THE RADIOLYSIS OF ORGANIC SOLUTIONS:

II. THE BENZOPHENONE-PROPANOL-2 SYSTEM

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II. THE BENZOPHENONE-PROPANOL-2 SYSTEM

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ABSTRACT

Mixtures of benzophenone with propanol-2 have been irradiated with Cobalt-60 gamma rays. It has been found that the yield of hydrogen from propanol-2 is very sensitive to benzophenone addition; 1% benzophenone lowers $\underline{G}(H_2)$ from 3.0 to 2.0. Addition of benzophenone also lowers the yield of methane from propanol-2. It is concluded that benzophenone probably functions principally as a hydrogen atom scavenger. It was also observed that radiolysis of these mixtures produced benzpinacol with a $\underline{G}$ of 6.60 (as semipinacol units) concurrent with a disappearance of benzophenone with a $\underline{G}$ of 7.2 and the formation of acetone with a $\underline{G}$ of 9.1. It is concluded that hydrogen transfer between the components of a system composed of a ketone molecule solvated with carbinol molecules is an important factor in the formation of the pinacol.

I. INTRODUCTION

In a previous paper[1] the possibility that ketones could serve as scavengers for radiolytically produced hydrogen atoms was discussed and evidence presented to show that acetone did indeed scavenge the hydrogen atoms produced in the radiolysis of propanol-2. The present paper reports an extension of this investigation to the ketone, benzophenone. The ability of benzophenone to scavenge the radiolytic hydrogen atoms from propanol-2 has been evaluated.

An interesting side issue accompanied the study of the benzophenone-propanol-2 system: the radiation-induced formation of acetone and benzpinacol. It is well known in photochemistry that illumination with sunlight or ultraviolet light, of solutions of benzophenone in propanol-2 (and other carbinols), converts the benzophenone quantitatively into benzpinacol (1, 1, 2, 2-tetraphenylethanediol-1, 2) and an equivalent amount of propanol-2 into acetone.[2]

Pinacols can similarly be produced by ultraviolet irradiation of numerous other ketone-carbinol solutions.[2] More recent work[3] has suggested that a complex radical formed by addition of a semipinacol radical to another ketone molecule is intermediate in pinacol formation. It has also been shown,[3] by carbon-14 labeling, that the benzpinacol formed by reaction between benzophenone and benzhydrol arises entirely from the ketone. The quantum yield of benzpinacol has been observed[3] to be 0.5.

The absorption of energy in the photochemical reaction is entirely by the benzophenone, since this substance possesses absorption maxima[4] at 258 microns (aromatic ring) and 338 microns (carbonyl group); whereas, propanol-2, like other saturated aliphatic carbinols, is transparent in the near ultraviolet region. Thus formation of the pinacol must be initiated by excitation of the ketone, and proceed by interaction of the excited ketone molecule with carbinol molecules. However, in the radiation-induced process, the absorption of ionizing radiation by the two components is in proportion to the electron fraction of each in the mixture. For the concentration of the ketones employed here (2-5 mole %), the absorption of energy is predominantly by the carbinol. Thus one must distinguish between pinacolization initiated by excitation (or ionization) of the carbinol and that initiated by excitation of the ketone. This distinction will be important in a later discussion.

II. EXPERIMENTAL

A. MATERIALS

Propanol-2, Mallinckrodt analytical reagent grade, was carefully fraction-ated in a 50-plate column and the heart fraction dried over Drierite. Very high chemical purity was confirmed by examination in the gas chromatograph. Benzo-phenone, Eastman Kodak Company's white label grade, was assumed to be essentially free from isomers, homologs, and impurities. This was then vacuum distilled twice, each time retaining the heart fraction. A purity check on the gas chromatograph was unsuccessful as the benzophenone decomposed inside the column of the instrument. No impurities could be seen by infrared spectrophotometer analysis. Mixtures of benzophenone in isopropyl alcohol were made up in molar concentrations of 1, 2, 3, and 5% benzophenone. These solutions were noticeably unstable in the fluorescent light of the laboratory so they were either stored in the dark or freshly prepared for the radiolyses.

B. IRRADIATIONS

Ampules for the benzophenone-propanol-2 solutions were prepared from sections of 12 mm pyrex tubing, constricted to capillary diameter at one end, and sealed at the other end. The internal volumes were about 2.5 ml, and the overall lengths about 60 to 70 mm. One ml samples of the solutions were pipetted into the ampules through the construction, the liquids degassed on a high vacuum line by the conventional freeze-melt technique, and the ampules then sealed off under vacuum.

The benzophenone-propanol-2 solutions were irradiated to a total dose of about 1.1×10^{21} ev. The intensity of the source was 1.50×10^{18} ev/ml water-min, and the ambient temperature was about 40°C.

C. BENZPINACOL FORMATION

Essentially 100% conversion of benzophenone to benzpinacol could be accom-plished by irradiating the degassed benzophenone-propanol-2 solutions. The pinacol crystallized spontaneously from the solutions. Irradiation of solutions open to the air produced a much lower yield of pinacol (10 to 15%). The pinacol crystals obtained from either solution were colored, but since the color annealed

out upon heating, it was evidently normal F-center coloring. The pinacol was identified by melting point, mixture melting point with authentic benzpinacol, and iodine-catalyzed conversion to pinacolone.*

D. ANALYSES

$\underline{G}$ values, for gaseous products, were measured by opening the ampules in a high vacuum system containing a liquid nitrogen-cooled trap. The non-condensable gases were Toeplered into a calibrated gas burette[1] where the volumes and temperatures were measured. Composition of the gaseous products was determined by mass spectrometry on a modified Consolidated 21-620 mass spectrometer.

After removal of the non-condensable gases from the irradiated benzophenone-propanol-2 solutions, the volatile components of the solution were distilled into the liquid nitrogen-cooled trap of the vacuum line and then removed. This faction was analyzed for volatile ketone (acetone) by measuring the transmission in the infrared at 5.84 microns. Solutions of acetone in propanol-2 were used as standards and a portion of the unirradiated radiolysis solution used as the reference standard for zero ketone content. The non-volatile fraction of the radiolysis product was removed from the vacuum line, dissolved in chloroform, and made up to the volume of the original radiolysis sample. Benzophenone content was measured by the transmission in the infrared at 6.02 microns, and nonvolatile carbinol by the transmission at 2.80 microns. Reference standards were solutions of benzophenone in chloroform, and solutions of benzpinacol in carbon disulfide (the molar transmission of the OH stretching band for benzpinacol was shown to be the same in carbon disulfide and in chloroform). Although this non-volatile carbinol probably includes some glycol from the propanol, no attempt was made to distinguish this carbinol from the benzpinacol, and the analyses are reported as percent benzpinacol (since the atmospheric boiling point of pinacol is 176°C, and the working pressure of the vacuum line was about 10^{-5} mm, it was considered probable that most of the glycol distilled away from the benzpinacol).

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*It was observed that the melting point of pinacol depends markedly upon the rate of heating, and the literature value could be approached only if the rate of heating were quite slow as with a capillary tube and heating bath. Faster heating as on a hot bench produced a melting point raised by 20 to 30°.

III. DISCUSSION AND CONCLUSIONS

A. HYDROGEN ATOM SCAVENGING AND ENERGY TRANSFER

Evidence was presented in the previous paper[1] of this series to show that the effect of dissolved acetone upon the yield of radiolytic hydrogen from propanol-2 could be explained by trapping of hydrogen atoms (from the propanol-2) by the carbonyl group of the ketone. This evidence consisted principally in the fact that the hydrogen and methane originated from the acetone in yields which were directly proportional to the absorption of energy in the acetone. The yields of hydrogen and methane from radiolysis of solutions of benzophenone in propanol-2 are shown in Figure 1. It was subsequently found that, for reasons
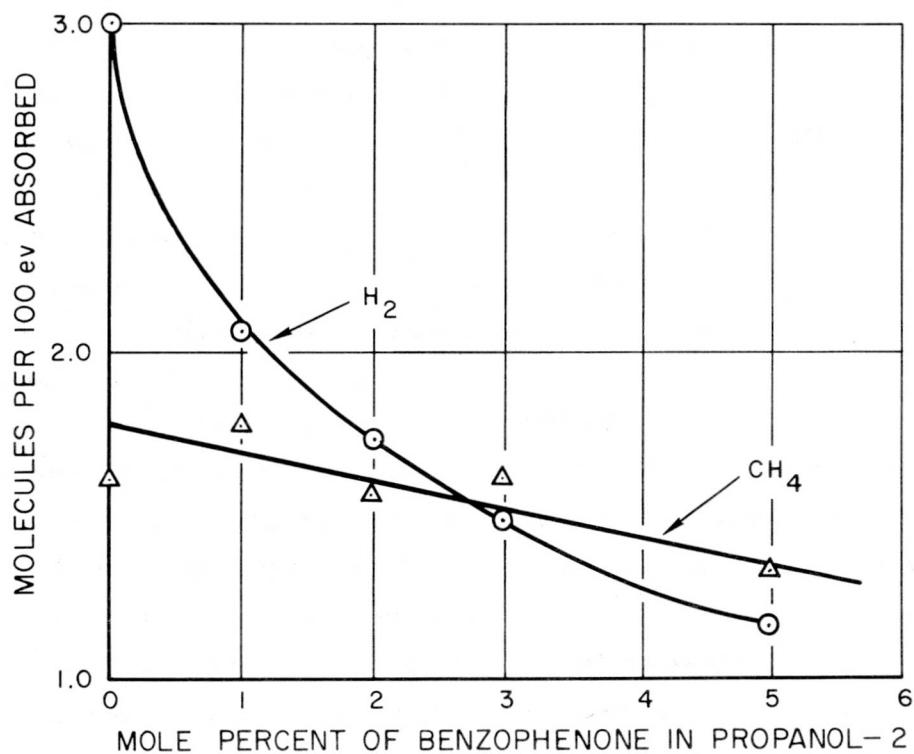

Figure 1. Gas Yields from Benzophenone-Propanol Solutions

discussed below, benzophenone disappeared from these solutions at a very high rate (in contrast to the acetone solutions,[1] where acetone concentration remained essentially constant). During the irradiations, whose results are cited in Figure 1, approximately one-half of the benzophenone was consumed

and an amount of acetone was formed nearly equivalent to the amount of benzophenone consumed. Therefore, we studied the yields of hydrogen and methane from a 2% solution of benzophenone in propanol-2 as a function of dose. The yields so obtained were linear with dose and could be extrapolated to zero dose to obtain initial yields. The data of Figure 1 thus corrected to present the initial yields of hydrogen are shown in Figure 2, together with the corresponding data for solutions of acetone in propanol-2. Figure 2 also contains curves for the difference in hydrogen yield $\left[\Delta G(H_2)\right]$ for these two types of solution at equal molar concentrations of the two ketones.

It is instructive to compare the results obtained in this investigation with the corresponding data for solutions of acetone in propanol-2. This comparison is shown in Figure 2. At low concentrations of ketone (0.5%), the slope $\Delta G(H_2)$ /Δ (ketone) for benzophenone solutions is about twice that for the acetone solutions; thus benzophenone is about twice as effective as acetone in reducing the hydrogen yield from propanol-2.

Acetone had no observable effect upon the methane yield from propanol-2 (this was measured with the use of acetone-d_6), whereas 2% of benzophenone reduces the methane yeild from 1.8 to 1.4. In the case of solute acetone, it was possible to show that the carbonyl group of the acetone does not appear able to trap methyl radicals.

This difference in effectiveness of two solutes so similar in structure (namely, each consisting of two hydrocarbon residues attached to a carbonyl group) is quite in contrast to the similar effectiveness of other solutes in reducing hydrogen yields. For example, Schuler[5] found that iodine, methyl iodide, ethyl iodide, methyl bromide, sulfur dioxide, methyl iodide plus iodine, and methyl iodide plus triphenylmethane, were equally effective in reducing the hydrogen yield from cyclohexane. Similarly Ausloos and Paulson[6] found that both iodine and DPPH were about equally effective in reducing the hydrogen yield and methane yield from irradiated liquid acetone.

It appears then that the differences in structure between acetone and benzophenone are quite important. This fact can be best rationalized on the basis that the effect of both ketones upon the hydrogen yield from propanol-2 is caused by the scavenging of hydrogen atoms. It is well known that aryl rings can trap
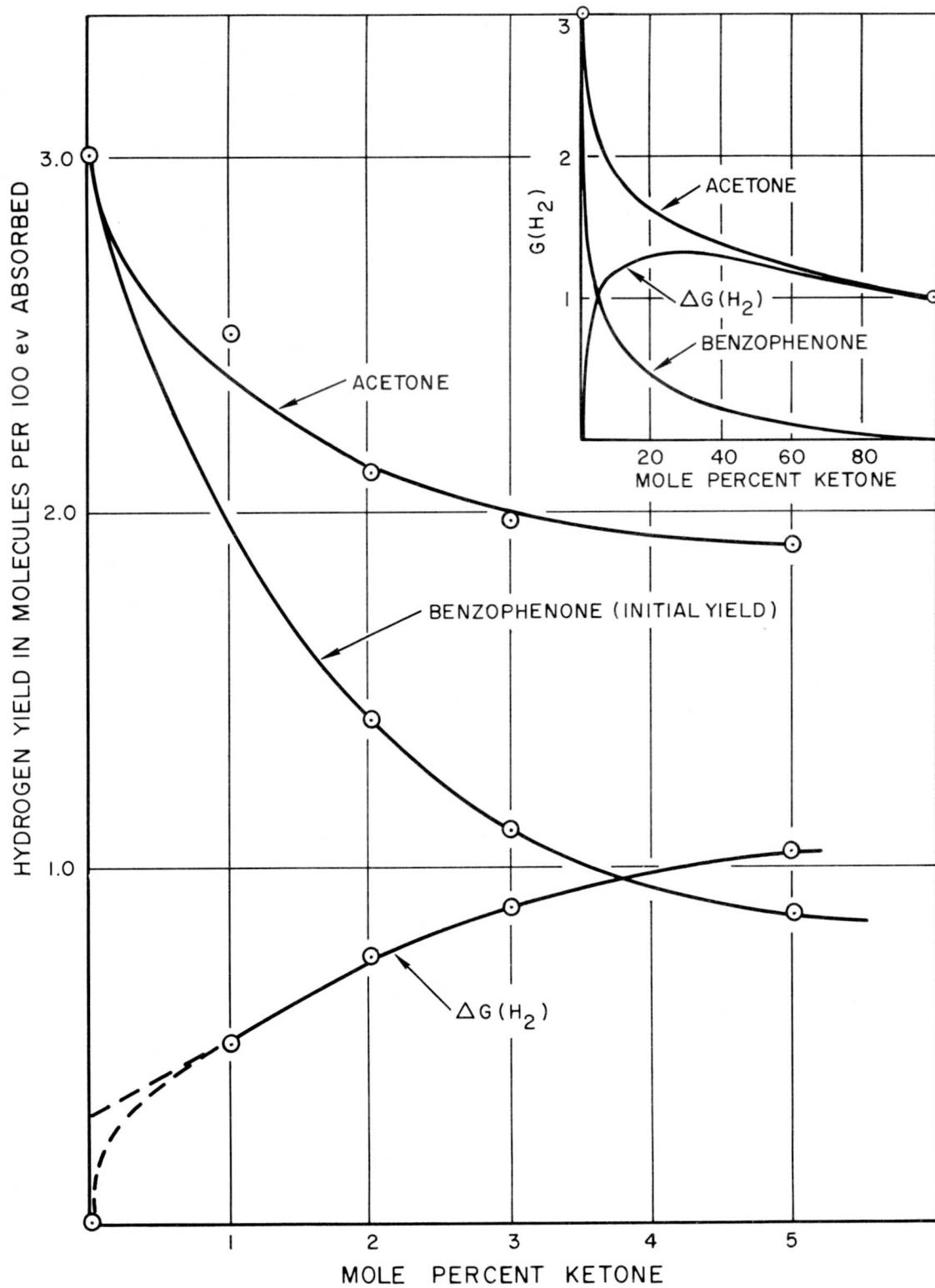
Figure 2. Gas Yields from Solutions of Ketone in Propanol-2

hydrogen atoms by an addition reaction, both in the gas phase[7] and in the liquid phase.[8] It is also known that methyl radicals add readily to aromatic rings.[9] Benzophenone, for the purposes of this discussion, can be regarded as a collection of six carbon-carbon double bonds and one carbon-oxygen double bond; each double bond is capable of scavenging at least the hydrogen atoms. Thus a solution of benzophenone, equal in molar concentration to a particular acetone solution, contains a concentration of scavenger groups seven times that of the acetone solution. This is consistent with our observation that benzophenone is more effective in reducing hydrogen yield than acetone.

Evidence was produced in the earlier paper that the acetone carbonyl group does not scavenge the thermal methyl radicals produced in the radiolysis of acetone; presumably the carbonyl group of benzophenone would be even less effective as a methyl radical scavenger owing to the greater steric demand of that carbonyl group. However, the ability of dissolved benzophenone to reduce the methane yield from propanol-2 can be logically attributed to scavenging of the methyl radicals by the aromatic rings of the benzophenone.

We have no direct evidence to exclude energy transfer as an important factor in the radiolysis of the benzophenone-propanol-2 solutions. However, it is difficult to reconcile the assumption of extensive energy transfer here with the indicated absence of such processes in the acetone-propanol-2 radiolysis,[1] because energy transfer from propanol-2 to acetone seems at least as energetically favorable as that from propanol-2 to benzophenone. The excitation energies and ionization potentials of the two ketones are quite similar (since in both cases the electrons of the carbonyl oxygen unshared pair are the ones principally involved in these transitions).

B.   BENZPINACOL FORMATION

The yields of acetone and benzpinacol and the yield for benzophenone consumption were measured as a function of dose. All three yields were found to be linear with dose; the data for acetone and benzpinacol formation could be extrapolated to indicate zero yield at zero dose. We suggest, therefore, that these data represent observation of primary chemical reactions in the radio-lyses.

The yield for acetone formation was found to be 9.1 molecules per 100 ev absorbed, the yield of benzpinacol (as semipinacol units) to be 6.6

molecules per 100 ev absorbed, and the yield for consumption of benzophenone to be 7.2 molecules per 100 ev absorbed. It may be noted that the yield of semipinacol units and the yield for consumption of benzophenone are nearly equal - i.e., one-half molecule of benzpinacol appears for every molecule of benzophenone which disappears. On the other hand the yield of acetone is distinctly higher. The higher yield of acetone than semipinacol units may be accounted for by postulating that acetone is formed via two processes: 1) the direct radiolysis of propanol-2, and 2) a radiation-induced reaction between the ketone and the carbinol.

1) $(CH_3)_2CHOH \xrightarrow{\quad\text{\scriptsize \Large\char"2240}\quad} (CH_3)_2CO + H_2$

2) a)
$$\underset{C_6H_5}{\overset{C_6H_5}{>}}C = O \cdots H\text{-}O\text{-}CH\underset{CH_3}{\overset{CH_3}{<}} \longrightarrow \underset{C_6H_5}{\overset{C_6H_5}{>}}\overset{\circ}{C}\text{ - OH} + .O - CH\underset{CH_3}{\overset{CH_3}{<}}$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\text{I}\quad\quad\quad\quad\text{II}$$

b) $(C_6H_5)_2\overset{\circ}{C}$ - OH + $(C_6H_5)_2$ CO $\longrightarrow (C_6H_5)_2\overset{\overset{OH}{|}}{C}\text{---}\overset{\overset{O}{|}}{C}(C_6H_5)_2$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\text{III}$$

c) III + $(CH_3)_2$ CHOH $\longrightarrow \left[(C_6H_5)_2\overset{|}{C}\text{ - OH}\right]_2 + (CH_3)_2\overset{\circ}{C}\text{ - OH}$

d)
$$\underset{CH_3}{\overset{CH_3}{>}}CHO \longrightarrow \underset{CH_3}{\overset{CH_3}{>}}C = O + H$$
$$\quad\quad\quad\text{II}$$

e) 2 $\underset{CH_3}{\overset{CH_3}{>}}CHO \longrightarrow \underset{CH_3}{\overset{CH_3}{>}}CHOH + \underset{CH_3}{\overset{CH_3}{>}}C = O$
$$\quad\quad\quad\text{II}$$

3) H + $(C_6H_5)_2$ CO $\longrightarrow (C_6H_5)_2\overset{|}{C}$ - OH or $(C_6H_5)_2\overset{\overset{H}{|}}{C}$ - O -
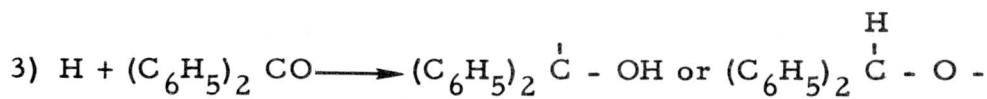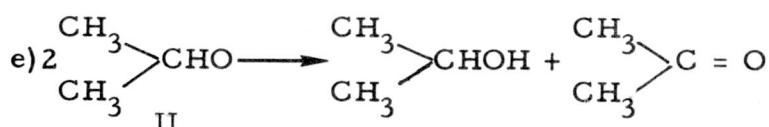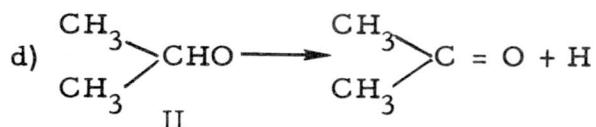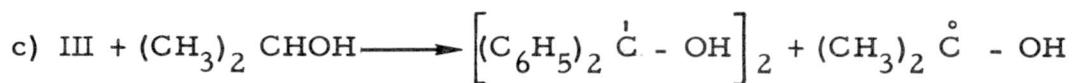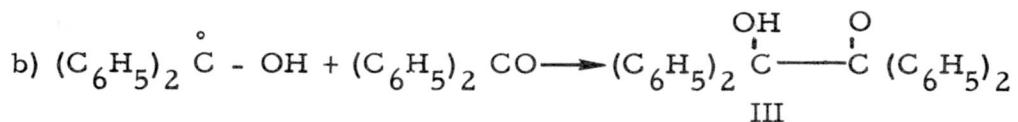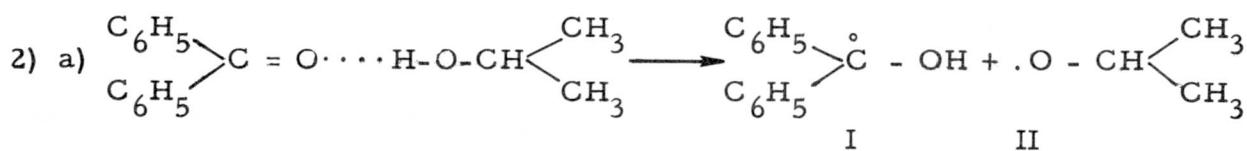
The radiolysis of propanol-2 is known[10] to produce acetone with a $\underline{G}$ value of about 3; the difference between our $\underline{G}$ for acetone, 9.1, and the $\underline{G}$ for semi-pinacol formation, 6.6, is 2.5. The fact that the $\underline{G}$ value for benzophenone consumption is higher than the $\underline{G}$ value for pinacol production can be attributed to consumption of benzophenone through hydrogen atom trapping equation 3). However, the accuracy of these values is insufficient to warrant much discussion of processes which are measured by the differences among the observed values. We can simply say that these differences are in the right directions and of reasonable magnitudes.

It is also to be noted that the $\underline{G}$ values reported above are based upon the energy absorption by the entire solution. If the consumption of benzophenone is calculated upon the basis of energy absorption only by benzophenone, the $\underline{G}$ value is about 350. This very high value suggests a) a high rate of energy transfer from propanol-2 to benzophenone; or b) a chain reaction for benzophenone consumption; or c) a reaction which can be initiated by absorption of very small amounts of energy-i.e., of the order of 0.3 ev, or about 6 to 7 kcal/mole. In the foregoing discussion it was concluded that energy transfer from propanol-2 to the dissolved benzophenone was not likely in these radiolyses. We have been unable to think of any logical or defensible chain reaction involving benzophenone and propanol-2, so we think explanation b) is unlikely.

However, it is highly probable that a substantial amount of hydrogen bonding exists between the ketone and the carbinol hydroxyl hydrogen, as shown in equation 2), a). It seems quite probable that absorption of a relatively small amount of radiant energy could effect a reversible shift of the hydrogen atom from the carbinol oxygen to the ketone oxygen. The two radicals I and II thus produced could be the source of the two reaction products, benzpinacol and acetone.

We have no evidence bearing upon the mechanism of pinacol and acetone formation subsequent to the presumed formation of the two semipinacol intermediates. We can say that formation of acetone from II by reaction 2), d) is endothermic and thus unlikely; that formation of acetone directly from II by the disproportionation 2), e) can be ruled out since this would produce only one acetone molecule for every two benzophenone molecules consumed. We can also say that the sequence of reactions 2), a), b), c), is in agreement with

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the stoichiometry observed, and seems the most probable sequence which can be proposed in the absence of any specific knowledge of the reaction intermediates. We do not know what process converts the $(CH_3)_2 COH$ radicals into acetone.

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