Photolysis of benzil in 2-propanol and in cumene

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Benzil has been irradiated in 2-propanol and in cumene with a mercury lamp filtered through Pyrex. The principal products are benzoin, 1,2,3,4-tetraphenyl-2,3-dihydroxybutane-1,4-dione (**3**), benzoin benzoate, benzaldehyde, benzoic acid, 1,2,3,4-tetraphenyl-2,3-dihydroxybutane-1,4-dione dibenzoate (**5**), and some unidentified high molecular weight compounds. The yield of **3** is strongly dependent on initial benzil concentration and temperature and on the solvent used. The quantum yield of benzil disappearance depends on initial benzil concentration to a lower limit which varies with solvent. At an initial benzil concentration of 0.083 moles/l, the quantum yield of benzil disappearance is 0.11 in 2-propanol and 0.018 in cyclohexane. Compound **3** does not appear to be formed by a coupling of the appropriate ketyl radicals, as in the benzophenone case but instead, a complex is formed between a benzil molecule and the ketyl radical. Compound **3** decomposes at temperatures as low as 25°. The principal path for the formation of benzaldehyde and benzoyl radicals is the dissociation of the ketyl radical. Excited benzil abstracts a hydrogen from 2-propanol at least ten times faster than it dissociates into two benzoyl radicals.

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Introduction

The photo-reaction of benzil in cyclohexane has already been reported (1). This study has been extended using 2-propanol and cumene as solvents. Differences in kinds of products formed, in product distribution, and in concentration dependence, result when different solvents are used, particularly in the appearance of benzil pinacol (1,2,3,4-tetraphenyl-2,3-dihydroxy-1,4-butanedione). These differences seem to be related to the ease with which a hydrogen atom may be abstracted from the solvent. Benzoic acid appears as a product in all solvents used despite exclusion of oxygen during irradiation. Although similar to the photo-reduction of benzophenone (**2**) in the initial chemical step, subsequent reactions are more complicated.

Experimental

Materials

Benzil was from Eastman Organic Chemicals, and benzoin was Matheson, Coleman, and Bell, reagent grade. These were twice recrystallized from methanol. 2-Propanol and benzene, Fisher certified reagents, were freshly distilled. Cumene, Eastman Organic Chemicals, was distilled each time immediately before use. The silica gel used in column chromatography was 100–200 mesh Fisher certified grade, heated to 150 °C for 1 h and cooled to room temperature in a desiccator. Eastman Chromagram Sheet 6060 (silica gel with fluorescent indicator) was used in thin-layer chromatography (t.l.c.) and was heated to 100° for 20 min before use. Naphthalene, anthracene, and pyrene were chromatographed through activated alumina (3). Tri-*n*-butyltin hydride was prepared from tri-*n*-butyltin chloride (Aldrich Chemical Co. Inc.) by reduction with lithium aluminium hydride and vacuum distilled prior to use (4). Benzoin benzoate had been prepared previously. All other solvents used were freshly distilled.

Apparatus

All melting points were taken on a Fisher–Johns melting point apparatus and/or checked with a Mel-Temp melting point apparatus. Infrared (i.r.) spectra were determined on a Beckman IR 8 double beam spectrophotometer. Elemental analyses were done by Schwarzkopf Microanalytical Laboratory, 56–19 37th Avenue, Woodside, New York 11377, except for the dibenzoate analysis which was done by Dr. C. Daessle, Montreal, Quebec. Molecular weights were determined on a Hitachi Perkin–Elmer Model 115 molecular weight apparatus which uses an isopiestic method. Gas–liquid chromatography (g.l.c.) was performed on a Burrell model K-1 with a thermal conductivity detector. A 250 cm × $\frac{1}{4}$ in. internal diameter column filled with 20% Dow Corning high vacuum silicone grease on 80–100 mesh Chromosorb W was used for all compounds except acetone, for which 15% Apiezon L on the same supporting material was used. Standard solutions were run alternately with the irradiated solution for each peak of interest. Nuclear magnetic resonance (n.m.r.) spectra were obtained on a Varian A-60-A spectrometer, by courtesy of Dr. B. M. Lynch.

Three Raymaster Uviarc high pressure mercury lamps 420-UI (George W. Gates and Co., Inc., Franklin Square, Long Island, New York 11 010) were used in all irradiations except the actinometry runs. For these an Osram HBO 100 W/2 mercury super (high) pressure lamp (George W. Gates) with an arc size of 0.3 mm × 0.3 mm was used. Quantitative measurements were made on thin-layer chromatograms by a Photovolt Densicord, model 542 densitometer with a light source of 254 mμ.

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Irradiation

Three types of irradiation were carried out. In the first type, 0.6 g of benzil were weighed into a 50 ml tube and made up to 35 ml with 2-propanol. This was attached to a vacuum line and, after degassing by at least three freeze pump thaw cycles, was sealed off the line and allowed to warm to room temperature. After solution of the benzil, it was irradiated for 7 min with external water cooling.

In the second type, 34.2 g of benzil were dissolved in 2 l of 2-propanol. The resulting solution was poured into a 3 l three-necked round bottom Pyrex flask fitted with reflux condenser and nitrogen sparger connections. The flask was surrounded by the 3 Uviarc mercury lamps and, after thorough flushing with nitrogen, it was irradiated. The temperature during irradiation was the boiling point of 2-propanol (82–85 °C).

Most of the irradiations were carried out using the third arrangement. In this, varying amounts of benzil and sometimes other reagents were dissolved in 500 ml of 2-propanol or other solvent and placed in a Vycor cylinder with a 600 ml capacity. This cylinder was placed inside a larger Pyrex cylinder and distilled water (25 °C) circulated through the Pyrex cylinder by means of a vibrostatic pump. Nitrogen was flushed through the solution for 30 min before irradiation and during the course of the irradiation. The few runs where nitrogen was not used are indicated.

Thin-Layer Chromatography

Standards were run at the same time as the irradiated solution. The developing solvent was hexane:ethyl ether (2:1). Quantitative analysis was carried out by measuring the area recorded on the densitometer and comparing it to the area produced by a standard solution. Using standard solutions, it was seen that there was a linear relationship between the area and amount of substance.

Column Chromatography

A check by t.l.c. showed no difference in the kinds of products between the sealed tube photolyses and the nitrogen flushed ones, so no further work was done on the sealed tube runs. In those runs in which a precipitate appeared, it was first filtered off and the filtrate treated the same as in those runs where there was no precipitate.

The 2-propanol was removed from the clear solution under reduced pressure. About 5 g of the residue were redissolved in 50 ml of ethyl ether and were added to 15 ml of saturated sodium bisulfite solution with continuous shaking. After separation, the ether layer was washed with 30 ml of saturated sodium bicarbonate twice, followed by two 50 ml portions of distilled water, and then dried over anhydrous sodium sulfate. The ether solution was then added to 30 g of silica gel, and the ether removed in a rotary evaporator. The dried residue was ground in a mortar with *n*-hexane and the mixture placed on top of 300 g of silica gel in a packed column. The column was eluted with 6 l of ethyl ether - hexane which varied in concentration from 0 to 60% ether (v/v), then 2.5 l of acetone. Each fraction was examined by either t.l.c. or g.l.c. Ether (5%) eluted the unreacted benzil and ether (15%) eluted the benzoin benzoate. The fractions eluted by 25–35% ether were combined for further column chromatography and yielded benzoin and dibenzoin dibenzoate.

The material eluted from the first column by 50% ether and by acetone could not be separated any further and was brownish in color; presumably this material was a high molecular weight product. There was also a very little material which could not be removed from the column. Runs made after identification of all the products had been completed were analyzed by t.l.c. after removal of the benzaldehyde and benzoic acid.

Determination of Quantum Yield

The actinometer used was that of Hatchard and Parker (5) and was stirred by a current of nitrogen during irradiation. The light from the lamp was passed through a collimating hole and then a No. 7-83 filter from Corning glass works. This filter has a peak at 368 mμ and a half band width of 22 mμ. The percentage transmission at the maximum is 16%. The same cell with plane glass windows was used both for the benzil solutions and for the actinometer. Complete absorption of light, as measured by a photocell, took place in the benzil solutions.

Isolation, Identification, and Estimation of Products

Benzil Pinacol

This compound appeared as a white precipitate after some irradiations. As there was sometimes supersaturation, the solution was always allowed to stand for several hours after irradiation before filtration. After filtering, the precipitate was purified by immersion in acetone for 24 h, filtered again, and dried in a vacuum desiccator. The i.r. spectrum showed a strong hydroxy peak at 3400 cm^{-1} and a carbonyl absorption at 1650 cm^{-1}. The melting point was 204° measured on a Koffler hot bench but decomposed at 130° when heated slowly in a capillary tube. If air was present, the decomposition product was benzil. When heated in a sealed degassed tube the decomposition products were benzoin and benzil. Quantitative analysis (weighing the total decomposition product and measuring the benzil by ultraviolet (u.v.) spectrometry) showed that the two were present in a 1:1 mole ratio.

Anal. Calcd. for $C_{28}H_{22}O_4$: C, 79.60; H, 5.25. Found: C, 79.14, 79.19; H, 5.20, 5.18.

The formula weight is 422. An outside laboratory reported a molecular weight of 278. Using tetrahydrofuran as solvent, we found the molecular weight to be 403 when measured as soon as the solution was made up. After standing for 4 h in tetrahydrofuran (0.9 g/100 ml at room temperature) the compound changed completely to benzil. The compound also dissolved in dioxane (0.7 g/100 ml at room temperature), and slightly in dimethyl sulfoxide. It was insoluble in all other solvents tried, changing in some of them to benzil (DMF 5 min, diphenylmethane 24 h). Alcohols and acetone at room temperature had absolutely no effect on either, neither did 1 *N* alcoholic NaOH. The fact that it changes to benzil over a period of hours would explain the molecular weight results. The insolubility in NaOH and the white color exclude the enol structure which might be expected in analogy with the dimerization of triphenylmethyl radicals to produce 1-diphenylmethylene-4-trityl-2,5-cyclohexadiene (6).

The n.m.r. spectrum in DMSO was run 6 times over a period of 135 min. The ratio of the area of the aromatic hydrogen and hydroxy hydrogen was plotted against time and extrapolated to zero time. The intercept ArH/OH was 12. A ratio of 10 would be expected on the basis of the structure **3**. An excess of the compound was shaken with tetrahydrofuran, centrifuged, and the n.m.r. spectrum taken immediately. A value of 9.6 was obtained for the same ratio. When refluxed in 2-propanol or even just heated to 50 °C in 2-propanol, the compound changed to benzil. When added to styrene at room temperature the rate of polymerization increased. When added to a benzene solution of iodine which was then degassed and sealed, the color disappeared on warming to 50 °C. Apparently, the benzil pinacol dissociates very easily into two ketyl radicals. In the absence of oxygen, they disproportionate to benzil and benzoin. When O_2 is present, benzil is the sole product. Neckers and Schaap have recently reported that benzpinacol dissociates into free radicals at a temperature as low as 130 °C (7).

Benzaldehyde

This compound was measured by g.l.c. and its identity was checked by comparing its retention time with that of an authentic sample, and also by precipitating the 2,4-dinitrophenylhydrazone.

Unreacted Benzil

This compound was identified by its i.r. spectrum. It was measured by g.l.c.; one half of the benzoin had been subtracted. Benzoin disproportionates to benzil and deoxybenzoin on the g.l.c. column (8).

Benzoic Acid

This was recovered by acidification of the bicarbonate extract to pH 2 followed by two extractions with ether. The ether was washed, dried, and evaporated; the residue was identified by its m.p. and i.r. spectrum, and was weighed.

Benzoin Benzoate

The fraction eluted with 15% ethyl ether gave a substance which after recrystallization had m.p. 126 °C, lit. (17) 125 °C. The mixed m.p. with benzoin benzoate showed no depression and the i.r. and n.m.r. spectra were identical with authentic benzoin benzoate. The singlet at δ 7.19 in the n.m.r. spectrum is assigned to the aliphatic proton. It was measured either by weighing or by t.l.c.

Benzoin

This was obtained from column chromatography. It was identified by its m.p. and i.r. spectrum. It was measured either by weighing after column chromatography or by densitometry after t.l.c.

1,2,3,4-Tetraphenyl-2,3-dihydroxy-1,4-butanedione Dibenzoate (5) (di-(Benzoin Benzoate))

The second fraction after rechromatography yielded a compound which after recrystallization from *n*-hexane had m.p. 112–113 °C. It was first measured quantitatively by weighing and later by densitometry after t.l.c.

Anal. Calcd. for $C_{42}H_{30}O_6$ (mol. wt., 630.7): C, 79.98; H, 4.80. Found (mol. wt., 640): C, 78.82; H, 4.88.

The i.r. spectrum showed no aliphatic hydrogens or hydroxy groups and had the characteristic bands of the benzoyl group. The n.m.r. spectrum in dimethyl sulfoxide consisted only of unresolved aromatic absorption.

Further identification was made in two ways. The radicals produced by the abstraction of the aliphatic hydrogen of benzoin benzoate should couple to produce **5**. A mixture of benzoin benzoate with benzophenone was irradiated in a benzene–cyclohexane solvent (1:1, v/v). The solution was evaporated to dryness and the residue separated by column chromatography. One of the compounds obtained had an i.r. spectrum identical with that of **5** and m.p. 112 °C. A mixed m.p. with **5** showed no depression.

Rust *et al.* (9) found that heating benzaldehyde with *tert*-butyl peroxide leads to the formation of dihydrobenzoin dibenzoate by a mechanism involving the attack of benzoyl radicals on the oxygen of another benzaldehyde molecule, followed by a coupling of the resulting radicals. It was earlier reported by Bunbury and Wang (1) that adding benzil to the mixture of benzaldehyde and *tert*-butyl peroxide did not lead to the production of the dibenzoate. However, a careful check of the products from heating benzil, benzaldehyde, and *tert*-butyl peroxide leads to the isolation of several compounds. One of these compounds had m.p. 110–112 °C on recrystallization from *n*-hexane. The elementary analysis was C, 78.94; H, 4.80 and the measured molecular weight 648. A mixed m.p. with the product from the benzil in 2-propanol irradiation showed no depression. The n.m.r. spectrum showed only unresolved aromatic absorption.

Acetone

This was measured by g.l.c. and identified by its 2,4-dinitrophenylhydrazone.

Bicumyl

After irradiation of a cumene solution of benzil, the solvent was removed under reduced pressure, and the residue separated by column chromatography. The first fraction eluted with *n*-hexane was proved to be bicumyl by its m.p. and by comparison of its i.r. spectrum with that of an authentic sample. It was weighed.

Results and Discussion

The percentage of high molecular weight compounds appearing in Table I was obtained by difference. All runs in this table were carried to about 50% decomposition of the benzil.

Reducing the benzil concentration at constant light intensity has three effects: (1) the rate of benzil disappearance becomes steadily less until a constant value is reached, see runs 4–9, Table I and Fig. 1 curve A; (2) the percentage of benzil pinacol falls off to zero, see runs 4–9, Table I and Fig. 1 curve C; and (3) there is an increase in the amount of benzoin benzoate formed and even more in the amount of dibenzoin dibenzoate formed, see runs 4–9, Table I. Further, the initial concentration at which the benzil pinacol production becomes zero is the same as that at which the rate of benzil disappearance becomes constant.

Reducing the 2-propanol concentration with benzene leads to a marked reduction in rate and an elimination of benzil pinacol as a product, see run 13 Table I.

TABLE I

Reaction conditions and products of benzil photolysis in 2-propanol

						Products (% of benzil lost)						
Run number*	Reaction conditions	Solvent	Sample concentration (mmoles/l)	Time (min)	Benzil destroyed	Benzil pinacol	Benzaldehyde	Benzoic acid	Benzoin	Benzoin benzoate	Dibenzoin dibenzoate	High mol. wt. compound§
1	N_2-flushed	2-Propanol	83.1	185	84.2	‡	13.2	10.6	28.6	24.7	8.3	14.6
2	O_2-flushed	2-Propanol	83.0	81	22.3	‡	‡	91.2	‡	‡	‡	8.8
3	Stoppered	2-Propanol	83.5	70	20.3	28.6	4.5	14.7	14.5	10.2	5.4	22.1
4	N_2-flushed	2-Propanol	84.0	57	21.6	34.5	4.4	10.9	17.5	14.2	5.7	12.8
5	N_2-flushed	2-Propanol	51.9	51	11.4	20.3	5.7	11.1	18.0	16.1	11.2	17.6
6	N_2-flushed	2-Propanol	30.5	62	8.4	7.6	6.2	13.2	17.4	19.8	16.5	19.3
7	N_2-flushed	2-Propanol	16.6	55	4.4	0.4	5.9	12.0	20.5	19.3	17.3	24.6
8	N_2-flushed	2-Propanol	15.2	54	4.3	‡	†	†	†	†	†	†
9	N_2-flushed	2-Propanol	9.5	35	3	‡	7	11	20	17	18	27
10	N_2-flushed	Cumene	84.5	120	14.2	‡	†	†	†	†	†	†
11	N_2-flushed	Cumene	335.8	765	54.0	30.8	7.4	11.4	10.7	4.6	‡	35.1
12	N_2-flushed	Benzene	80.5	325	‡	‡	†	†	†	†	†	†
13	N_2-flushed	10% 2-propanol in benzene (v/v)	83.5	552	23.2	‡	15.3	18.8	17.1	18.4	10.2	20.2
19	N_2-flushed	2-Propanol	83.2	600	6.9	32.5	†	†	†	†	†	†

*Bath temperature was 25–30° in all runs except run 1; here it was 82–85°. The sample volume was 0.5 l except in run 1; here it was 2 l. Acetone (17 mmoles) was found in run 4, and 7 mmoles of bicumyl was found in run 11. There was weak light intensity in run 19. Runs were carried to 50% decomposition.

†Not measured.

‡None were found.

§High molecular weight compounds were obtained by difference.

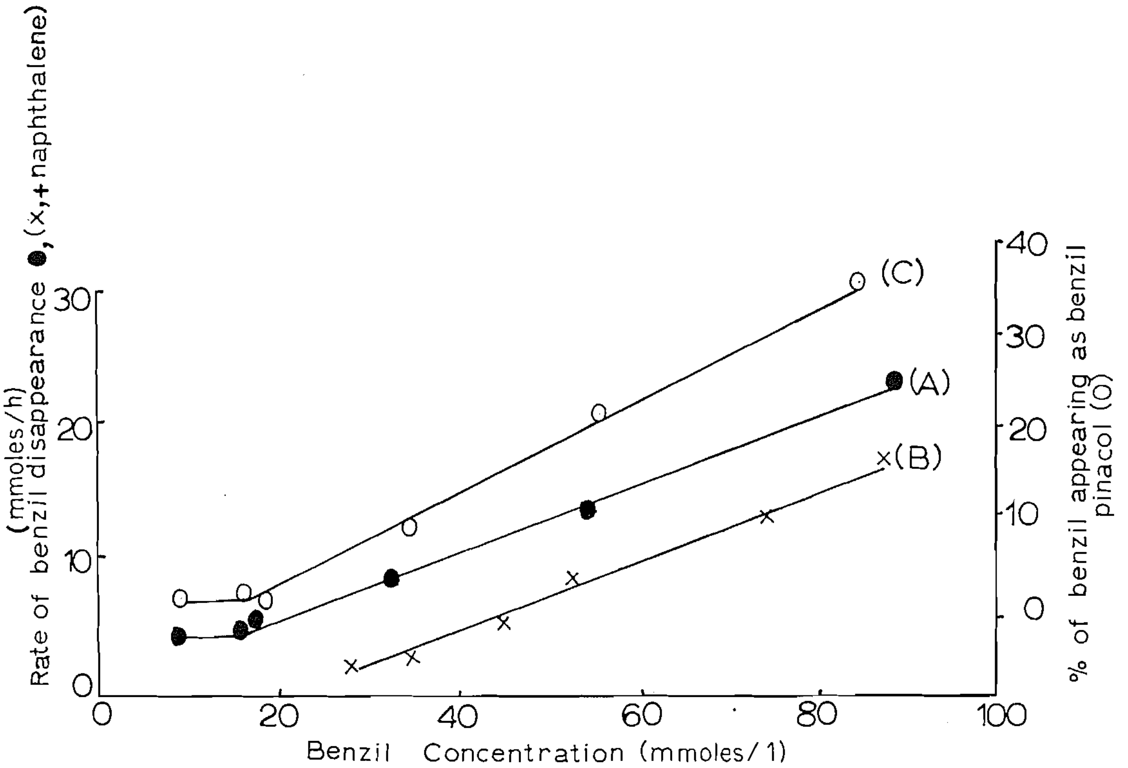


FIG. 1. Rate of benzil disappearance and pinacol formation as a function of benzil concentration in 2-propanol. Each curve was a separate series: curves A and B, 10% destruction of benzil; curve C, 40% destruction of benzil.

TABLE II

Reaction conditions and products of benzil photolysis in cumene

Run number*	Initial concentration of benzil (mole/l)	Rate of decomposition (mmole/h)	% benzil pinacol formed (% of decomposed benzil)	Benzoin	Benzoin benzoate	Benzaldehyde
1	0.405	3.54	23.0	7	3	†
2	0.362	3.15	15.7	7	5	†
3	0.272	2.50	9.4	10	5	†
4	0.248	2.38	0	14	10	†
5	0.226	2.33	0	13	13	†
6	0.092	2.60	0	†	†	†

*Total volume for irradiation is 50 ml of cumene solution. About 15% benzil was destroyed in each run. All runs were degassed.
†Not measured.

The behavior in cumene differs from that in 2-propanol in the following ways. The benzil concentration below which no benzil pinacol is formed is 250 mmoles/l in cumene as compared to 18 mmoles/l in 2-propanol. At a given concentration the rate is slower. The rate of change of the rate with concentration is 0.009 mmoles/h//mmoles/l while in 2-propanol it is 0.25 mmoles/h//mmoles/l. This is shown by runs 4, 10, and 11 in Table I, by Table II, and by Figs. 1 and 2.

The following series of steps seems best for rationalizing the results.

$$[1] \quad C_6H_5COCOC_6H_5 \xrightarrow{h\nu} \underset{\mathbf{1}}{C_6H_5COCOC_6H_5^*}$$

$$[2] \quad C_6H_5COCOC_6H_5^* \rightarrow C_6H_5COCOC_6H_5$$

TABLE III

Effect of various adducts on the photolysis of benzil in 2-propanol*

Run number	Quencher	Concentration of quencher (mmoles/l)	Solvent	Benzil concentration (mmoles/l)	Time (min)	% benzil destroyed	Products (% benzil lost)			
							Benzil pinacol	Benzoin	Benzoin benzoate	Benzoic acid
4	‡	‡	2-Propanol	84.0	57	51.5	34.5	17.5	14.2	10.9
14	Naphthalene	3.75	2-Propanol	80.0	90	56.4	30.8	‡	‡	‡
15	Pyrene	4.05	2-Propanol	82.1	120	21.5	31.4	14.5	16.0	‡
16	Anthracene	3.1	Benzene (16.7%) in 2-propanol	81.7	120	24.5	32.2	13.6	17.4	‡
17†	Tri-*n*-butyltin hydride	40.3	2-Propanol	83.1	115	17.3	§	22.4	25.2	13.5
18	Iodine	1.0	2-Propanol	80.7	120	§	§	‡	‡	‡

*Reaction conditions: temperature 25–30 °C; volume 500 ml; nitrogen was flushed in all runs.
†Benzoin (0.41 mmoles) and 0.28 mmoles of benzoin benzoate were found in the dark and subtracted from the total to give the figures in the table.
‡Not measured.
§None were found.

TABLE IV

Rates of benzil disappearance and product appearance at constant light intensity for selected runs

Run number	Benzil concentration	mmoles benzil destroyed/h	Rates in mmoles/h					BB+2D*	Benzoin C_6H_5CHO	BB+2D* *o*-CHO
			Pinacol	Benzaldehyde	Benzoin	Benzoin benzoate	Dimer			
1	83.1	27.3	0.0	3.68	7.81	4.50	0.753	5.306	2.2	1.45
4	84.0	22.73	3.92	2.0	3.975	2.183	0.432	3.047	4.0	1.524
5	51.9	13.41	1.362	1.53	2.413	1.43	0.502	2.434	3.2	1.589
6	30.5	8.13	0.309	1.01	1.414	1.072	0.447	1.966	2.8	1.946
7	16.6	4.8	0.01	0.566	0.984	0.619	0.277	1.173	3.5	2.075
9	9.5	5.14	0.0	0.72	1.027	0.582	0.308	1.198	2.9	1.666

*Benzoin benzoate ≡ BB, dimer ≡ D.

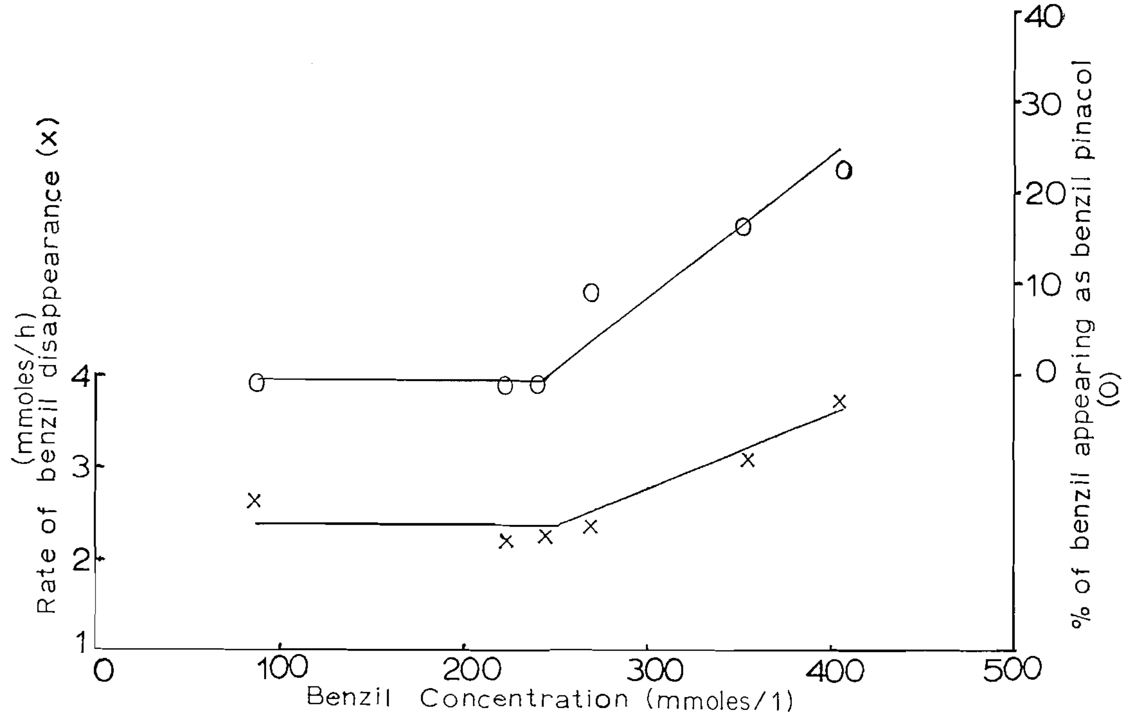


FIG. 2. Rate of benzil disappearance and pinacol formation as a function of benzil concentration in cumene.

[3] $C_6H_5COCOC_6H_5^* \rightarrow 2C_6H_5CO\cdot$

[4] $C_6H_5COCOC_6H_5^* + CH_3CHOHCH_3 \rightarrow \underset{\mathbf{2}}{C_6H_5\dot{C}OHCOC_6H_5} + CH_3\dot{C}OHCH_3$

[5] $\mathbf{1} + CH_3\dot{C}OHCH_3 \rightarrow \mathbf{2} + CH_3COCH_3$

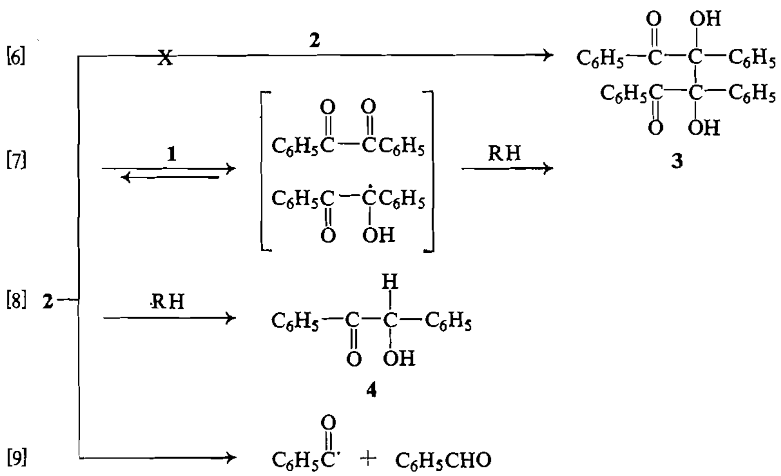
After reaction [1] the excited benzil molecule can do three things; lose its energy and revert to the ground state [2], split into two benzoyl radicals [3], or abstract a hydrogen atom from the solvent to form the ketyl radical [4]. That reaction [2] does occur is shown by the fact that the quantum yield of benzil decomposed depends strongly on the ease with which hydrogen is lost by the solvent. At an initial concentration of 83.4 mmoles/l the quantum yield of benzil disappearance in 2-propanol is 0.11 and in cyclohexane, 0.018. Anthracene and pyrene which have triplet energies below that of benzil are much more effective in slowing down the reaction than is naphthalene, the triplet energy of which is greater (*10a*), see Table III.

Reaction [3] is a minor reaction. Assume for the sake of argument that the benzoyl radicals so produced either abstract hydrogen from the solvent or react with benzil as proposed by Bunbury and Wang (1). Then the proportion of benzaldehyde should increase with the ease of hydrogen abstraction from the solvent but no such correlation is found; cyclohexane 6.2%, cumene 7.4%, 2-propanol 6%. Further, at lower benzil concentrations there should be an increase in the amount of benzaldehyde as there is less benzil to compete with the solvent for the benzoyl radicals. No such increase is found (Table I). The rate of decomposition in pure benzene, where reactions [4] and [5] cannot occur was found to be 0.323 mmoles/h at a concentration of 8 mmoles/l, and 0.526 mmoles/h at a concentration of 82.8 mmoles/l, under the same conditions as the runs in Table IV.

With the exception of the formation of benzoic acid, reactions [4] and [5] are the principal ones leading to products.

Reactions [6]–[9] show the different possible fates of the ketyl radical (**2**).

Reaction [6] shows the formation of benzil in a manner analogous to the formation of benzpinacol in the photolysis of benzophenone, **2.**



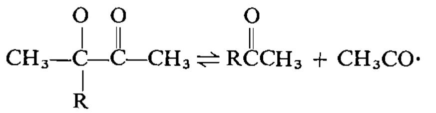
Dimerization of two ketyl radicals does not occur to any extent in the benzil system. If the benzil pinacol was produced by the combination of two ketyl radicals, its rate of production compared to that of benzoin should drastically decrease with a reduction in light intensity as the steady state concentration of ketyl radicals was reduced. No such decrease was found (run 19, Table I). Added quenchers which also reduce the steady state concentration of excited benzil, reduced the rate but had no effect on the proportion of benzil pinacol produced (Table III).

Since reduction of the benzil concentration causes a marked decrease in the production of benzil pinacol, we postulate a reversible complex formed between the ketyl radical and an unexcited benzil molecule and that this complex can abstract a hydrogen atom to form the benzil pinacol, reaction [7]. Also, since formation of the pinacol by this route uses a benzil molecule that would not otherwise be used, part of the fall in the quantum yield of benzil disappearance with fall in initial benzil concentration is explained. If the complex between the ketyl radical and a benzil molecule is a poor hydrogen abstractor, there should be an effect of solvent on pinacol formation. If we compare the reaction in cyclohexane, cumene, and 2-propanol, it is seen that there is no pinacol production in cyclohexane, and that the pinacol production becomes zero in cumene at an initial benzil concentration of 0.25 moles/l, and zero in 2-propanol at an initial benzil concentration of about 0.018 moles/l.

Metzger (11), in a study of the thermal decomposition of 1,1,2,2-tetraphenylethanol and of α-benzhydrylbenzoin says ". . . the experimental evidence leads to the conclusion that benzil is forming π-complexes with the radical intermediates . . .". One of the radicals for which complexes are postulated is the same ketyl radical as we have here.

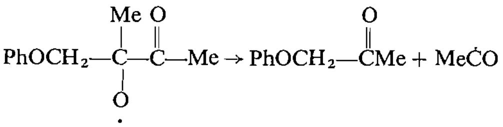
In a recent paper, Filipescu and Minn (12) have shown that there is a long-lived intermediate formed between the $Ph\dot{C}OH$ radicals and the $Me_2\dot{C}OH$ radical during the photolysis of benzophenone in 2-propanol. This intermediate undergoes a slow dark reaction with benzophenone in the absence of oxygen to produce two $Ph\dot{C}OH$ radicals. Since the benzil pinacol usually took some time to precipitate after irradiation, we thought that perhaps an intermediate was intervening in a similar way. Shaking the irradiated mixture with air immediately after turning out the lights had no effect on the amount of benzil pinacol produced.

As mentioned above, the hydrogen-donating properties of the solvent have no effect on benzaldehyde production, therefore, benzaldehyde does not appear to be produced by hydrogen abstraction of benzoyl radicals. Further, the rate of benzoyl radical production by reaction [3] (as measured in pure benzene) is not nearly great enough to account for the rate of production of benzoin benzoate and its dimer (Table IV). Therefore, another source of benzoyl radicals, as well as a route for the production of benzaldehyde, is needed. Reaction [9] is suggested as a source of both benzaldehyde and benzoyl radicals. This reaction is similar to reaction [10]

[10]


$$\mathrm{CH_3{-}\overset{O}{\underset{R}{C}}{-}\overset{O}{\overset{\|}{C}}{-}CH_3 \rightleftharpoons R\overset{O}{\overset{\|}{C}}CH_3 + CH_3CO\cdot}$$

proposed by Bentrude and Darnall (13) in both biacetyl photochemistry and the reaction of biacetyl with thermally generated radicals, and

[11]


$$\mathrm{PhOCH_2{-}\overset{Me}{\underset{\dot{O}}{C}}{-}\overset{O}{\overset{\|}{C}}{-}Me \rightarrow PhOCH_2{-}\overset{O}{\overset{\|}{C}}Me + Me\dot{C}O}$$

also to reaction [11] suggested by Baum and Norman (14) in a study of the photochemical reactions of biacetyl with some benzenoid compounds. In the photolysis of acetaldehyde, Zeldes and Livingston (15) propose reaction [12] which is the reverse of reaction [9] with methyls instead of phenyls

[12] $\mathrm{CH_3CO\cdot + CH_3CHO \rightarrow CH_3COCOHCH_3}$

Reaction [9] is also supported by the finding that both benzoin and *benzoin benzoate* are produced by tri-*n*-butyl tin hydride acting on benzil in 2-propanol in the dark (Table III). Presumably, the tin hydride transfers a hydrogen atom to benzil forming the same ketyl radical, some of which then dissociates according to reaction [9]. In a given solvent the benzoin/benzaldehyde ratio would be expected to be independent of the benzil concentration as a certain fraction of the ketyl radicals would split and a certain fraction abstract hydrogen to form benzoin. On examining runs 4–7 in Table IV this is seen to be so. An increase in temperature would increase the rate of both reaction [8] and reaction [9] so the change in the ratio is not predictable. The ratio in fact shows slight if any change from 82–85 °C to 25–30 °C, 2.2 to 3.3. The more difficult it is to abstract a hydrogen atom from the solvent, the greater the amount of dissociation to benzoin formation would become. The benzoin/benzaldehyde ratio is 1.4 for cumene at 25°, and 1.1 for 10% 2-propanol in benzene at 25°.

If it is assumed that the rate of dissociation is the same in 2-propanol as in cumene, a comparison of the benzoin/benzaldehyde ratio in the two solvents gives the relative ease of hydrogen abstraction by the ketyl radical. The additional assumption that reaction [13]

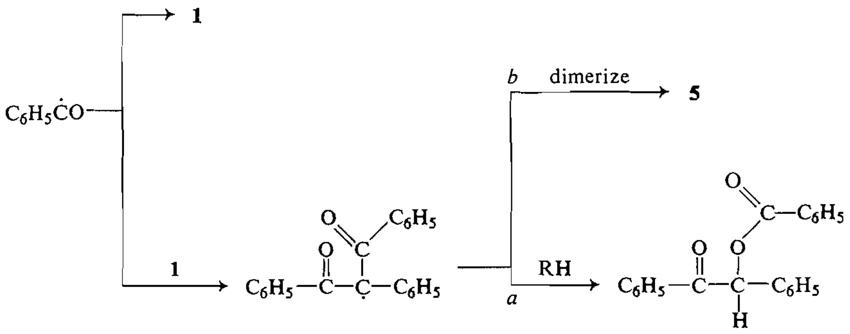
[13] $\mathrm{\mathbf{2} + CH_3\dot{C}OHCH_3 \rightarrow \mathbf{4} + CH_3COCH_3}$

does not take place to any appreciable extent must also be made. This appears to be so in the case of benzophenone; i.e. benzhydrol is not produced (10*b*).

With unsubstituted benzil, reaction [14] only results in a reduction of the quantum yield but it cannot be ruled out. Reaction [15] leads to benzoin benzoate, and di-(benzoin benzoate). Presumably, the high molecular weight compounds may be formed by other reactions involving benzoyl radicals. If reaction [9] was the only one forming benzoyl radicals, the moles of benzaldehyde should not be less than the moles of benzoin benzoate, plus twice the moles of benzoin benzoate dimer; further, the ratio of the two should remain constant. As can be seen from Table IV, the relative amount of benzoin benzoate and dimer increase with decreasing benzil concentration. Reaction [3] must be providing the additional benzoyl radicals. The thin-layer chromatogram of the pure benzene runs

[14]

[15]



showed only two product spots, one that did not move and one that had an R_f corresponding to the dimer of benzoin benzoate. Apparently the sequence [1], [3], [15*b*] is followed in benzene. If twice the rate of decomposition in pure benzene (about 0.4 mmoles/h) is subtracted from the sum of the rate of benzoin benzoate formation and twice that of its dimer, the difference is approximately the rate of benzaldehyde production: i.e. benzaldehyde to benzoin benzoate plus twice the dimer ratio becomes more or less constant.

Apparently then, at constant light intensity, benzil dissociates into benzoyl radicals at a certain slow rate that is concentration independent, and also abstracts hydrogen from the solvent at a much faster rate that is solvent and, in some cases, concentration dependent. Thus, the proportion of benzil dissociating into two benzoyl radicals would become progressively larger at lower benzil concentrations (until the steady value is reached) thus explaining the relative increase in products involving the benzoyl radical as starting concentrations of benzil are reduced.

The decrease in the quantum yield of benzil destruction with decreasing benzil concentration is more than can be accounted for by the decrease in pinacol production. If each mole of pinacol is formed from an excited benzil molecule and one in the ground state, the rate of benzil disappearance when pinacol production reaches zero should be $22.7 - 3.9 = 18.8$ mmoles/h. Instead, it falls to about 5 mmoles/h (Table IV). If at high benzil concentrations, reaction [5] is important and at low benzil concentrations becomes much less so, the 2-hydroxy-2-propyl radicals disappearing by disproportionation, this could account for an additional fall in the rate to about 9 mmoles/h. In cumene, the concentration effect disappears at a much higher initial benzil concentration and is much less marked than in 2-propanol; 0.009 mmoles/h//mmoles/l compared to 0.25 mmoles/h//mmoles/l.

It was originally thought that the tri-*n*-butyl tin hydride would suppress benzil pinacol formation by giving a hydrogen to the benzoin radicals before they had a chance to dimerize. Since that is apparently not the path of benzil pinacol formation we have no explanation for the suppression of benzil pinacol formation or for the fact that the tin hydride also slows down the rate of photochemical reaction.

That such a small amount of iodine should suppress the photochemical reaction is surprising (Table III). The iodine must either be a very efficient quencher or reacting in such a way that it is constantly being regenerated. For example, the following steps, [16] and [17], would provide such a path

$$[16] \qquad \mathbf{2} + \underset{(\mathrm{I})}{\mathrm{I_2}} \rightarrow \mathbf{1} + \underset{(\mathrm{HI})}{\mathrm{HI}} + \mathrm{I}$$

$$[17] \quad \mathrm{CH_3\dot{C}(OH)CH_3 + HI \rightarrow CH_3CHOHCH_3 + I}$$

This sequence is the same as the one proposed by Cohen *et al.* (16) for inhibition by disulfides and thiols in low concentration, of the photo-reduction of benzophenone, reactions [18] and [19].

$$[18] \qquad \mathrm{Ph_2\dot{C}OH} + \underset{(\mathrm{R_2S_2})}{\mathrm{RS\cdot}} \rightarrow \mathrm{Ph_2CO} + \underset{(\mathrm{RSH\,+\,RS\cdot})}{\mathrm{RSH}}$$

$$[19] \qquad \mathrm{Me_2\dot{C}OH + RSH \rightarrow Me_2CHOH + RS\cdot}$$

The path to benzoic acid remains obscure. It is produced in all solvents used so far, cyclohexane (1), 2-propanol, cumene, and in later work here[2], triethylamine. The poorer hydrogen donors produce a larger percentage of benzoic acid. On the other hand, the presence of the very strong hydrogen donor, tri-*n*-butyl tin hydride does not affect the percentage of benzoic acid formed in 2-propanol. The reaction leading to the benzoic acid precursor must be a rapid one. The fact that it can exist in the presence of the tin hydride argues against it being a radical. It is not produced by oxygen during the reaction. When carried out in sealed degassed tubes, the same products were found comparable to run 4, Table I, benzil pinacol (not measured), benzoin 20%, benzoin benzoate 15%, benzoic acid 10% (analysis by t.l.c. only), and dibenzoin dibenzoate. Varying the flushing period before irradiation to a minimum of 15 min had no effect on the products. The u.v. spectrum (360–480 mμ) of a degassed sample was taken before irradiation, after irradiation, and after being opened to the air. The changes were not pronounced. Deliberately adding oxygen to the reaction mixture during irradiation leads to benzoic acid as the sole identifiable product with a reduction in rate

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[2] Runs by Miss Han Ping Mak.

from 22.7 mmoles/h to 16.5 mmoles/h.[3] In oxygen-free solutions, the compound leading to benzoic acid might be an intermediate of the type proposed by Filipescu and Minn (12). In the case of benzophenone, it regenerates benzophenone on exposure to oxygen. In the case of benzil, it could lead to benzoic acid.

Acknowledgments

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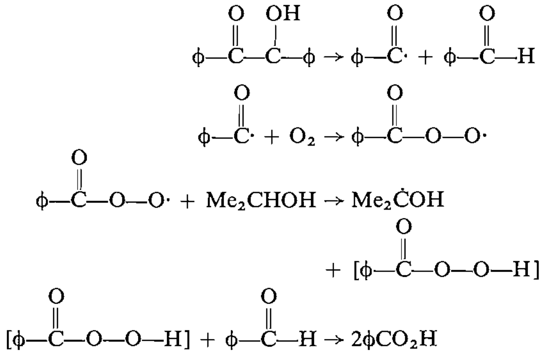
[3] A referee has suggested that in this case the following chain leads to benzoic acid when oxygen is present.



$$\phi\text{—}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—}\overset{\overset{\mathrm{OH}}{|}}{\mathrm{C}}\text{—}\phi \rightarrow \phi\text{—}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\cdot + \phi\text{—}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—H}$$

$$\phi\text{—}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\cdot + \mathrm{O_2} \rightarrow \phi\text{—}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—O—O}\cdot$$

$$\phi\text{—}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—O—O}\cdot + \mathrm{Me_2CHOH} \rightarrow \mathrm{Me_2\dot{C}OH} + [\phi\text{—}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—O—O—H}]$$

$$[\phi\text{—}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—O—O—H}] + \phi\text{—}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—H} \rightarrow 2\phi\mathrm{CO_2H}$$