

Quenching, Radical Formation, and Disproportionation in the Photoreduction of 4-Carboxybenzophenone by 4-Carboxybenzhydrol, Hydrazine, and Hydrazinium Ion[†]

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Abstract: Laser flash and steady irradiation studies have been carried out on the 4-carboxybenzophenone (CB)-4-carboxybenzhydrol (CBH₂) and CB-hydrazine systems over the pH range 5.8-12. In reaction with CBH₂, CB triplet is quenched in part by the carboxylate, $k_q \approx 4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$; total reaction, $k_4 = 3.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, leads to the ketyl radical CBH•, $\varphi = 1.7$. Absorption spectra were recorded for CB triplet, $\lambda_{\text{max}} = 535 \text{ nm}$ ($\epsilon = 6600 \text{ M}^{-1} \text{ cm}^{-1}$), for CBH•, $\lambda_{\text{max}} = 570 \text{ nm}$ ($\epsilon = 5500$), and for the radical anion CB^{-•}, $\lambda_{\text{max}} = 660 \text{ nm}$ ($\epsilon = 8100$). The $\text{p}K_a$ of CBH• was determined, 8.2. Rate constants were determined: for combination of CBH• to pinacol, $2k_6 = 1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; for reactions of CBH• with CB^{-•}, $k_7 = 1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; for disproportionation of 2CB^{-•}, $2k_8 = 9.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Factors to convert observed yields of photoreduction by hydrazine to yields of ketyl radical leading to pinacol and hydrol were determined from effects of pH on quantum yields of reduction of CB by CBH₂. Reduction of CB triplet by neutral hydrazine occurs with $k_{\text{ir}} = 6.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, forming ketyl radical with $\varphi = 1.0$, measured relative to the CBH₂ reaction. The reaction with protonated hydrazine is slower, $k'_{\text{ir}} = 4.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Computer simulation, using the measured rate constants, $\text{p}K_a$ and primary yields, and literature constants for pure hydrazine systems, leads to calculated reduction yields very similar to the observed values, with $\varphi_{\text{ketyl}} \approx 0.0$ for reaction of triplet with protonated hydrazine, and ratios of rate constants for ketyl-hydrazyl disproportionations appropriately close to unity.

In an earlier study,¹ the quantum yield of photoreduction of 4-carboxybenzophenone (CB) by hydrazine (N) was measured as function of N concentration and pH, over the range 5.8-12. The yields of ketyl radical which reacted to form pinacol and hydrol went through a maximum, $\varphi' \approx 0.35$, at pH ~ 7.5 , fell off sharply at lower pH and decreased more gradually at higher pH. In interpreting these results, we observe that CB exists as the anion throughout this pH range, but both neutral hydrazine and hydrazinium ion are involved in the initial reaction with the ketone triplet. Moreover, these reactions may lead either to radical formation or to quenching. Consideration must also be given to acid-base equilibria involving both the ketyl and hydrazyl radical products, whose neutral or ionic forms may react either by disproportionation or combination, further influencing the overall photoreduction yield.

The quantum yield at pH 9, ~ 0.20 , was insensitive to concentration of hydrazine, and at all concentrations studied there was sufficient free hydrazine to trap the triplet. However, at low pH the quantum yield was very low despite ample protonated hydrazine to react with the triplet. This indicated that free hydrazine is the active reducing agent, while reaction with protonated hydrazine leads largely to quenching. The decrease in quantum yield at high pH would be due to disproportionation of ketyl radical anion, CB^{-•}, with hydrazyl radical, competing very effectively with formation of hydrol or pinacol from CB^{-•}. The rather low peak yield, 0.35, in the reaction with free hydrazine at neutral pH might be caused by partial quenching in the primary step and/or by disproportionation of ketyl radical, CBH•, with hydrazyl radical. The overall kinetics would not distinguish between these two sources of inefficiency.

This ambiguity, quenching vs. disproportionation, is encountered quite generally in photoreductions with quantum yields less than unity, as in the reaction of triplet benzophenone with amines,² thiols,³ and thioethers.³ The question has been resolved in those cases by flash photolytic measurements of the quantum yield of

primary ketyl radical formation. Such measurements require knowledge of the relative extinction coefficients of the triplet and ketyl radical, ϵ_T/ϵ_R . This may be obtained from the ratio $r = \Delta D_{R^\infty}/\Delta D_T^0$, where ΔD_T^0 and ΔD_{R^∞} are the observed transient absorptions at appropriate wavelengths, corresponding respectively to initial formation of triplet and to total formation of radical;⁴ r is proportional to the quantum yield and may be converted to the absolute value $\varphi = r\epsilon_T/\epsilon_R$, by comparison with r for a related reaction in which the yield of the same radical is known. In the case of benzophenone photoreductions^{2,3} we have calibrated r by the value observed by using benzhydrol as reductant, for which we may take $\varphi_{\text{ketyl}} = 2.0$.⁵

However, preliminary experiments using the CB-4-carboxybenzhydrol (CBH₂) system as reference, with the analogous assumption that $\varphi_{\text{ketyl}} = 2.0$, led to r values corresponding to φ_{ketyl} greater than unity in the CB-hydrazine system. This indicated the need for a detailed study of ketyl and overall reduction quantum yields in the CB-CBH₂ reaction. In addition to providing a reference standard for ketyl yields in other CB-reductant systems, this would allow determination of the products and rate constants for the ketyl radical reactions CBH• + CBH•, CBH• + CB^{-•}, and CB^{-•} + CB^{-•}. Also in mechanistic analysis of the hydrazine system, values are needed, at each pH, for the yields of pinacol and hydrol, from combination and disproportionation, respectively, of ketyl radical and anion. In the previous work,¹ these yields were based on pinacol yields obtained as a function of pH in photoreduction by aqueous 2-propanol.⁶ Study of CB-CBH₂ in water would be more relevant to other CB-reductant systems in water, since solvent may greatly affect the relative magnitudes of rate constants for ketyl-ketyl and ketyl-ketyl radical anion reactions.⁷

We now report on a laser flash study of these two systems.

Materials and Methods

Materials. Water was triply distilled from potassium permanganate

[†] Dedicated to Professor George S. Hammond on the occasion of his 60th birthday.

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and sodium dichromate. Buffers¹ were prepared from sodium tetraborate decahydrate (Baker Analyzed), above pH 8.3 and potassium dihydrogen phosphate (Fisher Certified) below pH 8.3, and were in the range 0.03–0.05 M. Hydrazine (Aldrich) was distilled and stored under nitrogen at –18 °C. 4-Carboxybenzophenone (Aldrich) was recrystallized from ethanol, mp 199–200 °C. 4-Carboxybenzhydrol, CBH₂, was prepared by reduction of the ketone by sodium borohydride, mp 172–172.5 °C, from ethyl acetate–chloroform (lit.⁸ mp 167–168 °C). 4-*tert*-Butylbenzoic acid (Aldrich), was recrystallized from methanol, mp 167–168 °C (lit.⁹ mp 165–166 °C).

α -Methyl-4-carboxybenzhydrol: 4-carboxybenzophenone (5.65 g, 0.025 mol) in 50 mL of dry tetrahydrofuran was added slowly to 25 mL of a stirred 3 M solution of methylmagnesium bromide in ether (Aldrich). The mixture was boiled for 24 h, treated with 50 mL of 10% sulfuric acid, and extracted with ether. The sodium carbonate extract of this solution was acidified and extracted with ether, leading to the product, mp 150–151.5 °C, from chloroform, 1.9 g (31% yield). Anal. Calcd for C₁₅H₁₄O₃: C, 74.36; H, 5.82. Found: C, 73.34; H, 5.76 (Galbraith).

Methods. Laser flash photolysis with excitation at 347 nm was carried out using apparatus and procedures described previously.¹⁰ Buffered solutions, in 1 × 1-cm Pyrex cells fitted with Teflon closures, were degassed by three freeze–thaw cycles and left under argon. Spectra of the transients, corrected for variation in flash intensity, were obtained over the range 360–700 nm. First- and second-order decay rate constants of transients were determined from the first- and second-order plots of the time-resolved absorbances, at appropriate wavelengths for the triplet, ketyl radical, CBH•, and radical anion, CB^{•-} (see below). Rate constants, k_{ir} , for interaction of excited triplet with quenchers or reductants were determined from the dependence of the effective pseudo-first-order triplet decay constant on concentration of reactant (eq 1). In such experiments,

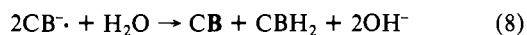
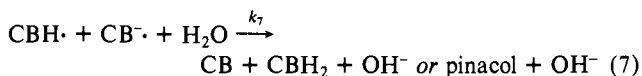
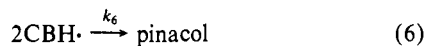
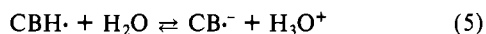
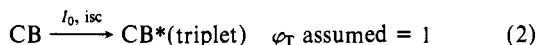
$$k_{eff} = k_0 + k_{ir}(Q) \quad (1)$$

a set of about five samples were prepared and degassed together. These included a full range of reactant concentrations and blank, treated identically to minimize irreproducibilities in triplet lifetime caused by variations in residual oxygen or solvent impurities.

Steady Illumination Photo-reduction Yields. Test solutions in 1-cm Pyrex cells, deoxygenated as above, were mounted on a rotating wheel and irradiated with a GE HA-85 lamp. Decrease in ketone concentration with time was followed by absorption measurements at 330–340 nm, in a 1-mm side-arm quartz cell, and the initial slope computed by least squares. Quantum yields were obtained by comparison with the "Aberchrome" actinometer, for which $\phi = 0.20$.¹¹

Results and Discussion

A. The CB–CBH₂ System. As a framework for discussion, it is helpful first to list pertinent reactions in this system.



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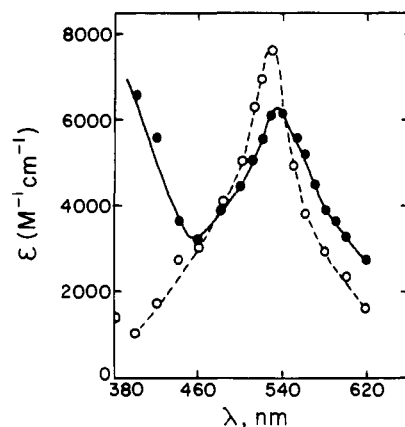


Figure 1. Triplet spectra: benzophenone in benzene, O; 4-carboxybenzophenone in water, pH 7, ●.

In this scheme, we do not include disproportionation of 2CBH₂• nor pinacol formation from 2CB^{•-} (see below, A-7).

1. Triplet of 4-Carboxybenzophenone (CB). Laser flash irradiation of CB in deoxygenated aqueous solution, pH 7, gave a transient whose absorption, measured from 380 to 620 nm, peaked at $\lambda_{max} = 535$ nm. The spectrum, shown in Figure 1, is close to that of benzophenone triplet¹² and is safely assigned to the benzophenone carboxylate triplet. In this paper, where we report data only at pH > 5.8, it will be understood that the CB triplet is always in its carboxylate anion form. The decadic molar extinction coefficient was determined by reference to the known absorption of benzophenone triplet in benzene, $\epsilon_{525} = 7630 \text{ M}^{-1} \text{ cm}^{-1}$.¹³ Triplet spectra were obtained for benzophenone, 0.0020 M in benzene, and CB, 0.00156 M in buffer, pH 7, which have similar absorptions ($A \approx 0.265$) at 347 nm. From the relative absorbances of the two transients, corrected for variations in flash intensity and for small differences in absorption, we find $\epsilon_{525} = 6150 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon_{max} (535 \text{ nm}) = 6600$ for the CB triplet.

The triplet decay was first order, with total rate constant, k_d , in the range $(1.5\text{--}2.0) \times 10^5 \text{ s}^{-1}$ at 0.002 M CB, consistent with earlier phosphorescence data.¹

2. Quenching of CB Triplet by Benzoate. Since 4-carboxybenzhydrol differs from benzhydrol in its carboxyl group, the effect of the benzoate moiety of CBH₂• on the lifetime of CB triplet was examined by flash irradiation of 0.002 M CB in the presence of 0.01–0.5 M sodium benzoate, pH 7, and 0.02–0.16 M sodium 4-*tert*-butylbenzoate, pH 7. These anions decreased the lifetime of CB triplet without leading to ketyl radicals or other long-lived transients. Values of k_q of $1.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $3.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ were obtained for the two compounds, respectively. As a closer model for study of quenching by CBH₂•, a homologue which lacks the easily abstracted carbinol hydrogen, α -methyl-4-carboxybenzhydrol, was prepared. This compound, 0.02–0.20 M, pH 7, also quenched CB triplet without forming other transients. The rate constant was slightly higher, $k_q = 4.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, and this was taken as the contribution to quenching by the benzoate group of CBH₂•. This quenching by the carboxylate is consistent with the effect of ground-state CB on CB triplet, previously observed¹ by phosphorescence quenching, $k_q = 6.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, and with quenching of aromatic carbonyl triplets by inorganic anions without formation of ketyl radicals.¹⁴ Alternatively, the quenching may involve ring interactions, as has been postulated to explain self-quenching of benzophenone triplet in aqueous media.⁷

3. Reaction of CB Triplet with CBH₂•. In the presence of CBH₂• the lifetime of the CB triplet was decreased and longer lived transients appeared. On the basis of the effects of pH on their spectra (Figure 2), these are identified as the ketyl radical and

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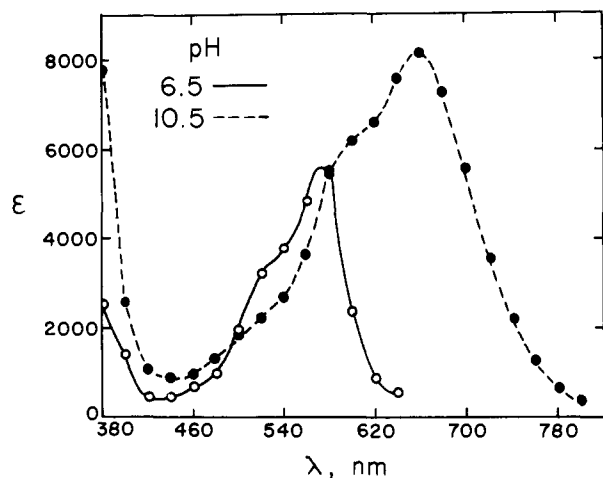


Figure 2. Radical spectra: 4-carboxybenzophenone ketyl, $\text{CBH}\cdot$, \circ ; radical anion, $\text{CB}\cdot^-$, \bullet .

Table I. pK_a of 4-Carboxybenzophenone Ketyl, $\text{CBH}\cdot^a$

pH	$r_{660\text{ nm}}$	$(\text{CB}\cdot^-)/(\text{CBH}\cdot)$	$\log(\text{CB}\cdot^-)/(\text{CBH}\cdot)$
6.0	0.15		
7.0	0.50	0.057	-1.24
7.5	1.09	0.24	-0.62
8.0	2.21	0.48	-0.32
8.5	5.37	4.24	0.63
9.0	5.63	5.81	0.76
9.5	6.12	13.60	1.13
10.5	6.62		
11.5	6.59		

^a Effect of pH on $r_{660\text{ nm}} = \Delta D_R / \Delta D_T$; flash irradiation, 347 nm; 0.002 M CB, 0.15 M CBH_2 .

radical anion (see below). The lifetimes of the triplet and radical species were well separated, permitting ready determination of rate constants and initial triplet and total radical absorbances, ΔD_T^0 and ΔD_R^∞ .⁴ At pH 7, in 0.002 M CB, the triplet decay constant was linear in CBH_2 concentration in the range 0.01–0.12 M, leading to $k_4 = 3.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. From this result, together with the benzoate quenching rate constant, $4.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ obtained above, we conclude that 14% of the CB triplets are quenched in the CBH_2 interaction and 86% abstract α -H from the hydrol. The total radical yield, ϕ_{ketyl} , would be twice this, or 1.7, compared with 2.0 in the benzophenone–benzhydrol system.⁵

4. Radical and Radical Anion Spectra. Spectra of the ketyl radical anion, $\text{CB}\cdot^-$, were obtained by flash excitation at 347 nm of 0.0020 M CB and 0.10 M CBH_2 at pH 6.5 and 10.5, respectively: $\lambda_{\text{max}}(\text{ketyl}) = 570 \text{ nm}$; $\lambda_{\text{max}}(\text{ketyl anion}) = 660 \text{ nm}$ (Figure 2). The extinction coefficient of the ketyl radical was determined by reference to $\epsilon_{525} = 6150$ of the triplet determined above and the quantum yield for formation of ketyl radical. In this experiment, 96% of the triplet reacted with the hydrol, generating ketyl with a quantum yield of 1.7. The ratio of $\text{CBH}\cdot$ to triplet absorption at 525 nm, 0.955, leads to $\epsilon_{525\text{ nm}} = 3600$ and $\epsilon_{570} = 5500$ for $\text{CBH}\cdot$ at λ_{max} . On the assumption of the same yield of $\text{CBH}\cdot$ at pH 10.5, followed by rapid deprotonation to $\text{CB}\cdot^-$, the ratio of absorption of $\text{CB}\cdot^-$ to triplet absorption at 525 nm, 0.637, leads to extinction coefficients for $\text{CB}\cdot^-$, $\epsilon_{525} = 2400 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon_{660} = 8100$ at λ_{max} .

5. pK_a of the Ketyl Radical. The ketyl radical has very low absorption at 660 nm, where the anion has its λ_{max} (Figure 2). The ratio, $r = \Delta D_R / \Delta D_T^0$, measured at this wavelength, has the low value due essentially to $\text{CBH}\cdot$ when irradiation is carried out at pH 6 and the high value due to $\text{CB}\cdot^-$ after flashing at pH 10.5. Measurements of $r_{660\text{ nm}}$ in 0.0020 M CB and 0.15 M CBH_2 as a function of pH from 6.0 to 10.5 are given in Table I and Figure 3. The ratio, $f = (\text{CB}\cdot^-)/(\text{CBH}\cdot)$ at a given pH is, to a close approximation, given by the ratio $(r_{\text{pH}} - r_{\text{pH } 6.0}) / (r_{\text{pH } 10.5} - r_{\text{pH}})$. The log plot, Figure 4, leads to $pK_a = 8.2$ for $\text{CBH}\cdot$. This may

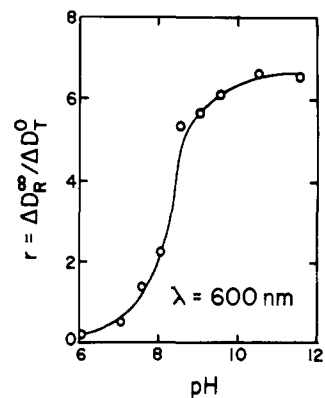


Figure 3. $r = \Delta D_R^\infty / \Delta D_T^0$, as a function of pH ($\lambda = 660 \text{ nm}$).

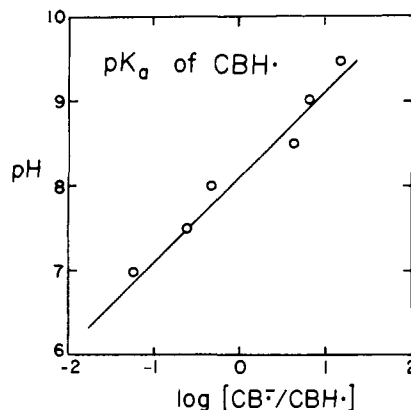
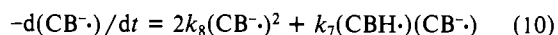
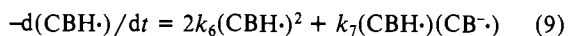


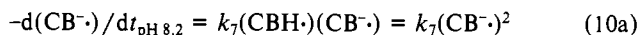
Figure 4. Determination of pK_a of 4-carboxybenzophenone ketyl radical.

be compared with the value given for benzophenone ketyl radical, $pK_a = 9.2$, in 50% 2-propanol–water.¹⁵

6. Rate Constants for Ketyl-Ketyl Reactions. In the CB – CBH_2 system, $\text{CBH}\cdot$ and $\text{CB}\cdot^-$ react to form pinacol and/or hydrol (eq 6–10). At pH 6.3 only $\text{CBH}\cdot$ is present. A solution, 0.0020 M



CB and 0.08 M CBH_2 was flashed, and the value of k_6 was calculated from the second-order decay curve (Figure 5A) of the absorption at 525 nm, $\epsilon_{525} = 3600$: $2k_6 = 1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Similarly, at pH 11, where $\text{CBH}\cdot$ may be neglected, the second-order decay of the absorption at 660 nm due to $\text{CB}\cdot^-$, $\epsilon_{660} = 8100$, led to $2k_8 = 9.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. At pH 8.2, $\text{CBH}\cdot$ and $\text{CB}\cdot^-$ are present initially at equal concentrations, the low value of k_8 allows the first term in eq 10 to be neglected, and eq 10 may be simplified to eq 10a, valid as $t \rightarrow 0$. The second-order plot of



decay of absorption of $\text{CB}\cdot^-$ at 660 nm led to $k_7 = 1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Figure 5B). The values found here for $2k_6$ and k_7 are close to those given for the corresponding reactions of benzophenone ketyl and ketyl anion in water.⁷

7. Photoreduction of CB by CBH_2 . The rates of photoreduction of 0.004 M CB by 0.10 M CBH_2 under steady irradiation were measured over the pH range 6–11 and are given in Table II, relative to the rate at pH 6, taken as unity. These were converted to absolute values by measurements at pH 6.5 by using the Aberchrome actinometer,¹¹ with irradiation at 334 nm, $\phi_{\text{pH } 6.5}$ was 0.74. The fraction of triplet not trapped by reduction at this CBH_2 concentration was 10%, as derived from the values of k_d for the blanks in this experiment. Correcting for this gives $\phi_{\text{pH } 6.5} = 0.82$.

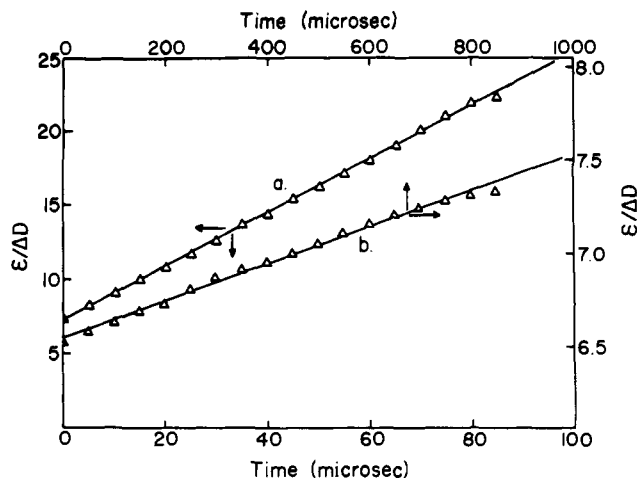


Figure 5. Second-order decay: a, $\text{CBH}\cdot$, pH 6.3; b, $\text{CB}\cdot^-$, pH 11.0.

Table II. Effect of pH on Observed Rates of Photo-reduction of 0.004 M 4-Carboxybenzophenone, CB, by 0.10 M 4-Carboxybenzhydrol, CBH_2

pH	rel rate (p) ^a	φ_{red}	$q^b = 2/(1+p)$
6.0	1.00	0.84	1.00
6.5	0.98	0.82	1.01
7.0	0.93	0.78	1.04
8.0	0.63	0.53	1.23
8.5	0.45	0.38	1.38
9.0	0.31	0.26	1.53
10.0	0.15	0.125	1.74
11.0	0.05	0.042	1.89

^a Fraction of ketyl converted to pinacol. ^b Correction factor for conversion of observed reduction quantum yield to φ'_{ketyl} (Figure 7).

At pH 6 all ketyl radicals combine (k_6) to form pinacol.⁶ We thus obtain the maximum value of $\varphi_{\text{red}} = 0.84$ in good agreement with $\varphi_{\text{red}} = 0.86$, derived solely from flash measurements of the k_{ir} 's for triplet interaction with CBH_2 and its α -methyl derivative. This agreement supports the assumption made earlier that in the primary $\text{CB}\cdot^- - \text{CBH}_2$ interaction, the only quenching effect is that associated with the benzoate group of the donor. The efficiency of the triplet in abstracting H from a neutral carbinol does not decrease in alkali,⁸ and the decrease in φ_{red} at higher pH is assigned to increasing disproportionation of ketyl radical and its anion, largely regenerating starting materials.

The respective yields of pinacol in the ketyl-ketyl anion (k_7) and anion-anion (k_8) reactions were estimated from the observed dependence of φ_{red} on pH (Figure 6). From the reaction scheme given above, we have, for reduction of CB by CBH_2

$$\varphi_{\text{red}} = 0.86 \frac{2k_6 + f k_7 \varphi_7 + f^2 k_8 \varphi_8}{2k_6 + f k_7 + f^2 k_8} \quad (11)$$

The asymptotic approach of φ_{red} to zero with increasing pH shows that the pinacol yield, φ_8 , of the $\text{CB}\cdot^- + \text{CB}\cdot^-$ reaction must be very low, and within the precision of our data, we take this to be zero. Assuming the pinacol yield, φ_7 , of the $\text{CBH}\cdot + \text{CB}\cdot^-$ reaction also to be zero, with values of the remaining constants measured above, leads to the dotted curve in Figure 6. Yields calculated taking $\varphi_7 = 0.15$ are shown by the open circles. The difference is well outside experimental error and remains so over a reasonable range of error in the determination of $\text{p}K_a$ for ketyl. We conclude that the pinacol yield in the ketyl-ketyl anion reaction is about 15%.

Decrease in yield of pinacol with increasing negative charge in the ketyl moieties is to be expected. Since ionization of the pinacol hydroxyl in strong alkali leads to rupture of the intrinsically weak central C-C bond,⁶ the reaction of two ketyl moieties in which one or both are and remain anionic has diminished tendency

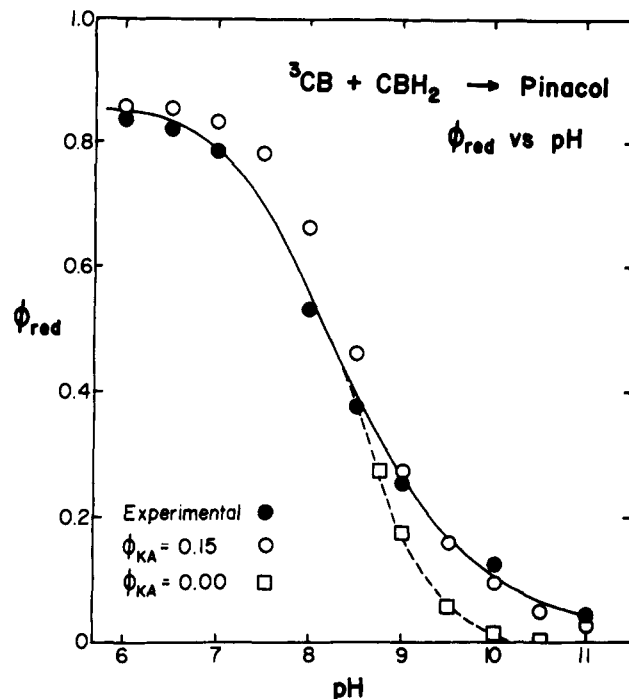


Figure 6. Reduction of 4-carboxybenzophenone by 4-carboxybenzhydrol (φ_{red} vs. pH): ●, observed; ○, calculated, eq 11, assuming $\varphi_7 = 0.15$; □, calculated, eq 11, assuming $\varphi_7 = 0$.

to form this bond but leads preferably to disproportionation. A mechanism involving initial formation of pinacol followed by cleavage to ketone and hydrol is unlikely, since earlier studies have shown the pinacol to be stable in a pH region in which pinacol yields were diminished and much hydrol was formed.⁶

It is noteworthy that the combination of ketyl radicals, k_6 , and the disproportionation of ketyl radical and radical anion, k_7 , proceed at essentially the same, very high rate. This suggests that both reactions pass through similar configurations, with disproportionation being closely accompanied by protonation at the α -carbon, without formation of either a pinacol or free carbanion. The disproportionation of the two radical anions proceeds at a rapid but substantially slower rate, $k_8 \approx 10^7 \text{ M}^{-1} \text{ s}^{-1}$. This redox reaction must also be closely coupled to proton-transfer processes involving surrounding or complexed water, in which fluctuations will influence the direction of electron transfer between the initially symmetrical reagents. The possibility may also be suggested of electron transfer involving the phenyl rings interacting hydrophobically, assisted by appreciable charge delocalization.

Tables III and IV summarize respectively properties of the triplet and radical intermediates and reaction rate constants, determined above.

B. The CB-Hydrazine System. 1. CB Triplet-Hydrazine Reaction. Flash irradiation of CB-hydrazine solutions at pH 7 and 11 gave triplet and long-lived transient spectra identical with those observed in $\text{CB} - \text{CBH}_2$ solutions at these pHs. No absorption attributable to radicals other than neutral and anionic ketyl was observed in the region 380–680 nm. The effect of hydrazine on triplet lifetime was measured over the range 0.004–0.01 M at pH 7 and 0.0001–0.0004 M at pH 11. The pseudo-first-order decay constant was linear in free hydrazine ($\text{p}K_a = 8.0^{16}$), giving $k_{\text{ir}} = 5.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at pH 7 and $7.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at pH 11 for the reaction with free hydrazine. These results may be compared with $k_{\text{ir}} = 6.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ derived from phosphorescence quenching data.¹

2. Primary Ketyl Yield. In solutions 0.0020 M in CB and 0.0010 M in hydrazine, the values of $r = \Delta D_{\text{R}}^{\text{tr}} / \Delta D_{\text{T}}^{\text{tr}}$, measured

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Table III. Properties of CB* (Triplet), CBH· (Ketyl Radical) and CB⁻· (Radical Anion)

species	λ_{\max} , nm	ϵ_{\max}^a , M ⁻¹ cm ⁻¹	pK _a
CB*	535	6600	
CBH·	570	5500	8.2
CB ⁻ ·	660	8100	

^a Relative to benzophenone triplet, ϵ_{525} 7630 M⁻¹ cm⁻¹³.

Table IV. Summary of Rate Constants and Reaction Products

system	reaction	value
CB*	k_d	1.5×10^5 s ⁻¹
CB* + CB	k_{q1}	4.2×10^6 M ⁻¹ s ⁻¹
CB* + CBH ₂	k_{q2}	3.0×10^7 M ⁻¹ s ⁻¹
CBH· + CBH·	$2k_6^b$	1.8×10^9 M ⁻¹ s ⁻¹
CBH· + CB ⁻ ·	k_7^c	1.1×10^9 M ⁻¹ s ⁻¹
CB ⁻ · + CB ⁻ ·	$2k_8^d$	9.8×10^6 M ⁻¹ s ⁻¹
CB* + H ₂ NNH ₂	k_{ir}^e	6.8×10^8 M ⁻¹ s ⁻¹
CB* + H ₂ NNH ₃	k_{ir}^f	4.4×10^6 M ⁻¹ s ⁻¹

^a 14% quenching; 86% CBH· formation (see text). ^b Pinacol formation. ^c 85% disproportionation, 15% pinacol formation (see text). ^d Disproportionation (see text). ^e Radical yield, $a = 1.0$ ^f Radical yield, $a' = 0-0.2$.

at 660 nm, were 2.05 at pH 9 and 2.49 at pH 11. At pH 9, only about 87% of ketyl (pK_a = 8.2) is present as the highly absorbing CB⁻·. Correction for this gives $r_{pH 9(corr)} = 2.40$, corresponding to the total radical formed. Thus, the primary radical yield is essentially the same in the two solutions, in contrast to the decrease in overall reduction yields with rising pH, $\phi_{red} = 0.35, 0.23$, and 0.05 at pH 7.5, 9.0, and 11, respectively.¹

Spectra of the triplet and CBH· were scanned around λ_{\max} , over the range 530–580 nm, in a solution 0.002 M in CB and 0.04 M in hydrazine at pH 7. Under these conditions 95% of the triplet reacts with hydrazine. The absorptions at the maxima of these transients were measured, corrected for variations in flash intensity, and the ratio was determined: $r_{\lambda_{\max}} = \Delta D_{R,570} / \Delta D_{T,535} = 0.78$. From the ratio $(\epsilon_T / \epsilon_R)_{\lambda_{\max}} = 0.83$ and correction for untrapped triplet, the quantum yield of CBH· is found to be $\phi_{ketyl} = 0.98$. A similar experiment with 0.002 M CB and 0.06 M CBH₂ gave $r_{\lambda_{\max}} = 1.29$. The ratio $1.29/0.78 = 1.7$ corresponds to the value obtained from the benzoate quenching experiments, indicating that the data are consistent and supporting our interpretations.

In a second procedure, the ratios r_{λ} were measured at pH 7.0 at $\lambda = 380, 390$, and 500 nm, for two 0.002 M CB solutions, containing respectively 0.08 M CBH₂ and 0.04 M hydrazine. Values of r_{λ} at the three wavelengths were respectively 0.72, 0.51, and 0.71 for the reference CBH₂ solution and 0.44, 0.30, and 0.45 for the hydrazine solution. On the basis of $\phi_{ketyl} = 1.7$ for the reference, the ratios of the r_{λ} 's lead to ϕ_{ketyl} values for primary reduction by hydrazine of 1.0, 1.0, and 1.1, measured at the three wavelengths. We conclude that ketyl is formed with unit quantum efficiency in reaction of CB triplet with neutral hydrazine. Low reduction in the corresponding pH region must be assigned to disproportionation.

3. Reaction Mechanisms in Photoreduction of CB by Hydrazine. Primary Ketyl Yield in Reaction of CB Triplet and Hydrazinium Ion. In developing mechanisms for these systems we first note that in the reduction of a ketone by its hydrol, the only reaction leading to net disappearance of ketone is pinacol formation. This reduction will vary with pH to the extent that disproportionation regenerates the starting materials. However, reduction by other reagents differs in that a second molecule of ketone may be reduced by reductant-derived radical, ketone will be consumed in formation of both pinacol and hydrol, and ketone–reductant coupling products may be formed. In the particular case of reduction by hydrazine, low quantum yields indicate no secondary reduction process, and products of ketone–hydrazine interaction were not observed. We conclude that reactions of hydrazine-derived radicals either regenerate starting materials (eq 16–18) or simply remove these radicals from the scene (eq 19–21). The

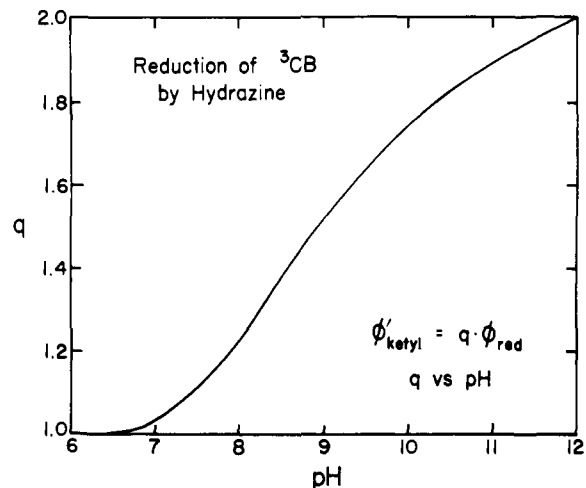


Figure 7. Correction factor, q , for converting observed ϕ_{red} to ϕ'_{ketyl} in reduction of 4-carboxybenzophenone by hydrazine.

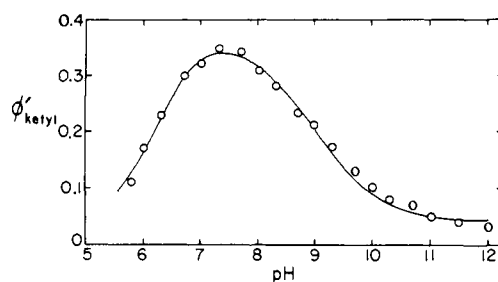
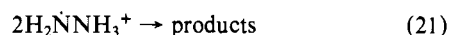
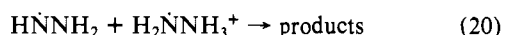
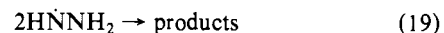
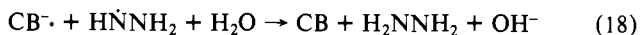
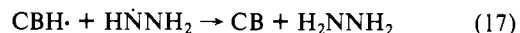
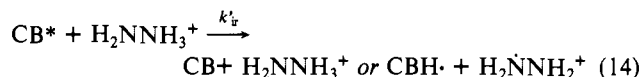
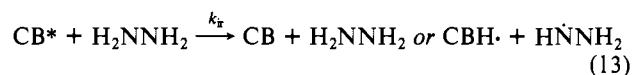


Figure 8. Photoreduction of 4-carboxybenzophenone by hydrazine (ϕ'_{ketyl} vs. pH): O, observed; —, calculated, eq 22.

overall yield of ketone reduction will then be determined by ϕ'_{ketyl} , the yield of primary ketyl radicals that react to form pinacol and hydrol, and by the partitioning between these reactions. No indication of ground-state interaction between hydrazine and CB was observed.

We thus consider reactions 12–21 for the CB–hydrazine system, in addition to those given above for the CB triplet and radical species.



On the basis of this scheme, using the steady-state approximation and neglecting reactions 3' and 4 in view of the much faster reactions with hydrazine, we derive the following expression for ϕ'_{ketyl} at a given pH in terms of the total concentration of hydrazine (N), the primary rate constants, and competition between ketyl–ketyl and ketyl–hydrazyl reactions.

$$\phi'_{\text{ketyl}} = \frac{(ak_{\text{ir}}/k_{\text{d}} + a'gk'_{\text{ir}}/kd)(N)}{1 + g + k_{\text{ir}}/k_{\text{d}} + gk'_{\text{ir}}/k_{\text{d}}} \frac{1}{1 + k_{18}/2k_6^{1/2}k_{19}^{1/2} \frac{(f + jk_{16}/k_{18} + k_{17}/k_{18})}{(1 + fk_7/k_6 + f^2k_8/k_6)^{1/2}(1 + jk_{20}/k_{19} + j^2k_{21}/k_{19})^{1/2}}} \quad (22)$$

In eq 22, a and a' are the primary radical yields in the reaction of ketone triplet with neutral and protonated hydrazine, respectively, eq 13 and 14; $f = (\text{CB}^-)/(\text{CBH}\cdot)$; $g = (\text{H}_2\text{NNH}_3^+)/(\text{H}_2\text{NNH}_2)$; $j = (\text{H}_2\text{NNH}_2^+)/(\text{HNNH}_2)$.

For comparison with experiment, we obtain ϕ'_{ketyl} for reduction by hydrazine, as a function of pH, from the observed overall ketone reduction yield, ϕ_{red} ,¹ and the data on the CB-CBH₂ reaction, as follows. When n ketyl radicals or radical anions react, the fraction p forms $np/2$ pinacol molecules and fraction $(1-p)$ forms $n(1-p)/2$ hydrol and an equal number of ketone molecules. The observed disappearance of ketone is $[n - (n/2)(1-p)] = n(1+p)/2$. The ratio $\phi'_{\text{ketyl}}/\phi_{\text{obsd}} = n/n(1+p)/2 = 2/(1+p) = q$, where q is the factor for converting ϕ_{obsd} to ϕ'_{ketyl} . The values of p , as function of pH, are given directly by the relative rates of CB reduction by CBH₂, leading to the corresponding values of q listed in Table II and shown in Figure 7. The resulting values of ϕ'_{ketyl} over the range of pH are given in Figure 8.

Evaluation of the parameters in eq 22 requires knowledge of 15 rate and equilibrium constants in the reaction scheme, eq 2-8, 12-21. Of these, five are available in the literature, e.g., the pK_a 's of hydrazine and hydrazinium radical cation (7.1¹⁷) and the rate constants k_{19} , k_{20} , and k_{21} .^{1,18} The flash experiments described here have established six more constants, k_{ir} , k_{d} , k_6 , k_7 , k_8 , and the pK_a of the CBH \cdot radical, while k'_{ir} is known from earlier phosphorescence quenching data.¹ Moreover, we have shown above that a , the yield of ketyl radicals in reduction of triplet by neutral hydrazine is unity. The direct determination of a' , the yield of ketyl from reduction of triplet by protonated hydrazine, is possible, in principle, by flash technique at low pH. However, this is difficult for technical reasons. The reaction of ketone triplet with neutral hydrazine ($k_{\text{ir}} = 6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) is so much faster than that with hydrazinium ion ($k'_{\text{ir}} = 4.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) that quite acid conditions are required to isolate the latter reaction. However, in such pH ranges, the CB anion begins to be protonated, leading to complications, including precipitation of the acid. Accordingly, a' was estimated by optimizing the fit of eq 22 to the ϕ'_{ketyl} data. In the accessible pH range below about 6.2 the shape of the yield curve is dominated by competition between neutral and protonated hydrazine in the primary interaction. The sharp drop in yield in this region indicates a very low value of a' . There remain also to be determined values of the terms in eq 22 containing the rate constants k_{16} , k_{17} , and k_{18} , for disproportionation between ketyl and hydrazyl moieties. Values of rate constants in this system for reactions between uncharged and charged and uncharged radicals of like species, k_6 and k_7 , and k_{19} and k_{20} , are high and similar, and it is expected that the ratios of rate constants in eq 22, corresponding to these radical reactions, would all be close to unity. Figure 8 shows the fit obtained by computer optimization of these parameters, giving $k_{18}/2k_6^{1/2}k_{19}^{1/2} = 1.35$, $k_{16}/k_{18} = 1.45$, and $k_{17}/k_{18} = 1.40$ and $a' = 0$.

While considerable latitude exists in adjusting these ratios, taking account also of the uncertainty in the pK_a 's, variations by

as much as 1 order of magnitude from the optimized values can be definitely excluded. The essential conclusion is that the data may be fitted by a reasonable choice of the undetermined rate constants, in a situation where the experimentally established parameters impose severe restrictions. The uncertainty in the value of a' derives from the same factors which limit its direct measurement. Raising a' from 0 to 1 increases the value of ϕ at pH 5.8 by about 25%, which is far outside experimental error. We estimate the upper limit for a' to be about 0.2.

The direct observation of unit quantum yield of ketyl radical in the reaction of triplet ketone with free hydrazine, eq 13, eliminates the possibility that low overall reduction yields in this process are caused by partial quenching within the primary excited reaction complex. On the basis of Figure 8 and the reasonable values found for the pertinent rate constants, we conclude that the maximum reduction quantum yields, ~ 0.35 , observed around pH 7-8 are lower than ketyl quantum yields because of disproportionation of ketyl and hydrazyl moieties, eq 16-18. Such regeneration of ketone by disproportionation with heteroatom-centered radicals, either by direct hydrogen transfer or after combination, is also seen in reactions with aminyl,² anilino,¹⁹ and thiy²⁰ radicals. Reduction quantum yields are diminished further at low pH as decreased concentration of free hydrazine allows larger proportions of decay of triplet, k_{d} , and quenching by protonated hydrazine, in addition to the disproportionations. At high pH low reduction quantum yields result as ketyl radical anion, CB $^-$, is formed and largely regenerates ketone by disproportionation with hydrazyl, eq 18; its self-disproportionation to hydrol and ketone is much slower. It remains preferable, however, to continue to formulate the initial triplet-reductant interaction in terms of charge transfer instead of direct hydrogen abstraction, because of the high rate constant, k_{ir} , and the general effectiveness of reduction by amines,²¹ the occurrence of quenching within the primary complex in reactions of amino ketones²²⁻²³ and sulfur compounds,^{3,24} the ready decarboxylation of amino acids by excited triplet,²⁴ and the observation of initial electron transfer in picosecond studies of the reaction of benzophenone with 3 M triethylamine, in benzene.²⁵

Acknowledgment. We appreciate support of this work by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, Contract EY-76-02-3117 (H.L.), by the National Science Foundation, Grant CHE 78-09333, and by the Cobar Fund, Brandeis University (S.G.C.).

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