

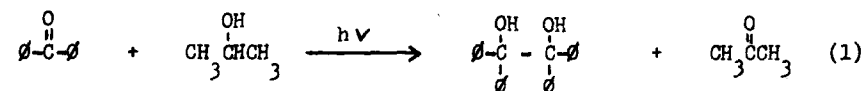
REACTIONS OF α -HYDROXYBENZYL RADICALS
 V THE THERMAL DECOMPOSITION OF TETRAARYL PINACOLS¹

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The photoreduction of benzophenone is, perhaps, the classic organic photochemical reaction. Discovered by Ciamician and Silber in 1900², the reaction involves reductive dimerization of the aryl ketone (1).



In spite of the fact that benzophenone photoreductions are sufficiently well known to be included in the undergraduate laboratory, even the most trivial change in the absorbing ketone,³ the solvent,⁴ or the temperature often causes the reduction to take either a different course or to become much less efficient.

In an effort to better understand the factors influencing photoreduction reactions, we have undertaken a study of the free radical intermediates presumed important in these processes.⁵ We report now, preliminary results of a kinetic study aimed at elucidating the factors responsible for product formation in photoreduction reactions.

Results:

Benzophenone reduces quantitatively to benzpinacol when irradiated in alcohols. The mechanism for the reaction requires genesis and destruction of α -hydroxydiphenylmethyl radicals in solution. Irradiation at sufficiently higher temperatures produces more benzhydrol such that at 150°, it becomes nearly the exclusive product, Figure 1

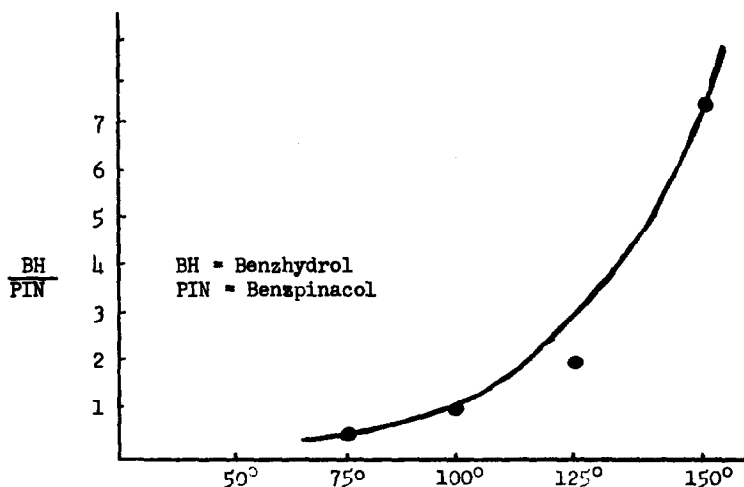
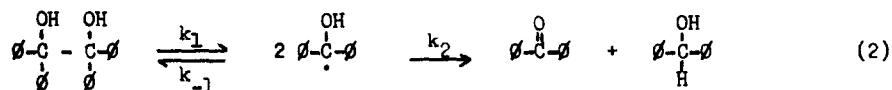


Figure 1

In the absence of additives, benzhydrol production results from the thermal instability of the product benzpinacol. Thus, benzpinacol decomposes smoothly to benzophenone and benzhydrol in a variety of solvents, providing oxygen is carefully excluded. A mechanism encompassing the first order kinetics observed for this reaction is shown in (2).



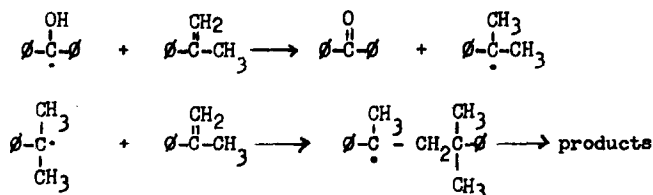
First order rate constants for the decomposition process measured by benzophenone appearance are displayed in Table I.

Table I

Rate Constants for the Decomposition of Benzpinacol

Temp.	Conc.	$\frac{k_1 k_2}{k_{-1} + k_2} (\text{sec}^{-1}) \times 10^6$
92.0°	0.010m	0.84
94.0°	0.010m	0.91
107.0°	0.010m	6.30

A half life of four hours at 125° and relatively low activation parameters ($\Delta H^* = 33.8$ kcal/mole, $\Delta S^* = 7.8$ e.u.) point to the facility of the process⁶. We suggest, for example, that benzpinacol might prove useful as an initiator for vinyl polymerization. The use of benzpinacol as an initiator for polymerization is attractive for it would provide a hydrogen atom end group for the polymer. The facility of hydrogen atom transfer from the benzpinacol derived α -hydroxydiphenylmethyl radical to a vinyl monomer, α -methylstyrene demonstrates the ease of such a process, Scheme I.



Scheme I

In the presence of oxygen, a rapid oxidation of the α -hydroxydiphenylmethyl radical occurs and benzophenone becomes the exclusive product from the decomposition of benzpinacol. A second product, hydrogen peroxide, destroys itself at the temperatures of the reaction eventually oxidizing the solvent, diphenyl ether. This observation extends an observation made some years ago by Moore, Hammond and Foss⁷ concerning oxygen quenching of benzophenone photoreduction. Because oxidation of the α -hydroxydiphenylmethyl radical (3) is a facile process, a competitive alternative to oxygen quenching of benzophenone triplets, a spectroscopically observable process, involves chemical oxidation of the reaction intermediate.



It is apparent that oxygen markedly effects the rate of benzophenone appearance derived from decomposing benzpinacol in diphenyl ether. Rate constants for the two reactions, degassed and oxygenated, are compared in Table II. Because no acidic products are observed in this oxidation, we prefer to think of this reaction as a

hydrogen atom transfer also, but more will be reported on these studies later.

Table II

Rate Constants, Benzpinacol Decomposition in Presence of Oxygen

<u>System</u>	<u>T</u>	<u>k (sec⁻¹) x 10⁶</u> <u>obs.</u>
Degassed	109°	7.13
Oxygen Bubbling	109°	68.5
Degassed	113°	11.6
Oxygen Bubbling	112.5°	118.0

Our studies on the effect of oxygen on the thermal decomposition process are being continued, as are studies on the effect of other additives (thiol, amines, etc.). Further attempts to ferret the photochemistry from the free radical chemistry in photoreduction systems are also being made. These studies will be published in detail shortly.⁸

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6. Compare, for example, di-*t*-butyl peroxide, half life = 14 hours (T=125°).
 $\Delta H^\ddagger = 36.8$ kcal/mole, $\Delta S^\ddagger = 11.3$ e.u. (Calculated from the data of J. H. Raley, F. F. Rust and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 1337 (1948)).
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8. We acknowledge the experimental assistance of Thomas Elwood and James Hardy in the early aspects of this work. Financial support from the Petroleum Research Fund (2739-B) administered by the American Chemical Society, the Research Corporation, and the Eli Lilly Corporation is gratefully acknowledged.