# Effects of Quenchers on Photoreduction of *p*-Benzoylbenzenesulfonic Acid in Aqueous 2-Propanol[1]

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**Abstract:** Sodium *p*-benzoylbenzenesulfonate, SBBS, has been prepared from *p*-aminobenzophenone, and its photoreduction studied in aqueous 2-propanol, pH 6.4. The product is the pinacol. Photoreduction shows an initial rapid phase, $\varphi \sim 1.6$, followed by a zero-order slower one, $\varphi \sim 1.4$. The kinetics are complicated by formation of light-absorbing intermediates. At high concentrations of physical quenchers formation of the intermediate is suppressed, zero-order kinetics are observed, and extrapolation of plots of inverse rate *vs.* concentration of quencher lead to limiting quantum yields of 2, $k_r \cong 10^6\ M^{-1}\ \text{sec}^{-1}$. The standard kinetic treatment may not be applied when substantial concentrations of intermediate are present. Naphthalene is about 65% as effective in quenching SBBS as it is in quenching benzophenone. A positively charged quencher, 1-naphthyltrimethylammonium tosylate, is 80% as effective as naphthalene in quenching SBBS; a negatively charged one, naphthalene-2-sulfonic acid, is 67% as effective. The photoreduction of SBBS is also retarded efficiently by a mercaptan, dimethylaminoethanethiol hydrochloride, presumably by free radical hydrogen atom transfer repair reactions.

Study of photoreduction of aromatic ketones containing water solubilizing groups is of interest to us intrinsically and in relation to inhibition by mercaptans[3] of photochemical and radiation-induced reactions in aqueous media. Aminobenzophenones are photoreduced by aqueous alcohols in acidic solutions in which the amino groups are protonated,[4] but strongly acidic conditions may decrease quantum yields as compared with photoreduction of benzophenone in neutral aqueous alcohol. *p*-Aminobenzophenone is photoreduced by tertiary amines in hydrocarbon solution,[5] but in polar media the reaction fails, largely because of inefficient intersystem crossing.[6] *p*-Benzoylphenyltrimethylammonium salts are photoreduced by aqueous alcohols and amines,[7] and may be studied in neutral, acidic, and alkaline solutions. Photoreduction in neutral 1:1 aqueous 2-propanol of the quaternary ammonium substituted ketone is seriously complicated by formation of light-absorbing transients, and quantum yields are ~0.6, about one-half that for photoreduction of benzophenone itself under similar conditions.[7] Photoreduction of the positively charged ketone is quenched by naphthalene, N, about one-fourth as effectively as is unsubstituted benzophenone.[7] A negatively charged quencher, naphthalene-2-sulfonic acid, NS$^-$, showed similar efficiency to naphthalene in quenching photoreduction of the positively charged ketone, and it was somewhat less efficient than naphthalene in quenching benzophenone.[7] A positively charged naphthalene, 2-naphthyltrimethylammonium tosylate, was about half as efficient as naphthalene in quenching photoreduction of benzophenone, but it was very inefficient in quenching the positively charged quaternary ammonium substituted benzophenone.[7] We now report on photoreduction in aqueous media of a ketone containing an anionic substituent, sodium *p*-benzoylbenzenesulfonate, SBBS, and on effects of the naphthalenes and a mercaptan on the photoreduction.

## Experimental Section

Irradiation procedures and analytical instruments were the same as those described previously.[5b] Aliquots (4 or 5 ml) of 0.1 *M* sodium *p*-benzoylbenzenesulfonate were degassed by the freeze-thaw method and irradiated in Pyrex tubes under argon on a turntable 8 cm from an Osram Mercury Spectrallampe, 220 V, 1.2 A. In the preliminary experiments cylindrical Thunberg tubes were used. In subsequent work the irradiation tubes were 1 × 1 cm precision square tubing fitted with Fisher-Porter Teflon closures. Tubes were calibrated for transmission. After irradiation the tubes were opened to air, shaken, and allowed to stand overnight for decomposition of intermediate. Aliquots were taken with a syringe and diluted in volumetric flasks, and absorbance was measured on a Beckman DU or Cary 14 spectrophotometer at 333 nm ($\epsilon$ 194) in 95% ethanol, or at 258 nm ($\epsilon$ 21,310) in 1:1 2-propanol-water. At 258 nm a correction was applied for absorption by the pinacol product, estimated to be $\epsilon$ 1216, twice that of the hydrol. Analyses for pinacol formation were made by treatment of diluted aliquots with alkali and measurement of increase in absorbance due to formation of ketone from decomposition of pinacol.[5b]

Quantum yields were determined by ferrioxalate actinometry.[8] Irradiation was by an Osram SP-200 lamp in a Bausch and Lomb 38-86-01 monochromator. In typical experiments $6 \times 10^{-3}$ ferrioxalate solutions were irradiated for ~1 min at 313 nm, or ~2 min at 334 nm, with rates of reaction 0.0725 $M\ \text{hr}^{-1}$ and 0.0405 $M\ \text{hr}^{-1}$, and quantum yields 1.24 and 1.23, respectively.

In the study of light-absorbing transients, irradiations were carried out in a 1-cm tube to which was sealed a 1-mm quartz absorption cell. The solution was degassed and the initial absorption spectrum was obtained, $A_0$; the solution was irradiated and the absorption spectrum was obtained immediately, $A_t$. Air was admitted, the contents were stirred and allowed to stand overnight in the dark, and the absorption spectrum was obtained again, $A_t'$. The absorption spectrum of the intermediate is $A_t - A_t'$. The value of $A_0 - A_t'$ is a measure of the amount of ketone photoreduced. The fraction of light being absorbed by the ketone at the end of the irradiation period at the wavelength of irradiation is given by the fraction $\text{OD}_t'/\text{OD}_t$, and that absorbed by the intermediate, $(\text{OD}_t - \text{OD}_t')/\text{OD}_t$. It was also observed that the absorbance due to the intermediate decreased on standing without exposure to air.

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Benzophenone was Fisher Certified grade, mp 47.5–48.5°. 2-Propanol was Eastman Spectrograde. Naphthalene-2-sulfonic acid trihydrate (NS$^-$, Eastman Kodak Co.) was recrystallized from acetonitrile, mp 82–83°. 1-Naphthyltrimethylammonium tosylate (NT$^+$), available from previous work,[7] was recrystallized from chloroform, mp 165–166°. Dimethylaminoethanethiol hydrochloride was from Aldrich, mp 158–160°.

**$p$-Benzoylbenzenesulfonyl chloride** was prepared from $p$-aminobenzophenone by a procedure for replacement of the amino by the sulfonyl chloride group.[9] Glacial acetic acid, 40 ml, was saturated with *ca.* 15 g (0.23 mol) of sulfur dioxide at 5–10°, and a solution of 0.42 g (0.0025 mol) of $CuCl_2 \cdot 2H_2O$ in 2 ml of water was added. A suspension of 4.93 g (0.025 mol, Aldrich Chemical Co.) of $p$-aminobenzophenone in 30 ml of concentrated HCl was prepared and to it was added in 1.5 hr at 0° a solution of 2.43 g (0.035 mol) of sodium nitrite. Excess nitrous acid was destroyed by sulfamic acid, and the solution of the diazonium chloride was filtered into the stirred acetic acid solution. After 15 min the solution was warmed to room temperature, stirred for 15 min, and diluted with water, leading to $p$-benzoylbenzenesulfonyl chloride, 5.8 g (0.020 mol), 80% yield, mp 93–93.5°, from hexane.

*Anal.* Calcd for $C_{13}H_9O_3SCl$: C, 55.6; H, 3.2; S, 11.4. Found: C, 55.7; H, 3.3; S, 11.3 (Dr. C. Fitz).

**Sodium $p$-Benzoylbenzenesulfonate, SBBS.** The sulfonyl chloride (1.8 g, 6.3 mmol) was heated with 9 ml of 2 $N$ NaOH to form a clear solution. This was diluted with 40 ml of hot water, neutralized with concentrated HCl, cooled, and filtered through Celite. The filtrate was placed on an Amberlite XAD-2 column, *ca.* 250 ml, eluted with water until free of chloride ion (500 ml), and then with 500 ml of 95% ethanol. The ethanol was evaporated and the residue, SBBS, 1.8 g, was dissolved in a minimum volume of cold water, filtered through Celite, and taken to dryness. The residue was crystallized from 95% ethanol, 1.2 g.

*Anal.* Calcd for $C_{13}H_9O_4SNa$: C, 54.9; H, 3.2; S, 11.3; Na, 8.1. Found: C, 54.8; H, 3.2; S, 11.2; Na, 8.0 (Dr. C. Fitz).

**Pinacol of Sodium $p$-Benzoylbenzenesulfonate.** An aliquot of a 0.1 $M$ solution of SBBS in 3.25 $M$ 2-propanol in water was irradiated for 60 min. The absorbance, at 257.5 nm after appropriate dilutions and corrections, fell from 0.855 to 0.471 during irradiation, and rose to 0.661 on treatment of the irradiated solution with alkali. This corresponded to 98% formation of pinacol from the photoreduced ketone.

Solutions of 0.1 $M$ SBBS in 3:1 2-propanol–water from irradiation studies were combined, *ca.* 20 ml, degassed, and irradiated for 24 hr. The absorbance indicated 96% reduction of the ketone. The solution was concentrated under vacuum, the residue was dissolved in water, and the pinacol was precipitated with dioxane, 0.58 g, white needles from water–dioxane. It showed an unusual flat shoulder at 252–264 nm, apparent $\epsilon$ 2200, in 1:1 2-propanol–water.

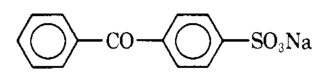
*Anal.* Calcd for $C_{26}H_{20}O_8S_2Na_2 \cdot 2H_2O$: C, 51.8; H, 4.0. Found: C, 51.6; H, 4.5 (Dr. C. Fitz).

**Reduction of SBBS by Sodium Borohydride.** Sodium borohydride (0.045 g, 1.2 mmol) was added to a stirred aqueous solution of 0.57 g (2.0 mmol) of SBBS and stirring was continued overnight. The mixture was acidified with concentrated HCl, neutralized with 5 $N$ NaOH, and chromatographed on Amberlite XAD-2. Water removed inorganic material and 95% ethanol eluted the carbinol, 0.50 g. This was recrystallized from 95% ethanol. The compound showed $\lambda_{max}$ 262 nm ($\epsilon$ 644, $\epsilon_{25}$, 608) in 1:1 2-propanol–water.

*Anal.* Calcd for $C_{13}H_{11}O_4SNa \cdot H_2O$: C, 51.3; H, 4.3; S, 10.5; Na, 7.6. Found: C, 51.3; H, 4.5; S, 10.3; Na, 7.4 (Dr. C. Fitz).

## Results

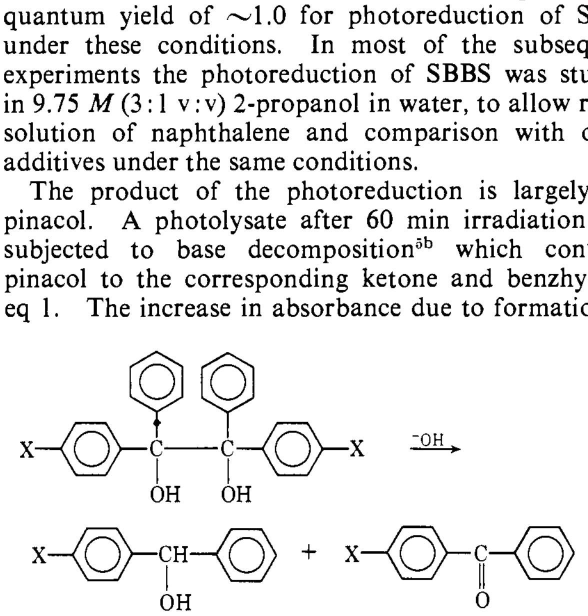
$p$-Benzoylbenzenesulfonyl chloride was prepared from $p$-aminobenzophenone, by diazotization and treatment of the diazonium compound with sulfur dioxide and cupric chloride. The sulfonyl chloride was hydrolyzed with sodium hydroxide, leading to sodium $p$-benzoylbenzenesulfonate, which was purified by chromatography on Amberlite XAD-2.



SBBS

Aliquots of 0.1 $M$ SBBS in aqueous 2-propanol were irradiated under argon in Pyrex on a rotating wheel, with light from an Osram mercury lamp. In preliminary experiments effect of concentration of 2-propanol was examined, 1.0, 3.25, 6.5, and 9.75 $M$. Rates of photoreduction were compared with that of a standard solution, 0.1 $M$ benzophenone in 2-butylamine. For SBBS there were observed an initial rapid decrease in absorbance for a few minutes, then a constant linear decrease in absorbance for about 1 hr, 35–40% reaction, followed by a slower reaction. Rates were calculated for comparison from the zero-order part of the reaction. The rates were insensitive within experimental error to this range of concentration of 2-propanol, 0.034 ± 0.001 $M$ hr$^{-1}$, as compared with 0.037 $M$ hr$^{-1}$ for the standard, and correspond to a quantum yield of ~1.0 for photoreduction of SBBS under these conditions. In most of the subsequent experiments the photoreduction of SBBS was studied in 9.75 $M$ (3:1 v:v) 2-propanol in water, to allow ready solution of naphthalene and comparison with other additives under the same conditions.

The product of the photoreduction is largely the pinacol. A photolysate after 60 min irradiation was subjected to base decomposition[5b] which converts pinacol to the corresponding ketone and benzhydrol, eq 1. The increase in absorbance due to formation of the ketone as compared with the decrease in absorbance due to irradiation indicated that the photoreduction had led to 98% pinacol. Some photolysates from kinetic runs were irradiated for 24 hr and the product was isolated. Analysis by alkaline decomposition indicated that the isolated product contained only about 85% pinacol, but it was not brought readily to a high state of purity.



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That the photoreduction showed an initial rapid rate followed by a slower approximately zero-order rate indicated that a light-absorbing intermediate formed and perhaps persisted for a period at a steady level. In a study of the absorbing intermediate a solution of 0.10 $M$ SBBS in 3:1 2-propanol–water was irradiated at 334 nm, at the exit slit of the monochromator for 24 min. The absorbance at $\lambda_{max}$ 333 nm fell from 1.948 initially to 1.878 immediately after irradiation, and after 15 hr in the dark to 1.524. At high light intensity the decrease in absorbance at $\lambda_{max}$ due to photoreduction is largely masked, immediately after irradiation, by the increase in absorbance due to the intermediate. When irradiation was carried out at a lower (63%) light intensity, the absorbance at 333 nm fell from 1.957 initially to 1.740 after irradiation, and further to 1.441 after 17 hr in the dark. At lower light intensity there is somewhat less internal masking

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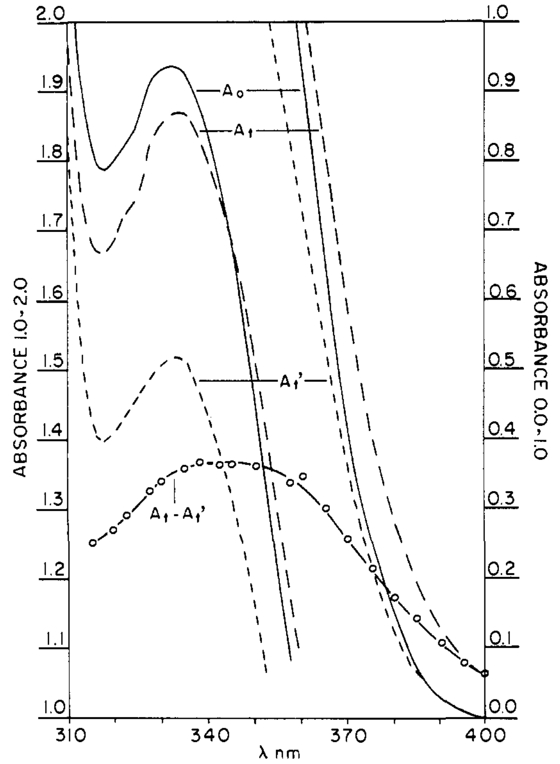

Figure 1. Absorption spectra, irradiation at 334 nm, high light intensity, of 0.10 *M* SBBS in 3:1 2-propanol-water: $A_0$, initial spectrum, ———; $A_t$, spectrum immediately after irradiation for 24 min, — — —; $A_t'$, spectrum after irradiated solution was allowed to stand for 15 hr, ------; $A_t - A_t'$, spectrum of the intermediate —O—O—O—O—, OD 0.0–1.0 scale.

due to the transient. The difference between the spectra after irradiation and after standing was determined and indicates that the intermediate has a broad absorption band centering at 345 nm and extending beyond 400 nm. Some spectra are shown in Figure 1.

Studies were made, in irradiations on the wheel, of the effects of a physical quencher, naphthalene. Times of irradiation were increased as the initial concentration of naphthalene was increased to allow equal extents of photoreduction. The effects were examined during the initial rapid phase, at 7–10% reaction, and during the intermediate slower zero-order rate phases, at ~25% reaction. Photoreduction of benzophenone was examined at the same time. Some results are summarized in Table I. The unquenched rate during the initial phase was greater than that in the later phase, and the early rapid rate was somewhat more sensitive to quenching. Plots of inverse rate against concentration of quencher at low concentration of quencher deviate from linearity. The highly quenched photoreduction of SBBS at 0.020 *M* naphthalene (and also at 0.015 *M*) followed zero-order kinetics, and did not show rapid initial rate and subsequent slower rates. Examination of these photolysates indicated that essentially no light-absorbing transient accumulated to complicate the kinetics.

Table I. Effect of Naphthalene on the Photoreduction of 0.10 *M* SBBS and 0.1 *M* Benzophenone, B, in 3:1 2-Propanol-Water

| Ketone | Naphthalene, *M* | Rate,[a] *M* hr$^{-1}$ | Rate,[b] *M* hr$^{-1}$ |
|---|---|---|---|
| SBBS | | 0.054 | 0.041 |
| SBBS | 0.0050 | 0.041 | 0.029 |
| SBBS | 0.0100 | 0.031 | 0.025 |
| SBBS | 0.0200 | 0.021 | 0.020 |
| B | | | 0.038 |
| B | 0.0050 | | 0.021 |
| B | 0.0100 | | 0.015 |

[a] Rates during 7–10% reaction, rates normalized for lamp variation. [b] Rates during 24–27% reaction.

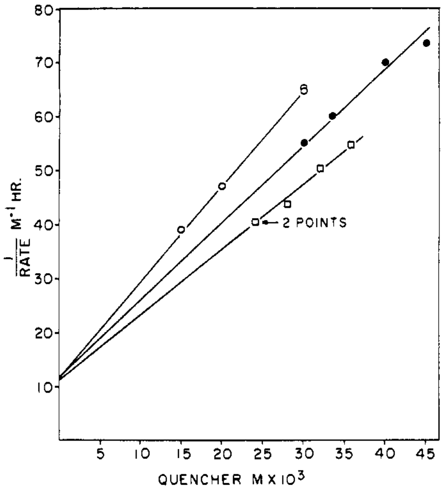

Figure 2. Quenching of photoreduction of 0.10 *M* SBBS in 3:1 2-propanol-water: by naphthalene, N, —O——O—; by 1-naphthyltrimethylammonium tosylate, NT$^+$, —●——●—; by naphthalene-2-sulfonic acid, NS$^-$, —□——□—.

Studies were then made of quenching of photoreduction of 0.10 *M* SBBS by naphthalene (N), naphthalene-2-sulfonic (NS$^-$), and 1-naphthyltrimethylammonium tosylate (NT$^+$), at concentrations above 0.015 *M*, at which interference from the light-absorbing intermediate might be avoided. Photoreduction of 0.10 *M* benzophenone by 2-butylamine, $\varphi = 1.1$, was carried out simultaneously as a standard. Rates of photoreduction and rates relative to that of the standard are given in Table II. Linear plots of inverse rate against concentration of quencher may be constructed, Figure 2. The slopes are, for naphthalene 1800 $M^{-2}$ hr, for naphthalene-2-sulfonic acid, 1200 $M^{-2}$ hr,

Table II. Photoreduction of 0.10 *M* SBBS in 3:1 2-Propanol-Water. Effects of High Concentrations, >0.015 *M* of Quenchers, Naphthalene (N), Naphthalene-2-sulfonic Acid (NS$^-$), and Naphthyltrimethylammonium Tosylate (NT$^+$)

| Quencher | | Photoreduction | |
|---|---|---|---|
| Compd | *M* | *M* hr$^{-1}$ | Rel rate |
| N | 0.015 | 0.024 | 0.51[a] |
| N | 0.020 | 0.020 | 0.43[a] |
| N | 0.030 | 0.014 | 0.30[a] |
| N | 0.030 | 0.015 | 0.30[c] |
| NS$^-$ | 0.024 | 0.024 | 0.50[b] |
| NS$^-$ | 0.028 | 0.0225 | 0.46[b] |
| NS$^-$ | 0.032 | 0.020 | 0.41[b] |
| NS$^-$ | 0.036 | 0.018 | 0.37[b] |
| NT$^+$ | 0.016 | 0.035 | 0.72[b] |
| NT$^+$ | 0.030 | 0.018 | 0.37[c] |
| NT$^+$ | 0.035 | 0.0165 | 0.33[c] |
| NT$^+$ | 0.040 | 0.014 | 0.29[c] |
| NT$^+$ | 0.045 | 0.0135 | 0.27[c] |

[a] Rate of photoreduction of 0.10 *M* benzophenone in 2-butylamine, standard, 0.0467 *M* hr$^{-1}$. [b] Rate of standard 0.0487 *M* hr$^{-1}$. [c] Rate of standard 0.0497 *M* hr$^{-1}$.

Table III. Quantum Yields by Ferrioxalate Actinometry of Photoreduction of 0.10 $M$ SBBS, in 2-Propanol–Water

| Expt no. | Irradiation λ, nm | Irradiation Time, min | Reaction $M$ hr$^{-1}$ | Reaction % | $\varphi$ | Additive Compd | Additive $M$ |
|---|---|---|---|---|---|---|---|
| 1$^a$ | 313 | 21 | 0.0760 | 26 | 1.30 | | |
| 2$^a$ | 334 | 10 | 0.0516 | 8 | 1.57 | | |
| 3$^a$ | 334 | 38 | 0.0447 | 28 | 1.36 | | |
| 4$^a$ | 334 | 103 | 0.0117 | 20 | 0.37 | Naphthalene | 0.030 |
| 6$^b$ | 334 | 161 | 0.0119 | 33 | 0.35 | DMAET | 0.024 |

$^a$ In 3:1 2-propanol–water. $^b$ In 1:3 2-propanol–water, pH 5.9.

and for 1-naphthyltrimethylammonium tosylate, 1440 $M^{-2}$ hr. Extrapoation of each of these plots to zero concentration of quencher leads to a single value of the limiting rate, 0.090 $M$ hr$^{-1}$, 1.85 times the observed rate of photoreduction of benzophenone by 2-butylamine, corresponding to a high theoretical limiting quantum yield, ~2.

Quantum yields were determined by ferrioxalate actinometry for photoreduction of 0.10 $M$ SBBS in 3:1 2-propanol–water under varying conditions. Some results are summarized in Table III. Solutions irradiated on the monochromator showed quantum yields $\varphi$ = 1.30 and 1.36 at 313 and 334 nm, respectively, at equivalent, moderately high conversions, 26 and 28% (experiments 1 and 3). The slightly lower quantum yield at 313 nm may be due to a larger fraction of the light being absorbed by the intermediate at this wavelength. At low extent of reaction, 8% (experiment 2), the quantum yield at 334 nm was substantially higher, 1.57, corresponding to the initial fast rate, less encumbered by transient. Quantum yields were also determined in the presence of a quencher, naphthalene, and an inhibitor, dimethylaminoethanethiol.

Retardation by dimethylaminoethanethiol hydrochloride, DMAET, of photoreduction of 0.10 $M$ SBBS in 1:3 2-propanol–water was examined. Titration indicated p$K_a$ values of 7.8 (–SH) and 10.7 ($-NR_2H^+$), which may be compared with reported values of 7.95 and 10.7 in 1:1 methanol–water.[10] The irradiations were carried out at pH 5.75 in 0.05 $M$ phosphate buffer; at this pH the amino group is essentially completely protonated. Irradiations were carried out for one period of irradiation at each concentration of mercaptan, and extents of reaction varied. Results are summarized in Table IV.

Table IV. Effects of Dimethylaminoethanethiol, DMAET, on Photoreduction of 0.10 $M$ SBBS in 1:3 2-Propanol–Water, pH 5.9$^a$

| DMAET, $M$ | Reaction % | Reaction $M$ hr$^{-1}$ |
|---|---|---|
| 0 | 48 | 0.047 |
| 0.0060 | 56 | 0.042 |
| 0.012 | 46 | 0.028 |
| 0.024 | 38 | 0.016 |

$^a$ Rate of 0.10 $M$ benzophenone in 2-butylamine, irradiated concurrently, 0.049 $M$ hr$^{-1}$, $\varphi$ = 1.1.

## Discussion

Attainment of the maximum quantum yield, $\varphi$ = 2, for the photoreduction of an aromatic ketone by an alcohol requires quantitative efficiency in a sequence of processes: absorption of the incident light by the ketone, intersystem crossing to the excited triplet, abstraction of hydrogen from the carbinol carbon of the alcohol, eq 2, and transfer of hydrogen from the alcohol-derived radical to a second molecule of ketone, eq 3.[11–13] For a system operating under these ideal

$$\mathrm{Ar,Ar'C{=}O^*(T_1) + R,R'CHOH} \xrightarrow{k_r} \mathrm{Ar,Ar'\dot{C}OH + R,R'\dot{C}OH} \quad (2)$$

$$\mathrm{Ar,Ar'C{=}O + R,R'\dot{C}OH} \longrightarrow \mathrm{Ar,Ar'\dot{C}OH + R,R'C{=}O} \quad (3)$$

conditions the following relation may be derived[12]

$$1/\varphi = {}^1/_2 + \frac{k_d}{2k_r(\mathrm{RH})} \quad (4)$$

The observed quantum yield may be 2 when the self- and solvent-induced deactivation of the triplet, rate constant $k_d$, is very small compared with reaction 2, $k_r$(RH).

However the kinetics of photoreduction of aromatic ketones by alcohols[1,14–18] and by secondary and tertiary amines[19] are complicated by light-absorbing transients. The observed quantum yield of photoreduction of benzophenone by neat 2-propanol at moderately high light intensity was only about 1.1, and it decreased with extent of reaction as the light-absorbing transient increased. The quantum yield *increased* on dilution with benzene to ~1.6 at 0.72 $M$ 2-propanol, and then decreased on further dilution with rising value of the fraction $k_d/k_r$(RH). The inverse plot of quantum yield *vs.* concentration of 2-propanol for the data below ~1 $M$ 2-propanol extrapolated to the hypothetical quantum yield of ~2.[20] The photoreduction in neat 2-propanol is accompanied by much light-absorbing transient, and far less is formed in dilute solution in benzene. The indicated variations in quantum yields may be largely due to the varying concentrations of the intermediate. The intermediate appears to be the product of para coupling of the initially formed radicals,[18] eq 5. The lower quantum yields at high concentrations of 2-propanol may not be due to higher $k_d$ or lower $k_r$, since a quantum yield

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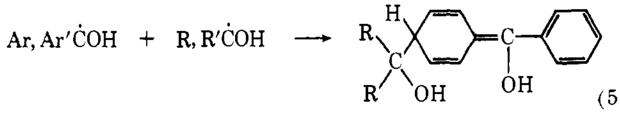

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of 2 was reported[13] for photoreduction of benzophenone in 2-propanol at very low light intensity and moderately high concentration of benzophenone, conditions which allow reaction 3 to be faster than reaction 5. Dilution of 2-propanol with *tert*-butyl alcohol instead of with benzene led to no increase in quantum yield and to development of much absorbing intermediate.[20] Similarly in the photoreduction of *p*-benzoylphenyltrimethylammonium ion by 2-propanol, dilution of the alcohol with water led to no increase in quantum yield and to much light-absorbing intermediate.[7] The para coupling process to form the intermediate may be favored in hydroxylic solvents because of solvation of the $\alpha$-hydroxyls and hindrance to $\alpha$-coupling. The intermediate leads subsequently in dark reactions to the isolated products, pinacols.

The characteristics of the photoreduction of SBBS by 2-propanol are those of a reaction accompanied by substantial formation of an intermediate, eq 5, much like the photoreduction of benzophenone under similar conditions. The absorption spectrum of the intermediate, Figure 1, obtained from the difference in spectra immediately after a period of irradiation and after decomposition of the intermediate, is similar to that from benzophenone.[18] Since these studies are entirely in hydroxylic media absorbing intermediates will prevent observation of the high extrapolated quantum yield of 2.

Physical quenchers lead to complex kinetic effects in such a system. Ideally, for a system which includes an added quencher, Q, eq 6 may be derived.[12] A plot of

$$1/\varphi = \frac{k_d + k_r(\mathrm{RH})}{2k_r(\mathrm{RH})} + \frac{k_q(\mathrm{Q})}{2k_r(\mathrm{RH})} \qquad (6)$$

$1/\varphi$ against concentration of quencher has slope $= k_q/2k_r(\mathrm{RH})$, and ratio of slope to intercept $= k_q/(k_d + k_r(\mathrm{RH}))$. The value of $k_q$ may be calculated if it is diffusion controlled, or sometimes obtained from phosphorescence quenching,[21] and application of eq 4 and 6 leads to calculation of $k_d$ and $k_r$. The intercept in such a plot is a measure of the unquenched quantum yield under the conditions of solvent and reducing agent of the experiments. In the present photoreduction of SBBS, during the early rapid stage before the concentration of intermediate has built up, formation of triplet and physical quenching both occur with high efficiency. During the later phase of photoreduction, which is retarded by intermediate, less triplet is formed and apparently less quenching occurs for a given concentration of quencher, Table I. However, the quenched reactions show less development of intermediate. Quenching may lead to less intermediate by decreasing the rate of initial formation of radicals, as does low light intensity, but it is not clear that this accounts fully for the observed effect. At low concentrations of quencher some intermediate is present and the reaction shows retardation due to both intermediate and quencher. At high concentrations of quencher intermediate is fully suppressed, all the light is absorbed by the ketone, retardation results only from action of the added quencher and the photoreductions show simple zero-order kinetics. In a plot of $1/\varphi$ *vs.* [Q], low concentrations of quencher, would appear to be more effective than their concentration should allow. The slope of the line would be less than it should be or it would show upward curvature as it is extrapolated to zero quencher. High values of intercept or low extrapolated values of limiting quantum yield in absence of quencher would be observed. Such a treatment of the data of Table I would lead to a limiting unquenched rate of 0.070 $M$ hr$^{-1}$, $\varphi \sim 1.6$, for the data at low conversion (<10%), and to 0.050 $M$ hr$^{-1}$, $\varphi \sim 1.1$, for the data at higher conversion.

When only the results obtained at high concentration of quenchers, Table II, are used, effects of the intermediate are avoided and linear plots may be constructed of inverse rate *vs.* concentration of quenchers, Figure 2. Three quenchers were compared, naphthalene, N, the positive 1-naphthyltrimethylammonium tosylate, NT$^+$, and the negatively charged naphthalene-2-sulfonic, acid NS$^-$. Of these naphthalene is most effective, about 65% as effective in quenching SBBS as it is in quenching uncharged benzophenone. The positively charged naphthalene is 80% as effective as naphthalene, and the negatively charged compound is 67% as effective. The previous study[7] of the positively charged benzoylphenyltrimethylammonium chloride indicated that ketone was generally less sensitive than benzophenone to quenching, and very insensitive to NT$^+$. Ionic charge, whether in the ketone or the quencher, leads to decreased quenching efficiency, possibly because of solvation barriers and lower diffusion rates, and a charged ketone is quenched more efficiently by a quencher of opposite charge than by one of the same charge.

The linear plots of Figure 2 for the three quenchers extrapolate to rates corresponding to a quantum yield of $\sim 2$. When complication due to the intermediate is avoided, in this case by strong quenching, the system behaves in accord with eq 2–4. The slope of the plot for quenching by naphthalene is 1800 $M^{-2}$ hr, the ratio of slope to intercept is 160 $M^{-1}$, and, from eq 6, if $k_d \ll k_r(\mathrm{RH})$, this ratio $= k_q/k_r(\mathrm{RH})$, $k_q/k_r = 1600$, $k_r = 1.1 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$, based on $k_q = 1.8 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$. This value of $k_r$ for abstraction of hydrogen from 2-propanol by SBBS triplet is slightly less than those for the same abstraction by the triplets of benzophenone and of the 4-benzoylbenzoate anion in water–pyridine.[22] The slope of the plot for quenching by NT$^+$ is 1440 $M^{-2}$ hr, indicating $k_q = 1.4 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$, and the corresponding values for NS$^-$ are 1200 $M^{-2}$ hr and $1.2 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$, both based on $1.8 \times 10^9\ M^{-1}$ for quenching by naphthalene.

Quantum yields for photoreduction of SBBS by aqueous 2-propanol, Table III, determined on a monochromator by comparison with a primary actinometer, ferrioxalate, were higher at low conversion, $\varphi = 1.57$, 334 nm, than at higher conversion, $\varphi = 1.36$, 334 nm, $\varphi = 1.30$, 313 nm. This is consistent with the preceding discussion of development of intermediate. The values are higher than those calculated from irradiation on the wheel with all light passed by Pyrex and comparison with the secondary actinometer, benzophenone-2-butyl-

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(21) W. D. K. Clark, A. D. Litt, and C. Steel, *J. Amer. Chem. Soc.*, **91**, 5413 (1969).

(22) S. G. Cohen and N. Stein, *ibid.*, **91**, 3690 (1969).

amine, $\varphi = 1.1$. In the polychromatic irradiation a larger proportion of the light is absorbed by the transient than in irradiation at 334 nm, near $\lambda_{max}$ of SBBS, and lower apparent quantum yields result. When the quantum yield at 334 nm in the presence of 0.030 $M$ naphthalene, $\varphi = 0.38$, is applied to the corresponding experiment of Table II and to the data at lower concentrations of quencher, extrapolation leads to a limiting $\varphi = 2.2$. This is higher than the theoretical maximum, $\varphi = 2.0$, and may reflect the errors in these experiments and in translating data obtained on the monochromator to those obtained with polychromatic light.

Photoreduction of SBBS by aqueous 2-propanol was also strongly retarded by a mercaptan, dimethylaminoethanethiol, DMAET, used as the hydrochloride at pH 5.75, Table IV. Although amines interact rapidly with ketone triplets,[19] the unshared electrons of nitrogen appear to be required and the protonated amino group probably does not interfere. The retardation presumably arises from the previously described repeating sequence of hydrogen atom transfer reactions,[3] reduction of the alcohol derived radical by mercaptan and oxidation of the ketone derived radical by thiyl radical, eq 7 and 8. Although the mechanism is quite different from

$$\mathrm{R,R'\dot{C}OH + MSH \longrightarrow R,R'CHOH + MS\cdot} \qquad (7)$$

$$\mathrm{Ar,Ar'\dot{C}OH + MS\cdot \longrightarrow Ar,Ar'C{=}O + MSH} \qquad (8)$$

that of physical quenching of triplet, a not dissimilar kinetic expression may be derived.[23] A plot of inverse rate against concentration of mercaptan may be constructed, with slope = 2000 $M^{-2}$ hr, similar to that for naphthalene. The mercaptan keeps the concentration of alcohol derived radical low, the absorbing intermediate is not observed, and the plot is linear. The extrapolated rate in the absence of mercaptan is 0.083 $M$ hr$^{-1}$, 1.7 times that of the standard, benzophenone-2-butylamine, corresponding to a hypothetical uninhibited quantum yield of $\sim$1.9. The quantum yield was also determined at 334 nm by ferrioxalate actinometry in the presence of 0.024 $M$ DMAET, experiment 5, Table III, $\varphi = 0.35$. When this value is applied to the data of Table IV, the corresponding rate, 0.016 $M$ hr$^{-1}$, and the extrapolated rate, 0.083 $M$ hr$^{-1}$, lead to a hypothetical quantum yield in the absence of mercaptan, $\varphi = 1.8$. This high nearly maximum extrapolated value of quantum yield arises from absence of intermediate in the presence of mercaptan, and stands in contrast to the lower quantum yield, $\varphi = 1.1$, actually observed in the absence of mercaptan.

[23] S. G. Cohen, D. A. Laufer, and W. V. Sherman, *J. Amer. Chem. Soc.*, **86**, 3060 (1964).

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# Oxidation of 2-Methoxyethanol to Methoxyacetic Acid by Nitric Acid Solutions

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**Abstract:** The oxidation of 2-methoxyethanol by nitric acid in sulfuric acid solution was studied using 60-MHz nmr to follow the rate of disappearance of the alcohol. Nitric oxide evolution and $N_2O_3$ and HONO in solution were also monitored. An activation energy of 17.9 kcal/mol was obtained for the overall reaction in the temperature range 4–27°. The rate of disappearance of 2-methoxyethanol follows first-order kinetics well in the range of 20–80% conversion. A plot of the logarithm of the rate constants *vs.* the acidity function $H_0$ gives a unit slope. A deuterium isotope effect of 3.9 was observed and indicates the rate-determining step involves cleavage of the 1-C–H bond. A mechanism is proposed which involves nitrosonium ion ($NO^+$) as the active oxidizing agent. A rapid equilibrium between 2-methoxyethanol and 2-methoxyethyl nitrite exists under our oxidation conditions. The oxidation of 2-methoxyethanol by nitrosonium fluoroborate was studied and provides additional support for the role assigned to nitrosonium ion.

Although nitric acid has often been used in the oxidation of alcohols to organic acids, only a few studies have been made to determine the oxidation path. Ogata and his coworkers[1] have studied separately the kinetics of nitric acid oxidation of benzyl alcohol to benzaldehyde (which proceeds in dilute $HNO_3$) and the oxidation of benzaldehyde to benzoic acid (which proceeds only under strongly acid conditions). Ogata and Sawaki[1c] have suggested that the radical ion, $HNO_2^+$, is the oxidizing agent in the oxidation of benzyl alcohol to benzaldehyde in aqueous dioxane. They postulated an abstraction of a hydrogen atom by $HNO_2^+$ followed by nitrite formation between the resulting organic radical and $NO_2$. The nitrite ester then could hydrolyze to the aldehyde. For the oxidation of benzaldehyde to benzoic acid in aqueous dioxane–$H_2SO_4$, Ogata, Tezuka, and Sawaki[1b] proposed a mechanism involving a rate-determining hydrogen abstraction from both hydrated and free benzaldehyde by protonated nitrogen dioxide, followed by rapid hydrolysis of the so-formed benzoyl nitrites to benzoic acid. The oxidation of ethanol by aqueous nitric acid at 100–200° and 30–40 atm has been studied by Silakhtarian, Blümberg, Nonkov, and Emanuel.[2] They proposed a chain reaction involving

[1] (a) Y. Ogata, Y. Sawaki, F. Matsunaga and H. Tezuka, *Tetrahedron*, **22**, 2655 (1966); (b) Y. Ogata, H. Tezuka, and Y. Sawaki, *ibid.*, **23**, 1007 (1967); (c) Y. Ogata and Y. Sawaki, *J. Amer. Chem. Soc.*, **88**, 5832 (1966).

[2] N. T. Silakhtarian, E. A. Blümberg, U. D. Nonkov, and N. M. Emanuel, *Dokl. Akad. Nauk SSSR*, **184**, 376 (1969).