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Phenylethanol derivatives as triplet sensitizers for 1-azidoadamantane

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Laser flash photolysis, phosphorescence and density functional calculations were used to characterize the triplet excited states of phenylethanol derivatives 1, 2, 3 and 4. In acetonitrile, the triplet excited states of these alcohols were formed with rate constants on the order of ~10⁷ s⁻¹ and decayed with rate constants between 10⁵ and 10⁶ s⁻¹. The energies of these triplet excited states were between 80 and 83 kcal/mol. Furthermore, 3 can be used as a triplet sensitizer for alkyl azides to form triplet nitrene intermediates. Copyright © 2011 John Wiley & Sons, Ltd.

Keywords: alky nitrene; laser flash photolysis; triplet sensitization

INTRODUCTION

Triplet sensitization makes it possible to form various triplet excited states and reactive intermediates that cannot be formed by direct irradiation. For example, direct irradiation of alkyl azides does not lead to the formation of triplet alkyl nitrenes but rather to imine products either via a concerted reaction of the singlet excited state of the alkyl azide or by the formation of a singlet alkyl nitrene intermediate, which rearranges as shown in Scheme 1.[1-4] Thus, intersystem crossing, either from the singlet excited state of the alkyl azide to its triplet excited state or from the singlet nitrene to its triplet configuration, must be slower than the formation of the imine product. However, triplet alkyl nitrenes can be formed by intermolecular and intramolecular sensitization of alkyl azides with acetophenone derivatives.^[5–10] Acetophenone derivatives are excellent triplet sensitizers for alkyl azides because they absorb light at longer wavelengths than alkyl azides. In addition, acetophenone derivatives undergo intersystem crossing to their triplet states efficiently, with rate constants on the order of 10¹¹ s⁻¹ and with quantum yields approaching unity.^[11–13] In our continuing effort to study triplet intermediates using sensitization, we characterized the triplet states of phenylethanol derivatives and showed that they can be used as triplet sensitizers for alkyl azides to form triplet nitrenes.

Here, we describe the characterization of the first excited triplet state (T_1) of phenylethanol derivatives 1, 2, 3 and 4 by phosphorescence, laser flash photolysis and density functional calculations (Scheme 2). The T_1 of 1, 2, 3 and 4 are located between 83 and 80 kcal/mol above their ground state (S_0). The T_1 of these phenylethanol derivatives have lifetimes of a few microseconds in acetonitrile, but the intersystem crossing rate constants to form the triplet excited states are only on the order of ~10⁷ s⁻¹. Alcohol 3 can be used as an efficient sensitizer for azidoadamantane to form a triplet alkyl nitrene, whereas 1, 2 and 4 are less suitable.

SYNTHESIS OF STARTING MATERIALS

1-Azidoadmantane and phenylethanol derivatives 1, 2 and 3 are commercially available. We prepared 4 as described below.

Synthesis of 1-(4-methoxy-2,5-dimethylphenyl) ethanone

To a solution of 2-methoxy-1,4-dimethylbenzene (4.80 g, 0.035 mol) in dichloromethane (10 mL) at 0 °C was added CH₃COCI (2.75 g, 0.035 mol) in dichloromethane (10 mL). AlCl₃ (9.34 g, 0.070 mol) was added in small portions to the solution. The resulting mixture was stirred for 4 h and poured into an ice bath. The mixture was acidified by adding a saturated solution of NH₄Cl. The reaction mixture was extracted with dichloromethane and washed with water. The organic layer was dried with anhydrous MgSO₄ and the solvent was removed under vacuum to yield 1-(4-methoxy-2,5-dimethylphenyl)ethanone (2.68 g, 0.015 mol, 43% yield).

Synthesis of 1-(4-methoxy-2,5-dimethylphenyl)ethanol (4)

CeCl₃.7H₂O (7.45 g, 0.02 mol) was added to a solution of 1-(4methoxy-2,5-dimethylphenyl)ethanone (2.68 g, 0.015 mol) in methanol at ambient temperature while stirring.^[14] The reaction mixture was cooled to 0 °C and NaBH₄ (0.76 g, 0.020 mol) was added in small portions. The resulting mixture was stirred for 25 min and a saturated solution of NH₄Cl (15 mL) added. The reaction mixture was extracted with diethyl ether and washed with water. The organic layer was dried with anhydrous MgSO₄ and the solvent was removed under vacuum to give 4 (2.08 g). The crude was purified on silica column eluted with ethyl acetate in hexane mixture (1:4) to yield 4 (0.74 g, 4.1 mmol, 27% yield).

¹H NMR (CDCl₃, 400 MHz): δ 1.45 (d, *J* = 5 Hz, 3H), 1.62 (br s, 1H), 2.20 (s, 3H), 2.33 (s, 3H), 3.81 (s, 3H), 5.07 (q, *J* = 5 Hz, 1H), 6.59 (s, 1H), 7.26 (s, 1H) ppm. GC/MS (EI): *m/z* 180 (M⁺), 162 (100%), 147, 137, 131, 122, 115, 105, 91, 77, 65, 51.

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Scheme 1. Photoreactivity of Alkyl Azides

COMPUTATIONAL DETAILS

The calculations were performed using density functional theory (DFT) at the Becke, three-parameter, Lee-Yang-Parr (B3LYP) level of theory and with the 6-31 + G(d) basis sets as implemented in GAUSSIAN 09 (Gaussian Inc., Wallingford, CT, USA).[15-17] It has been shown that the B3LYP method can successfully predict energies for open-shell systems such as triplet nitrenes.^[18] All of the geometries were optimized at the B3LYP/6-31 + G(d) level of theory, and for each stationary point, the second derivative of the energy was calculated to confirm that these structures represent local energy minima. Solvation effects were evaluated for acetonitrile and methanol using the integral equation formalism polarizable continuum model with complete geometry optimizations and vibrational frequency analyses at the B3LYP/6-31 + G(d) level of theory.^[19-22] The energies of the excited states and the absorption spectra were calculated using time-dependent density functional theory (TD-DFT).^[23-27] Spin contamination was negligible for all of these open-shell molecules. All of the calculations were performed at the Ohio Supercomputer Center.

LASER FLASH PHOTOLYSIS

Laser flash photolysis was performed with an Excimer (Lambda Physik, Inc.Fort Lauderdale, FL, USA) laser (308 nm, 17 ns), using a previously described system.^[28] Stock solutions of alcohols 1, 2, 3 and 4 in methanol and acetonitrile were prepared with spectroscopic grade solvents such that the solutions had absorptions between 0.3 and 0.8 at 308 nm. Typically, $\sim 2 \text{ mL}$ of the stock solution was placed in a 48-mm-long quartz cuvette cell (10 mm 10 mm in cross-section) and purged with argon for 5 min or

oxygen for 15 min. The rate constants were obtained by fitting an average of three to eight kinetic traces.

Quenching studies of T_1 of 3 with azidoadamantane were done as follows. A stock solution of 25 mM 3 (0.760 g, 5 mmol) in acetonitrile (200 mL) was prepared. A series of solutions were made by dissolving 4.6 mg, 8.9 mg, 24.0 mg, 31.6 mg, and 43.8 mg of azidoadamantane in 25 mL of the stock solution of 3 to: yield 1.0 mM, 2.0 mM, 5.0 mM, 7.0 mM and 10.0 mM solutions of azidoadamantane.

PHOSPHORESCENCE

The phosphorescence spectra were obtained on a phosphorimeter in ethanol glasses at 77 K. The solutions were irradiated at 260 nm and the emission spectra recorded between 300 and 600 nm.

TRIPLET SENSITIZATION

A mixture of 1, 2, 3 or 4 (0.2 mmol) and 1-azidoadamantane (35 mg, 0.2 mmol) was dissolved in CH_3CN (2 mL, 0.1 M solution), and the resulting solution was purged with argon for 5 min. This solution was irradiated through a Pyrex (Corning, Lowell, MA, USA) filter, and the reaction mixture was analyzed by gas chromatography-mass spectroscopy (GC-MS).

RESULTS AND DISCUSSION

Product studies

Prolonged irradiation of 1, 2, and 3 through a Pyrex filter in both argon-saturated and oxygen-saturated solution did not yield any photoproducts. In comparison, photolysis of 4 did result in the formation of a small amount of dimeric products that we did not characterize further.

We photolyzed a 1:1 solution of 0.1 M 1, 2, 3 or 4 and azidoadamantane through a Pyrex filter. We followed the reaction with GC-MS and kept the conversion below 20%. Sensitization of azidoadamantane with 3 yielded azo-dimer 5 as its only product, whereas sensitization with 1 and 4 resulted in the formation of 5 and 6 (Scheme 3). Dimer 5 has been shown to form by the dimerization of two triplet alkyl nitrene intermediates,^[7] whereas 6 is formed via the singlet reactivity of azidoadamantane to form 7, which is trapped with an alcohol.^[29,30] Photolysis of azidoadamantane with 2 or toluene as a sensitizer did not yield any photoproducts. The product studies show that 3 is an efficient triplet sensitizer for azidoadamantane, because sensitization with 3 completely bypassed the singlet reactivity of azidoadamantane. In comparison, 1 and 4 were not as efficient triplet sensitizers as they gave products that can be attributed to both



Scheme 2. Molecular Structure of Alcohols 1, 2, 3 and 4



Scheme 3. Triplet Sensitization of Azidoadamantane

singlet and triplet reactivity of azidoadamantane, whereas sensitization with 2 and toluene was not successful.

UV absorption

To better evaluate the ability of 1, 2, 3 and 4 as triplet sensitizers for azidoadamantane; we compared the absorption spectra of alcohols 1, 2, 3 and 4 with the absorption spectra of toluene and acetophenone (Table 1). Alcohols 3 and 4 have an absorption band at ~280 nm that trails out to 300 nm (Figure 1), whereas 1 and 2 have weaker absorption bands at a somewhat shorter wavelength, similar to the absorption spectrum of toluene. The absorption of 1, 2, 3 and 4 above 300 nm is weaker than for the acetophenone, which has an (n, π^*) absorption band around 320 nm (ε = 50, Table 1) ^[31], and has been shown to be an efficient triplet sensitizer for azidoadamantane^[7]. However, we conclude that toluene, 1 and 2 are not as effective triplet sensitizers because their ground state absorption is similar to azidoadamantane, which has a weak absorption band at 286 nm (ε = 25 M⁻¹ cm⁻¹).^[32]

Calculations

To further analyze the ability of 1, 2, 3 and 4 to be used as sensitizers for azido compounds, we calculated their triplet excited states and compared them with the triplet excited

Table 1. The ground state UV absorption λ_{max} and ϵ for 1, $^{[33]}$ 2, 3 and 4					
	λ _{max} (ε)	λ _{max} (ε)	λ _{max} (ε)		
	nm (M ⁻¹ cm ⁻¹)	nm (M ⁻¹ cm ⁻¹)	nm (M ⁻¹ cm ⁻¹)		
Acetophenone ^[34]	320 (50)	278 (1110)	240 (1.3 $ imes$ 10 ⁴)		
Toluene ^[34]	262 (174)	208 (2460)			
1	259 (300)	252 (300)			
2	277 (250)	268 (300)			
3	282 (2200)	276 (2400)			
4	284 (2600)	278 (2600)			
1-	286 (25)				
Azidoadamantane. ^[32]					

state of toluene. We optimized the ground state (S_0) of 1, 2, 3, 4 and toluene and performed TD-DFT calculations to estimate the energies of their first excited singlet and triplet states (S_1 and T_1). We found that the S_1 are located 122 kcal/mol above the S_0 for 1 and toluene. The S_1 of 2 is located 116 kcal/mol above its S_0 whereas the S_1 of 3 and 4 are 114 kcal/mol above their S_0 (Table 2). The T_1 of 1, 2, 3, 4 and toluene were placed between 82 and 86 kcal/mol above their S_0 . Inspection of the molecular orbitals demonstrates that S_1 is due to a (π , π^*) electronic transition. In comparison, the T_1 in 1, 2 and 3 are due to a mixed electronic transition from a π -orbital and the lone pair on the alcohol



Figure 1. UV absorption spectra for 0.20 mM solutions of 1, 2, 3 and 4 in ethanol

Table 2.	Calculated energies in kcal/mol for S_1 and T_1 of 1, 2,
3, 4 and 1	toluene

		TD-DFT			Optimized T_1			
	S ₁	$S_1 \qquad T_1$			<i>T</i> ₂	Г ₂		
	GP	GP	EtOH	MeCN	GP	GP	EtOH	MeCN
1	122	86	86	87	106	86	87	87
2	116	83	84	84	102	80	80	80
3	114	84	85	85	94	80	80	80
4	114	82	82	82	96	78	78	78
Toluene	122	86	86	86	105	85	85	85
GP: Gas phase.								

moiety into a π^* -orbital (Figure 2), whereas the T_1 of 4 is mainly due to a (π,π^*) electronic transition, similar as observed for T_1 of toluene. Solvation in ethanol or acetonitrile did not change the calculated energies of S_1 and T_1 of 1, 2, 3, 4 and toluene significantly.

In addition, we optimized the T_1 of 1, 2, 3, 4 and toluene (Figure 3). The most significant difference between the optimized S_0 and the T_1 of 1, 2, 3 and 4 is that the carbon–carbon bonds in the aromatic ring are no longer equivalent; some of

the bonds became longer and others shorter, as has been observed for the T_1 of benzene and toluene.^[35] The optimized structure of the T_1 of toluene is similar to what Cogan *et al.* have reported using Complete Active Space Self Consistent Field (CASSCF) calculations.^[36] We found that the energies obtained from the optimized structures were 3–4 kcal/mol lower in energy than those obtained by TD-DFT calculations for 2, 3 and 4, whereas the energy calculated for the T_1 of 1 and toluene was similar by both methods. Thus, unrestricted Becke, three-parameter,





Figure 2. The orbitals involved in the lowest energy electronic transitions for the T_1 of 3 (TD-DFT in CH₃CN)



C-C bond distances are in Å



Lee–Yang–Parr (UB3LYP) optimization of 1, 2, 3 and 4 yielded energies that are in good agreement with those obtained from TD-DFT calculations. We have previously shown that UB3LYP significantly underestimates the adiabatic energy of triplet ketones with (n,π^*) configuration, whereas UB3LYP assessment of the adiabatic energy of triplet ketones with (π,π^*) configuration is excellent.^[37,38]

The DFT calculations show that 1, 2, 3 and 4 have their T_1 with similar or slightly lower energy than T_1 of toluene.

Phosphorescence

We measured the phosphorescence of 1, 2, 3 and 4 in ethanol glasses at 77 K. These spectra are shown in Fig. 4, and the energies of the (0,0) bands are listed in Table 3. The emission spectra for 1 and 2 have a resolved fine structure that makes it possible to locate their (0,0) transitions, whereas the emission for 3 and 4 are not sufficiently resolved to locate the (0,0) transitions. Therefore, we used the onset of the emissions at the shortest wavelength as an estimate for the (0,0) transitions for 3 and 4. The intensity of the phosphorescence was somewhat lower for 4 than 1, 2 and 3.

The measured energies of the T_1 in 1, 2, 3 and 4 in ethanol glasses and the calculated values are in good agreement. The calculated energies of the T_1 for 1, 2, 3 and 4 are within ~3 kcal/mol of the measured energies. The energies of the T_1 in 1, 2, 3 and 4 are similar to the reported energies of the T_1 in toluene (83 kcal/mol) and benzene (81 kcal/mol).^[39] Furthermore, the calculated energy of T_1 in toluene fits well with the measured one. Thus, the phosphorescence studies verify that DFT calculations are suitable for optimizing the triplet excited state of phenyl ethanol derivatives.





Figure 4. Phosphorescence spectra for (a) 1, (b) 2, (c) 3 and (d) 4 obtained in ethanol at 77 K with 260 nm irradiation

Table 3.	The	(0,0)	bands	obtained	from	phosphorescence
spectra of	[:] 1, 2	, 3 an	d 4 in e	ethanol at	77 K	

	(0,0) nm	kcal/mol
Acetophenone ^[39]		74
Toluene ^[39]		83
1	344	83
2	357	80
3	355	81
4	357	80

LASER FLASH PHOTOLYSIS

We performed laser flash photolysis of 1, 2, 3 and 4 to further characterize their T_1 . Laser flash photolysis of 1 in acetonitrile resulted in a transient spectrum with λ_{max} at 320 and 350 nm (Figure 5). The transient absorption was quenched in an oxygen-saturated solution. In addition, the rate constant for the transient formation at 320 nm was $2 \times 10^7 \text{ s}^{-1}$, whereas the transient decayed with a rate constant of $3 \times 10^5 \text{ s}^{-1}$. Based on the TD-DFT calculations, we assigned this transient to the T_1 of 1. Laser flash photolysis of 1 in methanol resulted in a similar transient spectrum, whereas the decay rate constant for the T_1 of 1 was somewhat slower at $4 \times 10^4 \text{ s}^{-1}$.

Laser flash photolysis of 2 in argon-saturated acetonitrile resulted in a transient spectrum with λ_{max} around 360 nm, which we assigned to the T_1 of 2 based on the TD-DFT calculations (Figure 6). We did not measure the transient absorption below 330 nm because of interference by the fluoroscence from S_1 of 2. This transient absorption was quenched in oxygen-saturated acetonitrile. The transient was formed with a rate constant of $1.7 \times 10^7 \text{ s}^{-1}$ and decayed at a rate constant of $1.3 \times 10^6 \text{ s}^{-1}$.



Figure 5. Laser flash photolysis of 1. (a) Kinetic trace obtained at 320 nm in argon-saturated methanol; (b) transient spectrum in argon-saturated acetonitrile immediately after the laser pulse; and (c) calculated TD-DFT spectrum for the T_1 of 1 in acetonitrile



Figure 6. Laser flash photolysis of 2 in argon-saturated acetonitrile. (a) Kinetic trace obtained at 370 nm; (b) transient spectrum obtained right after the laser pulse; and (c) calculated TD-DFT spectrum for the T_1 of 2 in acetonitrile

Laser flash photolysis of 3 resulted in a broad transient spectrum with λ_{max} at 410 nm (Figure 7). This transient was formed faster than the resolution of the laser flash apparatus (17 ns), but it was quenched in oxygen saturated-acetonitrile. The rate constant for the decay of this transient was measured at 410 nm and found to be 4.6 \times 10⁵ s⁻¹.

Laser flash photolysis of 4 resulted in broad transient absorption as shown in Fig. 8, and we assigned it to the T_1 of 4. This transient absorption was quenched efficiently in oxygen-saturated acetonitrile. The transient was formed with a rate constant of $7 \times 10^6 \text{ s}^{-1}$ and it decayed with a rate constant of $2 \times 10^5 \text{ s}^{-1}$.



Figure 7. Laser flash photolysis of 3 in argon-saturated acetonitrile. (a) Kinetic trace obtained at 410 nm; (b) transient spectrum immediately after the laser pulse; and (c) calculated TD-DFT spectrum for the T_1 of 3 in acetonitrile



Figure 8. Laser flash photolysis of 4 in argon-saturated acetonitrile. (a) Kinetic trace obtained at 460 nm; (b) transient spectrum obtained immediately after the laser pulse; and (c) calculated TD-DFT spectrum for the T_1 of 4 in acetonitrile

Thus, laser flash photolysis allowed for the direct detection of the T_1 of 1, 2, 3 and 4 at ambient temperature. The T_1 of 1, 3 and 4 have lifetimes of several microseconds in acetonitrile, whereas the T_1 of 2 is somewhat shorter lived. We were able to measure the rate constants for forming T_1 of 1, 2 and 4 directly, and they are on the order of ~10⁷ s⁻¹. This is similar to the reported rate constants for the formation of the T_1 of benzene and toluene. Furthermore, laser flash photolysis of *p*-methylphenylethanol has been reported to produce its T_1 , which has an absorption between 300 and 400 nm and a lifetime of 2 µs.^[40]



Figure 9. (a) Kinetic traces at 400 nm for the T_1 of 3 at various azidoadamantane concentrations. (b) The decay rate constants for the T_1 of 3 at various azidoadamantane concentrations

Journal of Physical Organic Chemistry Because 3 and 4 have similar S_0 absorption, but 4 is not as an efficient sensitizer as 3, we propose that the smaller rate constant for intersystem crossing in 4 causes it to be both a singlet and triplet sensitizer for azidoadamantane. Furthermore, the shorter lifetime of the T_1 of 2 causes it to be a less effective sensitizer than 1.

We measured the rate for quenching the T_1 of 3 with azidoadamantane (Figure 9). The decay rate constant of T_1 of 3, increased with increasing concentration of azidoadamantane. A plot of the decay rate constants for T_1 of 3 versus the azidoadamantane concentration was fitted with a straight line, with a slope of $1.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The rate for azidoadamantane quenching the T_1 of 3, is similar as to what is been reported as the rate of azidoadamantane quenching the T_1 of acetophenone.^[7]

CONCLUSION

We used phosphorescence and laser flash photolysis to characterize the T_1 of 1, 2, 3 and 4. The T_1 are formed with rate constants on the order of ~10⁷ s⁻¹ and have lifetimes of several microseconds in solution. The energies of the T_1 are between 80 and 83 kcal/mol, which makes them valuable as high-energy triplet sensitizers. However, only 3 is an efficient triplet sensitizer for azidoadamantane, because its intersystem crossing rate constant is fast enough to prevent singlet sensitization from competing with the triplet sensitization. In comparison the slow intersystem crossing in 4, results in both singlet and triplet sensitization of azidoadamantane. Alcohols 1 and 2 are not as efficient sensitizers as 3, because their ground state absorption does not differ sufficiently from azidoadamantane in addition to slow intersystem crossing rate constants.

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