol. Degassing of the solution was performed in a test tube which had a sidearm with a 7/25 joint to which the esr cell could be attached. Three freeze-pump-thaw cycles to an ultimate pressure of 2 × 10^{-4} mm were performed before sealing the cell.

Nonaqueous samples were contained in quartz 3 mm tubes and there degassed by the same procedure.

III. RESULTS

Studies of Phenoxy Radical in Aqueous Solution

Phenol was flash photolyzed as a 1.0×10^{-3} M aqueous solution in quartz flash cells. Under these conditions, phenoxy radical was readily observable. Double flash photolysis techniques were utilized to obtain the spectrum of phenoxy radical (Figure III), in close agreement with that appearing in the literature.[7,12]

The decay of phenoxy radical was monitored at its 400 nm maximum, and was clearly second-order, as demonstrated by the following typical analysis (Figure IV).

The rate constant of $(1.2 \pm 0.1) \times 10^{9}$ M^{-1} sec^{-1} was derived as the result of six different measurements on fresh, degassed samples of aqueous phenol. The range of values of k_2/ε was $(5.45 \pm 0.30) \times 10^{5}$ cm sec^{-1}.

The decay kinetics were reproducible and unquestionably second-order only on the first flash, however. If the sample is subjected to further flashes, the fit to second-order kinetics becomes progressively worse, and if a rate constant is extracted from the data, it decreases sharply. The effect of continued flashing upon the apparent second-order rate constant is shown in Figure V.

Apparently, new photoproducts develop rapidly and in subsequent flashes undergo reactions which interfere

Figure III

The Electronic Absorption Spectrum
of Phenoxy Radical

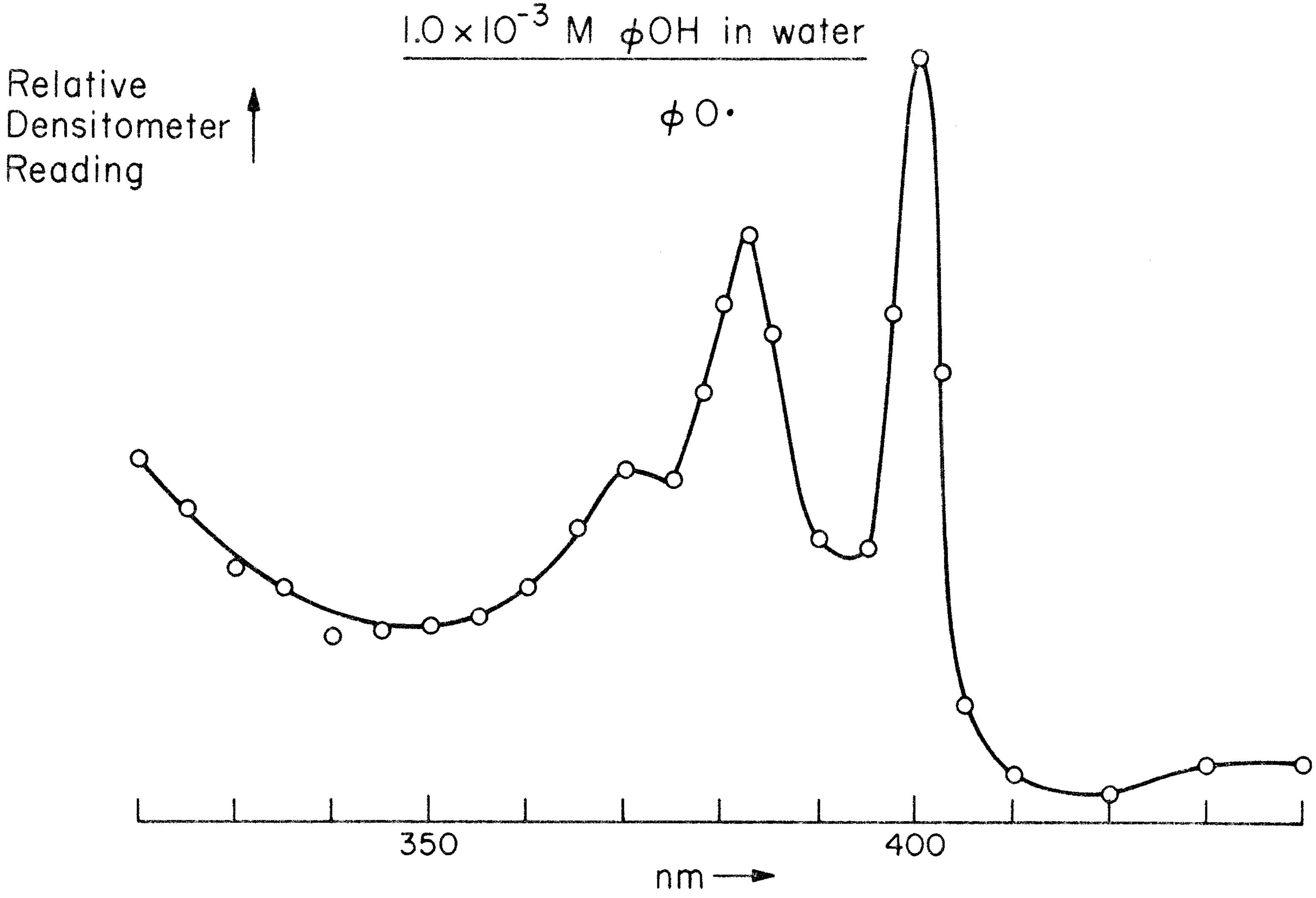

1.0×10^{-3} M φOH in water
φO·
Relative Densitometer Reading
350
400
nm

Figure IV

The Second-Order Decay of Phenoxy Radical

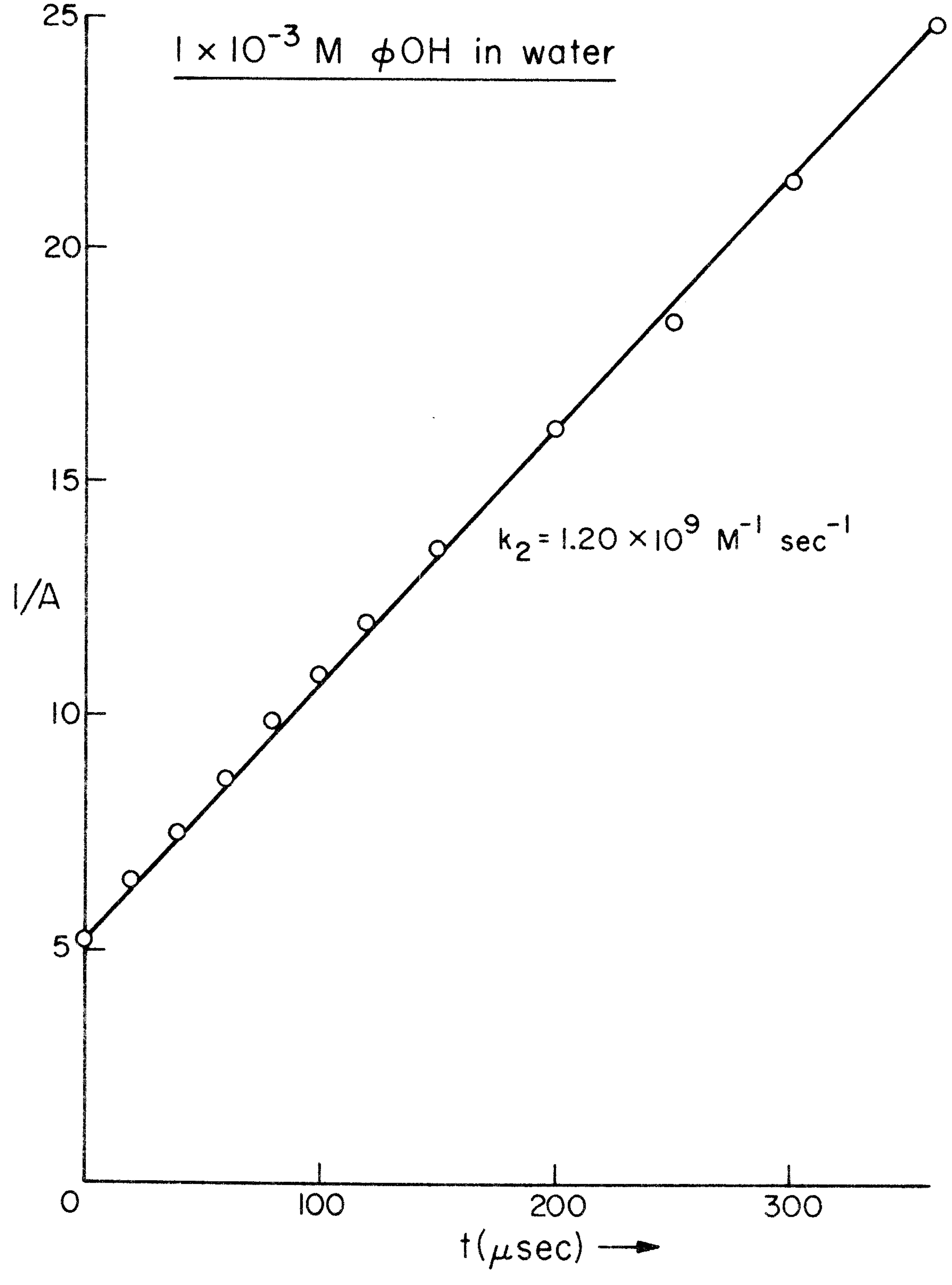
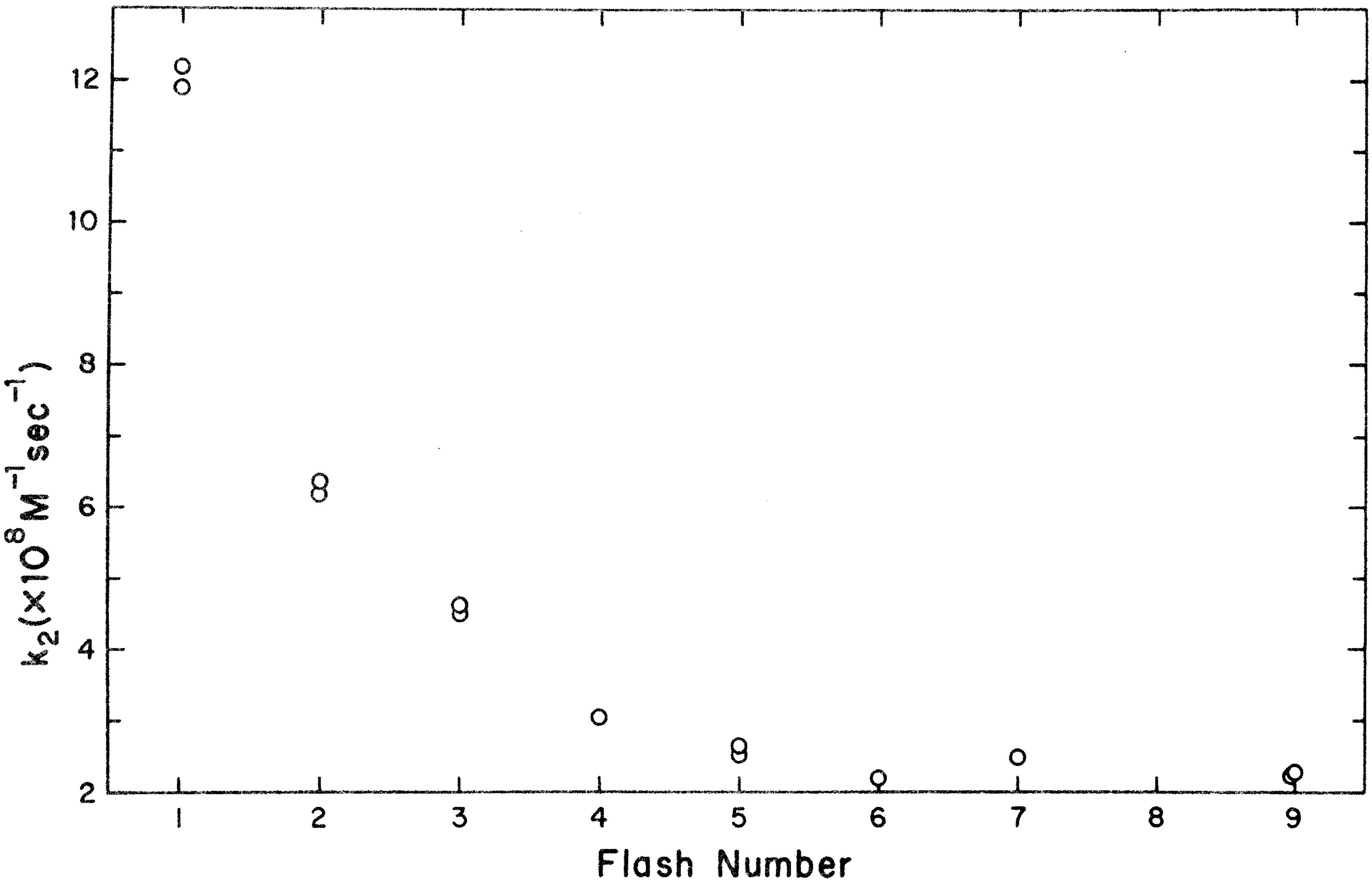

1 × 10⁻³ M φOH in water
k₂ = 1.20 × 10⁹ M⁻¹ sec⁻¹
1/A
25
20
15
10
5
0
100
200
300
t(μsec) →

Figure V

The Effect of Continued Flashing
Upon the Apparent Second-Order Decay
of Phenoxy Radical


12
10
8
6
4
2
$k_2(\times 10^8 M^{-1} sec^{-1})$
1
2
3
4
5
6
7
8
9
Flash Number

with the kinetic analysis for phenoxy radical. This is supported by the fact that the transient absorption spectra obtained upon subsequent flashes differ somewhat from the spectrum of phenoxy radical. The products arising from photolysis of aqueous phenol have been characterized.[28] They include dimers of phenoxy radical of all types, including substituted phenols. Such products could give rise to substituted phenoxy radicals, which would probably absorb at 400 nm,[29] and should be expected to decay at different, probably slower, rates. At 400 nm, the maximum optical density attained directly after the excitation flash is about 0.2, from which the concentration of phenoxy radicals may be placed at about 5×10^{-6} M, or 0.5% conversion per flash. Since conversion of phenol in the first flash is not extensive, it is unlikely that the new transient species are formed by direct photolysis. These new radicals are probably formed by secondary reactions of the primary photoproducts, either energy transfer or attack by transients formed from photolysis of phenol.

Electron spin resonance studies were also undertaken, using the apparatus and methods of Weiner and Hammond.[20] Irradiation of an aqueous solution of 5×10^{-2} M phenol gradually produced a paramagnetic signal which was light-dependent. A satisfactory decay curve could not be obtained, however. The signal was unsymmetrical, broad, and weak, and required prolonged photolysis before its appearance. For these reasons, it was considered to be the result of some secondary photointermediates, in accord with the findings upon repeated flash photolyses. The appearance of a white precipitate demonstrated that species of higher molecular weight were being formed in significant yield.

Flash Photolysis of Phenol in Nonaqueous Solvents

It was discovered that water is by far the superior solvent for observation of phenoxy radicals by photolysis of phenol. In ethanol or 2-propanol, an unidentified transient absorption was noted. Absorption at 400 nm was weak, with much stronger absorption at 313 nm. The lifetime was about 200 μsec, but the decay was neither first- nor second-order. Presumably in these solvents phenoxy radical decays rapidly by hydrogen abstraction from the solvent. The transients which were observed probably reflect secondary processes such as attack of solvent radicals upon phenol.

In the hydrocarbon solvents, hexane and cyclohexane, no transient intermediate could be observed at all. In paraffin oil as solvent, flash photolysis of phenol did give rise to a very weak transient absorption assignable to phenoxy radical.

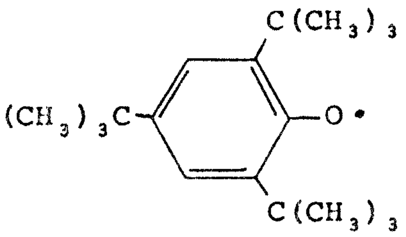
Other Possible Sources of Phenoxy Radical

Since phenoxy radical has been implicated in a number of photoreactions, some other possible sources of phenoxy radical were explored. The photo-Fries reaction of phenyl esters may proceed through free phenoxy radicals.[30] However, flash photolysis of 1.0×10^{-3} M phenyl benzoate in hexane, ether, or ethanol gave no transient absorption at all. Furthermore, the absorption due to the rearrangement products, o- and p-hydroxybenzophenone, appears immediately (< 10 μsec) after the excitation flash.[31] The implication with regard to the mechanism of the photo-Fries rearrangement is that "free" phenoxy radicals cannot be present in significant concentrations.

Phenyl t-butyl ether was prepared in the hopes that phenoxy radical could be more readily produced if it were offered a more stable counter-radical. However, flash photolysis of phenyl t-butyl ether showed no transient absorption at all. Furthermore, esr monitoring during irradiation of a neat sample of phenyl t-butyl ether showed no paramagnetic signal, even though the sample was considerably yellowed under the photolysis conditions. It was concluded that phenyl t-butyl ether was not a convenient source of phenoxy radicals.

Studies with 2,4,6-Tri-t-butylphenoxy Radical

Phenoxy radicals substituted with bulky groups in the ortho and para positions are stable species, since the normal coupling reactions are strongly hindered.[3] With only moderate precautions for the exclusion of oxygen, 2,4,6-tri-t-butylphenoxy radical (I) is readily



(I)

prepared and handled. Flash photolysis of a 10^{-3} M solution of I in hexane did show the appearance of a transient absorption at 4358 A. Only at 4358 A was there sufficient monitoring intensity to observe this intermediate. Its decay was approximately first-order, $k = 3 \times 10^{3}$ sec^{-1}. This intermediate could represent an excited state of I, perhaps a quartet state, or may represent a free radical of some sort.

Esr studies were undertaken in the hopes of observing the spectrum due to the photointermediate found in the flash photolysis experiments. A hexane solution of 10^{-4} M I gave a well-defined esr spectrum, in agreement with that appearing in the literature - a(meta) =

1.3 gauss.[32] Irradiation with light in the range of 200-400 nm rapidly destroys this esr signal. However, no new signal could be observed, either during or after the photolysis.

IV. DISCUSSION

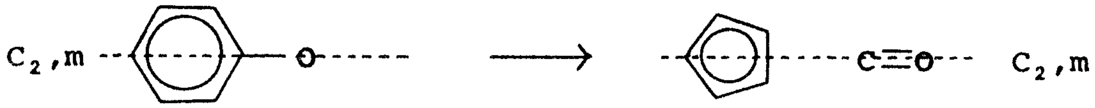
This research was undertaken in order to elucidate the mechanism of formation of cyclopentadienyl radical from phenol. The first stage of the reaction, formation of phenoxy radical, was carefully characterized. However, the formation of cyclopentadienyl radical was not observed under the conditions of this work.

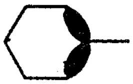
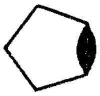
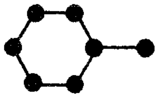
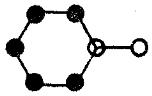
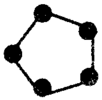
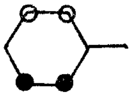
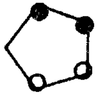
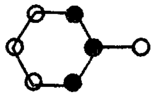
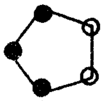
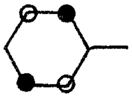
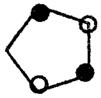
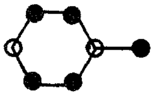
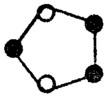
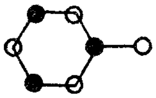
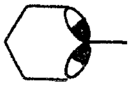
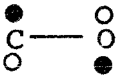
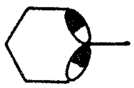
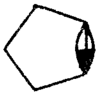
The absorption spectrum and the decay kinetics of phenoxy radical were determined, both in agreement with data available in the literature. In the case of the decay kinetics, the bimolecular termination rate is probably an improvement on previously reported values because a revised value of the extinction coefficient was used.

The conversion of phenoxy radical to cyclopentadienyl radical can be handled by Woodward-Hoffmann molecular orbital symmetry correlations.[33] It can be shown that there is a symmetry-allowed concerted conversion of ground-state phenoxy radical to ground state cyclopentadienyl radical (Figure VI). The concerted extrusion of carbon monoxide from phenoxy radical maintains two symmetry elements at all times - a twofold axis (C_2) and a mirror plane (m) - oriented as shown through O, C_1, and C_4. The symmetry of all eleven molecular orbitals are shown both before and after the reaction. However, only two molecular

Figure VI

Molecular Orbital Correlations
for the Conversion of Phenoxy Radical
to Cyclopentadienyl Radical and Carbon Monoxide



	Phenoxy Radical	C_2	m		Products	C_2	m
ψ_1		+	+	ϕ_1		+	+
ψ_2		−	−	ϕ_2		−	−
ψ_3		−	+	ϕ_3		−	+
ψ_4		−	+	ϕ_4		−	+
ψ_5		+	−	ϕ_5		+	−
ψ_6		−	+	ϕ_6		−	+
ψ_7		+	−	ϕ_7		+	−
ψ_8		−	+	ϕ_8		−	+
ψ_9		−	+	ϕ_9		−	+
ψ_{10}		+	+	ϕ_{10}		−	−
ψ_{11}		−	−	ϕ_{11}		−	−

● ○ p orbitals

 σ orbitals

Ground State Symmetry Correlations

Phenoxy radical ground state:

	$(\psi_1)^2$	$(\psi_2)^2$	$(\psi_3)^2$	$(\psi_4)^2$	$(\psi_5)^2$	$(\psi_6)^1$
C_2	++	--	--	--	++	-
m	++	--	++	++	--	+

Product ground states:

	$(\phi_1)^2$	$(\phi_2)^2$	$(\phi_3)^2$	$(\phi_4)^2$	$(\phi_5)^2$	$(\phi_6)^1$
C_2	++	--	--	--	++	-
m	++	--	++	++	--	+

There is a ground-state correlation.

In simpler terms, the only orbitals which are affected by the reaction are the two defined by the bonds which are made and broken.

$$(\psi_1)^2 \rightarrow (\phi_1)^2$$

$$(\psi_2)^2 \rightarrow (\phi_2)^2$$

Excited State Symmetry Correlations

Phenoxy radical lowest excited state:

	$(\psi_1)^2$	$(\psi_2)^2$	$(\psi_3)^2$	$(\psi_4)^2$	$(\psi_5)^2$	$(\psi_7)^1$
C_2	++	--	--	--	++	+
m	++	--	++	++	--	-

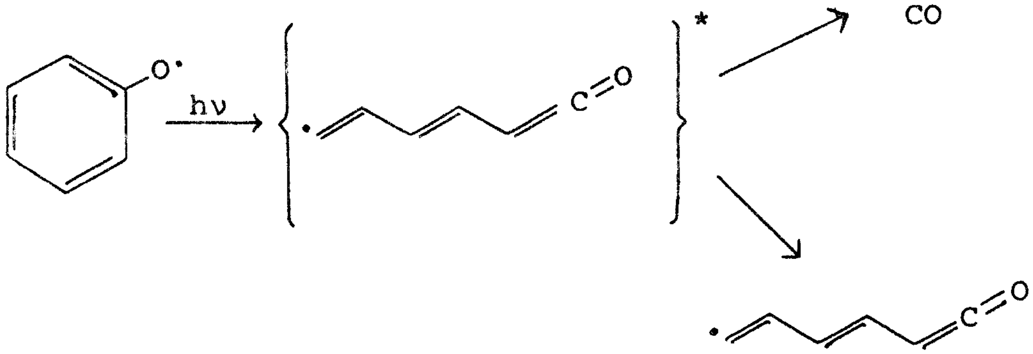
This correlates with upper excited states of the products and is orbital symmetry forbidden.

orbitals are substantially altered in the reaction and this simplified correlation is also shown.

Since the orbital symmetry correlations point to an allowed concerted transition from phenoxy radical to cyclopentadienyl radical, it was hoped that the reaction could be observed. Of course, the availability of a symmetry-allowed pathway does not necessitate that the pathway will be of very low energy.

Correlations for photoexcited phenoxy radical are more difficult to predict due to the multiplicity of excited states available to phenoxy radical. The spectrum of phenoxy radical displays absorption maxima at 296, 382, 400, and 600 nm.[8] These bands have not been assigned to the excited states, although it is believed that the lowest excited state corresponds to excitation of the lone oxygen electron.[8] If this is the case, there is not a correlation between this excited state and ground state cyclopentadienyl radical (Figure VI).

These orbital symmetry considerations do, in fact, correlate the known reactions of phenoxy radical. In a nitrogen matrix at 4° K, phenoxy radical has been produced from phenol, isolated and photolyzed.[13] The products of photolysis of phenoxy radical are the ring-opened 6-oxo-1,3,5-hexatrienyl-1 radical and some carbon monoxide.



Genuine thermal reactions of phenoxy radical are somewhat more difficult to validate. Probably the gas phase flash photolysis experiments of Porter and Ward[14,15] represent thermal decomposition of photolytically-produced phenoxy radical, rather than a two-quantum process. In the vapor phase, thermal fragmentations are enhanced by the lack of cage effects and by the longer lifetimes of vibrationally excited states. Furthermore, pyrolysis of phenol at 1000° leads to mass spectral fragments at C_6H_5O, C_5H_5, and CO.[17] These thermal reactions form cyclopentadienyl radical from phenoxy radical, while a different reaction occurs upon photolysis of phenoxy radical. These observations are in accord with orbital symmetry considerations.

The failure to observe the formation of cyclopentadienyl radical in this work can be traced to several causes. Studies were restricted to the solution phase, where the reaction may be expected to be less favorable than in the vapor phase. In condensed phases, bond breaking reactions are hindered by cage effects which prevent separation of the initially formed fragments. This would be a serious hindrance only if the two fragments are capable of reverting back to the starting molecule, however. There is no evidence that the reaction of phenoxy radical to give carbon monoxide plus cyclopentadienyl radical is at all reversible.

The major difference between reactions in the vapor phase and in condensed phases lies in the vibrational relaxation times. Vibrationally excited states are quenched in condensed phases in the order of 10^{-11} sec.[34] In the vapor phase, lifetimes of vibrationally excited states are highly pressure-dependent, and can be several orders of magnitude longer. Reactions of these vibrationally excited states are thereby enhanced in the vapor phase.

Finally, the belated publication of the experimental procedure of Porter and Ward[15] attests to the elaborate techniques required to observe the presence of cyclopentadienyl radical in the vapor phase flash photolysis of phenol. A combination of long path lengths (up to 10 m) by multiple reflections and the high dispersion of a 21 ft.

grating spectrograph (2.33 Å/mm and 1.16 Å/mm in the second order) were necessary to characterize the spectrum of cyclopentadienyl radical. These conditions could not be approached using the apparatus available for this work. Furthermore, the expected difficulties of condensed phase photofragmentations also worked against the detection of cyclopentadienyl radical. Thus in retrospect, cyclopentadienyl radical is not an expected photointermediate from the flash photolysis of phenol under standard solution-phase conditions.

V. REFERENCES

[1] A. I. Scott, *Quart. Rev.* (London), *19*, 1 (1965).

[2] H. Musso, *Angew. Chem. Int. Ed. Eng.*, *2*, 723 (1963).

[3] E. R. Altwicker, *Chem. Rev.*, *67*, 475 (1967).

[4] T. J. Stone and W. A. Waters, *Proc. Chem. Soc.*, 253 (1962).

[5] B. T. Allen and W. Vanneste, *Nature*, *204*, 991 (1964).

[6] G. Porter and F. J. Wright, *Trans. Faraday Soc.*, *51*, 1469 (1955).

[7] E. J. Land, G. Porter and E. Strachan, *Trans. Faraday Soc.*, *57*, 1885 (1961).

[8] E. J. Land and G. Porter, *Trans. Faraday Soc.*, *59*, 2016 (1963).

[9] L. I. Grossweiner and W. A. Mulac, *Radiat. Res.*, *10*, 515 (1959).

[10] G. Dobson and L. I. Grossweiner, *Trans. Faraday Soc.*, *61*, 708 (1965).

[11] I. Norman and G. Porter, *Proc. Roy. Soc., Ser. A*, *230*, 399 (1955).

[12] E. J. Land and M. Ebert, *Trans. Faraday Soc.*, *63*, 1181 (1967).

[13] J. L. Roebber, *J. Chem. Phys.*, *37*, 1974 (1962).

[14] G. Porter and B. Ward, *Proc. Chem. Soc.*, 288 (1964).

[15] G. Porter and B. Ward, *Proc. Roy. Soc., Ser. A*, *303*, 139 (1968).

[16] B. A. Thrush, *Nature*, *178*, 155 (1956).

[17] A. G. Harrison, L. R. Honnen, H. J. Dauben, and F. P. Lossing, *J. Amer. Chem. Soc.*, *82*, 5593 (1960).

[18] P. M. Collins and H. Hart, *J. Chem. Soc.*, *C*, 1197 (1967).

[19] Professor J. D. Roberts' HK6 program.

[20] S. A. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, *90*, 1659 (1968).

[21] S. A. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, *91*, 986 (1969).

[22] W. G. Herkstroeter, Ph.D. Thesis, California Institute of Technology, Pasadena, California, 1965.

[23] W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, *88*, 4769 (1966).

[24] C. D. Cook and R. C. Woodworth, *J. Amer. Chem. Soc.*, *75*, 6242 (1953).

[25] M. R. V. Sahyun and D. J. Cram, *Org. Syn.*, *45*, 89 (1965).

[26] A Bausch and Lomb Two-Meter Prism Spectrograph (no. 749) was kindly loaned by Professor G. W. Robinson.

[27] Property of Professor G. W. Robinson.

[28] H. I. Joschek and S. I. Miller, *J. Amer. Chem. Soc.*, *88*, 3273 (1966).

[29] Absorption spectra for a variety of phenoxy radicals appear in references 7 and 8.

[30] M. R. Sandner, E. Hedaya and D. J. Trecker, *J. Amer. Chem. Soc.*, *90*, 7249 (1968).

[31] Experiment performed with Mr. James W. Meyer.

[32] J. K. Becconsall, S. Chough and G. Scott, *Trans. Faraday Soc.*, *56*, 459 (1960).

[33] R. Hoffmann and R. B. Woodward, *Accts. Chem. Res.*, *1*, 17 (1968).

[34] P. M. Rentzepis, *Photochem. Photobiol.*, *8*, 579 (1968).

THE PHOTOREACTION OF MICHLER'S KETONE WITH BENZOPHENONE

I. INTRODUCTION

The reactions of carbonyl compounds have long been of interest to photochemists.[1,2] The photoreduction of benzophenone by 2-propanol to give benzpinacol is now one of the most well-known and well-studied photoreactions.[3-6] The key step in the photoreduction reaction is considered to be abstraction of a hydrogen atom by the n-π* triplet state of benzophenone.[7-10] The importance of the n-π* state is demonstrated by the fact that substituted benzophenones which have a lowest triplet state of charge-transfer or π-π* character are nearly totally unreactive in 2-propanol solution.[7-10] Michler's ketone (4,4'-bis [dimethylamino]benzophenone) shows this classic lack of photoreactivity - the quantum yield for disappearance in 2-propanol is less than 10^{-4},[10] in sharp contrast to the quantum efficiency for benzophenone disappearance which can approach 2.[3] Only in nonpolar solvents does Michler's ketone become somewhat photoreactive, due to the shift of the reactive n-π* triplet level below that of the unreactive charge-transfer triplet.[11]

With this classical understanding of the reactivity of the n-π* state and the nonreactivity of π-π* or charge-transfer states, it was somewhat startling to discover that Michler's ketone undergoes a photoreaction with benzophenone in 2-propanol. This discovery was, in fact, made by Dr. Katherine Chang at the Photoproducts Division of the Dupont Experimental Station, Wilmington, Delaware. We are deeply grateful to have been offered to take a part in this discovery.

The initial experiments indicated that a mixture of Michler's ketone and benzophenone provides better photoinitiation of free radical reactions than either of the two individual sensitizers. Such a result was entirely unexpected on the basis of the known photochemistry of Michler's ketone and benzophenone. The most reasonable prediction would have been that mixtures of Michler's ketone and benzophenone would show no photoreactivity at all. The excited states of Michler's ketone are unreactive in 2-propanol.[10] Benzophenone is photoreactive in 2-propanol, but scarcely any light can be absorbed by benzophenone in the presence of Michler's ketone. Furthermore, Michler's ketone will act as a quencher for benzophenone excited states.

The problem was rendered more and more fascinating by the ease with which mechanistic possibilities could be disposed with. For example, it is thermodynamically impossible for the reactive benzophenone triplet state to be formed by triplet energy transfer from Michler's ketone, since this process is endothermic by over 7 kcal/mole.[12] Furthermore, the photoreaction cannot be initiated by an excited state of Michler's ketone, since these are not reactive in 2-propanol.[10] At the very outset of this work, the unique character of the mechanism was forced upon us. Important clues towards the mechanistic interpretation became available in the chemical literature on the photoreactions of benzophenone with amines.

Benzophenones are efficiently photoreduced by primary or secondary amines bearing α-hydrogens.[13] In the case of many amines, a mechanism exactly analogous to the 2-propanol photoreduction is appropriate.[13] However, recent evidence demonstrates that intermolecular charge-transfer interactions are very important with amines of relatively low ionization potential, particularly in polar solvents.[14-17] Undoubtedly the most convincing evidence for charge transfer interactions are the observations of Davidson and Lambeth, who established the intermediacy of the tri-*p*-tolylamine radical cation in the flash photolysis of benzophenone and tri-*p*-tolylamine in acetonitrile.[15] Also significant is their finding that naphthalene is a poor quencher for the photoreduction of benzophenone by N,N-dimethylaniline, while ferric chelates are much better quenchers.[16] These data suggest that triplet benzophenone is quenched very rapidly by electron transfer from the amine.

Only one example exists in the chemical literature describing the interaction of excited amines with ground-state benzophenone. Irradiation of solid solutions of benzophenone and diphenylamine in alcohol glasses at 77° K, such that diphenylamine absorbs >90% of the light, generates benzophenone ketyl, benzophenone radical anion, and diphenylamine radical cation, as characterized by their ultraviolet and esr spectra.[18] The variation of total product yield with light intensity points to a two-quantum process, leading the authors to suggest a mechanism in which the triplet state of the amine absorbs the second quantum of light, thereby initiating the ionization process.[18]

Finally, consideration of Michler's ketone as an amine rather than a ketone led to a different insight upon the problem. However, the reaction again demanded a unique interpretation. It cannot be described as a normal interaction of an amine with triplet benzophenone, since triplet benzophenone simply cannot be present. At every turn, the reaction suggested the intermediacy of triplet benzophenone, while the existence of triplet benzophenone in such a system defied photochemical intuition.

Mechanistic studies were undertaken with the uncommon stimulation of a guarantee of an unusual mechanism.

II. EXPERIMENTAL

Materials

Michler's ketone (Eastman) was sublimed once, m.p. 174-175°.

Benzophenone (Matheson, Coleman and Bell) was recrystallized twice from petroleum ether, m.p. 49-50°.

1,3-Cyclohexadiene (Aldrich) was distilled from lithium aluminum hydride under nitrogen by Mr. Thomas L. Penner. It was degassed and sealed immediately and kept in a freezer until use.

2-Propanol (Matheson, Coleman and Bell spectroquality solvent) was used without further purification.

C-14 Methyl iodide (Tracerlab lot number 70-45-11) had a specific activity of 1.0 mcurie/mmole. The sample had a distinct violet color, but purification was found to be unnecessary.

Methylene chloride (Matheson, Coleman and Bell spectroquality solvent) was used without further purification.

C-14 Toluene radioactivity standard (New England Nuclear Corporation lot number 282-222A) had a specific activity of 4.36×10^5 dpm/ml and was kindly provided by Professor J. H. Richards.

Bray's scintillation solution[19] was prepared from 60 g naphthalene (Eastman, recrystallized), 4 g PPO (Packard

Instrument Co.), 0.2 g POPOP (Packard), 20 ml ethylene glycol, and 100 ml methanol, diluted to one liter with p-dioxane (Baker and Adamson reagent).

Preparative Scale Irradiations

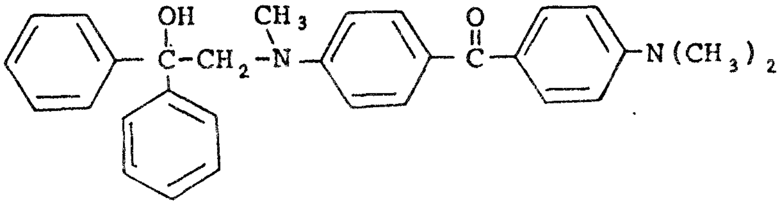
Michler's ketone (268 mg - 1.0 mmole) and benzophenone (455 mg - 2.5 mmole) were dissolved in 250 ml of 2-propanol. The solution was poured into a 250 ml pyrex reactor and degassed by bubbling with nitrogen, pre-saturated with 2-propanol, for at least thirty minutes. The center well contained a Hanovia 450 watt medium-pressure lamp with a uranium glass filter. To prevent overheating of the lamp inside the uranium glass filter, a slow stream of dry nitrogen was passed in from the bottom of the well.

The solution was irradiated for about three hours with a slow bubbling of nitrogen to agitate the solution. A large amount of yellow precipitate formed during the irradiation. The precipitate was filtered, washed with 2-propanol, and dried by suction. Typical yields were about 250-350 mg, representing a 55-75% conversion of Michler's ketone. The crude photoproduct contained small amounts of benzpinacol, which could be removed by a few hours of Soxhlet extraction with boiling 95% ethanol. The remaining material was shown to be homogeneous by thin layer chromatography on silica gel with elution by about twenty different solvents. Its melting point was 173-175°.

One experiment was performed exactly as above, using benzene rather than 2-propanol as solvent. The same photoproduct was obtained with 31% conversion in 3 hours, about half as efficient as the reaction in 2-propanol.

Identification of the Photoproduct

The photoproduct was considered to be 4-[N,N-dimethylamino]-4'-[N'-(2",2"-diphenyl-2"-hydroxyethyl)-N'-methylamino]benzophenone (I).



(I)

This assignment was based upon the consistency of the following data with the above structure.

Infrared spectrum - A broad carbonyl stretching frequency appeared at 1600 cm^{-1}. The carbonyl stretching frequency of Michler's ketone appears at the same frequency. The extremely low frequency has been related to the strong electron-donating effects of the two dialkylamino groups.[20]

A broad hydroxyl O-H stretch appears at 3400 cm^{-1}.

Ultraviolet spectrum - The ultraviolet spectrum in dichloromethane appeared very similar to that of Michler's ketone, with a slightly longer tail into the visible.

λ_{max} = 356 nm ($\varepsilon = 3.5 \times 10^4\ M^{-1}\ cm^{-1}$)

λ_{max} = 245 nm ($\varepsilon = 1.9 \times 10^4\ M^{-1}\ cm^{-1}$)

Nuclear magnetic resonance spectrum - All attempts at obtaining a 60 MHz nmr spectrum gave disappointing results - the peaks were unexpectedly broad and weak. Most of the expected qualitative features could be discerned, however.

<u>60 MHz Nmr Absorptions (in δ)</u>

Photoproduct (I)	Michler's Ketone	Benzpinacol	Assignment
2.96	3.00		N-Methyls
6.52	6.60		
6.70	6.75		Aromatic
7.43	7.67		AA'BB'
7.69	7.85		Quartet
7.1 - 7.4 broad		7.0 - 7.4 multiplet	Aromatic Multiplet
2.55		3.00	Hydroxyl

Mass spectrum - The mass spectrum [23,24] showed a parent molecular ion at 450 mass units. Although the 450 peak was considerably smaller than the 448 peak, the ratio of the M:M+1:M+2 peaks allowed unequivocal assignment of 450 as the parent molecular ion.[25]

Calculated for $C_{30}H_{30}N_2O_2$:

$$M:M+1:M+2 = 100:35:3$$

$$450:451:452 = 100:30:7$$

$$448:449:450 = 100:36:21$$

Furthermore, the mass spectrum showed many of the expected peaks.

Mass Number	Relative Intensity	Cation Assignment
450	10	M
449	17	M - H
448	47	M - 2H
268	165	$M - \phi_2CO$
267	190	$M - \phi_2COH$
254	500	$M - \phi_2CO - CH_3 + H$
253	470	$M - \phi_2CO - CH_3$
240	45	$M - \phi_2CO - 2CH_3 + 2H$
239	60	$M - \phi_2CO - 2CH_3 + H$

Mass Number	Relative Intensity	Cation Assignment
224	45	$M - \phi_2CO - N(CH_3)_2$
182	2500	ϕ_2CO
148	480	$(CH_3)_2N\phi CO$
121	45	$(CH_3)_2N\phi + H$
119	45	$(CH_3)_2N\phi - H$
105	5500	ϕ-CO
77	2800	ϕ
51	890	$\phi - C_2H_2$

M = Photoproduct (I) $\phi = C_6H_5$

The mass spectrum of Michler's ketone showed corresponding peaks at 268, 254, 240, 224, 148, 120, 77, and 51.

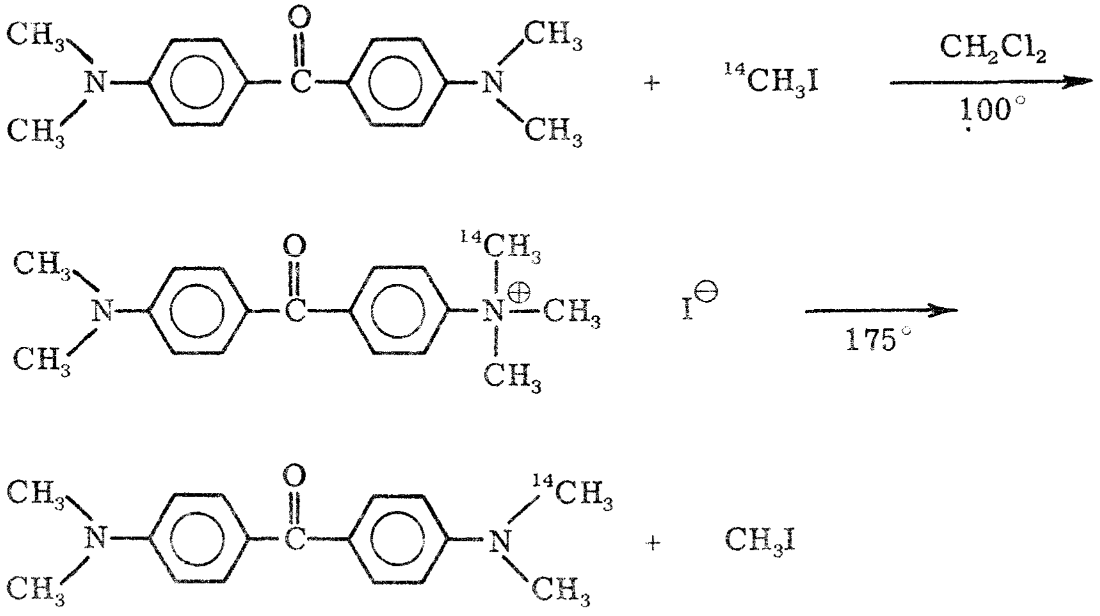
Meta-stable transitions were observed for 148 → 120 (97.3), 77 → 76 (75.0), 182 → 105 (60.6), 105 → 77 (56.5), and 77 → 51 (33.8).

Elemental Analysis - The microanalytical data[26] for photoproduct I were only in fair agreement with the expected composition.

	Calculated	Found
C	79.97	78.77
H	6.71	6.50
N	6.22	6.58
O	(7.10)	(8.15)

C-14 Labelling of Michler's Ketone

A simple, highly efficient method was developed for the incorporation of a C-14 label into Michler's ketone. The amine functions of Michler's ketone were quaternized with C-14 methyl iodide and the resulting quaternary iodide pyrolyzed to yield a statistical incorporation of C-14 methyl groups into the Michler's ketone.



The apparatus in which two quaternization-pyrolysis cycles were performed is shown in Figure I.

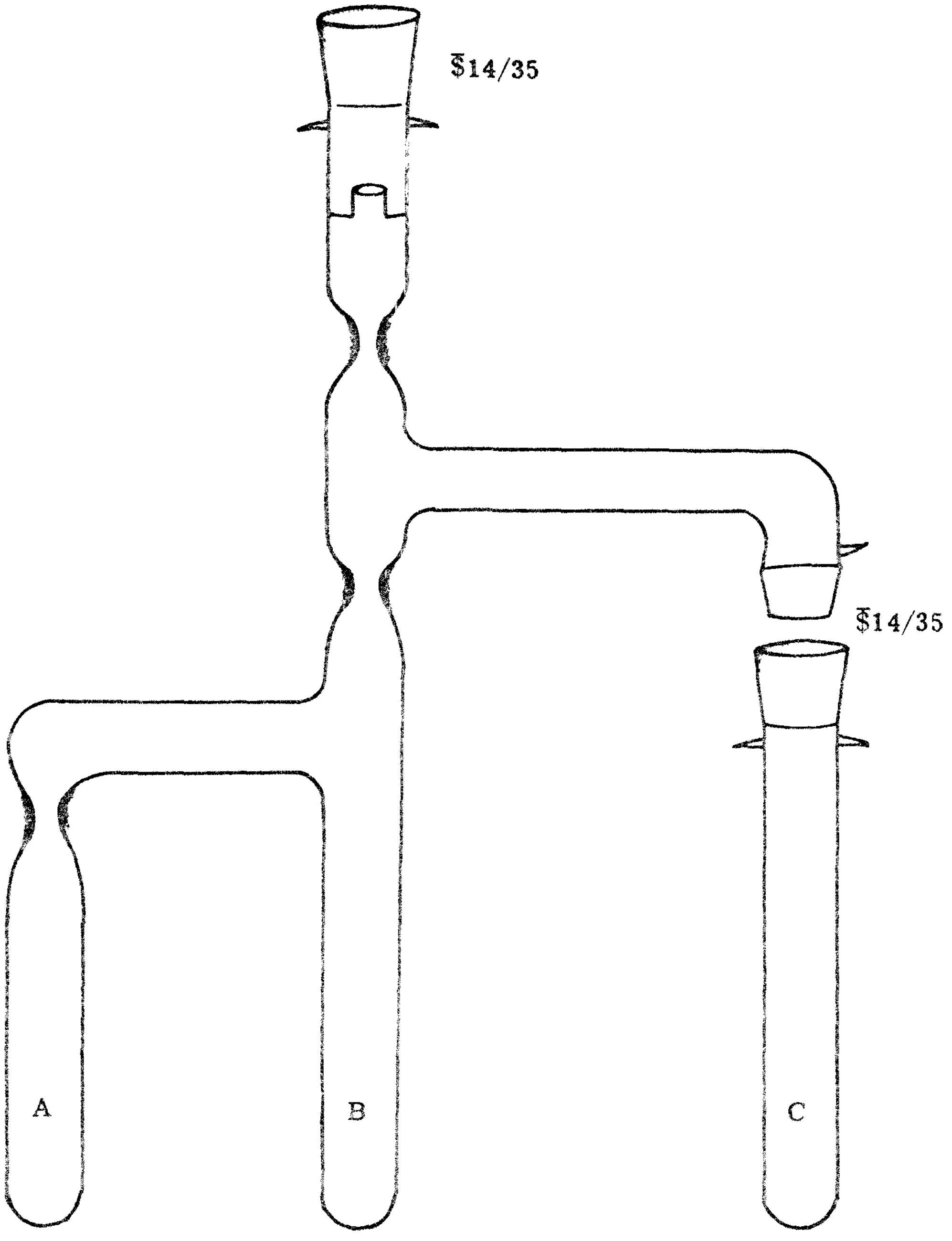
A solution of 134 mg (0.50 mmole) of Michler's ketone in 4 ml of methylene chloride was placed by syringe into tube B of the apparatus. An additional 1 ml of solvent was used to rinse the syringe to assure quantitative transferral of the Michler's ketone. Into tube C was placed the breakseal tube containing 71 mg (0.50 mmole) of C-14 methyl iodide (total activity 0.50 mcurie). A steel magnet was very carefully placed on top of the breakseal. The apparatus was then attached to a vacuum manifold and degassed through two freeze-pump-thaw cycles to pressures of 1×10^{-3} mm and 5×10^{-4} mm. The upper constriction was sealed, annealed, and allowed to cool while the solution in tube B remained frozen in liquid nitrogen. The breakseal tube was then broken and the methyl iodide quickly distilled into tube B. After more than sufficient time for complete distillation, the liquid nitrogen level was raised well above the region where the methyl iodide had condensed and the next constriction was sealed. This thick-wall seal was subjected to thorough annealing while the sample remained frozen in liquid nitrogen. After attaining room temperature, the reaction cell was immersed in an oil bath held at 95-105° for 60 hours. During this period, the reaction solution turned from yellow to pink-

Figure I

Apparatus for the C-14 Labelling of

Michler's Ketone

Apparatus for C-14 Labelling of Michler's Ketone



1/2" thick wall pyrex

orange. Occasionally solvent would distill into sidearm A and was simply poured back.

After 60 hours of reaction, the solvent was distilled into tube A by removing tube A from the oil bath. Removal of the last traces of solvent from tube B was rendered difficult by bumping. Cooling tube A in Dry Ice-acetone with tube B at room temperature seemed most effective. The remaining red solid in tube B was then pyrolyzed by heating gradually to its melting point. Melting began at about 172° and was marked by vigorous gas evolution. Tube A was frozen in liquid nitrogen to assure collection of the evolved methyl iodide. Heating was continued to 180°, although melting and gas evolution ceased at 176°.

After this first cycle, the two tubes containing solid and solvent were allowed to return to room temperature. The solvent was poured back into tube B to initiate an exact repetition of the quaternization-pyrolysis cycle. After the second such cycle, the solvent, frozen in liquid nitrogen, was sealed off. Tube B was cooled and then opened by cutting rather near the bottom, leaving the solid residue in a convenient cup. From there, it was transferred quantitatively to a sublimator. A single sublimation at 150°, 0.05 mm, yielded beautiful pale yellow needles of weight 100 mg (75%) and m.p. 173-173.5°.

A stock solution was prepared from 42.3 mg of the product in 50 ml of 2-propanol (calculated 3.15×10^{-3} M). This solution was diluted 1:100 for an ultraviolet absorption spectrum, which confirmed that the solution was 3.1×10^{-3} M. Exactly 1 ml of the diluted solution was taken for scintillation counting. By comparison with 20 μl of C-14 toluene radioactivity standard (4.36×10^{5} dpm/ml), the labelled Michler's ketone was shown to have a specific activity of 0.71 mcurie/mmole. This corresponds to a 71% incorporation of C-14 methyl groups into the Michler's ketone. It is notable that the maximum statistical incorporation would be 80%, if there were complete equilibration of the five equivalents of methyl groups.

Quantum Yield Determinations

Solutions for irradiation were prepared from stock solutions of 3.0×10^{-3} M Michler's ketone (specific activity 0.071 mc/mmole) and 3.0×10^{-3} M benzophenone in 2-propanol. Exactly 3 ml of solution was pipetted into half-inch thick-wall pyrex tubes with constrictions. The thick-wall tubing was found necessary to eliminate cracking during the freeze-pump-thaw degassing cycles. The tubes were degassed by three freeze-pump-thaw cycles to pressures of 1×10^{-3} mm, 5×10^{-4} mm, and 5×10^{-4} mm. The tubes were carefully annealed after sealing, and kept in the dark as much as possible. The tubes were irradiated on a 366 nm merry-go-round apparatus.[21] Ferrioxalate actinometry[22] was performed in two half-inch thick-wall pyrex tubes, identical to the tubes in which the irradiations were performed. The lamp intensity was measured immediately before and immediately after irradiation periods and was reproducible within 5%.

The irradiated tubes were opened and the solvent completely evaporated at room temperature by blowing nitrogen over the sample. A small amount of nonradioactive photoproduct was added to the residue to enhance the visibility of the photoproduct spot in the subsequent thin layer chromatographic separation. The solid material was then completely dissolved in a small amount of chloroform, and all of the solution was streaked onto two silical gel plates. The plates were prepared from 230 g Silical Gel PF (254 + 366) in 150 ml methanol and 450 ml distilled water, spread 1 mm thick on 5 cm × 20 cm plates. The photoreaction mixture was eluted with 2% methanol in chloroform, usually giving a good separation of Michler's ketone ($R_f = 0.3$) and the photoproduct ($R_f = 0.0\text{-}0.1$). The two bands were distinctly yellow and were easily located. Use of an ultraviolet lamp further enhanced their visibility and also located the benzophenone band ($R_f = 0.6$). The lower two bands were scraped off the plate into Büchner filter funnels, and the silica gel was eluted with three 3 ml portions of 60% methanol in chloroform. This procedure was shown to elute over 98% of the radioactivity. It was found necessary to elute the material from the silica gel because the scintillation counting showed substantial quenching in the presence of silica gel. It was further noted that both Michler's ketone and the photoproduct seemed to undergo a slow reaction on silica gel, as indicated by a slow darkening of the bands. The elution was performed as quickly as possible after the chromatographic elution and drying of the plates.

The radioactive fractions were eluted directly into a scintillation vial, where the solvent was evaporated by blowing nitrogen over the sample which was warmed in a hot water bath. Bray's scintillation solution (15 ml) was added and the residue completely dissolved by vigorous shaking. Scintillation counting was performed on a Packard Instrument Co. Tri-Carb Liquid Scintillation Counter. Each tube was subjected to two independent analyses and each scintillation vial was counted twice on each of the three independent channels. Background counts were subtracted and the percentage of the total count in each fraction was determined. It was demonstrated that an insignificant amount of radioactivity (less than 0.1%) lay outside of the two fractions normally collected.

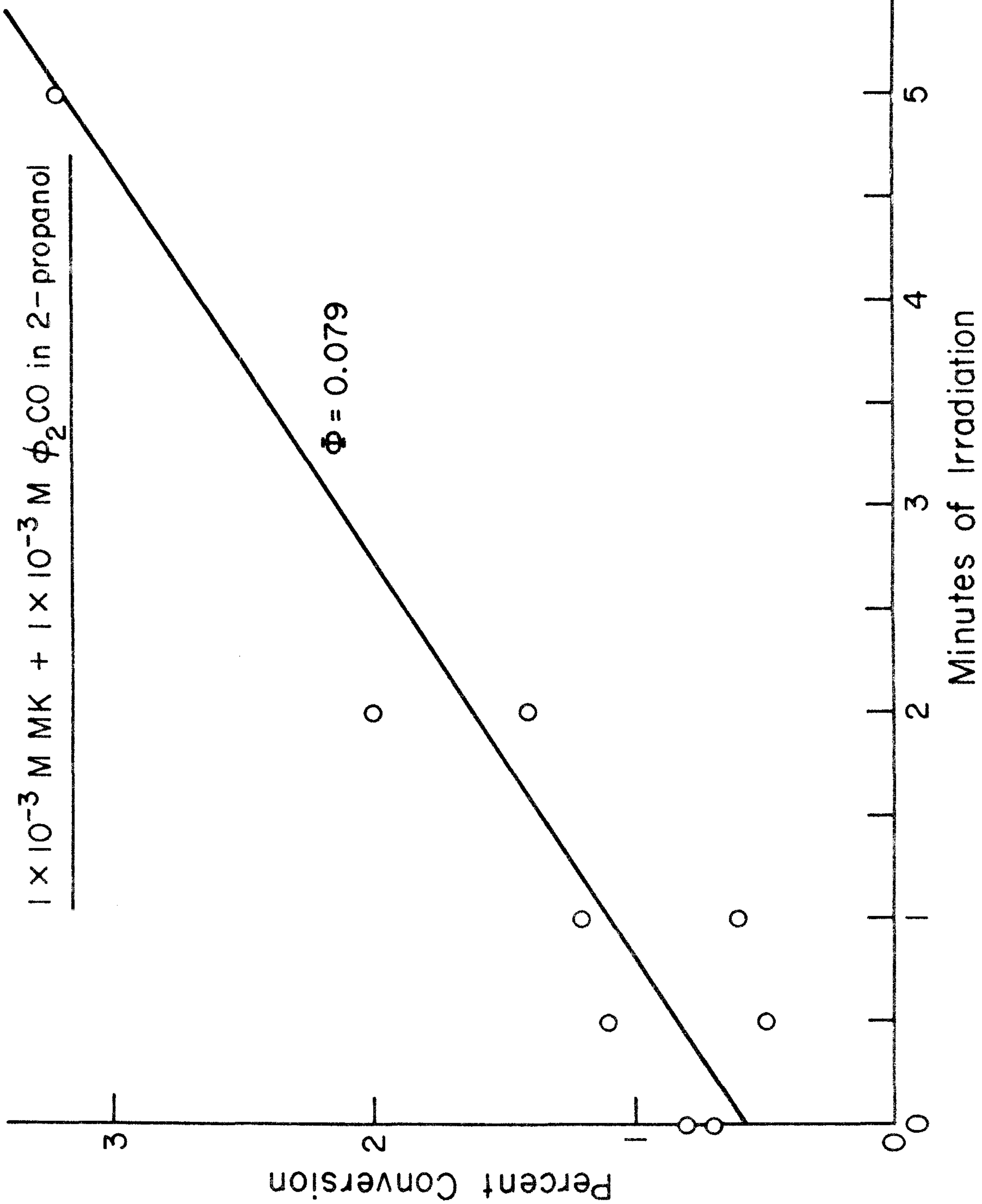
The total count in a tube containing 1 × 10^{-3} M Michler's ketone was 370,000 cpm. Normally well over 100,000 cpm was applied to each of the two plates, so that counting was quick (one minute sufficed) and precise. The accuracy was limited mainly by the effectiveness of the chromatographic separation. Most of the scatter in the points in Figure II can probably be attributed to this problem.

Each quantum yield determination was the result of duplicate analyses on at least five tubes, representing different irradiation times (as in Figure II). Percent conversion was plotted as a function of time and the best straight line was fitted by least-squares analysis. Correlation coefficients were normally greater than 0.90, despite the appearance of substantial scatter. The slope of the straight line, the amount of substrate irradiated, and the incident light intensity led directly to the quantum yield:

$$\Phi = \frac{(\text{conversion per minute})(\text{moles irradiated})}{(\text{einsteins per minute})}$$

Figure II

Quantum Yield for Photoproduct Formation


1 × 10^{-3} M MK + 1 × 10^{-3} M ϕ_2CO in 2-propanol
$\Phi = 0.079$
Percent Conversion
Minutes of Irradiation
0
1
2
3
0
1
2
3
4
5

Flash Photolysis Procedures

The apparatus and general procedures for the flash photolysis studies were exactly as described in part I of this thesis.

III. RESULTS

In the photoreaction of Michler's ketone with benzophenone, several different types of intermediates may possibly be anticipated - excited states, neutral radicals, and radical ions. Two powerful techniques are available for the study of photointermediates of these types. Esr spectra and decay kinetics have been obtained for photolytically-produced free radicals.[27,28] In addition, flash photolysis studies can offer a wealth of information regarding the electronic absorption spectrum and decay kinetics of photointermediates.[29]

Esr Studies

Irradiation of 1×10^{-2} M Michler's ketone plus 5×10^{-2} M benzophenone in 2-propanol in an esr cavity gave rise to no observable paramagnetic signal. Slightly improved results were obtained upon irradiation of 1×10^{-3} M Michler's ketone plus 3×10^{-3} M benzophenone in 2-propanol in a flow system through the esr cavity. In this case, a weak signal was observed, corresponding in width (7 gauss) and position (free spin) to that of benzophenone ketyl. The spectrum could be neither resolved nor analyzed for decay kinetics, however.

Later quantum yield studies suggested that the quantum efficiency of the photoreaction was somewhat too low to produce a suitable steady-state concentration of photointermediates. Irradiation of 5×10^{-2} M benzophenone in 2-propanol, a high quantum yield reaction, did give the characteristic esr spectrum and decay kinetics[30] of benzophenone ketyl radical.

Flash Photolysis of Michler's Ketone

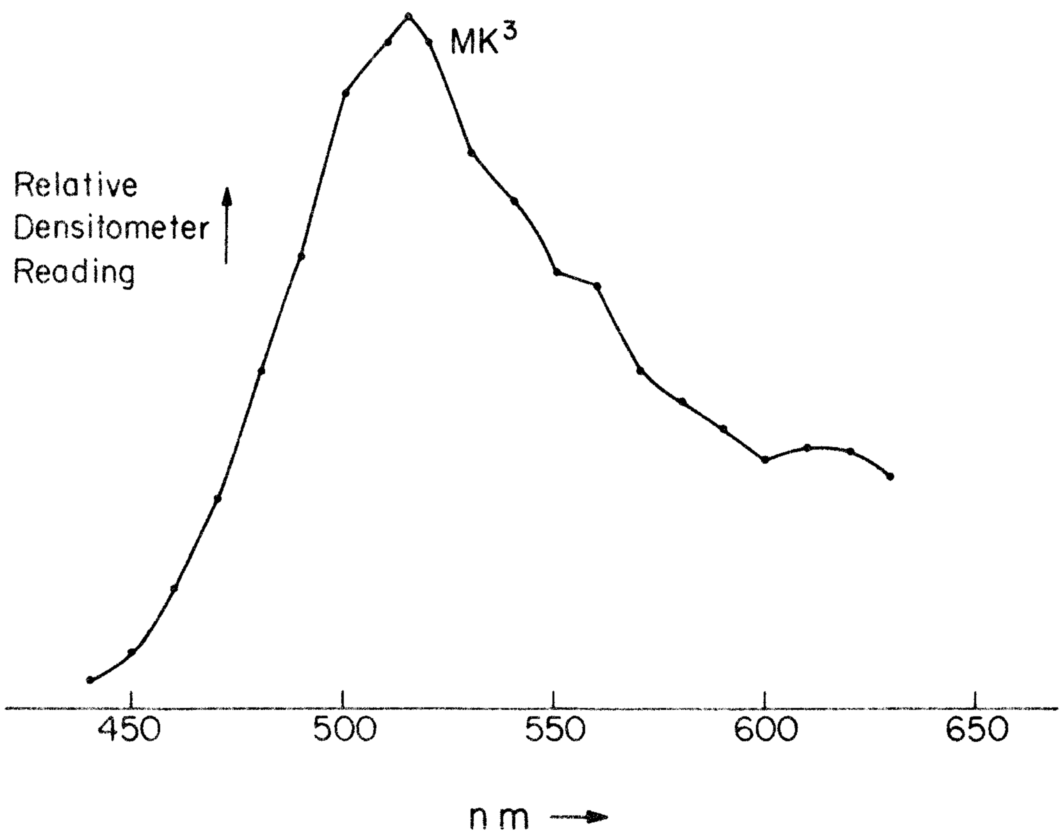
Flash photolysis of 1×10^{-4} M Michler's ketone in 2-propanol produced an intermediate with the absorption spectrum shown in Figure III. This spectrum was assigned to the triplet state of Michler's ketone.

The kinetics for the disappearance of Michler's ketone triplet were measured at both 500 nm and 600 nm and found to be identical. The decay was rather cleanly first-order, as shown in Figure IV. This is quite typical for triplet decay in fluid solution, and is the result of quenching of the excited state by traces of impurities.[31] Nevertheless, the calculated first-order rate constant, $k_1 = 1.4 \times 10^4$ sec^{-1}, was repeatedly reproducible within ± 20%.

Flash photolysis of 1×10^{-4} M Michler's ketone in toluene or hexane gave a different transient absorption spectrum. The spectrum was broader and the lifetime con-

Figure III

Absorption Spectrum of Michler's Ketone Triplet

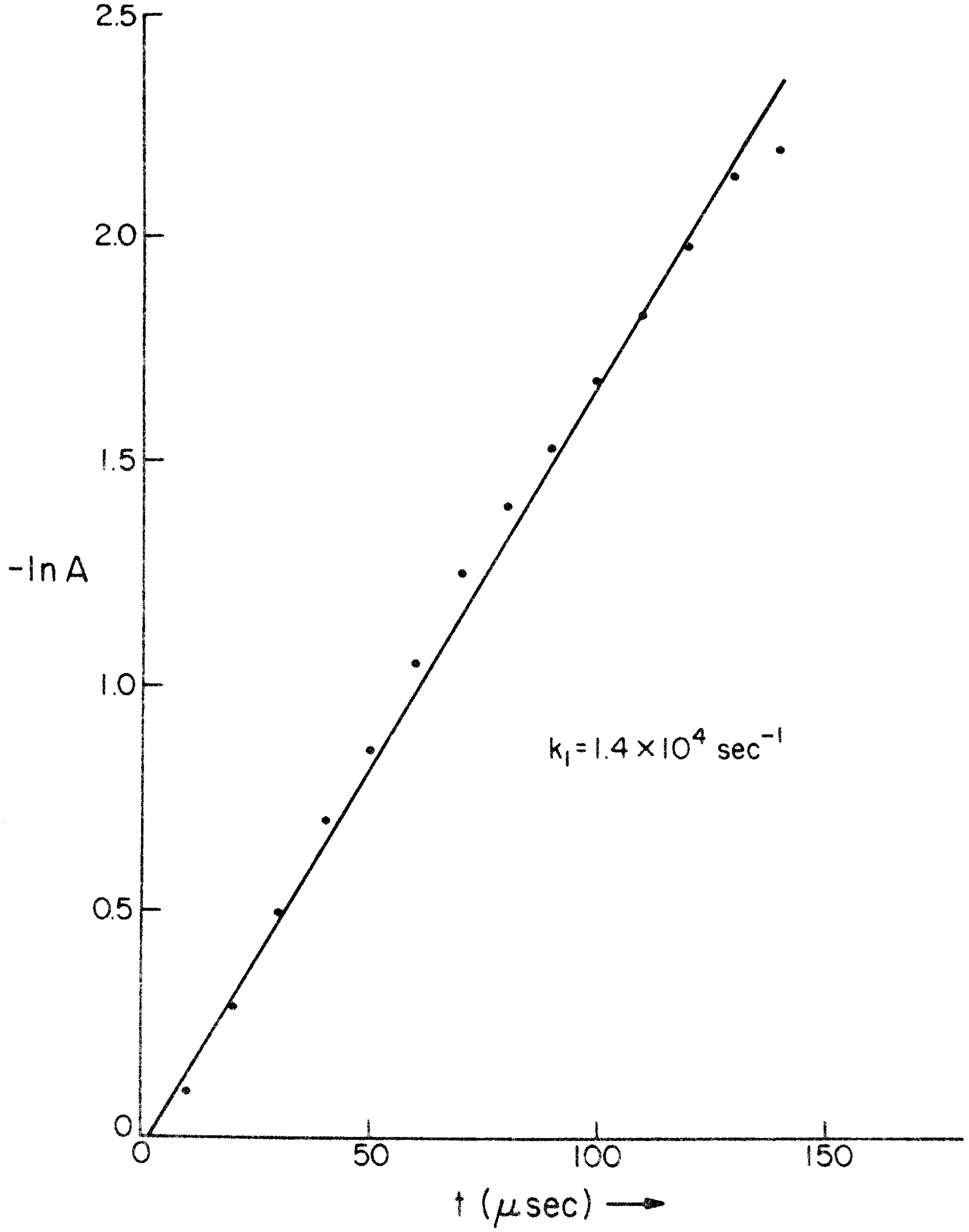


1×10^{-4} M MK in 2-propanol

Figure IV

Decay Kinetics for Michler's Ketone Triplet

1×10⁻⁴ M MK in 2-propanol



siderably longer than for Michler's ketone triplet. This photointermediate was tentatively considered to be the ketyl of Michler's ketone, on the basis of the known reactivity of Michler's ketone in such nonpolar solvents.[11]

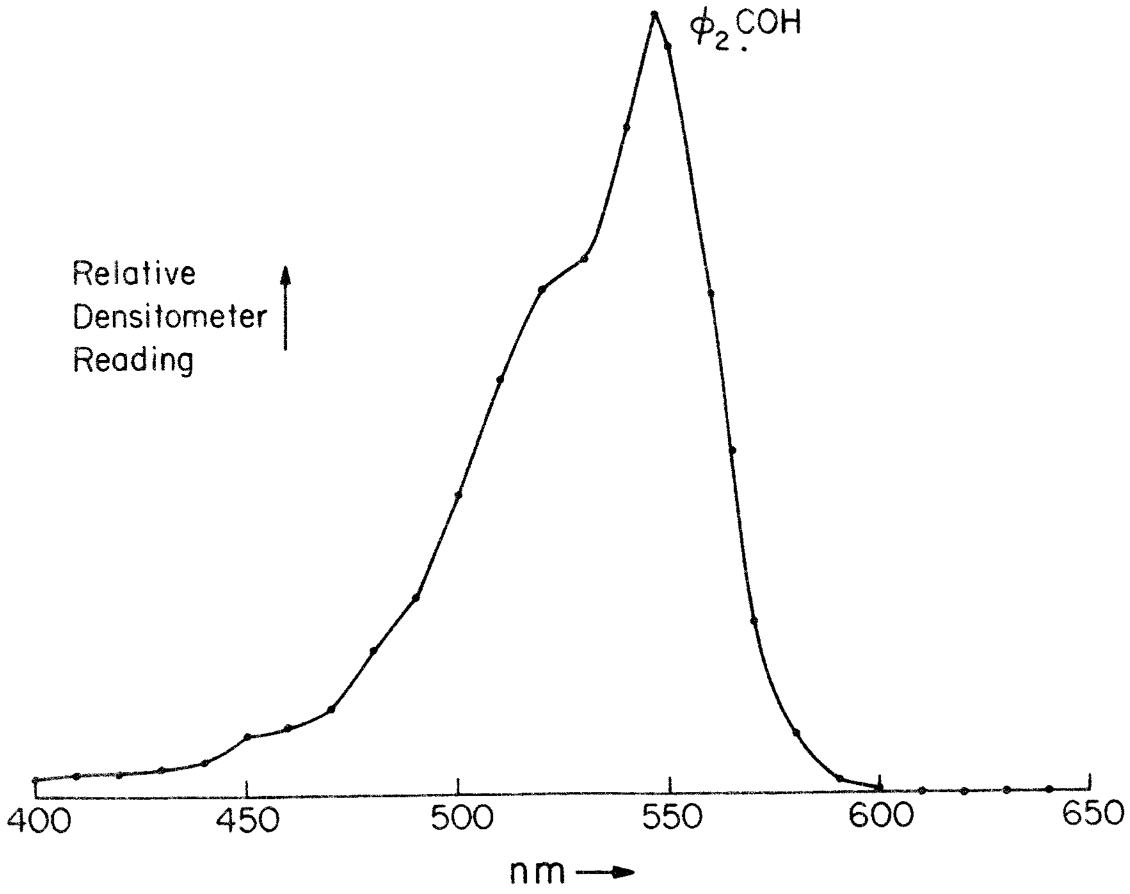
Flash Photolysis of Benzophenone in 2-Propanol

Flash irradiation of 5×10^{-4} M benzophenone in 2-propanol gave rise to the well-known spectrum of the benzophenone ketyl radical[32] (Figure V). The kinetics of disappearance were monitored at the 546 nm absorption maximum, where the extinction coefficient is known.[3] The decay fit second-order kinetics very nicely and the rate constant extracted was 3.1×10^{7} M^{-1} sec^{-1} (Figure VI). This rate constant differs from the best value appearing in the literature[3] only by a factor of 2, which this author feels is appropriate to include in the definition of the rate constant:

$$-d[\phi_2\underset{\bullet}{C}OH]/dt = 2k_2[\phi_2\underset{\bullet}{C}OH]^2$$

Figure V

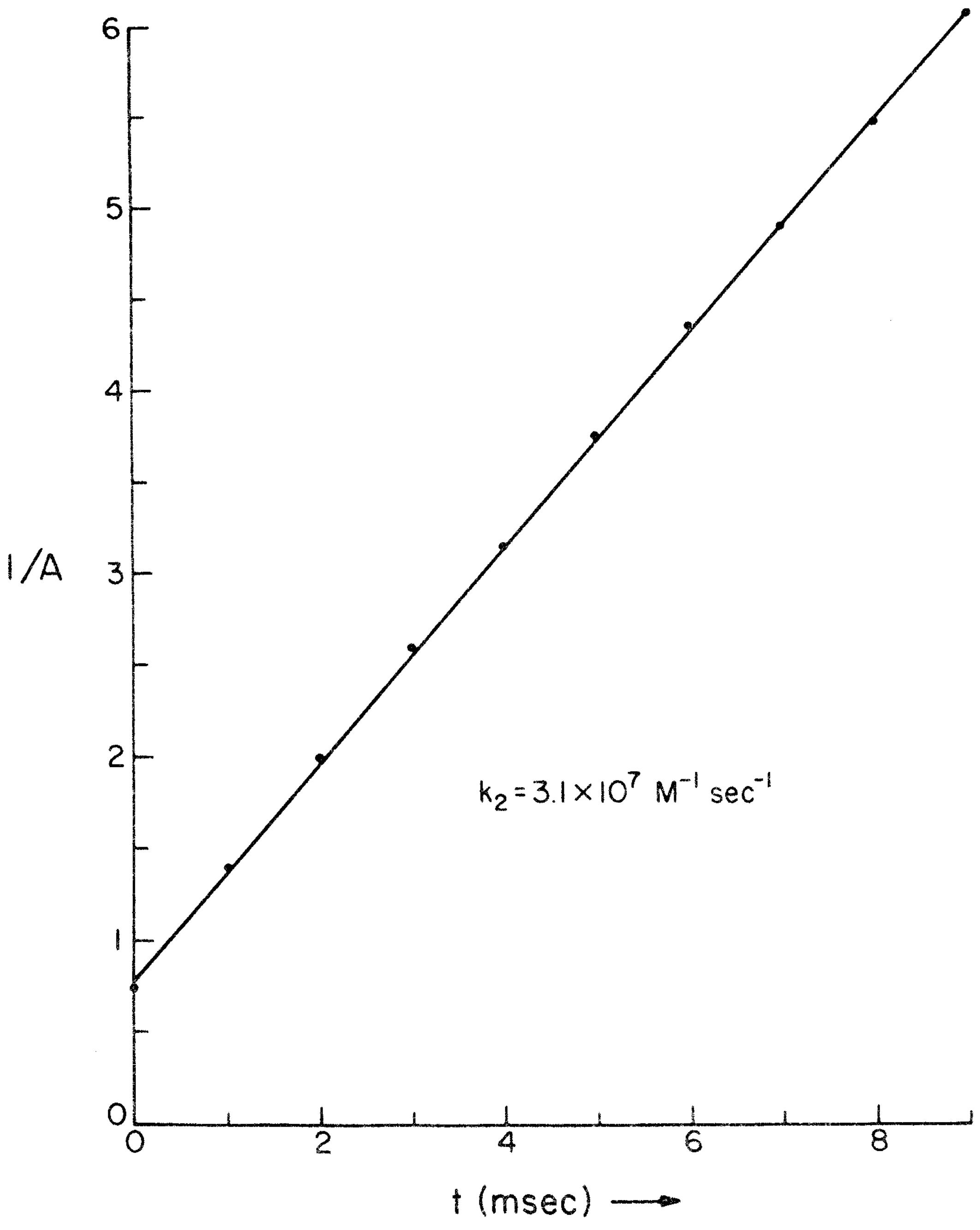
Absorption Spectrum of Benzophenone Ketyl



5×10^{-4} M ϕ_2CO in 2-propanol

Figure VI

Decay Kinetics for Benzophenone Ketyl



$5 \times 10^{-4} M\ \phi_2CO$ in 2-propanol

$k_2 = 3.1 \times 10^7\ M^{-1}\ sec^{-1}$

Flash Photolysis of Michler's Ketone Plus Benzophenone in 2-Propanol

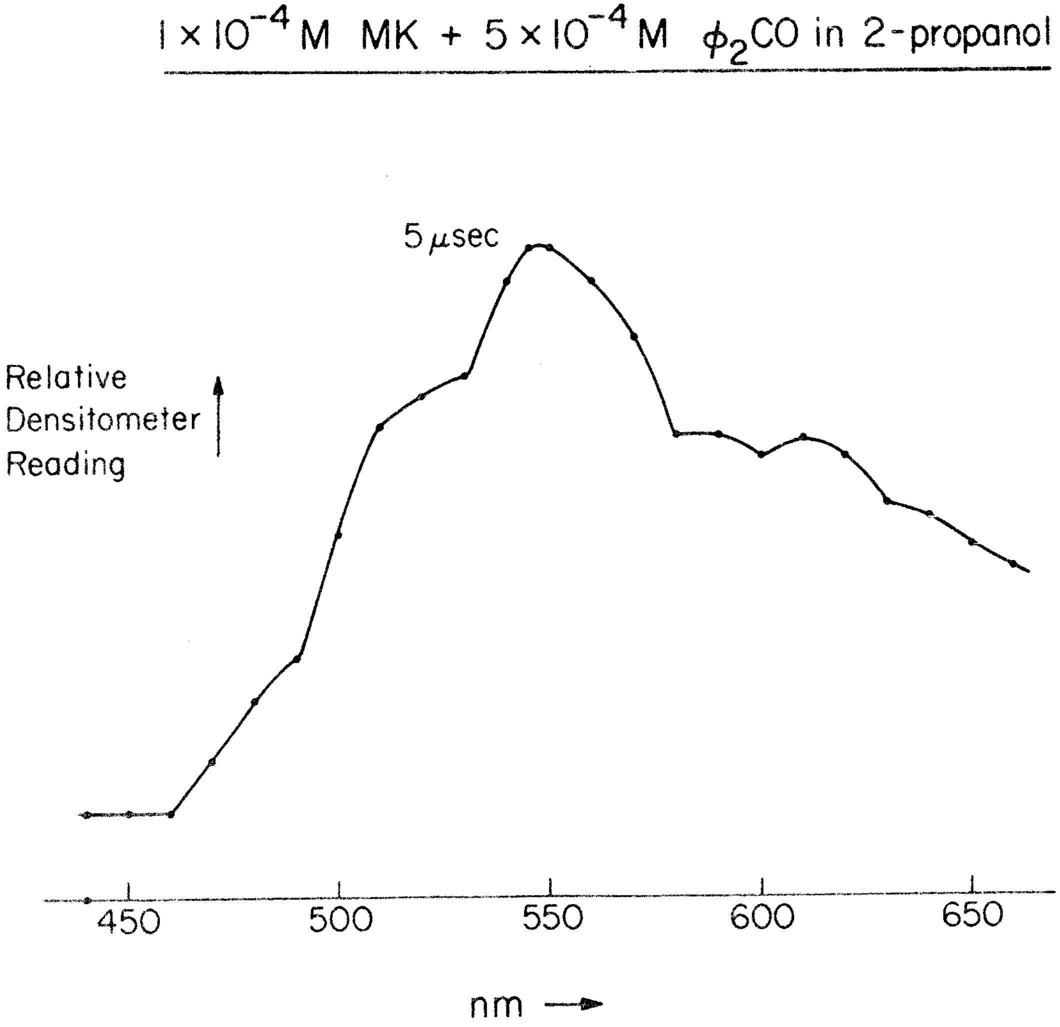
Spectra

Flash photolysis of 1×10^{-4} M Michler's ketone plus 5×10^{-4} M benzophenone in 2-propanol solution produced a broad transient absorption spectrum with several apparent maxima (Figure VII). This spectrum was taken 5 μsec after initiation of the excitation flash and represents the shortest delay time available. The spectrum is mainly reminiscent of the Michler's ketone triplet spectrum (Figure III), except for the absorption maximum near 546 nm, which would be characteristic of the benzophenone ketyl spectrum (Figure V).

As the transient spectrum decayed, however, its features changed (Figure VIII). At decay times of 1 msec and more, the spectrum of benzophenone ketyl clearly predominated. It should be reemphasized at this point that the entire spectrum had decayed substantially up to 1 msec, so that the excess benzophenone ketyl was really not a very large fraction of the total initial ketyl concentration. The import of the changing transient spectrum is the demonstration that there are at least two absorbing photointermediates in the Michler's ketone-benzophenone system. One intermediate is the benzophenone

Figure VII

Photointermediates
in the Michler's Ketone-Benzophenone System
at 5 μsec



1×10^{-4} M MK + 5×10^{-4} M ϕ_2CO in 2-propanol
5 μsec
Relative Densitometer Reading
450
500
550
600
650
nm →

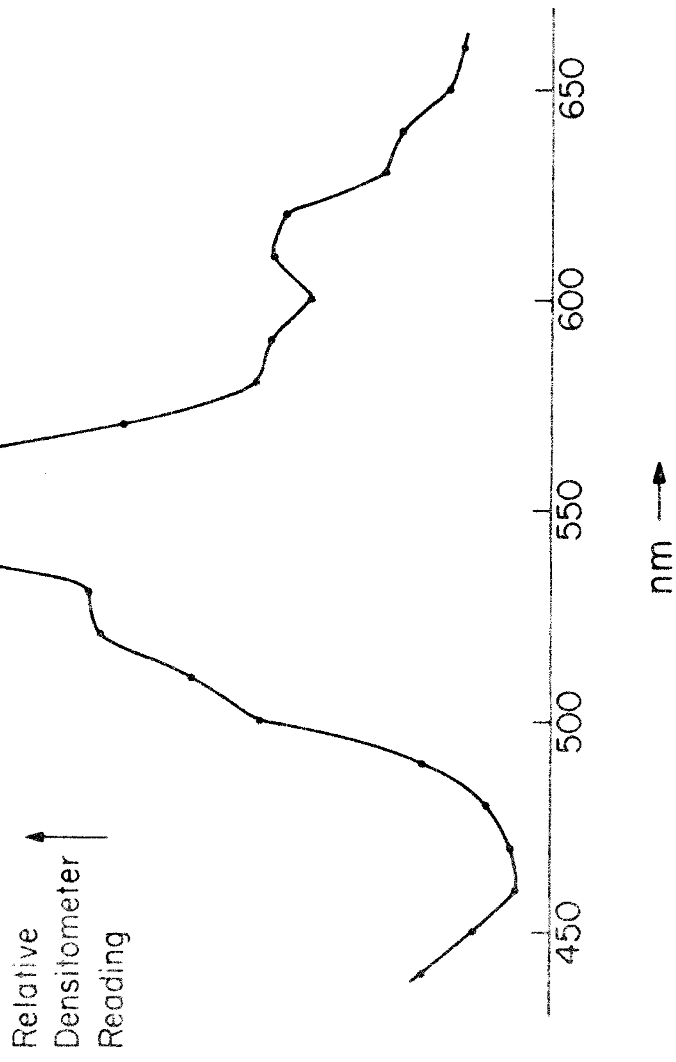
Figure VIII

Photointermediates

in the Michler's Ketone-Benzophenone System

at 1 msec

1×10^{-4} M MK + 5×10^{-4} M ϕ_2CO in 2-propanol



ketyl radical and the second would appear to be derived from Michler's ketone.

Decay Kinetics

An analysis of the decay kinetics in the Michler's ketone-benzophenone system also pointed directly to the presence of two photointermediates. The decay of the 546 nm absorption was a clear case of a two-component decay curve (Figure IX). At decay times greater than 1 msec, the decay curve could be fit to second-order kinetics. In fact, the rate constant was precisely what would be expected for benzophenone ketyl. This is in full accord with the finding that a residual spectrum of benzophenone ketyl remains after the other photointermediate has died away. These data suggest that benzpinacol should appear as a minor photoproduct. Thin layer chromatographic analyses suggested that traces of benzpinacol were present, but it was never isolated.

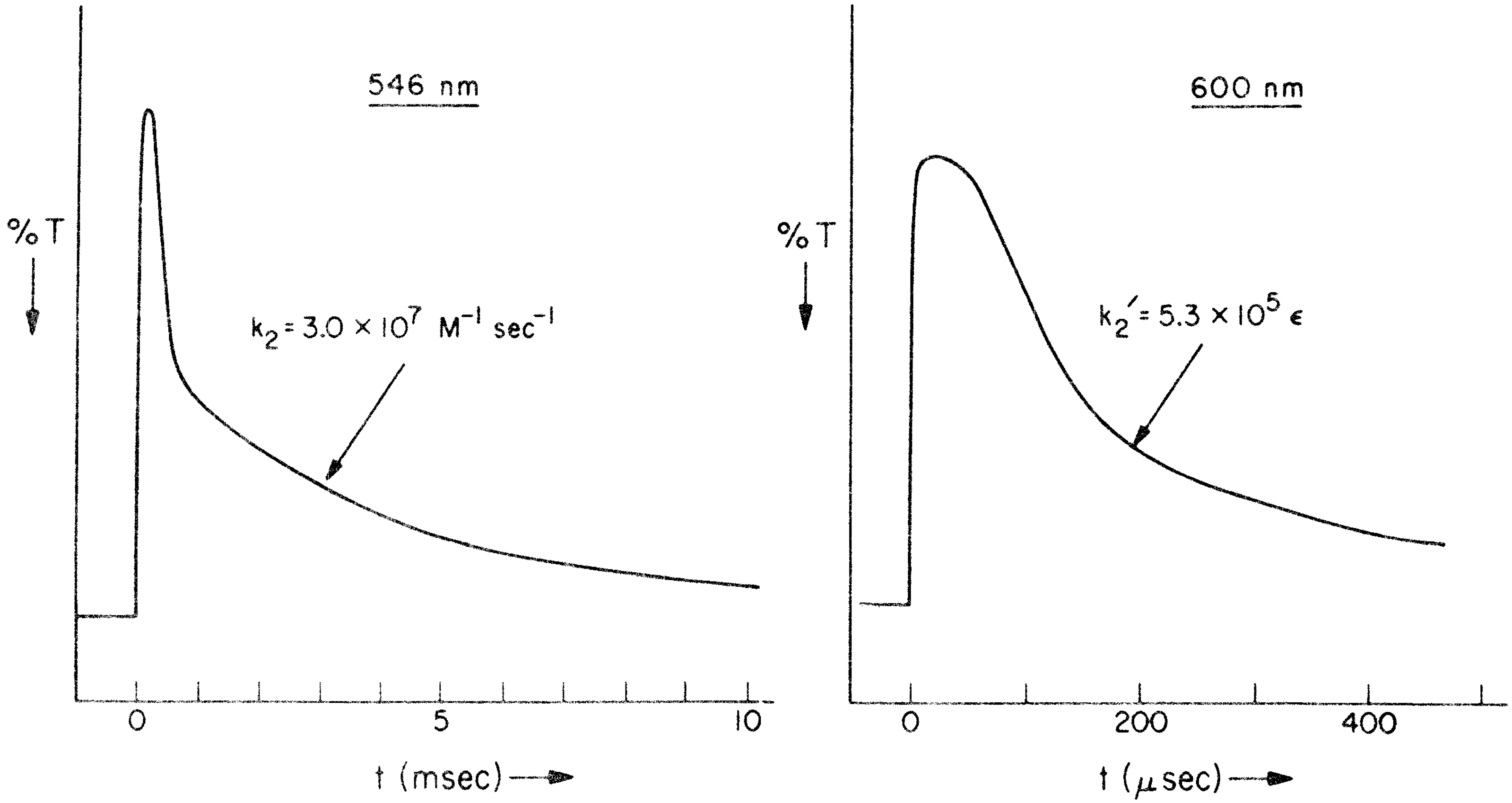
The initial rapid decay represents the great majority of the total reaction, since the initial decay goes from 2% to 67% transmittance (or > 90% of the optical density). This decay was able to be isolated by monitoring at 600 nm, where benzophenone ketyl does not absorb (Figure IX). An independent flash photolysis analysis of benzophenone in

Figure IX

Decay Curves

in the Michler's Ketone-Benzophenone System

1×10^{-4} M MK + 5×10^{-4} M ϕ_2CO in 2-propanol



2-propanol confirmed that there was no interference from benzophenone photointermediates at 600 nm. The decay kinetics at 600 nm in the Michler's ketone-benzophenone system were very cleanly second-order (Figure X). However, the second-order rate constant can only be put in terms of the extinction coefficient of the photointermediate at 600 nm, $k_2' = 5.3 \times 10^5\ \varepsilon$.

The effect of benzophenone concentration on the decay of the 600 nm absorption was studied. Without benzophenone, the absorbing species is simply Michler's ketone triplet and the decay is first-order. As benzophenone is added, the decay gradually moves to second-order. At concentrations of benzophenone of 2×10^{-4} M and lower, the decay is mixed first- and second-order. At concentrations greater than 2×10^{-4} M, the decay is cleanly second-order and is independent of benzophenone concentration. The change from first- to second-order kinetics and an increase in overall lifetime with added quencher was truly a unique observation. However, it must be borne in mind that the quenching act is giving rise to a new intermediate, of longer lifetime and with second-order decay kinetics.

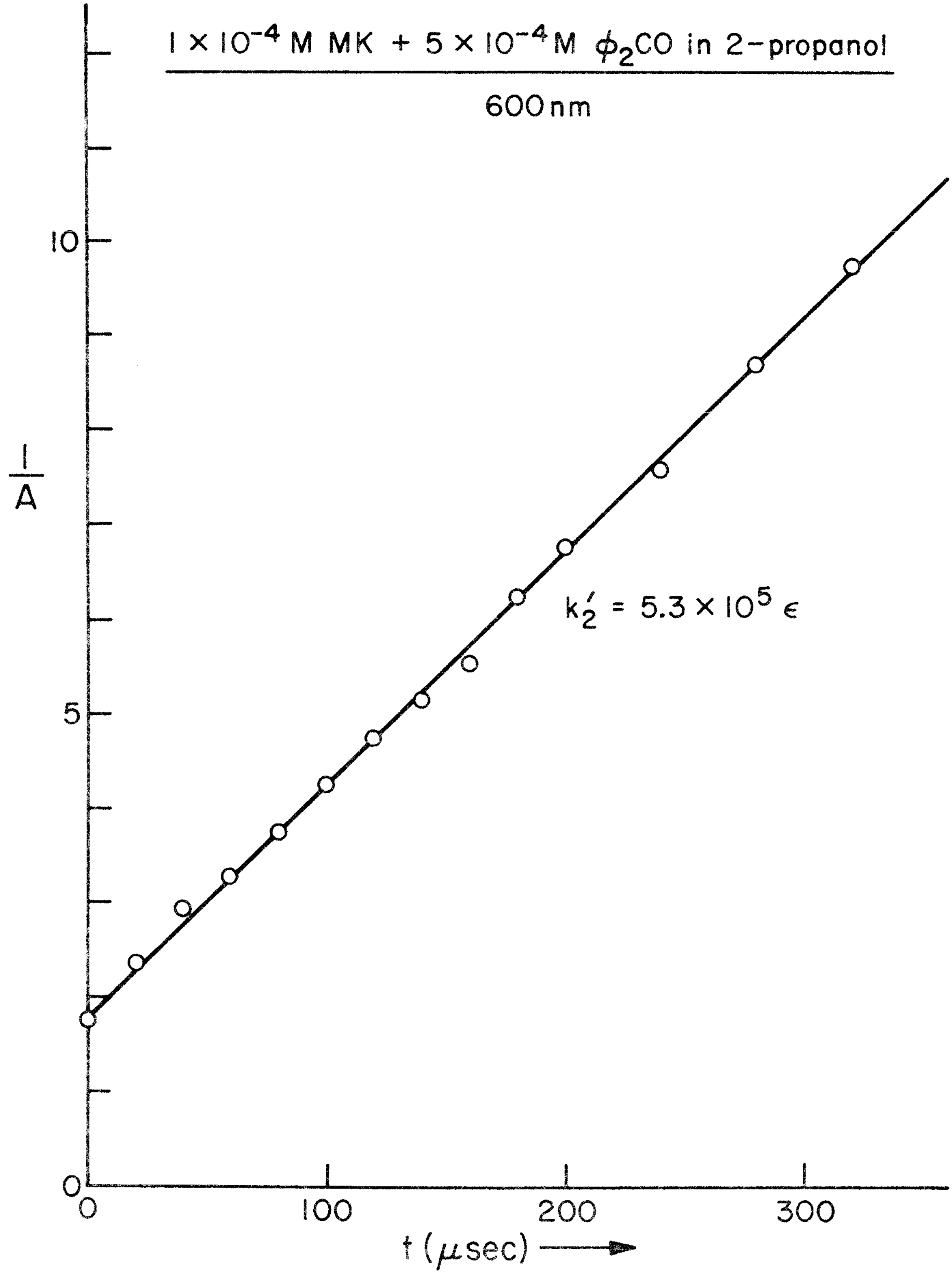
Thus the main decay mode of the Michler's ketone photointermediate is a second-order disappearance. There also exists a small amount of residual benzophenone ketyl

Figure X

Decay Kinetics

for the Michler's Ketone-Benzophenone Photointermediate

at 600 nm


1×10^{-4} M MK + 5×10^{-4} M ϕ_2CO in 2-propanol
600 nm
$\frac{1}{A}$
10
5
0
$k_2' = 5.3 \times 10^5\ \epsilon$
0
100
200
300
t (μsec)

which decays by its normal second-order coupling reaction.

Quenching Experiments

In order to ascertain the nature of the photointermediate absorbing at 600 nm, quenching experiments with 1,3-cyclohexadiene were undertaken. 1,3-Cyclohexadiene is an excellent triplet quencher because it has a relatively low triplet energy - 54 kcal/mole.[33] Lifetime quenching experiments monitored at both 500 nm and 600 nm demonstrated that Michler's ketone triplet was quenched by 1,3-cyclohexadiene at a rate of 1.8×10^9 M^{-1} sec^{-1}, very near the expected maximum rate in 2-propanol.[34] Concentrations of the diene of about 1×10^{-5} M were sufficient to substantially decrease the triplet lifetime of Michler's ketone.

In sharp contrast to these findings, the 600 nm absorption in the Michler's ketone-benzophenone system decayed at exactly the same rate with added concentrations of 1,3-cyclohexadiene up to 5×10^{-4} M. The lack of any lifetime quenching rules out a triplet state as the identity of the 600 nm photointermediate. Most likely, the intermediate is a radical ion or free radical derived from Michler's ketone.

Although the 600 nm decay kinetics were unaffected by added 1,3-cyclohexadiene quencher, the initial intensity of the 600 nm absorption was much lower than in the absence of diene. This can certainly be attributed to quenching of Michler's ketone triplet, the precursor to the 600 nm intermediate. The rate of quenching by benzophenone can be estimated by the relative competition between benzophenone and 1,3-cyclohexadiene for Michler's ketone triplets. It can be estimated that the intensity of the 600 nm absorption was diminished to one-half by about 10^{-5} M diene. The concentration of benzophenone in this series of experiments was 3×10^{-4} M, so 1,3-cyclohexadiene is at least thirty times as good as a quencher for Michler's ketone triplets. This suggests a benzophenone quenching rate of the order of 10^{7} M^{-1} sec^{-1}. The exact rate is best obtained from quantum yield studies, however.

Quantum Yield Determinations

The quantum efficiency for conversion of Michler's ketone into photoproduct I was determined by thin layer chromatographic separation of the photoreaction mixture of labelled Michler's ketone and benzophenone. It was demonstrated that no radioactivity lay outside the photoproduct band and the Michler's ketone band, so the quantum yields presented here represent both the quantum yield of photoproduct formation and the quantum efficiency of Michler's ketone disappearance. All studies were performed with 366 nm irradiation.

The quantum efficiency of the photoreaction was found to be 0.079 ± 0.010 at concentrations of 1×10^{-3} M Michler's ketone plus 1×10^{-3} M benzophenone. Under these conditions, Michler's ketone absorbs > 99.6% of the incident light at 366 nm.

The effect of doubling the concentration of either Michler's ketone or benzophenone was found to be quite small. The quantum yield for photoproduct formation was 0.071 ± 0.010 for 2×10^{-3} M Michler's ketone plus 1×10^{-3} M benzophenone and 0.073 ± 0.010 for 1×10^{-3} M Michler's ketone plus 2×10^{-3} M benzophenone. The invariance of the quantum yield with benzophenone concentration suggests that all the Michler's ketone triplet states are being quenched by benzophenone. If this is the case, it should be expected that the quantum efficiency of the photoreaction is insensitive to benzophenone concentration, at least in the range of concentrations for which it is convenient to measure quantum yields.

An alternative method for obtaining the benzophenone quenching rate constant is to compare it with another added quencher. 1,3-Cyclohexadiene was shown to quench the triplet state of Michler's ketone at a rate of 1.8×10^9 M^{-1} sec^{-1}, and does not quench any of the other photointermediates. Hence a direct competition between benzophenone and 1,3-cyclohexadiene for Michler's ketone triplets can be established. The result of these studies is shown in Figure XI.

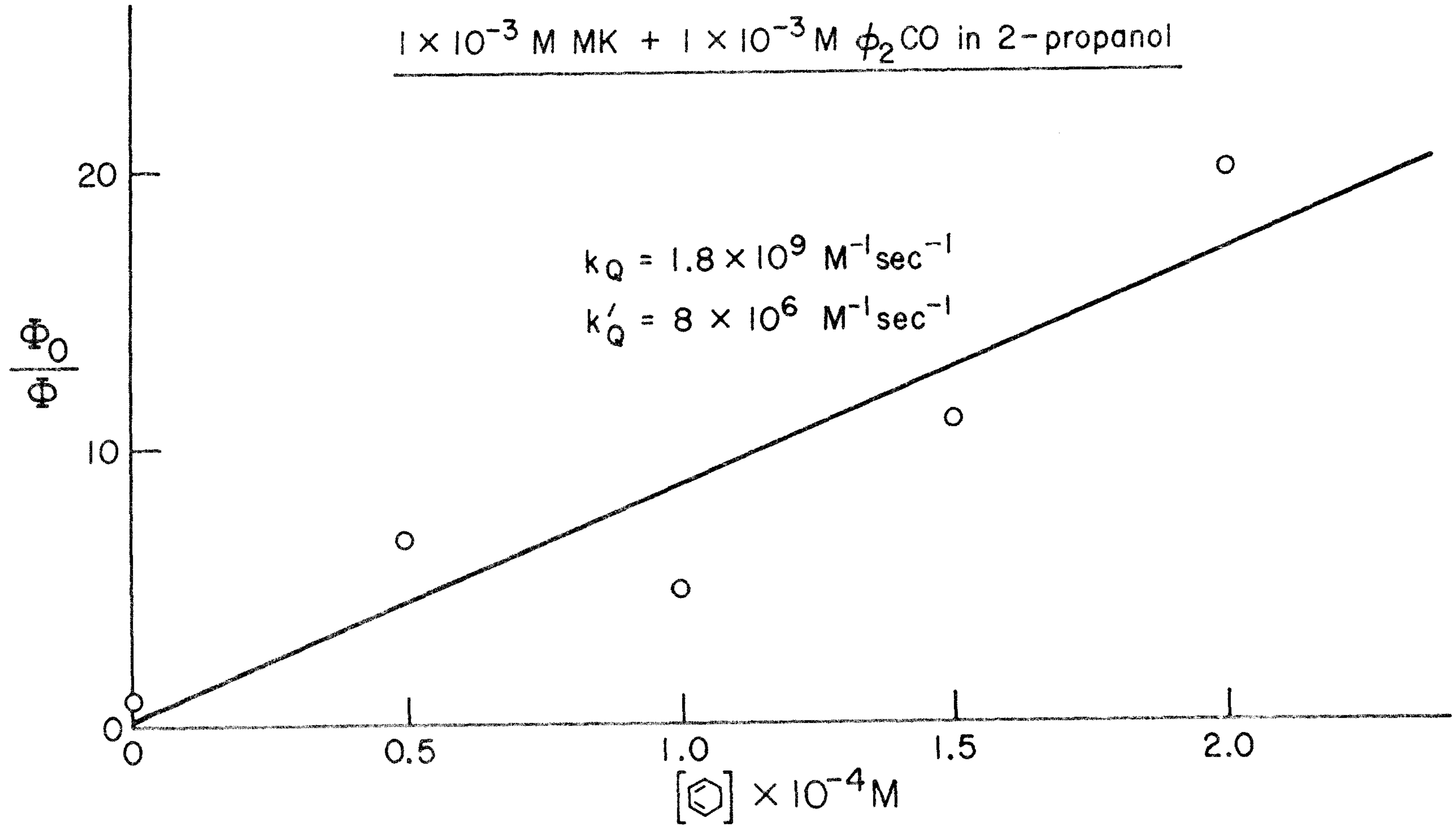
The slope of the least-squares line is 8.3×10^4 M^{-1}, with correlation coefficient 0.919. Since the quenching rate for 1,3-cyclohexadiene is $k_Q = 1.8 \times 10^9$ M^{-1} sec^{-1}, this points to a triplet decay rate for Michler's ketone of 2.2×10^4 sec^{-1}. Since the decay rate in the absence of benzophenone is 1.4×10^4 sec^{-1}, the benzophenone accounts for a decay of 8×10^3 sec^{-1}, or $k_Q' = 8 \times 10^6$ M^{-1} sec^{-1}.

Visible-Ultraviolet Spectra of Mixtures of Michler's Ketone and Benzophenone

The electronic absorption spectra of mixtures of Michler's ketone and benzophenone, at a variety of relative concentrations and with either benzene or 2-propanol as solvent, were always the exact sum of the component absorption spectra. These findings rule out any strong ground-state interactions between benzophenone and Michler's ketone.

Figure XI

Quenching of the Quantum Yield
for Photoproduct Formation
by 1,3-Cyclohexadiene


1 × 10^{-3} M MK + 1 × 10^{-3} M ϕ_2CO in 2-propanol
$k_Q = 1.8 \times 10^9\ M^{-1} sec^{-1}$
$k'_Q = 8 \times 10^6\ M^{-1} sec^{-1}$
$\frac{\Phi_0}{\Phi}$
20
10
0
0
0.5
1.0
1.5
2.0
[⌬] × 10^{-4}M

IV. DISCUSSION

On the basis of the results just described, the following mechanism is proposed to account for the photoreaction of Michler's ketone with benzophenone in 2-propanol.

Proposed Mechanism

$$MK \xrightarrow{h\nu} MK^1 \xrightarrow{\qquad} MK^3$$

$$MK^3 \xrightarrow{k_1} MK$$

$$MK^3 + \phi_2CO \xrightarrow{k_2} [MK\cdots\cdot\phi_2CO]^3$$

$$MK^3 + CHD \xrightarrow{k_3} MK + CHD^3$$

$$[MK\cdots\cdot\phi_2CO]^3 \xrightarrow{k_4} MK\cdot + \phi_2\underset{\bullet}{C}OH$$

$$[MK\cdots\cdot\phi_2CO]^3 \xrightarrow{k_5} MK + \phi_2CO$$

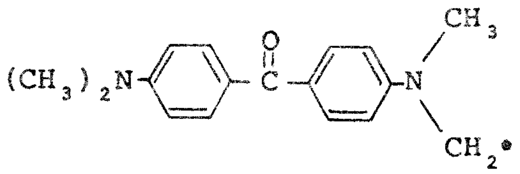
$$MK\cdot + \phi_2\underset{\bullet}{C}OH \xrightarrow{k_6} I$$

$$MK\cdot + \phi_2\underset{\bullet}{C}OH \xrightarrow{k_7} MK + \phi_2CO$$

CHD = 1,3-Cyclohexadiene

MK = Michler's Ketone

MK· =



The mechanism must certainly begin with the triplet state of Michler's ketone. There are no known reactions of the singlet states of either benzophenone or Michler's ketone, since the intersystem crossing is so efficient.[35] Essentially all of the incident light is absorbed by the Michler's ketone, due to its mammoth charge-transfer absorption band between 300-400 nm ($\varepsilon_{max} = 3.6 \times 10^4\ M^{-1}\ cm^{-1}$). Furthermore, if any excitation did reach the benzophenone molecules, the concentrations of Michler's ketone were such that nearly all of the benzophenone triplets would be quenched by direct triplet energy transfer to Michler's ketone. Hence quantitative formation of Michler's ketone triplet is expected as the initial step in the photoreaction.

The unique character of this reaction lies in the manner by which the excitation residing in the Michler's ketone triplet can be utilized in the subsequent reactions. Michler's ketone triplet is normally unreactive in 2-propanol solution.[11] The subsequent reaction amounts to a hydrogen atom transfer from Michler's ketone triplet to benzophenone. This step, of course, strongly recalls the characteristic reaction of triplet benzophenone - hydrogen abstraction. However, the intermediacy of triplet benzophenone in this reaction can be rather firmly ruled out. Transfer of the triplet excitation from Michler's ketone to benzophenone would be endothermic by over 7 kcal/mole.[12]

This is sufficient to rule out triplet energy transfer at any significant rate.[36,37]

Alternatively, the reaction may be visualized as similar to amine quenching of triplet benzophenone by charge transfer.[14-17] Such charge-transfer reactions again are characteristic of excited benzophenone, and only doubly excited amines have been shown capable of charge-transfer to ground state benzophenone.[18]

For these reasons, it is most useful to consider that Michler's ketone triplet and benzophenone interact by forming some sort of excited complex, or "exciplex".[38] Such an interaction is simply visualized as a means by which Michler's ketone and benzophenone "share" the triplet energy. It is convenient to consider that benzophenone is imparted partial triplet character in this interaction, because the hydrogen abstraction reaction so closely resembles reactions of triplet benzophenone. It should be emphasized that the exciplex need not be a genuine intermediate with a measurable lifetime. The exciplex is simply postulated as a means to better visualize the type of interaction which must take place between Michler's ketone and benzophenone.

The possibility that the hydrogen transfer reaction is actually a charge transfer step followed by proton transfer is quite reasonable. The lowest excited states of Michler's ketone are of charge-transfer character,[9] so that an intermolecular charge-transfer may not be totally foreign to the nature of Michler's ketone. It may certainly be that the exciplex derives its strength of interaction from charge-transfer interactions. It may even be the case that the exciplex is an ion pair and that proton transfer is a distinct succeeding step. This possibility is difficult to rule out in view of the abundant literature dealing with excited state interactions between amines and benzophenones.[13-18] However, one argument may be presented in favor of the simpler, one-step hydrogen transfer. The reaction proceeds very well when benzene is the solvent rather than 2-propanol. The same photoproduct is obtained, although in reduced yield. Most of the reduction in yield can be accounted for by the shift in the absorption spectrum of Michler's ketone in going from 2-propanol to benzene. Michler's ketone in benzene (λ_{max} = 347 nm) absorbs much less light through a uranium glass filter than Michler's ketone in 2-propanol (λ_{max} = 360 nm). Thus it appears that the photoreactivity in benzene parallels the photoreactivity in 2-propanol. If an ion pair is a discrete intermediate stage in the photoreaction, there would be expected a large decrease in the efficiency of the photoreaction in proceeding from the polar to nonpolar solvent. The lack of a strong solvent effect points to the intermediacy of radicals rather than ions.

Perhaps the best way to visualize the interaction between Michler's ketone triplet and benzophenone is with as few specific details as possible. The net result of the interaction is hydrogen transfer from Michler's ketone to benzophenone.

The exciplex interaction thus leads to a pair of radicals, benzophenone ketyl and the corresponding radical derived from Michler's ketone (MK·). The latter free radical is responsible for the transient absorption at 600 nm and longer wavelengths. Its decay is purely second-order, which is a potential source of confusion since the radical does not couple with itself according to product analyses. The decay is second-order because MK· couples only with benzophenone ketyl, which is present in essentially equal concentrations at all times.

$$-d[MK\cdot]/dt = k_2'[MK\cdot][\phi_2\underset{\bullet}{C}OH]$$

but if $[\phi_2\underset{\bullet}{C}OH] = [MK\cdot]$ at all times

$$-d[MK\cdot]/dt = k_2'[MK\cdot]^2$$

$$k_2' = 5.3 \times 10^5\ \varepsilon \text{ at } 600\text{ nm}$$

As previously noted, at least 90% of the disappearance of the optical density at 546 nm occurs in this rapid second-order reaction. However, the presence of some side reactions is demonstrated by the existence of residual benzophenone ketyl after this initial disappearance of MK·. There are two means of explaining this phenomenon. Either benzophenone ketyl is initially formed in larger concentrations than MK·, or MK· undergoes some side reactions which cause it to disappear before all the benzophenone ketyl is used up. The first possibility would be difficult to understand unless some excitation were actually reaching the benzophenone. This seems quite unlikely, since calculations point to absorption of over 99% of the light by Michler's ketone. A very plausible scheme can be conceived, however, which not only destroys some MK·, but creates extra benzophenone ketyl. MK· may abstract hydrogen from 2-propanol to return to Michler's ketone and produce the 2-hydroxy-2-propyl radical. This radical can then transfer hydrogen to benzophenone, forming acetone and benzophenone ketyl.[3]

$$\mathrm{MK}\cdot + (\mathrm{CH_3})_2\mathrm{CHOH} \longrightarrow \mathrm{MK} + (\mathrm{CH_3})_2\underset{\bullet}{\mathrm{C}}\mathrm{OH}$$

$$(\mathrm{CH_3})_2\underset{\bullet}{\mathrm{C}}\mathrm{OH} + \phi_2\mathrm{CO} \longrightarrow (\mathrm{CH_3})_2\mathrm{CO} + \phi_2\underset{\bullet}{\mathrm{C}}\mathrm{OH}$$

In order to reemphasize the perspective, such a scheme would represent side reactions amounting to less than 10% of the total reaction.

Quantum Yield Analysis

The proposed mechanism leads to the following kinetic analyses for the quantum yield of formation of photoproduct I.

$$\Phi = \frac{abk_2[\phi_2CO]}{k_1 + k_2[\phi_2CO] + k_3[CHD]}$$

$$\Phi_0 = \frac{abk_2[\phi_2CO]}{k_1 + k_2[\phi_2CO]}$$

$$\frac{\Phi_0}{\Phi} = 1 + \left(\frac{k_3[CHD]}{k_1 + k_2[\phi_2CO]}\right)$$

$$a = (k_4/k_4 + k_5) \qquad b = (k_6/k_6 + k_7)$$

$$k_1 = 1.4 \times 10^4 \text{ sec}^{-1}$$

$$k_2 = 8 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$$

$$k_3 = 1.8 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$$

$$(ab) = 0.22$$

The rate constants for the first three steps have been measured. The second-order disappearance of MK· was also measured, but must be expressed in terms of the unknown extinction coefficient of MK· at 600 nm - $k_6 + k_7 = 5.3 \times 10^5 \epsilon$. Decay kinetics for the exciplex, k_3 and k_4, were impossible to measure, but are probably exceedingly rapid in view of our interpretation of the exciplex. The factors a and b represent partitioning ratios of the exciplex and the radicals, respectively. It is certainly impossible to determine how much of the inefficiency occurs at each of these two points. The significance of the product (ab) = 0.22 is that this represents the maximum quantum yield for the reaction, at infinite benzophenone concentration.

Concluding Remarks

At this point, some concluding remarks concerning the novelty of this reaction mechanism would be appropriate. The mechanism is highlighted by the postulated exciplex between the triplet state of Michler's ketone and benzophenone. Descriptions of the interactions which define this exciplex were consciously avoided because specific details of that nature would be difficult, if not meaningless, to attempt to characterize. A sufficient description is that the exciplex is an interaction which leads to hydrogen transfer from triplet Michler's ketone to benzophenone.

To our knowledge, this is the first postulation of a triplet exciplex in a photochemical reaction. However, there are several reactions, such as the Paterno-Büchi oxetane formation reaction,[39] which could very well be described in terms of a triplet exciplex. We fully expect the triplet exciplex to be a useful concept in photochemistry, more commonplace than novel.

V. REFERENCES

[1] G. Ciamician and P. Silber, <u>Chem. Ber.</u>, <u>33</u>, 2911 (1900).

[2] G. Ciamician and P. Silber, <u>Chem. Ber.</u>, <u>34</u>, 1541 (1901).

[3] A. Beckett and G. Porter, <u>Trans. Faraday Soc.</u>, <u>59</u>, 2038 (1963).

[4] J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald and R. B. Martin, <u>J. Amer. Chem. Soc.</u>, <u>81</u>, 1068 (1959).

[5] H. L. J. Bäckström and K. Sandros, <u>Acta Chem. Scand.</u>, <u>14</u>, 48 (1960).

[6] N. Filipescu and F. L. Minn, <u>J. Amer. Chem. Soc.</u>, <u>90</u>, 1544 (1968).

[7] J. N. Pitts, H. W. Johnson and T. Kuwana, <u>J. Phys. Chem.</u>, <u>66</u>, 2456 (1962).

[8] A. Beckett and G. Porter, <u>Trans. Faraday Soc.</u>, <u>59</u>, 2051 (1963).

[9] G. Porter and P. Suppan, <u>Trans. Faraday Soc.</u>, <u>61</u>, 1664 (1965).

[10] G. Porter and P. Suppan, <u>Pure Appl. Chem.</u>, <u>9</u>, 499 (1965).

[11] P. Suppan, <u>Ber. Bunsenges. Phys. Chem.</u>, <u>72</u>, 321 (1968).

[12] W. G. Herkstroeter, A. A. Lamola and G. S. Hammond, <u>J. Amer. Chem. Soc.</u>, <u>86</u>, 4537 (1964).

[13] S. G. Cohen and R. J. Baumgarten, <u>J. Amer. Chem. Soc.</u>, <u>89</u>, 3471 (1967).

[14] R. S. Davidson and P. F. Lambeth, <u>Chem. Comm.</u>, 1265 (1967).

[15] R. S. Davidson, P. F. Lambeth, J. F. McKellar, P. H. Turner and R. Wilson, <u>Chem. Comm.</u>, 732 (1969).

[16] R. S. Davidson and P. F Lambeth, <u>Chem. Comm.</u>, 511 (1968).

[17] S. G. Cohen and H. M. Chao, J. Amer. Chem. Soc., 90, 165 (1968).

[18] Kh. S. Bagdasar'yan and Z. A. Sinitsyna, Dokl. Akad. Nauk SSSR, 175, 627 (1967).

[19] G. Bray, Anal. Biochem., 1, 279 (1960).

[20] N. Fuson, M. L. Josien and E. M. Shelton, J. Amer. Chem. Soc., 76, 2526 (1964).

[21] F. G. Moses, R. S. H. Liu and B. M. Monroe, Mol. Photochem., 1, 245 (1969).

[22] C. G. Hatchard and C. A. Parker, Proc. Roy. Soc., Ser. A, 235, 518 (1956).

[23] Taken by Dr. Alan Duffield with the Stanford University MS-9 Low Resolution Mass Spectrometer.

[24] Expert assistance in the interpretation was generously provided by Dr. Jean Kossanyi.

[25] Calculations based upon tables in J. Lederberg, Computation of Molecular Formulas for Mass Spectrometry, Holden-Day, Inc., San Francisco, 1964, p. 65.

[26] Spang Microanalytical Laboratories, Ann Arbor, Michigan.

[27] S. A. Weiner and G. S. Hammond, J. Amer. Chem. Soc., 91, 986 (1969).

[28] B. M. Monroe and S. A. Weiner, J. Amer. Chem. Soc., 91, 450 (1969).

[29] G. Porter, Science, 160, 1299 (1968).

[30] S. A. Weiner and G. S. Hammond, J. Amer. Chem. Soc., in press.

[31] S. Cheng Tsai and G. W. Robinson, J. Chem. Phys., 49, 3184 (1968).

[32] G. Porter and F. Wilkinson, Trans. Faraday Soc., 57, 1686 (1961).

[33] D. F. Evans, J. Chem. Soc., 1987 (1961).

[34] J. G. Calvert and J. N. Pitts, Photochemistry, John Wiley and Sons, Inc., New York, 1966, p. 627.

[35] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, *43*, 2129 (1965).

[36] W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, *88*, 4769 (1966).

[37] K. Sandros, *Acta Chem. Scand.*, *18*, 2355 (1964).

[38] J. B. Birks, *Nature*, *214*, 1187 (1967).

[39] D. R. Arnold, *Advan. Photochem.*, *6*, 301 (1968).

PROPOSITIONS

PROPOSITION 1

It is proposed that the phenomenon of steric hindrance to electronic energy transfer be characterized by studies of the rates at which substituted azo compounds quench a variety of sensitizer triplet states.

The process of triplet-triplet energy transfer is normally considered to require actual contact between the donor and acceptor molecules. This conclusion has been reached by spectroscopic studies in rigid media.[1] This requirement of contact between donor and acceptor raises the problem of steric hindrance whenever this contact is rendered difficult by bulky substituents. In a few cases, steric hindrance to energy transfer has been postulated in order to explain unexpected photochemical results.[2,3] However, a definitive characterization of the problems of steric bulk in photochemistry has yet to appear.

At the request of Professor P. D. Bartlett of Harvard University, I have performed a few flash photolysis experiments in support of a research project of P. S. Engel and P. D. Bartlett.[4] As a sidelight to these results, it appeared that the rate of quenching of triphenylene triplets by azo-2-methyl-2-propane (I) was slower than would be expected.

$$(CH_3)_3C - N = N - C(CH_3)_3$$

(I)

The triplet energy of triphenylene is 66.6 kcal/mole, while the triplet energy of I is reasonably estimated at 60 kcal/mole.[4] Thus a diffusion-controlled quenching rate (about $5 \times 10^9\ M^{-1}\ sec^{-1}$ in benzene at room temperature) was expected.[5] The quenching rate measured by flash photolysis studies was $7.7 \times 10^8\ M^{-1}\ sec^{-1}$. Probably the best explanation for this observation is that the <u>t</u>-butyl groups sterically protect the azo chromophore, making energy transfer from the aromatic sensitizer less efficient. Because the quencher (I) is such a simple molecule, this effect seems to point clearly to steric hindrance to energy transfer.

Aliphatic azo compounds are ideally suited as quenchers in studies of this type for three main reasons. 1) They undergo a characteristic, easily-monitored photochemical reaction - loss of nitrogen. 2) The portion of the molecule into which the electronic energy is accepted is relatively small and highly localized. 3) The azo functional group can be surrounded on both sides by substituents with varying steric properties.

The experiments which would clarify this phenomenon would run in two major channels - use of a variety of sensitizers and use of a variety of azo compounds. Study of a series of sensitizers with a single azo quencher will show the correlation of triplet energy with energy transfer rate. The normal correlation is an energy transfer rate at the diffusion-controlled limit while the sensitizer has a triplet energy greater than that of the acceptor by 3 kcal/mole or more. With sensitizers of lower triplet energy, the energy transfer rate falls off rapidly.[5] If steric hindrance to energy transfer is important, the expected correlation would be that energy transfer rates do not rise to the diffusion-controlled limit as rapidly as usual. In fact, it will be of interest to ascertain whether diffusion-controlled transfer ("maximum" efficiency) can be attained at all to a sterically hindered quencher. Probably, raising the sensitizer energy in order to increase the exothermicity of the transfer reaction would not be effective in making the reaction more efficient, since the cause of the inefficiency is inherent in the molecule. Energy transfer to sterically hindered quenchers would probably proceed at rates which rise slowly to some limit, below the diffusion-controlled rate. If this prediction is validated, these limiting rates may well provide a convenient scale to quantify steric hindrance of substituents.

The second type of experiments then, would compare the effects of various substituents in producing steric hindrance to energy transfer. The use of azo compounds substituted with groups more bulky than t-butyl should provide more startling examples of steric hindrance. Azo compounds substituted with less bulky substituents will provide meaningful criteria concerning the minimum requirements for steric interference.

References

[1] J. G. Calvert and J. N. Pitts, Photochemistry, John Wiley and Sons, Inc., New York, 1966, p. 342 ff.

[2] W. G. Herkstroeter, L. B. Jones and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4777 (1966).

[3] G. S. Hammond and R. S. Cole, *J. Amer. Chem. Soc.*, **87**, 3256 (1965).

[4] P. S. Engel, submitted for publication.

[5] W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).

PROPOSITION 2

It is proposed that the new technique of laser pulse photolysis be utilized for a direct observation of electronic energy transfer processes.

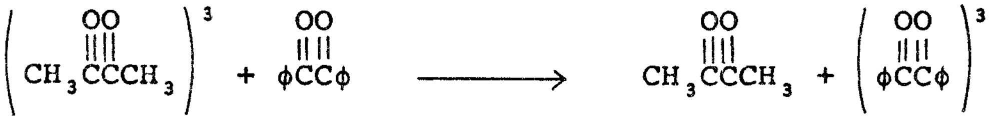
Flash photolysis is unparalleled as a technique for the observation of short-lived photochemical intermediates. It has long been restricted to the range of microseconds, however, due to the difficulty of obtaining high intensity flashes in shorter times. The advent of lasers has made available a high intensity source which can be pulsed with very short lifetimes. The first laser pulse photolysis apparatus has recently been described.[1] An ultraviolet excitation pulse of 347 nm light is obtained by passage of a Q-switched ruby laser pulse (694 nm) through a frequency doubling crystal of KDP, with 3% efficiency. The pulse lasts about 30 nsec, an improvement of about two orders of magnitude over the time resolution of conventional flash photolysis.

Suitable monitoring sources are available with a good variety of properties. The undoubled laser pulse can be separated from the excitation pulse by a prism and focused on a gas-filled cell, producing a spark which is suitable as a continuous background spectrum. By varying the gas, flash monitoring pulses with lifetimes from 30 nsec to 1 μsec are available.[1] The monitoring pulses may be delayed after the excitation flash by adding extra path length to the monitoring beam. Presumably, use of a continuous monitoring beam and a monochromator with photoelectric recording should allow decay curves to be obtained. Nanosecond response phototubes are available.[2]

On photolyzing coronene, Windsor and Novak observed spectroscopically the decay of the lowest excited singlet state and the growth of the lowest excited triplet state.[1] This is a remarkably direct observation of the process of intersystem crossing. Use of photoelectric recording to observe the kinetics of intersystem crossing is an obvious and valuable extension of this work. Unfortunately, a kinetic analysis of intersystem crossing requires a knowledge of absolute concentrations of the singlet and triplet states. Absorbance, not concentration, is measured, making it necessary to determine extinction coefficients for the absorptions of the singlet and triplet. Such determinations have been successfully carried out in flash photolysis studies by simultaneously measuring the absorbance of the triplet state and the depletion of absorbance of the ground state.[3] The improved time resolution of laser pulse photolysis should allow this method to be applied to short-lived triplet species and to singlet states. The kinetic analysis which leads to a determination of the intersystem crossing rate is presented in the appendix. Other methods for determining intersystem crossing rates are quite indirect.[4]

Direct observation of intersystem crossing suggests that this technique will lend itself readily to studies of other primary photochemical processes, such as energy transfer. For example, the heavily-studied case of triplet energy transfer from benzophenone to naphthalene[5] should be observable. Naphthalene will not absorb light at 347 nm, while benzophenone has an absorption maximum at 347 nm. Benzophenone can be selectively excited, the decay of its triplet observed spectroscopically, and the appearance of the naphthalene triplet simultaneously observed. The naphthalene triplet and the benzophenone triplet can be monitored independently at different wavelengths. Furthermore, the time scale of this energy transfer will be convenient. Benzophenone triplet has a lifetime which is relatively short, but still readily observable (2 μsec).[6] Naphthalene triplet has a long lifetime,[7] and to a first approximation will not decay during the energy transfer process. For the first time, independent determinations of the rate of energy transfer can be made by simultaneous measurement of donor decay and acceptor appearance. The kinetic analysis again requires a knowledge of extinction coefficients for the species involved. The analysis is presented in the appendix.

The ultimate value of a study of energy transfer by this technique will be in the elucidation of the processes involved in cases of inefficient energy transfer. In one system, it has been noted that the rate of triplet quenching does not equal the rate of triplet sensitization.[8]



$$\left(CH_3\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}CH_3\right)^3 + \phi\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}\phi \longrightarrow CH_3\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}CH_3 + \left(\phi\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}\phi\right)^3$$

$$K_{\text{quenching}} = 900\ M^{-1}$$

$$K_{\text{sensitization}} = 390\ M^{-1}$$

In cases of inefficient energy transfer, such as "nonvertical" energy transfer,[9] it may not be unusual that the donor triplet is quenched without an equivalent population of acceptor triplet states. When quenching rates fall far below the diffusion-controlled limit, it is quite important to differentiate between various quenching modes. If direct triplet energy transfer is energetically unfavorable, other quenching routes which do not proceed through the acceptor triplet may become important. Quenching which takes the form of a pure deactivation of an excited state has been characterized[10] and may be more common than originally considered.

Appendix

I. Intersystem Crossing Rates

$$A \xrightarrow{h\nu} A^1$$

$$A^1 \xrightarrow{k_1} A$$

$$A^1 \xrightarrow{k_2} A + h\nu'$$

$$A^1 \xrightarrow{k_3} A^3$$

$$-d[A^1]/dt = (k_1 + k_2 + k_3)\ [A^1]$$

$$d[A^3]/dt = k_3\ [A^1]$$

$$-\ell n[A^1] + \ell n\ [A^1]_0 = (k_1 + k_2 + k_3)\ t$$

A plot of $-\ell n[A^1]$ versus time will give a straight line with slope $(k_1 + k_2 + k_3)$.

$$-d[A^3]/d[A^1] = k_3/(k_1 + k_2 + k_3) \equiv \Phi_{ic}$$

A plot of $\Delta[A^3]$ versus $-\Delta[A^1]$ will give a straight line with slope $k_3/(k_1 + k_2 + k_3)$, from which k_3 may be calculated.

II. Quenching Rates and Sensitization Rates

D = donor molecule

A = acceptor molecule

$$D \xrightarrow{h\nu} D^1 \longrightarrow D^3$$

$$D^3 \xrightarrow{k_1} D$$

$$D^3 + A \xrightarrow{k_2} D + A^3$$

$$D^3 + A \xrightarrow{k_3} D + A$$

$$-d[D^3]/dt = \{k_1 + (k_2 + k_3)\ [A]\}\ [D^3]$$

$$d[A^3]/dt = k_2[A][D^3]$$

$$-\ell n[D^3] + \ell n[D^3]_0 = \{k_1 + (k_2 + k_3)[A]\}\ t$$

A plot of $-\ell n[D^3]$ versus time will give a straight line with slope $\{k_1 + (k_2 + k_3)[A]\}$. Since k_1 is available from the corresponding plot at $[A] = 0$, the sum $(k_2 + k_3)$ can be obtained.

$$-d[A^3]/d[D^3] = k_2[A]/\{k_1 + (k_2 + k_3)[A]\}$$

A plot of $\Delta[A^3]$ versus $-\Delta[D^3]$ will give a straight line with slope $k_2[A]/\{k_1 + (k_2 + k_3)[A]\}$, from which k_2 may be calculated.

References

[1] J. R. Novak and M. W. Windsor, Proc. Roy. Soc., Ser. A, 308, 95 (1968).

[2] ITT Industrial Laboratories, Fort Wayne, Indiana.

[3] G. Porter and M. W. Windsor, Proc. Roy. Soc., Ser. A, 245, 238 (1958).

[4] N. J. Turro, Molecular Photochemistry, W. A. Benjamin, Inc., New York, 1965, pp. 73-75.

[5] J. G. Calvert and J. N. Pitts, Photochemistry, John Wiley and Sons, Inc., New York 1966, pp. 342 ff.

[6] J. A. Bell and H. Linschitz, J. Amer. Chem. Soc., 85, 528 (1963).

[7] S. Cheng Tsai and G. W. Robinson, J. Chem. Phys., 49, 3184 (1968).

[8] H. H. Richtol and A. Belorit, J. Chem. Phys., 45, 35 (1966).

[9] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt and C. Dalton, J. Amer. Chem. Soc., 86, 3197 (1964).

[10] L. M. Stephenson and G. S. Hammond, Angew. Chem. Inter. Ed. Eng., 8, 261 (1969).

PROPOSITION 3

It is proposed that the transfer of iodine from iodobenzene to phenyl radical be studied by electron spin resonance techniques.

Abstraction of a halogen atom is a well-known reaction of free radicals. In general, facility of halogen abstraction follows the order I>Br>Cl, which is in accord with normal covalent bond strengths.[1] One of the strongest covalent bonds to iodine is found in aryl iodides (61 kcal/mole for iodobenzene[2]). Nevertheless, removal of iodine from iodobenzenes by aryl radicals is a facile reaction.[3] This iodine exchange reaction occurs more rapidly than

$$\mathrm{Ar\cdot} + \mathrm{Ar'{-}I} \rightleftharpoons \mathrm{Ar{-}I} + \mathrm{Ar'\cdot}$$

the better-known reaction of aryl radicals with aromatic compounds, arylation of the nucleus.[3]

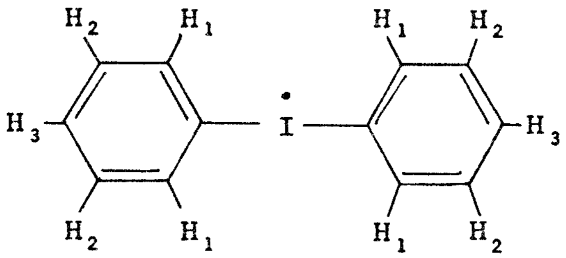
Phenyl radicals have now been prepared in concentrations suitable for esr studies. In the most recent work, phenyl radicals were formed by irradiation of iodobenzene in an argon matrix at 4° K.[4] The spectrum was sharp and all the hyperfine splitting constants were measurable - a(ortho) = 17.4 gauss, a(meta) = 5.9 gauss, and a(para) = 1.9 gauss.[4]

Earlier, an esr spectrum of phenyl radical was obtained from iodobenzene and sodium or potassium in inert matrices at 77° K.[5] When iodobenzene was used as its own matrix, there was a very pronounced broadening of the spectrum. Curiously, the same broadening effect, although not the same spectrum, was observed in a xenon matrix. It seems reasonable that the broadening effect is due to exchange of iodine between iodobenzene and phenyl radicals, although this was not one of the rationalizations offered.[5] The clarity of the esr spectrum at 4° K suggests that the exchange reaction was "frozen out" at this temperature.

The abstraction of iodine from iodobenzene by phenyl radical suggests the interesting species diphenyliodine as an intermediate. There is good evidence that diphenyliodine is produced by the one-electron polarographic reduction of diphenyliodonium cation, since at low concentrations, the polarographic wave is reversible, which suggests that diphenyliodine enjoys a finite lifetime.[6] However, exhaustive controlled-potential experiments led only to iodobenzene and products derived from phenyl radical.[6] Diphenyliodine has also been suggested as the product of electron transfer to diphenyliodonium cation from anions such as diethyl malonate.[7]

Esr studies of the iodobenzene-phenyl radical system would be more informative if carried out in solution. Anisotropies observed in the semi-rigid matrix will be averaged to zero, and this may lead to improved resolution of hyperfine splittings. Furthermore, rate studies can be attempted, since the phenyl radicals observed in solution will necessarily represent a steady-state condition, reflecting a dynamic balance of initiation and termination rates. The difficulty with solution studies is the attainment of a sufficient steady-state concentration. Rapid decomposition of benzoyl peroxide, a superb source of phenyl radicals,[8] should be suitable. A suitable inert solvent, such as perfluorocyclohexane,[5] is a necessity. Techniques have been developed for both thermal[9] and photochemical[10] decompositions which lead to observable steady-state concentrations of radicals in solution.

Two different answers may be resolved by these experiments. First, it will be interesting to note if the combination of phenyl radicals plus iodobenzene provides any evidence for the existence of diphenyliodine. At low concentrations, diphenyliodine may have a lifetime which is long on the esr time scale.[6] Its spectrum would be complex, but certainly characteristic.



Splittings should be expected for four equivalent H_1 protons, four equivalent H_2 protons, and two equivalent H_3 protons. This would lead to a spectrum of up to 75 lines. Unfortunately, splittings due to iodine atom are not observable in solution. Only recently have esr spectra of iodine atoms in the vapor phase been reported.[11] The presence of iodine will have a very beneficial effect on the spectrum, however. The g-value of diphenyliodine should be considerable higher than that of phenyl radical, due to large spin-orbit coupling with iodine. A g-value between 2.005 and 2.010 should probably be expected for diphenyliodine, while a g-value of 2.0023 is representative of a free electron and most organic radicals without large spin-orbit coupling.[12] This would lead to a separation of four to twelve gauss between the centers of the diphenyliodine spectrum and the phenyl radical spectrum.

Use of a higher microwave frequency would further increase the separation, if necessary.

Whether or not diphenyliodine can be detected in this system, the rate of phenyl radical attack on iodobenzene can be measured. In the limit of a very short lifetime of diphenyliodine (a transition state rather

$$\phi\cdot + \phi I \underset{k'}{\overset{k}{\rightleftarrows}} \phi-\dot{I}-\phi \underset{k}{\overset{k'}{\rightleftarrows}} \phi I + \phi\cdot$$

than an intermediate), the process is simply iodine atom exchange. If diphenyliodine has a substantial lifetime, the process is an equilibrium between two different radicals. In either case, the average lifetime of a phenyl radical, with respect to this exchange, will be $1/k[\phi I]$. The frequency of exchange, $k[\phi I]$, will manifest itself in the width of the hyperfine splitting lines, according to the equation

$$\delta w = w + k[\phi I]$$

where δw is the line width and w is the natural line width in the absence of the exchange process. A plot of the line width versus concentration of iodobenzene will give a slope of k and an intercept of w.

The range of rates which can be measured in this manner is easily approximated. From the reported spectrum of phenyl radical, a broadening of one gauss (or about 3 MHz) should be distinguishable. This broadening will be in effect when $k[\phi I] = 3 \times 10^6\ sec^{-1}$. If the exchange rate is $1 \times 10^{10}\ M^{-1}\ sec^{-1}$, the maximum, diffusion-controlled rate, no line broadening would be observed until the concentration of iodobenzene approached 3×10^{-4} M. Alternatively, the slowest rate observable would be about $3 \times 10^5\ M^{-1}\ sec^{-1}$, if neat iodobenzene (9 M) were just sufficient to bring about a one gauss line broadening. Thus an iodine exchange rate greater than or equal to $3 \times 10^5\ M^{-1}\ sec^{-1}$ should be measurable by this technique.

References

[1] C. Walling, Free Radicals in Solution, John Wiley and Sons, Inc., New York, 1957, pp. 155, 255.

[2] V. I. Vedeneyev, et. al., Bond Energies, Ionization Potentials and Electron Affinities, St. Martin's Press, New York, 1966, p. 63.

[3] J. F. Bunnett and C. C. Wamser, J. Amer. Chem. Soc., 88, 5534 (1966).

[4] P. H. Dasai, E. Hedaya and E. B. Whipple, J. Amer. Chem. Soc., 91, 4364 (1969).

[5] J. E. Bennett, B. Mile and A. Thomas, Proc. Roy. Soc., Ser. A, 293, 246 (1966).

[6] H. E. Bachofner, F. M. Beringer and L. Meites, J. Amer. Chem. Soc., 80, 4269, 4274 (1958).

[7] F. M. Beringer and P. S. Forgione, J. Org. Chem., 28, 714 (1963).

[8] D. F. DeTar, J. Amer. Chem. Soc., 89, 4058 (1967).

[9] A. A. Bichutinskii, A. I. Prokof'ev and V. A. Shabalkin, Russ. J. Phys. Chem., 38, 534 (1964).

[10] S. A. Weiner and G. S. Hammond, J. Amer. Chem. Soc., 90, 1659 (1968).

[11] S. Aditya and J. E. Willard, J. Chem. Phys., 44, 833 (1966).

[12] M. Bersohn and J. C. Baird, An Introduction to Electron Paramagnetic Resonance, W. A. Benjamin, Inc., New York, 1966, p. 70.

PROPOSITION 4

It is proposed that flash photolysis studies be undertaken to measure rates of triplet energy transfer between the chlorophylls and other pigments of potential importance in photosynthesis.

The essence of photosynthesis is the collection of light energy and the transfer of this energy to a reactive site where useful chemistry can be performed.[1] The nature of the reaction center and the mechanism of energy transfer remain the chief problems of photosynthesis.[2] A careful study of energy transfer processes among the chlorophylls, carotenoids, and other components of photosynthetic cells would be a valuable aid in the determination of the path of the light energy in the photosynthetic process.

The role of the triplet state of chlorophyll in photosynthesis is still a subject of controversy.[2,3] Chlorophyll triplets have been implicated in some photoreactions which may bear upon photosynthesis, such as photooxidation and electron transfer reactions.[1] Carotenes are known to protect chlorophyll from such photoreactions.[4] A more detailed knowledge of the reactions of chlorophyll triplets with other such components of photosynthetic cells may well be valuable in resolving the controversy.

Flash photolysis of chlorophyll *in vitro* leads to heavy population of the triplet state.[5] The quantum yields for triplet formation are $\Phi_{ta} = 0.64$ for chlorophyll a and $\Phi_{tb} = 0.88$ for chlorophyll b in polar solvents.[6] These correlate well with the fluorescence quantum efficiencies, which are $\Phi_{fa} = 0.32$ and $\Phi_{fb} = 0.12$ for chlorophyll a and b, respectively.[7] Similar irradiation of chloroplasts, *in vivo* chlorophyll, shows that the formation of triplet states of chlorophyll is substantially decreased.[8] This indicates either that the triplet state is strongly quenched or the precursor singlet state is strongly quenched in the living photosynthetic cell. An analysis of chlorophyll triplet quenching rates obtained *in vitro* will provide a quantitative basis for description of potentially important energy transfer processes *in vivo*.

The techniques of flash photolysis are ideally suited for such a study. Relatively low energy flashes (50 joules) are sufficient to populate the triplet state to the extent of 90%.[5] The triplet lifetime of chlorophyll b is about 1 msec in solution,[5] a conveniently long lifetime which will allow sensitive detection and measurement of quenching.

On the other hand, there may well be some formidable experimental difficulties due to competing absorptions. For each substrate-quencher pair to be studied, 1) the excitation flash must be carefully filtered to assure excitation of only the substrate and 2) the transient spectra must be well-known in order to allow independent monitoring of the decay of donor excited states, and perhaps simultaneous appearance of acceptor excited states. These two problems of competitive absorption may be solved by finding specific wavelength regions where only the desired species absorb. Otherwise, correctional calculations would be required.

References

[1] R. K. Clayton, Molecular Physics in Photosynthesis, Blaisdell Publishing Co., New York, 1965.

[2] G. W. Robinson, Brookhaven Symposia in Biology, 19, 16 (1966).

[3] G. M. Maggiora and L. L. Ingraham, Struct. Bonding, 2, 126 (1967).

[4] H. Claes, Z. Naturforschung, 166, 445 (1961).

[5] G. Porter, Proc. Roy. Soc., Ser. B, 157, 293 (1963).

[6] P. G. Bowers and G. Porter, Proc. Roy. Soc., Ser. A, 296, 435 (1966).

[7] G. Weber and J. W. F. Teale, Trans. Faraday Soc., 53, 646 (1957).

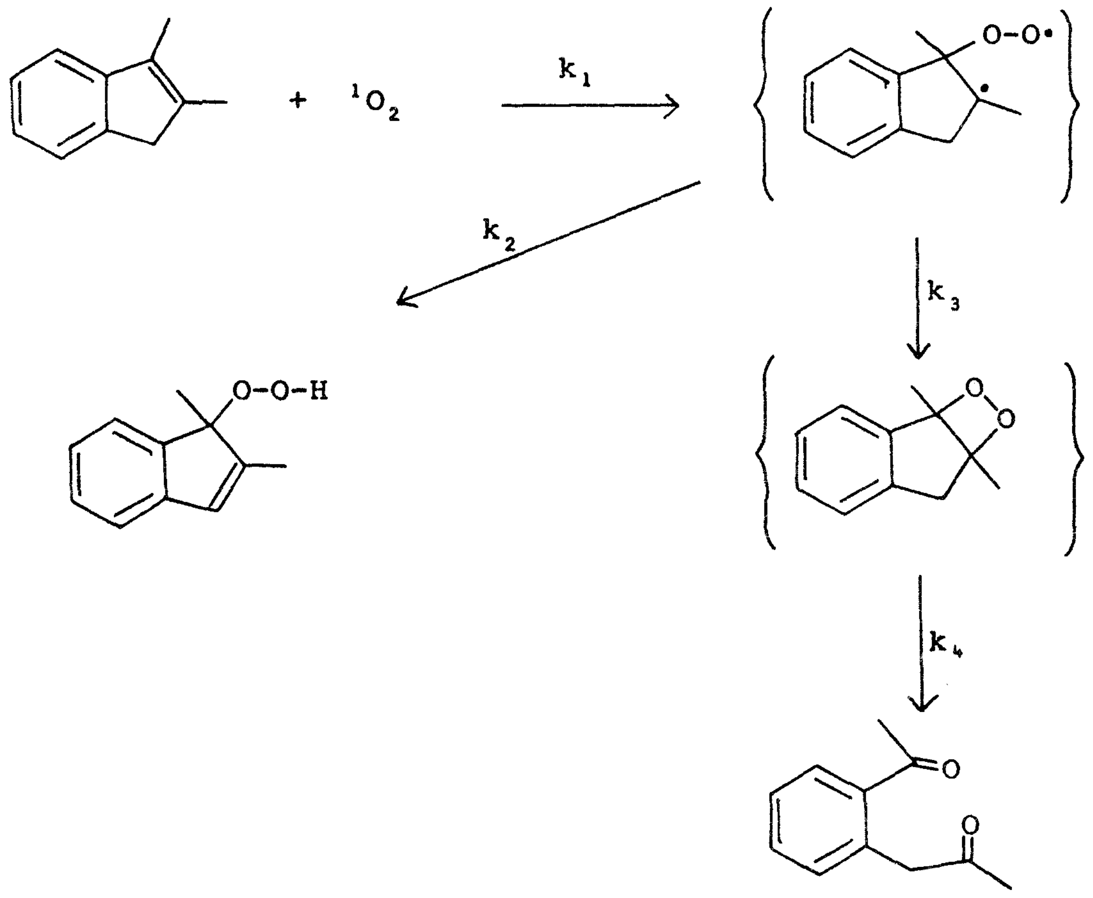
[8] A. Müller, B. Rumberg and H. T. Witt, Proc. Roy. Soc., Ser. B, 157, 313 (1963).

PROPOSITION 5

Experiments are proposed which will demonstrate whether the reactions of singlet oxygen with olefins, giving rearranged allylic hydroperoxides or carbonyl fragments, share a common intermediate.

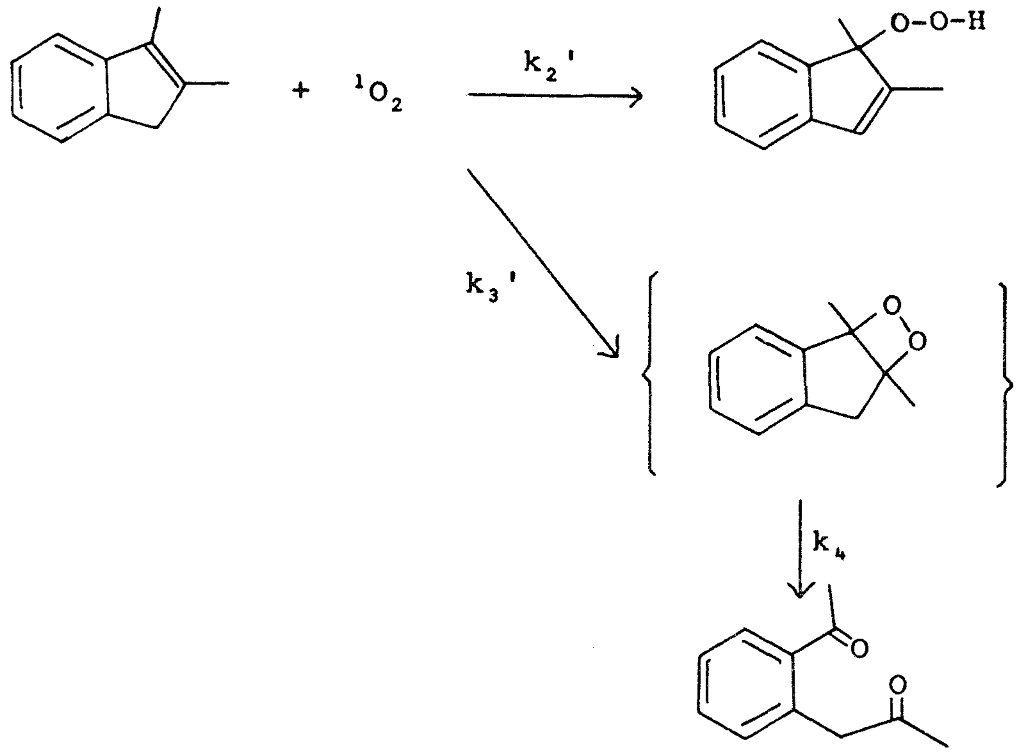
Singlet oxygen reacts with most olefins to produce rearranged allylic hydroperoxides.[1] Another rather common reaction pathway, however, is oxidation to carbonyl fragments.[1] The mechanism of the hydroperoxide formation is most often described as a concerted "ene" reaction.[1,2] The relationship between the hydroperoxide formation and the carbonyl formation reactions is only now being clarified. It had been considered that the carbonyl fragmentation represented a further reaction of the allylic hydroperoxide.[1] This possibility has now been ruled out by the isolation of indene hydroperoxide and the demonstration that it does not produce the carbonyl fragments which are observed in the oxidation of indene.[3] The best hypothesis at present is that the carbonyl fragmentation occurs by thermal decomposition of a 1,2-dioxetane intermediate.[3,4] Recently, 3,3,4-trimethyl-1,2-dioxetane has been isolated and shown to give quantitative yields of the carbonyl fragments, acetone and acetaldehyde (as well as carbonyl luminescence, which is a fascinating story in its own right).[4] Thus the conceptions of the two mechanisms of singlet oxygen reaction with olefins have been diverging. If the mechanisms share any intermediate at all, it must be at the very earliest stage of the reaction, as shown in Scheme I. The reaction is illustrated with 2,3-dimethylindene, since this is the only olefin known to show significant yields of both oxidation products.[3]

Scheme I



Alternatively, the possibility of completely separate, concerted mechanistic pathways is shown in Scheme II.

Scheme II



These two mechanisms are differentiable only if the partitioning of the proposed diradical intermediate can be affected in a predictable way. It is proposed that this can be accomplished by a study of the relative kinetics of oxidation and the relative product distributions of 2,3-dimethylindene and 1,1-dideuterio-2,3-dimethylindene with singlet oxygen. Such an analysis has been successfully utilized in clarifying the mechanism of decomposition of 4-methyl-1-pyrazoline.[5]

In Scheme I, the rate constant for disappearance of olefin, k_I, and the ratio of hydroperoxide product to carbonyl product, R_I, are derived as follows:

$$\text{Rate} = k_1 \, [\text{In}] \, [{}^1O_2]$$

In = 2,3-dimethylindene

$$k_I = k_1$$

$$R_I = k_2/k_3$$

The corresponding values for Scheme II are the following:

$$\text{Rate} = (k_2' + k_3') \, [\text{In}] \, [{}^1O_2]$$

$$k_{II} = k_2' + k_3'$$

$$R_{II} = k_2'/k_3'$$

Deuteration at the 1-position should substantially affect only the hydrogen abstraction rates, k_2 and k_2'. An isotope effect of about 4 might be expected.[6] Thus either mechanistic scheme would predict a decrease in the hydroperoxide fraction of the total oxidation products. Scheme II would further predict a corresponding decrease in the overall rate of disappearance of the indene, however. If there is no corresponding decrease in the rate of oxidation upon deuteration, then the hydrogen abstraction reaction must occur after the rate-determining step and the diradical intermediate of Scheme I is validated.

References

[1] K. Gollnick, Advan. Photochem., 6, 1 (1968).

[2] A. Nickon and J. F. Bagli, J. Amer. Chem. Soc., 83, 1498 (1961).

[3] W. Fenical, D. R. Kearns and P. Radlick, J. Amer. Chem. Soc., 91, 3396 (1969).

[4] K. R. Kopecky and C. Mumford, Can. J. Chem., 47, 709 (1969).

[5] This work was pointed out by Dr. R. G. Bergman: R. J. Crawford and A. Mishra, J. Amer. Chem. Soc., 88, 3963 (1966).

[6] K. B. Wiberg, Chem. Rev., 55, 713 (1955).