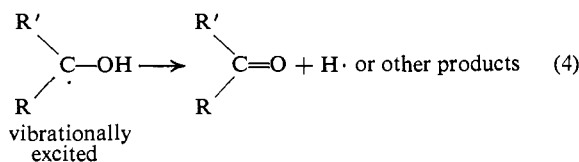
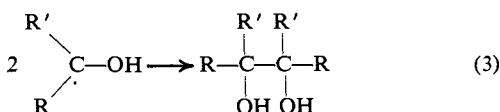
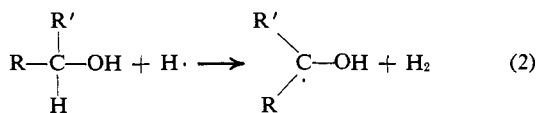
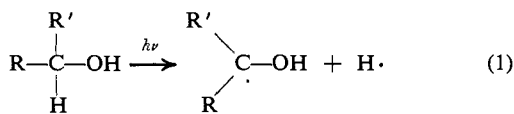


2-propanol, and 2-methyl-2-propanol are summarized below, and the products are expressed in units of mmoles per hour: methanol: H₂, 2.97; CO, 0.098; CH₄, 0.012; HCHO, 0.32; (CH₂OH)₂, 1.92; glycerine, 0.26; ethanol: H₂, 2.54; CO, 0.75; CH₄, 0.81; CH₃CHO, 0.10; 2,3-dihydroxybutane, 1.63; 2-propanol: H₂, 1.72; CO, 0.68; CH₄, 1.27; C₂H₆, 0.05; acetone, 0.23; pinacol, 1.52; 2-methyl-2-propanol: CH₄, 5.10; CO, 0.42; acetone, 0.35; pinacol, 1.25; 3-hydroxy-3-methyl-2-butanone, 0.33; 2,5-dihydroxy-2,5-dimethylhexane, 1.74.

The gas evolutions in these photolyses were inhibited by cyclohexene and were completely suppressed by the presence of 5% of cyclohexene (0.6 M). In all cases, cyclohexene only absorbs a minor portion of the light. In the case of photolysis of 2-propanol in the presence of 5% of cyclohexene, the following products were obtained in units of millimoles per hour: acetone, 2.0; pinacol, 0.09; cyclohexane, 0.60; cyclohexyldimethylcarbinol, 0.51; cyclohexenyldimethylcarbinol, 0.40; bicyclohexyl, 0.12; cyclohexenylcyclohexane, 0.05; high boiling residue (0.04 g/hr).

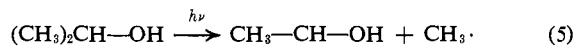
The principal gaseous product is hydrogen in all cases except 2-methyl-2-propanol and the principal higher boiling products are the corresponding carbonyl compounds and the glycol. When the results of photolysis of 2-propanol in the presence of cyclohexene, a radical scavenger, were compared with the results of photolysis of pure 2-propanol, it is interesting to note that the evolution of hydrogen, methane, and carbon monoxide was completely suppressed and the yield of acetone became much higher. On the basis of the above observations, hydrogen is most likely formed from a radical process such as indicated by reactions 1 and 2 and acetone is not formed directly from 2-propanol by a molecular elimination of hydrogen. One possible



explanation is that the 2-hydroxy-2-propyl radical formed in reaction 1 may be vibrationally excited. The light at 185 m μ is very energetic and is equivalent to 6.5 eV or 148.7 kcal/einstein. After the initial cleavage of the α -C-H bond in photoexcited 2-propanol, which has a bond energy estimated at about 85 kcal, the excess energy may remain preferably in the form of vibrational energy in the 2-hydroxy-2-propyl radical rather than in the form of kinetic energy of the hydrogen atom. The vibrationally excited 2-hydroxy-2-

propyl radical thus generated may differ in its behavior from the normal 2-hydroxy-2-propyl radical which usually dimerizes to give pinacol (reaction 3) or is scavenged by cyclohexene. It is probable that the vibrationally excited 2-hydroxy-2-propyl radical may disproportionate, dissociate, or react with cyclohexene to give acetone prior to its deactivation (reaction 4). The accumulation of acetone in the photolysis of 2-propanol in the presence of cyclohexene may be attributed to the quenching effect of cyclohexene on the secondary decomposition of acetone by the 254-m μ emission of the light source.

The α -C-C bond in 2-propanol has a bond energy comparable to that of the α -C-H bond. An initial cleavage of photoexcited 2-propanol will give a methyl radical and a 1-hydroxyethyl radical (reaction 5). The products which may be derived from these radicals are conspicuously absent in the photolysis of 2-propanol in the presence of cyclohexene or among the higher boiling products in the photolysis of pure 2-propanol. Therefore, the formation of methane and carbon monoxide in the photolysis of 2-propanol is probably derived from the secondary photolysis of acetone. This fact was readily demonstrated by photolyzing acetone in 2-propanol.^{5,9}



We wish to suggest that the principal primary process in the liquid phase photolysis of simple primary and secondary alcohols is the cleavage of an α -C-H bond, while the primary process for tertiary alcohols is the cleavage of an α -C-C bond. Our preliminary investigations indicate that photochemical reactions in the liquid phase with 185 m μ light might be quite selective and the investigations are being extended to other organic compounds.

Acknowledgment. The authors wish to thank the Atomic Energy Commission for the support of this work.

(9) A detailed analysis of gas evolved from the photolysis of 2-propanol at 60-min intervals indicated that the gas evolved earlier is considerably richer in hydrogen, but we are not able as yet to obtain a sample completely free of methane. Acetaldehyde, if formed, would have been detected under the reaction conditions.

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Dependence of the Quantum Yield of Photoreduction of Benzophenone in 2-Propanol on Light Intensity. Possibility of Triplet Quenching by the Radical Intermediates in Solution

Sir:

The photoreduction of benzophenone in 2-propanol has been extensively investigated.¹ The reaction is

(1) (a) G. Ciamician and P. Silber, *Ber.*, **34**, 1530 (1901); (b) J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *J. Am. Chem. Soc.*, **81**, 1068 (1959); (c) J. N. Pitts, Jr., H. W. Johnson, Jr., and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962); (d) W. M. Moore, G. S. Hammond, and R. P. Ross, *J. Am. Chem. Soc.*, **83**, 2789 (1961); (e) G. S. Hammond, W. P. Baker, and W. M. Moore, *ibid.*, **83**, 2795 (1961); (f) G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57**, 1686 (1961).

characterized by its high chemical yield of products,² benzpinacol and acetone, as well as by its high quantum efficiency as $\Phi_{-(C_6H_5)_2CO}$ approaches 2 under ordinary conditions.³ Contributions from various laboratories have demonstrated that the reactive intermediate of this reaction is the low-lying triplet state ($n \rightarrow \pi^*$) of benzophenone, and the intersystem crossing efficiency of the originally photoexcited singlet state to the low-lying triplet state is unity.^{1,4} In connection with our interest in the photochemistry of carbonyl compounds, we used a high intensity light source to investigate the quantum yields of low quantum efficiency photochemical reactions. We found that the quantum yield of the photoreduction of benzophenone in 2-propanol varies with light intensity. It varies over a range of about six with a 60-fold variation of light intensity.⁵

The system used in our investigation consisted of an Osram 200-w super-pressure mercury vapor point source with two lenses. The 313-m μ emission of mercury was isolated with an appropriate filtering system.⁶ Cylindrical quartz cells (1 cm) were used for the samples and were thermostated at 25.0° with a thermostated cell holder from a Cary 14 recording spectrometer. A quartz plate was set at 45° to the light beam in front of the sample cell to reflect about one-seventh of the light into a monitor actinometer solution. The reflectance/transmission ratio was determined by the use of actinometer solutions in both the sample cell and the monitor cell. The light intensity was determined with both ferrioxalate and uranyl oxalate actinometry and was monitored throughout the quantum yield determinations with the ferrioxalate actinometry.⁷ Solutions of zone-refined benzophenone in spectrograde 2-propanol (approximately 0.1 M) were degassed before each determination by repeated freezing-thawing under reduced pressure. The progress of photochemical reaction was followed by both the variation of absorbance of the unreacted benzophenone with a Cary 14 spectrometer or by the formation of acetone with a 20-ft Carbowax 20M column at 125° in a conventional gas chromatograph. The reaction was carried to $18 \pm 2\%$ completion. In several cases, the quantum yield of photoreduction was followed at various stages of completion, and it was found that the quantum yield was constant within the range investigated. The light intensities were changed by means of wire screens in front of the sample cells or by increasing the concentration of chromate ion in the filtering system. The experimental results are summarized in Table I. The experimental error in quantum yield determination is $\pm 5\%$.

The data indicated that the quantum yield of this photoreduction decreases with increasing light intensity,

(2) W. E. Bachman, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 71.

(3) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2039 (1963).

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

(5) The variation of quantum yield of photoreduction of benzophenone in 2-propanol, from 1.12 to 1.62, at low light intensity, 2.0×10^{15} to 2.0×10^{17} quanta/min, has been noted by Professor A. C. Testa, St. John's University: A. C. Testa, *J. Phys. Chem.*, **67**, 1341 (1963). We wish to thank Professor Testa for calling this to our attention.

(6) The filtering system consisted of a Corning 7-54 filter and 2.5 cm of a circulating aqueous solution containing 0.006 M potassium acid phthalate, 0.0005 M potassium chromate, and 0.03 M sodium hydroxide.

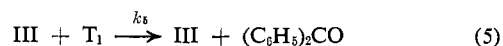
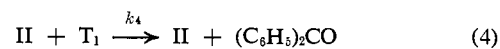
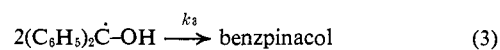
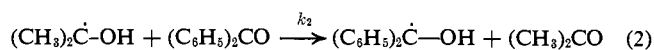
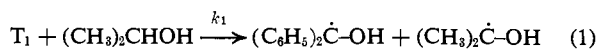
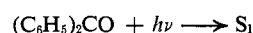
(7) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. (London)*, **A235**, 518 (1956).

Table I

Light intensity I (10^{16} quanta/min)	$I^{1/2}$	$\Phi_{-(C_6H_5)_2CO}$	$\Phi_{acetone}$	$\frac{2 - \Phi}{\Phi^{3/2}}$
5.3	2.43	1.47	...	0.30
17.7	4.20	1.21	0.66	0.59
33.8	5.81	1.08	0.57	0.82
55.3	7.43	0.97	0.51	1.08
74.9	8.64	0.76	0.39	1.86
97.6	9.87	0.64	...	2.66
129.0	11.4	0.53	0.27	3.76
256.0	16.0	0.42	0.21	5.85
343.0 ^a	18.5	0.37	0.18	7.21
14.3 ^b	...	0.80	0.40	...

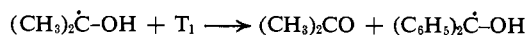
^a Our light source and optical system gave an intense spot on the sample cell; the rate of the triplet generated at this light intensity was estimated to be to the order of 0.1–1.0 mole l.⁻¹. ^b The reaction was carried out in $(CH_3)_2CHOD$.

and we did not detect appreciable variation in the nature of chemical reaction, *i.e.*, the conversion of benzophenone and 2-propanol to benzpinacol and acetone. A possible explanation of this variation of quantum yield with light intensity would be two concurrent processes involving the reactive intermediate, a first-order process which gives rise to the chemical reaction and a competing higher order process which is non-productive photochemically. As mentioned earlier,^{1,4} the reactive intermediate of photoreduction of benzophenone is the low-lying triplet state. The competing nonproductive process is then the quenching of the triplet state by other species in solution. The predominant paramagnetic species in solution which may act as the quencher are the intermediate radicals formed in photoreduction, the ketyl radical II and 2-hydroxy-2-propyl radical III. Since the interstate crossing of excited benzophenone is efficient and rapid as compared with other processes, the reaction may be represented by the following equations in which S_1 and T_1 represent the singlet and triplet excited states of benzophenone, respectively.^{8,9}



(8) Pitts, Schenk, Bäckstrom, and their collaborators reported the formation of a strongly absorbing by-product in the photoreduction of benzophenone in 2-propanol; see H. L. J. Bäckstrom, K. L. Appelgren, and R. J. V. Niklasson, *Acta Chem. Scand.*, **19**, 1555 (1965), and references therein. Our investigation indicated that the quantum yield of photoreduction does not vary with time while the by-product formation is linear with time; therefore, the by-product cannot play an important role in the quenching process.

(9) Since 2-hydroxy-2-propyl radical (III) is known to react with benzophenone to give the ketyl radical (II) and acetone (reaction 2), it is reasonable to assume that a similar reaction may take place between III and excited benzophenone to give the same products. If this reaction does occur, it will not affect the limited conclusion of our discussion.



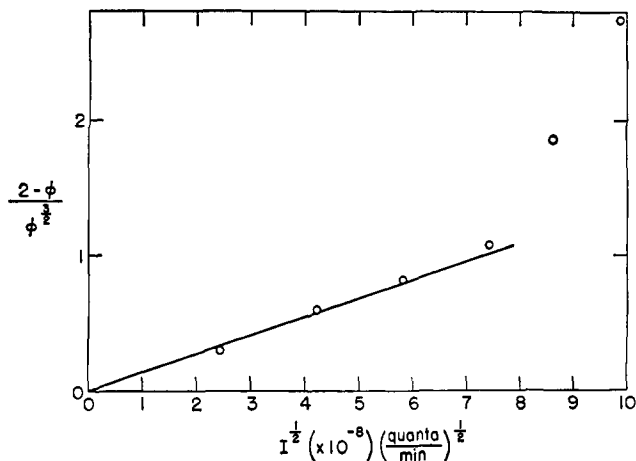


Figure 1.

The quantum yield of disappearance of benzophenone is defined as

$$\Phi_{-(C_6H_5)_2CO} = \frac{2k_1(T_1)}{I} \quad (6)$$

where I is the light intensity.

At steady state, the formation of T_1 , II, and III will be equal to the disappearance of these species.

$$I = k_1(T_1) + k_4(II)(T_1) + k_5(III)(T_1) \quad (7)$$

$$2k_3(II)^2 = k_1(T_1) + k_2(III) \quad (8)$$

$$k_1(T_1) = k_2(III) \quad (9)$$

Combining (8) and (9) and solving for II, we have

$$(II) = [k_1(T_1)/k_3]^{1/2} \quad (10)$$

Substituting (6), (9), and (10) into (7) and solving in terms of I , we have

$$\frac{2 - \Phi}{\Phi^{3/2}} = k'I^{1/2} + k''I\Phi^{1/2}$$

where $k' = k_4/k_1(2k_3)^{1/2}$ and $k'' = k_5/2k_1k_2$

At low light intensity, the second term may be relatively insignificant as compared to the first term. Physically it means that the quenching is mainly due to the ketyl radical (II) at low light intensity. If our explanation is correct, by plotting $(2 - \Phi)/\Phi^{3/2}$ against $I^{1/2}$ we will obtain a straight line at low light intensity. At high light intensity, there will be an increase in 2-hydroxy-2-propyl radical (III) concentration, and the second term becomes increasingly more significant and the line will deviate with an increasing slope. Our experimental results are represented in Figure 1.

It has been shown that O-deuteration on 2-propanol has no measurable isotope effect on the quantum yield of photoreduction of benzophenone in 2-propanol at low light intensity.¹⁰ It is reasonable to assume that O-deuteration will slow down reaction 2 and will increase the concentration of the solvent radical III. Therefore, the decrease in quantum yield with increasing light intensity will be more predominant in 2-propanol-*d*. A preliminary investigation was carried

(10) W. M. Moore and M. D. Ketchum, *J. Phys. Chem.*, **68**, 214 (1964).

out in 2-propanol-*d*. We found that this was indeed the case (see Table I).

The generality of this phenomenon and a quantitative treatment on the rates of these processes¹¹ are being investigated.

Acknowledgment. The authors wish to thank the National Science Foundation for the support of this work, the Esso Research Foundation for a fellowship to one of us (S. M.), and Professor D. S. McClure for his helpful discussions.

(11) By using the values reported by C. Walling and M. J. Gibian (*J. Am. Chem. Soc.*, **87**, 3361 (1965)) that $k_1 = 8.7 \times 10^4$ and by A. Beckett, A. D. Osborne, and G. Porter (*Trans. Faraday Soc.*, **60**, 873 (1964)) that $k_2 = 5.9 \times 10^7$, the value for k_4 was estimated at the order of 10^{10} .

(12) National Science Foundation Fellow, 1962–1965; Esso Research Foundation Fellow, 1965–1966.

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Nuclear Magnetic Resonance Studies of Plant Biosynthesis. Bacteriochlorophyll¹

Sir:

We wish to report experimental results, based upon the use of a deuterium-substituted substrate and proton magnetic resonance, that give new information about the biogenesis of bacteriochlorophyll in physiologically competent microorganisms.

Rhodospirillum rubrum (A.T.C.C. 11170) was grown in an ordinary water medium² with succinic acid-*d*₄ (>99 atom % D) as the only exogenous organic carbon source. Bacteriochlorophyll³ was isolated from these organisms and converted to methyl bacteriopheophorbide,⁴ which was purified by chromatography and crystallization. The nmr spectra of bacteriochlorophyll and methyl bacteriopheophorbide have been assigned⁵ by conventional techniques;⁶ hence we could accurately determine the relative abundance of hydrogen and deuterium at each position in the molecule.⁷

The ratio H/D at the hydrogen positions in the molecule reflects both the isotopic composition of the succinic acid and the exchange and hydrogen transfer reactions that occurred during biosynthesis. With deuterium decoupling, the hydrogen atoms at position 4'' (see 1 in Table I for numbering) in the H₂O-succinate-*d*₄ bacteriochlorophyll (0.12 M in C₃D₈O) ($\delta \sim 103$ cps) appeared as a sharp doublet ($J \sim 7.2$ cps). In the usual hydrogen bacteriochlorophyll, a triplet with the same coupling constant and chemical shift is ob-

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) J. G. Ormerod, K. S. Ormerod, and H. Gest, *Arch. Biochem. Biophys.*, **94**, 449 (1961).

(3) H. H. Strain, M. R. Thomas, H. L. Crespi, M. I. Blake, and J. J. Katz, *Ann. N. Y. Acad. Sci.*, **84**, 617 (1960).

(4) H. Fisher and A. Stern, "Die Chemie des Pyrrole," Band III, Akademische Verlagsgesellschaft, Leipzig, 1940, p 317.

(5) J. J. Katz, R. C. Dougherty, and L. J. Boucher, "Chlorophyll," L. P. Vernon and G. R. Seely, Ed., Academic Press Inc., New York, N. Y., in press.

(6) G. L. Closs, J. J. Katz, F. C. Pennington, M. R. Thomas, and H. H. Strain, *J. Am. Chem. Soc.*, **85**, 3809 (1963).

(7) The nmr spectra were recorded on a Varian HA-100 nmr spectrometer in the field-sweep mode. Deuterium decoupling was carried out with an N.M.R. Specialties Hetero-Nuclear Decoupler adjusted for decoupling the deuterons in acetone-*d*₆ at "zero power."