Geometrical Effects on Intramolecular Quenching of Aromatic Ketone (π,π*) Triplets by Remote Phenolic Hydrogen Abstraction

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Abstract: The photochemistry of a series of alkoxyacetophenone derivatives bearing remote phenolic groups has been studied using laser flash photolysis techniques. The compounds are structured with a *p*- or *m*-phenolic moiety attached via a *m*- or *p*-oxyethyl linkage to the carbonyl chromophore, and each have a lowest triplet state of π,π* configuration. The corresponding methoxy-substituted compounds have also been examined. The triplet lifetimes of the phenolic ketones vary with the positions of attachment (*meta* or *para*) of the oxyethyl spacer to the carbonyl and phenolic moieties, indicating a very strong dependence of the rate of intramolecular H-abstraction on geometric factors. For example, the para,para′-linked phenolic ketone has a lifetime $\tau_T \approx 12$ ns in dry MeCN solution at room temperature due to rapid intramolecular H-abstraction, while the meta,meta′-derivative exhibits a lifetime $\tau_T \geq 11.5$ μs at infinite dilution and no detectable intramolecular reactivity. The presence of as little as 0.03 M water in the solvent leads to a significant increase in triplet decay rate in all cases, in contrast to its retarding effect on the rate of bimolecular phenolic H-abstraction in model compounds. Semiempirical (PM3) calculations have been carried out to determine the optimum conformation for abstraction in each molecule as a function of substitution pattern. The variation in the rate constants for intramolecular H-abstraction throughout the series is consistent with a mechanism involving coupled electron/proton transfer within a hydrogen-bonded triplet exciplex, the overall rate of which depends critically on orbital overlap factors between the aromatic rings in the ketone and the phenol.

Introduction

It is well-known that aromatic ketones with lowest π,π* triplet states are normally much less reactive than those with lowest n,π* states toward inter- and intramolecular hydrogen abstraction.[1−7] With hydrocarbon, arene, and alcohol hydrogen donors, ketones with n,π* triplets react with bimolecular rate constants some 10−100 times faster than those with lowest π,π* states, all else being equal.[8,9] On the other hand, the configuration of the lowest triplet state is less important in abstractions from donors containing heteroatoms such as nitrogen or sulfur,[6] where the rate-determining step for quenching of the lowest triplet state is usually charge or electron transfer from the H-donor to the ketone; similar *gross* features are exhibited by hydrogen abstractions from phenols.

Quenching of aromatic ketone triplets by amines has been particularly well studied.[7,10−17] The mechanistic spectrum is a complicated one, depending on the solvent, the structure of the amine, and the possibility of secondary reactions of the primary intermediates, but most amine−ketone triplet quenching reactions are rapid. As well, numerous studies on the interactions

of excited ketones with sulfur-containing species have been reported. Such compounds include simple alkyl and aryl thiols and thioethers,[18−23] as well as compounds of biological importance such as amino acids and peptides.[24−27] In aqueous or mixed aqueous solution, the direct detection of radical ions[21,28]

(1) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604.

(2) Berger, M.; McAlpine, E.; Steel, C. *J. Am. Chem. Soc.* **1978**, *100*, 5147.

(3) Encinas, M. V.; Lissi, E. A.; Lemp, E.; Zanocco, A.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 1856.

(4) Wagner, P. J.; Truman, R. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 7093.

(5) Wagner, P. J.; Truman, R. J.; Puchalski, A. E.; Wake, R. *J. Am. Chem. Soc.* **1986**, *108*, 7727.

(6) Wagner, P. J.; Park, B.-S. *Org. Photochem.* **1991**, *11*, 227.

(7) Aspari, P.; Ghoneim, N.; Haselbach, E.; von Raumer, M.; Suppan, P.; Vauthey, E. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1689.

(8) Walling, C.; Gibian, M. J. *J. Am. Chem. Soc.* **1965**, *87*, 3361.

(9) Scaiano, J. C. *J. Photochem.* **1973**, *2*, 81.

(10) Cohen, S. G.; Parola, A.; Parsons, G. H., Jr. *Chem. Rev.* **1973**, *73*, 141.

(11) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 1048.

(12) Griller, D.; Howard, J. A.; Marriott, P. R.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 619.

(13) Haselbach, E.; Jacques, P.; Pilloud, D.; Suppan, P.; Vauthey, E. *J. Phys. Chem.* **1991**, *95*, 7115.

(14) Miyasaka, H.; Morita, K.; Kamada, K.; Mataga, N. *Chem. Phys. Lett.* **1991**, *178*, 504.

(15) Miyasaka, H.; Kiri, M.; Morita, K.; Mataga, N.; Tanimoto, Y. *Chem. Phys. Lett.* **1992**, *199*, 21.

(16) Peters, K. S.; Lee, J. *J. Phys. Chem.* **1993**, *97*, 3761.

(17) von Raumer, M.; Suppan, P.; Haselbach, E. *Helv. Chim. Acta* **1997**, *80*, 719.

(18) Guttenplan, J. B.; Cohen, S. G. *J. Org. Chem.* **1973**, *38*, 2001.

(19) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1982**, *104*, 1679.

(20) Ronfard-Haret, J. C.; Bensasson, R. V.; Gramain, J. C. *Chem. Phys. Lett.* **1983**, *96*, 31.

(21) Jones, G.; Malba, V.; Bergmark, W. R. *J. Am. Chem. Soc.* **1986**, *108*, 4214.

(22) Bobrowski, K.; Marciniak, B.; Hug, G. L. *J. Photochem. Photobiol. A: Chem.* **1994**, *81*, 159.

(23) Wakasa, M.; Hayashi, H. *J. Phys. Chem.* **1996**, *100*, 15640.

(24) Cohen, S. G.; Ojanpera, S. *J. Am. Chem. Soc.* **1975**, *97*, 5633.

(25) Bhattacharyya, S. N.; Das, P. K. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 1107.

(26) Encinas, M. V.; Lissi, E. A.; Olea, A. F. *Photochem. Photobiol.* **1985**, *42*, 347.

(27) Marciniak, B.; Bobrowski, K.; Hug, G. L. *J. Phys. Chem.* **1993**, *97*, 11937.

has clearly demonstrated that the mechanism involves electron transfer from the sulfur atom to the triplet ketone, and this is supported by theoretical calculations.[27]

The mechanism by which aromatic ketone triplets are quenched by phenols is not nearly so well understood. Early work by Becker indicated that photochemical *reaction* between aromatic ketones and phenols is efficient only in the presence of an acid catalyst.[29−31] Turro and co-workers compared the quenching of biacetyl singlet and triplet states by amines and phenols and noticed many similarities in behavior between the two, but they concluded that phenols react via fast, reversible abstraction of the phenolic hydrogen.[32,33] Scaiano and co-workers observed that the interaction between n,π* and π,π* triplet ketones and phenols leads to rapid quenching that is insensitive to lowest-triplet configuration, and verified that the primary products of the reaction are the corresponding phenoxyl and hemipinacol radicals, identified clearly on the basis of their transient absorption spectra.[34] The fast quenching rates and lack of state dependence suggested a charge- or electron-transfer component in the quenching process. A number of other mechanistic studies have been published since then, employing laser flash photolysis (LFP),[35−45] and other [46,47] techniques to shed additional light on the details of the primary quenching process.

Recently, we studied the triplet quenching of a series of substituted benzophenones by *p*-cresol in acetonitrile solution by laser flash photolysis techniques.[41] We found that a Hammett plot of the rate constants for quenching of donor-substituted (n,π*) benzophenone triplets by phenols gave rise to a negative Hammett ρ value, suggesting that the ketone triplet behaves as a *nucleophile* in the reaction. This behavior was proposed to stem from increased mixing of the lowest n,π* triplet with the higher-lying π,π* state (due to a reduced $(n,\pi^*)^3-(\pi,\pi^*)^3$ energy gap), coupled with increasing basicity of the π,π* state, as the electron-donating power of the substituent(s) increases. The mechanistic events were suggested to be initial formation of a hydrogen-bonded exciplex between the ketone and the phenol, followed by coupled electron/proton transfer to generate the resulting phenoxyl and hemipinacol radicals (eq 1).[41]

We further proposed that the main effect of hydrogen bonding in the putative triplet exciplex was to facilitate the electron-


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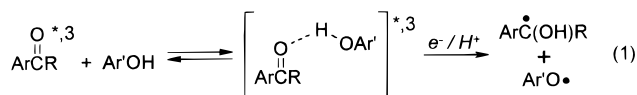
transfer component of the (net) hydrogen atom transfer process, by lowering both the reduction potential of the ketone (as a result of giving it more carbenium ion character) and the oxidation potential of the phenol (by giving it more phenoxide ion character). This adjustment of the redox potentials of the ketone triplet and phenol by the hydrogen bond is necessary to make the electron transfer thermodynamically favorable. A recent paper by Linschitz and co-workers on the quenching of fluorenone (π,π*) triplets by phenols reaches similar mechanistic conclusions,[43] and Shizuka and his group have also discovered a similar role for H-bond-mediated electron transfer in their study of benzophenone/naphthylamine exciplexes.[48]

The reaction has also been studied intramolecularly, in systems containing an aromatic ketone linked to a phenol via spacer groups of varying chain lengths. Das,[47] Levin,[38] and Hayashi[39] and their groups have reported that hemipinacol/phenoxyl biradicals are formed by exciting benzophenone−phenol systems linked by 5−12 atom chains, while our group has studied acetophenone−, indanone−, and benzophenone−phenol systems linked by a three-atom (oxyethyl) spacer through the *para* positions of the two aromatic rings (**1−4**).[36,41,49,50] The triplet lifetimes of **1−4** are in every case controlled by the rate of intramolecular phenolic hydrogen abstraction, which produces the corresponding hemipinacol/phenoxyl biradical. This process is slightly faster in **1** (a lowest π,π* triplet) than in **4** (a lowest n,π* triplet), in accord with the relative rate constants for bimolecular hydrogen abstraction by 4-methoxyacetophenone and 4-methoxybenzophenone from *p*-cresol.
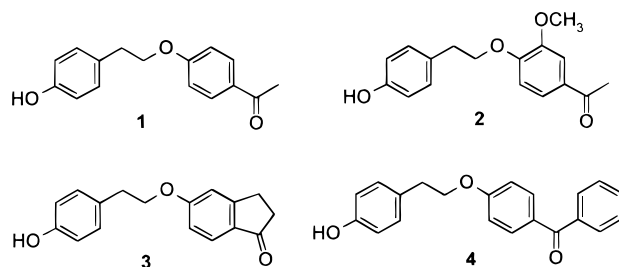
The fact that triplet decay is so fast in these compounds suggests that electron transfer within the triplet exciplex is efficient when the benzoyl and phenolic aromatic rings are oriented in a sandwich-like, face-to-face geometry, which is structurally enforced in compounds such as these as a result of the hydrogen bond (see eq 2). Clearly, our results do not exclude


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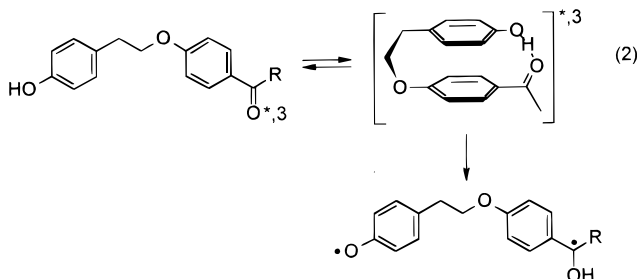
(28) Marciniak, B.; Andrzejewska, E.; Hug, G. L. *J. Photochem. Photobiol. A: Chem.* **1998**, *112*, 21.

(29) Becker, H.-D. *J. Org. Chem.* **1967**, *32*, 2115.

(30) Becker, H.-D. *J. Org. Chem.* **1967**, *32*, 2124.

(31) Becker, H.-D. *J. Org. Chem.* **1967**, *32*, 2140.

(32) Turro, N. J.; Engel, R. *J. Am. Chem. Soc.* **1969**, *91*, 7113.

(33) Turro, N. J.; Lee, T. J. *Mol. Photochem.* **1970**, *2*, 185.

(34) Das, P. K.; Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4154.

(35) Bobrowski, K.; Das, P. K. *Chem. Phys. Lett.* **1981**, *80*, 371.

(36) Scaiano, J. C.; McGimpsey, W. G.; Leigh, W. J.; Jakobs, S. *J. Org. Chem.* **1987**, *52*, 4540.

(37) Evans, C.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *4*, 4589.

(38) Levin, P. P.; Shafirovich, V. Y.; Batova, E. E.; Kuzmin, V. A. *Chem. Phys. Lett.* **1994**, *228*, 357.

(39) Wakasa, M.; Hayashi, H. *J. Phys. Chem.* **1995**, *99*, 17074.

(40) Yoshihara, T.; Yamaji, M.; Shizuka, H. *Chem. Phys. Lett.* **1996**, *261*, 431.

(41) Leigh, W. J.; Lathioor, E. C.; St. Pierre, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 12339.

(42) Jovanovic, S. V.; Morris, D. G.; Pliva, C. N.; Scaiano, J. C. *J. Photochem. Photobiol. A: Chem.* **1997**, *107*, 153.

(43) Biczok, L.; Berces, T.; Linschitz, H. *J. Am. Chem. Soc.* **1997**, *119*, 11071.

(44) Bhasikuttan, A. C.; Singh, A. K.; Palit, D. K.; Sapre, A. V.; Mittal, J. P. *J. Phys. Chem. A* **1998**, *102*, 3470.

(45) de Lucas, N. C.; Netto-Ferreira, J. C. *J. Photochem. Photobiol. A: Chem.* **1998**, *116*, 203.

(46) Niizuma, S.; Kawata, H. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1627.

(47) Das, R.; Bhatnagar, R.; Venkataraman, B. *Proc. Ind. Acad. Sci. (Chem. Sci.)* **1994**, *106*, 1681.

(48) Kiyota, T.; Yamaji, M.; Shizuka, H. *J. Phys. Chem.* **1996**, *100*, 672.

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other geometries for the triplet exciplex, but suggest that this one, at least, is a favorable one for fast electron/proton transfer.

The behavior of the indanone derivative **3** provides one other detail regarding the structure of the triplet exciplex. The triplet state of this compound is significantly longer-lived than that of **1**, even though both compounds have lowest π,π^* triplet states and 5-methoxyindanone abstracts hydrogen from *p*-cresol *faster* than does 4-methoxyacetophenone. This was interpreted as indicating that abstraction involves an interaction with the carbonyl n orbital, as would be expected for a mechanism involving hydrogen bonding of the phenol to the ketone triplet. This is geometrically more difficult in the linked indanone−phenol system than in the acetophenone derivative.

Inspection of molecular models suggests that modifications to the structures of **1−4**, in which the positions of attachment of the carbonyl and hydroxy substituents are varied between the *para* and *meta* positions relative to the oxyethyl spacer, should afford additional information on how the structure of the putative exciplex intermediate affects the overall rate constant for phenolic hydrogen abstraction. In this paper, we report the results of such a study, employing the series of phenolic acetophenones **5a−7a** and the corresponding methoxy analogues **5b−7b**. The triplet state of each compound has been

5 a. R = H
   b. R = Me

6 a. R = H
   b. R = Me

7 a. R = H
   b. R = Me
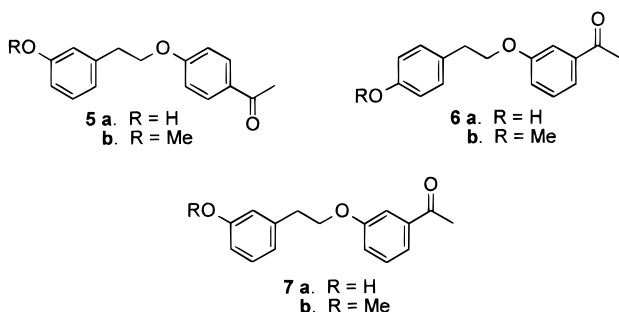
studied in detail using NLFP techniques and low-temperature phosphorescence emission spectroscopy. To assist in the analysis, we have also determined absolute rate constants for bimolecular quenching of *m*- and *p*-methoxyacetophenone (**8** and **9**, respectively) by *m*- and *p*-cresol under similar conditions and carried out semiempirical (PM3) theoretical calculations on the conformational properties of the four isomeric phenolic acetophenones as they pertain to intramolecular hydrogen abstraction.

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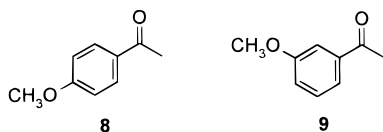
Results

Our initial attempts at the synthesis of **5a−7a** employed a similar procedure to that employed for our original preparation of **1**: reaction of *p*- or *m*-hydroxyacetophenone with *p*- or *m*-(trimethylsiloxy)phenethyl bromide.[36] With **6a** and **7a**, this resulted largely in elimination to the corresponding styrene derivative, and afforded the desired products in crude yields of only 5−20%. Much higher yields of the three ketones could be obtained using the ditosylate esters of *m*- and *p*-hydroxyphenethyl alcohol as substrates for the S_N2 substitutions with *p*- or *m*-hydroxyacetophenone (eq 3). The syntheses of the methoxy analogues **5b−7b** were carried out using both the *m*- and *p*-methoxyphenethyl bromides and tosylates, with the tosylate

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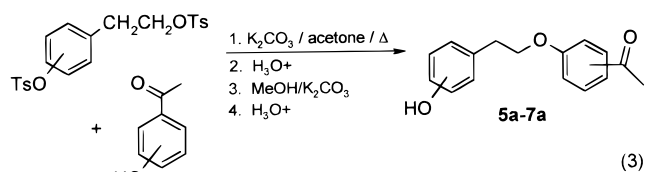
substitutions consistently affording higher yields of the desired product. The structures of each compound were assigned on the basis of spectroscopic and analytical data (see Supporting Information).

The ultraviolet absorption spectra of **5−7** in acetonitrile solution are indistinguishable from those of *p*- and *m*-methoxyacetophenone (**8** and **9**), and afford no evidence for ground-state interactions between the carbonyl chromophores and the remote phenolic moieties. Similarly, the phosphorescence emission spectra and phosphorescence lifetimes of **5−7**, which were recorded in 4:1 ethanol/methanol glasses at 77 K, are characteristic of the particular benzoyl chromophore present in each case and appear to be unaffected by the presence of the remote phenolic group. Triplet energies were estimated in each case from the short wavelength onset of the phosphorescence emission band; these are 73.8 ± 0.3 kcal/mol (τ = 240−260 ms) for **5a,b**, and 69.7 ± 0.1 kcal/mol (τ = 90−120 ms) for **6a,b** and **7a,b**. The general features of the emission spectra, triplet energies, and triplet lifetimes are the same, within experimental error, as measured under similar conditions for the corresponding model compounds **8** and **9**. From the absence of fine structure in the spectra and the lifetimes, the lowest triplet states of **5−7** can be assigned a π,π^* configuration. The presence of the remote phenolic moiety has no discernible effect on the configuration of the lowest triplet state, and no effect on the triplet lifetime in a solid matrix at low temperature.

As reported previously for **1−4**,[36,41] direct irradiation of deoxygenated 0.0025 M acetonitrile solutions of **5a−7a** with 300-nm light led to the inefficient formation of high molecular weight materials. Simultaneous irradiation of solutions of **5a−7a** and **1** (Φ_{-1} = 0.006 ± 0.002)[36] in a merry-go-round, with periodic monitoring of the solutions by gas chromatography, indicated the quantum yields for disappearance of ketone to be in the 0.001−0.01 range in all three cases. Under these conditions, triplet quenching by either intra- or intermolecular phenolic hydrogen abstraction can be expected to be reasonably efficient,[34,36,41] so these results merely verify that little net chemistry results from the reaction. This is well-known for bimolecular phenolic H-abstraction by ketone triplets in general.[29−33] As expected, the methoxy-substituted compounds (**5b−7b**) proved to be even less reactive under the same conditions.

Absolute rate constants for quenching of *p*- and *m*-methoxyacetophenone triplets (**8** and **9**, respectively) by *p*- and *m*-cresol were determined in deoxygenated acetonitrile and 5% aqueous acetonitrile solution at 27−29 °C by laser flash photolysis, using the pulses from a nitrogen laser (337 nm, ∼6 ns, ∼5 mJ) for excitation, and monitoring the decay of the strong triplet−triplet absorption spectra of the ketones at 380 nm. As expected, addition of the phenols resulted in an increase in triplet decay rate and the formation of new, long-lived absorptions assignable to *p*- or *m*-cresyloxyl radicals and the corresponding hemipinacol radicals. While these absorptions overlap with those due to the ketone triplets, they were sufficiently long-lived that triplet decay rate constants could generally be determined with reasonable accuracy by simply taking the absorption due to the radical products as the infinity level in the least squares analyses of

Table 1. Absolute Rate Constants for Quenching of *p*-Methoxyacetophenone (**8**) and *m*-Methoxyacetophenone (**9**) Triplets by *p*- and *m*-Cresol in Acetonitrile and 5% Aqueous Acetonitrile Solution at 27 ± 1 °C[a]

phenol	solvent	**8**	**9**
p-cresol	MeCN	1.24 ± 0.03	1.32 ± 0.04
	5% aqueous MeCN	0.75 ± 0.05	0.74 ± 0.05
m-cresol	MeCN	0.71 ± 0.02	1.06 ± 0.05
	5% aqueous MeCN	0.35 ± 0.02	0.49 ± 0.04

[a] Measured by 337-nm laser flash photolysis of 0.01−0.03 M solutions of the ketones in deoxygenated acetonitrile. In units of 10^9 M^{-1} s^{-1}.

the Δ-OD versus time data; at low phenol concentrations where the triplet lifetime was only ≤5 times shorter than those of the radicals, the triplet decay rates were determined by two-exponential least-squares fitting of the data. Bimolecular quenching rate constants (k_q) were determined from plots of the ketone triplet decay rate (k_{decay}) versus cresol concentration ([Q]) according to

$$k_{decay} = k_o + k_q[Q] \qquad (4)$$

where k_o is the pseudo-first-order rate constant for triplet decay in the absence of quencher. The results of these experiments are collected in Table 1. The bimolecular rate constant for quenching of the triplet state of **7b** by *m*-cresol was also determined and found to be $k_q = (1.17 \pm 0.03) \times 10^9$ M^{-1} s^{-1} in acetonitrile solution at 23 °C.

Laser flash photolysis experiments with **5**−**7** were carried out on extensively deoxygenated acetonitrile solutions in 3- or 7-mm path length cells, using the pulses from nitrogen, XeCl (308 nm, ~12 ns, ~50-mJ), or KrF (248 nm, 15−25 ns, 70−120 mJ) excimer lasers depending on the sample concentration. Flash photolysis of solutions of the methoxy ketones **5b**−**7b** led to the formation of strongly absorbing transients which decayed with clean pseudo-first-order kinetics (at low laser intensities) and exhibited lifetimes in the 3−10 μs range. These were assigned to the corresponding triplet states on the basis of their characteristic[51] absorption spectra ($\lambda_{max} \approx$ 380 nm) and the fact that they are quenched rapidly by 1,3-cyclohexadiene ($k_q = (7-10) \times 10^9$ M^{-1} s^{-1}) and oxygen ($k_q > 10^9$ M^{-1} s^{-1}).

Flash photolysis of deoxygenated, 10^{-5} to 10^{-4} M solutions of the phenolic ketones **5a**−**7a** in acetonitrile afforded transient absorptions which decayed with clean pseudo-first-order kinetics and exhibited similar absorption spectra to those from **5b**−**7b**. The lifetimes were in the 0.25−12.0-μs range depending on the concentrations of the ketone and water in the solvent. In all cases, addition of oxygen or 1,3-cyclohexadiene to the solutions resulted in shortening of the lifetime of the transient. Increasing the concentration of the ketone also caused the lifetime of the transient to shorten, and as well resulted in the formation of longer-lived residual absorptions which decayed over several tens of microseconds with mixed first- and second-order kinetics. On the basis of these experiments, the initial transient can be assigned to the triplet state of the ketone in all three cases, while the long-lived absorptions observed at higher ketone concentrations are assigned to the hemipinacol and phenoxyl monoradicals (**10a** and **11a**, respectively) formed by bimolecular hydrogen abstraction by the triplet from ground-state ketone ("self-quenching"; see eq 5).
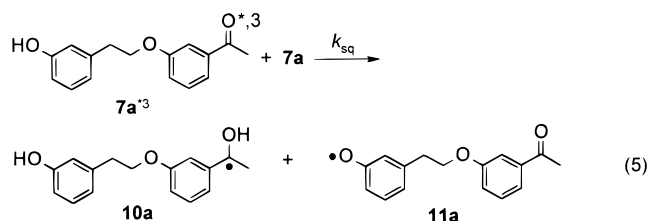
(49) Leigh, W. J.; Jakobs, S. *Tetrahedron* **1987**, *43*, 1393.
(50) Leigh, W. J.; Workentin, M. S.; Andrew, D. *J. Photochem. Photobiol. A: Chem.* **1991**, *57*, 97.
(51) Lutz, H.; Breheret, E.; Lindqvist, L. *J. Phys. Chem.* **1973**, *77*, 1758.

(5)

Figure 1 shows the triplet−triplet absorption spectra obtained by flash photolysis of deoxygenated acetonitrile solutions of **7a** (6×10^{-4} M) and **7b**. The spectra were recorded between 0.1 and 0.3 μs after the laser pulse. Typical transient decay profiles, recorded at 380 nm, are shown as inserts in the figures. Analogous spectra (available as Supporting Information) were obtained from **5** and **6** under similar conditions; those of **5a,b** are similar to those of **1**[36,41] while those of **6a,b** are similar to the spectra of **7a,b** shown in Figure 1.

Triplet decay rates were determined for **5a**−**7a** at 23 °C as a function of concentration, to account for contributions to the lifetimes from bimolecular self-quenching. As mentioned above, in all three cases the triplet lifetime decreased and the yield of long-lived monoradicals (as measured by the extrapolated initial intensity of the long-lived residual absorption) increased with increasing ketone concentration. Plots of k_{decay} vs ketone concentration ([K]) were linear in every case; a typical plot is shown for compound **7a** in Figure 2. The slope of the plot is the bimolecular self-quenching rate constant (k_{sq}), while the intercept is the rate constant for ketone triplet decay at infinite dilution, k_o (= $1/\tau_o$).

As mentioned above, the presence of water was found to have quite a significant effect on the behavior of the transient absorptions observed in NLFP experiments with these compounds, particularly with the *m*-acetyl derivatives **6a** and **7a**, whose triplet lifetimes in HPLC-grade acetonitrile were consistently 30−50% shorter than those determined in the same batch of solvent after drying with activated alumina or 4 Å molecular sieves ($[H_2O] \leq 10^{-4}$ M). Table 2 lists triplet lifetimes determined for **5a**−**7a** and **5b**−**7b** in dried acetonitrile and in acetonitrile containing 0.028 M H_2O and D_2O. In all cases, the lifetimes were determined in extensively deoxygenated solution, and at low enough laser intensities to avoid contributions to triplet decay from triplet−triplet annihilation. The values for **6a** and **7a** were obtained from the intercepts of dilution plots, and are thus completely free from contributions due to (bimolecular) self-quenching. For **7a**, (infinite dilution) triplet decay rates were also determined in acetonitrile containing higher concentrations of L_2O. The results of these experiments are shown in Figure 3. The slope of the plot for H_2O is $k_{H_2O} = (7.1 \pm 0.6) \times 10^5$ M^{-1} s^{-1}, while that for D_2O is indistinguishable from zero within experimental error (i.e. $k_{D_2O} < 10^4$ M^{-1} s^{-1}). Addition of water to acetonitrile solutions of **7b** led to a slight decrease in lifetime for $[H_2O] \leq 0.06$ M, but the effect did not persist at higher water concentrations. The plot of k_{decay} vs $[H_2O]$ for **7b** is also shown in Figure 3. Table 2 also contains the corresponding triplet lifetimes for **1**, which were redetermined in the course of this work. These agree well with those we previously reported for this compound.[41]

Finally, Arrhenius parameters for triplet decay were estimated for **5a**−**7a** from the lifetimes at several temperatures over the range 0−60 °C, and are listed in Table 3. Again, lifetimes for the shorter-lived ketone (**5a**) were determined with solutions of concentration ~10^{-4} M, while those for **6a** and **7a** were determined from the intercepts of dilution plots. The Arrhenius plots for triplet decay of all four of the phenolic acetophenone derivatives are shown in Figure 4.
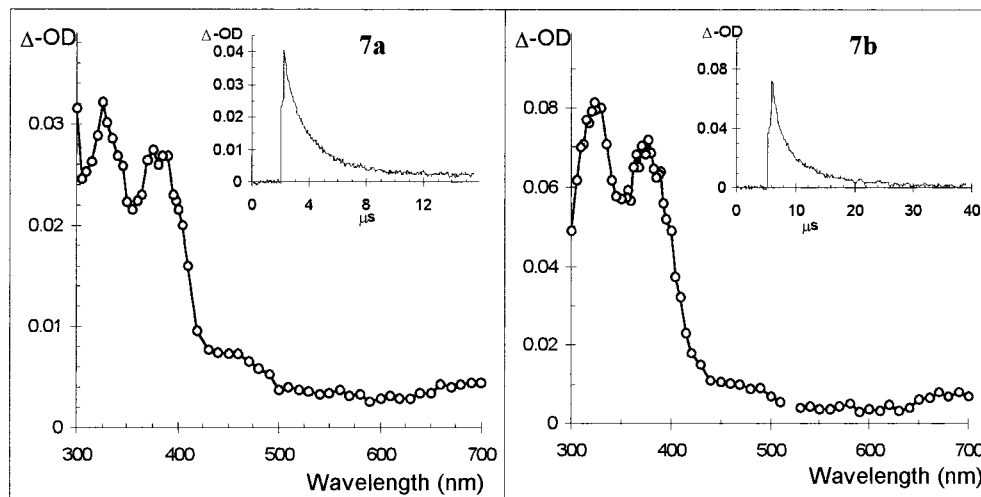
Figure 1. Triplet−triplet absorption spectra of ketones **7a** and **7b**, recorded by 248-nm laser flash photolysis of deoxygenated, optically matched acetonitrile solutions of the ketones (∼2 × 10⁻⁴ M) at 23 °C. The spectra were recorded 0−50 ns after the laser pulse. The inserts show decay traces recorded at 380 nm.

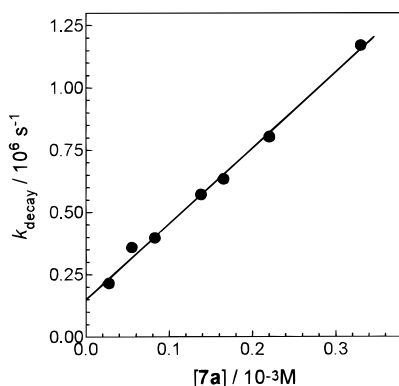**Figure 2.** Plot of k_{decay} vs ketone concentration from 248-nm laser flash photolysis of deoxygenated, dry ([H$_2$O] ≤ 10⁻⁴ M) acetonitrile solutions of **7a**.

Semiempirical (PM3) molecular orbital calculations were carried out on the four compounds, to estimate the effects of conformational factors on intramolecular hydrogen abstraction as a function of substitution pattern. Initial geometry optimizations showed that in all four cases, the most stable conformer has an *all-trans* geometry with respect to the ethylene bridge. Further geometry optimizations were then carried out after constraining the carbonyl oxygen−phenolic hydrogen distance to 2.65 Å and setting the degree of twist of the carbonyl from coplanarity with its attached phenyl ring to 45°. The 2.65 Å H-bonding distance was chosen on the basis of crystallographic data for hydrogen-bonded phenol−quinone pairs,[52] but it is also close to the optimum values for C−H abstraction by carbonyl n,π* triplets, as established by Scheffer and co-workers.[53] In every case except for **7a**, these constraints produced sandwich-like structures similar to the crude representation of eq 2. These are shown explicitly in Figure 5, along with the differences between the calculated heats of formation of the constrained and unconstrained (*all-trans*) conformers ($\Delta(\Delta H_f)$). In the case of the meta,meta′ derivative **7a**, two close-lying minima were found, one in which the phenyl rings were almost perpendicular, and another in which the rings were parallel to one another but not overlapping. Application of the additional constraints necessary to force a sandwich-like geometry similar to that

calculated for **1** led to substantial increases in the calculated energy. The structure of one such conformer, whose $\Delta(\Delta H_f)$ is similar to those of **1**, **5a**, and **6a**, is also shown in Figure 5.

Discussion

Mechanism of Triplet State Deactivation for Phenolic Ketones 5a−7a. The effect of varying the positions of attachment of the oxyethyl linker on the triplet lifetimes of these phenolic ketones is quite dramatic. The triplet lifetimes of **1** and **5a−7a** in acetonitrile solution vary by almost 3 orders of magnitude throughout the series, increasing in the order **1** < **5a** < **6a** ≪ **7a**. The self-quenching rate constants vary somewhat throughout the series (Table 2), but are similar to the bimolecular rate constants for quenching of *p*- and *m*-methoxyacetophenone (**8** and **9**, respectively) by *p*- and *m*-cresol (Table 1).
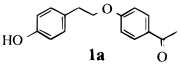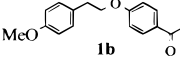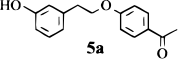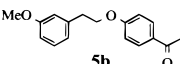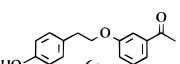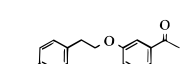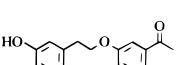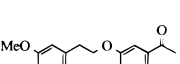
Comparison of the triplet lifetimes of **1**, **5a**, **6a**, and **7a** to those of the corresponding methoxy compounds suggests that the lifetimes of the first three compounds are dominated by the rate constant for intramolecular phenolic hydrogen abstraction, a conclusion which is verified by the deuterium isotope effects on the triplet lifetimes in 0.028 M aqueous acetonitrile. In contrast to **1**, for which signals due to both the triplet state (τ_T = 12 ns) and the resulting 1,13-biradical ($\tau \approx 140$ ns) could be observed,[36,41] only triplet signals are observed from **5a−7a** in dry acetonitrile solution. Since the steady-state irradiation experiments indicate that these compounds are relatively unreactive, we conclude that the corresponding biradicals have lifetimes which are comparable to or (more likely) shorter than those of the triplet precursors, and decay predominantly by back-hydrogen transfer to regenerate the precursor. This suggests that the biradical lifetimes are much less dependent on substrate structure than the triplet lifetimes throughout this series of compounds, as might be expected if biradical decay proceeds by (rate-determining) intersystem crossing followed by back-hydrogen transfer to regenerate the ground state of the ketone. The absence of a deuterium isotope effect on the infinite dilution lifetime of **7a**, coupled with its similarity to the lifetime of the methoxy analogue **7b**, suggests that the triplet state of this compound does not decay by intramolecular hydrogen abstraction to any significant extent.

Geometrical Effect on the Triplet Lifetimes. It is clear from the rate constants for bimolecular phenolic H-abstraction by the model compounds that the origin of the variation of the triplet

(52) Wallwork, S. C.; Harding, T. T. *Nature* **1953**, *171*, 40.
(53) Scheffer, J. R.; Garcia-Garibay, M. A.; Nalamasu, O. *Org. Photochem.* **1987**, *8*, 249.

Table 2. Lifetimes (*μ*s) of Carbonyl Triplets in Dry Acetonitrile ([H$_2$O] ≈ 10^{-4} M) and in Acetonitrile Containing 0.028 M H$_2$O or 0.028 M D$_2$O and Bimolecular Triplet Self-quenching Rate Constants at 23.0 ± 0.5 °C[a]

Compound	MeCN	0.028 M H$_2$O	0.028 M D$_2$O	KIE[b]	k_{sq} / 10^9 M^{-1}s^{-1}
1a	0.012 ± 0.002[c]	0.014 ± 0.002[c]	0.018 ± 0.002[c]	1.3 ± 0.2	-
1b	3.5 ± 0.2	2.9 ± 0.2	-	-	-
5a	0.34 ± 0.01[d]	0.32 ± 0.01[d]	0.80 ± 0.08	2.5 ± 0.3	3.8 ± 1.2
5b	8.8 ± 0.5	7.0 ± 0.7	-	-	-
6a	1.9 ± 0.2[d]	0.88 ± 0.02[d]	1.34 ± 0.02[d]	1.6 ± 0.2	2.2 ± 0.1
6b	12.3 ± 1.1	6.1 ± 0.6	-	-	-
7a	11.5 ± 1.8[d]	7.9 ± 2.3[d]	9.5 ± 1.1[d]	1.2 ± 0.2	1.2 ± 0.1
7b	8.5 ± 0.8	6.9 ± 0.7	-	-	-

[a] Measured directly by 248-nm NLFP, using rigorously deoxygenated, (0.8−1.2) × 10^{-4} M solutions, unless otherwise noted, and corrected for self-quenching. Errors are listed as twice the standard deviation of the mean of several determinations. [b] Ratio of lifetimes in acetonitrile containing 0.028 M D$_2$O and 0.028 M H$_2$O. [c] Measured by the 1-methylnaphthalene probe method. [d] From the intercepts of dilution plots.
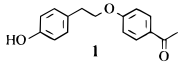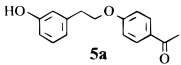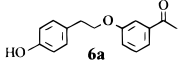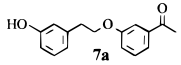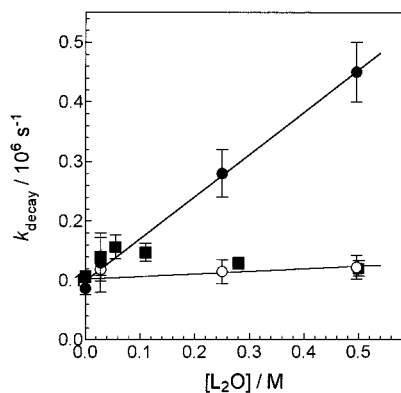

Figure 3. Plot of k_{decay} vs L$_2$O concentration for ketones **7a** (●, H$_2$O; ○, D$_2$O) and **7b** (■, H$_2$O) in deoxygenated acetonitrile solution. k_{decay} values for **7a** were obtained from the intercepts of dilution plots at each L$_2$O concentration.

lifetime in the phenolic ketones must be due to structural factors affecting the ease with which the molecules can adopt a conformation which allows fast (net) hydrogen atom transfer. The PM3 calculations suggest that all four molecules can adopt at least one conformation, of similar or lower energy to that of **1**, in which the phenolic hydrogen is within abstracting distance of the excited carbonyl. This verifies that the process is *not* just a simple H atom abstraction; if it were, then little variation in triplet lifetime throughout the series would be expected. At the same time, they verify that some bonding interaction between the phenolic hydrogen and carbonyl oxygen is required in order to "turn on" the quenching process; for example, a simple

charge- or electron-transfer interaction between the two aryl rings followed by rapid proton transfer, without prior hydrogen bonding, would also be expected to proceed with similar facility in the four compounds. In fact, the results provide good evidence in support of the hydrogen-bonded exciplex mechanism for phenolic hydrogen abstraction, and suggest that there are very specific structural requirements that must be met for the exciplex to decay to products rapidly. The variation in triplet lifetimes throughout the series indicates that these requirements must be different for (bimolecular) abstraction of phenolic hydrogens by *m*- and *p*-alkoxyphenyl alkyl ketones, but that both require some type of spatial overlap between the phenyl rings of the carbonyl and phenolic moieties.

Compound **1** is obviously capable of forming a "good" exciplex geometry for fast hydrogen transfer, one possibility for which is shown in Figure 5. Since this ketone is the most reactive one in the series, we take this as the prototype for a "good" exciplex geometry for fast electron/proton transfer to generate the corresponding biradical. Inspection of the Δ(ΔH_f) values from Figure 5 indicates that there is little difference in the abilities of **1**, **5a**, and **6a** to adopt an exciplex structure similar to that of **1**. While the rings are slightly skewed away from each other in **5a** and **6a**, there is clearly no structural reason which might account for the observed increases in lifetime observed, especially the ∼75-fold increase for **6a**, to the extent that our choice of constraints for the calculated abstraction geometries are reasonable. We do note, however, that constraining the hydrogen-bond distance to slightly shorter distances (e.g., 2.50 Å) has the effect of widening the spread in calculated Δ-

Table 3. Arrhenius Parameters for Intramolecular Phenolic Hydrogen Abstraction by the Triplet States of Ketones **1** and **5a−7a** in Deoxygenated Acetonitrile Solution[a]

Compound	Temperature Range	*log A*	E_A (kcal/mol)
1	-32 to 23°C	10.7 ± 0.3[b]	3.8 ± 0.3[b]
5a	-12 to 40°C	9.6 ± 0.5	4.2 ± 0.4
6a	5 to 65°C	7.8 ± 0.8	2.4 ± 0.8
7a	5 to 65°C	8.7 ± 0.6	4.7 ± 1.1

[a] Decay rate constants for **5a** were measured directly by 248-nm NLFP, using rigorously deoxygenated, $(0.8-1.2) \times 10^{-4}$ M solutions, and were not corrected for self-quenching. Those for **6a** and **7a** were obtained from the intercepts of dilution plots at each temperature. [b] Reference 41.
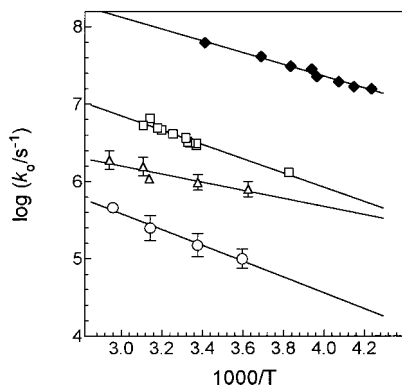
Figure 4. Arrhenius plots of the triplet decay rates (at infinite dilution) of phenolic ketones **1** (◆), **5a** (□), **6a** (△), and **7a** (○) in deoxygenated acetonitrile solution.

(ΔH_f) values for these three compounds, in a way which parallels the increase in triplet lifetime throughout the series. We obviously cannot comment on whether this is significant. Compound **7a** is unique in that there are at least two H-bonding conformations which are considerably lower in energy than those of the other three compounds. However, there is clearly minimal orbital overlap possible between the aryl rings in these conformers, a feature which would be expected to affect quite dramatically the rate of intramolecular electron transfer compared to those of other triplet decay processes.[54−58] As expected, a dramatic increase in energy accompanies any attempt to constrain the molecule in a sandwich-like geometry similar to that of **1**, but as the last picture in Figure 5 indicates, it appears possible for it to assume such a conformation with a similar expenditure in energy. In conclusion, these calculations do not readily explain why the triplet lifetimes for **5a** and **6a** differ from **1**, but do point toward the possibility that **7a** may only rarely sample the good exciplex geometry which is required for fast electron/proton transfer.

(54) Reimers, J. R.; Hush, N. S.; Sammeth, D. M.; Callis, P. R. *Chem. Phys. Lett.* **1990**, *169*, 622.
(55) Zeng, Y.; Zimmt, M. B. *J. Am. Chem. Soc.* **1991**, *113*, 5107.
(56) Verhoeven, J. W.; Kroon, J.; Paddon-Row, M. N.; Warman, J. M. In *Supramolecular Chemistry*; Balzani, V., DeCola, L., Eds.; Kluwer Academic Publishers: Dordrecht, 1992; pp 181−200.
(57) Jacques, P.; Allonas, X.; von Raumer, M.; Suppan, P.; Haselbach, E. *J. Photochem. Photobiol. A: Chem.* **1997**, *111*, 41.
(58) Haselbach, E.; Pilloud, D.; Suppan, P. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 3123.
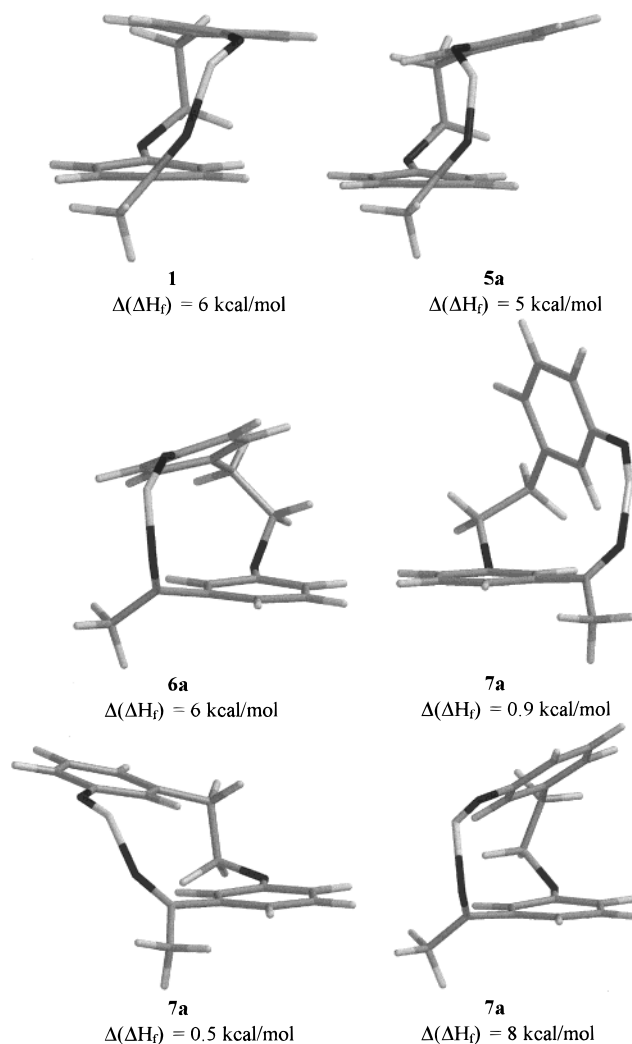
Figure 5. Calculated (PM3) quenching geometries and $\Delta(\Delta H_f)$ values for phenolic ketones **1** and **5a−7a**, where $\Delta(\Delta H_f)$ is the difference between the calculated heats of formation of the conformer shown and the relaxed *all-trans*-conformer (see text).

Symmetry-Restricted Electron Transfer. In these molecules, fast electron/proton transfer in the hydrogen-bonded triplet exciplex can be expected to require good spatial overlap between the frontier molecular orbitals associated with the

Scheme 1. Nodal Properties for *Para*-Substituted Methoxyacetophenone and Cresol Moieties (Left) and Their *Meta* Isomers (Right) from Extended Huckel Calculations
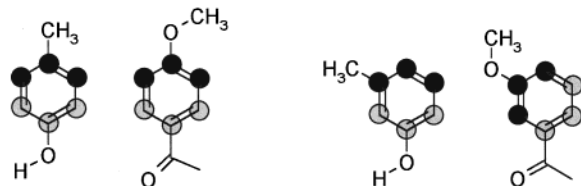
phenolic and alkoxybenzoyl donor/acceptor pairs.[54−58] These can be identified as the lower singly occupied molecular orbital of the ketone π,π^* triplet (the HOMO of the ground state ketone) and the HOMO of the phenol, which are both largely comprised of the benzenoid π_A molecular orbitals. The nodal properties of these MO's in *m*- and *p*-methoxyacetophenone and *m*- and *p*-cresol, at the simple Hückel level, are depicted in Scheme 1. To a first approximation, the degree of orbital overlap which is possible in the cyclophane-like conformations accessible to **1** and **7a** can then be assessed by simply superimposing the two rings in each of the ketone−phenol pairs.

Aligning the two *para*-substituted moieties in a sandwich-like orientation analogous to that shown in Figure 5 for **1** results in nearly perfect orbital overlap between all six carbons of the two aromatic rings, consistent with the very fast rate of intramolecular hydrogen transfer observed for the triplet state of this compound. In contrast, a nonsymmetric situation results when *m*-methoxyacetophenone and *m*-cresol are aligned similarly, leading to antibonding interactions between two centers and poorer net orbital overlap. We thus propose that for **7a**, and to a lesser extent **6a**, the orbital overlap required for fast electron transfer between the two aromatic rings is poorer than for **1a** and **5a**, resulting in a reduced rate constant for (net) hydrogen atom transfer once a "good" quenching geometry is attained. It is evident that these effects are general, since similar observations have been made in photoinduced charge- or electron-transfer processes in cyclophane derivatives,[59−62] donor−spacer−acceptor systems,[63−65] and various bimolecular systems,[66−68] as well as in singlet state photocycloaddition and dimerization reactions.[69−71] On the other hand, there is no precedent that we are aware of for a kinetic effect of the magnitude reported here for **1a** and **7a**. It is possible that other factors also contribute to the observed differences in reactivity, which are more difficult to assess at the present time. One possibility is electronic effects associated with the oxyethyl tethers, which are conformationally locked in the H-bonded exciplex geometries. This could alter the carbonyl triplet pK_a

(for example), which would affect both the equilibrium constant for exciplex formation and the rate of coupled electron/proton transfer within the exciplex in unanticipated ways.

Overall, the combination of a geometrical effect on achieving an appropriate quenching conformation and the ease with which electron transfer may occur from that geometry are responsible for the ∼1000-fold variation in rate constant for intramolecular phenolic hydrogen abstraction in this series of compounds. For **1**, the sandwich-like exciplex geometry is the only one attainable, there are no symmetry restrictions to electron transfer in this geometry, and electron/proton transfer is consequently facile. On the other hand, **7a** can form several hydrogen-bonded conformers of much lower energy than the sandwich-like geometry, none of these allow the good orbital overlap necessary for fast electron transfer, and intramolecular H atom abstraction is consequently much slower than nonproductive decay of the ketone triplet state. Further work will address the possible role of electronic effects, associated with the restricted mobility about the C_{aryl}−O bond in the oxyethyl tether, in contributing to the substantial variation in the rate of intramolecular phenolic H abstraction within this series of compounds.

Arrhenius Data and Lifetimes of the Methoxy Ketones. The Arrhenius parameters for intramolecular quenching of the triplet states of **1** and **5a**−**7a** in acetonitrile solution (Table 3) are not particularly informative. The main variable throughout the series is the preexponential factor, suggesting that entropic factors are significantly more pronounced for the *meta*-substituted ketones, probably due to the effects of conformational and orbital overlap factors on the quenching process.

As far as the triplet states of the methoxy analogues of **1** and **5a**−**7a** are concerned, it is clear that all are significantly shorter-lived than *p*- and *m*-methoxyacetophenone (**8** and **9**). We have previously proposed for the methoxy analogue of **1** that this is due to intramolecular quenching by a (nonproductive) charge-transfer mechanism.[41] The triplet lifetimes of the linked anisyl ketones follow the same trend as their phenolic analogues, but vary by a factor of only 2−3 throughout the series. Such a process also requires good orbital overlap between the donor and acceptor,[59,62] but because intramolecular hydrogen bonding is not a factor, the oxyethyl-linked anisyl ketones are free to assume a geometry in which such overlap is maximized and thus geometrical differences are minimized.

The Effect of Water on the Triplet Lifetimes of 1 and 5a−7a. As we found previously for **1−4**,[41] the addition of water to acetonitrile solutions of **5a**−**7a** results in a significant reduction in triplet lifetime in all cases. With **5a**, this is also accompanied by the appearance of intense fluorescence from the sample, which made lifetime determinations difficult at water concentrations higher than ∼0.06 M. This was not a problem with **6a** and **7a**, and the shorter-lived signals obtained in the presence of water could be verified to be due to the triplet states by quenching with 1,3-cyclohexadiene. In contrast, the presence of water has a *retarding* influence on bimolecular phenolic hydrogen abstraction by the methoxyacetophenones **8** and **9** from *m*- and *p*-cresol (Table 1). This effect is well-known for H abstraction by other aromatic ketone triplets[34,35,37,41] as well as alkoxyl free radicals,[37,72,73] and is due to a reduction in the concentration of free phenol through hydrogen bonding with water.[74] It is quite small compared to that on the triplet lifetimes

(59) Zsom, R. L. J.; Schroff, L. G.; Bakker, C. J.; Verhoeven, J. W.; De Boer, Th. J.; Wright, J. D.; Kuroda, H. *Tetrahedron* **1978**, *34*, 3225.

(60) Staab, H. A.; Rebafka, W. *Chem. Ber.* **1977**, *110*, 3333.

(61) Staab, H. A.; Herz, C. P.; Krieger, C.; Rentea, M. *Chem. Ber.* **1977**, *110*, 3351.

(62) Staab, H. A.; Herz, C. P.; Krieger, C.; Rentea, M. *Chem. Ber.* **1983**, *116*, 3813.

(63) Sakata, Y.; Tsue, H.; Goto, Y.; Misumi, S.; Asahi, T.; Nishikawa, S.; Okada, T.; Mataga, N. *Chem. Lett.* **1991**, 1307.

(64) Fiebig, T.; Kuhnle, W.; Staerk, H. *Chem. Phys. Lett.* **1998**, *282*, 7.

(65) Helsen, N.; Viaene, L.; Van der Auweraer, M.; De Schryver, F. C. *J. Phys. Chem.* **1994**, *98*, 1532.

(66) Nagaoka, S.-I.; Nagashima, U. *Chem. Phys.* **1996**, *206*, 353.

(67) Tramer, A.; Brenner, V.; Millie, P.; Piuzzi, F. *J. Phys. Chem.* **1998**, *102*, 2798.

(68) Tramer, A.; Brenner, V.; Millie, P.; Piuzzi, F. *J. Phys. Chem.* **1998**, *102*, 2808.

(69) Lewis, F. D.; Hoyle, C. E.; Johnson, D. E. *J. Am. Chem. Soc.* **1974**, *97*, 3267.

(70) Michl, J. *Tetrahedron* **1977**, *25*, 141.

(71) Caldwell, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 4004.

(72) Wayner, D. D. M.; Lusztyk, J.; Page, D.; Ingold, K. U.; Mulder, P.; Laarhoven, L. J. J.; Aldrich, H. S. *J. Am. Chem. Soc.* **1995**, *117*, 8737.

(73) Valgimigli, L.; Banks, J. T.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1995**, *117*, 9966.

(74) Banks, J. T.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1996**, *118*, 6790.

of **5a**−**7a**, however. Even the triplet lifetime of **7b** shows some sensitivity to the presence of water, although only at very low concentrations (≤0.1 M).

One possible explanation for the effect of water on the triplet lifetimes of the phenolic ketones is that it causes aggregation of the substrate, which could lead to enhanced triplet decay due to an increased contribution from bimolecular hydrogen abstraction by self-quenching.[41] This explanation can be ruled out, since the dilution plots for **6a** and **7a** in aqueous acetonitrile show no hint of the positive curvature that would be expected for such a mechanism, and no lifetime reduction is exhibited by **7a** in the presence of D_2O rather than H_2O. In fact, the latter suggests strongly that the effect involves hydrogen bonding in some way. One possibility is that water can assist in intramolecular H transfer by acting as a bridge between the phenolic hydrogen and carbonyl oxygen in the triplet exciplex. This could result in a "looser", more flexible exciplex in which the orbital overlap required for electron-transfer might be achieved more easily.

Conclusions

Bimolecular phenolic hydrogen abstraction by lowest π,π^* triplet ketones, or lowest n,π^* triplets with proximate π,π^* triplet states, has earlier been proposed to proceed by a mechanism involving the initial formation of a hydrogen-bonded triplet exciplex followed by coupled electron/proton transfer to generate the corresponding phenoxyl and hemipinacol radicals.[41,43] The results reported here provide excellent indirect evidence for the involvement of the hydrogen-bonded triplet exciplex and for the role of electron transfer in this reaction. In bimolecular systems, hydrogen bonding serves to adjust the redox potentials of the excited ketone and phenol so that electron transfer is thermodynamically favorable; the two partners in the process are then free to adopt whatever relative orientation is necessary for maximum orbital overlap and fast electron/proton transfer. In the intramolecular examples studied in the present work, electron transfer must proceed via a cyclophane-like geometry in which the relative orientation of the aromatic rings is rigidly controlled by the hydrogen bond and the oxyethyl linker group. The ease with which an appropriate geometry can be attained, as well as orbital overlap factors, vary depending on the positions of attachment of the oxyethyl linker to the two aryl rings. This has very large effects on the rate of electron/proton transfer in the putative triplet exciplex.

Photochemical hydrogen abstraction by aromatic ketones from phenols is a reaction of considerable importance in natural materials, where it often must occur in restrictive environments such as the solid state or at solid−liquid interfaces.[75] The results reported here demonstrate that the efficiency of such processes is likely to be affected not only by diffusional factors, but also by the ability of the medium to afford the reacting molecules sufficient conformational freedom that the correct geometry for abstraction can be attained. We are currently investigating the geometrical requirements of the process in ketones of other lowest triplet configurations, the results of which will be reported in due course.

Experimental Section

Details regarding the materials and synthetic procedures employed for the preparation of **5**−**7**, and analytical and spectroscopic data for all compounds, are available as Supporting Information.

Nanosecond laser flash photolysis experiments employed the pulses from a Lumonics TE-861M excimer laser filled with Xe/HCl/H_2/He (308 nm, 15 ns, ∼40 mJ) or N_2/He (337 nm, 6 ns, ∼4 mJ), a Lumonics 510 excimer laser filled with Kr/F_2/He (248 nm, 20 ns, ∼60 mJ), or a Lambda Physik Compex 120 filled with Kr/F_2/Ne (248 nm, 25 ns, 100−140 mJ), and a computer-controlled detection system which has been described elsewhere.[50,76] All samples were contained in 3 × 7 mm or 7 × 7 mm Suprasil quartz cells which were sealed with rubber septa. Substrate concentrations were adjusted to yield an absorbance between 0.2 and 0.9 at the excitation wavelength. Each solution was degassed with dry nitrogen or argon until constant lifetimes were achieved. Quenchers were added as aliquots of standard solutions.

Phosphorescence emission spectra and lifetimes were determined with a Photon Technologies LS-100 spectrofluorimeter utilizing the manufacturer's software. Sample concentrations were ∼1 mg/mL and were contained in 2 mm i.d. Suprasil quartz tubes that were sealed with rubber septa and deoxygenated with dry nitrogen.

Steady-state irradiations were performed in a Rayonet Reactor (New England Ultraviolet Co.) using RPR-300 lamps and a merry-go-round apparatus. Samples were contained in 3 mm i.d. quartz tubes sealed with rubber septa, and were deoxygenated with nitrogen. Progress of the photolyses was monitored periodically by GC using the disappearance of **1a** as an actinometer. The internal standard was either dodecane or hexadecane.

The PM3 calculations were carried out using Spartan 5.0.3 (Wavefunction, Inc.) on a dual-processor Silicon Graphics Octane workstation.

(75) Heitner, C. In *Photochemistry of lignocellulosic materials*; Heitner, C., Scaiano, J. C., Eds.; ACS Symposium Series 531; American Chemical Society: Washington, 1993; pp 1−24.

(76) Bradaric, C. J.; Leigh, W. J. *Can. J. Chem.* **1997**, *75*, 1393.