Hydrogen Transfer and Energy Transfer in the γ-Radiolysis of Benzophenone–2-Propanol. Effects of Naphthalene and of Phenyl Disulfide

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γ-Ray irradiation of 2-propanol leads to zero-order formation of acetone which is little affected by phenyl disulfide. γ-Ray irradiation of benzophenone in 2-propanol leads to benzpinacol, with rate zero order in benzophenone, and to an equimolar additional quantity of acetone. Naphthalene has essentially no effect in this system, indicating that triplet benzophenone may not be an intermediate in the γ-ray-induced reaction, in contrast to the ultraviolet radiation-induced reaction. Phenyl disulfide inhibits both light and γ-ray-induced reductions of benzophenone. The radical $(C_6H_5)_2\dot{C}OH$ is an intermediate for consumption of benzophenone and formation of benzpinacol in both systems. Disulfide and mercaptan protect solvent and solute against radiation by repeated hydrogen transfer reactions (eq. 1 and 2).

Introduction

Preliminary results have been reported,[3] indicating that aromatic mercaptans and disulfides inhibit the ^{60}Co γ-ray-induced conversion of benzophenone to benzpinacol in 2-propanol. The present work reports a more detailed study of the effects of phenyl disulfide and of naphthalene on the ^{60}Co γ-ray-induced reaction, carried out to ascertain whether the first excited triplet of benzophenone and/or the benzophenone ketyl radical ($(C_6H_5)_2\dot{C}OH$, I) and alcohol-derived radicals are important intermediates in this reaction. Measurements have been made of rates of formation of acetone and acetaldehyde, of disappearance of benzophenone, and of appearance of benzpinacol as functions of concentrations of benzophenone, phenyl disulfide, and naphthalene.

Results and Discussion

Radiolysis of 2-propanol led to acetone, $G = 2.6$, and a lower yield of acetaldehyde, $G = 0.4$, yields being directly proportional to dose and little if at all affected by 2.56×10^{-3} M phenyl disulfide. These two products of radiolysis of the solvent may be formed partly in radiation tracks and partly from fragments or other species which go into the solution and react too rapidly to be affected much by this solute present in low concentration.

Irradiation of 0.1 and 0.5 M solutions of benzophenone in 2-propanol led to disappearance of benzophenone and formation of acetone with rates zero order in benzophenone. The extents of these reactions appeared to depend only upon the quantity of radiation absorbed when followed to 80% disappearance of benzophenone. The G-value for benzophenone disappearance was 6.4. In representative reactions, both under these conditions and in the presence of phenyl disulfide, benzpinacol was isolated and characterized,[3] and found to account satisfactorily for the quantity of benzophenone which had reacted. The G-value for acetone formation was 5.5. It appears that approximately one molecule of acetone is formed per two molecules of benzophenone reduced to benzpinacol in addition to that which is normally formed from radiolysis of the solvent alone under these circumstances. This is similar to the relative yields in the photochemical reaction[4] and confirms our preliminary

results,[3] but indicates lower yield of acetone than reported previously.[5]

Acetaldehyde, formed with $G = 0.4$ from 2-propanol alone, showed increased G with increasing concentration of benzophenone, $G = 1.0$ and 1.3 in 0.1 and 0.5 M benzophenone, respectively. The reactions leading to this product appear relatively insensitive to the presence of either naphthalene or disulfide. 1-Hydroxyethyl radical, $CH_3\dot{C}HOH$, a possible product of radiolysis of 2-propanol, may transfer hydrogen to benzophenone, leading to increased yield of acetaldehyde and to the radical I, $(C_6H_5)_2\dot{C}OH$, in a reaction analogous to that proposed for the 2-hydroxy-2-propyl radical.[4]

Naphthalene, 0.01 and 0.05 M, had no effect which we could detect on the rate of reduction of benzophenone in the radiolysis of 0.1 M benzophenone in 2-propanol. This indicates that the γ-ray-induced reaction does not involve the same metastable triplet state of benzophenone which is the chemically reactive intermediate in the light-induced process[4,6] and which is effectively quenched by naphthalene.[7a,b,8] It is not at present clear whether other higher excited states of benzophenone, which may not be quenched by naphthalene, could themselves enter into chemical reactions[9a,b] leading to benzpinacol, or whether they would degrade very rapidly to the first excited triplet state.[10a-c] If the latter should be the case the insensitivity of the reaction to naphthalene would tend to rule out direct excitation of benzophenone by γ-rays or energy transfer from excited solvent or solvent fragments as important mechanisms leading to disappearance of this solute. This is consistent with observations of liquid scintillation counters in which the energy efficiency of most scintillators in γ-irradiated organic solutions is less than 1%.[11]

Phenyl disulfide, in low concentrations, 10^{-3}–10^{-2} M, has a marked effectiveness as a retarder and inhibitor

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of the reduction of benzophenone and formation of acetone in radiolysis of 0.1 and 0.5 M benzophenone in 2-propanol. The data are summarized in Table I. Reduction of benzophenone and formation of acetone remain zero order but the rates are decreased, the decrease becoming more marked with increasing concentration of disulfide. The rate of reduction of benzophenone is decreased to one-half the uninhibited rate by about 0.6×10^{-3} M disulfide in 0.1 M benzophenone in 2-propanol, and by about 2.7×10^{-3} M disulfide in 0.5 M benzophenone. The reduction of 0.1 and 0.5 M benzophenone in 2-propanol are essentially completely inhibited by about 6×10^{-3} and 10×10^{-3} M disulfide, respectively.
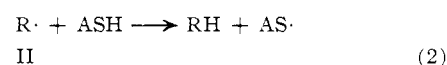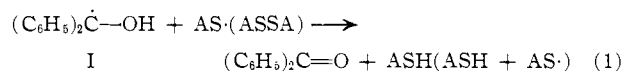
TABLE I

EFFECT OF PHENYL DISULFIDE ON THE RADIOLYSIS OF BENZOPHENONE IN 2-PROPANOL

Init. benzophenone, mole l.$^{-1}$	Phenyl disulfide, mole l.$^{-1}$	G		
		Acetaldehyde	Acetone	—Benzophenone
0	0	0.40[a]	2.6[a]	...
0	2.56	.40	2.5	...
0.10	0	.90[b]	5.4[b]	6.4[b]
.10	0.37	..	..	4.3
.10	.49	..	..	3.6[c]
.10	.74	..	2.6	2.8
.10	1.04	0.96[c]	2.8[c]	2.5[c]
.10	1.25	1.0[b]	2.2[c]	2.1[c]
.10	2.58	0.96	1.9	0.7
.10	6.40	..	..	0[c]
.10	10.3	0.90[c]	1.4[c]	0[c]
.50	0	1.4	5.7	6.4
.50	0.77	..	..	5.6
.50	1.50	1.7[d]	5.3[d]	5.4[d]
.50	2.50	1.4[d]	4.1[d]	3.7[d]
.50	3.20	1.0	2.4	2.5
.50	6.70	1.3[d]	2.0[d]	1.5[d]
.50	9.00	1.0[d]	1.7[d]	0.7[d]
.50	12.0	1.4	1.7	0

[a] Yields unchanged by 1×10^{-2} M naphthalene. [b] Yields unchanged by 1×10^{-2} and 5×10^{-2} M naphthalene. [c,d] G-Value calculated from product formed by a dose of 9.75 and 24.4×10^{20} e.v. ml.$^{-1}$, respectively. All other yields were determined from the slope of the observed linear plot of yield vs. dose over the dose range 0–30 $\times 10^{20}$ e.v. ml.$^{-1}$.

The decrease in reduction of benzophenone due to disulfide is accompanied by decrease in formation of acetone. The G-value for acetone decreases somewhat more than G(benzpinacol), indicating that additional solvent may be protected over that which is converted to acetone in the reactions leading to benzpinacol. At concentrations of disulfide where reduction of benzophenone is virtually completely inhibited G-(acetone) falls to about 1.7, which is below that found in the radiolysis of 2-propanol, alone and in the presence of 2.5×10^{-3} M disulfide, $G = 2.6$. The combination of benzophenone and disulfide may offer some protection to the solvent itself, but confirmation of this would depend upon more complete analyses for the other products which may be formed.

The disulfide shows an inhibitory effect in radiolysis which is similar, quantitatively, to its effect in the photochemical reaction. In these inhibitions small quantities of the sulfur compounds protect manyfold larger quantities of benzophenone from reduction and of 2-propanol from oxidation. In the experiments in which total protection of benzophenone is noted, the radiation doses would otherwise have led to reduction of benzophenone and oxidation of 2-propanol, each in molar quantities ten times as great as the amount of disulfide present. The irradiations were carried out for arbitrary lengths of time and protection would undoubtedly be present for even greater doses. The quencher naphthalene has no such effect and the sulfur compound, in any event, is not a quencher for photoexcited benzophenone.[3,12,13] The mixture of disulfide and mercaptan, which is presumably present in this system undergoing a radiation-induced oxidation–reduction, inhibits or protects by participating repeatedly in free radical reactions involving rapid hydrogen transfers similar to those postulated previously in the photochemical system, eq. 1 and 2.

$$(C_6H_5)_2\dot{C}\!\!-\!\!OH + AS \cdot (ASSA) \longrightarrow$$

$$I \qquad (C_6H_5)_2C\!\!=\!\!O + ASH(ASH + AS\cdot) \quad (1)$$

$$R \cdot + ASH \longrightarrow RH + AS \cdot$$

$$II \qquad\qquad\qquad (2)$$

Radical I may be formed from products of radiolysis of 2-propanol: by attachment of an electron[14] followed by a proton, by addition of a hydrogen atom, and by transfer of a hydrogen atom from solvent-derived free radicals. These radicals, of type II, $(CH_3)_2$-$\dot{C}OH$, $\cdot CH_2CHOHCH_3$, and $(CH_3)_2CHO\cdot$, may react with benzophenone to form acetone and radical I, which normally dimerizes to benzpinacol. As described previously,[3] in the presence of the sulfur compounds, radical I may be reoxidized to benzophenone by disulfide or thiyl radical (eq. 1); radicals II may be reconverted to 2-propanol by mercaptan (eq. 2). Solute and solvent are protected; the sulfur compounds are regenerated in their two valence states and used repeatedly.[3] To the extent that the radiation leads to rupture of bonds other than those binding hydrogen, the sulfur compounds alter the course of subsequent reactions, but do not afford true protection.

From Fig. 1 it appears that for a given benzophenone concentration there is an approximately linear relationship between $1/G$ and concentration of disulfide at low concentrations of the latter and moderate degrees of retardation. A higher order dependence of inhibition on concentration of sulfur compound is evident at higher disulfide concentrations, $1/G$ rising rapidly. The disulfide appears about five times more effective in 0.1 M benzophenone than in 0.5 M solution. This appears consistent with the processes considered above. Benzophenone and the sulfur compound compete for fragments from solvent, which may convert benzophenone to radical I. At higher concentration benzophenone competes more successfully, and the G-value for radical I and thus for benzpinacol is higher. Beyond this initial competition, the disulfide inhibits by oxidizing radical I to benzophenone. A dependence of $1/G$ on a function of the ratio of concentration of sulfur compound to benzophenone was earlier predicted in the photochemical process.[12]

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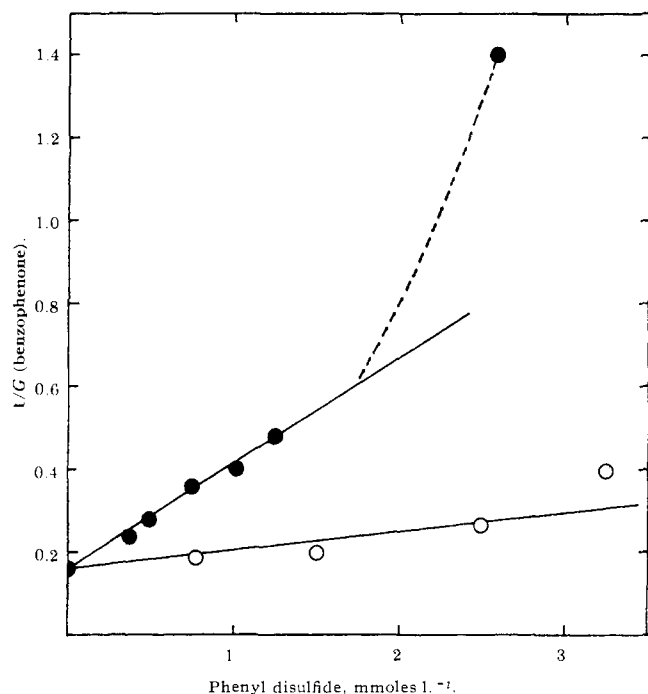(14) M. R. Ronayne, J. P. Guarina, and W. H. Hamill, ibid., **84**, 4230 (1962).

Fig. 1.—γ-Radiolysis of 0.1 and 0.5 M benzophenone in 2-propanol; effect of phenyl disulfide on reduction of benzophenone: -●-●-, 0.1 M benzophenone; -O-O-, 0.5 M benzophenone.

Experimental

Materials.—Benzophenone (Fisher) was crystallized from ethyl alcohol; m.p. 47°. 2-Propanol (Fisher spectroscopic or reagent grade) was found free from impurity by gas chromatographic analysis and used without further treatment. Naphthalene (Fisher) and phenyl disulfide (Eastman) were used as received; m.p. 78–79 and 59°, respectively.

Preparation and Irradiation of Solutions.—Standard solutions of 0.1 and 0.5 M benzophenone in 2-propanol were prepared. For the experiments with naphthalene and phenyl disulfide these materials were weighed into a volumetric flask and made up to the mark with standard benzophenone solution. Aliquots (2 ml.) of the reaction mixture were placed in 150 × 12 mm. Pyrex tubes and degassed by the freeze–thaw method (three cycles)

on a vacuum line at 0.02 mm. The tubes were then irradiated with a nominal 1.25-Mc. cobalt-60 source. The radiation doses received by the solutions were determined with a ferrous–copper dosimeter[15] (a solution of 10^{-3} N ferrous sulfate and 10^{-2} N copper sulfate in 10^{-2} N sulfuric acid, taking $G_{Fe^{3+}-(Cu^{2+})} = 0.66$). The dose rate at the commencement of the experiments was 4.06 Mrads hr.$^{-1}$ dropping to 3.91 Mrads hr.$^{-1}$ at the end. The electron densities of the dosimeter and 2-propanol are 0.554 and 0.432 electron mole ml.$^{-1}$, respectively. To calculate the dose received by the reaction solutions, the dose received by the same volume of the ferrous–copper dosimeter was multiplied by a factor $0.432/0.554 = 0.780$.

Analysis.—After the irradiation period the reaction tube was opened and 0.5 ml. of the reaction mixture was removed and mixed with a weighed (1 mmole) amount of 2-butanol. This solution was gas chromatographed on an Aerograph A700. A 6-ft. column of 10% polymeric butyl glycol adipate (Rubber Corporation of America B.G.A.) on 80–100 Chromosorb-W (Johns Manville) was used at 40°. The carrier gas was helium and a thermal conductivity detector was used. The acetone formed was identified by its retention time and infrared spectrum of a sample collected at the exit port of the gas chromatograph. Acetaldehyde was identified by its retention time and typical odor at the exit port. The concentration of acetaldehyde was determined by comparison of its peak area with that of the added 2-butanol, while acetone was determined by comparison with both 2-butanol and 2-propanol peaks. From calibration curves the mole ratios of 2-propanol/acetone, 2-butanol/acetone, and 2-butanol/acetaldehyde were found to be 1.00, 0.90, and 0.76 × peak area ratio, respectively. Benzophenone was estimated by removing a 1-ml. aliquot, diluting with 2-propanol, and measuring the absorption at 333, 340, 350, and 360 mμ on a Perkin–Elmer Model 202 spectrophotometer. Extinction coefficients at these wave lengths were 150, 140, 108, and 68, respectively.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY, CAMBRIDGE, MASS.]

Oxidative Decarboxylation[1]

By LOUIS F. FIESER AND MAKHLUF J. HADDADIN

A convenient synthesis of p-terphenyl reported in the literature from the adduct 1 of *trans,trans*-1,4-diphenyl-butadiene and dimethyl acetylenedicarboxylate involves a hitherto unrecognized alkaline isomerization of 1 to 2 prior to saponification to 3. Elucidation of the true structure of 3 provides the basis for a rational interpretation of the ready decarboxylation of this bisallylic diacid to p-terphenyl by alkaline ferricyanide (6 → 7 → 4). Further examples of the reaction with diacids of the dihydronaphthalene and dihydrobenzene series are recorded.

Lohaus[2] briefly reported the synthesis of p-terphenyl (**4**) by Diels–Alder addition of *trans,trans*-1,4-diphenyl-butadiene to diethyl acetylenedicarboxylate (5 hr. at 150°), saponification, and oxidation with potassium ferricyanide in sodium carbonate solution. McDonald and Campbell[3] repeated the synthesis without isolation of intermediates and extended the scheme to the synthesis of a number of polyphenyls, including p-

quinquephenyl.[4] These authors formulated each oxidation as involving a diacid corresponding in structure to the diester adduct saponified, for example 1. Such an oxidative decarboxylation seemed to us surprising enough to call for a reinvestigation.

We prepared *trans,trans*-1,4-diphenylbutadiene by a simplified version of the phosphate modification of the Wittig reaction,[5] particularly as developed by Seus

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