# Solvent Effects upon the Phosphorescence Lifetimes and Photoreactivity of Butyrophenone

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**Abstract:** Excitation of butyrophenone in moderately hydrogen bonding, polar glasses gives rise to dual component phosphorescence emission, one component relatively short lived (~0.001 sec) and other relatively long lived (~0.05 sec). On the basis of previous investigations, it is probable that these arise from the pure $^3(n,\pi^*)$ state in the former and from a state having both $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ characteristics in the latter. The long-lived component emission is undetected in hydrocarbon solvents, while in highly polar solvents the short-lived component is absent. The effect is best explained on the basis of local solvent effects. The photoreactivity of butyrophenone is also found to be a function of solvent polarity and is maximized in solvents where polarity is moderately high, but not high enough to significantly introduce relatively inert $\pi,\pi^*$ character in the reacting $^3(n,\pi^*)$ excited state.

The effect of solvent upon the excited states of aromatic carbonyl compounds has been a subject of current interest.[2-5] Recently, Lamola[4] has demonstrated that the relative disposition of the $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ states of acetophenone is reversed in highly polar media compared to that in nonpolar media. The long-lived $^3(\pi,\pi^*)$ state becomes the triplet of lowest energy in 50% ethylene glycol–water (EGW), in a methylcyclohexane–silica gel slurry, in glacial acetic acid, in formamide, and in 85% phosphoric acid. This is attributed to the rise in the $^3(n,\pi^*)$ and decrease in the $^3(\pi,\pi^*)$ energy with increasing solvent polarity. Lamola also reported two types of phosphorescent emission from acetophenone in ethanol, a short-lived and a long-lived component, and suggested the possibility of two kinds of solvation sites.[4] Yang has observed two phosphorescent states in 1-inadanone in both methylcyclohexane (MCH) and EPA (ether–isopentane–ethanol), one of pure $n,\pi^*$ character and a longer-lived species having a mixture of $n,\pi^*$ and $\pi,\pi^*$ characteristics.[3]

Wagner[2] has to some extent correlated solvent polarity with the propensity of butyrophenone, valerophenone, and 2-hexanone to undergo the Norrish type II elimination. In all three cases a general increase in the quantum yield for disappearance of ketone in passing from hydrocarbon solvents to *t*-butyl alcohol was observed. The quantum yield based upon the formation of photoelimination products also shows a marked increase with solvent polarity, but only in media which are poor donors of radical hydrogen so that competing photoreduction is minimized.[2]

Much has been published on the effects of electron-donating substituents upon the lifetimes and photoreactivity of aryl ketones.[6-11] The reactive excited state in the photoreduction and the photoelimination of these compounds has been presumed to be the $n,\pi^*$ triplet. The relative energetic disposition of the $n,\pi^*$ triplet to the $\pi,\pi^*$ triplet in phenyl alkyl ketones becomes reversed upon the introduction of methyl, methoxy, and hydroxyl substituents causing the excited molecules to be less reactive.[5-8] Furthermore, quantum yields based upon elimination products in substituted butyrophenones[7] and upon reduction products in substituted acetophenones[5] have an inverse relationship to their phosphorescence lifetimes, lending additional evidence for the $\pi,\pi^*$ character of the lowest triplet state in the inert compounds. The pertinent data are given in Table I.

**Table I.** Quantum Yields and Phosphorescence Lifetimes of Some Substituted Butyrophenones and Acetophenones

| Substituent | —Acetophenone[a]— $\tau_p$, sec | $\phi_{\text{ketone}}$[c] | —Butyrophenone[b]— $\tau_p$, sec | $\phi_{\text{ethylene}}$ |
|---|---|---|---|---|
| None | 0.004 | 0.68 | 0.002 | 0.42 |
| *p*-Me | 0.084 | 0.66 | 0.009 | 0.39 |
| *p*-F | ... | ... | 0.004 | 0.29 |
| *p*-OMe | 0.26 | 0.04 | 0.051 | 0.10 |
| *m*-OMe | 0.71 | 0.006 | ... | ... |
| *p*-OH | ... | ... | 0.084 | 0.00 |
| *o*-OH | ... | ... | ... | 0.00 |
| *p*-$NH_2$ | ... | ... | 0.084 | 0.00 |

[a] All values for $\tau_p$ and $\phi_{\text{ketone}}$ are reproduced from Yang's recent paper.[5] Photolyses were carried out in *n*-propyl alcohol. [b] All values for $\tau_p$ and for $\phi_{\text{ethylene}}$ reproduced from Calvert and Pitts,[7] p 383. The quantum yields measure the extent of photoelimination. Lifetimes were recorded in an ethanol glass, quantum yields in benzene. [c] At 3130 Å.

In light of these investigations, the purpose of the present study is to demonstrate that solvent effects parallel the effects of inductive group substitution upon the photoreactivity of aryl ketones and to elucidate further the mechanism of solvent intervention in these reactions. Butyrophenone is an excellent compound for such a study. Not only do the $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ states lie very close in energy, as in acetophenone, but also the compound undergoes the Norrish type II elimination as well as photoreduction. The efficiency

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(1) Alfred P. Sloan Fellow, 1967–1969.
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of both reactions at room temperature may be correlated with the 1/*e* phosphorescent lifetimes of butyrophenone in a variety of solvents at 77°K.

One must be cautious in correlations of ambient temperature photochemistry with data about electronic states determined at much lower (liquid nitrogen) temperatures. In the research to be discussed, however, such correlations are not only meaningful but also very useful. We make no attempt to *quantitatively* correlate *natural* phosphorescence lifetime with photoreactivity. Our objective is to characterize excited states by their lifetimes—"long," "short," or both—at 77°K. On the assumption that solute–solvent interactions are not *wholly* different at 298 *vs.* 77°K, we then infer that the emitting states (at 77°K) are essentially the same as the chemically active states at room temperature (at which no emission can be detected). We do want to introduce the qualification that many more solute–solvent contacts will be explored per unit time at room temperature so that interconversion of nearly degenerate triplet states will be more facile.

## Experimental Section

**Materials.** Butyrophenone was obtained from Aldrich Chemical Company and was distilled at reduced pressure before use. All solvents were of spectroscopic or reagent grade and were used without further purification. Silica gel was Grace Davidson Commerical, 100–200 mesh, and was oven dried at 200°.

**Emission Lifetimes.** Phosphorescence lifetimes were measured at 77°K on an Aminco-Bowman spectrophotofluorimeter with a rotating can attachment. The instrument was equipped with a Tetronix Type 561A oscilloscope with a plug-in Type 3A75 amplifier and a Type 2B67 time base. Decay curves were recorded using a Polaroid camera attachment.

**Photolysis.** Photolyses were carried out at room temperature with predominantly 2537-Å light. A Rayonet reactor manufactured by Southern New England Ultraviolet Co. of Middletown, Conn., equipped with a merry-go-round apparatus was used. Cells were 8-mm diameter Vycor glass tubes sealed at one end and capped with serum caps through which a hypodermic needle outlet was placed to relieve internal pressure. Samples of 4 ml were used, each charged with 0.01 ml of dodecane which served as an internal standard. All reaction times were 90 min. Analysis was conducted using glpc techniques (column: 5 ft × 0.25 in., 10% silicon polar oil on Chromosorb support; column temperature, 150°; injector block temperature, 220°), and relative peak areas were estimated using the "cut out and weigh" method.

**Actinometers.** The quantum yields based upon disappearance of butyrophenone and upon appearance of acetophenone in methanol are reported by Wagner as being 0.80 and 0.35, respectively, for a 0.2 *M* degassed solution of butyrophenone irradiated at 3130 Å. These results were checked using a benzophenone–benzhydrol actinometer.[12] The quantum yields for the same solution were found to agree quite closely when the reaction was carried out under nondegassed conditions using a 2537-Å source, being 0.78 and 0.33 for disappearance and appearance, respectively. Once this was determined, all samples were run under the same conditions and quantum yields were computed relative to these values.

**Table II.** Phosphorescence Lifetime[a] of Butyrophenone in Various Solvents

| Solvent | $\tau_p$ (short component), sec | $\tau_p$ (long component), sec |
|---|---|---|
| MCH | $0.8 \times 10^{-3}$ | None |
| 3-Methylpentane | $1.0 \times 10^{-3}$ | None |
| EPA | $3.0 \times 10^{-3}$ | $2.0 \times 10^{-2}$ |
| *t*-BuOH | $3.0 \times 10^{-3}$ | $1.5 \times 10^{-2}$ |
| EtOH | $3.5 \times 10^{-3}$ | $3.0 \times 10^{-2}$ |
| MeOH | $7.0 \times 10^{-3}$ | $3.5 \times 10^{-2}$ |
| EtOH–EG | | |
| 2:1 | $8.0 \times 10^{-3}$ | $3.0 \times 10^{-2}$ |
| 1:1 | $8.0 \times 10^{-3}$ | $3.0 \times 10^{-2}$ |
| 2:3 | $8.0 \times 10^{-3}$ | $3.0 \times 10^{-2}$ |
| 1:5 | $7.0 \times 10^{-3}$ | $3.5 \times 10^{-2}$ |
| EGW | | |
| 9.5:1 | . . . | $3.0 \times 10^{-2}$ |
| 4:1 | . . . | $5.0 \times 10^{-2}$ |
| 2.3:1 | . . . | $6.0 \times 10^{-2}$ |
| 1:1 | None | $8.0 \times 10^{-2}$ |
| 1:1.5 | None | $1.0 \times 10^{-1}$ |
| EtOH–HCl | | |
| 0.5% | $4 \times 10^{-3}$ | $4.0 \times 10^{-2}$ |
| 1.0% | . . . | $5.0 \times 10^{-2}$ |
| 5.0% | $5 \times 10^{-3}$ | $7.0 \times 10^{-2}$ |
| MCH,$SiO_2$ | None | $7.5 \times 10^{-2}$ |
| EG–EtOH–HOAc, 1:1:2 | $2.5 \times 10^{-3}$ | $5.0 \times 10^{-2}$ |
| HOAc–EGW 1:1 | $2.5 \times 10^{-3}$ | $9.0 \times 10^{-2}$ |
| $H_3PO_4$ (85%) | None | $8.0 \times 10^{-1}$ |

[a] Lifetimes of excited states are uncorrected for nonradiative processes and thus are only estimates, since absolute and relative quantum yields for emission were not determined.

## Results and Discussion

Table II provides a list of measured phosphorescence lifetimes for butyrophenone in a number of solvents which form a glass at 77°K. (Since quantum yields for emission were not determined, these can only be *estimates* of natural radiative lifetimes.) These solvents, or solvent systems, may be roughly divided into three categories: (1) those in which only a short-lived phosphorescent component is evident,[13] (2) those which exhibit two components, one short lived and one long lived, and (3) those which exhibit only a long-lived component. (Where two components were found, we were not able to determine quantitatively the relative contribution of each. For our purposes this is important but not critical.) It is evident from Table II that there is no specific point at which the $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ states are definitely reversed. In MCH and in 3-methylpentane, only a short-lived triplet (~0.001 sec), presumably n,$\pi^*$ in character, is noticed. These solvents are not at all polar, thus the n electrons have little interaction with solvent in this case, so that it is not unreasonable that the lowest and emitting triplet is clearly n,$\pi^*$ (see Figure 1a). In media of intermediate polarity, such as ethanol, methanol, *t*-butyl alcohol, and glacial acetic acid, solvation may surely take place in a variety of ways (as suggested by Lamola[4] in the case of acetophenone in ethanol). Some molecules will then be in locally polar environments, others will not. The result will be equilibration of two possible nearly degenerate triplet species. Dual component emission is observed in these cases.

The shorter lived component is pure $\pi^* \rightarrow$ n in character and arises from molecules in mostly nonpolar solvent situations in which the carbonyl is left relatively unperturbed. The other emission arises from molecules whose n electrons are hydrogen bonded to the solvent, in which case the energy of the $^3(n,\pi^*)$ state becomes nearly equivalent to that of the $^3(\pi,\pi^*)$ state. The energy of the latter state is correspondingly lowered due to solvent perturbation which leads to increased mixing

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(12) W. M. Moore and M. Ketchum, *J. Am. Chem. Soc.*, **84**, 1368 (1962).

(13) Yang[3] reports finding two phosphorescent components for 1-indanone in methylcyclohexane. We find no "long-lived" component for butyrophenone in hydrocarbon solvents, but one may exist which is beyond our range of detection.

**Table III.** Phosphorescence Lifetimes and Quantum Yields for Disappearance of Butyrophenone and Appearance of Acetophenone in Various Solvents

| Solvent | Component $\tau_p$, sec | $\phi$ Butyrophenone | $\phi$ Acetophenone | $-\Delta$acetophenone/ $\Delta$butyrophenone |
|---|---|---|---|---|
| MCH | $0.8 \times 10^{-3}$ | 0.33 | 0.24 | 0.70 |
| *n*-Hexane | Est 0.001 | 0.39[a] | 0.27[a] | 0.74 |
| *t*-BuOH[b] | $3 \times 10^{-3}$, $1.5 \times 10^{-2}$ | 1.00[a] | 0.86[a] | 0.86 |
| $CH_3CN$ | . . . | 0.90[a] | 0.81[a] | 0.90 |
| HOAc | $3.5 \times 10^{-3}$, $3.0 \times 10^{-2}$ | 1.0 | 0.90 | 0.90 |
| EG–EtOH–HOAc, 1:1:2 | $2.5 \times 10^{-3}$, $3 \times 10^{-2}$ | 1.0 | 0.63 | 0.63 |
| EGW–HOAc, 1:1 | $2.5 \times 10^{-3}$, $9.0 \times 10^{-2}$ | 0.94 | 0.83 | 0.95 |
| MeOH | $4 \times 10^{-3}$, $3.5 \times 10^{-2}$ | 0.78 | 0.36 | 0.43 |
| EG–EtOH, 5:1 | $2.5 \times 10^{-3}$, $3.5 \times 10^{-2}$ | 0.74 | 0.45 | 0.60 |
| EtOH | $3.5 \times 10^{-3}$, $3.0 \times 10^{-2}$ | 0.66 | 0.26 | 0.40 |
| EtOH–0.5% HCl | $4 \times 10^{-3}$, $4 \times 10^{-2}$ | 0.48 | 0.18 | 0.38 |
| EtOH–1% HCl | . . . | 0.46 | 0.17 | 0.37 |
| EtOH–5% HCl | $5 \times 10^{-3}$, $8 \times 10^{-2}$ | 0.33 | 0.12 | 0.34 |
| $MCH–SiO_2$ | $8 \times 10^{-2}$ | . . . | 0.045 | . . . |
| EGW | $1.0 \times 10^{-1}$ | <0.02 | <0.02 | . . . |
| $H_3PO_4$ (85%) | $8.0 \times 10^{-1}$ | <0.02 | . . . | . . . |

[a] Values taken from data obtained by Wagner.[2] [b] Since *t*-BuOH does not form a glass at 77°K, it phosphorescence lifetime was obtained by extrapolation of lifetimes of several *t*-BuOH–EtOH solutions.

in of higher $\pi,\pi^*$ states.[4] The exact energetic dispositions of the $^3(n,\pi^*)$ state and the $^3(\pi,\pi^*)$ state in this long-lived triplet remain unclear, but it is assumed that they are very close (Figure 1b). In solvents of high polarity (EGW, $MCH-SiO_2$, and $H_3PO_4$) the n electrons of butyrophenone in the ground state are strongly hydrogen bonded, raising the energy of the $^3(n,\pi^*)$ state with respect to the $^3(\pi,\pi^*)$ state to such an extent that their dispositions are reversed and phosphorescent emission shows no discernible short-lived component (Figure 1c).

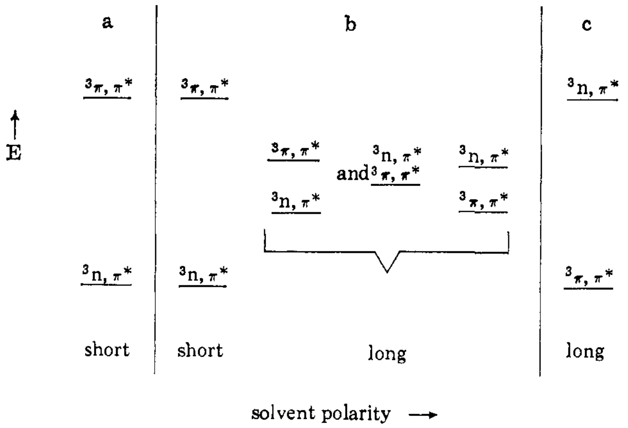
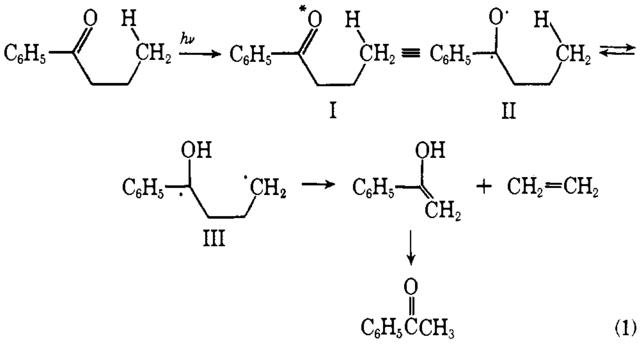


Figure 1. The relative dispositions of the low-lying triplet states for short and long emissive components in (a) nonpolar solvents, (b) moderately polar solvents, and (c) highly polar solvents.

In view of these observations, it is now possible to explain how the nature of the solvent affects the photoreactivity of butyrophenone. Butyrophenone is known to undergo the Norrish type II elimination, the mechanism of which has been elucidated by several investigators[14–17] (eq 1). Not only should solvent polarity influence the energy of $^3(n,\pi^*)$ triplet excited state (I, II), but also, as has been shown by Wagner,[2] should hinder reverse γ-hydrogen transfer (III → II) and thus facilitate



(1)

$$\text{II} \xrightarrow{\text{RH}} \text{reduction products} \qquad (2)$$

photoelimination. A further complication, however, is the ability of the solvent to donate radical hydrogen; efficient donors (such as methanol) giving a high yield of photoreduction products (eq 2).

In the present investigation, 0.2 *M* butyrophenone was irradiated at 2537 Å in a variety of solvents ranging in polarity from methylcyclohexane to 85% phosphoric acid. The quantum yields based upon the disappearance of butyrophenone ($\phi_B$) and upon the appearance of acetophenone ($\phi_A$) are reported in Table III. In light of the lifetime data, the results, in most cases, are quite predictable.

Unlike the situation in alkyl ketones, the effect of solvent upon the photoreactivity of aryl carbonyl compounds is observed as twofold. On one hand, as demonstrated by Wagner,[2] the reactivity of the excited state is enhanced by moderately hydrogen-bonding media. However, as the (primarily) $n,\pi^*$ triplet becomes more energetic, it begins to assume more inert $\pi,\pi^*$ character. The point at which the photoreactivity of *n*-butyrophenone reaches a maximum, then, is when solvent polarity is moderately high, but not high enough to decrease the reactivity of the $^3(n,\pi^*)$ state. This is the case when methanol, *t*-butyl alcohol, acetonitrile,[2] and acetic acid are used as solvents.

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(17) P. J. Wagner and G. S. Hammond, *ibid.*, **87**, 4009 (1965); **88**, 1245 (1966).

However, quantum yields drop to less than 0.1 in EGW, MCH-$SiO_2$, and 85% $H_3PO_4$, highly polar solvents in which only long-lived component phosphorescence is observed at 77°K (Table II). This long-lived emission, as in acetophenone and certain substituted aryl ketones, must be predominantly $\pi^* \rightarrow \pi$ in character, indicating that the lowest excited state is predominantly the *relatively* (see, however, ref 5 and 14) unreactive $^3(\pi,\pi^*)$. Further increases in triplet lifetime, from 0.075 sec in MCH-$SiO_2$ to 0.8 sec in 85% $H_3PO_4$ (at 77°K) are caused by decreasing perturbations from n,$\pi^*$ states,[4] and we observe correspondingly that butyrophenone in phosphoric acid is essentially photostable (Table III) at room temperature under normal irradiation conditions.

The difference between $\phi_B$ and $\phi_A$, or alternatively, the quantity $-(\Delta\text{acetophenone}/\Delta\text{butyrophenone})$ is a measure of the extent the Norrish type II elimination, and is smallest in solvents capable of donating radical hydrogen. Irradiation of solutions of butyrophenone in ethanol shows a marked decrease in $\phi_B$ when 0.5% concentrated HCl is added and an even greater decrease when 1 and 5% concentrated HCl is added. These results are fully expected in light of the increase in lifetime of the long-lived triplet state in butyrophenone upon the addition of small amounts of hydrogen ion. (This effect was also observed by Lamola in the case of acetophenone.[4]) However, the *relative* extent of the Norrish type II elimination shows little change with increasing acidity, the decrease in $\phi_B$ being nearly proportional to the decrease in $\phi_A$. Unexpectedly the over-all reaction goes quite efficiently in glacial acetic acid, in 50% EGW-acetic acid, and in 1:1:2 ethanol–ethylene glycol–acetic acid solution; glacial acetic acid, like *t*-butyl alcohol, apparently provides optimal reaction conditions for reasons that are not readily explained. The quantity $-(\Delta\text{ acetophenone}/\Delta\text{butyrophenone})$ is relatively high in all three cases, but lowest when ethanol is present, since ethanol, an excellent donor of radical hydrogen, tends to promote photoreduction.

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# Primary Processes in the Photochemistry of Bicyclic Azo Compounds[1,2]

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**Abstract:** The primary processes in the photochemistry of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) and of 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) have been investigated. In the gas phase the quantum yields of decomposition are 0.85 ± 0.1 and 0.50 ± 0.1, respectively. In isooctane solution the yields are 1.0 ± 0.1 (DBH) and 0.08 ± 0.01 (DBO). Both molecules fluoresce in the gas phase with yields of 0.014 ± 0.0015 (DBH) and 0.56 ± 0.10 (DBO). In solution, however, DBH does not fluoresce. This is consistent with the existence of a pressure-induced dissociation, DBH* + X → products + X, which can also be observed in the gas phase when "inert" gases X are added to the system. In the case of DBO there is still strong emission in solutions such as isooctane and water, $\phi = 0.20 \pm 0.02$ and $0.22 \pm 0.02$, respectively, and "inert" gases are ineffective quenchers in the gas phase. However, the emission can be quenched both in the gas phase and in solution by oxygen, dienes, and olefins, DBO* + Q → DBO + Q. In the direct photolysis of both DBO and DBH there is no evidence for the intermediacy of a triplet state, although molecules in their triplet states, which have been produced by energy transfer, do dissociate. The emission lifetimes of DBO* both in the gas phase and in isooctane solution have been measured, yielding $\tau = 1.0 \times 10^{-6}$ and $0.33 \times 10^{-6}$ sec, respectively.

Although the production of radicals by the photochemical decomposition of aliphatic azo compounds has been widely studied,[4-6] relatively little is known of the details of the primary processes involved in the photochemistry of azo compounds. This is in sharp contrast to the extensive investigations into the detailed photochemistry of ketones, both cyclic and acyclic,[7,8] to which azo compounds have several strong analogies. During recent studies into the production of vibrationally excited molecules by the photodecomposition of cyclic azo compounds,[9-11] it became of

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[2] A preliminary report on this work was given at Division of Physical Chemistry, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

[3] Author to whom inquiries should be addressed.

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