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Journal of Photochemistry and Photobiology A: Chemistry 99 (1996) 93–96

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A: CHEMISTRY

Picosecond investigation of the effect of solvent on the photochemistry of benzoin

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Received 29 February 1996; revised 17 April 1996

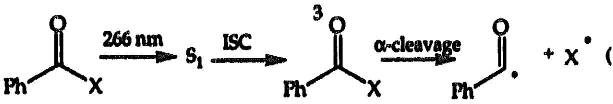
Abstract

Picosecond transient absorption studies of the Type I α-cleavage of the triplet state of benzoin and two derivatives have been investigated as a function of solvent polarity and solvent temperature. The rate of α-cleavage of the triplet state of benzoin increases by a factor of about 50 from hexanes as the solvent to acetonitrile or methanol. Solvent mixtures of hexanes and methanol yield median rates of α-cleavage. The roles of polar and steric factors on the α-cleavage reaction are discussed.

Keywords: benzoin; α-cleavage; Picosecond transient absorption

1. Introduction

In a pioneering investigation of the α-cleavage of ketones Eq. 1, Lewis and coworkers [1] employed the Stern–Volmer analysis of quenching of product yields to determine the triplet lifetimes of benzoin (Bz, Fig. 1) and a number of its derivatives in benzene. All of the measured triplet lifetimes were found to acceptably fit a Hammett plot with $\rho = -1.1$, except for the anomolous behavior of Bz. Although the Hammett relationship predicts that a hydroxy group stabilizes a positive charge better than a methoxy group does, [2] ^{3}Bz cleaves at less than one tenth the rate of its methyl ether (MeBz, Fig. 1).



(1)

The observed Hammett correlation is consistent with a mechanism in which substituents that stabilize a partial positive charge on the cleaving α-carbon lower the barrier to triplet state α-cleavage. Given the widespread use of benzoin derivatives as radical polymerization initiators, [3–6] it seemed of interest to investigate the anomolous behavior of Bz in order to obtain information on the origin of the anomaly Furthermore, the role of conformation on the reactivity of the triplet state of benzophenone (BP) [7,8] towards hydrogen abstraction and electron transfer and of the triplet state of dibenzylketone (DBK) [9] towards α-cleavage have recently been investigated. The major primary photochemical process of Bz is the same as that for DBK (α-cleavage) and, as an aromatic ketone, Bz should have a triplet state whose characteristics are similar to that of BP. Thus, an understanding of Bz's anomolously slow rate of α-cleavage in hexane might provide information of broader significance to ketone photochemistry in general.

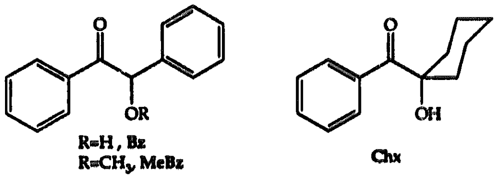


Fig. 1. The ketones studied in this work.

2. Experimental details

Bz is from Aldrich; Chx, from Ciba–Geigy. MeBz was prepared by deprotonating Bz with sodium hydride followed by quenching with methyl iodide and purification by silica column chromatography. All three ketones were >99% pure as measured by gas chromatography (HP5890, SE30 or DB 17 column, flame ionization detection).

Hexanes were from Fisher, ACS grade; methanol from Mallinckrodt, analytical reagent grade; acetonitrile from Burdick and Jackson, UV grade. All three solvents were transparent at 266 nm and were used as received.

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PII S1010-6030(96)04399-7

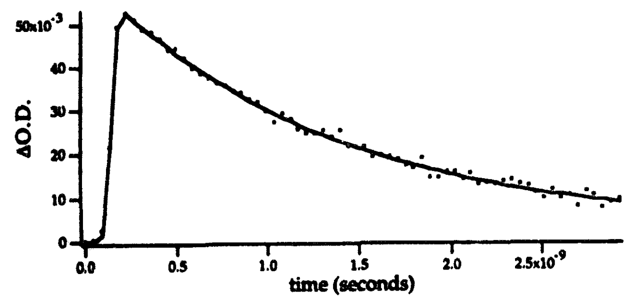


Fig. 2. Kinetic trace of ^{3}Bz in hexanes. Excitation @ 266 nm. Probe @ 355 nm.

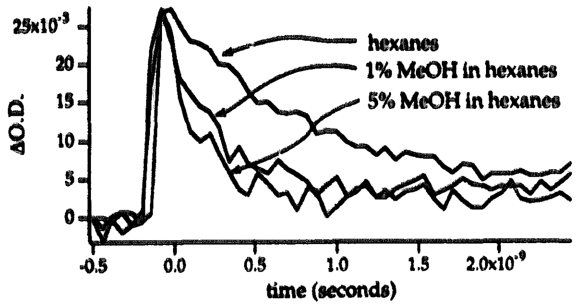


Fig. 3. Effect of added methanol on the rate of α-cleavage of ^{3}Bz in hexanes. Percent methanol is by volume. Peak intensity of traces with added methanol are normalized to that in pure hexanes.

A detailed description of the picosecond pump-probe experiment has been reported elsewhere [10]. The laser is a Continuum (PY61C-10) Nd:YAG (~30 ps FWHM). All samples were pumped at 266 nm (~100 μJ focused to 2 mm at the sample) and probed at 355 nm. The probe intensity is measured by Oriel 71902 UV-enhanced photodiodes interfaced to a Stanford (SRS 250) boxcar integrator.

Samples were prepared so as to exhibit a ground state optical density of 1.5 at 266 nm and were cycled through a 1 cm quartz cuvette throughout the experiment from a ~250 ml reservoir immersed in a temperature controlled water bath.

Typically 100 data points were collected per run. Each point is the average of 25 laser shots and the delay between points is 5–15 ps. The trace shown in Fig. 2 is the average of six runs; those shown in Fig. 3 are the average of two runs and are normalized to the intensity of ^{3}Bz in pure hexanes. Traces shown in this article are point grouped for display purposes.

The observed transient signal results from the convolution of the instrument response function with the absorption of the transient species. The instrument response function results from the convolution of the pump and probe pulse and was fitted to the analytical form of a Gaussian [10].

3. Results

Picosecond pump-probe spectroscopy was employed to directly measure the lifetime of the triplet state of Bz and two related ketones (MeBz and Chx, Fig. 1) as a function of the solvent. The ketones were excited at 266 nm and their triplet concentrations were probed at 355 nm, the absorption maximum of triplet acetophenone [11].

Table 1
Rates of triplet decays of the ketones studied. Errors are estimated from fits of multiple data sets. ᵃ These rate constants are not as accurate as those for Bz and Chx. See text for explanation

Ketone	Solvent	Rate (x10^9 s^{-1})
Bz	hexanes	1.2 ± 0.4
	1% methanol in hexanes	3.8 ± 0.5
	5% methanol in hexanes	8.0 ± 0.3
	methanol	about 50 ᵃ
	acetonitrile	about 50 ᵃ
MeBz	hexanes	about 50 ᵃ
	methanol	about 50 ᵃ
	acetonitrile	about 50 ᵃ
Chx	hexanes	2.6 ± 0.4
	methanol	6.1 ± 0.3
	acetonitrile	4.6 ± 0.4

As an example of the data obtained, Fig. 2 shows the kinetic decay of ^{3}Bz in hexanes. A rate constant for the decay of ^{3}Bz in hexanes of $1.2\text{x}10^9$ s^{-1}, determined by fitting the data to a first order decay, is in good agreement with the value reported by Lewis and coworkers for steady state quenching of ^{3}Bz in benzene [1]. Fig. 3 shows the transient absorption decay of ^{3}Bz in hexanes as a function of added methanol with trace intensity normalized to that of ^{3}Bz in pure hexanes. Table 1 lists the lifetimes of the three ketones shown in Fig. 1 measured by the pulse-probe method in hexanes, acetonitrile, and methanol. Analogous to acetophenone [12], the ketones are expected to intersystem cross from their excited singlet manifold at a rate of about $1\text{x}10^{11}$ s^{-1}. The response function of our experiment is 20 ± 4 ps. The uncertainty in these two values leads to little uncertainty in our fits to transients with lifetimes longer than about 100 ps. However, fitting of the shorter lived transients is not as accurate. For example, changing the rate of intersystem crossing used by our fitting routine from $4\text{x}10^{10}$–$1\text{x}10^{11}$ s^{-1} decreases the fit rate of α-cleavage from $7.0\text{x}10^{10}$–$2.4\text{x}10^{10}$ s^{-1} while increasing the sum of squares residuals by 0.26%. We estimate the triplet lifetime of ^{3}MeBz in all solvents and ^{3}Bz in methanol and acetonitrile as being about $50\text{x}10^{10}$ s^{-1}. We further note that since these shorter lived transients decay at a rate only one tenth as slow as they are formed, their transient absorptions are weak relative to those of the longer lived triplet states.

The lifetime of ^{3}Bz in hexanes as a function of temperature was measurerd and an Arrhenius plot of the data is shown in Fig. 4. From this plot, we obtain activation parameters for the α-cleavage of ^{3}Bz of Ea = 6.7 ± 0.6 kcal mole^{-1} and ln(A) = 32 ± 1.1 (A ≈ $8.5\text{x}10^{13}$ s^{-1}).

4. Discussion

Previous results have demonstated that the dominant primary photochemical reaction of the triplet state of the ketones

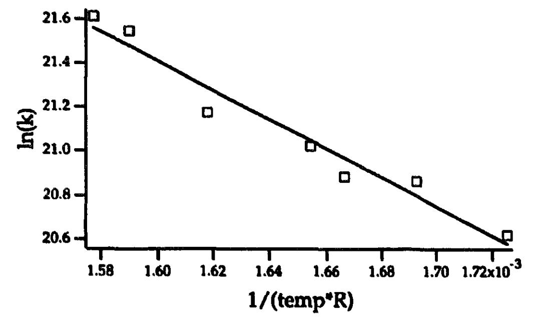


Fig. 4. Arrhenius plot for the α-cleavage of ^{3}Bz in hexanes.

investigated is α-cleavage; therefore, we shall assume the results of Table 1 refer to α-cleavage. From Table 1, it is seen that in hexanes, ^{3}MeBz undergoes α-cleavage about fifty times more rapidly than does ^{3}Bz. However, in methanol or acetonitrile, the two ketones undergo α-cleavage at comparable rates. The rate of α-cleavage of ^{3}Bz increases substantially upon the addition of methanol to hexanes reaching a value about 50 times greater in pure methanol. ^{3}Bz appears to react at comparable rates in methanol and acetonitrile. ^{3}Chx α-cleaves more rapidly in acetonitrile and methanol than it does in hexanes, although the solvent effect is not as dramatic as found for ^{3}Bz.

A Monte Carlo search of the ground state conformations of Bz with Macromodel [13] found that all confomations in the lowest 5 kcal mole^{-1} exhibit an intramolecular hydrogen bond (Fig. 5). In polar (and especially in hydrogen bonding) solvents, intermolecular hydrogen bonding will likely lower the concentration of intramolecularly hydrogen bonded species. This intramolecular hydrogen bond can perhaps control the rate of triplet reaction by (1) changing the extent of ππ* character in the ketone's triplet state and (2) 'locking' the conformation of the α-phenyl ring relative to the carbonyl moiety.

The nature of the triplet states of the ketones in our study is not clear. Triplet acetophenone, based on low temperature phosphorescence, transient absorption, and reactivity towards hydrogen abstraction, [11,14] displays predominantly nπ* character in non-polar solvents and predominantly ππ* character in polar solvents. Since ^{3}ππ* ketones are typically much less reactive towards α-cleavage than ^{3}nπ* ketones [14], it is possible that the intramolecular hydrogen bond Bz exhibits in its ground state in non-polar solvents increases the ππ* character of the ketone's triplet state relative to the triplet state of MeBz which may not form an intramolecular hydrogen bond.

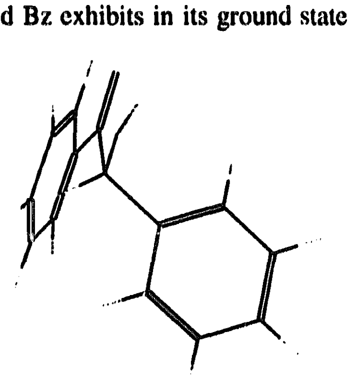
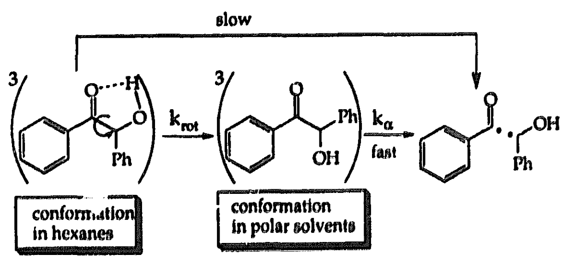


Fig. 5. Global minimum conformation found for the ground state of benzoin by molecular mechanics. See text for details.

An interpretation of an investigation into the triplet state of benzophenone [8] considers the half occupied n-orbital of ^{3}nπ* aromatic ketones as an oxygen p-orbital rotated 90° from the carbonyl π-bond. The phenyl ring is in the plane of the carbonyl bond, thus providing maximum overlap between the phenyl π-system and the carbonyl π-bond and zero overlap between the phenyl π-system and the half filled n-orbital on oxygen. Rotation of the phenyl ring around the carbonyl-phenyl bond decreases the phenyl-carbonyl π-interaction while increasing the overlap between the phenyl π-system and the half-filled n-orbital in oxygen. At 90° rotation, there is no overlap between the phenyl π-system and the carbonyl π-orbitals and maximum overlap between the phenyl π-system and the oxygen n-orbital. An electron may then easily transfer from the HOMO of the phenyl π-system to the oxygen n-orbital creating a ππ* triplet with many characteristics of a charge transfer state — a cation radical localized in the phenyl ring, a formal negative charge on the oxygen, and a radical localized on the carbonyl carbon — a state that would clearly be stabilized both by polar solvents and by hydrogen bonding to the negatively charged carbonyl oxygen. Based on this model, it is not expected that ^{3}MeBz reacts at the same rate in hexanes as in methanol, as observed.

A second possible interpretation of the effect of the intramolecular hydrogen bond of Bz on its triplet state reactivity is available from the results of Wagner and Stratton [15] who showed that the conformation of the phenyl ring in α-phenylcyclohexanone relative to the carbonyl moiety acts as an on/off switch for the triplet state α-cleavage. Computational evidence has recently been produced which indicates that the amount of unpaired electron density delocalized into the phenyl rings of the triplet state of dibenzylketone is sensitive to the conformation of the phenyl ring relative to the carbonyl moiety and conformations with increased unpaired electron density in the phenyl ring experience a lower barrier to α-cleavage. A conformational interpretation of the results is shown in Eq. 2, in which conformations for which there is an intramolecular hydrogen bond are shown to undergo α-cleavage more slowly than conformations for which the bond is broken or structurally absent. The role of polar solvent is to competitively break the intramolecular hydrogen bond.



(2)

It has long been known that substitution to the α-phenyl ring of benzoin and derivatives affects the nπ* absorption of its singlet state [16,17]. This is analogous to earlier observation that β,γ-unsaturated ketones possess enhanced nπ* absorptions. Although this coupling is observed in the singlet manifold, it is perhaps reasonable to assume that similar coupling exists for the triplet as well. Furthermore, strong electronic coupling between the α-phenyl ring and the carbonyl moiety in the triplet states of a number of benzoin acetates has been proposed [16,17].

We included Chx in this study since it presumably displays an intramolecular hydrogen bond similar to that of Bz, but has no α-phenyl ring which may interact with the carbonyl moiety in the ketone's triplet state. As is the case with ^{3}Bz, the lifetime of ^{3}Chx is measurably shorter in the polar solvents acetonitrile and methanol than it is in non-polar hexanes, but as opposed to the 50 time decrease seen for ^{3}Bz, the lifetime of ^{3}Chx decreases by only a factor of two.

Finally, we report Arrhenius parameters for the α-cleavage of ^{3}Bz in hexanes of $Ea = 6.7 \pm 0.6$ kcal mole^{-1} and $A = 8.5\times10^{13}$ s^{-1}. As reference, values reported for the triplet state α-cleavage of 2-methylpentan-3-one [18] in n-hexane/iso-octane solvent are $Ea = 7.2$ kcal mole^{-1} and $A = 3.1\times10^{13}$ s^{-1}. Fragmentation reactions often exhibit large entropic driving forces leading to large Arrhenius pre-exponential factors, since two fragments are created from one. If the triplet state of benzoin reacted from its hydrogen bonded conformation, the triplet radical pair formed would perhaps exhibit an intra-radical hydrogen bond leading to a smaller entropic driving force (and a correspondingly smaller Arrhenius pre-factor) than is normally observed in fragmentation reactions. However, from the Arrhenius parameters we report here, this does not appear to be the case[1]. An intriguing speculation is that the activation parameters refer to a rate limiting breaking of the intramolecular hydrogen bond followed by rapid α-cleavage, but further investigations are required to support or reject this possibility.

5. Conclusions

The anomolously slow α-cleavage of the triplet state of Bz in apolar solvents such as benzene [1] and hexanes is due to the occurrence of a strong intramolecular hydrogen bond which reduces reactivity either by increasing the π,π* character of the ketone's lowest triplet state or by 'locking' the ketone in a conformation unfavorable to reaction (or a mixture of both). In the polar solvents acetonitrile and methanol, the intramolecular hydrogen bond of benzoin is much weaker or broken and its triplet lifetime shortens considerably, becoming comparable to that of MeBz, a ketone structurally unable to form an intramolecular hydrogen bond.

Acknowledgements

We thank the National Science Foundation and the Air Force Office of Scientific Research for support of this work and Prof. K.S. Peters for the use of his facilities. The work in Professor Peters' lab was supported by a grant from the National Science Foundation, CHE 9408354. The authors also thank Dr. Peter F. McGarry for helpful discussions.

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