

RESEARCH NOTE

**Photoreduction of 4-Phenylbenzophenone [1].
Kinetic Analysis of Hydrogen Abstraction
by a π , π^* -Ketone Triplet**

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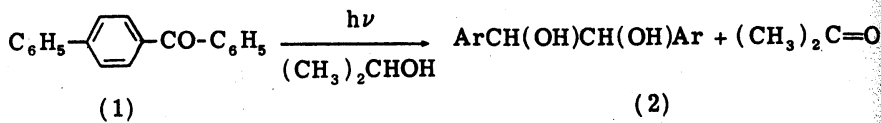
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INTRODUCTION

The photochemistry of 4-phenylbenzophenone (1) is of interest because the lowest triplet of this molecule possesses the spectroscopic characteristics of a π, π^* state [2], but its photochemical efficiency with respect to reactions with alcohols has been reported to be in the range of 0.1-0.2 [3]. Evaluation of the mechanistic meaning of such efficiencies is somewhat difficult because no one laboratory has done a study of product formation, efficiency, and kinetics for the reaction of 1 with alcohols. Such a study is reported here.

RESULTS AND DISCUSSION

The system of 1 in isopropyl alcohol was chosen for study, since the rate constants for an efficiency toward hydrogen abstraction from alcohols are known for many aryl ketones [4]. Irradiation of an isopropanol solution (10^{-2} M) of 1 with 366 nm light results in the formation of 4-phenylbenzophenone pinacol (2) as the sole photoreduction product. No mixed pinacol or 4-phenylbenzhydrol was detected by TLC analysis. Acetone is the other product reaction [3], but its concentration was not monitored. It was found that irradiation of 2 through Pyrex results in photolysis and at least two



new products were formed. The result severely complicates interpretation of previous results which used wavelengths shorter than 366 nm for excitation [3], since the yield of pinacol is wavelength dependent and the products may absorb a significant fraction of the exciting radiation. If UV analysis were employed for ketone disappearance, the new products could well be absorbing at wavelengths used for analysis.

Analyses for disappearance of 1 were made by measurement of the disappearance of UV absorption at 366 nm. Degassed benzophenone-benzhydrol (both 0.1 M) in benzene was used as an actinometer [5]. The maximum conversions of the actinometer solutions were approximately 10%. The quantum yield for disappearance of 1 in neat isopropanol was found to be 0.30 ± 0.01 at 366 nm excitation and room temperature [6].

A study of the quantum yield for the disappearance of 1 as a function of isopropyl alcohol concentration was analyzed according to Eq. (1), a standard Stern-Volmer relationship, in which a ρ is the efficiency of formation of the chemically active state times the probability that intermediates will go on to product, k_d is the unimolecular rate constant of deactivation of the chemically active state, k_r is the bimolecular rate constant for hydrogen abstraction and ϕ_{-k} is the quantum yield for the disappearance of 1 at various concentrations of isopropyl alcohol. The maximum conversion of 1 at any concentration was 30%.

Plotting the data according to Eq. (1) leads to a linear relationship (Fig. 1) with slope equal to $29 \pm 10\%$ and intercept of $1.0 \pm 10\%$. We can immediately conclude that since a $\rho = 1$ there is essentially unit efficiency for the formation of the chemically active state and for the probability that any intermediates go on to product. Furthermore, since we were unable to detect any luminescence from 1 at room temperature, even in very "inert" [7] solvents and since Sandros [8] has measured Φ_{ST} for 1 to be 1.0, we conclude that only triplet states of 1 are involved in the pinacol forming reaction. This allows us to assume the accompanying mechanistic scheme for analysis of the data.

The slope and intercept of Fig. 1 allow us to calculate that $k_d/k_r = 29 \pm 10\%$. Next, we sought to decouple these two rate constants. Two methods were employed: (a) direct measurement of k_d by flash spectroscopy and (b) diffusion-controlled quenching of T_1 of 1.

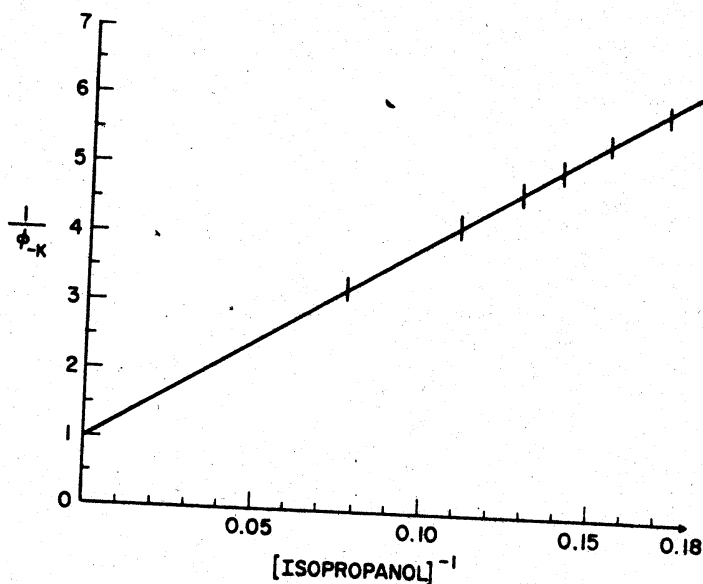
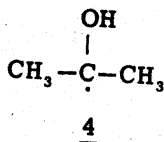
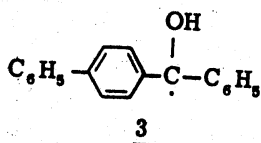
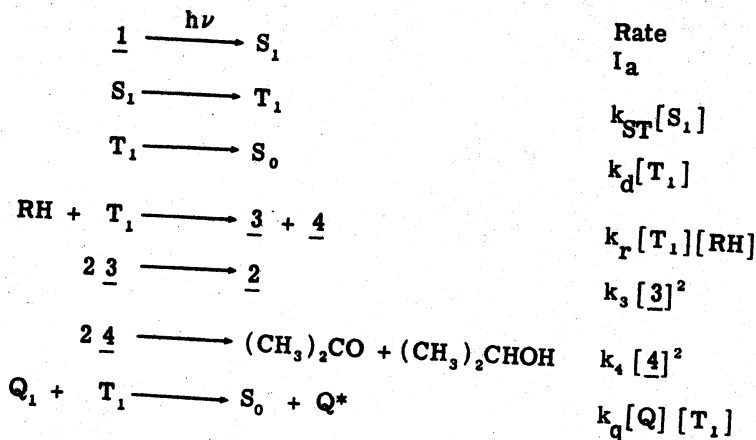


FIG. 1. Variation of quantum yield for disappearance of 1 in acetonitrile (366 nm excitation) as a function of isopropanol concentration plotted according to Eq. (1) in text. Slope equals 29 + 10% M and intercept = 1 ± 10%.



$$\frac{1}{\phi_{-k}} = \frac{1}{a\rho} + \frac{k_d}{a\rho k_r [(\text{CH}_3)_2\text{CHOH}]} \quad (1)$$

By method (a) we detected a transient whose absorption spectrum in CH_3CN was attributed to triplet 1. The decay of the absorption of this transient in CH_3CN at 400 nm was first order and corresponded to a lifetime of $(2.9 \pm 10\%) \times 10^{-5}$ sec, or a k_d of $(3.5 \pm 10\%) \times 10^4 \text{ sec}^{-1}$. Assuming that the transient has been correctly identified as T_1 , we calculate that $k_r = k_d/29 = 1.2 \times 10^3/\text{M sec}$.

Method (b) was used as a check of our kinetic analysis. Camphorquinone, 5, was found to be a suitable quencher since (1) irradiation of 10^{-2} M solution of 5 in isopropyl alcohol at 366 nm leads to no reaction, as indicated by the invariance of the UV maximum of 5 at 470 nm after extended irradiation. In addition, none of the well-known fluorescence or phosphorescence of 5 was excited by 366 nm excitation under our conditions. This result obtains from the very low extinction of 5 at 366 nm ($\epsilon < 1$), assuring us that competitive absorption by 5 would not be significant when we excite 1 with 366 nm light and that UV analysis at 366 nm for disappearance of 1 was still valid. Very low concentrations (approximately 10^{-6} M) of 5 effectively quench the photoreduction of 1 in isopropanol-acetonitrile solution. Analyzing our quenching data (at 9.1 M isopropanol) in terms of standard Stern-Volmer equations (2) or (3) (Figs. 2 and 3) we obtain $k_q/k_d = 2 \pm 5\% \times 10^5/\text{M}$ from Eq. (2) and $k_q/k_r = (7.4 \pm 5\%) \times 10^6$ and $k_d/k_r = 26 \pm 5\%$ from Eq. (3).

$$\frac{\phi_{-k}^0}{\phi_{-k}^Q} = 1 + \frac{k_q[Q]}{k_d} \quad (2)$$

$$\frac{1}{\phi_{-k}^Q} = 1 + \frac{k_d}{k_r [(\text{CH}_3)_2\text{CHOH}]} + \frac{k_q[Q]}{k_r [(\text{CH}_3)_2\text{CHOH}]} \quad (3)$$

We assumed in the above analysis that only triplet-triplet energy transfer is occurring. This assumption is strongly supported by the observation that only the phosphorescence of 5 is sensitized by 1. If we assume $k_q = 7 \times 10^9/\text{M sec}$ [9], we calculate $k_d = 3.5 \times 10^4/\text{sec}$

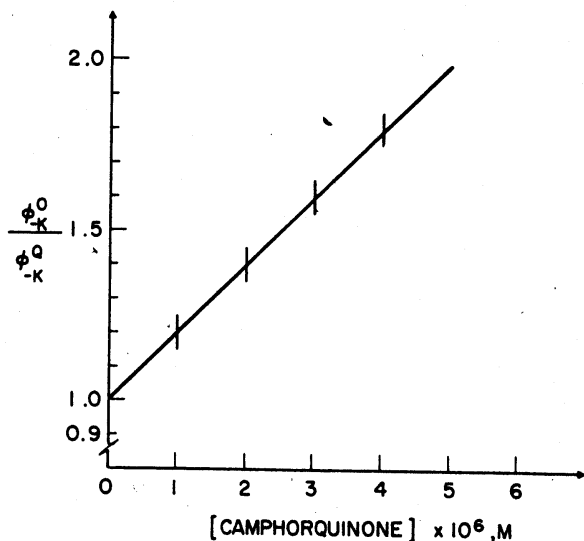


FIG. 2. Stern-Volmer plot [Eq. (2)] of the disappearance of **1** in an acetonitrile solution (9.1 M in isopropanol) with camphorquinone as quencher. Slope equals $2 \times 10^5 \pm 5\% \text{ M}^{-1}$.

and $k_r = 0.94 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ (in excellent agreement with the rate constants from combined flash lifetime and data of Fig. 1).

The excellent internal consistency of data derived from flash spectroscopy, and three different types of Stern-Volmer analyses, convince us of the well-behaved chemical nature of the systems studied and of the correctness of the indicated assumptions.

CONCLUSION

The evidence presented above allows us to state, with considerable confidence, the following conclusions: (1) the photoreaction of 4-phenylbenzophenone (**1**) with isopropanol is a photoreduction which yields 4-phenylbenzopinacol as the major (and probably exclusive) product derived from **1** (acetone being produced as the major oxidation product); (2) the efficiency of the hydrogen abstraction step is moderate, with yields of pinacol up to ~ 0.3 being possible; (3) the rate constant for the hydrogen abstraction step is $k_r \cong 1 \times 10^3 / \text{M sec}$, the rate constant for triplet decay of **1** is $k_d = 3.5 \times 10^4 / \text{sec}$; and

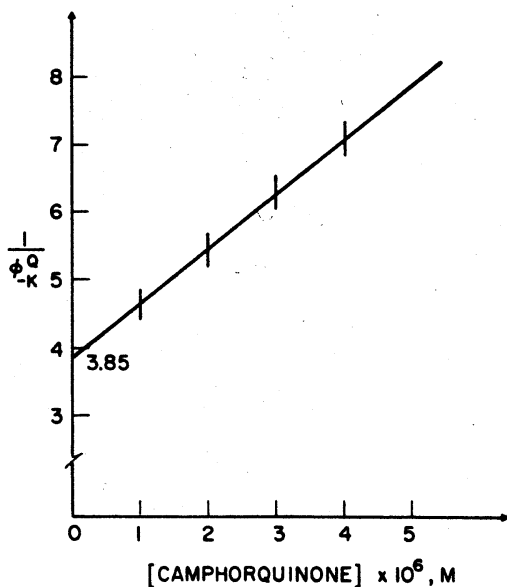


FIG. 3. Variation of quantum for disappearance of 1 in an acetonitrile solution (9.1 M in isopropanol) with camphorquinone as quencher. Slope equals $8.1 \times 10^5 \pm 5\% \text{ M}^{-1}$.

(4) the triplet of 1 is the sole reactive species in the photoreduction.

It should be pointed out that this rate constant, k_r , is to our knowledge the smallest ever measured for intermolecular hydrogen abstraction from isopropyl alcohol by an aryl ketone [10], and attests to the π, π^* character of T_1 [11]. We compare this rate constant to other values in the literature (Table 1) and note that the relatively high efficiency of photoreduction of 1 by isopropyl alcohol (0.3) masked a relatively low reactivity.

Finally, we point out that it seems unlikely to us that k_d is a true unimolecular decay constant. More likely, this rate constant reflects some pseudo-unimolecular process such as self-quenching [12] or (minute) impurity quenching [13]. This is a situation which has bedeviled nearly all studies of relatively long-lived ($k_d < 10/\text{sec}$) triplets in fluid solution [14]. Our results are summarized in Table 2 and can be compared to other literature values for photoreduction of aryl ketones by isopropanol given in Table 1.

TABLE 1. Rate Constants for Photoinduced Intermolecular Hydrogen Abstraction from Isopropanol by Aryl Ketones

| Ketone | $k_r, M^{-1} \text{ sec}^{-1}$ |
|--------------------------------------|---|
| $C_6H_5COC_6H_5$ | $1.3 \times 10^8 \text{ a,b}$ |
| $4-CF_3C_6H_4COC_6H_5$ | $2.2 \times 10^8 \text{ b}$ |
| $4-CH_3C_6H_4COC_6H_5$ | $0.85 \times 10^8 \text{ b}$ |
| $4,4' \text{-di-}CH_3C_6H_4COC_6H_5$ | $0.70 \times 10^8 \text{ b}$ |
| $C_6H_5COCH_3$ | $4.3 \times 10^5 \text{ b; } 7.5 \times 10^5 \text{ c}$ |
| $4-CF_3C_6H_4COCH_3$ | $2.8 \times 10^6 \text{ d}$ |
| $3,4\text{-di-}CH_3C_6H_4COCH_3$ | $8.4 \times 10^3 \text{ d}$ |
| $4-CH_3C_6H_4COCH_3$ | $3.9 \times 10^4 \text{ d}$ |
| $C_6H_5COCH_2CH_3$ | $4.4 \times 10^5 \text{ c}$ |
| $C_6H_5COCH(CH_3)_2$ | $1.3 \times 10^5 \text{ c}$ |

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^cF. D. Lewis, Tetrahedron Letters, **1970**, 1373.

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TABLE 2. Summary of Rate Constants for 4-Phenylbenzophenone Photoreduction by Isopropanol

$$k_d = (3.5 \pm 10\%) \times 10^4 \text{ sec}$$

$$\frac{k_d}{k_r} = 29 \pm 10\% \text{ M}$$

$$\frac{k_q}{k_d} = 2 \pm 5\% \times 10^5 \text{ M}^{-1}$$

$$\frac{k_q}{k_r} = (7.4 \pm 5\%) \times 10^6$$

$$k_r = 1.0 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$$

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- [6] 0.01 M, 3660 Å light, Hanovia 450-W lamp, Corning filter, degassed to less than 10^{-3} mm. Irradiation performed on a "merry-go-round" apparatus.
- [7] No fluorescence and phosphorescence were detected in Freon nor in benzene at room temperature.
- [8] K. Sandros, Acta Chem. Scand., **23**, 2815 (1969).
- [9] Calculated diffusion rates are $k_q = 11 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ in neat CH_3CN ; $k_q = 2.7 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ in neat isopropyl alcohol. We take an average value of $k_q = 7 \times 10^9$ in acetonitrile-2-propanol solution.
- [10] P. Suppan (Ber. Bunsenge., 1968, 321) has reported that $k_r = 4.90 \times 10^1 \text{ M}^{-1} \text{ sec}^{-1}$ at 20°C for 2-acetonaphthone in ethanol. This was not a measured value but assumed $k_d = 3 \times 10^5 \text{ sec}^{-1}$.
- [11] N. C. Yang and R. L. Dusenberry, J. Am. Chem. Soc., **90**, 5899 (1968); We find E_s of 1 to be 59.5 and 60.9 kcal/mole in methyl cyclohexane and ethanol at 77°K , respectively. The phosphorescence lifetime of 1 under these conditions is about 0.3 sec. These data are impressive support for the π, π^* nature of T_1 at room temperature in fluid solution.
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