

The Mechanistic Photochemistry of 4-Hydroxybenzophenone

by

NICHOLAS JOHN COWLEY

A thesis submitted to the Department of Chemistry

in conformity with the requirements for

the degree of Master of Science

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ABSTRACT

The photochemical reactions of 4-hydroxybenzophenone with a variety of reactants were studied by UV-visible spectrophotometry and continuous wave (CW) and time-resolved ESR spectroscopy (TR-ESR).

The absorption spectra of benzophenone in solvents such as cyclohexane and isopropanol were used to assign the π,π^* and n,π^* electronic transitions based on the extinction coefficients and the shifts in the absorption maxima with different solvents. A n,π^* band for 4-hydroxybenzophenone was not clearly identified.

Photoreduction at 308 nm of 4-hydroxybenzophenone was not shown with isopropanol or lactic acid, but hydrogen abstraction from 2,6-di-*t*-butyl phenol to form the 4-hydroxybenzophenone ketyl radical in acetonitrile is suggested. Photoreduction by electron transfer to form the 4-hydroxybenzophenone ketyl radical anion from sulfur-oxygen anions is put forward. Photochemical hydrogen abstraction from 4-hydroxybenzophenone, by quinones and pyruvic acid, to form the 4-hydroxybenzophenone phenoxyl radical is further suggested on the basis a simulated spectrum. These interpretations are based on the chemically induced dynamic electron spin-polarization of the radicals observed, which may be explained by contributions from both the Triplet Mechanism (TM) and the Radical Pair Mechanism (RPM).

Hydrogen abstraction from 4-hydroxybenzophenone by di-*t*-butyl peroxide is consistent with the UV-visible absorption spectra before and after irradiation ($\lambda > 300$ nm).

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CHAPTER ONE

INTRODUCTION

Compounds derived from benzophenone are widely used as UV stabilizers for many materials such as paints, paper and plastics. These compounds are also used as sunscreens in tanning lotions and cosmetics due to their highly energetic but selective UV absorption below 350 nm. 4-Hydroxybenzophenone, as shown below in Figure 1, has two functional groups, a carbonyl and a phenolic hydroxyl group.

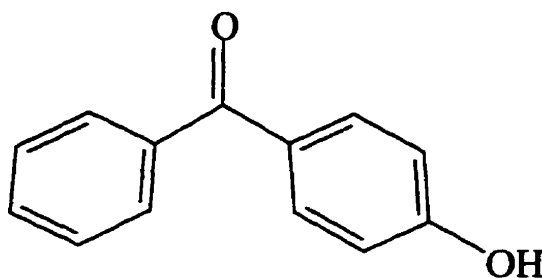


Figure 1. The structural formula of 4-hydroxybenzophenone showing the two functional groups.

The carbonyl group typically undergoes photoreduction by hydrogen abstraction, while the phenolic hydroxyl group affords the possibility of hydrogen donation, a sensitivity to changes in pH, and enhanced aqueous solubility. The chemist's view of 4-hydroxybenzophenone is that it is a good hydrogen donor but is less readily photoreduced by hydrogen abstraction from alcoholic media than benzophenone. The duality in the possible photochemical reaction pathways, and the sensitivity to both solvent and acidity, make 4-hydroxybenzophenone an interesting molecule for photochemical study.

The emphasis of this thesis is concerned with the effect that the addition of a phenolic hydroxyl group has on the photochemical behaviour of 4-hydroxybenzophenone in comparison to benzophenone and acetone.

The study of fast photoreactions requires sensitive investigative tools such as the techniques of UV-visible spectrophotometry and electron spin resonance (ESR) spectroscopy. Appropriate experiments can be designed to maximize the potential of these techniques. Although transient optical spectroscopy is the most widely used method for the detection of free radicals produced by flash photolysis, it suffers from low spectral resolution and cannot yield positive species identification. Steady-state or continuous wave (CW-ESR), however, can often show the spectra of the dominant radicals formed upon photolysis from which the hyperfine coupling constants (hfcc) can be obtained, aiding in their identification. Further, the sensitivity and phase-sensitive nature of the CIDEP technique may allow the determination of the excited state character of the molecular precursor. This technique, therefore, has the advantage over product analysis studies in that the primary reaction mechanisms can be more fully understood.

The current work highlights that the carbonyl group of 4-hydroxybenzophenone is less readily photoreduced, to form the ketyl radical in alcoholic solvents, than benzophenone. It also illustrates several photochemical systems which may warrant more detailed investigation.

1.1 PHOTOCHEMISTRY OF THE CARBONYL GROUP

The photochemistry of carbonyl compounds has been extensively studied in solution.^{1,2} The reactive excited state for benzophenone is the n,π^* state. On excitation, an electron from the oxygen nonbonding orbital is transferred to the π antibonding orbital of the carbonyl group. The singlet is initially formed, but rapid intersystem crossing (ISC) to the triplet can occur. In both excited states, the molecule is pyramidal, the C-O bond is stretched, and the dipole moment is reduced. This is due to transfer of electron density from an orbital that is localized on oxygen to one that encompasses the carbon atom.

An alternative excited state available to carbonyl compounds involves promotion of a bonding π electron to the antibonding π^* orbital. This is called a π,π^* transition and is most likely to occur when the carbonyl group is conjugated with an extensive π bonding system.

One of the most common reactions of photoexcited carbonyl compounds is hydrogen abstraction from the solvent, or some other hydrogen atom donor, by the oxygen of the carbonyl group. Many aromatic carbonyls, such as benzophenone, undergo hydrogen abstraction followed by coupling of the resulting ketyl (α -hydroxyl) radicals. Such reactions have high quantum yields for ketyl radical formation, in solvents that have easily abstractable hydrogens, such as isopropanol. These reactions usually occur via the triplet excited state T_1 .

The ISC of the initially formed singlet is so fast ($k = 10^{10} \text{ s}^{-1}$) in liquid solutions, that reactions of the singlet state of aromatic ketones, such as benzophenone, are usually

not observed in solutions. Photochemical hydrogen abstraction by benzophenone (BP) in isopropanol (RH), can be shown as follows:



This can be represented pictorially, as shown below, to form the two ketyl radicals.

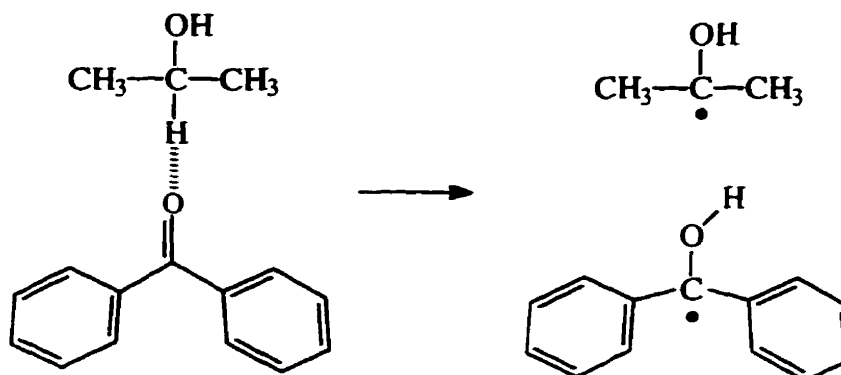


Figure 2. Hydrogen atom abstraction from isopropanol by the triplet state of benzophenone.

The intermediate benzophenone ketyl radical (BPH^*) has been detected after generation by flash photolysis.³ Photolysis of benzophenone, in benzene solution, results in the formation of two detectable radicals or intermediates depending on the hydrogen donor. One of these intermediates is the benzophenone ketyl radical which disappears by combination with another radical in a second-order process. A much shorter-lived species disappears with first-order kinetics, in the presence of excess amounts of various hydrogen atom donors, and has been assigned to the triplet excited state of benzophenone.

The efficiency of reduction of benzophenones is greatly reduced when an electron donating substituent, such as the hydroxyl or the amino group, located in the para

position, is present. The polarity and hydrogen bonding ability of the solvent also affects the efficiency of reduction as shown in Table 1.⁴

Table 1. Quantum Yields for Photoreduction of Various Substituted Benzophenones in Isopropanol and Cyclohexane.

Substituted Benzophenone	Quantum Yield For Photoreduction	
	Isopropanol	Cyclohexane
Benzophenone	1.0	0.50
4-Hydroxybenzophenone	0.02	0.90
4-Aminobenzophenone	-0	0.20

The much lower quantum yields for the substituted benzophenones relative to benzophenone are suggestive that other processes may compete with ketyl radical formation. Among these could be processes such as intramolecular deactivation modes, including emission, (fluorescence or phosphorescence) or radiationless internal conversion. Intermolecular deactivation modes such as energy transfer or charge transfer with the solvent may also occur.

CHAPTER TWO

THEORY

2.1 ELECTRON SPIN RESONANCE

The electron spin resonance technique is the observation of the magnetic field needed to bring the separation of electron spin energy levels into resonance with a microwave electromagnetic field. The identification of a free radical can be realized in its ESR spectrum and is expected to be independent of the preparation method.⁵

As the details of the basic principles and theory are the subject of many texts and comprehensive reviews,⁶ only the general concepts of continuous wave electron spin resonance spectroscopy (CW-ESR) and time-resolved electron spin resonance spectroscopy (TR-ESR), also known as the chemically induced dynamic electron polarization technique (CIDEP), will be presented.

The electron possesses a spin magnetic moment which has two permitted orientations corresponding to different spin states, α and β , which in the presence of a magnetic field have different energies. An electron spin undergoes a transition $\alpha \rightarrow \beta$ when the energy separation of the two states matches the energy of the microwave photon, as shown in Figure 3. Here, the sample and the electromagnetic field are in resonance. This occurs in a field of approximately 3,000 G or 0.3 T, with microwave radiation in the X-band. This corresponds to a frequency of 9.6 GHz and a wavelength of 3 cm.

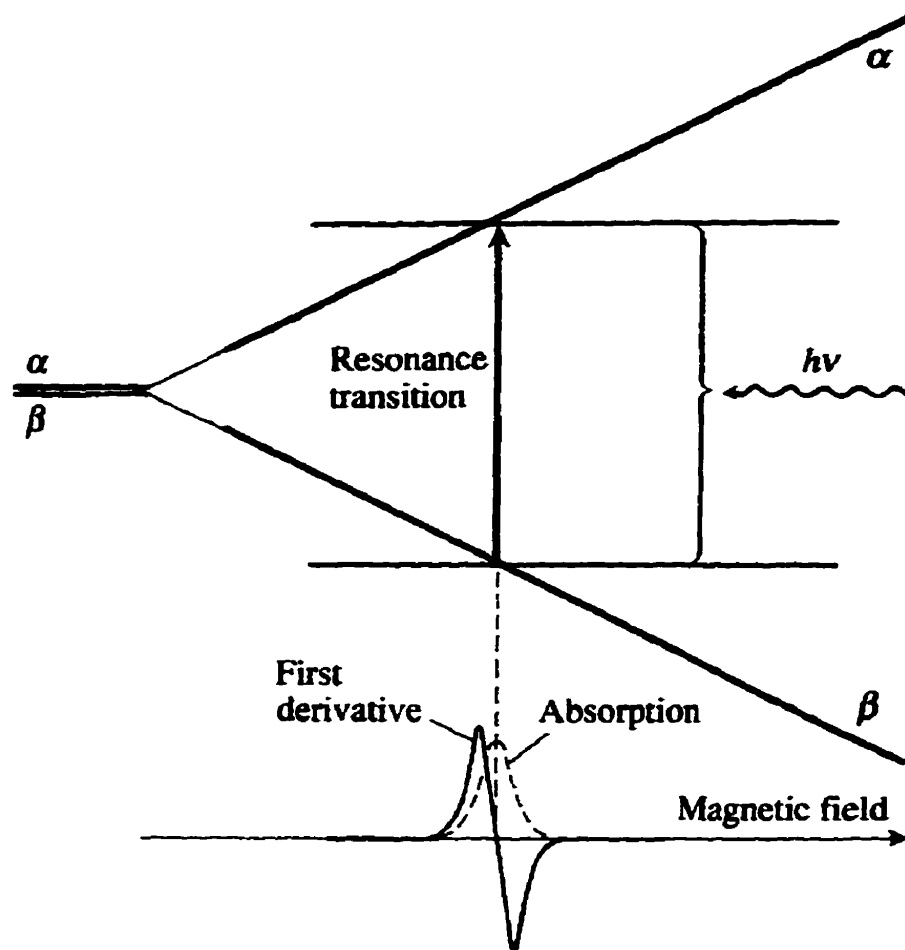


Figure 3. The fundamental basis of ESR. The energies of the α and β states of an electron diverge in a magnetic field.

The apparatus is composed of a strong magnet, a source of microwaves (a klystron) and a detector to monitor the absorption. The observation is performed by monitoring the absorption as the applied field is changed while the sample is exposed to a constant microwave radiation. The first derivative of the absorption signal is shown against the magnetic field. The appearance of the spectra arise from the phase-sensitive detection technique.

Three important types of information about the radicals, which provide an insight into possible structures of the species present, are able to be derived. These are the central position of the spectrum expressed by the g-factor, the hyperfine structure, and the line widths.

2.1.1 The Resonance Condition

For a given microwave frequency, the resonance condition is attained at the same local field. Therefore, at slightly different applied fields in different species, a characteristic g-factor can be found, where h is Planck's constant, ν is the frequency of the microwave radiation, μ_B is the Bohr magneton, and B is the external magnetic field.

$$h\nu = g\mu_B B \quad (3)$$

The g-factor can then be interpreted in terms of the electronic structure of the paramagnetic species and, if sufficiently distinctive, may be used to identify the species. In general, for organic radicals in solution g varies little. Hyperfine structure must be used for determination of the identity of the radical.

2.1.2 Line Intensity

If the electron spin system attains thermal equilibrium, the observed line intensity is proportional to the population difference between the upper and lower spin states:

$$I = N_\beta - N_\alpha \quad (4)$$

The Boltzmann distribution of the spin populations at equilibrium is given by:

$$\frac{N_{\alpha}}{N_{\beta}} = \exp \frac{g \mu_B B}{kT} \quad (5)$$

Thus, at room temperature, kT is greater than $g\mu_B B$, and the population difference between the two states is less than 1% for a typical magnetic field of 0.3T. This shows that reducing the temperature may be favorable if a suitable signal cannot be seen at room temperature.

2.1.3 Hyperfine Interaction

The hyperfine structure of an ESR spectrum arises from the interaction of an electron with nuclei with a spin magnetic moment. Such magnetic nuclei give rise to a local magnetic field, which, depending on the relative orientation of the nuclear spin and the applied field, can increase or decrease the local field experienced by the electron. As a consequence of this, electrons near these nuclei resonate at different applied fields. The magnitude of the isotropic proton hyperfine coupling (hfc) a_H is directly related to the unpaired spin density on the atom bearing the proton or other magnetic nuclei. The hyperfine splitting may be interpreted in terms of the distribution of electrons near the magnetic nucleus, and the electron distribution can be mapped over the magnetic nuclei in the molecule. For example, if a benzene molecule has an extra electron, it becomes a paramagnetic species with one unpaired electron, a free radical. The spectrum, however, does not consist of one line, but of seven, due to the presence of the six protons with magnetic nuclei with spin = 1/2 as shown in Figure 4.

The intensity ratio is binomial, 1:6:15:20:15:6:1. Each line arises from a molecule with different numbers of α and β proton spins.

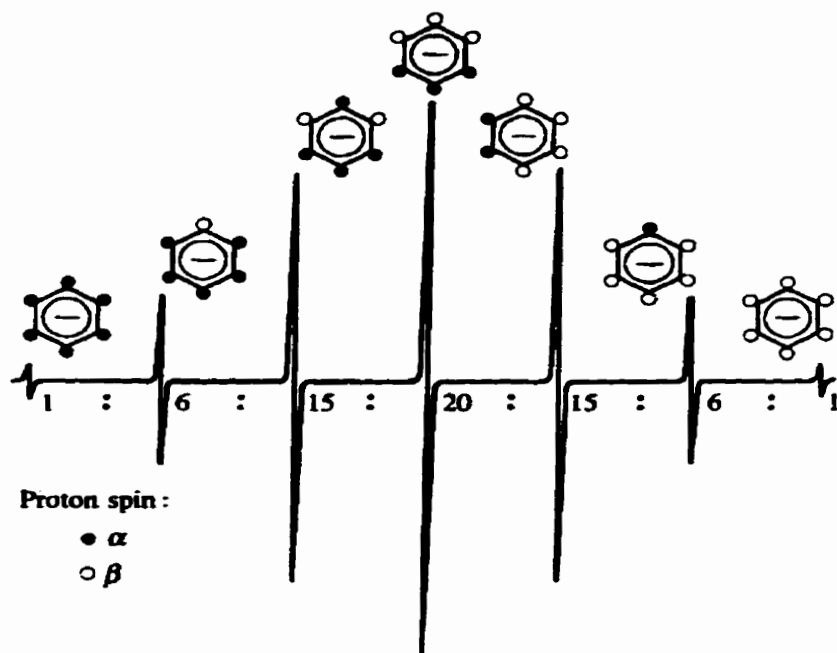


Figure 4. The theoretical hyperfine structure of the ESR spectrum of the benzene radical anion.

The appearance of the experimental spectrum is somewhat different and, as is often the case, the weakest outermost lines may hardly be observed as shown in Figure 5.



Figure 5. The experimental spectrum of the benzene anion in a solution of dimethoxyethane and tetrahydrofuran at 170K. [Spectrum taken from J.R. Bolton, *Mol. Phys.*, 6, 219 (1963)].

2.2 CHEMICALLY INDUCED DYNAMIC ELECTRON POLARIZATION (CIDEP)

In the course of the work undertaken, the most rapid progress in experimental results came with the application of TR-ESR (CIDEP). The CIDEP technique can be as much as three orders of magnitude more sensitive than conventional CW-ESR. CW-ESR is independent of the method of preparation of the free radical under investigation, and the low steady state of radicals can be quite persistent, of the order of seconds, minutes or even hours. CIDEP spectra, on the other hand, appear to be anomalous in intensity and persist only for a few microseconds. CIDEP is also useful in that it may allow the identification of the precursor multiplicity, i.e. whether the initial radical came from a singlet or triplet state.

CIDEP is simply an expression of the deviation of the population of electron spin Zeeman levels from the Boltzmann population shown earlier in Equation 5. The intensities of the lines in the spectrum may possess enhanced absorption or emission. A population of electron spins, that differs from the Boltzmann population, is described as being polarized. Overpopulation of lower energy spin levels results in enhanced absorption (A), and overpopulation of upper spin levels results in emission (E).

There are two main CIDEP mechanisms, each producing a characteristic intensity pattern. These are termed the Radical Pair Mechanism (RPM) and the Triplet Mechanism (TM). Numerous articles and reviews give a more in-depth discussion of the origins of CIDEP,⁷ as the current work has only used the CIDEP technique as a tool.

CHAPTER THREE

EXPERIMENTAL SECTION

3.1 UV-VISIBLE SPECTROPHOTOMETRY

3.1.1 Absorption Maxima of Benzophenone and 4-Hydroxybenzophenone in Different Solvents

Optical absorption spectra were recorded on a Cary5E UV-vis-NIR Spectrophotometer (Varian) with associated proprietary software, v3.00, using two matched 1 cm path length quartz cells to correct for solvent absorption. The spectra were recorded from 200 to 500 nm, at a scan rate of 132 nm/min, a data interval of 0.22 nm, and a spectral bandwidth of 1 nm. The absorption maxima were obtained using Peakfit™ v4. non-linear curve fitting software (Jandell Scientific).

A typical experiment involved making up a 0.1 M solution of benzophenone (Fischer Scientific) or 4-hydroxybenzophenone (Aldrich) in the solvent to observe the n,π^* transition, followed by dilution, (1 ml in 100 ml), to give a 0.1 mM solution from which the π,π^* transitions could be observed. All experiments were carried out at room temperature (25°C), and reagent grade solvents were used as supplied. 4-Hydroxybenzophenone and benzophenone were purified by three recrystallizations from ethanol.

3.1.2 Absorption Maxima of Benzophenone and 4-Hydroxybenzophenone in Ethanol with Acetic Acid or Sodium Acetate

Acidic solutions were made up using acetic acid (1 mM, 10 mM and 1 M) in absolute ethanol with benzophenone or 4-hydroxybenzophenone, (0.1 mM). Basic solutions were similarly made up using sodium acetate (BDH Chemicals Ltd) in ethanol.

3.1.3 Steady State Photolysis Experiments

A typical sample (10 mM) would be irradiated for several minutes in neat solvent, unless otherwise stated, using a 200 W mercury arc lamp (Ushio-Super High Pressure, Type USH - 05D, 3.5A) with a 1 cm diameter Pyrex filter to cut out light of wavelengths less than 300 nm. A 8451A Diode Array UV-visible spectrometer (Hewlett-Packard) was used to measure the UV-visible absorption of samples in the range of 200 to 400 nm. Matched quartz cells of 1 cm path length were used for solvent correction.

3.2 ELECTRON SPIN RESONANCE SPECTROSCOPY

3.2.1 Steady State Photolysis Experiments

The samples were contained in narrow, cylindrical quartz or Pyrex tubes of 1 - 4 mm internal diameter and were irradiated inside the ESR cavity with high pressure mercury arc lamps which were focused via a quartz lens. CW-ESR experiments were carried out using a E-104 (Varian) or customized spectrometer (Bruker) operated with a 100 kHz field modulation. Typical instrument settings were a centre field of 3355 G, scan time of 8 minutes, modulation of 1 G, a time constant of 1 second, power of 1 - 20 mW, amplifier gain of 10^4 and microwave frequency of 9.165 GHz. Data was acquired

by a VC-6025 digital storage oscilloscope (Hitachi), a model SR245 computer interface module (Stanford Research Systems) and a custom data acquisition program (OSC) written by Dr. Wayne King and modified for Microsoft Windows™ by Dr. Mikhail Ioffe. Spectral data were stored as ASCII type and were handled by GRAPHER™ for Windows v1.2, (Golden Software). The CW spectra were simulated using a program (ESRSim) written by Dr. Mikhail Ioffe.

3.2.2 Time-Resolved Experiments

For the CIDEF experiments, the samples were dissolved in a mixed solvent typically 1:2 (v/v) water and ethanol. Acetone (Fischer Scientific), sodium sulfite (Anachemia), sodium dithionite (BDH), lactic acid, pyruvic acid and t-butyl peroxide, 98% (Aldrich) were used as received. The samples were prepared with distilled water and thoroughly purged with nitrogen, to remove dissolved oxygen. Solutions were flowed (10 ml/hr), to minimize radicals from secondary reactions, with a 341B syringe pump (SAGE Instruments). Either an EMG 101-MSX XeCl excimer laser (Lambda-Physik), 308 nm or a GCR-11 YAG laser (Quanta-Ray), 355 nm, was used for photolysis of the samples. The repetition rate was 10 Hz. CIDEF spectra were obtained using a SR250 gated integrator (Stanford Research Systems). The signal from the spectrometers was obtained after a laser-triggered pulse which permitted integrated and time-gated data to be amplified by a factor of up to 200 by a Model SR240 fast preamplifier (Stanford Research Systems). The gate-width was typically 500 ns - 1 μ s, after a delay of 100 ns - 2 μ s. The spectra have a typical width of 25 - 160 G and were collected over a period of 8 minutes which is long enough for the field to remain constant as the signal is sampled.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 UV-VISIBLE SPECTROPHOTOMETRY OF BENZOPHENONE AND 4-HYDROXYBENZOPHENONE IN DIFFERENT SOLVENTS

Two maxima or bands are observed in the UV-visible absorption spectrum of benzophenone in ethanol, one at 252 (± 1) nm and the other at 331 (± 1) nm, as shown below in Figure 6. The band below 220 nm is not considered due to absorption by the solvent. These broad absorption regions are due to different electronic transitions in the molecule. The low-intensity band at long wavelength, which has a maximum extinction coefficient (ϵ_{\max}) of 148 (± 1), can be assigned to a n,π^* transition. The 252 nm transition is more intense and can be assigned to a π,π^* transition ($\epsilon_{\max} = 17,230 (\pm 10)$). The difference in ϵ_{\max} requires a one hundred-fold change in the concentration (0.1 mM and 10 mM), and explains why two curves are shown below in Figure 6. These assignments are in agreement with the literature.⁸

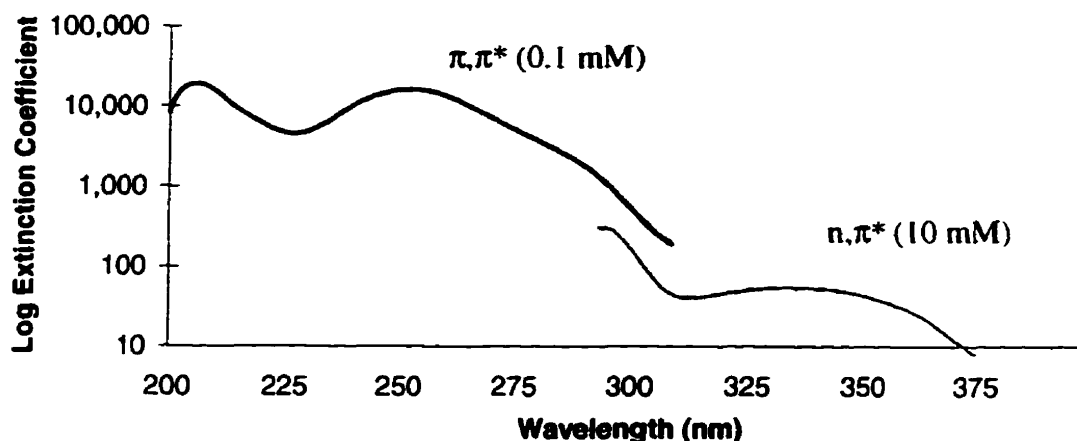


Figure 6. The absorption spectra of benzophenone (0.1 mM and 10 mM) in ethanol.

For 4-hydroxybenzophenone at least three overlapping bands are observed as shown in Figure 7. The band at 295 nm may be attributed to a π,π^* transition due to the relative insensitivity of its position to solvent (Table 2.) and a high value for ϵ_{max} . The position of a possible n,π^* band is shown below but is not sufficiently distinct to be assigned. The bands are more clearly seen if absorbance is plotted instead of the log of the extinction coefficient.

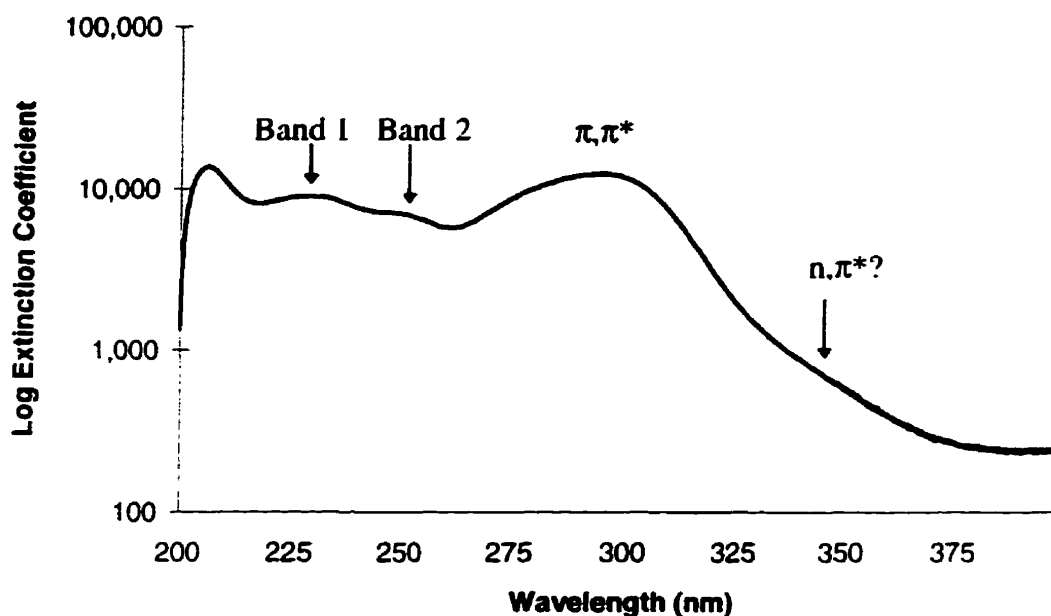


Figure 7. The absorption spectrum of 4-hydroxybenzophenone (10 mM) in ethanol.

The effect of solvents on the energy of the orbitals involved in n,π^* and π,π^* transitions is different. For the n,π^* transitions, solvents that can form a hydrogen bond with the carbonyl oxygen, make excitation of the nonbonding electrons more difficult. This leads to the well known blue shift of λ_{max} in the absorption spectrum as the energy of the excited state increases. The π,π^* transition is less affected by the solvent, but nevertheless, a slight red shift is seen due to the lowering of the energy of the π,π^* state.⁹

Measurement of λ_{max} of benzophenone and 4-hydroxybenzophenone in several different solvents gave the following results (Tables 2 and 3).

Table 2. The Absorption Maxima for Benzophenone in Different Solvents.

Solvent	Wavelength (nm)	
	π,π^*	n,π^*
Cyclohexane	249	350
Acetonitrile	251	339
Isopropanol	252	339
Ethanol	252	331
Water: Ethanol (3:1)	258	320

As the solvents change from cyclohexane to water, it is apparent that the small red shift is consistent with a π,π^* transition, and a large blue shift is consistent with a n,π^* transition. The π,π^* band is at shorter wavelength or higher energy because more energy is required for excitation of a π electron; π electrons are more firmly bound in the ground state than are the nonbonding oxygen electrons. The π^* orbital covers the entire molecule rather than being localized in the carbonyl group and is the same as the one involved in the n,π^* transition. This discussion is an oversimplification as a change in the electronic configuration of a molecule, from photoexcitation, changes all the orbitals due to electron-electron interactions.

Table 3. The Absorption Maxima for 4-Hydroxybenzophenone in Different Solvents.

Solvent	Wavelength (nm)	
	π,π^*	π,π^*
Cyclohexane	248	287
Acetonitrile	249	285
Isopropanol	255	296
Ethanol	254	295
Water: Ethanol (1:1)	254	295
Water	260	294

As the solvent changes from cyclohexane to water, both bands undergo a small red shift which is consistent with π,π^* transitions. Careful inspection of the spectra and peak fitting with Peakfit™ software showed that there appears to be other bands hidden beneath the strong π,π^* transitions, but there was no observation of a band which can be definitively attributed to a n,π^* transition. If such a transition exists it may well be hidden by the intense π,π^* transitions as shown earlier in Figure 7.

The shifts may be correlated with polarity except for the fact that acetonitrile is more polar than isopropanol and yet does not red shift the π,π^* band (285 to 296 nm) as much. This suggests that a hydrogen bonding interaction could be significant.

The effect of adding acetic acid or sodium acetate to 4-hydroxybenzophenone is shown below in Figures 8 and 9.

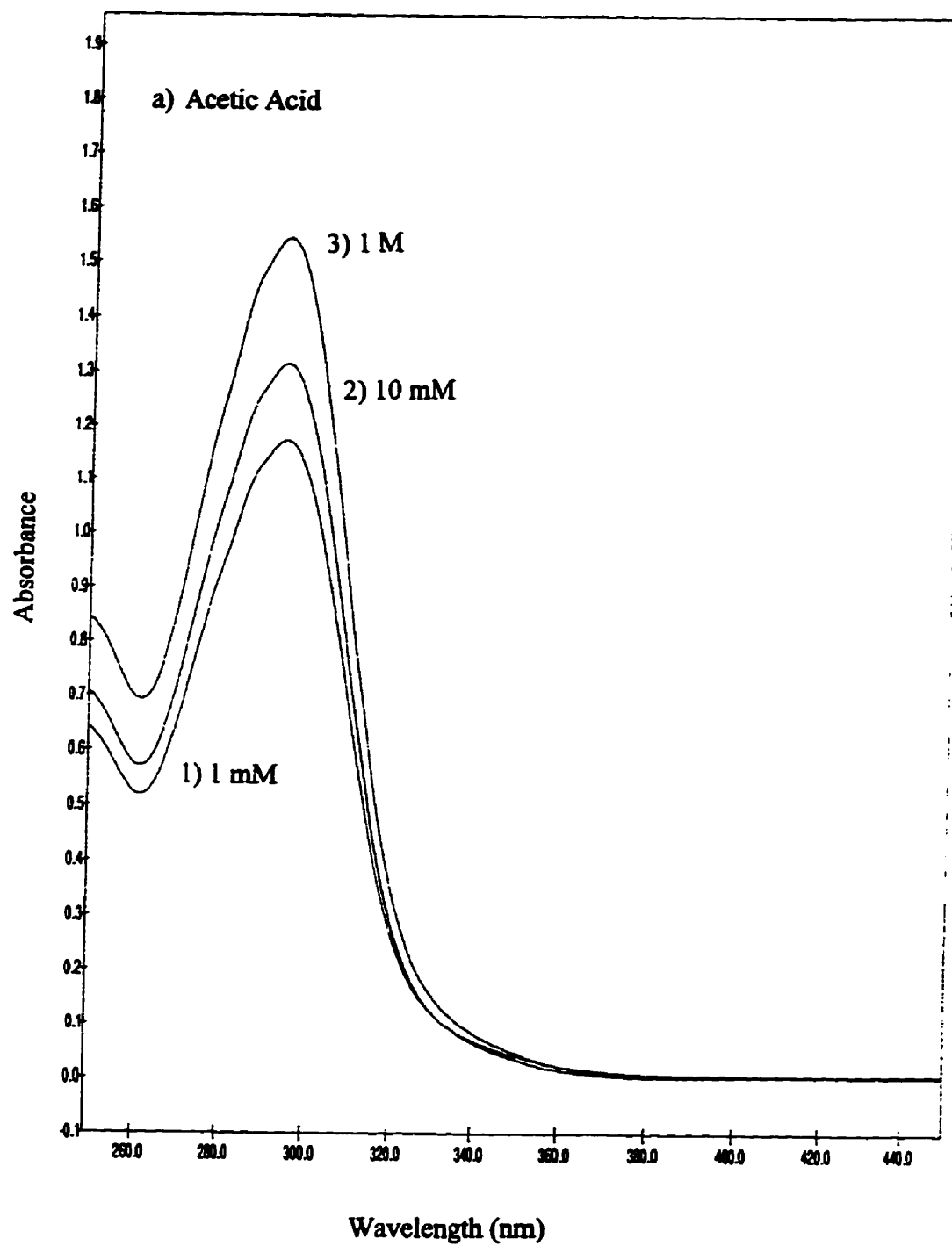


Figure 8. The absorption spectra of 4-hydroxybenzophenone in ethanol with acetic acid, 1) 1 mM, 2) 10 mM and 3) 1M.

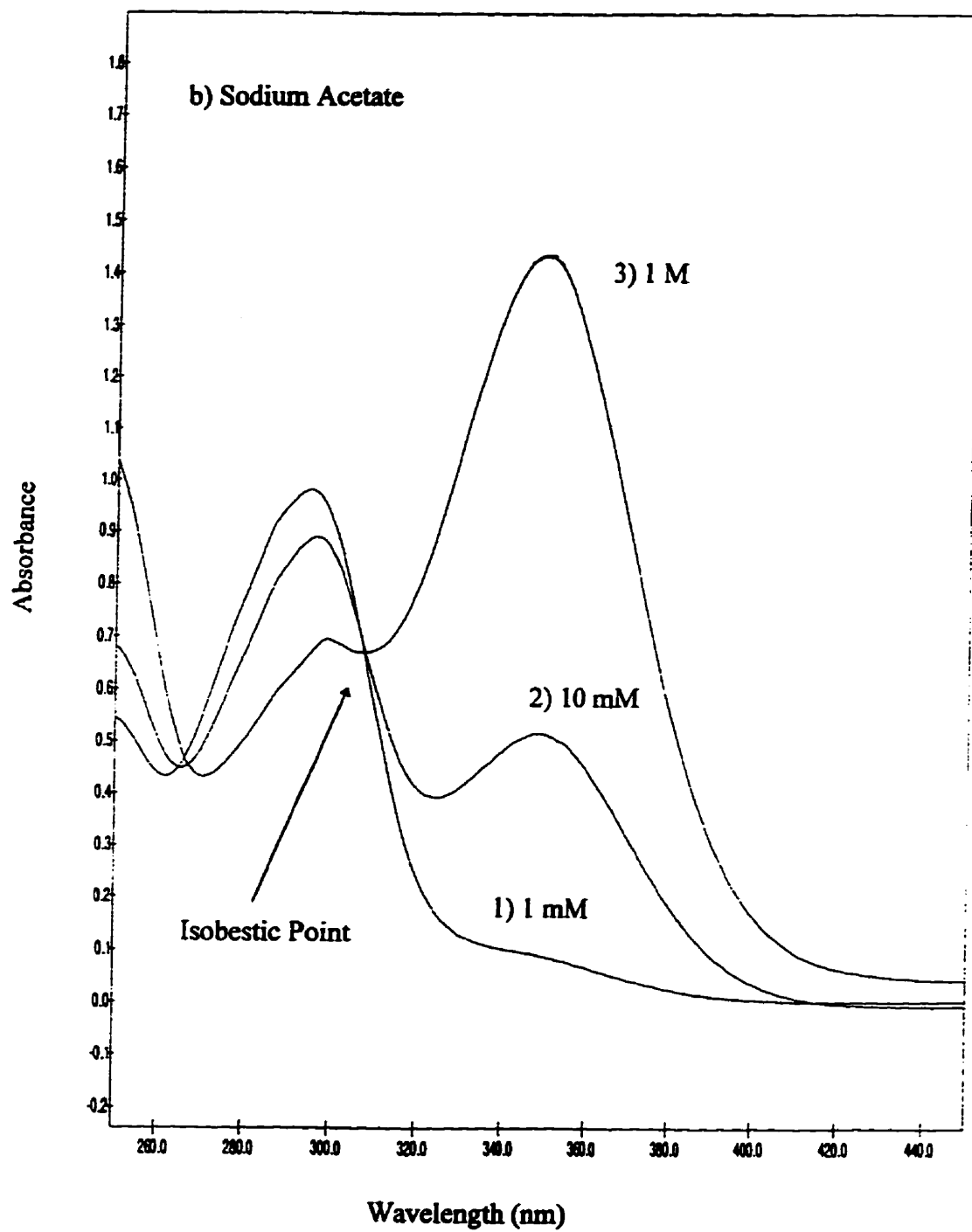


Figure 9. The absorption spectra of 4-hydroxybenzophenone in ethanol with sodium acetate, 1) 1 mM, 2) 10 mM and 3) 1 M.

Figure 8. shows that the affect of acidic media (acetic acid, 1 mM - 1 M, in ethanol) is slight in comparison to the dramatic change, shown in Figure 9., in the spectra of 4-hydroxybenzophenone (0.1 mM) as the solution becomes more basic (sodium acetate, 1 mM - 1 M, in ethanol). The longest wavelength band shifts from 295 to 349 nm and the isobestic point is evidence for the interconversion of two species. If deprotonation of 4-hydroxybenzophenone is occurring, the new species may well be one in which significant conjugation has occurred. A possible resonance form of 4-hydroxybenzophenone in basic media might be depicted as shown below in Figure 10.

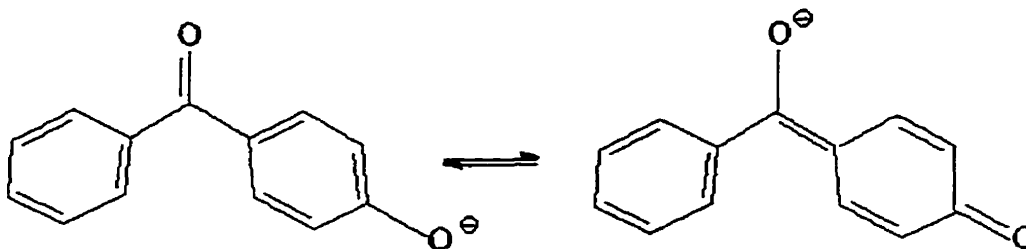


Figure 10. A possible resonance form of 4-hydroxybenzophenone in basic media.

4.2 PHOTOREDUCTION OF 4-HYDROXYBENZOPHENONE BY HYDROGEN ABSTRACTION IN DIFFERENT SOLVENTS

4.2.1 Related Work Reported in the Literature on Photoreduction by Hydrogen Abstraction

Conventional flash photolysis studies have confirmed that deprotonation of the excited state singlet of 4-hydroxybenzophenone in ethanol is responsible for the low quantum yield of photoreduction in alcohols.¹⁰ Hoshino, using nanosecond absorption spectroscopy,¹¹ has identified two transients formed on photolysis of 4-hydroxybenzophenone in ethanol. The first, observed 20 ns after the laser pulse at 355 nm, has absorption bands located in the region shorter than 430 nm, was quenched by naphthalene, and was assigned to the photoexcited triplet state of 4-hydroxybenzophenone. The first species decayed within 200 ns leaving the second long-lived transient which had an absorption maximum around 350 nm. As it was unaffected by the presence of naphthalene, this second transient was ascribed to the 4-hydroxybenzophenone anion that is derived from deprotonation of the excited singlet state.¹² A transient was not observed which could be attributed to the 4-hydroxybenzophenone ketyl radical. The lowest excited triplet state of 4-hydroxybenzophenone cannot abstract a hydrogen atom from ethanol and was assigned π,π^* and not n,π^* in nature.

This supports the UV-visible results of the current work which show that the lowest energy absorption band appears to arise from a π,π^* transition. Hydrogen abstraction can still occur from a π,π^* state of aromatic ketones, as illustrated by xanthone, as shown in Figure 11.

Xanthone shows hydrogen abstraction in alcoholic media and is known to have π,π^* orbital character in polar solvents.¹³

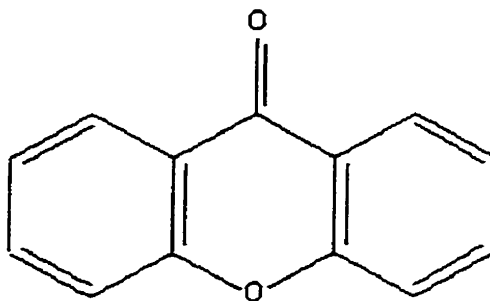


Figure 11. Structural formula of xanthone.

There is also a higher n,π^* triplet state located close to the π,π^* triplet state and the separation between these two states is very sensitive to the environment. The nature of the photochemical reactions is thought to be determined by the relative energy of the n,π^* and π,π^* triplet states. Kuwata,¹⁴ rationalized the difference in the photochemical reactivity between benzophenone and xanthone by the different orbital characters of their excited states. He postulated that hydrogen abstraction by the excited state of xanthone from ethanol is not a direct process, and proposed that an electron initially transfers from ethanol to the excited triplet state of xanthone. A proton or deuteron then transfers from the hydroxyl group of the ethanol cation to the xanthone anion as shown below. This resembles the photoreduction of some aromatic carbonyls with amines.¹⁵





Xn and $^*\text{XnH}$ represent xanthone and its ketyl radical respectively. It is apparent that xanthone and 4-hydroxybenzophenone have closely-spaced triplet states that are sensitive to factors, such as the substituent, solvent and temperature.

4.2.2 Steady State Photolysis of 4-Hydroxybenzophenone in Polar and Non-Polar Solvents Monitored by UV-Visible Absorption

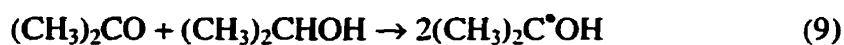
Photolysis ($\lambda > 300$ nm) of 4-hydroxybenzophenone in t-butyl benzene showed that the absorption spectrum was identical before and after irradiation, with no color change in the solution, which is suggestive that no significant reaction had occurred. Experiments were also performed with irradiation of 4-hydroxybenzophenone in dichloromethane. Here, the irradiated solution acquired a pale yellow color with a tail in the absorption spectrum to 500 nm. A blank experiment without 4-hydroxybenzophenone failed to show any coloration. This suggested that a photochemical reaction may have been occurring and CIDEP experiments were conducted.

4.2.3 Photolysis of 4-Hydroxybenzophenone in Ethanol and Isopropanol

Several photolysis experiments were conducted with irradiation (308 nm) of 4-hydroxybenzophenone (3 mM) in ethanol and in a mixed solvent 1:2 (v/v) water and ethanol. However, no characterizable spectra were observed which suggested that 4-hydroxybenzophenone does photoreduce to form its ketyl radical in ethanol or in a mixed solvent 1:2 (v/v) water and ethanol.

The rates of hydrogen abstraction by carbonyls are approximately ten times greater for tertiary hydrogens relative to secondary hydrogens, and a hundred times greater than for primary hydrogens in solution.¹⁶ Therefore, hydrogen abstraction of the tertiary hydrogen of isopropanol by 4-hydroxybenzophenone might occur sufficiently fast to allow the opportunity for observation of CIDEP.

One of the standard systems that can be used to verify the laser intensity is that of acetone and isopropanol. The two radicals produced on photolysis are identical, as shown below in Equation 9.



Irradiation of a solution of acetone, isopropanol and water 2:1:2 (v/v) gave a TR-ESR spectrum of seven lines polarized with E/A* phase as shown in Figure 12.

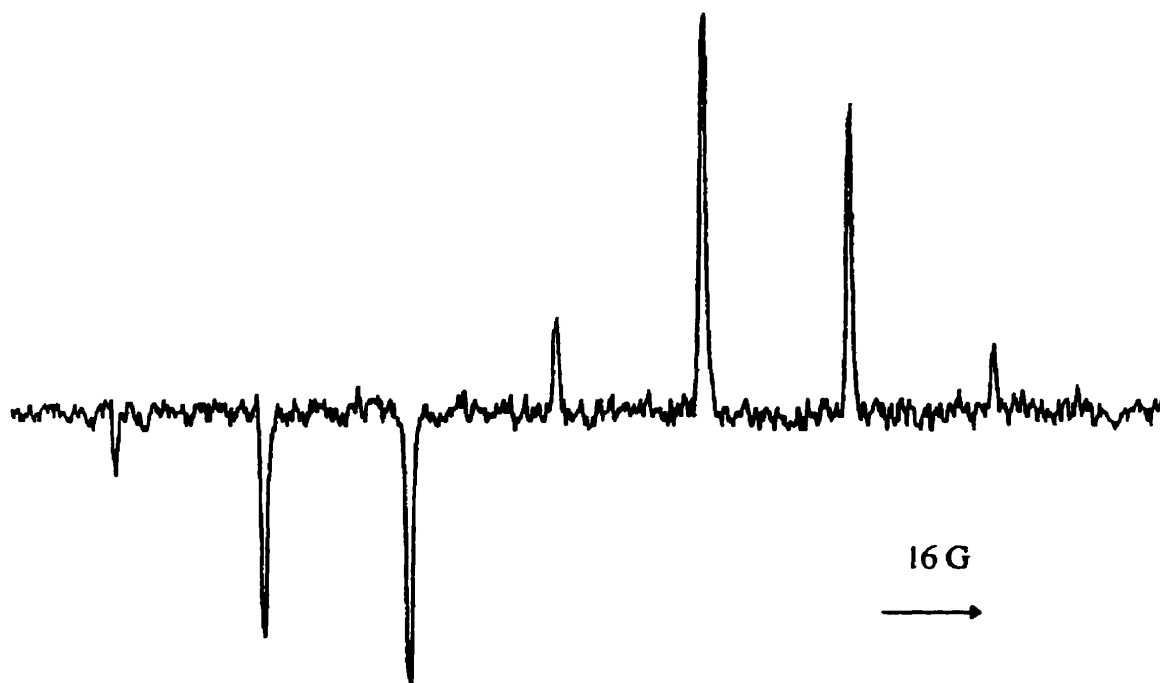


Figure 12. CIDEP spectrum from photolysis of acetone in isopropanol and water, 2:1:2 (v/v); time delay 1 μ s.

The sharp, strong signals arise from coupling to six equivalent methyl protons with a hyperfine coupling constant of approximately 20G. This is consistent with the isopropyl ketyl radical. Both TM and RPM polarization contribute to the spectrum giving the observed E/A + A or E/A* pattern.

Photolysis of a) benzophenone (0.1 M) in isopropanol and b) 4-hydroxybenzophenone (10 mM) in isopropanol, gives rise to the spectra shown in Figure 13.

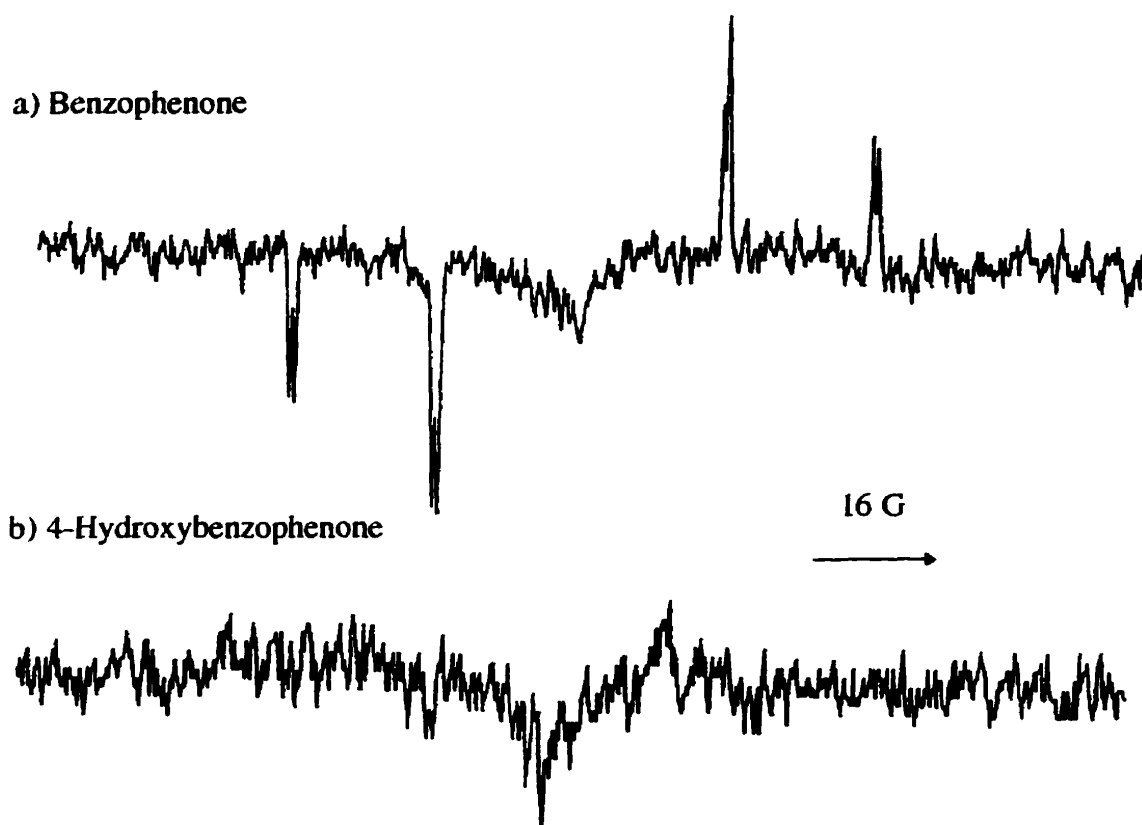


Figure 13. CIDEP spectra from irradiation of a) benzophenone and b) 4-hydroxybenzophenone in isopropanol at 308 nm.

The spectrum, Figure 13 a) from photolysis of benzophenone, appears in emission for the lower field lines and in absorption for the higher field lines. The splitting and position of the sharp lines is consistent with the isopropyl radical and the broad central peak may be the benzophenone ketyl radical. This suggests that hydrogen abstraction by the triplet state of benzophenone may have occurred and that the total polarization exhibited also has a strong contribution from the RPM. In the experiment with 4-hydroxybenzophenone, Figure 13 b), the central part of the spectrum appears similar to that obtained with benzophenone, i.e. an E/A pattern. This may be suggestive of photoreduction by hydrogen abstraction to form the 4-hydroxybenzophenone ketyl radical, but it is not conclusive as there is no evidence of polarized lines from the isopropyl ketyl radical. Either 4-hydroxybenzophenone reacts with itself or reacts much more slowly with isopropanol than does benzophenone. ISC may also be less efficient than with benzophenone.

Photolysis of benzophenone (0.1 M) in isopropanol at 355 nm gave the spectrum shown in Figure 14 a). The central portion of the spectrum has E/A character but the presence of the counter isopropyl ketyl radicals is barely distinguishable. Figure 14 b) shows a strong emissive signal in the central part of the spectrum but the lack of the counter ketyl radical again, precludes further statement as to the identity of the species.

As far as can be seen from the CIDEP spectral results, hydrogen abstraction by 4-hydroxybenzophenone can not be seen to be occurring to any great extent in isopropanol.

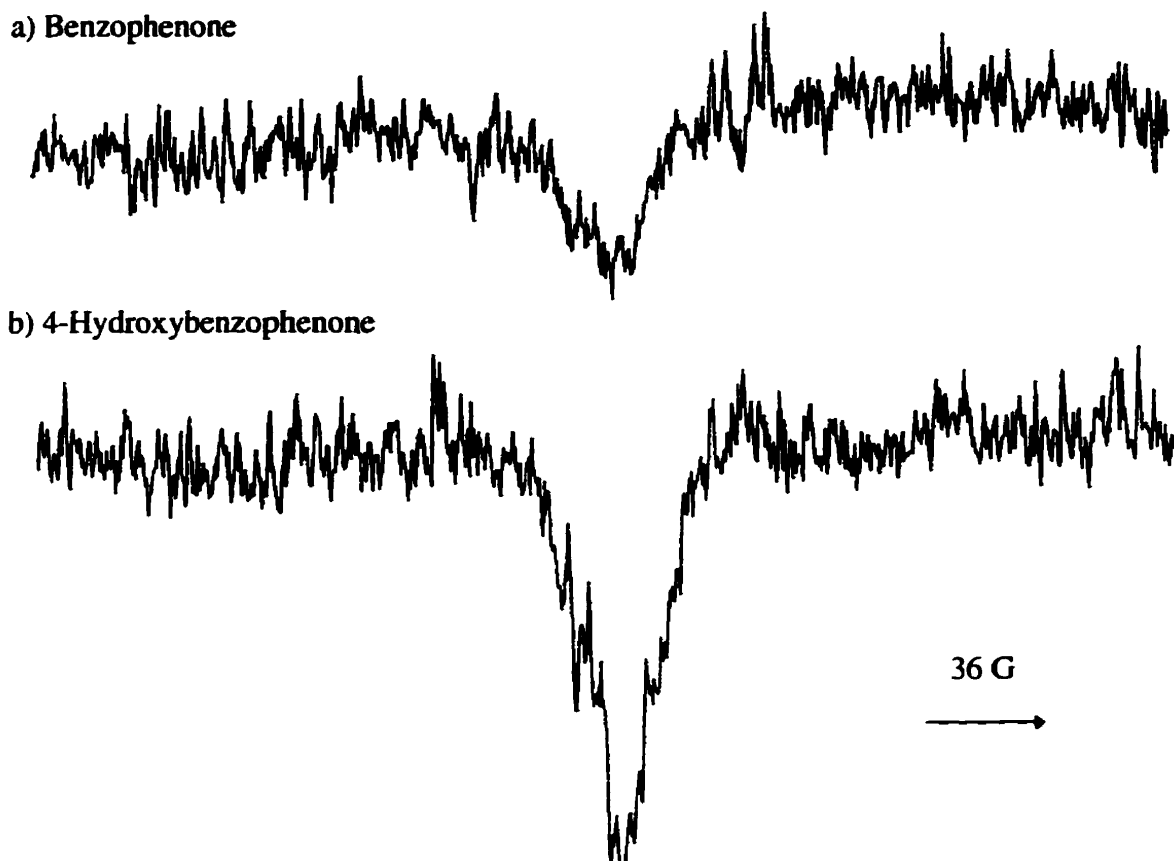


Figure 14. CIDEP spectra from irradiation of a) benzophenone and b) 4-hydroxybenzophenone in isopropanol at 355 nm.

4.2.4 Photolysis of 4-Hydroxybenzophenone with 2,6-di-*t*-Butyl Phenol in Acetonitrile

Phenol photochemistry in liquid solution is dominated by the formation of phenoxyl radicals in photooxidation reactions. With sterically-hindered phenols, such as 2,6-di-*t*-butyl phenol, the resulting phenoxyl radical, formed from photooxidation in benzene, is persistent and can be seen with conventional CW-ESR. CIDEP spectra are totally emissive which is consistent with the radical cation formed by the TM as shown in Equation 10.¹⁷



The phenol radical cation may rapidly deprotonate to give the more stable phenoxyl radical as shown in Equation 11.

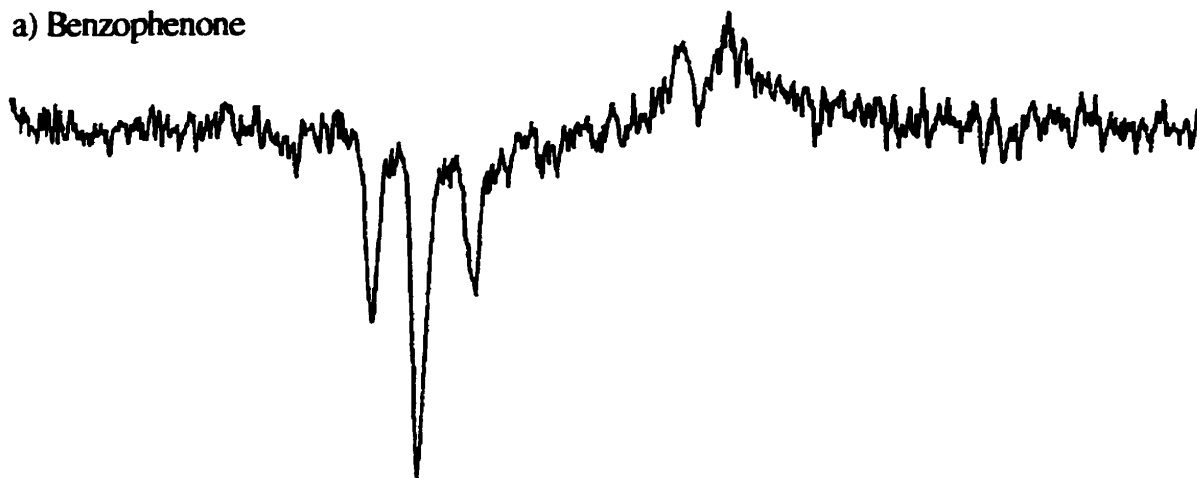


Substituted phenols have also been used as hydrogen donors in the photoreduction of quinones. In fact, the photoreduction of quinones with phenols was the reaction first used to establish the TM.¹⁸ Triplet benzophenone is known to hydrogen abstract from 2,4,6-tri-*t*-butyl phenol in benzene with a rate constant of $6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.¹⁹ It is important to note that although the photooxidation of these phenols was observed in benzene, a similar experiment in acetonitrile did not lead to observation of the radical cation.

Experiments were performed with irradiation at 308 nm for 2,6-di-*t*-butyl phenol with benzophenone (0.1 M) or 4-hydroxybenzophenone (10 mM) in acetonitrile. For 4-hydroxybenzophenone, Figure 15. b) an emissive doublet of triplets is observed which is consistent with the phenoxyl radical. An underlying broad, unresolved emissive resonance is also apparent. This is consistent with a predominantly TM of polarization, which would seem to suggest that hydrogen abstraction by 4-hydroxybenzophenone is occurring. For benzophenone, Figure 15. a) E/A character is more apparent which is consistent with contributions to the polarization from both the RPM and the TM. Similar experiments with other phenols such as 2,6-dimethyl phenol and 2,5-di-*t*-butyl phenol also gave emissive spectra with slight E/A character when photolyzed with

4-hydroxybenzophenone in acetonitrile suggesting that contamination of the phenol was not leading to observation of the phenoxy radical.

a) Benzophenone



b) 4-Hydroxybenzophenone

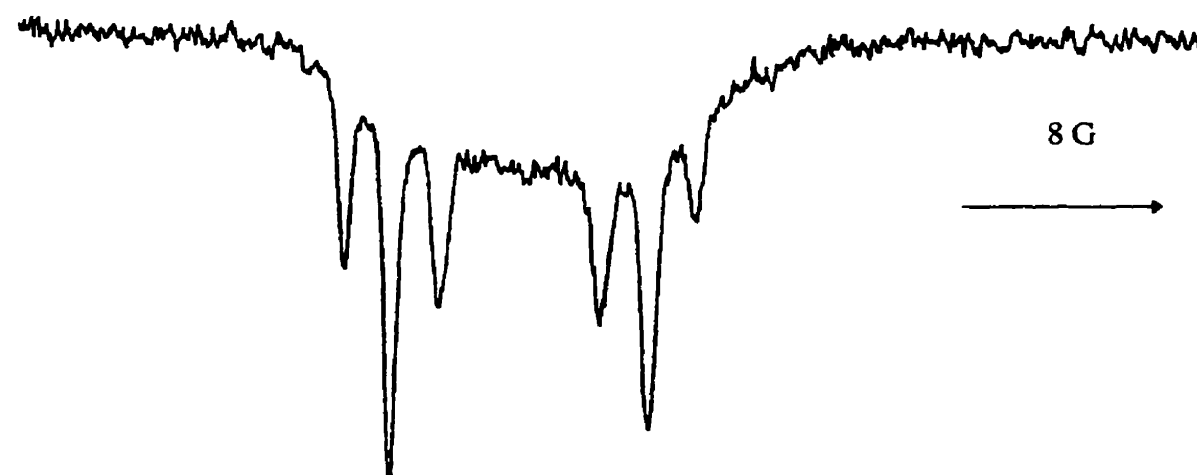


Figure 15. CIDEP spectra from irradiation of a) benzophenone and b) 4-hydroxybenzophenone with 2,6-di-*t*-butyl phenol at 308 nm, delay 1 μ s, power 5 mW.

The control experiments with irradiation of the phenol alone, did not give a signal, indicating that phenoxy radical formation was not observed. Hydrogen abstraction by compounds usually thought of as poor hydrogen abstractors is not, however, uncommon as 4-alkoxyacetophenones have been shown to react very efficiently

when the donor is a phenol.²⁰ There is evidence for hydrogen abstraction in these phenol systems, however, reactions such as direct absorption of light by the phenol may generate electronically excited states which can also lead to the observation of a phenoxyl radical.²¹

4.2.5 Photolysis of 4-Hydroxybenzophenone with Lactic Acid

Lactic acid can also act as a hydrogen donor. Irradiation of acetone in lactic acid 5:1 (v/v) gives rise to the spectrum, Figure 16. a), which shows the presence of two radicals which are consistent with the ketyl radicals derived from lactic acid and acetone. The E/A form and symmetry of the low and high field lines is suggestive of the RPM. Irradiation at 308 nm, of a 1:1 (v/v) mixture of pyruvic acid and lactic acid, Figure 16. b), shows four lines of doublets arising from the ketyl radical and, again, is suggestive of hydrogen abstraction of lactic acid by the triplet state of pyruvic acid. Similar irradiation of benzophenone, Figure 16. c), also shows a spectrum with E/A character with the signals arising from the lactic acid ketyl radical and a central unresolved multiplet which may be the benzophenone ketyl radical. This is suggestive of hydrogen abstraction of lactic acid by the triplet state of benzophenone. Irradiation of 4-hydroxybenzophenone with lactic acid, Figure 16. d), however, does not show a well-resolved spectrum, although careful inspection does reveal some E/A character. In other words, lactic acid appears to be a less effective hydrogen donor towards aromatic carbonyls than do the substituted phenols. The abstraction reaction may be slow so that the triplet polarization decays before reaction has occurred.

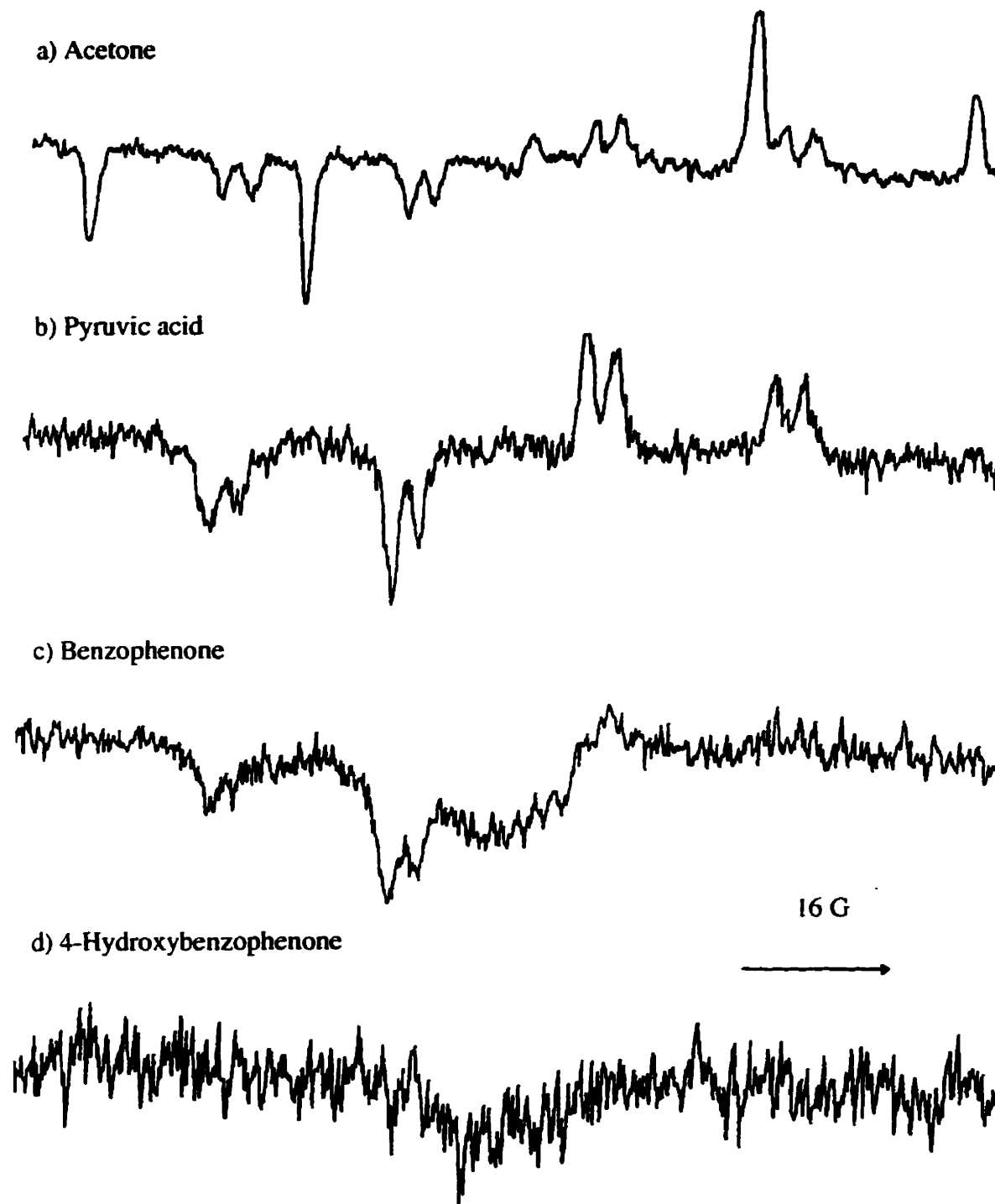


Figure 16. CIDEP spectra from irradiation of a) acetone, b) pyruvic acid, c) benzophenone and d) 4-hydroxybenzophenone in lactic acid at 308 nm.

4.3 PHOTOREDUCTION OF 4-HYDROXYBENZOPHENONE BY ELECTRON TRANSFER

4.3.1 Related Work Reported in the Literature on Photoreduction by Electron Transfer

Recent study of the rates and radical yields in electron transfer interactions, between organic triplets and simple anions,^{22,23} have shown that the reactivity of the organic triplet depends essentially on its thermodynamic properties, i.e. reduction potential and triplet energy. This contrasts with the well established fact that π,π^* states of carbonyl triplets are much less reactive than n,π^* states in direct hydrogen atom abstraction reactions. However, reactions from π,π^* states are commonly observed with donors of high ionization potential and are characterized by significant deuterium isotope effects.²⁴ It should be noted that the problem of evaluating electron transfer contributions to the rate of hydrogen atom abstraction reactions is complicated by the possibility of close-lying or mixed n,π^* and π,π^* states, which may be the case for 4-hydroxybenzophenone.

The photochemistry of sulfur-oxygen anions in aqueous solutions is complex and aerobic oxidation of sulfite SO_3^{2-} has been shown to lead to sulfate SO_4^{2-} and dithionite $\text{S}_2\text{O}_4^{2-}$ as the main products.²⁵ Sodium dithionite has also been shown to lead to at least five species even under anaerobic conditions.²⁶

Nevertheless, it has been shown in a recent study that, electron transfer from sulfite SO_3^{2-} , metabisulfite $\text{S}_2\text{O}_5^{2-}$, and dithionite $\text{S}_2\text{O}_4^{2-}$, occurred to the triplet states of acetone and benzophenone.²⁷ Electron transfer from sulfite and metabisulfite gave rise to the sulfite anion radical $\text{SO}_3^{\bullet-}$. Electron transfer from dithionite gave rise to the $\text{SO}_2^{\bullet-}$

radical through formation of the $S_2O_4^{\bullet-}$ radical followed by dissociation to SO_2 and $SO_2^{\bullet-}$. The mechanisms were established by the CIDEP spectra of the $SO_2^{\bullet-}$ and $SO_3^{\bullet-}$ radicals observed after the laser pulses. The spectra were absorptive in the case of acetone, and emissive for benzophenone, which can be accounted for by the TM.

As pure electron transfer can be exemplified by anion quenching, it seems reasonable that the excited triplet state of 4-hydroxybenzophenone may be quenched by sulfur-oxygen anions such as sodium dithionite or sodium metabisulfite. The effect of the addition of acetic acid (0.1 - 1M) and sodium hydroxide (0.1 - 1M) was also investigated.

4.3.2 Photolysis of Acetone with Sodium Metabisulfite

Preliminary experiments with irradiation of acetone and sodium dithionite in a mixed solvent 3:1 (v/v) water and acetone showed the presence of two lines in absorption. The g-factors of 2.003 and 2.006, are consistent with $SO_3^{\bullet-}$ and $SO_2^{\bullet-}$ respectively. These g-factors agree with the values obtained by other workers in studies of similar systems.^{28,29} Only one line consistent with $SO_3^{\bullet-}$, was observed in a solution made basic with sodium hydroxide, (a pellet in a few ml of mixed solvent). The presence of the ketyl radical was not detected presumably because of a fast reaction with SO_2 formed from the dissociation of $S_2O_4^{\bullet-}$ with a rate constant near the diffusion limit.³⁰ This result indicates that rapid decomposition of the dithionite solution to sulfite may be responsible for the presence of $SO_3^{\bullet-}$ as opposed to the $SO_2^{\bullet-}$. Due to the instability of the dithionite solution and the lack of detection of the counter ketyl radical, sodium metabisulfite was used as the anion of choice. Irradiation of a sodium metabisulfite and

acetone solution 3:1 (v/v) water and acetone lead to observation of a spectrum consistent with the isopropyl ketyl radical, Figure 17. b). Addition of sodium hydroxide (1 pellet in a few ml) to a fresh solution lead to the enhancement of the central line i.e. the single line which is suggestive of $\text{SO}_3^{\cdot-}$ and the central line of the ketyl radical have very similar g-factors, Figure 17. a).

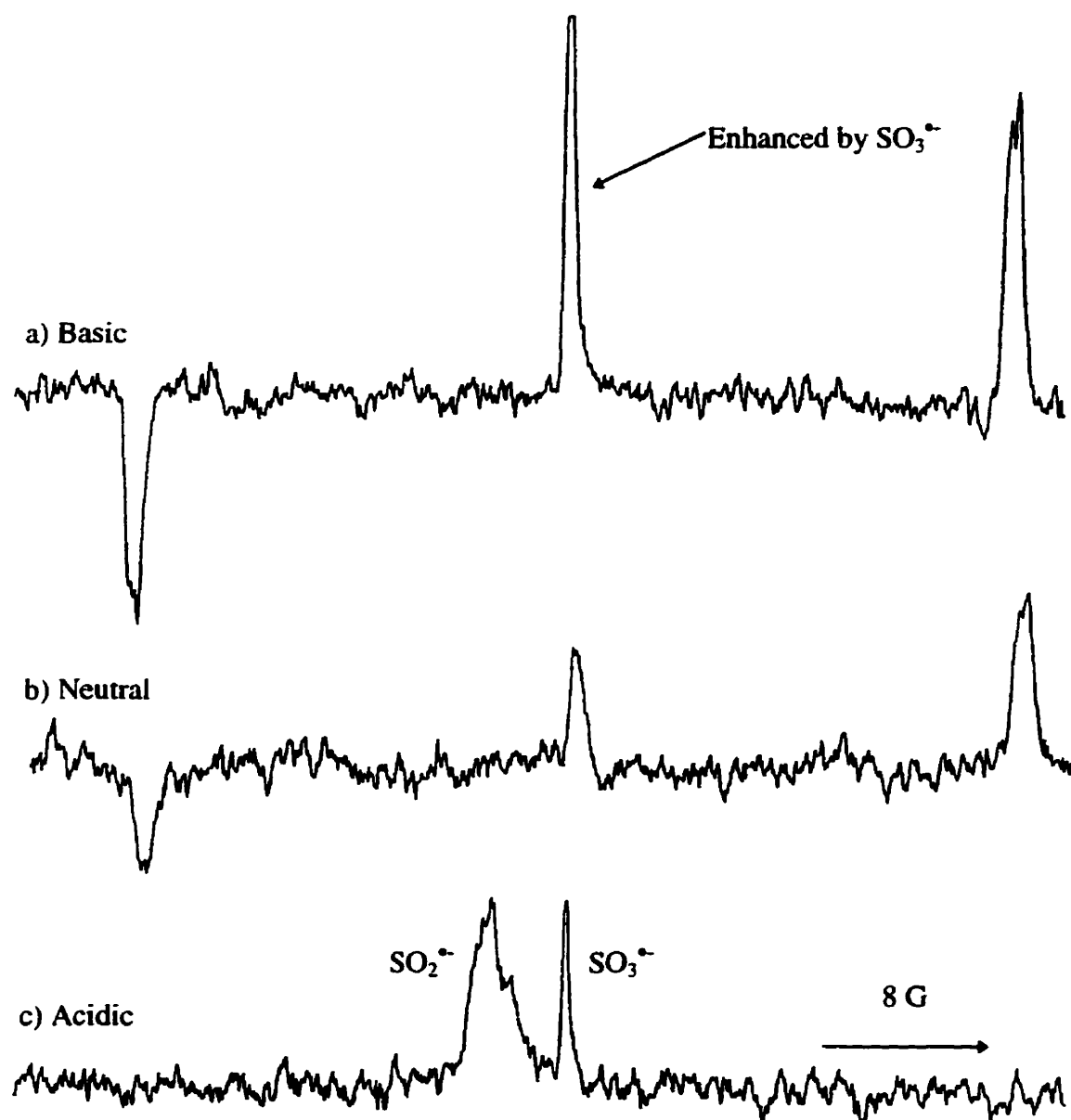


Figure 17. CIDEP spectra from irradiation of acetone and sodium metabisulfite in a) basic, b) neutral and c) acidic 3:1 (v/v) water and ethanol.

Acidification of a fresh solution with a few of acetic acid, Figure 17 c), apparently removes the lines consistent with the ketyl radical leaving the $\text{SO}_3^{\cdot-}$, with the accompanying appearance of a broader line consistent with the $\text{SO}_2^{\cdot-}$ radical. This strongly suggests fast electron transfer to from the triplet ketyl radical to SO_2 as noted above for the acetone:dithionite system. Figure 18.a) and b), show the spectra from a high resolution scan of 10 Gauss of a fresh basic and acidic system. They show several unknown lines (?) in addition to the lines consistent with $\text{SO}_2^{\cdot-}$ and $\text{SO}_3^{\cdot-}$ radicals.

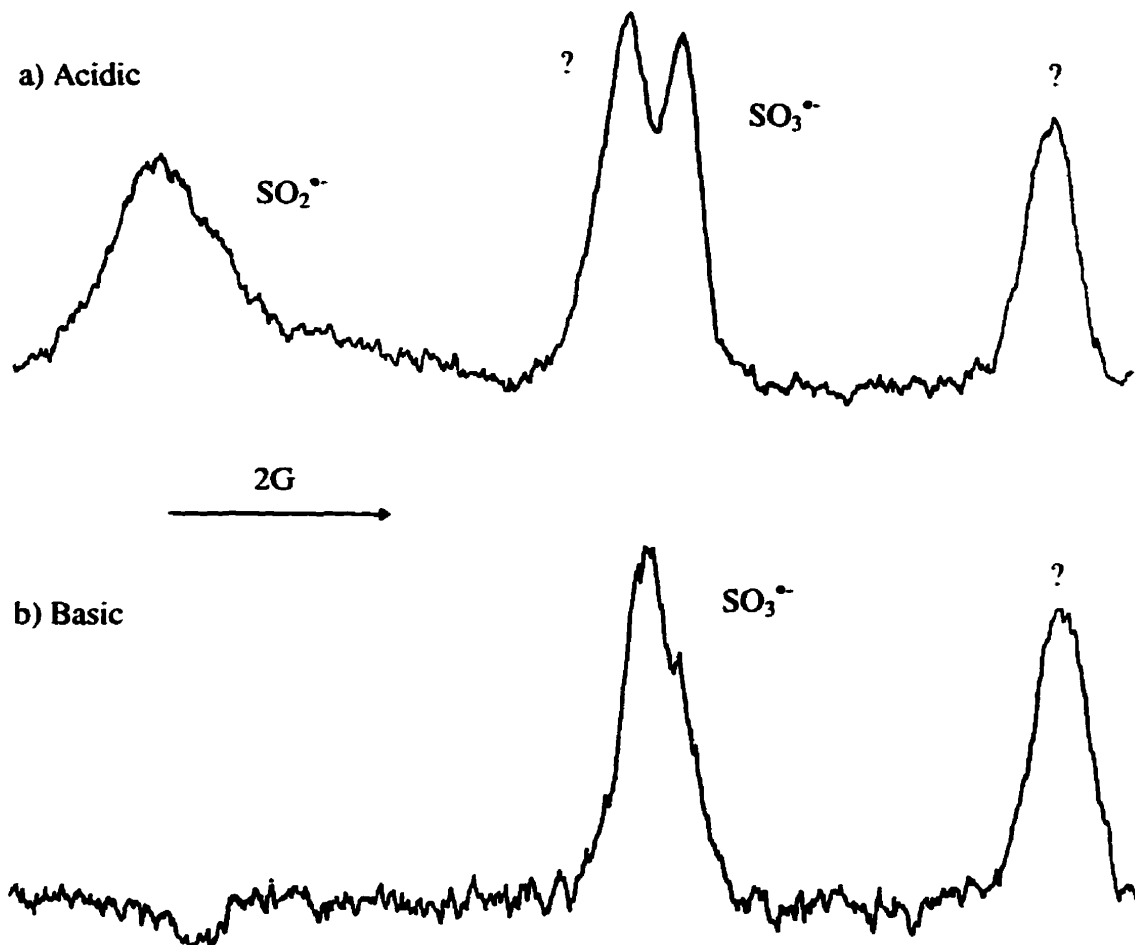


Figure 18. Irradiation of acetone and sodium metabisulfite in a) acidic and b) basic 3:1 (v/v) water and acetone solutions.

4.3.3 Photolysis of 4-Hydroxybenzophenone with Sodium Metabisulfite in a Mixed Solvent 1:2 (v/v) Water and Ethanol

Photolysis of a mixed solvent 1:2 (v/v) water and ethanol solution of 4-hydroxybenzophenone (3 mM) and sodium metabisulfite (60 mM) gave the spectrum shown in Figure 19.

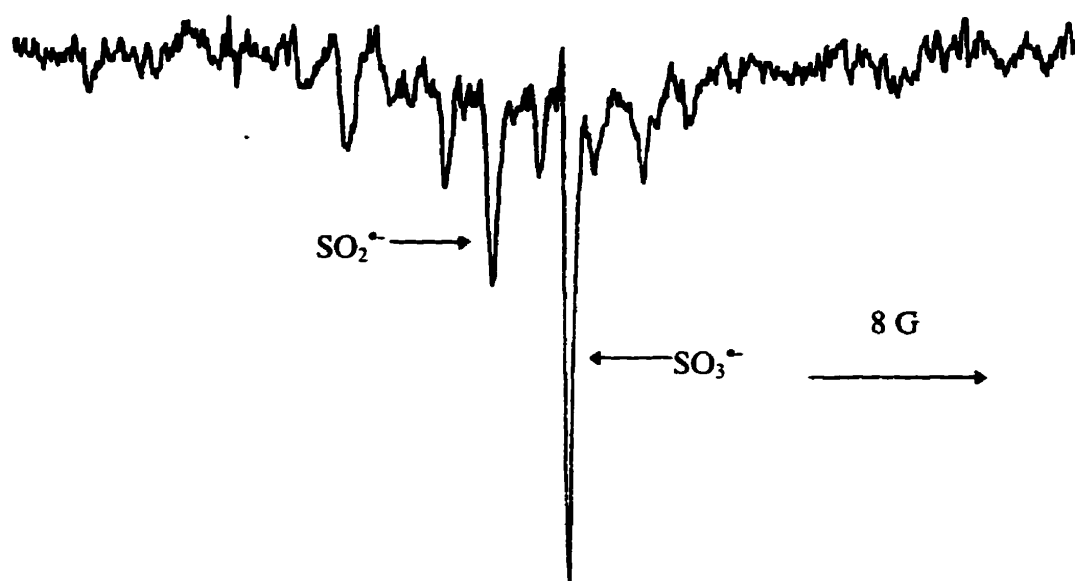


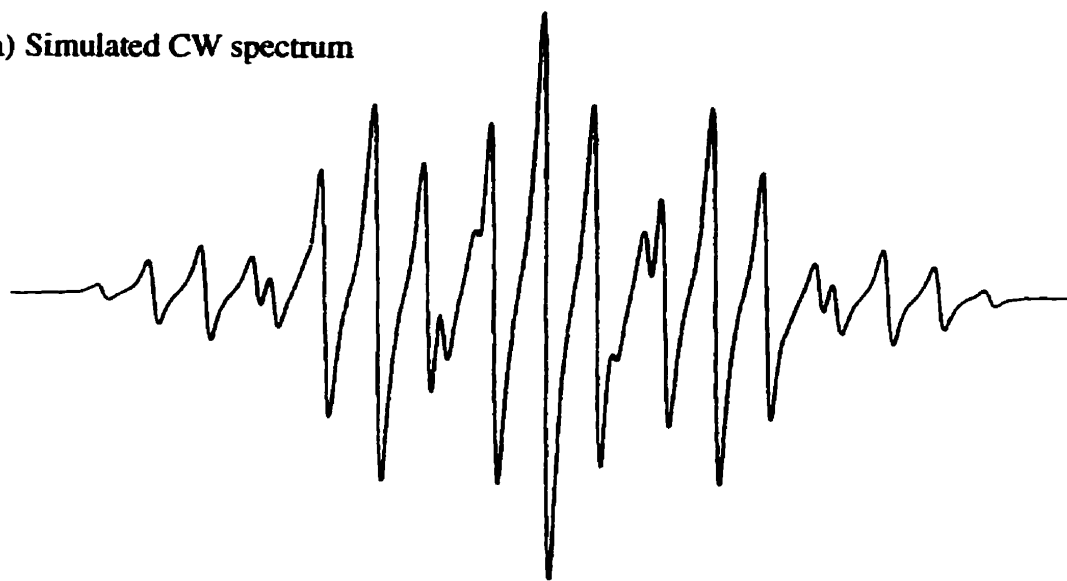
Figure 19. CIDEP spectrum from irradiation of sodium metabisulfite and 4-hydroxybenzophenone in a mixed solvent 1:2 (v/v) water and ethanol.

The sharp emissive singlets are consistent with $\text{SO}_3^{\bullet-}$ and $\text{SO}_2^{\bullet-}$. Photolysis of a fresh solution with a few drops of acetic acid, in addition to the components detailed above, lead the spectrum shown in Figure 20. b). The underlying multiplet in both Figure 19. and Figure 20. b) is suggestive of the 4-hydroxybenzophenone phenoxy radical, as simulated in Figure 20 a). As a control, irradiation of the acidic mixed solvent solution without sodium metabisulfite did not give a discernible spectrum. It is proposed

that the 4-hydroxybenzophenone phenoxyl radical (4-O^\bullet) may arise from hydrogen abstraction by the reactive sulfur-oxygen radicals, $\text{SO}_3^{\bullet-}$ and $\text{SO}_2^{\bullet-}$.



a) Simulated CW spectrum



b) Experimental CIDEP spectrum

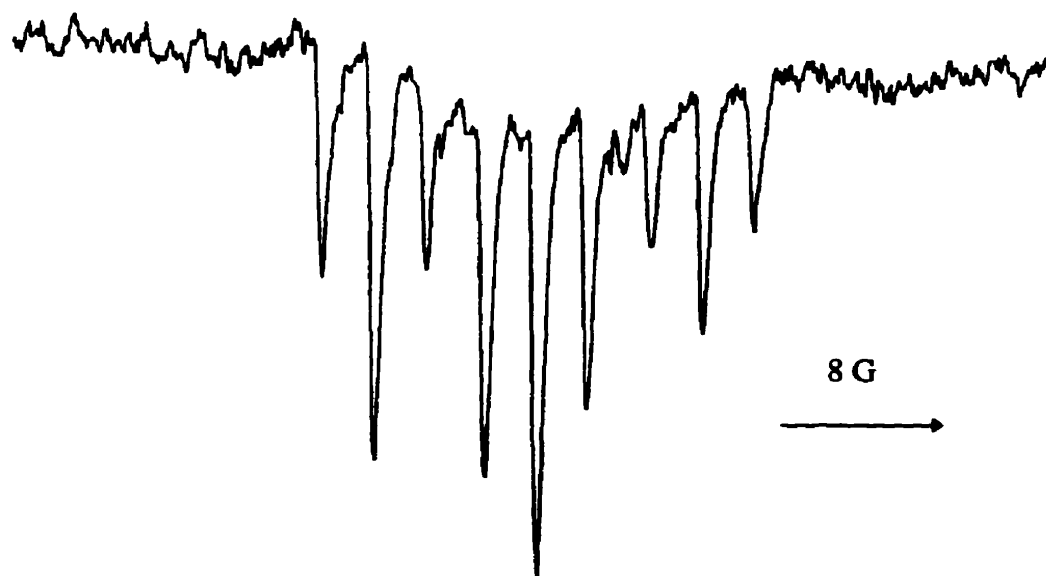


Figure 20. a) Simulated CW spectrum of the 4-hydroxybenzophenone phenoxyl radical and b) CIDEP spectrum from irradiation of 4-hydroxybenzophenone and sodium metabisulfite in mixed solvent 1:2 (v/v) water and ethanol with a few drops of acetic acid.

Although the dominant radical observed may not be the ketyl radical from 4-hydroxybenzophenone, the ketyl radical may have reacted via electron transfer with SO_2 forming the $\text{SO}_2^{\bullet-}$ or reacted with another 4-hydroxybenzophenone molecule.

The addition of sodium hydroxide to a solution of 4-hydroxybenzophenone may form the resonance-stabilized anion, whose UV-visible absorption spectrum is entirely different to the molecule in neutral or acidic media, as shown earlier in Figure 10. Figure 21. shows the spectrum recorded from irradiation of 4-hydroxybenzophenone (3 mM) and sodium metabisulfite (60 mM) with sodium hydroxide, (1 pellet in 5 ml) in a mixed solvent 1:2 (v/v) water and ethanol.

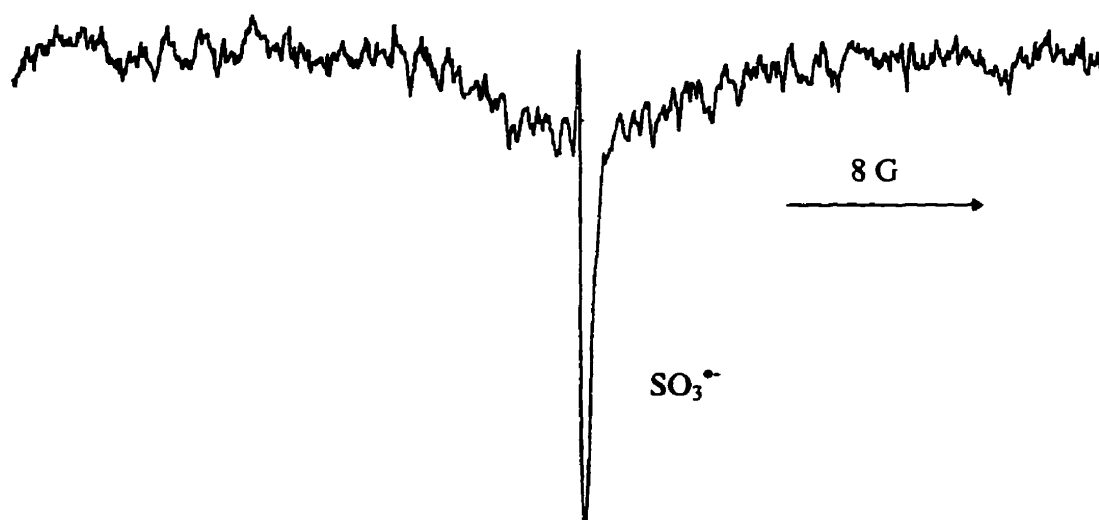


Figure 21. CIDEP spectrum from irradiation of sodium metabisulfite and 4-hydroxybenzophenone in mixed solvent 1:2 (v/v) water and ethanol with sodium hydroxide.

Only one emissive line is observed and is consistent with $\text{SO}_3^{\bullet-}$. This could indicate electron transfer to the anion of 4-hydroxybenzophenone. The broad emissive multiplet which is also present cannot be definitively assigned.

4.4 PHOTOOXIDATION OF 4-HYDROXYBENZOPHENONE BY HYDROGEN DONATION

4.4.1 Steady State Photolysis of 4-Hydroxybenzophenone with di-t-Butyl Peroxide Monitored by UV-Visible Absorption Spectrophotometry.

Photolysis of di-t-butyl peroxide is expected to produce a singlet pair of identical radicals as shown in Equation 14.



Photolysis ($\lambda > 300$ nm) of 4-hydroxybenzophenone (10 mg) in a mixed solvent 1:1 (v/v) di-t-butyl peroxide and dichloromethane (5ml) leads to formation of a cloudy yellow solution which precipitates under prolonged irradiation. Removal of the supernatant leaves a yellow precipitate which is soluble in methanol. After irradiation, the UV-visible absorption spectrum of the yellow precipitate dissolved in methanol shows a broadening of the absorption peak at 350 nm and an absorption tail into the 500 nm range after irradiation. This may be interpreted as hydrogen abstraction by t-butoxyl radicals which abstract the hydroxyl hydrogen from 4-hydroxybenzophenone forming the anion and t-butyl alcohol which is insoluble in the non-polar solvent.

An experiment with 4-hydroxybenzophenone (10 mg) in dichloromethane (5 ml) with a few drops of t-butyl peroxide suggests that the absorption peak at 295 nm, which is consistent with a π,π^* band, was decreased upon irradiation ($\lambda > 300$ nm). This suggests possible removal of the hydroxyl hydrogen by t-butoxyl radicals as shown in Figure 22.

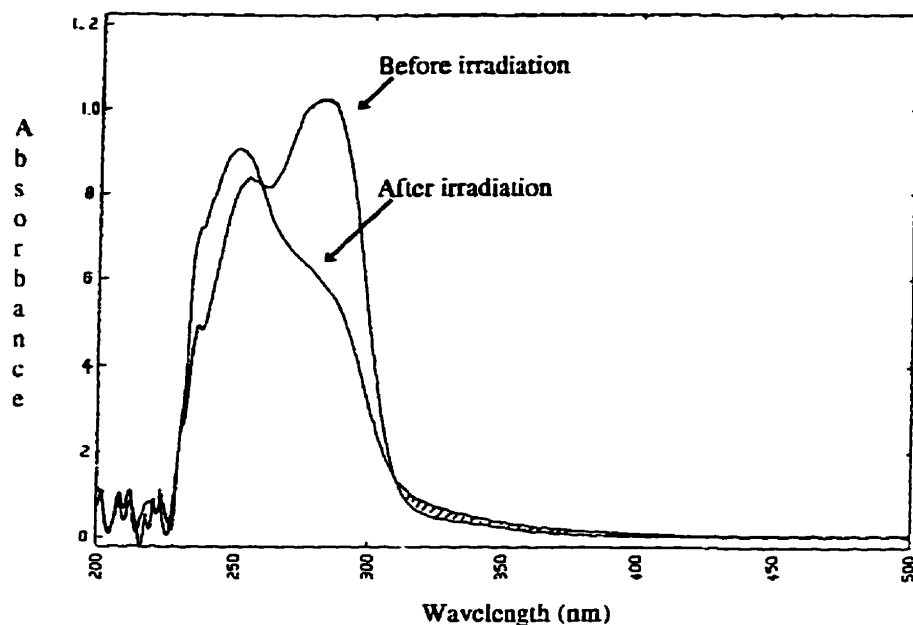


Figure 22. Absorption spectra of 4-hydroxybenzophenone with a few drops of di-tert-butyl peroxide in dichloromethane, before and after irradiation for several minutes, $\lambda > 300$ nm.

4.4.2 Photolysis of 4-Hydroxybenzophenone with Duroquinone in Benzene

The excited state of duroquinone undergoes ISC from an excited singlet to triplet state on the absorption of light, with a quantum yield of approximately 1 in ethanol or in water.³¹ The excited states can decay by many processes, but photoreduction is a major mode which can proceed via electron transfer or hydrogen abstraction. When the triplet state of the quinone lies below the triplet state of the molecule being quenched, electronic energy transfer can also occur. However, if electron transfer is energetically feasible, such reaction is often favoured. As can be seen in Table 4., oxygen, amines and phenol are very effective triplet quenchers for the excited triplet state of duroquinone.^{32,33}

Quantum yields for reduction of 0.5-1.0 are common for quinones with low-lying n,π^* states. Substitution of quinones by electron-donating groups give rise to low-lying π,π^* states with an accompanying decrease in photoreduction reactivities from which a comparison to 4-hydroxybenzophenone can be made. The substituent effects on reaction rates can be accounted for by a change in reduction potentials and by the nature and energy of the excited states. Although theory predicts that π,π^* states have an intrinsic reactivity which is two to four orders of magnitude less than the n,π^* states, when both levels are energetically close, the observed reactivity is due to the thermally equilibrated population of the two states.³⁴

Table 4. Quenching Rate Constants for Duroquinone in Different Solvents.

Quencher/ Hydrogen Donor	Solvent	$k_q (M^{-1}s^{-1})$	Reference
Oxygen	Toluene	2.1×10^9	32
Triethylamine	Toluene	3.6×10^8	35
Phenol	Ethanol	2×10^8	36
Acetone	Ethanol	5×10^4	33
IPA	Ethanol	1.8×10^4	37
Ethanol	Ethanol	$(0.64-1.6) \times 10^4$	35

The photoreduction of quinones remained controversial with regard to whether the primary reaction of the triplet state of quinones was an electron transfer or direct hydrogen atom abstraction. In basic alcoholic media, however, it is generally considered

to involve hydrogen abstraction from the solvent by the quinone. This is followed by dissociation of the semiquinone radical QH^\bullet to the semiquinone anion radical, as shown below in Equation 15. The initial polarization of the quinone triplet is transferred to both the semiquinone and the ketyl radical.



In the absence of basic media, disproportionation results in the formation of the hydroquinone, QH_2 and the presence of QH^\bullet has been indicated by ESR flash photolysis studies.¹⁸



Duroquinone's lowest triplet excited state shows a high abstraction reactivity toward ethanol and cyclohexane. However, changing the solvent to a 2:1 (v/v) mixture of water and ethanol reveals that ${}^3\text{DQ}^*$ does not abstract hydrogen, but rather an electron, from ethanol.³¹ CIDEP experiments with 4-hydroxybenzophenone were carried out with duroquinone with the desire to see the radical derived from 4-hydroxybenzophenone after hydrogen abstraction.

Photolysis of a solution of isopropyl alcohol (5 ml) and duroquinone (10 mg) leads to a signal which should theoretically be 13 lines from the radical anion. As shown in Equation 16, the neutral semiquinone radical (QH^\bullet) rapidly ionizes to the quinone radical anion ($\text{Q}^{\bullet-}$) and a proton. Addition of acetic acid (a few drops in 5 ml), keeps the

equilibrium to the left in Equation 16 and five of the seven septets, are observed due to primarily emissive TM polarization plus some RPM contribution as seen in Figure 23 a).

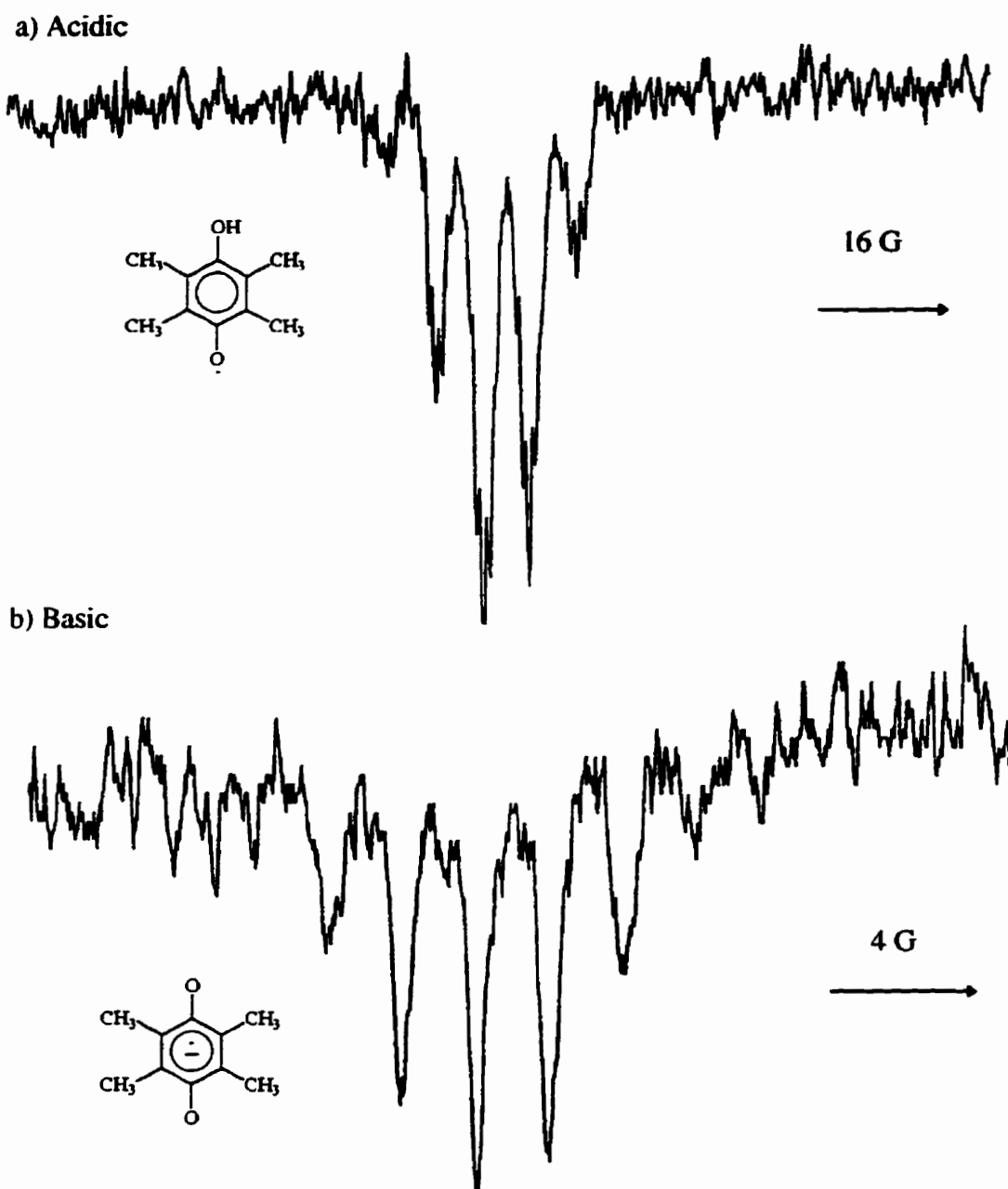


Figure 23. CIDEP spectra from irradiation of duroquinone in a) acidic and b) basic isopropanol.

Figure 23. a) appears to be E*/A in nature i.e. mainly E with some A/E superimposed. The addition of a few drops of sodium hydroxide (1 pellet in a few ml of water) in place of the acid leads to observation of the quinone radical anion with five of the thirteen lines being easily seen in Figure 23 b).

With 4-hydroxybenzophenone (2 mM) as the hydrogen donor, photolysis of an acidic (few drops of acetic acid in a 5 ml) benzene solution with duroquinone (20mM), leads to a strong emissive spectrum with five of the seven multiplets very clearly seen in Figure 24.

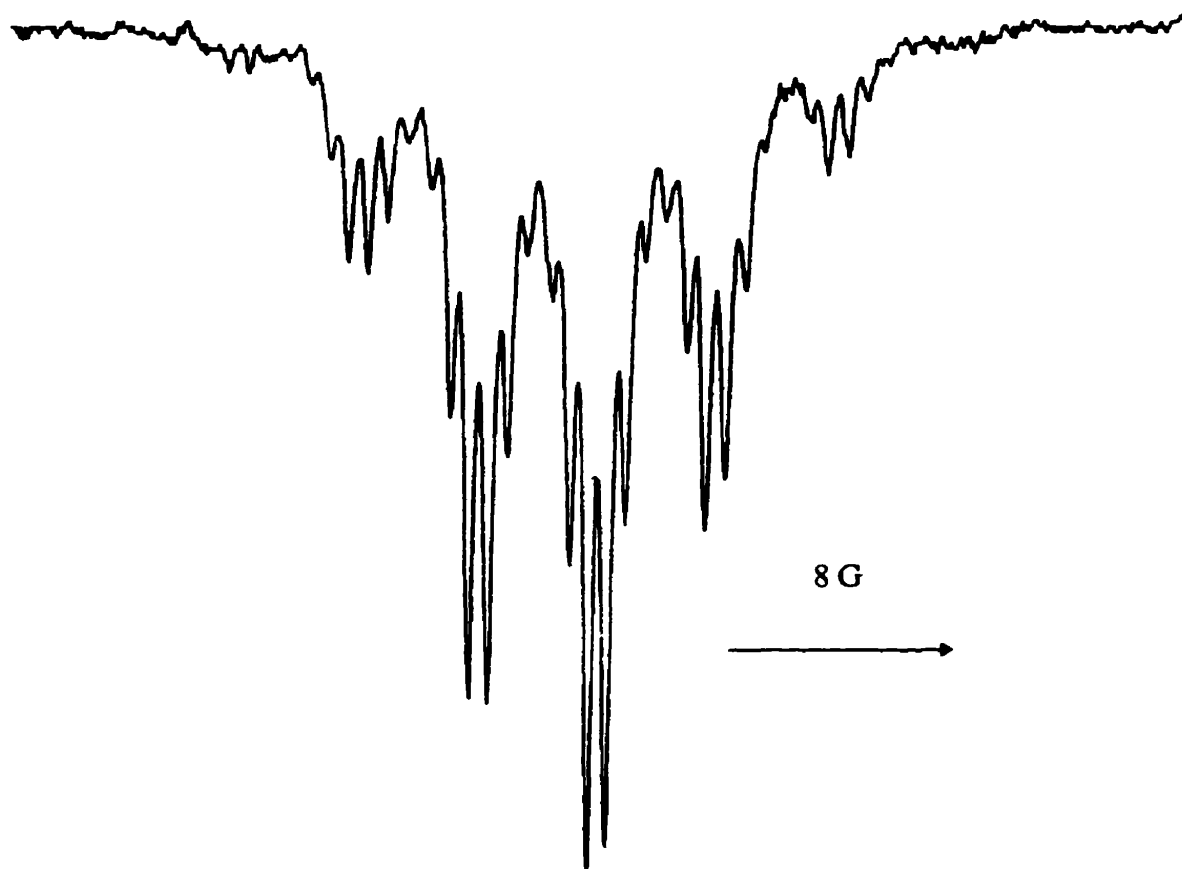


Figure 24. CIDEP spectrum from irradiation of 4-hydroxybenzophenone and duroquinone in benzene with acetic acid.

Experiments with phenol and duroquinone in acetonitrile with a few drops of acetic acid show five of the seven multiplets of the neutral semiquinone radical. In a similar experiment with a few drops of sodium hydroxide an emissive multiplet consistent with the semiquinone radical anion is observed. The latter spectrum presumably arises from the electron transfer from phenol to duroquinone. The failure of the observation of a similar result with 4-hydroxybenzophenone in acetonitrile with a few drops of sodium hydroxide indicates that it probably does not undergo hydrogen abstraction or electron transfer under basic conditions like phenol.

4-Hydroxybenzophenone can, therefore, donate hydrogen in neutral or acidic media and may be considered as a phenol. The bond dissociation energy of the hydroxyl hydrogen in 4-hydroxybenzophenone in comparison with phenol and the other substituted phenols is shown below in Table 4.³⁸ It can be seen that 4-hydroxybenzophenone has a high bond dissociation energy. Nevertheless the possibility of self-reaction whereby a photoexcited 4-hydroxybenzophenone abstracts a hydrogen from another ground state 4-hydroxybenzophenone molecule may be an important pathway which precludes the observation of the 4-hydroxybenzophenone ketyl radical.

Table 5. The Bond Dissociation Energies (BDE) of Various Phenols.

Phenol	BDE ^a (kJ mol ⁻¹)
4-Nitrophenol	392
4-Hydroxybenzophenone	383
Phenol	372
2,6-Dimethylphenol	354
1-Naphthol	348
2,6-Di-t-butylphenol	340

^a Estimate from $BDE(\text{kJ mol}^{-1}) = 1.37 \text{ pK}_{\text{HA}} + 23.06 E_{\text{ox}}(\text{A}) + C$ from F.G. Bordwell and X-M. Zhang, *J. Phy. Org. Chem.*, 8, 529 (1995)

4.4.3 Photolysis of 4-Hydroxybenzophenone with Pyruvic Acid

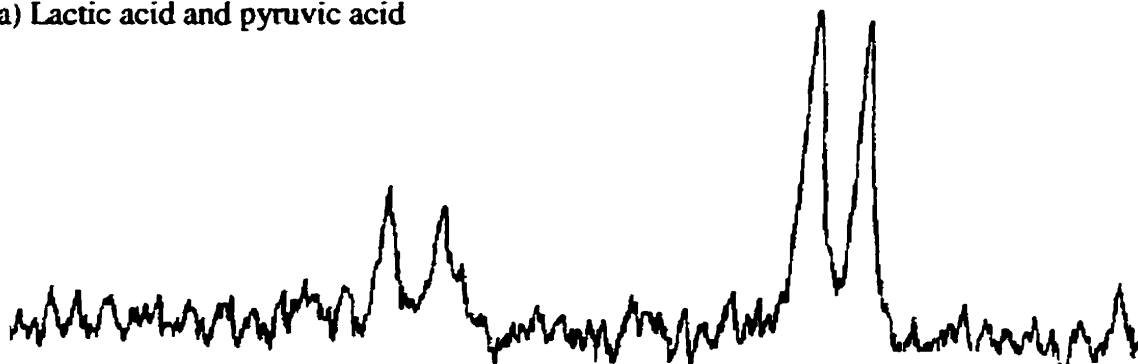
Pyruvic acid is well known to effect hydrogen abstraction from many hydrogen donors and a spectrum of four doublets can be obtained by photolyzing pyruvic acid with lactic acid which forms two equivalents of the ketyl radical as shown below, in Equation 18. The radical is characterized by a quartet of doublets, ($a_{\text{CH}_3}=18.2\text{G}$) and ($a_{\text{OH}}=2.8\text{G}$) which is in agreement with previous work.³⁹



Photolysis of pyruvic acid and lactic acid 1:1 (v/v) gives a spectrum consistent with the ketyl radical. Two of the four doublets are shown in Figure 25 a) which has a pattern characteristic of absorptive polarization from the TM and E/A from the RPM.

This is consistent with hydrogen abstraction by pyruvic acid as observed by other workers.⁴⁰ Irradiation of 4-hydroxybenzophenone (6 mM) in pyruvic acid, at 308 nm, gave the spectrum shown in Figure 25 b). The spectrum shows the presence of a radical consistent with the pyruvic acid ketyl radical in E*/A form and an emissive multiplet. The multiplet is suggestive of the phenoxy radical of 4-hydroxybenzophenone due to hydrogen abstraction by pyruvic acid.

a) Lactic acid and pyruvic acid



b) 4-Hydroxybenzophenone and pyruvic acid

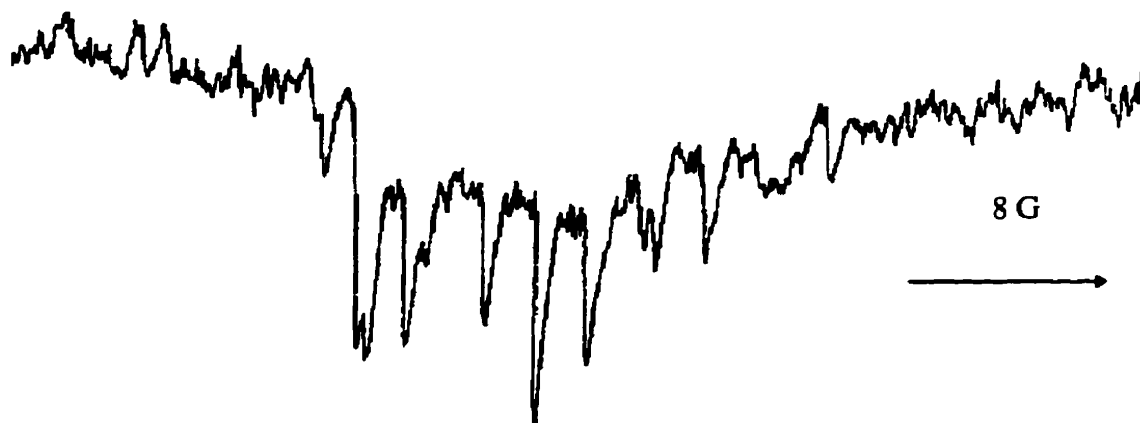


Figure 25. CIDEP spectra from irradiation of a) lactic acid and b) 4-hydroxybenzophenone in pyruvic acid.

CHAPTER FIVE

CONCLUSIONS

The current work has demonstrated that 4-hydroxybenzophenone does not appear to have an absorption band which is suggestive of a n,π^* transition. 4-Hydroxybenzophenone exhibits a marked solvent shift in a mixed solvent of 1:2 (v/v) water and ethanol with added sodium acetate. This is probably due to deprotonation of the phenolic hydroxyl group with likely formation of a resonance stabilized anion. The carbonyl group of 4-hydroxybenzophenone is less readily photoreduced to form the ketyl radical or ketyl radical anion in alcoholic solvents than benzophenone.

The high sensitivity of the CIDEP technique has, however, suggested that 4-hydroxybenzophenone undergoes photoreduction to form its ketyl radical with good hydrogen donors such as phenols. This is consistent with the observation of the phenoxyl radical from the phenol and the broad underlying multiplet which is suggestive of the 4-hydroxybenzophenone ketyl radical. The failure of an observation of the ketyl radical from isopropanol or lactic acid, indicates that photoreduction of 4-hydroxybenzophenone to form its ketyl radical in these hydrogen donors is inefficient. Other mechanisms such as self-reaction may become dominant in these solvents.

The photoreduction of the triplet state of 4-hydroxybenzophenone to form its ketyl radical anion with sulfur-oxygen anions may occur. The dominant radical observed, however, is thought to be the 4-hydroxybenzophenone phenoxyl radical and not the 4-hydroxybenzophenone ketyl radical which suggests photooxidation and not

photoreduction. It is possible that self-reaction may rapidly convert the ketyl radical to the phenoxyl radical or that rapid reaction with $\text{SO}_3^{\bullet-}$ or $\text{SO}_2^{\bullet-}$ may occur.

In summary, in the presence of molecules that can abstract hydrogen, 4-hydroxybenzophenone is reactive towards hydrogen abstraction as a donor and not as an acceptor.

Further work could involve experimentation with various concentrations of reactants, sequential time delays, different radiation wavelengths and different solvent systems. In particular, CIDEP experiments, with irradiation of 4-hydroxybenzophenone in non-polar solvents, should be undertaken in an attempt to resolve the ketyl radical derived from 4-hydroxybenzophenone and the corresponding counter radicals.

REFERENCES

1. G. J. Karvarnos and N.J. Turro, *Chem. Rev.*, **86**, 401 (1986).
2. P.J. Wagner, *Top. Curr. Chem.*, **66**, 1 (1979).
3. J.A. Bell and H. Linschitz, *J. Am. Chem. Soc.*, **85**, 528 (1963).
4. N.J. Turro, Modern Molecular Photochemistry, Benjamin Cumming, Menlo Park, (1978).
5. P.W. Atkins, Quanta: A Handbook of Concepts, 2nd Edition, Oxford University Press, New York, 104 (1991).
6. See, for example, P.W. Atkins, Physical Chemistry, 4th Edition, Oxford University Press, New York, 558 (1990); J.E. Wertz, J.R. Bolton, Electron Spin Resonance: Elementary Theory and Practical Applications, McGraw Hill, New York (1972); J.K. Kochi, (Ed.), Free Radicals, J. Wiley & Sons, New York, 2, 436 (1973); Poole C.P. Jr., ESR: A Comprehensive Treatise on Experimental Techniques, 2nd Edition, J. Wiley & Sons (1983).
7. See, for example, J.K.S. Wan, S.K. Wong and D.A. Hutchinson, *Acc. Chem. Res.*, **7**, 58 (1971); K.A. McLaughlan and D.G. Stevens, *Acc. Chem. Res.*, **21**, 54 (1988); N. Hirota, K. Tominaga and S. Yamauchi, *Bull. Chem. Soc. Japan*, **68**, 2997 (1995); K.A. McLaughlan and D.G. Stevens, *Acc. Chem. Res.*, **21**, 54 (1988); F.J. Adrian, *J. Chem. Phys.*, **61**, 11, 48 (1974); J.K.S. Wan in Advances in Photochemistry, J.N. Pitts and G.S. Hammond, (Eds.), K. Gollnick and D. Grosjean, (Ass.Eds.), John Wiley & Sons Inc., New York., 283 (1980) (and references therein).
8. J.B. Hendrickson, D.J. Cram and G.S. Hammond, Organic Chemistry, 3rd Edition, McGraw Hill, New York, 878 (1970).
9. C. Reichardt, Solvents and Solvent Effects in Organic Chemistry, VCH: Weinheim, Germany (1988).
10. M. Hoshino and M. Koizumi, *Bull. Chem. Soc. Jpn*, **45**, 2731 (1972).
11. M. Hoshino, *J. Phys. Chem.*, **91**, 6385 (1987).
12. T.S. Godfrey, G. Porter and P. Suppan, *Discuss. Faraday Soc.*, **31**, 194 (1965).
13. J.C. Scaiano, *J. Am. Chem. Soc.*, **102**, 7747 (1980).

14. K. Kuwata and H. Murai, *J. Phys. Chem.*, **95**, 6247 (1991).
15. H. Miyasaka and N. Mataga, *Bull. Chem. Soc. Jpn.*, **63**, 131 (1990).
16. K. Tominaga, S. Yamauchi and N. Hirota, *J. Chem. Phys.*, **88**, 553 (1988).
17. M.C. Depew, S. Emori and J.K.S. Wan, *Res. Chem. Int.*, **12**, 275 (1989).
18. M.C. Depew and J.K.S. Wan, in The Chemistry of the Quinoid Compounds, **2**, 963 (1988). S. Patai and Z. Rappoport, (Eds.), Wiley Interscience, London (and references therein).
19. Y. Kajii, M. Fujita, H. Hiratsuka, K. Obi, Y. Mori and I. Tanaka, *J. Phys. Chem.*, **91**, 2791 (1987).
20. P.K. Das, M.V. Encinas and J.C. Scaiano, *J. Am. Chem. Soc.*, **103**, 4154 (1981).
21. O. Brede, H. Orthner, V. Zubarev and R. Hermann, *J. Phys. Chem.*, **100**, 7097 (1996); I.A. Shkrob and A.D. Trifunac, *Radiat. Phys. Chem.*, **46**, 97 (1995); O. Brede, *Macromol. Symp.*, **100**, 71 (1995).
22. I. Loeff, A. Treinin and H. Linschitz, *J. Phys. Chem.*, **96**, 5264 (1992).
23. I. Loeff, A. Treinin and H. Linschitz, *J. Phys. Chem.*, **115**, **20**, 8933 (1993).
24. J.C. Scaiano, *J. Photochem.*, **2**, 81 (1973).
25. M. Fischer and P. Warneck, *J. Phys. Chem.*, **37**, 15111 (1996).
26. D.A. Holman and D.W. Bennett, *J. Phys. Chem.*, **98**, 13300 (1994).
27. M.C. Depew, P.Y. Jiang and J.K.S. Wan, *Res. Chem. Intermed.*, **23** (1997), in press.
28. A.S. Jeevarajan and R.W. Fessenden, *J. Phys. Chem.*, **96**, 1520 (1992).
29. R.S. Pemberton, M.C. Depew, C. Heitner and J.K.S. Wan, *J. Wood Chem. and Techn.*, **15**, **1**, 65 (1995).
30. P. Neta, R.E. Huie and A.J. Harriman, *J. Phys. Chem.*, **91**, 1606 (1987).
31. E. Amouyal and R. Bensasson, *J. Chem. Soc., Faraday Trans.*, **73**, **1**, 1561 (1977).
32. A.P. Darmanyan, *Chem. Phys. Lett.*, **96**, 383 (1983).

33. R. Scherer and M. Gratzel, *J. Am. Chem. Soc.*, **99**, 865 (1977).
34. S.J. Formosino, *J. Chem. Soc., Faraday Trans.*, **74**, 2 (1978).
35. P.W. Atkins, A.J. Dobbs and K.A. McLauchlan, *Chem. Phys. Lett.*, **29**, 616 (1974).
36. A.J. Elliot and J.K.S. Wan, *J. Phys. Chem.*, **82**, 444 (1978).
37. D.R. Kemp and G. Porter, *Proc. R. Soc. Lond. A.*, **326**, 117 (1971).
38. F.G. Bordwell, J-P. Cheng, *J. Am. Chem. Soc.*, **113**, 1736 (1991).
39. K.Y. Choo and J.K.S. Wan, *J. Am. Chem. Soc.*, **94**, 7127 (1975).
40. A.I. Grant and K.A. McLauchlan, *Chem. Phys. Lett.*, **101**, 120 (1983).