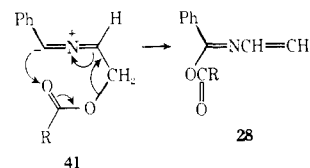


- (25) B. Castro, Y. Chapleur, B. Gross, and C. Selve, *Tetrahedron Lett.*, 5001 (1972); *Bull. Soc. Chem. Fr.*, 3034 (1973).
- (26) A. Hassner and L. A. Levy, *J. Am. Chem. Soc.*, **87**, 4203 (1965).
- (27) S. Sato, H. Kato, and M. Ohta, *Bull. Chem. Soc. Jpn.*, **40**, 2938 (1967).
- (28) F. W. Fowler and A. Hassner, *J. Am. Chem. Soc.*, **90**, 2875 (1968).
- (29) S. Sato, *Nippon Kagaku Zasshi*, **90**, 113 (1969).
- (30) P. B. Valkovich, J. L. Conger, F. A. Castiello, T. D. Brodie, and W. P. Weber, *J. Am. Chem. Soc.*, **97**, 90 (1975).
- (31) L. A. Wendling and R. G. Bergman, *J. Org. Chem.*, **41**, 831 (1976).
- (32) I. Ninomiya, T. Naito, and T. Kiguchi, *Tetrahedron Lett.*, 4451 (1970); *J. Chem. Soc., Perkin Trans. 1*, 1720, 762 (1975).
- (33) Y. Ogata, K. Takagi, and J. Ishino, *J. Org. Chem.*, **36**, 3975 (1971).
- (34) N. C. Yang and G. R. Lenz, *Tetrahedron Lett.*, 4897 (1967).
- (35) A. Orahovats, H. Heimgartner, and H. Schmid, *Helv. Chim. Acta*, **57**, 2626 (1974).
- (36) P. Claus, P. Gilgen, H. J. Hansen, H. Heimgartner, and H. Schmid, *Helv. Chim. Acta*, **57**, 2173 (1974).
- (37) A. Padwa, S. Clough, M. Dharan, J. Smolanoff, and S. I. Wetmore, Jr., *J. Am. Chem. Soc.*, **94**, 1395 (1972).
- (38) A. Padwa, J. Smolanoff, and S. I. Wetmore, Jr., *J. Org. Chem.*, **38**, 1333 (1973).
- (39) N. Gakis, M. Marky, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **55**, 748 (1972).
- (40) N. S. Narasimhan, H. Heimgartner, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **56**, 1351 (1973).
- (41) A. L. Logothetis, *J. Org. Chem.*, **29**, 3049 (1964).
- (42) V. Nair, *J. Org. Chem.*, **33**, 2121 (1968); *Tetrahedron Lett.*, 4831 (1971).
- (43) J. C. Dalton, P. A. Wriede, and N. J. Turro, *J. Am. Chem. Soc.*, **92**, 1318 (1970).
- (44) Previous work in our laboratory has shown that the relative reactivities of the nitrile ylides generated from different 2*H*-azirine precursors are very similar toward a given dipolarophile, thereby justifying this assumption; see A. Padwa, J. Smolanoff, and A. I. Tremper, *J. Am. Chem. Soc.*, **97**, 4682 (1975).
- (45) H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).
- (46) It should be noted that the available data do not exclude the alternate electronic description shown below. However, the magnitude of the reaction



- constant ρ seems to be more consistent with the ion pair description. Further experiments with ^{18}O -labeled esters are planned to distinguish between these two possibilities.
- (47) All melting points and boiling points are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, Ga. The infrared absorption spectra were determined on a Perkin-Elmer Model 137 infracord spectrophotometer. The ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrophotometer using 1-cm matched cells. The proton magnetic resonance spectra were determined at 100 MHz using a Varian XL-100 and a Jeolco MH-100 spectrometer. Mass spectra were determined with a Perkin-Elmer RMU6 mass spectrometer at an ionizing voltage of 70 eV. All preparative irradiations were carried out using a 450-W Hanovia medium-pressure mercury arc.
- (48) W. Borsche, *Ber.*, 737 (1907).
- (49) Q. E. Thompson, *J. Am. Chem. Soc.*, **73**, 5914 (1951).
- (50) D. Ben-Ishai and R. Giger, *Tetrahedron Lett.*, 4523 (1965).
- (51) P. T. Lansbury, J. G. Colson, and N. R. Mancusco, *J. Am. Chem. Soc.*, **86**, 5225 (1964).
- (52) Owing to the extreme hydrolytic sensitivity of this system, it has not been possible to obtain satisfactory elemental analyses.
- (53) The stereochemical assignment was based on the fact that proton H_2 in the exo isomer (τ 4.8) appears at a higher field than the related proton in the endo isomer (τ 4.25). This is compatible with the anisotropic shielding of this proton by the adjacent aziridine ring⁵⁴ and is also consistent with the assignments made for related azabicyclo[3.1.0]hex-3-enes.⁵⁵
- (54) K. Tosi, K. Kitahonoki, Y. Takano, H. Tanida, and T. Tsuji, *Tetrahedron Lett.*, 868 (1965).
- (55) A. Padwa and E. Glazer, *J. Am. Chem. Soc.*, **94**, 7788 (1972).

Effects of pH in Photoreduction by Hydrazine

Shai Inbar* and Saul G. Cohen*

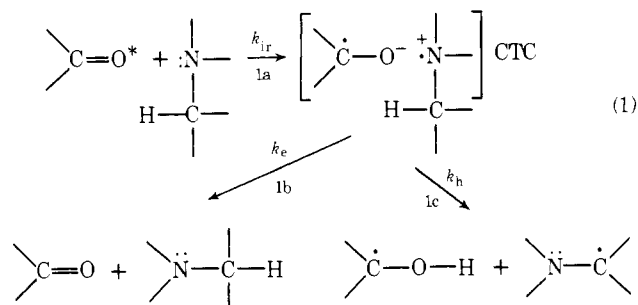
Contribution from the Department of Chemistry, Brandeis University, Waltham, Massachusetts 02154. Received October 11, 1977

Abstract: Quantum yields, ϕ_{ketyl} , for photoreduction of 0.005 M 4-benzoylbenzoate by 0.04 M hydrazine rise from 0.12 at pH 5.8 to 0.35 at pH 7.3 and fall to 0.03 at pH 12. Added ammonium ion and *tert*-butylammonium ion do not affect the reduction. Values of k_d , from phosphorescence decay, are $5.6 \times 10^4 \text{ s}^{-1}$ at pH 7 and $8.0 \times 10^4 \text{ s}^{-1}$ at pH 11.2, and are concentration dependent owing to quenching by ground-state ketone, $k_q = 6.2 \times 10^6$ and $8.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at pH 7 and 12. Quenching of phosphorescence, at pH 5.6–11.7, leads to $k_{\text{ir}} = 6.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for interaction with hydrazine, and $k'_{\text{ir}} = 4.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for interaction with protonated hydrazine. From the effects of concentration of hydrazine on quantum yields, ratios of kinetic constants are obtained, $k_{\text{ir}}/k_d = 7200 \text{ M}^{-1}$, $k'_{\text{ir}}/k_d = 9.9 \text{ M}^{-1}$, $k'_{\text{ir}}/k_{\text{ir}} = 1.4 \times 10^{-3}$. The effects of pH on quantum yields are considered in terms of quenching and reduction by both hydrazine and protonated hydrazine, accompanied by regeneration of starting materials by oxidation of ketyl radical anion by hydrazyl radical, importantly at high pH, and by oxidation of ketyl radical by protonated hydrazyl radical, importantly at low pH. Interaction of triplet with protonated hydrazine may lead only to quenching. Free hydrazine is the major reducing agent. A detailed kinetic scheme is developed, which leads to calculated quantum yields essentially the same as those observed over the entire range of pH. Earlier mechanistic proposals are corrected and remaining ambiguities are discussed.

While alcohols are effective photoreducing agents for aromatic carbonyl compounds with n, π^* excited triplets, amines may be quite general photoreducing agents, acting also on the generally less reactive $\pi-\pi^*$ and charge-transfer triplets.¹ Hydrogen on an atom α to the nitrogen is essential for reduction, while amino hydrogen is not. We have proposed that amines are both quenchers and photoreducing agents: the reaction proceeds via rapid initial formation, k_{ir} , of a charge-transfer complex, CTC; this may be followed either by transfer of an α hydrogen, rendered acidic by the radical-cationic nitrogen, or by spin inversion and return to the ground state, facilitated by mixing of the triplet carbonyl and singlet amine states, k_{h} and k_{e} , respectively, eq 1.^{2,3}

Formation of the CTC facilitates both reduction and

quenching, and makes reduction more general, but with inherent potential inefficiency.



Values of k_{ir} may be high, decreased by electron-withdrawing, increased by electron-donating groups in the amino compound, and approaching diffusion control when the donor has low ionization potential and highly stabilized radical cation.⁴ In the latter case unimolecular decay of the triplet, k_d , is unimportant and quantum yields for reduction are determined by the value of the fraction $r = k_h/(k_h + k_e)$. Electron-withdrawing groups, leading to low k_{ir} , may lead to sufficient charge transfer to cause quenching, lb, and to little reduction. Electron-donating groups increase k_{ir} , but they may stabilize the radical cation excessively, placing the CTC in a potential well from which exothermic decay to the ground state remains facile, while proton transfer and radical formation require activation. Thus, in photoreduction of fluorenone by *N,N*-dimethylanilines,⁵ the *p*-cyano and *p*-ethoxy compounds show lower and higher values of k_{ir} , respectively, than the unsubstituted compound, and both show lower quantum yields for reduction. *N,N,N',N'*-Tetramethyl-*p*-phenylenediamine, with a highly stabilized radical cation, and k_{ir} essentially diffusion controlled, leads to no photoreduction and acts as an exceedingly efficient quencher.

This led us to consider photoreduction by hydrazines, which are easily oxidized, effective reducing agents in thermal processes. Semiempirical calculations indicate that carbonyl triplets may abstract hydrogen from hydrazine.^{6a} In 1:1 water-pyridine at pH 12 hydrazine and alkylated hydrazines were found to act as very effective quenchers in processes accompanied by very little photoreduction.^{6b} In a study of effect of pH on photoreduction of 4-benzoylbenzoate in water, photoreduction by hydrazine was inefficient at pH 12, $\varphi \sim 0.02$, somewhat more efficient at pH 9, $\varphi \sim 0.2$, and more efficient at pH 7, $\varphi \sim 0.3$. We suggested that at pH 12 triplet interacted entirely with free hydrazine; the radical cation, $H_2NN^+H_2$, was highly stabilized like that of the phenylenediamine, and this led to quenching. At lower pH, triplet might interact in part with protonated hydrazine, $H_3N^+NH_2$, and the resulting species with radical dicationic character might protonate the radical anion in the CTC more effectively and lead to reduction.⁷ In the work which we will describe, observation of lower quantum yields at pH <7 indicates that this interpretation is incorrect and a more complex reaction scheme will be considered.

Experimental Section

Water was triply distilled. Hydrazine was distilled and stored under nitrogen. 4-Benzoylbenzoic acid (Aldrich) was crystallized from ethanol, mp 199–200 °C. Sodium 4-benzoylbenzenesulfonate was available from previous work.⁸ Sodium tetraborate decahydrate was Baker Analyzed reagent; potassium dihydrogen phosphate was Fisher Certified A.C.S.

Photoreduction. Solutions for irradiation were prepared from stock solutions of hydrazine in water, and of 4-benzoylbenzoic acid, dissolved in sodium hydroxide and brought to pH with buffer and a pH stat. From pH 5.9 to 8.0 phosphate, and from 8.3 to 11.0 borate, were used; at 11.5 and 12.0, sodium hydroxide alone. Commercial buffers may contain mold inhibitors which preclude their use in such studies. The pH did not change during the irradiations. Aliquots, 4 mL, in 1-cm square Pyrocell tubes fitted with a degassing bulb, a 1-mm quartz absorption cell, and a Teflon closure were degassed in four freeze-thaw cycles and closed under argon. No reaction occurred in the dark. Irradiations were on a rotating wheel fitted with a GE HA 85 lamp. The decrease in absorbance was followed at 330 and 340 nm and initial slopes were calculated by least-squares procedure. A solution of 0.005 M sodium benzoylbenzoate, 0.04 M triethylamine, pH 12, $\phi_{(-\rightarrow C=O)} = 0.70$,⁷ was irradiated simultaneously as a secondary actinometer. Quantum yields (Tables I and II) are each the average of three or four determinations and are accurate to ± 0.01 .

At pH 6 pinacol is formed; at pH 12 radical and radical anion disproportionate to ketone and hydrol. At intermediate values of pH combination and disproportionation occur. Rates for formation of ketyl at pH 6.3 and higher were corrected for disproportionation, and

quantum yields are for formation of ketyl radical. In the following the first number of each pair is pH and the second the correction factor: 12.0, 2.0; 11.5, 1.95; 11.0, 1.88; 10.7, 1.84; 10.5, 1.81; 10.3, 1.77; 10.0, 1.70; 9.7, 1.58; 9.3, 1.45; 9.0, 1.35; 8.1, 1.26; 8.3, 1.20; 8.0, 1.16; 7.7, 1.12; 7.3, 1.08; 7.0, 1.05; 6.7, 1.03; 6.3, 1.01.

Lifetime of the 4-benzoylbenzoate triplet was determined from decay of phosphorescence studied with an EG and G 549 Microflash System, 0.5 μ s, 5×10^7 candlepower beam. A Corning 7-60 (300–400 nm) filter was used on the excitation side, and Corning 4-96 (350–620 nm) and 3-72 (440–620 nm) filters were used on the emission side. 4-Benzoylbenzoic acid was dissolved in equivalent sodium hydroxide, pH was adjusted with hydrochloric acid and sodium hydroxide, and solutions were transferred to 1 \times 1 cm quartz cells fitted with Fisher-Porter Teflon valves and degassed in five freeze-thaw cycles. On the basis of near unimolecular decay, values of k_d (obsd) were taken from the slopes of linear plots of $\ln I$ against time. Observed slopes and values of k_d (obsd) showed a small dependence on concentration of ketone: at pH 7, 5.0×10^{-4} M, 5.8×10^4 s⁻¹; 1.0×10^{-3} M, 6.12×10^4 s⁻¹; 5.0×10^{-3} M, 8.7×10^4 s⁻¹; 1.0×10^{-2} M, 11.7×10^4 s⁻¹; at pH 11.2, 5.0×10^{-4} M, 8.3×10^4 s⁻¹; 1.0×10^{-3} M, 8.8×10^4 s⁻¹; 5.0×10^{-3} M, 12.1×10^4 s⁻¹; 1.0×10^{-2} M, 16.1×10^4 s⁻¹. The two sets of data led to linear plots of k_d (obsd) against concentration of ketone (CB), in accord with the equation

$$k_d(\text{obsd}) = k_d + k_q(\text{CB}) \quad (2)$$

and slopes and intercepts were obtained by least-squares treatment. At pH 7 the intercept, k_d , is $5.55 \pm 0.03 \times 10^4$ s⁻¹ and the slope, k_q , is $6.21 \pm 0.05 \times 10^6$ M⁻¹ s⁻¹; at pH 11.2 k_d is $7.97 \pm 0.03 \times 10^4$ s⁻¹ and k_q is $8.13 \pm 0.06 \times 10^6$ M⁻¹ s⁻¹. The value of k_d at 0.003 M ketone is 7.4×10^4 s⁻¹ at pH 7 and 10.4×10^4 s⁻¹ at pH 11.2.

Quenching of Phosphorescence. Phosphorescence intensity of 0.003 M 4-benzoylbenzoate was measured on a Perkin-Elmer MPF-4 spectrofluorimeter at 450 nm, excitation at 350 nm. Solutions were irradiated in round quartz tubes, fitted with Fisher-Porter Teflon valves, degassed in four freeze-thaw cycles. Five concentrations of hydrazine were examined in each run, in the range 2×10^{-5} to 8×10^{-3} M; linear plots of I_0/I vs. concentration of quencher were obtained. Phosphorescence intensities in the absence of hydrazine were the same over the pH range 6–9.7 and k_d from lifetime measurement at pH 7, 7.4×10^4 s⁻¹, was used in this range. Phosphorescence intensity is proportional to the inverse decay rate, $I \sim 1/(k_d + k_p)$, and with very low phosphorescence quantum yield, $k_d \gg k_p$, $I \sim 1/k_d$. The phosphorescence intensity at pH 11.7 was 0.65 relative to that at lower pH, leading to $k_d = 1.14 \times 10^5$ s⁻¹. The value from lifetime measurement was 1.04×10^5 s⁻¹; a value of 1.1×10^5 s⁻¹ at pH 11.7 was used. Background emission distorted results at high degree of quenching, and observations to 60% quenching were used. Duplicate runs were made at each pH and agreed within 5%.

Results

Since 4-benzoylbenzoic acid is insufficiently soluble at pH 5 for study at this pH, 4-benzoylbenzenesulfonic acid was examined. However, irradiation at pH below 7, with and without hydrazine, led to a precipitate which did not redissolve on addition of alkali but did dissolve with addition of alcohol. The compound apparently underwent desulfonation, and the study was carried out with 4-benzoylbenzoic acid, down to pH 5.8.

Quantum yields, corrected for formation of hydrol, for photoreduction of 0.005 M 4-benzoylbenzoate by 0.04 M hydrazine were determined over the pH range 5.8–12. Quantum yields rose sharply from 0.12 at pH 5.8 to a maximum of 0.35 at pH 7.3–7.7, and fell, somewhat more gradually, to 0.21 at pH 9, 0.07 at pH 10.7, and 0.03 at pH 12 (Table I and Figure 1).

The pK_a of hydrazine is 8.0,¹⁰ and it was possible that free hydrazine was needed for rapid formation of a CTC or free radical anion and cation, and that protonated hydrazine or something similar might be needed to protonate the radical anion rapidly and prevent back transfer of the electron and regeneration of the starting compounds. Effects of added ammonium and *tert*-butylammonium ion on rates of reduction were examined. At pH 8, ammonia, $pK_a = 9.25$,¹¹ is 95%

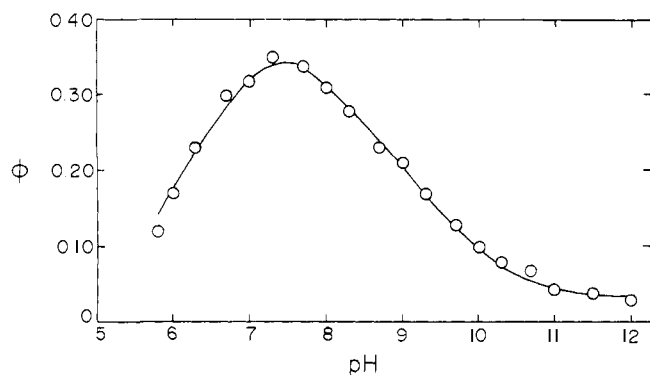


Figure 1. Effect on pH on quantum yield, photoreduction of 0.005 M 4-benzoylbenzoate by 0.04 M hydrazine: O, observed values; —, calculated curve.

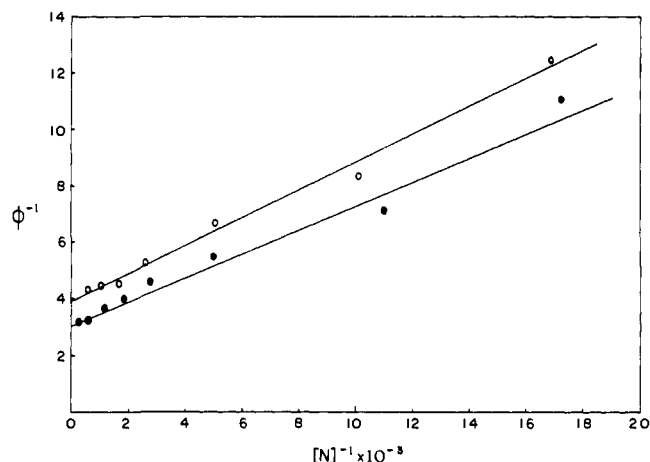


Figure 2. Effect of concentration of free hydrazine on photoreduction of 0.005 M 4-benzoylbenzoate: O, pH 6; ●, pH 7.

protonated and hydrazine is 50% protonated. Rates of photoreduction at this pH of 0.005 M 4-benzoylbenzoate by 0.04 M hydrazine were unaffected, within $\pm 5\%$ error, by 0.2 and 0.4 M ammonium ion. At pH 9.5 *tert*-butylamine, $pK_a = 10.68$,¹² is 94% protonated and hydrazine is 3% protonated. Photoreduction of 0.005 M 4-benzoylbenzoate by 0.2 M *tert*-butylammonium ion has $\varphi \sim 0.06$ compared with 0.15 by 0.04 M hydrazine. In the presence of both 0.04 M hydrazine and 0.2 M *tert*-butylammonium ion, the quantum yield was 0.18. At pH 10.5 the amine is 60% protonated, the hydrazine essentially free. Quantum yield for photoreduction by 0.04 M hydrazine is 0.07, for 0.04 M *tert*-butylamine 0.014, and for a combination of the two 0.07. Additional protonating species at fixed pH did not increase formation of products from ketyl radicals.

The effect of concentration of hydrazine on quantum yield was examined at pH 6, 7, and 9. Total concentration, hydrazine plus hydrazinium ion, was 0.0006–0.40 M. Results are summarized in Table II and Figure 2. At each pH quantum yields rise with total concentration of free and protonated hydrazine. At each total concentration, quantum yields are generally greater at pH 7 than at 6 or 9, consistent with the results at a single concentration (Table I). At pH 6 and 0.002 M total concentration, quantum yield is essentially zero, presumably because of very low concentration of free hydrazine. At this same concentration at pH 7 and 9 sufficient free hydrazine is present to allow substantial reduction, $\varphi = 0.20$ and 0.18, respectively. At lower total concentration, 0.001 M, quantum yields at pH 9 and 7 become equal, as the lower efficiency at pH 9, observed at higher concentrations, is compensated for

Table I. Photoreduction of 0.005 M 4-Benzoylbenzoate by 0.04 M Hydrazine (Total) Effect of pH on Quantum Yield

| pH | [N], ^a M | g^b | j^c | quantum yield | |
|------|------------------------|--------|--------|---------------|-------|
| | | | | obsd | calcd |
| 5.8 | 0.000 25 | 158. | 20.0 | 0.12 | 0.14 |
| 6.0 | 0.000 40 | 100. | 12.6 | 0.17 | 0.18 |
| 6.3 | 0.000 78 | 50.1 | 6.31 | 0.23 | 0.23 |
| 6.7 | 0.0019 | 20.0 | 2.51 | 0.30 | 0.29 |
| 7.0 | 0.0036 | 10.0 | 1.26 | 0.32 | 0.32 |
| 7.3 | 0.0067 | 5.01 | 0.631 | 0.35 | 0.34 |
| 7.7 | 0.013 | 2.00 | 0.251 | 0.34 | 0.34 |
| 8.0 | 0.020 | 1.00 | 0.126 | 0.31 | 0.32 |
| 8.3 | 0.027 | 0.501 | 0.0631 | 0.28 | 0.29 |
| 8.7 | 0.033 | 0.200 | 0.0251 | 0.23 | 0.24 |
| 9.0 | 0.036 | 0.100 | 0.0126 | 0.20 | 0.20 |
| 9.3 | 0.038 | 0.0501 | 0.0063 | 0.17 | 0.17 |
| 9.7 | 0.039 | 0.0200 | 0.0025 | 0.13 | 0.12 |
| 10.0 | 0.040 | 0.0100 | 0.0013 | 0.10 | 0.10 |
| 10.3 | 0.040 | 0.0050 | 0.0006 | 0.08 | 0.076 |
| 10.7 | 0.040 | 0.0020 | 0.0003 | 0.07 | 0.056 |
| 11.0 | 0.040 | 0.0010 | 0.0001 | 0.05 | 0.047 |
| 11.5 | 0.040 | 0.0003 | 0.0000 | 0.04 | 0.038 |
| 12.0 | 0.040 | 0.0001 | 0.0000 | 0.03 | 0.035 |

^a Concentration of free hydrazine. ^b Defined in eq 7b. ^c Defined in eq 7c.

Table II. Effect of Concentration of Hydrazine on Photoreduction of 0.005 M 4-Benzoylbenzoate, pH 6, 7, and 9

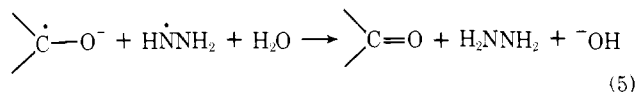
| H ₂ NN- H ₂ plus H ₂ N- NH ₃ ⁺ , 10 ³ M | H ₂ NNH ₂ (free), 10 ³ M | | | quantum yield | | |
|--|---|-------|------|---------------|------|------|
| | pH 6 | pH 7 | pH 9 | pH 6 | pH 7 | pH 9 |
| 400. | 3.96 | | | 0.22 | | |
| 200. | 1.98 | | | 0.23 | | |
| 100. | 0.99 | | | 0.22 | | |
| 60. | 0.59 | | | 0.22 | | |
| 40. | 0.39 | 3.6 | 36. | 0.19 | 0.32 | 0.20 |
| 20. | 0.20 | 1.8 | 18. | 0.15 | 0.31 | 0.20 |
| 10. | 0.099 | 0.91 | | 0.12 | 0.27 | |
| 6.0 | 0.059 | 0.55 | | 0.08 | 0.25 | |
| 4.0 | | 0.36 | 3.6 | | 0.22 | 0.19 |
| 2.0 | 0.020 | 0.18 | 1.8 | ~0 | 0.20 | 0.18 |
| 1.0 | | 0.091 | 0.91 | | 0.14 | 0.14 |
| 0.60 | | 0.055 | | | 0.09 | |

by the low concentration of free hydrazine at pH 7. Over the broad range of concentration, only at pH 9 is sufficient free hydrazine (90%) present to trap most of the triplet, and quantum yields at this pH are relatively insensitive to concentration. Linear plots of inverse quantum yield vs. inverse concentration of free hydrazine are obtained at pH 6 and 7 (Figure 2). Slopes and intercepts are, at pH 6, $0.000 49 \pm 0.000 02$ M and 3.93 ± 0.15 , $\varphi_{im} = 0.25$, and at pH 7, $0.000 42 \pm 0.000 02$ M and 3.06 ± 0.14 , $\varphi_{im} = 0.33$.

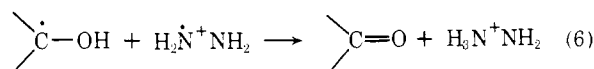
Values of k_d were determined from decay of phosphorescence of 4-benzoylbenzoate triplet at pH 7 and 11.2: 5.6×10^4 and 8.0×10^4 s⁻¹, respectively. The values are somewhat dependent on concentration owing to quenching by ground-state ketone, $k_q = 6.2 \times 10^6$ and 8.1×10^6 M⁻¹ s⁻¹ at pH 7 and 12, respectively. The reported value for quenching of benzophenone triplet by benzophenone in water is much higher,¹³ 1.2×10^8 M⁻¹ s⁻¹, and may reflect other effects.

Quenching of phosphorescence of 0.003 M 4-benzoylbenzoate by hydrazine plus hydrazinium ion was studied at pH 5.6–11.7. Plots of I_0/I , ratio of phosphorescence intensities in absence and presence of the quenchers, vs. the total concentration of hydrazine, N, plus hydrazinium ion, NH⁺, were

yield from pH 12 to 7, where the hydrazine is 90% protonated, had led us to suggest that the conjugate acid was the effective reducing agent. The values of k_{ir} and k'_{ir} , and that for k_d under these conditions, $8.7 \times 10^4 \text{ s}^{-1}$, show that at pH 7 at 0.04 M total hydrazine, 97% of the triplet is trapped by hydrazine and its conjugate acid, but 95% of this constitutes reaction with the small fraction of free hydrazine present. The great decrease in quantum yield at higher pH, where all triplet reacts with hydrazine, had led us to propose that free hydrazine does not reduce, but quenches. We now conclude that it is conversion of ketyl, $\text{p}K_a = 8-9$, to ketyl radical ion, and oxidation of the racial anion by hydrazyl radical which cause decreasing quantum yield with this increasing alkalinity:



Similarly, at low pH the increased proportion of hydrazinium radical cation, $\text{p}K_a = 7.1$,¹⁷ may lead to oxidation of ketyl radical and decreased quantum yield:



The maximum quantum yield is found near pH 7.5, where concentration of the two charged radical species is minimal.

In photoreduction by amines evidence has not been found for substantial regeneration of starting materials by intermolecular disproportionation of ketyl and α -aminoalkyl radicals.³ The latter either combines with ketyl radical to form a stable β -amino alcohol¹⁸ or reduces ground-state ketone.¹⁵ Bond energy considerations¹⁹ indicate that reduction of ground-state ketone by a hydrazyl radical may be less favored by $\sim 10-15 \text{ kcal/mol}$, and thus may not occur in competition with possible radical-radical reactions. Hydrazyl radical may oxidize ketyl radical to regenerate starting materials, eq 4d, either directly or by combination to the unstable α -hydrazino alcohol, which under the conditions of these studies will decompose to ketone and hydrazine.²⁰ While reactions of uncharged radicals may lead largely to combination, when important polar effects contribute to the transition states of reactions of unlike radicals disproportionation may dominate.²¹ A charged and uncharged radical, eq 5 and 6, may react more rapidly than a pair of uncharged radicals, and do so by disproportionation, as in the case of ketyl and ketyl radical anion.^{9,13,22} Electron transfer to nitrogen, as in the present system, may also be more favored than to the carbon-centered radicals in photoreduction by amines.

In the kinetic scheme, CB is 4-carboxybenzophenone, N is hydrazine, NH^+ is protonated hydrazine, $\text{CBH}\cdot$ is the ketyl radical, $\text{CB}^{\cdot-}$ is the ketyl radical anion, $\text{M}\cdot$ is the hydrazyl radical, and $\text{MH}^+\cdot$ is the hydrazyl radical cation or protonated hydrazyl. Rapid proton transfer and equilibration is assumed:

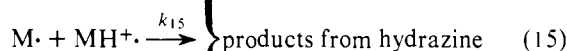
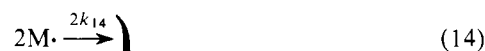
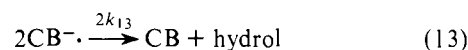
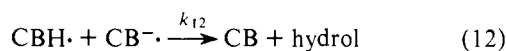
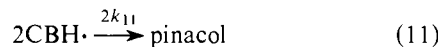
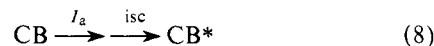
$$f = [\text{CB}^{\cdot-}]/[\text{CBH}\cdot] = K_1/[\text{H}^+] \quad (7a)$$

$$g = [\text{NH}^+]/[\text{N}] = [\text{H}^+]/K_2 = [\text{H}^+]/10^{-8.0} \quad (7b)$$

$$j = [\text{MH}^+\cdot]/[\text{M}\cdot] = [\text{H}^+]/K_3 = [\text{H}^+]/10^{-7.1} \quad (7c)$$

Light absorption and intersystem crossing lead to triplet, CB^* . This may decay, k_d , eq 9, react with N, k_{ir} , to form CTC, eq 4a, or react with NH^+ , k'_{ir} , to form CTC', eq 10a; CTC may lead to ground-state CB and N or to $\text{CBH}\cdot$ and $\text{M}\cdot$, k_e and k_h , eq 4b,c; CTC' may lead to CB and NH^+ or to $\text{CBH}\cdot$ and $\text{MH}^+\cdot$, k'_e and k'_h , eq 10b,c; $\text{CBH}\cdot$ may form pinacol, k_{11} , react with $\text{CB}^{\cdot-}$ to form CB and hydrol, k_{12} , or react with $\text{M}\cdot$, k_{14} , or $\text{MH}^+\cdot$, k_6 , to form CB and NH^+ ; $\text{CB}^{\cdot-}$ may disproportionate, k_{13} , or react with $\text{M}\cdot$, k_5 , to form CB and N; $\text{M}\cdot$

and $\text{MH}^+\cdot$ may form products of oxidation of hydrazine, k_{14} , k_{15} , k_{16} .



Reaction of k_{4d} is included in that of k_e , and, with steady-state approximations, expressions are obtained for $[\text{CB}^*]$, $[\text{CTC}]$, and $[\text{CTC}']$. Steady-state expressions are derived for $[\text{CBH}\cdot]$ in which $[\text{CB}^{\cdot-}]$ is written as $f[\text{CBH}\cdot]$, and for $[\text{M}\cdot]$ in which $[\text{MH}^+\cdot]$ is $j[\text{M}\cdot]$; $[\text{M}\cdot]$ is obtained in terms of $[\text{CBH}\cdot]$, and $[\text{CBH}\cdot]$ in terms of $[\text{CTC}]$ and $[\text{CTC}']$; r is set equal to $k_h/(k_h + k_e)$, and r' to $k'_h/(k'_h + k'_e)$. Dependence of quantum yield on concentration of free hydrazine, $[\text{N}]$, at a given pH is obtained:

$$1/\varphi_{\text{pH}} = K_{\text{pH}} \left(\frac{1 + gk'_{ir}/k_{ir}}{r + gr'k'_{ir}/k_{ir}} + \frac{k_d/k_{ir}}{r + gr'k'_{ir}/k_{ir}} \frac{1}{[\text{N}]} \right) \quad (17a)$$

where

$$K_{\text{pH}} = 1 +$$

$$\frac{(fk_5 + jk_6)}{2k_{11}^{1/2}k_{14}^{1/2} \left(1 + j \frac{k_{15}}{k_{14}} + j^2 \frac{k_{16}}{k_{14}} \right)^{1/2} \left(1 + \frac{fk_{12}}{k_{11}} + \frac{f^2k_{13}}{k_{11}} \right)^{1/2}} \quad (17b)$$

and the ratio of intercept to slope of a plot of φ^{-1} vs. $[\text{N}]^{-1}$ is

$$I/S = k_{ir}/k_d + gk'_{ir}/k_d \quad (18)$$

From the data at pH 6 and 7 (Table II and Figure 2) and g , from the $\text{p}K_a$ of hydrazine (Table I), $k'_{ir}/k_d = 9.9 \text{ M}^{-1}$, $k_{ir}/k_d = 7200 \text{ M}^{-1}$, $k_d/k_{ir} = 1.4 \times 10^{-4} \text{ M}$, and $k'_{ir}/k_{ir} = 1.4 \times 10^{-3}$. From the study of triplet decay and phosphorescence quenching, $k_d/k_{ir} = 1.2 \times 10^{-4} \text{ M}$, $k_d = 7.4 \times 10^4 \text{ s}^{-1}$, $k'_{ir}/k_{ir} = 6.9 \times 10^{-3}$. The values of k_d/k_{ir} and k'_{ir}/k_{ir} determined by the two quite different methods are similar. The values determined in the photoreduction experiments will be used in the calculations. The data at pH 9 (Table II) may also be converted to a plot of φ^{-1} vs. $[\text{N}]^{-1}$, slope = 0.0020 ± 0.0002 , intercept = 4.8 ± 0.1 , correlation 0.94, $\varphi_{\text{im}} = 0.21$, $S/I = 4.1 \times 10^{-4} \text{ M}$. At pH 9 the term in k'_{ir} , eq 18, may be neglected,

and $k_d/k_{ir} = 4.1 \times 10^{-4}$ M. Since quantum yield is insensitive to concentration at this pH (Table II), the accuracy is low and the value determined at pH 6 and 7, 1.4×10^{-4} , will be used.

Quantum yields may be calculated by computer optimization from the values of k_d/k_{ir} and k'_{ir}/k_{ir} , above, and eq 17a,b. The ratio k_{16}/k_{14} has been reported,¹⁷ and values of k_{14} , k_{15} , and k_{16} are available from flash photolysis and pulse radiolysis studies.²³ $k_{14} = 0.95 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $k_{15} = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $k_{16} = 2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$; g and j are obtained from the pK_a s of hydrazine¹⁰ and hydrazinium radical cation.¹⁷ Laser flash photolysis studies, to be reported later, indicate that the pK_a of carboxybenzophenone ketyl is somewhat lower than 9.2, the value reported for benzophenone ketyl,²⁴ and it was placed initially at $9.2 > pK_a \text{ CBH} \cdot > 8.0$. A relationship between r and r' may be derived from K_{pH} , eq 17b, at pH 6 and 7, using the values of k_{14} , k_{15} , k_{16} , and j , neglecting terms in f as compared with those of j at these low pH values. This leads to the equation

$$r' = 12.44r - 4.55 \quad (19)$$

This is imprecise, involving a small difference between large quantities of insufficient accuracy; r' was taken as a parameter in the optimization, and set initially at $0.6 > r' > 0$, and r was set at $0.45 > r > 0.39$, above the maximum observed quantum yield to allow for some disproportionation of charged ketyl and hydrazyl radicals. The radical-radical reactions were assumed to have rather similar rate constants,^{13,22} and limits were set, $1.2 > k_5/2k_{11}^{1/2}k_{14}^{1/2} > 0.5$, $1.2 > k_6/k_5 > 0.5$, $3.0 > k_{12}/k_{11} > 1.0$. Reaction of two radical anions is much less rapid than that of two radicals and $0.008 > k_{13}/k_{11} > 0.001$. A preliminary search was made for closer limits, and a new set was obtained: $0.44 > r > 0.40$, $0.4 > r' > 0.0$, $8.5 > pK_a \text{ CBH} \cdot > 0.8$, $0.8 > k_{15}/2k_{11}^{1/2}k_{14}^{1/2} > 0.4$, $0.8 > k_6/k_5 > 0.4$, $3.0 > k_{12}/k_{11} > 2.5$, and $0.005 > k_{13}/k_{11} > 0.003$. Final computer analysis to minimize the difference between calculated and observed quantum yields led to a gratifyingly close correspondence (Table I and Figure 1), with values of the parameters: $R = 0.40$, $r' = 0.0$, $pK_a \text{ CBH} \cdot = 8.2$, $k_5/2k_{11}^{1/2}k_{14}^{1/2} = 0.7$, $k_6/k_5 = 0.5$, $k_{12}/k_{11} = 2.9$, and $k_{13}/k_{11} = 0.004$.

With $r' = 0$, the results indicate that interaction of triplet with protonated hydrazine, eq 10a, k'_{ir} , leads only to quenching, and that formation of ketone- and hydrazine-derived radicals arises solely from reaction with free hydrazine. The positive group in protonated hydrazine, a strong electron-attracting substituent, may lead to little development of adjacent positive charge and only to quenching.⁵ At the lowest pH studied, 5.8 (Table I), with $k'_{ir}/k_{ir} = 1.4 \times 10^{-3}$, $k_{ir}/k_d = 7200 \text{ M}^{-1}$, and $k'_{ir}/k_d = 9.9 \text{ M}^{-1}$, 0.04 M protonated hydrazine and 0.000 25 M free hydrazine, 69% of triplet is trapped by total hydrazine and 31% decays; of that which is trapped, 18% is quenched by protonated hydrazine and the remainder, 56% of total triplet, reacts with free hydrazine. With $r = 0.40$, the quantum yield for ketyl formation would be 0.22; the observed quantum yield is 0.12, the remainder being lost by disproportionation of ketyl radical with hydrazyl radical cation, k_6 . With $k_6/k_5 = 0.5$, disproportionation of ketyl radical anion with neutral hydrazyl radical appears somewhat more rapid than that on the acid side, but at high pH essentially no triplet is lost by decay. That $k_{12}/k_{11} = 2.9$ confirms that disproportionation of charge and uncharged

ketyl species is somewhat more rapid than combination of the uncharged radicals,^{13,22} and the value of $k_5/2k_{11}^{1/2}k_{14}^{1/2}$ is also consistent with this; the low value of k_{13}/k_{11} indicates that two like charged species react far less rapidly, but this was built into the limits from data available from reactions of benzophenone.^{13,22}

Some ambiguity remains. We have attributed decreased quantum yields, at low pH to low concentration of free hydrazine, quenching by protonated hydrazine, and disproportionation of protonated hydrazyl with neutral ketyl, and, at high pH, to disproportionation of neutral hydrazyl with ketyl radical anion. We have omitted disproportionation of neutral hydrazyl with ketyl, eq 4d, in effect incorporating it in quenching in the CTC, k_c . An alternative analysis may be made, including high yield of ketyl and hydrazyl radicals, $r = 1$, with quantum yields of products decreased by disproportionation of the neutral radicals. This leads to eq 17a', eq 17a with $r = 1$, and to eq 17b', eq 17b in which k_{4d} is added to the terms in the numerator of the fraction. Computer optimization leads to an equally good fit of observed and calculated quantum yields, and to $r' = 0.0$, $pK_a \text{ CBH} \cdot = 8.2$, $k_5/2k_{11}^{1/2}k_{14}^{1/2} = 1.1$, $k_{4d}/k_5 = 1.9$, $k_6/k_5 = 1.6$, $k_{12}/k_{11} = 0.7$, $k_{13}/k_{11} = 0.002$. Our steady-state kinetics do not distinguish between these possibilities. Flash photolysis studies, which are in progress, may prove informative.

Acknowledgments. This work was supported by the National Science Foundation, CHE 75-09502. We are indebted to Dr. Abbas Farazdel for the computer calculations, and to Drs. J. W. Sutherland and P. Paysberg, Brookhaven National Laboratory, for their unpublished kinetic constants for reactions of hydrazyl radical.

Supplementary Material Available: Derivation of the kinetic expression (2 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) S. G. Cohen, A. Parola, and G. H. Parsons, Jr., *Chem. Rev.*, **73**, 141 (1973).
- (2) S. G. Cohen and J. I. Cohen, *J. Phys. Chem.*, **72**, 3782 (1968).
- (3) S. G. Cohen and H. M. Chao, *J. Am. Chem. Soc.*, **90**, 165 (1968).
- (4) J. B. Guttenplan and S. G. Cohen, *J. Am. Chem. Soc.*, **94**, 4040 (1972).
- (5) G. H. Parsons, Jr., and S. G. Cohen, *J. Am. Chem. Soc.*, **96**, 2948 (1974).
- (6) (a) C. M. Previtaly and J. C. Scaiano, *J. Chem. Soc., Perkin Trans. 2*, 934 (1975); (b) A. Parola, Ph.D. Thesis, Brandeis University, 1974.
- (7) S. Ojanpera, A. Parola, and S. G. Cohen, *J. Am. Chem. Soc.*, **96**, 7379 (1974).
- (8) G. C. Ramsay and S. G. Cohen, *J. Am. Chem. Soc.*, **93**, 1166 (1971).
- (9) S. G. Cohen, G. C. Ramsay, N. M. Stein, and S. Y. Weinstein, *J. Am. Chem. Soc.*, **96**, 5124 (1974).
- (10) (a) F. E. Condon, R. T. Reece, D. G. Shapiro, D. C. Thakkar, and T. B. Goldstein, *J. Chem. Soc., Perkin Trans. 2*, 1112 (1974); (b) R. L. Hinman, *J. Org. Chem.*, **23**, 1587 (1958).
- (11) D. H. Everett and D. A. Landoman, *Trans. Faraday Soc.*, **50**, 1221 (1954).
- (12) G. Girault-Verlearschi, *Bull. Soc. Chim. Fr.*, 589 (1956).
- (13) M. B. Ledger and G. Porter, *J. Chem. Soc., Faraday Trans. 1*, **68**, 539 (1972).
- (14) A. H. Parola, A. W. Rose, and S. G. Cohen, *J. Am. Chem. Soc.*, **97**, 6202 (1975).
- (15) S. G. Cohen and N. M. Stein, *J. Am. Chem. Soc.*, **93**, 6542 (1971).
- (16) S. F. Nelsen and J. M. Buschek, *J. Am. Chem. Soc.*, **96**, 2392 (1974).
- (17) E. Hayon and M. Simic, *J. Am. Chem. Soc.*, **94**, 42 (1972).
- (18) S. G. Cohen and J. B. Guttenplan, *Tetrahedron Lett.*, 5353 (1968).
- (19) G. E. Coates and L. E. Sutton, *J. Chem. Soc.*, 1187 (1948).
- (20) H. H. Szmant and C. McGinnis, *J. Am. Chem. Soc.*, **72**, 2890 (1950).
- (21) T. Bernath, G. H. Parsons, Jr., and S. G. Cohen, *J. Am. Chem. Soc.*, **97**, 2413 (1975).
- (22) A. Becket and G. Porter, *Trans. Faraday Soc.*, **59**, 2051 (1963).
- (23) J. W. Sutherland and P. Paysberg, private communication.
- (24) G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, 1686 (1961).