EFFECT OF MERCAPTAN ON PHOTOREDUCTION OF ACETONE. NON-REPAIR HYDROGEN TRANSFER REACTIONS[†]

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(Received 18 November 1968)

Abstract – Ultraviolet (u.v.) irradiation of solutions of benzhydrol in acetone leads to formation of 2-propanol, benzpinacol and some benzophenone, apparently from the free radicals $(CH_3)_2\dot{C}OH$, II, and $(C_6H_5)_2\dot{C}OH$, I. 2-Propanol is formed more rapidly and benzophenone is formed to a much larger extent and persists longer when the solution contains mesityl mercaptan, as radical II is reduced by mercaptan and radical I is oxidized by thiyl radical. The same hydrogen atom transfer reactions, which retard by a repair mechanism the photoreduction of benzophenone by 2-propanol, accelerate and alter the course of photoreduction of acetone by benzhydrol. Irradiation of acetone leads to 2-propanol, and this is formed more rapidly in the presence of mercaptan. Irradiation of benzophenone in acetone leads to no apparent reaction. The courses of reaction of the several systems are discussed.

INTRODUCTION

THE LIGHT induced reduction of benzophenone by 2-propanol proceeds via the first excited triplet of the ketone [1, 2] and the free radicals I and II.

$$(C_6H_5)_2C = O^* + (CH_3)_2CHOH \rightarrow (C_6H_5)_2\dot{C}OH + (CH_3)_2\dot{C}OH$$
(1)
I II

The reaction is an efficient one and the quantum yield for disappearance of the ketone may approach two at moderate concentrations of the ketone as the reaction of equation (2) becomes important [3].

$$(C_6H_5)_2C = O + II \rightarrow I + (CH_3)_2C = O$$
 (2)

The benzophenone ketyl radicals, I, dimerize, equation (3), and nearly quantitative yields of benzpinacol and acetone may be obtained. The four possible disproportionation reactions of the radicals I and II, although thermodynamically favorable, do not occur under these conditions to an important extent, the indicated reactions being more rapid.

The photoreduction may be inhibited very effectively by low concentrations, ~ 0.01 M, of mercaptan and disulfide[4] as new hydrogen transfer reactions, equations (4) and (5), are introduced which reconvert radicals I and II to the starting materials more rapidly than they undergo the normal product forming reactions of equations (2) and (3).

[†]This work was supported by the U.S. Atomic Energy Commission, AT(30-1)2499, and by a Summer College Teacher Grant, The National Science Foundation.

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$$(C_6H_5)_2\dot{C}OH + AS \rightarrow (C_6H_5)_2C = O + ASH$$
(4)

$$(CH_3)_2COH + ASH \rightarrow (CH_3)_2CHOH + AS$$
(5)

Disproportionation of the initially formed radicals is in effect catalyzed as the mercaptan and thiyl radical are regenerated and function repeatedly. A few molecules of sulfur compound negate the chemical consequences of many quanta and protect large quantities of ketone and alcohol. Mercaptans may offer protection in this way under a variety of conditions: against the ⁶⁰Co γ -ray induced reduction of benzophenone in 2-propanol [5, 6]: in photoreduction when only one intermediate radical is present, the benzophenone-benzhydrol and acetophenone- α -phenylmethylcarbinol systems, in which the intermediate radical is both oxidized by thiyl radical and reduced by mercaptan[7]; and in photoreductions in which an intermediate radical may consume the sulfur compound, the benzophenone-ether and benzophenone-hydrocarbon systems[8]. Evidence for this mechanism of protection by rapid hydrogen atom transfer reactions has been found in racemization and deuterium exchange studies[5, 7], in the equivalent effects of mercaptan and disulfide[5, 7], and in flash photolysis experiments[9].

According to this mechanism, when the benzophenone- and acetone-ketyl radicals I and II are formed in the presence of thiyl radical and mercaptan, the dominant reactions which result are those of equations (4) and (5), in which the radicals I and II are converted to benzophenone and 2-propanol respectively. If the radicals I and II are formed from benzophenone and 2-propanol the system is returned to its initial state and extended inhibition or protection is observed. As a corollary this would require that if the radicals I and II should be formed in the presence of the sulfur species, but not from benzophenone and 2-propanol, the radicals would be converted to these two compounds. The system would not be converted to its initial state, protection against radiation would not be observed, and the presence of the sulfur compound might instead change the course of the reaction from that observed in its absence. This situation might arise if acetone were irradiated in the presence of benzhydrol, and we wish to report the results of such experiments.

EXPERIMENTAL

Materials and procedures

Benzhydrol (Eastman, white label) was recrystallized from petroleum ether, $(30^{\circ}-60^{\circ})$, m.p. $68 \cdot 5^{\circ}-69 \cdot 5^{\circ}$. Benzophenone (Fisher reagent) was recrystallized from petroleum ether, (b.p. $30^{\circ}-60^{\circ}$), m.p. $48 \cdot 6^{\circ}-49^{\circ}$. Acetone (Fisher reagent) was used as received. 2-Mercaptomesitylene and 2-mesityl disulfide were available from previous work [5, 8].

Solutions were degassed by the freeze-thaw technique and irradiated under argon in 1 cm ground-glass closed Pyrex tubes. The tubes were mounted vertically in a rotating turntable and were irradiated either by a 55 W Osram mercury lamp, placed centrally 4 cm from the tubes, or by a G.E. RS sunlamp placed on the periphery 3 cm from the circle traced by the tubes.

Analyses for benzophenone were carried out by infrared absorption at 6.0μ in chloroform on a Perkin-Elmer Infracord. Content of benzophenone was determined by comparison with a calibration curve prepared from absorbance measurements of solutions of known concentrations. U.V. spectra were obtained in 95 per cent

ethanol in a Cary 14 spectrophotometer. Analyses for 2-propanol were carried out by glc on Aerograph A-90-P and 200 instruments, 10 and 15 per cent Ucon on 60-80 Chromosorb W, column temperature 40°. Determinations were made in some cases with 2-butanol as an internal standard and in other cases by comparison with a calibration curve prepared from peak heights of solutions of known concentration.

Benzpinacol from benzhydrol-acetone

Aliquots of a solution of 4.0 g, 0.022 mole, 1.1 M, of benzhydrol in 20 ml of acetone were irradiated with the G.E. lamp for 150 hr. The acetone was removed and the residue was crystallized from ethanol, leading to benzpinacol, 0.77 g 19 per cent yield, identified by i.r. spectrum and m.p. 187° - 188° .

Conversion of benzhydrol to benzophenone

(i) Aliquots, 5 ml, of 0.50 M solutions of benzhydrol in acetone and of 0.50 M benzhydrol and 0.040 M 2-mercaptomesitylene in acetone were irradiated with the G.E. lamp for 114, 138 and 145 hr and then taken to dryness. Residues from the solutions without mercaptan showed very minor absorbance at 6.0μ . The residues from the solutions irradiated with mercaptan, analyzed at 6.0μ , contained 0.036, 0.037 and 0.039 g of benzophenone respectively. One residue was treated with 2,4-dinitrophenyl-hydrazine in ethanol, leading to the 2,4-dinitrophenylhydrazone of benzophenone, m.p. 238°-239° dec.

(ii) Aliquots, 5 ml, of 0.025 M benzhydrol and 0.0025 M 2-mercaptomesitylene in acetone, were irradiated with the G.E. lamp for 20, 45, 70, and 118 hr, and then taken to dryness. Analysis of the residues at 6.0μ indicated the presence of 0.0059 M, 0.0077 M, 0.011 M and 0.0097 M benzophenone, respectively, after the stated periods of irradiation.

(iii) Aliquots, 5 ml, of $6\cdot 2 \times 10^{-3}$ M benzhydrol in acetone and of $6\cdot 2 \times 10^{-3}$ M benzhydrol and $8\cdot 6 \times 10^{-4}$ M 2-mercaptomesitylene in acetone were irradiated with the Osram lamp and then taken to dryness. Analysis of the residues for benzophenone indicated that, in the absence of mercaptan, 3×10^{-4} M, 6×10^{-4} M, 2×10^{-4} M, 1×10^{-4} M, and 1×10^{-4} M benzophenone were present after irradiation for 16, 27, 35, 47 and 58 hr respectively, Fig. 1. In the presence of mercaptan, $1\cdot 3 \times 10^{-3}$ M, $1\cdot 5 \times 10^{-3}$ M, $1\cdot 9 \times 10^{-3}$ M, $2\cdot 3 \times 10^{-3}$ M, $2\cdot 4 \times 10^{-3}$ M, $2\cdot 4 \times 10^{-3}$ M, $1\cdot 3 \times 10^{-3}$ M, and $1\cdot 4 \times 10^{-3}$ M benzophenone were present in the solutions after irradiation for 6, 11, 16, 26, 47, 72, 143 and 159 hr respectively, Fig. 1.

Conversion of acetone to 2-propanol

Aliquots, 5 ml, of acetone and acetone solutions were degassed, irradiated on the turntable with an Osram lamp for stated periods, and analyzed for 2-propanol by glc. The solutions were (a) $5 \cdot 0 \times 10^{-3}$ M benzhydrol in acetone; (b) $5 \cdot 0 \times 10^{-3}$ M benzhydrol and $5 \cdot 0 \times 10^{-4}$ M 2-mercaptomesitylene in acetone; (c) acetone alone; (d) $5 \cdot 0 \times 10^{-4}$ M 2-mercaptomesitylene in acetone; and (e) 5×10^{-2} M benzophenone in acetone. Results are given in Table 1.

RESULTS

In initial experiments 1 M benzhydrol in acetone was irradiated for ~ 20 hr and we were unable to isolate benzpinacol. When irradiation was extended to 150 hr, benzpina-

col was isolated in yield equivalent to 19 per cent of the benzhydrol initially present. The residue from evaporation of the mother liquors appeared from infrared spectrum to be largely recovered benzhydrol; the melting point was slightly depressed.

Residues from solutions of 1 M and 0.5 M benzhydrol in acetone, irradiated in excess of 100 hr, showed no substantial amounts of benzophenone. Residues from solutions of 0.5 M benzhydrol and 0.04 M 2-mercaptomesitylene in acetone, irradiated for 114–145 hr contained benzophenone corresponding to 0.040-0.043 M in the solutions. Analyses were by i.r. absorption, and the ketone was characterized as the 2,4-dinitrophenylhydrazone.

At lower initial concentrations, 0.025 M benzhydrol and 0.0025 M 2-mercaptomesitylene, 0.006 M benzophenone was present after irradiation for 20 hr, and it rose to 0.01 M, and persisted at that concentration, during irradiation from 70 to 118 hr. U.V. spectra from 225 to 300 nm were obtained for the initial solution, for the solution after irradiation for 119 hr, and for 0.01 M benzophenone. The sum of the spectra of the initial solution and of the benzophenone solution very closely approximated the spectrum of the irradiated solution.

Formation and consumption of benzophenone was then examined at still lower initial concentration of benzhydrol, $6 \cdot 2 \times 10^{-3}$ M in acetone, alone and in the presence of $8 \cdot 6 \times 10^{-4}$ M 2-mercaptomesitylene. In the absence of mercaptan, 6×10^{-4} M benzophenone was present after irradiation for 27 hr and then fell to a very low value in 47 hr. In the presence of the mercaptan the concentration of benzophenone rose rapidly to $2-2 \cdot 4 \times 10^{-3}$ M, 32-39 per cent of the initial concentration of benzhydrol, from 16 to 47 hr irradiation, and then decreased slowly but was still $1 \cdot 4 \times 10^{-3}$ M, corresponding to 23 per cent of the initial benzhydrol after 159 hr, Fig. 1.



Fig. 1. Formation of benzophenone in u.v. irradiation of benzhydrol in acetone; $-4 - 6 \cdot 2 \times 10^{-3}$ M benzhydrol in acetone; $-6 \cdot 2 \times 10^{-3}$ M benzhydrol and $8 \cdot 6 \times 10^{-4}$ M 2-mercaptomesitylene in acetone.

The formation of 2-propanol during irradiation of the benzhydrol-acetone and benzhydrol-acetone-mercaptan systems was then examined at low concentrations of benzhydrol, 5×10^{-3} M, and 2-mercaptomesitylene, 5×10^{-4} M, Table 1. The initial rate of formation of 2-propanol in the presence of mercaptan was about twice that in the absence of mercaptan; after irradiation for 71 hr, in the absence of mercaptan, 0.0049 M 2-propanol was present, 1 mole of 2-propanol per initial mole of benzhydrol, and 1.7 mole, 0.0087 M, was found in the presence of the mercaptan. 2-Propanol continued to be formed with prolonged irradiation. The concentration of 2-propanol rose to 0.013 M, after 240 hr irradiation in the absence of mercaptan, 2.6 moles per mole of benzhydrol, and to 0.014 M in the presence of mercaptan. The irradiation of acetone and acetone-mercaptan, 5×10^{-4} M, was then examined, with no benzhydrol present. 2-Propanol was formed even more rapidly than in the presence of benzhydrol, 0.009 M being present after irradiation for 72 hr in the absence of mercaptan, and 0.017 M in the presence of 5×10^{-4} M mercaptan. Irradiation of benzophenone, 0.05 M, in acetone was then examined, and the system appeared very inert, benzophenone did not disappear and 2-propanol was not formed.

Irradiation (hr)	2-Propanol, M				
	a	b	с	d	e
7	0.0014	0.0034			
24	0.0026	0.0055			
43	0-0037	0.0067			
71	0.0049	0.0087	0.0089	0.0169	0
137	0.0103	0.0118			
186	0.0113	0.0128			
240	0.0130	0.0142			

 Table 1. Formation of 2-propanol in u.v. irradiation of acetone and acetone solutions

a. 5.0×10^{-3} M benzhydrol in acetone.

b. 5.0×10^{-3} M benzhydrol and 5.0×10^{-4} M 2-mercaptomesitylene in acetone.

c. acetone.

d. 5.0×10^{-4} M 2-mercaptomesitylene in acetone.

e. 5×10^{-2} M benzophenone in acetone.

DISCUSSION

Irradiation of a solution of 1 M benzhydrol in acetone in Pyrex leads slowly to chemical reaction. The weak absorption band of acetone at 270 nm, $\epsilon \sim 13$, tails beyond the cutoff of Pyrex and probably results in reaction via excited acetone, equation (6), leading to the same products

$$(CH_3)_2 C = O^* + (C_6H_5)_2 CHOH \rightarrow (CH_3)_2 \dot{C} - OH + (C_6H_5)_2 \dot{C}OH$$

$$II \qquad I$$
(6)

as reaction 1, radicals I and II. Radical II survives in this system since in the absence of much benzophenone its consumption by reaction 2 is not rapid. Radicals I dimerized in part, equation (3), leading to benzpinacol. Direct evidence for the crossed coupling product and for the coupling product of II, pinacol, was not found, but these compounds may be formed.

During irradiation in the absence of mercaptan little benzophenone is detected. This may indicate that disproportionation reactions of radical I with radicals I or II, leading to benzophenone, are not important or that benzophenone is formed and disappears rapidly by excitation and reaction with benzhydrol. Benzhydrol, present initially, or 2-propanol, formed during irradiation, is required for removal of benzophenone which may be formed, since benzophenone does not react with acetone under irradiation in the time scale of these experiments.

In the presence of mesityl mercaptan benzophenone is formed substantially and efficiently, probably by reaction of the ketyl radical I with thiyl radical [9], equation (4), and it is readily detected. At high initial concentration of benzhydrol, 0.5 M, and mercaptan, 0.04 M, a quasi photostationary concentration of 0.04 M benzophenone is achieved for a long period. Much of the light is absorbed by this benzophenone, and the mercaptan inhibited benzophenone-benzhydrol[7] and benzophenone-2-propanol[4] systems may lead to the dominant reactions during this period, equations (7), (4) and (8) and (1), (4) and (5).

$$(C_6H_5)_2C = O^* + (C_6H_5)_2CHOH \rightarrow 2(C_6H_5)_2COH$$
 (7)

$$(C_6H_5)_2COH + AS \cdot \rightarrow (C_6H_5)_2C = O + ASH$$
(4)

$$(C_6H_5)_2\dot{C}OH + ASH \rightarrow (\dot{C}_6H_5)_2CHOH + AS \cdot$$
(8)

These reactions are competitive with others, a part of the light is absorbed by acetone and reaction (6) may also occur. Reaction (3) probably occurs at a much lower rate than in the absence of mercaptan as reactions (4) and (8) decrease the concentration of ketyl radical I.

At lower initial concentrations of benzhydrol, 0.025 M, and mercaptan, 0.0025 M, a lower quasi-stationary concentration of benzophenone is maintained, 0.01 M. But this corresponds to 40 per cent of the initial concentration of benzhydrol and it is maintained during an extended period by reactions (6), (7), (4) and (8).

At still lower concentrations, 6×10^{-3} M benzhydrol and 9×10^{-4} M mercaptan, the concentration of formed benzophenone again rises to 40 per cent of that of the initial benzhydrol. It does not remain stationary, but decreases, with continued irradiation, Fig. 1. The lower concentration of mercaptan may compete less effectively with the combination reactions of radicals I and II, and the small amount of benzhydrol initially present may be converted to the pinacol products of those reactions. At this low concentration of benzhydrol, in the absence of mercaptan a small concentration of benzophenone is found at intermediate irradiation times, Fig. 1. It disappears comparatively rapidly in the absence of the inhibiting and stabilizing effect of the mercaptan.

2-Propanol was formed during irradiation of the benzhydrol-acetone and benzhydrol-acetone-mercaptan systems, but it was formed even more rapidly in irradiation of acetone and acetone-mercaptan in the absence of benzhydrol, Table 1, a result which complicates interpretation.

In irradiation of acetone alone, excited acetone may abstract hydrogen from acetone, equation (9), leading to 2-hydroxy-2-propyl radical, II, and acetonyl radical, III.

$$(CH_3)_2C = O^* + (CH_3)_2C = O \rightarrow (CH_3)_2\dot{C} - OH + \cdot CH_2COCH_3$$
(9)
II III

Radicals II may disproportionate to 2-propanol and acetone or abstract hydrogen from acetone to form 2-propanol and acetonyl radical, III, equation (10). This abstraction has been described [11] in the γ -radiolysis of acetone and may be

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$$(CH_3)_2 \dot{C}OH + CH_3CCH_3 \rightarrow (CH_3)_2CHOH + \cdot CH_2CCH_3$$
(10)
II

favored by a polar contribution to the transition state.

$$\begin{bmatrix} O & O \\ \parallel \\ (CH_3)_2 C \cdot H \cdot CH_2 - C - CH_3 \longleftrightarrow (CH_3)_2 C^+ H \cdot \overline{CH_2 CCH_3} \\ OH & O \\ H \end{bmatrix}$$

The acetonyl radicals III may dimerize [10]. The increase in yield of 2-propanol, from 0.009 M to 0.017 M, when the irradiation of acetone was carried out in the presence of 0.0005 M mesityl mercaptan, indicates catalysis by mercaptan of abstraction of hydrogen from acetone. Mercaptan might effect this by replacing one hydrogen atom transfer by two more rapid transfers, as in the light induced decarbonylation of aldehydes [11]. Excited acetone of equation (9) and/or radical II of equation (10) may abstract hydrogen from mercaptan, and the thiyl radical so formed may abstract hydrogen from acetone, equation (11), and this sequence may be more efficient than the direct processes (9) and (10). The

$$\begin{array}{ccc} & & O \\ \parallel \\ AS \cdot + CH_3CCH_3 \rightarrow ASH + \cdot CH_2CCH_3 \end{array}$$
(11)

mercaptan thus might make hydrogen abstraction processes compete more favorably with other reactions of the excited ketone and/or radical II and lead to higher yield of 2-propanol. The small amount of mercaptan seemed to double the yield of 2-propanol and it is tempting to account for this by simply selecting two from the several possible processes: In the absence of mercaptan, 2-propanol may be formed largely by disproportionation of two radicals II formed by the process of equation (9), while in the presence of mercaptan radicals II may largely abstract hydrogen from mercaptan and form 2-propanol and thiyl radical, equation (5), and the thiyl radicals may abstract hydrogen from acetone, equation (11), to regenerate mercaptan for use in equation (5).

Also in the initial stages of the irradiation of 0.005 M benzhydrol in acetone, 2propanol was formed about twice as rapidly in the presence of 0.0005 M mercaptan as in its absence; in each solution 2-propanol was formed only about half as rapidly as in the irradiation of the corresponding acetone system in the absence of benzhydrol. Excited acetone may again abstract from acetone, equation (9), but abstraction of hydrogen from benzhydrol may dominate, equation (6). Formation of benzophenoneketyl radical, 1, in this system, and possible cross-coupling of radicals I and II may decrease formation of 2-propanol as compared with the pure acetone system. The increased formation of 2-propanol in the presence of mercaptan may again be due to the sequence of reactions (5) and (11). In any event, the effect of mercaptan in increasing formation of both 2-propanol and benzophenone indicates that the hydrogen transfer reactions (4) and (5), which inhibit the photoreduction of benzophenone by 2-propanol, take place in, and change the course of the irradiation of the acetone-benzhydrol system. With increased time of irradiation in the presence of mercaptan, the concentration of benzophenone rises to a substantial level, a large part of the light is absorbed by the benzophenone and leads to the benzophenone derived radical, I, instead of the acetone derived radical, II. 2-Propanol is then formed at a lower rate in the presence of mercaptan than in its absence. After prolonged irradiation similar quantities of 2-propanol are present in both the presence and absence of mercaptan, Table 1.

It is noteworthy that benzophenone in acetone appears unaffected by ultraviolet irradiation in Pyrex, since the concentration of benzophenone does not decrease[12] and propanol is not formed. This may indicate that excited benzophenone does not abstract hydrogen efficiently from acetone although excited acetone does, or that the abstraction is reversible and the products disproportionate to starting materials. It may also indicate that benzophenone may quench excited acetone, and this might, then, also occur to some extent in the acetone–benzhydrol systems.

The acetone-benzhydrol system is more complicated than the benzophenone-2propanol system because of the persistence and reactions of both initially formed radicals, and the photoreduction of acetone by acetone. Our results indicate that the same two radicals, I and II, are formed in the two systems and that the presence of mercaptan leads to the same two reactions, (4) and (5), conversion of the radicals to benzophenone and 2-propanol respectively. These reactions, which inhibit the photoreduction of benzophenone by 2-propanol by converting the radicals to the starting materials, in this case alter the course of the reaction and lead to the conversion of benzhydrol to benzophenone and of acetone to 2-propanol. The mercaptan and disulfide lead to the hydrogen atom transfer reactions which are the most rapid in the irradiated system; in some cases this offers protection, in others, it changes the reaction course and accelerates chemical change.

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