

Laser Flash Photolysis of 1,2-Diketopyracene and a Theoretical Study of the Phenolic Hydrogen Abstraction by the Triplet State of Cyclic α -Diketones

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Laser flash photolysis (LFP) studies, atoms in molecules (AIM) studies, and density functional theory (DFT) calculations have been performed in order to study the mechanism of the hydrogen abstraction by α -diketones in the presence of phenols. Laser irradiation of a degassed solution of 1,2-diketopyracene in acetonitrile resulted in the formation of a readily detectable transient with absorption at 610 nm, but with very low absorptivity. This transient decays with a lifetime of around 2 μ s. The quenching rate constant for substituted phenols, k_q , ranged from 1.10×10^8 L mol⁻¹ s⁻¹ (4-cyanophenol) to 3.87×10^9 L mol⁻¹ s⁻¹ (4-hydroxyphenol). The Hammett plot for the reaction of the triplet of 1,2-diketopyracene with phenols gave a reaction constant $\rho = -0.9$. DFT calculations (UB3LYP/6-311++G**//UB3LYP/6-31G*) of the triplet complex ketone–phenol revealed that hydrogen transfer has predominantly occurred and that the reaction with α -diketones are generally 7 kcal/mol less endothermic than the respective reactions of the monoketones. These results together with the geometries obtained from the DFT calculations, natural bond order (NBO) analysis, and AIM results indicate that hydrogen abstraction for α -diketones is facilitated by the electrophilicity of the ketone, instead of neighboring group participation by the second carbonyl group.

Introduction

It is known that photochemical hydrogen abstraction by aromatic ketones is dependent on the nature of their lowest triplet excited state, with the n,π^* triplet being the reactive state.¹ When the ketones have a lowest π,π^* triplet state they react predominantly via the higher energy n,π^* state, populated thermally from the lower energy state.^{2–4} Reduction potential, triplet energy, and the nature of the breaking bond influence the rate of hydrogen abstraction of n,π^* triplet ketones.² Electron transfer is relevant in ketone photoreduction of amines since its rate is faster than hydrogen abstraction from ketones.²

The mechanisms involved in the hydrogen abstraction process depend primarily on the bond energy of the hydrogen donor and of its oxidation potential. Thus, mechanisms ranging from “pure” alkoxy radical-like abstraction (as with alkanes or alcohols)^{5,6} to one initiated by full electron transfer (as with amines) have been identified.^{7–10} However, in the case of benzylic hydrogen abstraction, mechanisms which span both extremes have been observed and interpreted in terms of an initial formation of a charge-transfer complex.^{11,12}

Phenolic hydrogen abstraction by aromatic ketones is faster than the corresponding reaction of substituted toluenes.¹³ This is expected on the basis of the fact that phenol has both a lower

bond dissociation energy and lower oxidation potential than toluenes. It has been suggested that hydrogen abstraction from phenols occurs by a mechanism involving initial formation of a hydrogen-bonded triplet exciplex followed by coupled electron/proton transfer.^{13–17}

Several α -diketones have been found to be very reactive in the presence of hydrogen donors.^{18–20} Scaiano and co-workers have suggested that the triplet reactivity of cyclic α -diketones is due to hydrogen bonding in the transition state.²¹ However, it has been questioned by Wagner if a partial hydrogen bond would be sufficient to explain the increased reactivity.²

Our group has studied the triplet reactivity of acenaphthene-quinone (**1**) and 1-acenaphthenone (**2**) with phenols by laser flash photolysis (LFP). Diketone **1** was found to be more reactive than monoketone **2** and with both ketones the hydrogen abstraction reaction revealed a dependency upon the substitution on the phenol ($\rho = -1.5$).¹⁹ Still more interesting were the results observed with an analogous α -diketone, having a π,π^* configuration, i.e., 1,2-acanthrylenedione (**3**). In this case the reactivity with phenols was found to be 2 orders of magnitude less, but still exhibits a substituent effect ($\rho = -1.04$).²²

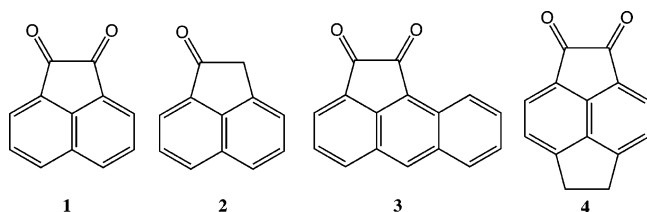
In this work we report the results of a systematic study of the reactivity of 1,2-diketopyracene (**4**) in the presence of substituted phenols employing the laser flash photolysis technique. Our interest in this system was to observe how a greater rigidity in the molecule would influence the reactivity of the triplet state with phenols. We have also performed a DFT, AIM, and NBO calculation study of the reaction of the triplet excited-state of **1–4** with phenol in order to investigate the mechanism of the hydrogen abstraction by α -diketones in the presence of phenols.

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Materials and Methods

Materials. Acetonitrile (VETEC spectrograde) was used as received. Phenol, 3-methoxyphenol, 4-methoxyphenol, 4-*tert*-butylphenol, 4-hydroxyphenol, 3-hydroxyphenol, 4-phenylphenol, 4-chlorophenol, 3-chlorophenol, 4-bromophenol, 3-bromophenol, 4-cyanophenol, 4-phenylphenol, 4-methylphenol, 3-methylphenol, and 4-fluorophenol from Aldrich, were used as received (purity >99%).

1,2-Diketopyracene (**4**) was prepared by the Friedel–Crafts reaction of acenaphthene with oxalyl bromide and aluminum bromide in carbon disulfide as described in the literature. Spectroscopic data and melting point are in accord with the structure proposed.²³

Laser Flash Photolysis. The laser flash photolysis experiments were carried out on a LuzChem Instrument model mLFP122. Samples were contained in a 10 mm × 10 mm cell made from Suprasil tubing and were deaerated by bubbling with oxygen-free nitrogen for about 30 min. The samples were irradiated with a Nd/YAG Surelite laser, using the third harmonic ($\lambda = 355$ nm, ~ 4 – 6 ns, ≥ 40 mJ/pulse), with the signal being detected by a Tektronix TDS2012 oscilloscope.

The 1,2-diketopyracene (**4**) concentration (~ 1 mM) was chosen in order to give an absorption in the wavelength of excitation (355 nm) of 0.3–0.5. Stock solutions of quenchers were prepared so that it was only necessary to add microliter volumes to the sample cell in order to obtain appropriate concentrations of the quencher.

Computational Methods. The geometries of several species were optimized using standard techniques,²⁴ and after geometry optimization, vibrational analysis was performed and the resulting geometries were checked with respect to being true minima on the potential energy surface, as shown by the absence of imaginary frequencies. Geometrical, energetic, and AIM calculations were performed at UB3LYP/6-311++G**//UB3LYP/6-31G* for all structures. NBO calculations were performed at UHF/6-311++G**//UB3LYP/6-31G* level. Energy differences correspond to enthalpy differences at 298 K and 1 atm. All calculations were performed with Gaussian 98 package of programs.²⁵ AIM^{26,27} (atoms in molecules) calculations were performed on AIM 2000, v2.0. The AIM theory was used to investigate the interactions involved in the triplet hydrogen abstraction reaction. This approach was used as it is capable of evaluating the existence of intermolecular interactions.

Results and Discussion

Laser Flash Photolysis Studies. Laser irradiation of a degassed solution of **4** in acetonitrile resulted in the formation of a readily detectable transient with absorption at 610 nm, but with a very low absorptivity (Figure 1). This transient decays by mixed first and second-order kinetics with a lifetime of around 2 μ s. (see inset in Figure 1) and shows similar lifetime and spectroscopic characteristics when compared to those of the triplet state of acenaphthenequinone (**1**).¹⁹ The triplet nature of this species was confirmed by quenching with β -carotene for which we obtained a diffusion-controlled quenching rate

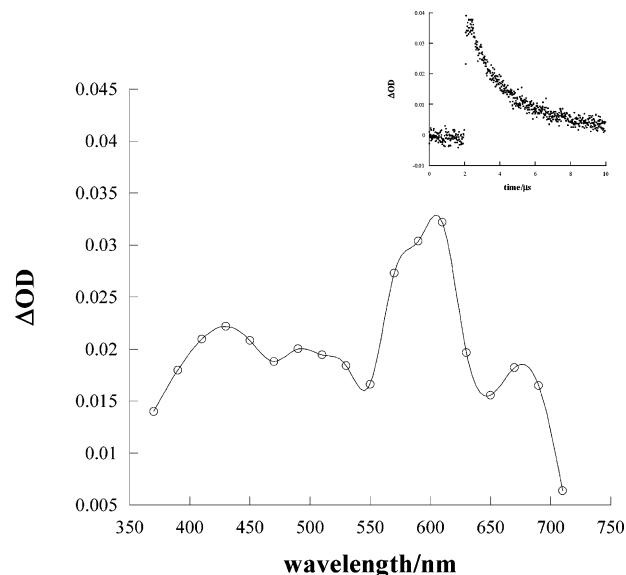


Figure 1. Transient absorption spectra obtained after 355 nm laser excitation of **4** (0.25 μ s after laser pulse) in acetonitrile solution. Inset: decay of the transient at 610 nm.

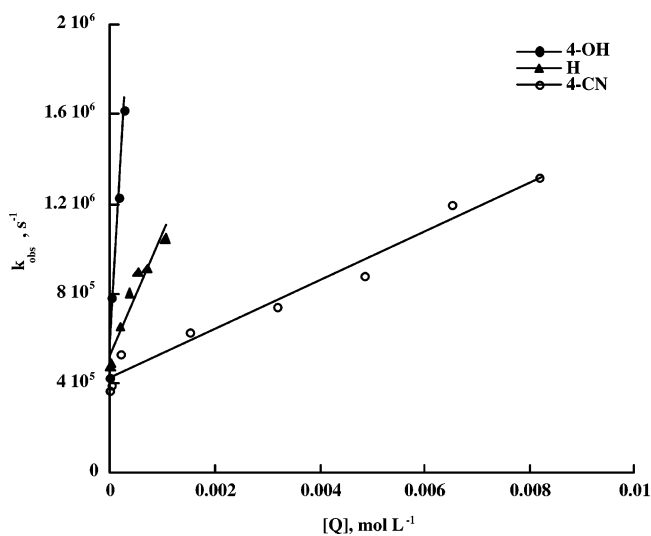


Figure 2. Quenching plots of the triplet of **4** by 4-hydroxyphenol, phenol, and 4-cyanophenol. $\lambda_{\text{exc}} = 355$ nm; $\lambda_{\text{mon}} = 610$ nm; solv = ACN.

constant, with the concomitant formation of the β -carotene triplet at $\lambda_{\text{max}} = 535$ nm.

Addition of phenols led to a shortening of the triplet lifetime of **4**. The triplet decay of this ketone followed pseudo-first-order kinetics in the presence of phenols, with the experimentally observed kinetic rate constant, k_{obs} , being related to the quenching rate constant, k_{q} , according to eq 1.

$$k_{\text{obs}} = k_0 + k_{\text{q}}[\text{Q}] \quad (1)$$

where k_0 is the decay rate constant of the triplet in the absence of the quencher, and $[\text{Q}]$ the quencher concentration. Plots based on this equation for the triplet of **4** being quenched by various phenols were found to be linear, from which one can determine the value of k_{q} . Figure 2 shows representative quenching plots for **4** by various phenols, and Table 1 shows the rate constants obtained from these plots, in acetonitrile.

Rate constants for the reaction of the triplet state of **4** toward phenols are faster than those observed for the triplet **1**,¹⁹ which is probably due to an increase in the rigidity of the former

TABLE 1: Rate Constants for Quenching of the Triplet State of 1–4 by Phenols in Acetonitrile

phenols	k_q^a L mol ⁻¹ s ⁻¹			
	1 ^b	2 ^b	3 ^c	4 ^d
4-methoxyphenol	3.1×10^9	3.6×10^7	7.0×10^6	3.0×10^9
4-hydroxyphenol	2.3×10^9	8.3×10^7	1.2×10^7	3.9×10^9
3-hydroxyphenol				2.1×10^9
4- <i>tert</i> -butylphenol	2.9×10^8	4.4×10^6	1.4×10^6	3.1×10^9
3-methoxyphenol	2.8×10^8	1.7×10^6	2.7×10^6	4.3×10^8
4-phenylphenol	2.4×10^8	2.9×10^6	1.1×10^6	1.4×10^9
3-methylphenol	1.5×10^8	1.0×10^6		8.6×10^8
4-methylphenol	9.3×10^7	3.3×10^6		1.1×10^9
4-chlorophenol	7.4×10^7	9.7×10^5	1.6×10^6	4.6×10^8
3-chlorophenol				5.0×10^8
phenol	6.9×10^7	1.0×10^6	3.3×10^5	5.7×10^8
4-bromophenol	5.3×10^7	1.2×10^6	6.9×10^5	
3-bromophenol				4.4×10^8
4-cyanophenol	1.5×10^7	4.0×10^5	2.1×10^5	1.0×10^8
4-fluorophenol				9.7×10^8
3-fluorophenol				2.1×10^8

^a Estimated to be accurate to $\pm 10\%$. ^b From ref 19. ^c From ref 22. ^d This work.

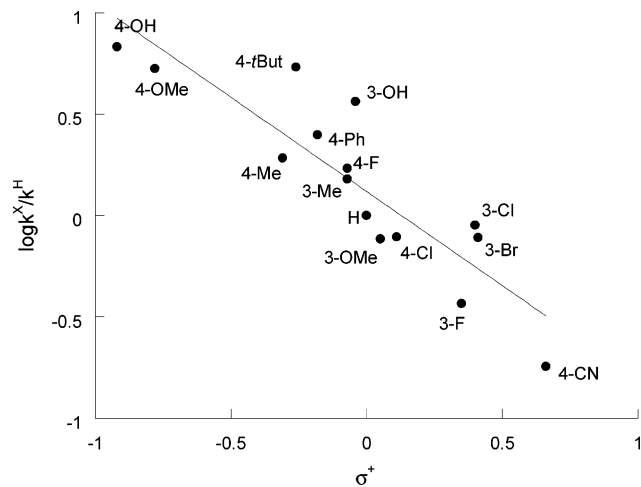
molecule, and are of the same order of magnitude for other n,π^* carbonyl triplets.¹³

The reaction of the triplet state of **4** with phenols leads to the formation of the corresponding phenoxy radical that was easily detected when laser flash photolysis experiments were performed in the presence of these hydrogen donors. For example, LFP of **4** in the presence of 4-methoxyphenol yields an absorption band centered at 400 nm, a region where 4-methoxyphenoxy radical strongly absorbs.²⁸

The Hammett correlation with the σ^+ -scale yields a negative value of $\rho = -0.9$ for the triplet state of **4** (Figure 3). Values of -1.5 , -1.48 , and -1.04 were obtained for the reaction constant ρ for **1**, **2**, and **3**, respectively.^{19,22} The negative values of ρ for all ketones is consistent with the known electrophilic character of a reactive n,π^* carbonyl triplet state.

Theoretical Calculations. The reaction mechanism for the triplets **1–4** with phenol was theoretically studied using computational methods. Recently, this method was employed to understand an analogous mechanism, the photoreduction of 2-benzoylthiophene by phenol.^{29,30} More recently, Pan et al. have used DFT calculations to investigate the photoreduction of *o*-naphthoquinones where they found that the ionization/affinity and redox potentials of the quinones gave a good correlation with experimental Hammett values.³¹ All computed geometries of the S_0 and T_1 excited states were performed without solvent effects. Hydrogen abstraction from phenol by triplet ketone, yielding the triplet radical pair, was rationalized in a three step mechanism. The first step was the formation of a triplet complex ketone/phenol, the second step was the transition state for hydrogen abstraction, and the third step was the formation of a triplet complex between the reduced ketone and the phenoxy radical after hydrogen abstraction (triplet radical pair). Figure 4 depicts the representative structures computed for the triplet complex ketone/phenol (a) and triplet radical pair (c) for diketone **1**.

Table 2 shows the computed geometric parameters for both triplet complexes and triplet radical pairs for ketones **1–4**. The calculated structures for the formation of the triplet complex ketone/phenol reveal a single hydrogen bond between the respective ketone and the phenol preceding hydrogen transfer (r1). The results of Table 2 show that the hydrogen bond in monoketone **2** is longer than that for the diketones **1** and **4** and the hydrogen bond in diketone **3** is the longest (1.877 Å),

**Figure 3.** Hammett plot for the hydrogen abstraction of the triplet of **4** by phenols, in acetonitrile.

reflecting the π,π^* configuration of the diketone.^{20,22} The dihedral angle between phenol and the respective ketone shows that only for the triplet complex **3**/phenol that both molecules are coplanar, but that after reaction takes place all diketone/phenol pairs are coplanar. This change is driven by a secondary hydrogen bond formed by an ortho phenolic hydrogen and the second carbonyl group on the diketone (r8 in Figure 4). As can be seen from Table 2, the bond length for this secondary H-bond interaction in the triplet radical pair complexes varies from 2.137 Å to 2.147 Å. These results illustrate the important participation of the second carbonyl group on the stability of the triplet radical pair. Once again it is interesting to note that this distance is marginally longer for the π,π^* diketone **3** triplet radical pair.

From the geometric parameters it can be seen that the monoketone **2** has the shorter O1–H_{transferring} (r1) bond and the longer O3–H_{transferring} (r2). These distances are similar among the diketones. The r3 distance is constant, independent of the ketone. The comparison between r5 and r6 indicates that the reacting carbonyl group has the longer bond length (r5). The r4 distance spans much larger values than the r1 values, though the values for ketones **1** and **4** are similar. The value for diketone **3** is larger than that compared with the ketones **1** and **4**. The transition state is found to be nonsymmetrical, revealing a localized hydrogen abstraction instead of vicinal carbonyl participation.

The calculated energies of the T_1 excited states are depicted in Table 3. Theoretical values are in reasonable agreement with the experimental results for the monoketone **2**.³² For diketone **1**, its value is lower than that from the literature.³³ For diketones **3** and **4**, there are no experimental values in the literature. However, the interesting point is the comparison among these values (triplet energy from Table 3), where the monoketone **2** has the larger value for T_1 (54.2 kcal/mol), while the diketones have values close to 44 kcal/mol. The solvent effects on the singlet and triplet states were not taken into account in the calculations. Differences in the solvation of mono and diketones may be important and could therefore result in the difference between calculated and experimental T_1 excited-state energies.

Table 3 also shows the calculated energy differences between the triplet radical pair and triplet complex ketone/phenol ($\Delta G_{\text{reaction}}$). From these results one can conclude that all the studied ketones have a triplet radical pair less energetic than the triplet complex ketone/phenol. These results support the experimental feasibility of hydrogen abstraction by the ketone triplet state. The monoketone **2** has the least energy difference

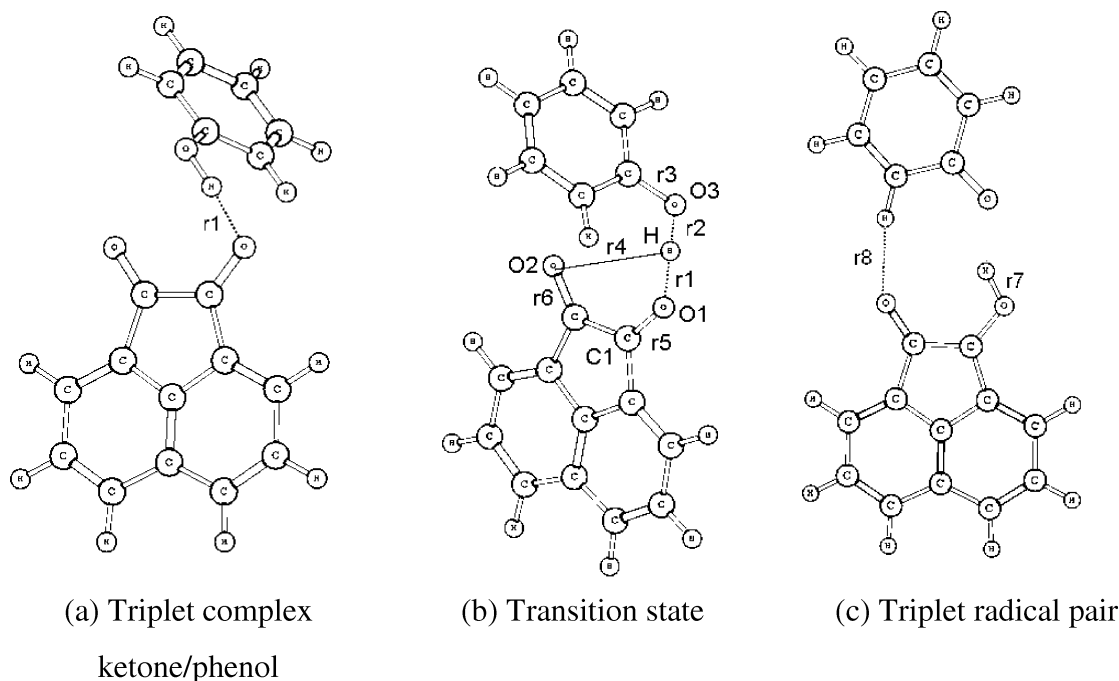


Figure 4. UB3LYP/6-31G* optimized structures for the computed reaction coordination of the hydrogen abstraction by diketone **1**.

TABLE 2: Geometric Parameters for the Triplet Complex Ketone/Phenol and for the Triplet Radical Pair

reaction coordinate	parameter	ketone			
		1	2	3	4
reactants	r1 (Å)	1.527 and 2.531 ^a	1.789	1.877 and 2.817 ^a	1.539 and 2.519 ^a
	dihedral angle between reactants (deg)	53.4	66.8	0	81.4
transition state	r1 (Å)	1.330	1.240	1.350	1.320
	r2 (Å)	1.110	1.150	1.090	1.110
	r3 (Å)	1.290	1.300	1.300	1.290
	r4 (Å)	2.879	-	3.170	2.862
	r5 (Å)	1.283	1.291	1.278	1.283
	r6 (Å)	1.260	-	1.250	1.250
product	dihedral angle between reactants (deg)	42.7	72.0	0	73.2
	r7(Å)	0.994	0.988	0.992	0.995
	r8(Å)	2.139	-	2.147	2.137
	dihedral angle between reactants (deg)	0.1	43.1	0	0.4

^a Values relative to the interaction between the acidic phenolic hydrogen and the second carbonyl group.

TABLE 3: Computed (UB3LYP/6-311++G//UB3LYP/6-31G*) Energetic Parameters for the Phenolic Hydrogen Abstraction**

ketone	triplet energy (kcal/mol)	ΔG^{\ddagger} activation (kcal/mol)	$\Delta G_{\text{reaction}}$ (kcal/mol) ^c
1	43.8 ^a	ca. 0	-12.6
2	54.2 ^b	2.4	-8.3
3	44.2	ca. 0	-12.0
4	45.4	ca. 0	-12.9

^a Experimental value 52 kcal/mol.^{33,35} ^b Experimental value 50 kcal/mol.³² ^c Difference between triplet complex ketone/phenol and triplet radical pair (see Figure 4).

(-8.3 kcal/mol) between both complexes, while diketones **1**, **3**, and **4** are about 12 kcal/mol more stabilized. These values are also in agreement with experimental results of reactivity toward phenols for the triplets **1**¹⁹ and **4** (Table 1).

Table 3 also depicts the activation energies for the transition state formed from the triplet complex ketone/phenol for all the studied reactions. The most important result is the positive activation barrier for the monoketone/phenol reaction while the diketone/phenol reactions are barrierless, ca. 0 kcal/mol.

The NBO population analysis in Table 4 depicts the electron distribution for hydrogen abstraction by ketones **1–4** in a three

TABLE 4: NBO Population of Ground and Triplet Excited States of Ketones 1–4, Triplet Complexes of Ketones 1–4/Phenol, Triplet Radical Pair Ketones 1–4/Phenol, and Their Transition States

	ketones NBO electron population ^a			
	1 (94)	2 (88)	3 (120)	4 (108)
triplet complex ketone/phenol	94.9	88.0	120.8	109.0
ketone-phenol transition state	94.9	88.7	120.8	109.0
triplet radical pair	95.0	89.0	121.0	109.0

^a Respective NBO total number of electrons in parenthesis

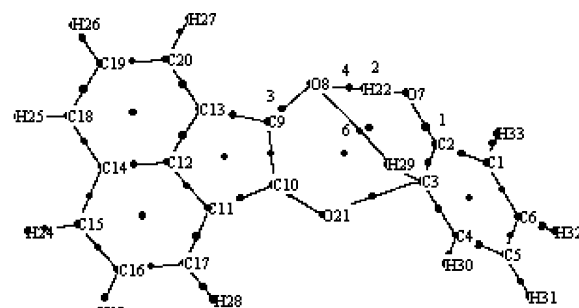
step sequence. From this table, one can see that three of the four ketones accept charge (q) from phenol at the triplet complex stage: for **1**, $q = 0.9e$; for **2**, $q = 0e$; for **3**, $q = 0.8e$; and for **4**, $q = 1.0e$. Here, e means unit charge density. The more electrophilic acceptor system is ketone **4**, followed by **1**, and then **3**. When analyzing the reaction, one can note that almost all the accepted charge by the ketones has been transferred at the initial triplet complex step. However in the case of **2**, the electron is transferred simultaneously with the H^+ in the transition state (i.e., a true hydrogen abstraction) thus, resulting in the positive activation energy for this reaction. On the other hand, the diketones **1**, **3**, and **4** have almost one electron transferred at the triplet complex, and therefore, they possess a

TABLE 5: Charge Density of Bond Critical Points of Ketones 1–4/phenol Complexes and Transition States

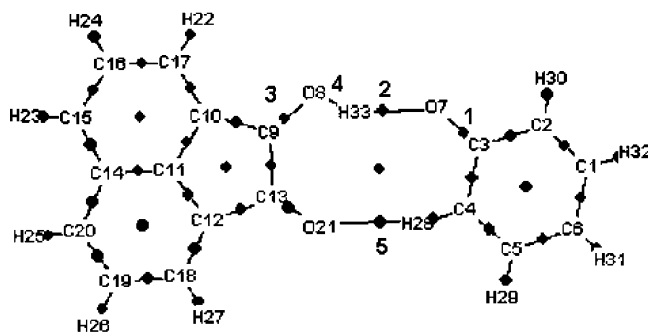
ketone	step	charge density of bond critical points (au)		
		BCP 2 ^a	BCP 4 ^a	BCP 5 ^a
1	triplet complex	0.290	0.292	
	transition state	0.226	0.118	
2	triplet radical pair	0.034	0.325	0.017
	triplet complex	0.335	0.037	
3	transition state	0.193	0.153	
	triplet radical pair	0.037	0.292	
4	triplet complex	0.232	0.107	0.023
	transition state	0.232	0.107	0.023
4	triplet radical pair	0.034	0.325	0.016
	triplet complex	0.223	0.121	-
4	transition state	0.223	0.121	-
	triplet radical pair	0.032	0.326	0.016

^a Bond critical points as depicted in Figure 5.

barrierless transition state involving H⁺ transfer. Finally, all the triplet products are reduced equally by 1.0e. Therefore, the NBO analysis reveals the importance of the electron transfer in the reactions between the diketones and phenol. On the basis of the energetics and NBO results, it can be seen that the diketones are very reactive and that this reactivity is due to their excited-state reduction potential. The NBO results reveal that for the diketones an electron is transferred before the transition state for proton transfer. The relative reactivity of the diketones can also be appreciated by the extent of electron transfer in the triplet complexes for the diketones, the greater the electron transfer the larger the values for k_q and the decreasing order of reactivity is 4, 1, and then 3. In the case of the calculated monoketone 2 with a n,π^* excited state, electron transfer in the triplet complex is not observed, reflecting a change in mechanism for the hydrogen abstraction reaction in comparison with the diketones. The NBO results for 2 reveal that a simultaneous electron/proton-transfer mechanism occurs during the transition state. These results are in agreement with the experimental values obtained recently by Leigh et al. for the hydrogen abstraction reaction from 4-methylphenol by a series of aromatic ketone triplets,³⁴ which are consistent with a reaction occurring via two different mechanisms. These mechanisms can be described as follows: (1) an electron-transfer mechanism, which applies to the n,π^* triplet ketones and those π,π^* triplets that possess particularly low reduction potentials; (2) a coupled electron-proton-transfer mechanism involving the intermediacy of a hydrogen-bonded exciplex, which applies to n,π^* and π,π^* ketone triplets that are less easily reduced. The former mechanism offers an explanation for our results for the diketones 1, 3, and 4 as discussed above, where the electron is almost completely transferred in the triplet complex, as a consequence of the expected low reduction potential for α -diketones that have either $n\pi^*$ or $\pi\pi^*$ triplet states. The results from the calculations are in accord with the experimental observation of the detection of the phenoxy radical and not the radical anion of the diketones as the subsequent ultrafast proton transfer to the radical anion must occur through an essentially barrierless transition state in the excited-state complex resulting in the radical pair. In the case of monoketone 2 despite being a $n\pi^*$ triplet state the reactivity is less than that observed with diketones 1 and 4 possibly due to a higher reduction potential, which results in a preference for a hydrogen abstraction via a hydrogen-bonded exciplex electron-proton-coupled transfer. The diminished reactivity of diketone 3 in relation to the diketones 1 and 4 is most likely due to the π,π^* nature of the excited-state of 3 where the basicity and the reduction potential have opposing effects. Indeed, as seen in Table 4, diketone 3 has a smaller electron



(a) transition state



(b) triplet radical pair

Figure 5. Molecular graphs for the (a) transition state and (b) triplet radical pair for diketone 1.

transferred NBO population in the triplet ketone/phenol complex in comparison to diketones 1 and 4.

A complementary study using AIM theory revealed an important feature: in the triplet state the magnitude of the CO-H interaction depends upon the extent of electron density transferred between the reactants. This parameter can be qualitatively evaluated by following the charge density values of bond critical points in the ketone/phenol triplet complexes and transition states (Table 5). In the triplet complexes the values for the charge density in the H(phenol)-O(ketone) bond (BCP 4) range from 0.107 to 0.292 au for the diketones, along with the low charge value for the monoketone 2 (0.037 au for BCP 4), are consistent with the observations made from the NBO analysis for the transfer of an electron in the case of the diketones and for a change in the reaction mechanism for monoketone 2. This is further confirmed by the largest density value for BCP 2 for the triplet complex involving 2, indicating the reduced charge transfer between phenol and the monoketone.

At the transition states, where an electron has been transferred in all cases, charge densities for BCP 4 no longer show a significant variation, with values varying from 0.107 to 0.153 au. This means that for the four studied transition states the CO-H bonds have almost the same nature.

As shown in Table 5, the diketones reveal a BCP 5 for the triplet radical pairs, and in the case of diketone 3, a BCP 5 is observed at all steps in the computed reaction coordinate, where the BCP 5 is related to a hydrogen bond like interaction between the second carbonyl group of the diketones and an ortho aromatic hydrogen of the phenol (H- Φ). This result is fully in accord with previous thermodynamic parameters found for the interaction of triplet 1 with 4-methoxyphenol.¹⁹ For this triplet an Arrhenius pre-exponential value of 10.2 was found, which indicates that an entropic factor has some contribution to the reactivity of the α -diketone 3 when compared to monoketones (for example, the pre-exponential factor for the reaction between benzophenone triplet and the same phenol is 12.5).¹³ Thus, the

more organized transition state for cisoid α -diketones can be a consequence of the extra interaction between the second carbonyl group of the diketones and the ortho aromatic hydrogen of the phenol.

It is important to note that no BCP was found between the transferring hydrogen atom and the vicinal carbonyl group (O2–H in Figures 4 and 5). This important feature evaluated by the AIM theory implies that no interaction between O2 and the transferring H atom is found at the transition state. That is, the second carbonyl group in the diketones does not act as an auxiliary group for phenol hydrogen abstraction, but instead, the presence of this group enhances the electron acceptor nature of the diketones.

Conclusion

Theoretical results are in agreement with experimental values. As discussed above, the Hammett correlation with σ^+ -scale yields a negative value of ρ (**1** = -1.5 , **2** = -1.48 , **3** = -1.04 , and **4** = -0.9 , Figure 3). These negative values of ρ for all ketones are consistent with the electrophilic character of the reactive carbonyl triplet states, which is in accordance with NBO analysis. Both theoretical and experimental results indicate that for these diketones the hydrogen abstraction from phenol is driven by an electron-transfer mechanism instead of a cooperative participation of the second carbonyl on the hydrogen abstraction step where n,π^* excited states are more reactive than π,π^* excited states.

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