Photoreaction of Valerophenone in Aqueous Solution

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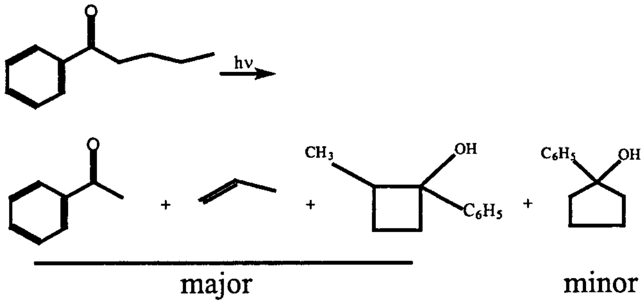
Kinetics and products of the photoreaction of the phenyl ketone valerophenone were investigated as a function of temperature, pH, and wavelength in aqueous solution. Under these conditions ($<10^{-4}$ M), the photoreactions are pseudo-first-order with respect to valerophenone concentration. Type II quantum yields for photoreaction were close to unity throughout the 290−330 nm spectral region and in the temperature range from 10 to 40 °C. The quantum yields for the photoproducts were 0.65 ± 0.04 for cleavage to acetophenone and propene and an overall yield of 0.32 ± 0.03 for cyclization to two cyclobutanols at 20 °C. A small amount of 1-phenylcyclopentanol (∼2% yield) also was formed. These photoreactions were quenchable by additions of the triplet quenchers sorbic alcohol or sorbic acid, and Stern−Volmer plots were linear up to at least 80% quenching of the photoreactions. On the basis of quenching studies with steady-state irradiations, the triplet lifetime of valerophenone at 20 °C was estimated to be 52 ns, ∼7 times longer than that observed in hydrocarbon solvents. Since the triplet lifetime is controlled by intramolecular hydrogen abstraction, these results indicate that the rate constant for H abstraction is significantly lowered in aqueous media. The slower H abstraction in aqueous solution is attributed to stabilization of the excited π,π^* state by water and vibronic mixing and slight inversion of the reactive n,π^* triplet and the unreactive π,π^* triplet states. This interpretation also is supported by changes in the UV absorption spectra of phenyl ketones in water compared to organic solvents. Red shifts, compared to the polar organic solvent acetonitrile, were observed in the $\pi-\pi^*$ transitions of valerophenone and acetophenone, reflecting stabilization of the excited π,π^* state by water. Other results indicated that the quantum yields for valerophenone photoreaction are pH-independent from pH 9 to pH 2 but decrease significantly below pH 2. The decrease at low pH is attributed to quenching of triplet reactivity via protonation of the excited triplet state. The use of valerophenone as a convenient actinometer for studies in water is discussed; its half-lives during midday exposure to summer sunlight in temperate latitudes are <30 min.

Introduction

Investigations of the photoreactions of aromatic alkyl ketones over the past several decades have provided a wealth of information concerning structural and solvent effects on triplet reactivities[1−9] and reactivities of biradical intermediates.[2,3,5,9−15] Aromatic ketones with hydrogen on γ- and δ-carbons on their alkyl side chains photoreact via their triplet states to produce 1,4- or 1,5-biradicals, respectively, that disproportionate back to starting ketone, cleave, or cyclize,[9−15] as illustrated by the valerophenone photoreactions shown below. Most studies of these reactions have been conducted in organic solvents, with a few in mixtures of polar organic solvents with water such as wet acetonitrile. Investigations of hydrophobic ketones in aqueous media have been limited by their low water solubility. Recent advances in analytical methodologies, however, have made it possible to conveniently study organic photoreactions in aqueous solutions.



Previous studies have indicated that the kinetics and products of aromatic ketone photoreactions may be altered significantly in water compared to organic solvents. First, the high polarity of water can have important effects on the relative energies of the lowest-lying n,π^* and π,π^* excited states of aromatic ketones. Solvent- and substituent-induced changes in the relative levels and mixing of reactive n,π^* triplets and unreactive π,π^* triplets of aromatic alkyl ketones are well-known to affect their triplet reactivities.[5−7] The π,π^* triplets are stabilized in high dielectric and hydrogen-bonding organic solvents.[16,17] Moreover, kinetics and products of the photoreactions of aromatic alkyl ketones with γ- and δ-carbon−hydrogen bonds can be altered by interactions of polar, hydrogen-bonding solvents with their 1,4- and 1,5-hydroxy biradical intermediates.[9−15] Polar and basic solvents such as water slow the disproportionation of biradical intermediates to starting ketone,

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thus enhancing biradical lifetimes and overall quantum efficiencies for photoreaction compared to nonpolar solvents.[5,6,13,14] Moreover, it has been suggested that the longer biradical lifetimes in hydrogen-bonding solvents reflect increased distance between radical sites, which decreases triplet to singlet intersystem crossing rates,[12] although subsequent studies by other groups appear to have discounted this interesting possibility.[11,14,15] Because biradical reactions and excited state reactivity are sensitive to conformational effects,[8,9,12,15] hydrophobic interactions between water and aromatic ketones that alter conformations of the alkyl moieties might have significant effects on the kinetics and product distributions. Finally, acid−base reactions of triplet ketones potentially may be an important consideration in aqueous media. Triplet aromatic ketones are 10^5-10^6 times more basic than corresponding ground state ketones, and protonation of triplets can influence aromatic ketone photophysics and photochemistry under strongly acidic conditions.[18−20]

Our interest in factors that affect the photoreactions of ketones in water is prompted by several considerations. First, aromatic ketone derivatives are increasingly being used as photoreactive probes that selectively generate free radical sites in aqueous biochemical studies.[21] Furthermore, carbonyl compounds likely are involved in photoreactions that affect carbon, nutrient, sulfur, and metal cycles in freshwater and marine environments and in atmospheric condensed phases.[22,23] Photoreactions enhance the biological availability of persistent natural organic polymers such as humic substances, cleaving them into lower molecular weight organic compounds that can be readily assimilated by microorganisms.[22,24,25] These aqueous photoreactions also produce gases such as carbon dioxide,[24d] carbon monoxide,[24c] and carbonyl sulfide,[22d] with concurrent reduction in UV absorbance that permits deeper penetration of harmful solar UV-B radiation (290−315 nm) into aquatic environments.[26] Reactive oxygen species produced on absorption of solar UV radiation have been shown to mediate these reactions.[27]

Although structural elucidation of the photoreactive chromophores in humic substances are scarce, a few studies suggest that carbonyl compounds are involved. The lignocellulose component of organic matter in freshwater and coastal marine environments has been shown to be photoreactive.[22d,28] Past research has demonstrated that type II cleavage of ketone moieties incorporated within synthetic organic polymers enhances their environmental degradability by sunlight.[29] Photochemical degradation of marine organic matter to produce various alkenes has been proposed to involve type II reaction of UV-absorbing carbonyl compounds.[30] A recent study further demonstrated that aromatic ketones likely are involved in photosensitized and free radical oxidations in condensed phases of the atmosphere (clouds, fog, and rain droplets).[23] In addition to their role in environmental reactions, photoreactions of phenyl alkyl ketones such as valerophenone may provide a convenient actinometer for measuring irradiance fluxes in the UV-B region (290−315 nm). Finally, synthetic contaminants that are introduced into lakes, rivers, and oceans by human activities have carbonyl constituents, for example, *p,p′*-dichlorobenzophenone, and studies of their photoreactions can provide useful information for mathematical models of their environmental fate and transport.[31] Photoreactions of halogenated phenyl ketones can be used to probe the excited state behavior of haloaromatic compounds.[32]

In this paper, we examine the kinetics and products of photoreactions of the phenyl alkyl ketone valerophenone in dilute aqueous solution as a function of temperature, wavelength, and pH. The results of these studies are then compared to previous observations in organic solvents, and the use of valerophenone for UV actinometry in aqueous systems is discussed.

Experimental Section

Chemicals. Valerophenone (99+%) and acetophenone were obtained from Aldrich Chemical Co. They were further purified by flash chromatography through silica gel followed by distillation under reduced pressure. Sorbic alcohol (2,4-hexadien-1-ol) was purchased from Aldrich, purified by distillation, and stored under nitrogen at 4 °C to slow oxidation. Reagent grade sorbic acid from Aldrich was used as received. Potassium ferrioxalate was either synthesized in this laboratory from $K_2C_2O_4$ and $FeCl_3$ as described by Hatchard and Parker or obtained from Alfa Products.[34] The results were identical for both the synthesized and commercial products. The Fe(II) analytical reagents, 1,10-phenanthroline and ferrozine, were obtained from Alfa Products and Aldrich Chemicals, respectively. A standard solution of 1000 ppm of Fe in 2% HNO_3 was obtained from Fisher Scientific. Reagent grade hydroxylamine hydrochloride from Matheson Scientific was used, and the source of ammonium acetate was Baker Chemical. Water was treated by a Barnstead Nanopure model D-7331 purification system. Acetonitrile (HPLC grade) from Burdick and Jackson and *n*-hexane (Sigma, 99+% pure) were used as received. All other chemicals were of reagent grade quality and used as received. Generally, phosphate buffer (5.0 mM) was used for the pH region 4.6−8.0. Addition of dilute HCl solution was used to adjust the pH below this range, and addition of dilute NaOH solution was employed above this range.

Preparation of Solutions for Kinetics Studies. Valerophenone solutions were prepared using two different methods for comparison. Stock solutions of valerophenone were prepared in pure water as previously described.[33] The aqueous solubility of valerophenone was found to be 8.1×10^{-4} M at 25 °C. This solution was diluted to concentrations $<7.0 \times 10^{-4}$ M for the measurements of UV−visible absorption spectra and for the photochemical kinetics studies. Alternatively, 5.0×10^{-6} M aqueous solutions of valerophenone that contained 0.05 vol % acetonitrile were prepared from 0.010 M stock solutions of valerophenone in acetonitrile. After addition of the acetonitrile solution to the water, the resulting solution was stirred magnetically for at least 2 h to ensure complete dissolution of the valerophenone. The photoreaction of valerophenone occurred at the same rate in pure water and in the solution containing 0.05% CH_3CN. Removal of oxygen by bubbling the solution with nitrogen or argon had no effect on the rate constant within experimental error, although bubbling did reduce the initial concentration of valerophenone by volatilization. Therefore, most of the photochemical studies were conducted using nondegassed water containing trace amounts of CH_3CN. The solutions were freshly prepared each day. Aliquots (3.00 mL) of the 5.0×10^{-6} M solutions of valerophenone were added to either 100 × 13 mm Pyrex test tubes (for the temperature studies) or 1.00 cm path length quartz cells (for the quantum yield studies) and tightly capped. Acidic solutions (0.100 N sulfuric acid) of potassium ferrioxalate were stored in the dark. All glassware was soaked in dilute hydrochloric acid before use to remove any traces of iron.

Irradiation Conditions. Temperature and pH studies were conducted by parallel irradiation of solutions in a rotating turntable photoreactor with a high-pressure quartz mercury vapor lamp.[33] Wavelengths below 300 nm were filtered out by a borosilicate sleeve in the immersion well surrounding the lamp. To isolate the 313 nm line for some of the experiments, the borosilicate filter was supplemented by a 1.0 cm thick solution of 0.002 M potassium chromate in 3% aqueous potassium carbonate. The photoreactor was immersed in an insulated water bath; a GCA Precision Scientific Group RDC 40 cooling system maintained the temperature of the photoreactor within ±0.2 °C by pumping thermostated coolant through copper tubing in the water bath. Quenching studies (313 nm) also were conducted in this photoreactor at 20 and 30 °C, as were studies that compared the kinetics of air-saturated and nitrogen-saturated solutions. The latter were conducted using completely filled, gastight tubes with Teflon-lined septum caps. Quantum yield studies of valerophenone at various wavelengths were conducted using the Spectral Energy Monochromatic Illumination System, which consists of a 1000-W xenon lamp, double monochromator, and sample compartment equipped with a magnetic stirrer. The band-pass of the monochromator was set at ±1.0 nm. To determine light intensity, well-stirred aqueous solutions of acidic potassium ferrioxalate (0.15 M in 0.1 N H_2SO_4) were used as actinometer. At each wavelength, three replicate samples of both valerophenone and potassium ferrioxalate solutions were irradiated with stirring, alternating valerophenone and ferrioxalate solutions.

Equipment. For the kinetics studies valerophenone and acetophenone were analyzed by direct injections of the aqueous solutions into an HPLC system consisting of a Waters Associates high-performance liquid chromatograph model 600 pump, a variable wavelength UV−visible detector (set at 245 nm), a Hewlett-Packard ChemStation for data acquisition and integration, and a Whatman Partisil ODS-3 column (70−30 or 75−25% acetonitrile/water as mobile phase). Electronic absorption spectra were measured using a Shimadzu 265 UV−visible spectrophotometer. Measurements of pH were made using an Orion Ross 8102 combination electrode calibrated using NIST buffers. Photoproduct mass spectra were obtained using a Hewlett-Packard Series II model 5890 gas chromatograph equipped with an HP 5972 Series mass selective detector with limited mass range.

Photoproduct Identification. An aqueous solution (50 mL) of valerophenone (4.00×10^{-4} M) was irradiated using borosilicate-filtered radiation from a mercury lamp until reaction had reached the first half-life. For comparison, a solution of valerophenone (4.00×10^{-4} M) in acetone was irradiated under the same conditions. The concentrations of valerophenone and acetophenone from the aqueous photoreaction were determined using HPLC analysis. The solution was transferred to a separatory funnel and extracted three times using methylene chloride. The extract was concentrated, dried over anhydrous sodium sulfate, and analyzed by GC/mass spectrometry using nonpolar and polar capillary columns to separate the products. Two capillary columns were used to separate the photoproducts: (1) a Chiraldex (β-cyclodextrin B-DM) column (30 m × 0.25 mm) purchased from Astec Co.; (2) a DB-5 column (30 m × 0.25 mm) that was purchased from J&W Co. The polar Chiraldex column was used isothermally (150 °C) with carrier gas flow at 1 mL min^{-1}, and the nonpolar DB-5 column, also with carrier gas flow at 1 mL min^{-1}, was programmed with an initial isothermal period at 55 °C (1.0 min) followed by a steady increase in temperature at a rate of 2 °C min^{-1}. Three major products were observed on both columns, in addition to unreacted valerophenone. Under the conditions used for the analysis, low molecular weight gases, for example, propene, were not detectable. The product that eluted first on both columns was acetophenone (*m*/*z* 120, 105, 77, 51, 43, 39). Two other products that were isomers of valerophenone also appeared. Although the retention times were similar, it was possible to achieve baseline separation on both capillary columns. Their mass spectra were virtually identical (*m*/*z* 162, 134, 133, 120, 105, 91, 78, 77, 51, 39), and their retention times were strongly affected by the nature of the GC column. On the nonpolar column, these products appeared prior to valerophenone, and on the polar column, they emerged after the valerophenone peak. Irradiation of valerophenone in acetone produced two isomers with the same retention times and mass spectra as those produced in water. Earlier studies demonstrated that *trans*-1-phenyl-2-methylcyclobutanol was the major cyclic photoproduct in acetone and the other isomer was the corresponding cis isomer.[35] The trans isomer also was the major cyclobutanol formed in water. In contrast to retention times observed on packed columns such as QF-1/Carbowax, the trans isomer emerged after the cis isomer on the capillary columns. The concentrations and yields of the cyclobutanols were computed from peak integrations of data obtained with flame ionization detection, assuming that the cyclobutanols had the same response as valerophenone. The yield of acetophenone was directly determined from the HPLC chromatographic data. In addition to these major products, another minor product (~2% yield, assuming the same response as valerophenone) was observed on the DB-5 column. The mass spectrum (*m*/*z* 144, 129, 115, 91, 77) exactly matched the spectrum of 1-phenylcyclopentanol that is included in the database of the NIST Mass Spectrometry Data Center.

Kinetics Procedures. The molar absorptivities of the iron(II)−ferrozine and iron(II)−phenanthroline complexes used to analyze Fe(II) in the ferrioxalate actinometers were determined experimentally under the same conditions used to analyze the ferrioxalate actinometers. The molar absorptivity of the Fe(II)− ferrozine complex [1.08×10^{-4} M ferrozine, $(1-10) \times 10^{-6}$ M Fe(II)] at pH 4.55 (0.020 M ammonium acetate buffer) was determined experimentally to be 27 300 L mol^{-1} cm^{-1} at 562 nm, in close agreement with previous studies.[36] The molar absorptivity of the Fe(II)−phenanthroline complex was 11 200 L mol^{-1} cm^{-1} at 510 nm, as previously reported.[34]

Two methods were used in the analysis of the potassium ferrioxalate actinometer (0.15 M). In the first, exposed potassium ferrioxalate solution (100 μL) was added to 3.00 mL of 1.0×10^{-4} M phenanthroline and allowed to react in the dark for 1 h. The absorbance of the solution was then measured at 510 nm. In the second method, exposed potassium ferrioxalate (60 μL) and 1 M ammonium acetate buffer (150 μL) were added to 3.00 mL of 1.0×10^{-4} M ferrozine. The reaction was complete within 5 min, after which time the absorbance of the solution was measured at 562 nm. The absorbances of unexposed blanks were determined using the same procedure. All analyses were performed in triplicate. The number of einsteins per liter that entered the cell per unit time (I_λ) was calculated using the equation

$$I_\lambda = (\mathrm{Abs}/\epsilon_{\mathrm{Fe}})(V_f/V_i)\,(t)/\Phi_{\mathrm{Fe(II)}} \qquad (1)$$

where Abs is the difference between absorbances of blank and exposed potassium ferrioxalate; ϵ_{Fe} the experimentally determined molar extinction coefficient for Fe(II) complex; V_f the final volume, either 3.21 or 3.10 mL; V_i the volume of solution taken, either 60 or 100 μL; *t* the exposure time in h; and $\Phi_{\mathrm{Fe(II)}}$ the quantum yield for Fe(II) photoproduction (from Hatchard and Parker[34]).

TABLE 1: Comparison of Yields of Valerophenone Type II Photoproducts in Water (20 °C)[a] and in Organic Solvents[b]

	yield, %		*trans:cis* ratio for	
solvent	acetophenone	cyclobutanols	cyclobutanols	reference
water	65 ± 4	32 ± 3[c]	2.4	this study
acetonitrile	85	15	2	37
tert-BuOH	90	10	2	37
acetone	*d*	*d*	2[e]	35, this study
	d	*d*	5.4[f]	this study
benzene	82	18	4.2	37, 38
hexane	87	13	5	37

[a] Valerophenone concentration 4.0×10^{-4} M for cyclobutanol measurements; acetophenone yield determined at valerophenone concentrations ranging from 5.0×10^{-6} to 4.0×10^{-4} M; average yield ± standard deviation for five replicates reported. [b] Valerophenone concentration 0.10 M except where noted. [c] 1-Phenyl-1-cyclopentanol also formed in ~2% yield. [d] Not determined. [e] 5% valerophenone in acetone; determined by elution chromatography in ref 35 and gas chromatography in this study. [f] 5.0×10^{-4} M valerophenone in acetone.

Valerophenone and acetophenone were analyzed by HPLC as noted above, using injections of 100 μL of the reaction solution. Concentrations were determined by comparing peak areas in the reaction mixtures to calibration standard curves. All chromatographic data were acquired and analyzed by computer using the HP ChemStation software.

Lotus 123 (v. 5) was used to conduct exponential regressions for the valerophenone or acetophenone concentrations versus time data. Pseudo-first-order rate constants were calculated from slopes of the regressions.

Results

Photoproducts in Water. Type II cleavage to acetophenone and propene and cyclization to two isomeric 1-phenyl-2-methylcyclobutan-1-ols were the dominant pathways for the photoreaction of valerophenone in water. The cyclic product, 1-phenylcyclopentanol, also formed with a low yield (~2%). As discussed below, the total quantum yields for these photoreactions are close to unity. The photoreaction can be followed by HPLC using reverse phase columns with a UV detector (245 nm). Acetophenone is the major detectable product. The cyclobutanols absorb UV radiation more weakly than valerophenone or acetophenone and are difficult to detect at submicromolar concentrations. In these studies the cyclobutanols and the cyclopentanol were identified by combined GC/MS and/or by comparisons of their retention times to authentic samples that were prepared by valerophenone photolysis in acetone.[35] At 20 °C cleavage accounted for 65 ± 3% of the photoreaction and cyclization for 32 ± 3% (mean ± standard deviation of results for five separate experiments). Although cleavage was, as expected, the predominant reaction, the ratio of cleavage to cyclization was considerably lower than that observed in organic solvents (Table 1). The difference is particularly pronounced in the case of comparisons with polar solvents, for example, alcohols, where cleavage usually accounts for 90% or more of the type II reaction and cyclization is a very minor reaction pathway. In aprotic solvents the trans:cis ratio of cyclobutanol products is in the 4−5 range; this ratio drops to 2.6 in water, about the same as observed in polar organic solvents (Table 1).

Quantum Yields. Studies of aromatic ketone photoreactions involving steady state irradiations in organic solvents often have been conducted under optically opaque conditions with low conversions to photoproducts. Under these conditions the photoreaction kinetics are zero-order with respect to ketone concentration and the photoreaction rate is proportional to the quantum yield for reaction as well as the light flux. The conditions are usually quite different in aqueous media. Due to solubility limitations, the concentrations of such ketones are typically sufficiently low that only a small fraction of the incident radiation is absorbed (i.e., with light path lengths <10 cm). Under these conditions the fraction of light absorbed by the ketone, and hence its light absorption rate, is approximately proportional to its concentration. Thus, the overall photoreaction rate of the ketone and the rate of production of nonphotoreactive products can be described by pseudo-first-order kinetic expressions.[43,44] The first-order rate constant is proportional to the reaction quantum yield and to the cross-product of the irradiance and the molar absorptivity of the ketone integrated over all the effective wavelengths of the light source. Moreover, because the photoproducts are fully exposed to the radiation, their buildup occurs only if they are much less photoreactive than their precursor.

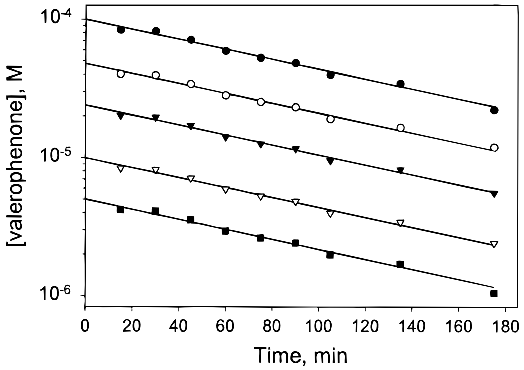


Figure 1. Effects of changing concentration on valerophenone photokinetics in aqueous solution. Slopes of first-order plots were linear out to 2 half-lives ($r^2 > 0.95$) with no change within experimental error over a 20-fold variation in initial concentration.

The solubility limit of valerophenone in water is 8.1×10^{-4} M, and even at its maximum solubility, the quantum yields could not be determined under conditions in which the radiation was completely absorbed. With continuous irradiations slopes of log plots of valerophenone concentration versus time were linear (r^2 values typically >0.95) with the same slopes at initial concentrations ranging from 5.0×10^{-6} to 1.0×10^{-4} M (Figure 1). An initial concentration of 1.0×10^{-5} M was used for most of the studies reported here. The quantum yield at wavelength λ ($\Phi_{\mathrm{II},\lambda}$) was computed from the first-order rate constants [$k_{\mathrm{obs}}(\lambda)$] using the equation[43,44]

$$\Phi_{\mathrm{II},\lambda} = \frac{k_{\mathrm{obs}}(\lambda)}{2.303(I_\lambda)(\epsilon_\lambda)(l)} \tag{2}$$

where I_λ is defined by eq 1, ϵ_λ is the molar absorptivity of valerophenone at wavelength λ, and l is the light path length. Ferrioxalate actinometry was used to measure I_λ. Quantum yields were found to be close to unity in the 290−330 nm range (Table 2). The quantum yield for acetophenone formation (0.65 ± 0.03) remained approximately constant out to >2 half-lives, and acetophenone was shown to be stable in this wavelength region during the period used for the irradiations. A series of experiments at various temperatures in the 10−20 °C range with borosilicate-filtered polychromatic radiation ($\lambda > 300$ nm) or 313 nm radiation from a mercury lamp at constant light intensity indicated that the first-order rate constant and thus the average Φ_{II} were temperature-independent (Table 2).

Variations in pH had no detectable effect on Φ_{II} over a broad pH range (from pH 9 to 2). At pH <2, however, the rate

TABLE 2: Molar Absorptivities and Quantum Yields for Total Norrish Type II Reaction (Cleavage and Cyclization) of Valerophenone (20 °C)

wavelength, nm	temp, °C	molar absorptivity (ϵ_λ) (M^{-1} cm^{-1})	quantum yields [$\Phi_{II}(\lambda)$][a]
290	25 ± 1	755	0.97 ± 0.03[b]
300	25 ± 1	287	0.98 ± 0.03[b]
310	25 ± 1	117	0.98 ± 0.04[b]
313	25 ± 1	101	0.99 ± 0.03[b]
320	25 ± 1	71.8	0.98 ± 0.04[b]
330	25 ± 1	40.2	0.97 ± 0.05[b]
313	10.0 ± 0.2	101	0.97 ± 0.04[b]
313	20.0 ± 0.2	101	0.99 ± 0.03[b]
313	30.0 ± 0.2	101	0.98 ± 0.03[b]
polychromatic	10.0 ± 0.2	*d*	0.98 ± 0.05[c]
polychromatic	20.0 ± 0.2	*d*	0.99 ± 0.05[c]
polychromatic	30.0 ± 0.2	*d*	0.98 ± 0.05[c]
polychromatic	40.0 ± 0.2	*d*	0.98 ± 0.05[c]

[a] Mean of triplicate experiments (±standard deviation); band-pass was ±1.0 nm for studies at 25 °C. [b] Computed using eq 1. [c] Average value computed by multiplying quantum yield at 313 nm by ratio of rate constant at temperature of experiment to that at 20 °C. [d] Not applicable.

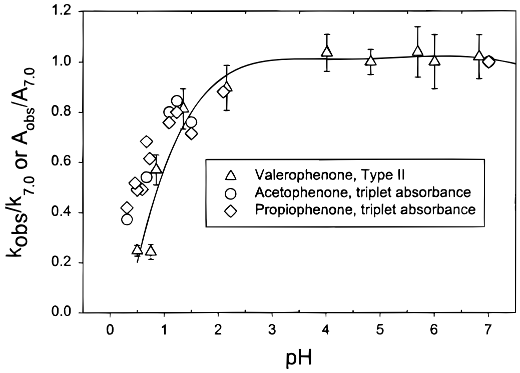


Figure 2. pH effects on first-order rate constants for photoreaction of valerophenone (1.0×10^{-5} M) and on triplet−triplet absorbances of acetophenone and propiophenone.[18] The valerophenone results are represented by a line fit to the data using a polynomial expression in Sigma Plot. The pH effects on the triplet absorbances of acetophenone and propiophenone were previously measured by Shizuka and Kimura.[18] All data were normalized to results at neutral pH.

constants dropped sharply with increasing acidity (Figure 2). To compare pH effects on valerophenone triplets with those previously determined for acetophenone and propiophenone triplet−triplet absorbance in 4:1 H_2O/CH_3CN,[18] the data for all three ketones were normalized to results obtained at pH 7 (Figure 2). This comparison shows that the titration plots for triplet absorbance reduction with acetophenone and propiophenone were quite similar to those observed for reduction of the valerophenone photoreaction rate constants in water.

UV Absorption Spectra. Unsubstituted phenyl ketones absorb UV radiation in the UV-B (280−315 nm) and UV-C (200−280 nm) spectral region (Figure 3). There is a pronounced solvent effect on the spectrum in this region, with a blue shift of the weakly absorbing n−π* transition in the UV-B region and a red shift of the π−π* (^1L_a) transition (237 to 245 nm λ_{max}) in changing from organic solvents to water. The shifts occur even in changing from polar solvents, such as acetonitrile, to water. Interestingly, the shift in going from nonpolar hexane to polar acetonitrile (+1.1 kcal mol^{-1}) is considerably lower than the shift in going to water (+4.2 kcal mol^{-1}).

Quenching Studies. The type II quantum yield for valerophenone can be reduced (and half-life increased) by addition of the triplet quenchers sorbic alcohol (2,4-hexadien-1-ol) or sorbic acid (2,4-hexadienoic acid) to the system. As shown in Figure 4, Stern−Volmer quenching plots of valerophenone photoreaction in water are linear out to >80% quenching. In Figure 4, $(\Phi_{II})_o$ and Φ_{II} are the quantum yields without and with added quencher, respectively; [Q] is the quencher concentration; and $k_q\tau$ is the quenching constant. At higher concentrations of sorbic acid, the rate constant also was reduced somewhat by light screening by the quencher. After correction for the light screening effect, the quenching constant for sorbic acid was the same as that for sorbic alcohol within experimental error. The value of the quenching constant in water in temperature-dependent, ranging from 152 M^{-1} at 20.0 °C to 138 M^{-1} at 30.0 °C. Therefore, when added quencher is present, the temperature must be well-defined to ensure reproducible, accurate results. Stern−Volmer quenching constants in water

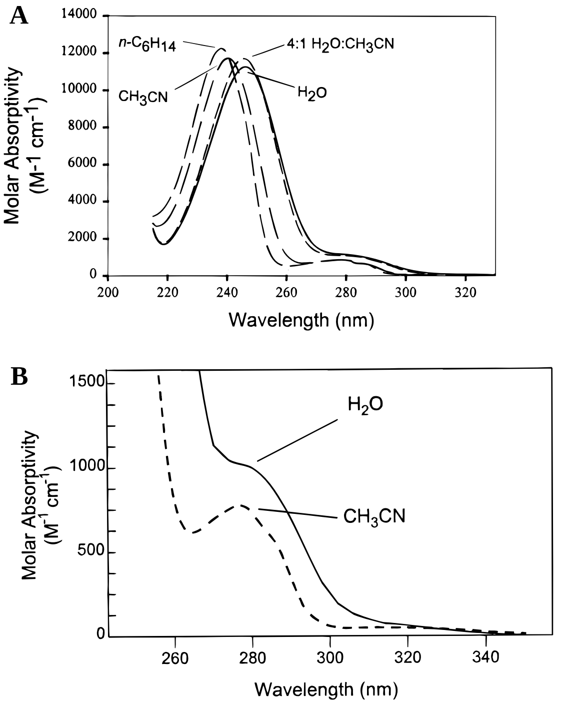


Figure 3. UV absorption spectra of valerophenone in aqueous solution compared to spectra in organic solvents and an acetonitrile/water mixture: (A) comparison of spectra in hexane, acetonitrile, 25% acetonitrile/water, and water, illustrating red shift in π−π* transitions; (B) long-wavelength part of absorption spectra compared, illustrating blue shift of n−π* transition and red shift of π−π* transitions in going from the polar organic solvent, CH_3CN, to water.

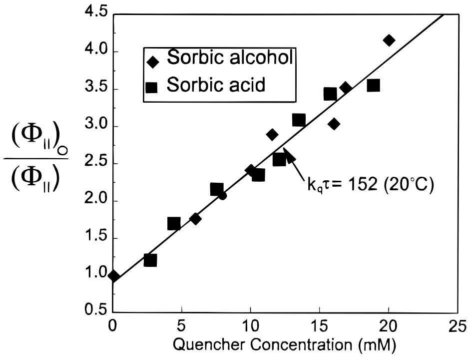


Figure 4. Comparison of Stern−Volmer quenching plots of valerophenone photoreaction in water at 20 °C using sorbic alcohol or sorbic acid as triplet quenchers. Quenching effect is the same for both dienes. The quenching data for sorbic acid were corrected for light screening effects; maximum correction was <10%.

TABLE 3: Quenching Constants and Triplet Lifetimes for Valerophenone in Water and Organic Solvents

solvent	$k_q\tau$, M^{-1}	k_q x 10^{-9}, M^{-1} s^{-1}	τ x 10^9, s	reference
water	152 ± 5[a]	2.9[b]	52	this study
	138 ± 4	3.6	38	
wet acetonitrile	63	7.2	8.7	39
acetonitrile	38	11	3.6	37
tert-BuOH	40	2.3	14	37
methanol	90	5.5	16	39
benzene	36	5.0	7.2	37
			5.6	7
hexane	78	11	7.2	37

[a] Mean of triplicate experiments (± standard deviation). [b] Quenching constant for sorbic alcohol in water.[33,40] Value at 30 °C computed by assuming temperature changes in k_q are inversely proportional to changes in viscosity of water (from ref 42).

are considerably higher than such constants that have been observed for valerophenone in organic solvents (Table 3).

Discussion

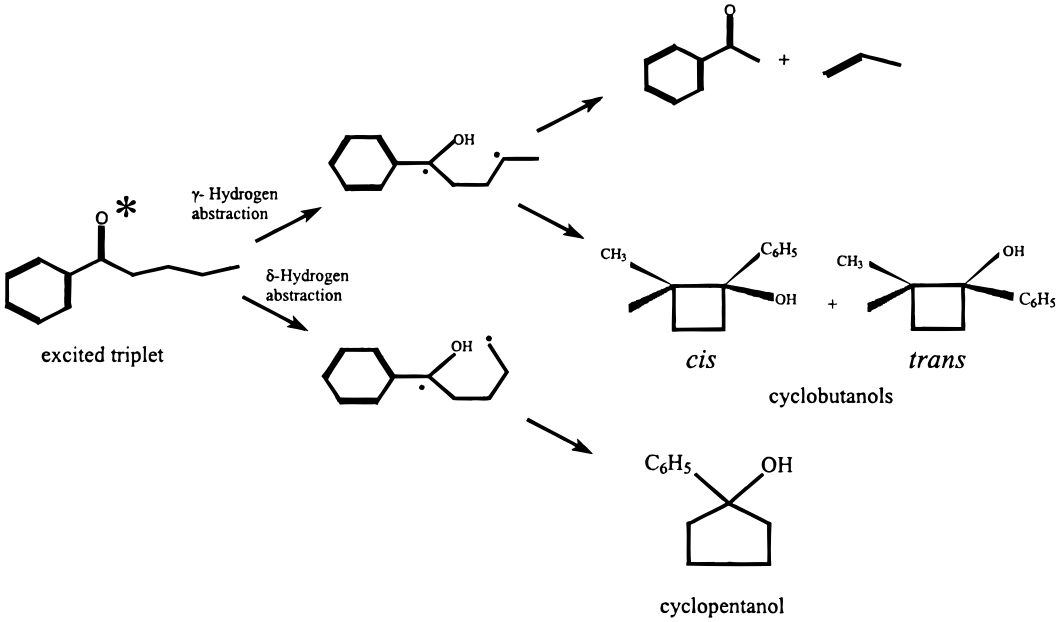
As discussed in the Introduction, solvent and pH effects on the photoreaction kinetics and products of phenyl alkyl ketone depend on several factors that relate to the nature of the lowest triplet as well as interactions of the biradical intermediate with the solvent. In the following discussion, we first consider the relationship between spectroscopic data, quenching results, and past studies of phenyl ketones to infer the effects of water on the triplet reactivity of valerophenone. The effects of water on the biradical reactivity are then discussed, taking into account the quantum yields and photoproduct distributions. Next, the mechanism for reduction of the quantum yield with increasing acidity is considered. Finally, we consider the potential use of valerophenone as an aqueous actinometer for the ultraviolet spectral region.

Triplet Reactivity in Water. Previously determined spectroscopic results have substantiated that phenyl alkyl ketones have lowest n,π* and π,π* excited states that are close in energy and vibronically coupled.[6,16,17] Stabilization of the π,π* triplet states occurs on addition of electron-releasing substituents such as *p*-methoxyl groups to the aromatic ring or on an increase in solvent dielectric constant and hydrogen-bonding ability.[6] Such stabilization is evidenced by red shifts of the $\pi-\pi$* electronic transitions, which are generally located in the 235−300 nm spectral region. Shifts in the λ_{max} of the second benzene transition (the ^1L_a band) in the UV absorption spectrum are most readily apparent. Water has a high dielectric constant and it is an excellent H-bonding solvent, so the ^1L_a band of valerophenone shifts significantly to longer wavelengths in aqueous media compared to organic solvents. In comparison, the λ_{max} for the ^1L_a band is shifted only slightly in going from nonpolar hexane to polar acetonitrile (Figure 3). The same is true for "wet" acetonitrile: addition of 2% up to 10% water hardly affected the UV absorption spectrum. Likewise, the triplet lifetime of valerophenone in acetonitrile and "wet" acetonitrile is similar to its lifetime in hydrocarbon media (Table 3). However, the spectrum in a 4:1 water/acetonitrile mixture was almost the same as in water (Figure 3). In water the S-^1L_a transition is lowered ~8 nm, corresponding to 4.2 kcal mol^{-1}, compared to hydrocarbon solvents (Figure 3A). At the same time the n−π* transition is increased ~2 kcal mol^{-1}, because the lowest n,π* state is less polar than the ground state (Figure 3B).

The solvent shift observed in water is remarkably similar to the shift observed when a *p*-methyl substituent is added to the benzene ring of valerophenone.[6] Interestingly, the triplet lifetime of valerophenone is prolonged to the same extent by *p*-methyl substitution[6] as by a solvent change from hydrocarbon to water (Table 3); ~7-fold increases were observed in both cases. Spectroscopic evidence indicates that *p*-methyl substitution inverts the reactive n,π* and unreactive π,π* triplets of phenyl ketones, thus reducing their triplet reactivities.[6] By analogy, the spectral shift and triplet lifetime increase observed for valerophenone in water support the proposition that these triplets have inverted in response to solvent perturbations. Wagner et al.[6] have argued that the lower triplet reactivity likely results from a combination of vibronic mixing of the n,π* and π,π* states which leads to a lowest energy, unreactive π,π* mixed state and a slightly more energetic reactive n,π* mixed triplet. It was further proposed that these two states may be at an equilibrium in which most of the triplets populate the unreactive state, thus reducing overall triplet reactivity. In further support of this idea, Scaiano's group[7] provided temperature studies of the triplet lifetimes of methoxyl-substituted phenyl ketones that indicated that their photoreactions proceed from reactive upper n,π* triplets that are thermally populated from lower energy, less reactive π,π* triplets. Detailed studies of temperature effects on the triplet lifetime of valerophenone were not conducted, but it was shown that the quenching constant dropped ~10% to 138 ± 4 in going from 20 to 30 °C, corresponding to an ≈37% increase in triplet reactivity (Table 3). The increase in reactivity in this temperature range is larger than that observed in organic solvents for valerophenone,[7,8] possibly reflecting a larger activation energy required to populate reactive upper n,π* triplets in aqueous medium.[6,7] Although valerophenone triplets are longer lived in water than in organic solvents, oxygen quenching of the triplets still is not experimentally detectable in air-saturated water, where O_2 concentrations are only ~0.2 mM.

Biradical Reactions in Water. As expected from earlier studies, the quantum yield for type II cleavage and cyclization of valerophenone jumps to nearly unity in water (Table 2), sharply higher than in nonpolar organic solvents. The quantum yield in water is essentially temperature- and wavelength-independent when the n−π* absorption band is irradiated (Table 2). Previous studies have established that the photoreactions of aromatic alkyl ketones with γ- and δ-carbon−hydrogen bonds can be altered by interactions of their 1,4- and 1,5-hydroxy biradical intermediates with polar, hydrogen-bonding solvents.[9−15] Abstraction of hydrogen from the γ-carbon to produce the 1,4-biradical is strongly favored over abstraction of the δ-hydrogen to form the 1,5-biradical (Scheme 1). Polar and basic solvents such as water slow the disproportionation of biradical intermediates to starting ketone, thus enhancing biradical lifetimes and overall quantum efficiencies for photoreaction compared to nonpolar solvents.[5,6,13,14] On the basis of previous observations that the cyclization efficiency decreases in changing from hydrocarbon solvents to alcohols,[37,38] we anticipated little or no cyclization in water. Instead, cyclization accounted for almost one-third of the reaction of the 1,4-hydroxy biradicals in water (Table 1). In addition to the cyclobutanols, we detected a small amount (~2% yield) of 1-phenylcyclopentanol, a product from cyclization of the 1,5-biradical formed from δ-hydrogen abstraction.[15,38] On the other hand, the 2.4:1 trans to cis ratio of cyclobutanols formed in water (Table 1) parallels the usual reduced selectivity that is observed in alcohols.[37] We assume that the higher yield of cyclic products may reflect the great sensitivity of the cleavage reaction to conformational factors.[8,9,12,15] Cleavage of a 1,4-biradical can occur efficiently

SCHEME 1



only in a conformation in which the two p orbitals are parallel to the carbon−carbon σ bond being broken. Hydrophobic interactions between water and the alkyl chain of the biradical may inhibit the assumption of such a conformation.

Although it has been reported that oxygen can affect the yield of type II photoproducts from valerophenone through scavenging of the biradical intermediate in organic solvents and “wet” acetonitrile,[41] these effects are observed at oxygen concentrations that are well above that found in air-saturated water. Oxygen is at least an order of magnitude less soluble in water than in organic solvents and, consequently, oxygen in air-saturated water (concentration is ∼0.2 mM) has no detectable quenching effect (<5%).

pH Effects on Valerophenone Photoreactions. Previous studies of the acid−base reactions of excited organic compounds have employed methods involving assumptions that the proton transfer reactions are sufficiently rapid that acid−base equilibrium can be achieved during the lifetime of the excited state. In the case of phenyl ketones, acid−base equilibria were shown to be established within the triplet state lifetimes of acetophenone, propiophenone, benzyl phenyl ketone, and benzophenone.[18,19] pK_a values of protonated triplet ketones were found to be 5−6 orders of magnitude larger than those for the corresponding ground states. pH effects on the triplets were quantified by measuring changes in the triplet absorbance and lifetime, both of which are reduced with increasing acidity.[19] The lifetimes of the phenyl alkyl ketones, acetophenone and propiophenone, are 1−1.2 μs in circumneutral water, ∼20−24 times longer than that of valerophenone. The shorter lifetime of the latter is attributable to its rapid γ-hydrogen abstraction, a reaction that is not available in the case of acetophenone and propiophenone. Thus, valerophenone triplets have considerably less time to reach acid−base equilibrium. To compare pH effects on valerophenone triplets with those on acetophenone and propiophenone triplets, we compared the previously determined pH dependence for the triplet absorbance data for acetophenone and propiophenone with the kinetic data for valerophenone photoreaction. To facilitate this comparison, the data for all three ketones were normalized to results obtained at pH 7 and a line depicting a polynomial fit to the kinetic data for the valerophenone results was obtained (Figure 2). The comparison shows that the reduction of the valerophenone photoreaction rates in water with decreasing pH was very similar to titration plots for triplet absorbance reduction with acetophenone and propiophenone in 4:1 H_2O/CH_3CN. The UV absorption spectra of phenyl ketones are almost the same in 4:1 H_2O/CH_3CN as in water (Figure 3), suggesting, as discussed above, that the triplet reactivity is about the same in both solvents. Assuming that the solvent difference has minimal influence on the results, these results indicate that acid−base equilibrium is achieved in the case of valerophenone, despite its much shorter excited state lifetime. Using the midpoint of the valerophenone titration curve, we estimate that the triplet pK_a of valerophenone is ∼0.9, within 0.3 unit of the pK_a values reported for the acetophenone and propiophenone triplets.[18] The pK_a for the propiophenone triplet is ∼0.15 unit higher than that for acetophenone,[18] likely due to an inductive effect caused by additional substitution on the alkyl side chain. The slightly higher value for valerophenone also likely is attributable to such an inductive effect.

Valerophenone as an Ultraviolet Actinometer. Valerophenone has long been used as a UV actinometer for laboratory studies in organic solvents.[3,6,14] The present study indicates that it is also a convenient, readily analyzed, optically thin actinometer for studies in weakly absorbing aqueous solutions. Organic solvents cannot be used for such studies due to refractive index effects that amplify the light flux entering the reaction cell. This is particularly true with multidirectional light sources such as sunlight impinging on curved surfaces such as test tubes. The photoreaction rates in dilute aqueous solution are unaffected by the photoproducts that form, and the lifetime of valerophenone is sufficiently brief that air-saturated solutions can be used without significant quenching effects.

Using data and equations discussed earlier, the number of einsteins per liter that enters the cell per unit time (I_λ) can be computed from the first-order rate constant for valerophenone photoreaction. For example, at 313 nm in a reactor with a 1.0 cm path length, a commonly used system for photochemical studies, $I_\lambda = 4.30 \times 10^{-3} k_{obs}$ einstein L^{-1} h^{-1}, where k_{obs} is the pseudo-first-order rate constant expressed in h^{-1}. The photolysis rates and half-lives ($t_{1/2}$) of dilute, aqueous valerophenone under

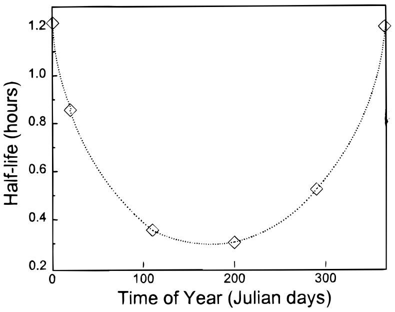


Figure 5. Half-lives computed for valerophenone photoreaction in sunlight on clear days at latitude 40° N. The half-lives were computed using a mathematical model[24c] that uses quantum yields, absorption coefficients, and simulated solar spectral irradiance to compute photolysis rate constants.

polychromatic light sources can be computed using the equations[44,45]

$$\text{rate} = [\mathrm{V}]\int 2.303 j^{-1} E_{\mathrm{o},\lambda}\epsilon_\lambda \Phi_{\mathrm{II},\lambda}\, \mathrm{d}\lambda = k_{\mathrm{obs}}[\mathrm{V}] \tag{3}$$

$$t_{1/2} = 0.693/k_{\mathrm{obs}} \tag{4}$$

where k_{obs} is the pseudo-first-order rate constant for the photoreaction; [V] the valerophenone concentration; $E_{\mathrm{o},\lambda}$ the scalar irradiance at wavelength λ; and j a unit conversion factor that, for example equals 6.02×10^{20} when the irradiance is expressed in units of photons $\mathrm{cm}^{-2}\ \mathrm{s}^{-1}$. The rates in sunlight also can be readily estimated using eq 3 along with mathematical models that simulate the solar spectral irradiance reaching the Earth's surface, the quantum yield data, and molar absorptivities (Table 2).[24c] The computed seasonal changes for this actinometer are illustrated in Figure 5. Half-lives of the valerophenone actinometer with no added quencher are <30 min in full, midday sunlight (July, latitude 40° N) or ~1 order of magnitude shorter than that of the *p*-nitroanisole actinometer.[45] Addition of sorbic acid or sorbic alcohol can be used to adjust the half-life of the valerophenone actinometer. Our computations using eq 3 and simulated solar spectral irradiance indicate that the broad-band irradiance measured by the valerophenone actinometer in sunlight during midday, midsummer at latitude 40° N corresponds to a peak response at 315 nm with a band-pass of ±10 nm.

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