

(CCl₄, 220 MHz) δ 5.15-5.24 (m, 1 H), 4.70-4.75 (br s, 2 H), 2.93-3.00 (br s, 2 H), 2.42 (m, 1 H), 1.82-1.95 (m, 2 H), 1.54 (d, $J = 6$ Hz, 3 H), 1.08 (d, $J = 6$ Hz, 3 H); mass spectrum, m/e (M^+) 122.

Fraction No. 3. The peak corresponding to this fraction had identical retention time and NMR spectrum as those reported for AS.

Fraction No. 4. The peak corresponding to this fraction had identical retention time and NMR spectrum as those reported for AA.

Kinetics. The pyrolysis apparatus for the kinetic study of C and T was the same used in the pyrolysis of DMCP-*d*₄. For a typical pyrolysis run, 8 μ L of pure sample was transferred into an evacuated 2-L well-conditioned bulb, timing being started when the bulb's valve was closed. After pyrolysis at the stated time interval, the pyrolysate was collected in a spiral coil trap at the temperature of liquid nitrogen and then vacuum transferred into a collector. The recovered pyrolysate was diluted with ~ 25 μ L of pentane and analyzed on a 200 ft \times 0.1 in. i.d. stainless-steel capillary column packed with DBTCP which separated all components to base line. Each run was analyzed from three to five times, and the average of these values for each time interval is reported. Since there is interconversion of C \rightleftharpoons T and the two reactants yield the same 1,3- and 3,3-shift products, the kinetics are not strictly first order. In order to account for this interconversion, we solved the kinetic scheme by using a numerical integration Runge-Kutta program. Table II shows the experimental and calculated mole fractions as a function of time, using the refined ten rate constants which define the system.

Pyrolysis of (-)-(4*R*,5*R*)-trans-4,5-Dimethyl-1,3-dimethylenecyclopentane and -1,3-Bis(dideuteriomethylene)cyclopentane [(-)-T^{H4} and (-)-T^{D4}]. In a typical pyrolysis run ~ 25 -35 μ L of each compound was pyrolyzed at 360.4 °C for 24 h. The recovered pyrolysate was separated by VPC (6 ft \times 0.25 in., 20% DBTCP, 90 °C). Because of difficulties found in the separation of C and T and S from A, the collected fractions

are mixtures of the corresponding isomers. Quantitative analysis of the recovered pyrolysate was done in the same conditions as for T and C. The values of the optical activity for the recovered starting materials (-)-T^{H4} and (-)-T^{D4} are the average of two experiments at the respective wavelengths, (Table IV).

Degradation of (+)-(+*S*)-anti-1-ethylidene-3-methylene-4-methylcyclopentane [(+)-A] to (-)-(S)-Methylsuccinic Anhydride. The collected fraction of (+)-A ($\sim 7\%$ contaminated with S) from the pyrolysis of (-)-T^{H4} was ozonized and oxidatively degraded under the same conditions as described for the degradation of DMCP to succinic acid; however the conversion of methylsuccinic acid to its anhydride was modified. Treatment of the crude product from the degradation with a 20:1 mixture of acetyl chloride/thionyl chloride at 45 °C for 1.5 h gave a semisolid after purification by vacuum distillation (70-90 °C (1 torr)). This semisolid showed IR and MS spectral characteristics identical with those for synthetic methylsuccinic anhydride. The optical purity of this material was determined by comparing its optical rotatory power value ($[\alpha]_D -6.1^\circ \pm 0.2$, $[\alpha]_{365} -16.2 \pm 0.4$ (c 6.8 mg/mL in ethanol)) with the highest value reported ($[\alpha]_D +32.97$).^{11,25}

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(25) The initial report of this work¹ used a value for the highest rotation reported which was shown to be incorrect.¹⁴

Laser Flash Photolysis Study of the Reactions of Carbonyl Triplets with Phenols and Photochemistry of *p*-Hydroxypropiofenone

P. K. Das, M. V. Encinas, and J. C. Scaiano*¹

Contribution from the Radiation Laboratory,² University of Notre Dame, Notre Dame, Indiana 46556. Received November 12, 1980

Abstract: The quenching of aromatic carbonyl triplets by phenols is a very fast process for both n,π^* and π,π^* states. Representative rate constants for benzophenone triplets in benzene are 1.3×10^9 (phenol) and 8.1×10^8 (*m*-fluorophenol) $M^{-1} s^{-1}$, while for *p*-methoxypropiofenone the values are 4.9×10^9 and $5.0 \times 10^9 M^{-1} s^{-1}$ for the same pair of substrates; 18 different phenols were examined. The rate constants are smaller in wet acetonitrile as a result of hydrogen bonding; for example for the benzophenone-phenol system we measured $8.0 \times 10^7 M^{-1} s^{-1}$. Isotope effects are larger for *p*-methoxypropiofenone than for benzophenone: for example in the case of phenol the values of k_H/k_D are 3.9 and 1.2, respectively (in wet acetonitrile). The quenching reaction leads to the efficient, but not quantitative, formation of phenoxy and ketyl radicals, with the only exception of *p*-nitrophenol where the process involves electronic energy transfer. The temperature dependence of a few representative systems, as well as the quenching by methyl ethers of similar structure, has also been examined. The photochemistry of *p*-hydroxypropiofenone is characterized by efficient self-quenching involving a head-to-tail hydrogen-transfer reaction.

Carbonyl triplets abstract hydrogen atoms from a variety of substrates,³ including hydrocarbons, alcohols and amines; these reactions have been proposed to occur by either an atom-transfer or an electron-transfer mechanism. In the latter case, the reaction is usually followed by proton transfer. Although there have been numerous studies regarding intermolecular and intramolecular hydrogen abstraction reactions³⁻⁵ of carbonyl triplets, the photo-

chemistry of carbonyl compounds in the presence of phenols has received only limited attention. In particular, Turro et al.^{6,7} have examined the photochemistry of biacetyl in the presence of phenols and observed that efficient triplet quenching was not accompanied by product formation. It was suggested that the

(1) To whom correspondence should be addressed at the Division of Chemistry, National Research Council, Ottawa, Canada K1A 0R6.

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reaction proceeded via reversible hydrogen abstraction; in support of this suggestion was the kinetic isotope effect of 3.4. A Hammett plot⁷ of the rate constants for phosphorescence quenching by six substituted phenols yielded $\rho = -1.15$.

No data on the absolute rates of interaction of aromatic carbonyl triplets with phenols have so far been reported. Becker⁸ has studied the photolysis of several aromatic ketones in the presence of phenols and isolated products which could be rationalized in terms of a mechanism involving reversible hydrogen abstraction by the carbonyl triplets from phenols. The formation of ketyl radical during the photolysis of acetophenone-phenol mixtures has also been demonstrated in CIDNP studies.^{9,10}

The photochemistry of *p*-hydroxypropiophenone (or *p*-hydroxyacetophenone) has not been examined before. In a related system, Favaro¹¹ has reported that *p*-hydroxybenzophenone undergoes efficient self-quenching with a rate constant of $1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in benzene at room temperature. While the mechanism of self-quenching could involve a head-to-tail hydrogen abstraction process, no evidence for the formation of phenoxy radicals has been reported.

A structurally related group of molecules, including 2-hydroxybenzophenones as the most common example, is frequently used as polymer photostabilizers and has been the subject of several studies.¹²⁻¹⁴ Their role is known to involve UV screening followed by efficient energy wasting, but there is evidence suggesting that their role may be more complex than this.¹²

In this paper we report the results of a laser flash photolysis study of the quenching of carbonyl triplets by substituted phenols and compare the data with the results obtained in the photochemistry of *p*-hydroxypropiophenone. In the following paper¹⁵ we shall present the results of a similar study with *tert*-butoxy radicals and make a comparison between the reactions of carbonyl triplets and alkoxy radicals with phenols.

Results

All the flash experiments in the present study were carried out by using the pulses from a nitrogen laser (337.1 nm, $\sim 8 \text{ ns}$, $\sim 3 \text{ mJ}$) for excitation. In most cases, the kinetic measurements required the averaging of only two to four traces and were carried out on static samples. The transient spectra were determined by using a flow system. All the data was obtained under oxygen-free conditions.

(a) Carbonyl Triplet Quenching by Phenols. The rates of interaction of carbonyl triplets with several phenols were determined by monitoring the transient T-T absorptions due to the carbonyl triplets as a function of the concentration of substrate. The basic mechanism is shown in reactions 1-5.



Figure 1 shows two traces obtained in the case of benzophenone in benzene using phenols as a quencher. The traces at 535 and 400 nm do not decay to the original (i.e., prepulse) level. The offset can be attributed to reaction 3, leading to the formation of phenoxy and ketyl radicals which absorb strongly at 400 and

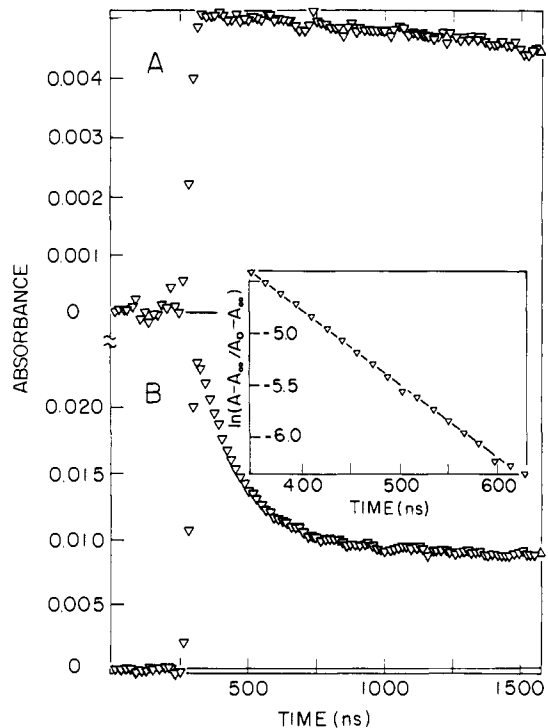


Figure 1. Experimental trace obtained in the benzophenone (0.01 M)-phenol (0.0043 M) system in benzene (at low doses) monitored at 400 nm (A) and 535 nm (B). Insert: plot of the data at 535 nm according to eq 6.

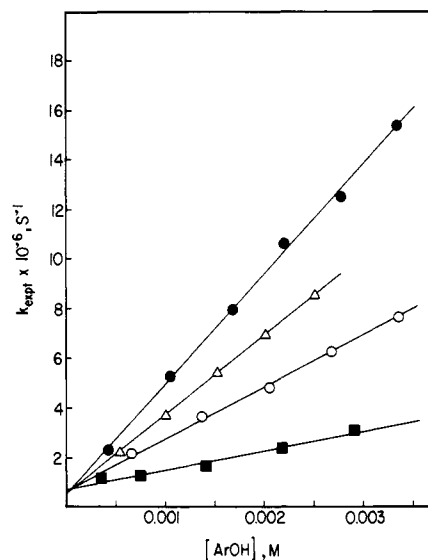


Figure 2. Kinetic data for the quenching of benzophenone triplets in benzene by *p*-methoxyphenol (●), *p*-nitrophenol (Δ), *p*-iodophenol (○), and *p*-cyanophenol (■).

535 nm, respectively.¹⁶⁻¹⁹ We note that in the time scale of our experiments the radicals are long-lived enough that their decay does not need to be taken into consideration. Kinetic analysis for a system of this type is straightforward; the carbonyl triplet

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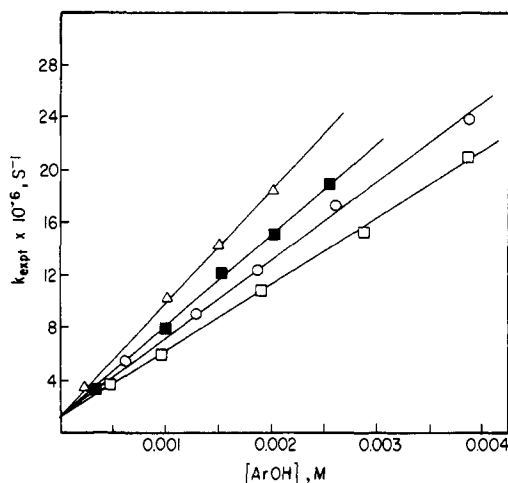


Figure 3. Kinetic data for the quenching of *p*-methoxypropiophenone triplets in benzene by *p*-nitrophenol (Δ), *p*-bromophenol (\blacksquare), *p*-cresol (\circ), and phenol (\square).

Table I. Rate Constants for the Quenching of Carbonyl Triplets by Substituted Phenols in Benzene at 22 °C

substituent	$k_q, M^{-1} s^{-1}$	
	benzophenone	<i>p</i> -methoxypropiophenone
H	1.3×10^9	4.9×10^9
<i>p</i> -OCH ₃	4.5×10^9	6.7×10^9
<i>p</i> -OC ₂ H ₅	4.7×10^9	6.0×10^9
<i>p</i> -C(CH ₃) ₃	2.4×10^9	4.9×10^9
<i>p</i> -C ₂ H ₅	2.9×10^9	5.3×10^9
<i>p</i> -CH ₃	2.6×10^9	6.0×10^9
<i>p</i> -F	1.7×10^9	5.6×10^9
<i>p</i> -Cl	2.0×10^9	6.4×10^9
<i>p</i> -Br	1.8×10^9	7.0×10^9
<i>p</i> -I	2.0×10^9	6.6×10^9
<i>p</i> -CN	6.5×10^8	6.2×10^9
<i>p</i> -NO ₂	2.9×10^9	8.7×10^9
<i>m</i> -OH	2.8×10^9	7.2×10^9
<i>m</i> -OCH ₃	2.4×10^9	5.0×10^9
<i>m</i> -CH ₃	1.9×10^9	5.7×10^9
<i>m</i> -F	8.1×10^8	5.0×10^9
<i>m</i> -Br	1.1×10^9	5.2×10^9
<i>m</i> -CN	5.9×10^8	5.5×10^9

disappears with the same kinetics with which the radicals are formed. In this case, the experimental rate constant can be obtained following the analysis of the data according to eq 6 and 7,²⁰ where A_0 is the transient absorption immediately after the

$$\ln \left(\frac{A - A_\infty}{A_0 - A_\infty} \right) = -k_{\text{exptl}} t \quad (6)$$

$$k_{\text{exptl}} = k_2 + (k_3 + k_4 + k_5)[\text{ArOH}] \quad (7a)$$

$$k_{\text{exptl}} = k_2 + k_q[\text{ArOH}] \quad (7b)$$

$$k_q = k_3 + k_4 + k_5 \quad (7c)$$

laser pulse, A_∞ the absorption after the triplet decay is complete, and A the absorption at time t . We note that k_q contains all the quenching rate constants; i.e., it includes both chemical and physical quenching processes. Figures 2 and 3 show a few representative plots according to eq 7 for benzophenone (monitored at 535 nm) and *p*-methoxypropiophenone (at 395 nm). The kinetic data for various substituted phenols in benzene have been summarized in Table I.

As pointed out earlier, the long-lived absorptions observed at the end of triplet decay can be attributed to a mixture of ketyl

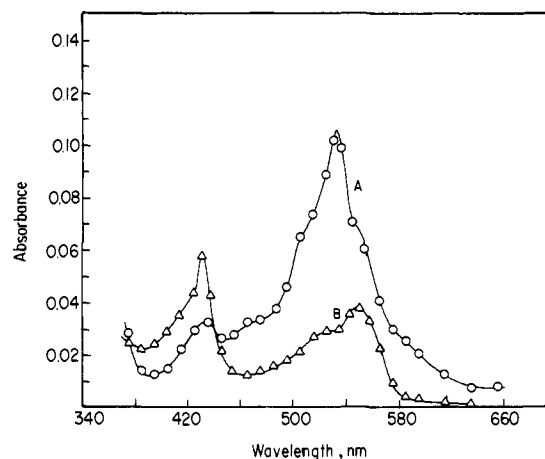


Figure 4. Spectra obtained in the benzophenone (0.028 M)-*p*-bromophenol (0.0027 M) system in benzene: A, end of pulse; B, after 1.3 μ s.

Table II. Yields of Phenoxy or Ketyl Radical in the Reaction of Carbonyl Triplets with Phenols in Benzene at 22 °C

phenol	ketyl or phenoxy yield	
	benzophenone ^{a,b}	<i>p</i> -methoxypropiophenone ^{b,c}
phenol	0.84	
hydroquinone	0.84	
<i>p</i> -methoxyphenol	0.79	
<i>p</i> -cresol	0.83	
<i>p</i> -fluorophenol	0.91	
<i>p</i> -chlorophenol	0.75	
<i>p</i> -bromophenol	0.71	0.55
<i>p</i> -iodophenol	0.61	0.21
<i>p</i> -cyanophenol	0.88	0.56

^a Ketyl yield. ^b See text for assumptions in the determination of yields. ^c Phenoxy yield.

and phenoxy radicals. For example, Figure 4 shows the transient spectra of benzophenone-*p*-bromophenol system recorded immediately after the laser pulse ("end-of-pulse" spectrum) and after ca. 7 triplet lifetimes, when less than 1% of the triplets remain. The "end-of-pulse" spectrum is in full agreement with that of benzophenone triplet,¹⁹ while the transient absorption following triplet decay is consistent with a mixture of ketyl and *p*-bromophenoxy radicals for which spectral data are available in the literature.^{18b,19}

In the case of benzophenone the maximum of absorption due to the ketyl radical (~ 545 nm) is well separated from the spectral absorptions due to the phenoxy radicals. In order to throw some light on the relative importance of the various pathways (reactions 3-5) responsible for triplet quenching, we carried out experiments to estimate the yields of the ketyl radical using various para-substituted phenols, *p*-XC₆H₄OH, as substrates. With use of a relatively concentrated solution of benzophenone in benzene in matched cells, the absorbances due to the ketyl radical were measured at 545 nm at room temperature following the completion of the triplet decay. The concentrations of the phenols were so adjusted that 95% of the carbonyl triplets were quenched by the phenols in each case. With X = OCH₃, CH₃, C₂H₅, C(CH₃)₃, H, F, Cl, and CN, the ketyl yields differed by less than 10%. In comparison to the average of the ketyl yields for these phenols, the ketyl yields were found to be significantly lower for *p*-bromophenol (15% less) and *p*-iodophenol (30% less). Similar results were also obtained in 1:9 water-acetonitrile; the ketyl yield was again significantly lower for *p*-iodophenol (40% reduction), compared to the average yield for the other phenols (Table II).

We also compared the ketyl yields observed under conditions where the benzophenone triplets were totally quenched by phenols with the triplet yield in the absence of any quencher. For several phenols, X = H, OCH₃, C(CH₃)₃ and F, in benzene, we found $A_{\text{triplet}}/A_{\text{ketyl}} = 2.8 \pm 0.5$, where A_{triplet} is the "end-of-pulse" absorbance due to benzophenone triplet monitored at 533 nm in the

(20) For a detailed kinetic analysis in a similar system, see: Encinas, M. V.; Wagner, P. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 1357-60.

absence of quencher and A_{ketyl} is the absorbance due to the ketyl radical monitored at 545 nm in the presence of sufficiently high concentration of phenols. Using a ratio of extinction coefficients at the maximum for the benzophenone triplet and the ketyl radical of 2.36,^{19c,21,23} we estimate that ~85% of the quenching events lead to free radical generation. Given the uncertainty in extinction coefficients, the efficiency is not significantly different from 100%. However, we observe that when the temperature is reduced, the yields of free radicals decrease substantially, even under conditions of quantitative quenching by phenols. At -70 °C the yields are one-fourth to one-fifth of the ones at room temperature (in toluene). At low temperatures there is no question on the occurrence of quenching processes which do not yield radicals.

In the case of *p*-methoxypropiofenone, the absorption spectrum of the ketyl radical overlaps considerably with the spectra of most of the phenoxy radicals (390–430 nm). Experiments, similar to the ones described above for benzophenone, to measure ketyl yields, were not possible for *p*-methoxypropiofenone. However, for some of the phenols the absorption maxima of the phenoxy radicals are located at relatively long wavelengths, e.g., *p*-cyanophenol ($\lambda_{\text{max}} = 440$ nm), *p*-bromophenol ($\lambda_{\text{max}} = 430$ nm), and *p*-iodophenol ($\lambda_{\text{max}} = 470$ nm). For these systems, the absorbances due to the phenoxy radicals could be monitored at or near the respective wavelength maxima without significant contribution from the ketyl radicals. The absorbances could then be converted into relative yields using the respective extinction coefficients, or their ratios, available from the study of hydrogen abstraction by *tert*-butoxy radicals (see following paper).¹⁵ For *p*-bromophenol and *p*-cyanophenol, the yields of the phenoxy radicals in benzene were found to be practically the same, whereas for iodophenol, the phenoxy yield was found to be 60% lower than the average of the yields for *p*-bromo- and *p*-cyanophenol (Table II).

A rough estimate of the percentage of the ketone that is quenched but does not lead to hydrogen abstraction was also made in the case of *p*-methoxypropiofenone-*p*-bromophenol system. We measured $A_{\text{triplet}}/A_{\text{phenoxy}} = 3.3 \pm 0.3$, where A_{triplet} is the "end-of-pulse" absorbance due to the ketone triplet monitored at 390 nm (λ_{max}) in the absence of any quencher and A_{phenoxy} is the "end-of-pulse" absorbance primarily due to phenoxy radical (and partly due to ketyl radical) monitored at 430 nm in the presence of excess of *p*-bromophenol. On the basis of extinction coefficients ($12\,000\text{ M}^{-1}\text{ cm}^{-1}$ for the ketone triplet²⁴ at 390 nm, $5900\text{ M}^{-1}\text{ cm}^{-1}$ for *p*-bromophenoxy radical²⁵ at 430 nm, and $\sim 700\text{ M}^{-1}\text{ cm}^{-1}$ for ketyl radical²⁶), we should obtain a ratio of 1.8, providing every quenching event leads to hydrogen abstraction. Roughly 45% of the quenching at room temperature takes place by pathways that do not lead to radical formation. The difference from the expected ratio for "quantitative quenching" is large enough to be beyond the cumulative errors of the measurements.

With *p*-nitrophenol, no significant absorption attributable to ketyl or phenoxy radical²⁸ was observed in the 360–600-nm range at the end of the triplet decay for benzophenone or *p*-methoxy-

Table III. Rate Constants for the Quenching of Carbonyl Triplets by Phenyl Ethers in Benzene at 22 °C

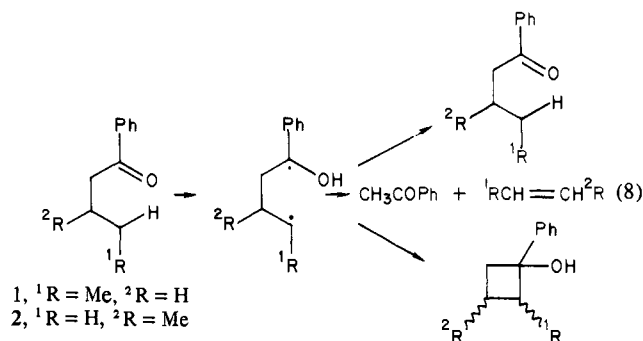
phenyl ether	$k, \text{M}^{-1} \text{s}^{-1}$	
	benzophenone	<i>p</i> -methoxypropiofenone
diphenyl ether	6.2×10^5 ^a	$<1 \times 10^6$
anisole	$<1 \times 10^6$	$<1 \times 10^6$
<i>p</i> -dimethoxybenzene	4.5×10^8	$<1 \times 10^6$
<i>p</i> -methylanisole	2.8×10^7	$<1 \times 10^6$
<i>p</i> -fluoroanisole	3.2×10^7	9.1×10^7
<i>p</i> -chloroanisole	6.2×10^6	8.1×10^6
<i>p</i> -bromoanisole	6.1×10^6	2.0×10^6
<i>p</i> -iodoanisole	1.6×10^7	1.5×10^7
<i>p</i> -anisonitrile	$\sim 1 \times 10^6$	$<1 \times 10^6$
<i>p</i> -nitroanisole	2.5×10^9	7.5×10^9

^a See ref 29.

propiofenone. The quenching of the ketone triplets by *p*-nitrophenol appears to be the result of energy rather than hydrogen transfer. Further evidence in support of this will be given below.

(b) Carbonyl Triplet Quenching by Phenyl Ethers. In order to determine the role of electronic energy transfer and possible complications due to reaction at the sites other than the phenolic OH groups (e.g., benzene nucleus,²⁹ methyl group in *p*-cresol), we have carried out quenching experiments with a number of para-substituted phenyl methyl ethers in benzene. The results are summarized in Table III. The kinetics and spectra with *p*-nitroanisole were found to be very similar to those with *p*-nitrophenol. The quenching rate constants for other substituted phenyl ethers are at least 50 times slower than those for the corresponding phenols, except in the case of dimethoxybenzene-benzophenone system. The rate constant for the quenching of benzophenone triplet by dimethoxybenzene is about 10% of that by *p*-methoxy- and *p*-ethoxyphenols.

(c) Photofragmentation of Valerophenone and Isovalerophenone in the Presence of Phenols. A study of the reaction between acetophenone or propiofenone with phenol using laser flash photolysis techniques was difficult, largely as a result of extensive overlap between the corresponding T-T absorptions and the spectra of phenoxy and ketyl radicals. The basic problem is that the three species absorb in the 400-nm region with extinction coefficients^{16,18,27} in the neighborhood of 1000 to 2000 $\text{M}^{-1}\text{ cm}^{-1}$. In order to obtain an estimate of the rate constant for a simple phenyl alkyl ketone, we examined the quenching of the Norrish Type II photofragmentation of valerophenone (1) and isovalerophenone (2) by phenol. Reaction 8 shows the photofragmentation mechanism.^{5,30}



If the yields of acetophenone in the presence of phenol decrease solely as a result of triplet quenching, then the quantum yields in the absence (ϕ_{II}^0) and presence (ϕ_{II}) of phenol should be related by a simple Stern-Volmer dependence (eq 9), where τ_{T} is the

$$\frac{\phi_{\text{II}}^0}{\phi_{\text{II}}} = 1 + k_{\text{q}}\tau_{\text{T}}[\text{PhOH}] \quad (9)$$

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(22) Other reported values for ϵ_{max} of benzophenone triplet in benzene are 10 300^{19c} and 7400²³ $\text{M}^{-1}\text{ cm}^{-1}$. On the basis of the energy transfer to naphthalene ($\epsilon_{\text{max}} = 13\,000\text{ M}^{-1}\text{ cm}^{-1}$, $\lambda_{\text{max}} = 425$ nm in benzene),²¹ we estimated a value of $7100 \pm 800\text{ M}^{-1}\text{ cm}^{-1}$ for ϵ_{max} of benzophenone triplet in benzene.

(23) Bell, J. A.; Linschitz, H. *J. Am. Chem. Soc.* **1963**, *85*, 528–32.

(24) The extinction coefficient for *p*-methoxypropiofenone triplet was obtained by energy transfer to naphthalene in benzene. The value is in good agreement with the extinction coefficient reported²⁷ for *p*-methoxyacetophenone triplet in cyclohexane ($\sim 11\,000\text{ M}^{-1}\text{ cm}^{-1}$).

(25) The value of ϵ_{max} for the *p*-bromophenoxy radical was obtained¹⁵ by hydrogen transfer between *p*-bromophenol and *tert*-butoxy radicals in di-*tert*-butyl peroxide-benzene (2:1) and is in good agreement with the value reported in water.^{18b}

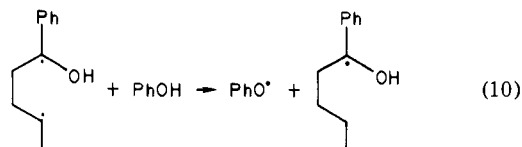
(26) The estimate for the extinction coefficient of the ketyl radical of *p*-methoxypropiofenone was made from the spectra reported²⁷ for ketyl radicals of various para-substituted acetophenones in cyclohexane.

(27) Lutz, H.; Breheret, E.; Lindqvist, L. *J. Phys. Chem.* **1973**, *77*, 1758–62.

(28) No information is available in the literature for *p*-nitrophenoxy radical. Our attempts to observe this species by reaction between *tert*-butoxy radicals and *p*-nitrophenol were also unsuccessful.

triplet lifetime. In the case of **2** the plots are linear and lead to $k_q = 1.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for phenol and $2.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for *p*-*tert*-butylphenol in 9:1 acetonitrile–water. These values are based on $\tau_T = 27 \text{ ns}$.³¹

The case of valerophenone (where higher phenol concentrations are required) is not as simple, since the Stern–Volmer plots according to eq 9 are found to be nonlinear (Figure 5). This curvature must reflect a change in mechanism. The effect is not uncommon; e.g., the quenching of the photofragmentation of valerophenone by di-*tert*-butyl selenoketone³² follows the same pattern. The curvature of the Stern–Volmer plots of Figure 5 is tentatively attributed to biradical scavenging by phenol, which most likely involves hydrogen transfer, as shown in eq 10. Kinetic

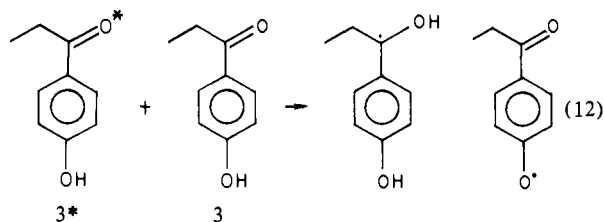


analysis for a system involving triplet quenching and biradical scavenging by the same substrate leads to a quadratic type of Stern–Volmer dependence.³²

$$\frac{\phi_{II}^0}{\phi_{II}} = 1 + (k_s\tau_B + k_q\tau_T)[\text{PhOH}] + k_s\tau_B k_q\tau_T[\text{PhOH}]^2 \quad (11)$$

As pointed out in earlier work,³² separating the biradical (k_s) and triplet state (k_q) components from this type of data is quite difficult. In addition, a nonnegligible contribution to the curvature at the relatively high concentrations of phenol arises from the screening of the exciting light (350 nm) by phenol itself. However, if we assume that the rate of triplet quenching should be the same for **1** and **2**, then, given the triplet lifetime of **1** (from the literature),³³ we can estimate $k_s\tau_B$. Such an analysis using the data of relatively low concentrations of phenol lead to $k_s\tau_B \leq 0.1 \text{ M}^{-1}$ which, given a biradical lifetime $\tau_B \approx 70 \text{ ns}$,^{33,34} leads to $k_s \leq 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

(d) Photochemistry of *p*-Hydroxypropiofenone. Laser flash photolysis examination of samples of *p*-hydroxypropiofenone (**3**) in wet acetonitrile (0.2 M) leads to the “end-of-pulse” transient spectrum shown in Figure 6A. We assign this rather featureless spectrum to the T–T absorption of the carbonyl triplet. The spectrum observed 0.5 μs after the laser pulse is that shown in Figure 6B and is very similar to what is observed in the *p*-methoxypropiofenone–phenol system. We assign the spectrum of Figure 6B to the 1:1 mixture of ketyl and phenoxy radicals produced in the “head-to-tail” abstraction of reaction 12.



The triplet lifetimes observed are rather short as a result of the occurrence of reaction 12; e.g., $\tau_T = 230 \text{ ns}$ at a concentration of 0.06 M in wet acetonitrile. The rates of self-quenching can be determined from a plot of the pseudo-first-order rate constant

(31) $\tau_T = 27 \text{ ns}$ for **2**, based on quenching studies using 2,5-dimethyl-2,4-hexadiene: Encinas, M. V., unpublished work. These experiments need to be carried out in a hydroxilic solvent to avoid the otherwise likely enhancement of the yields as a result of hydrogen bonding by the phenols; see ref 5.

(32) Scaiano, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 1494–8.

(33) Small, R. D., Jr.; Scaiano, J. C. *J. Phys. Chem.* **1977**, *81*, 2126–31.

(34) Small, R. D., Jr.; Scaiano, J. C. *Chem. Phys. Lett.* **1978**, *59*, 246–8.

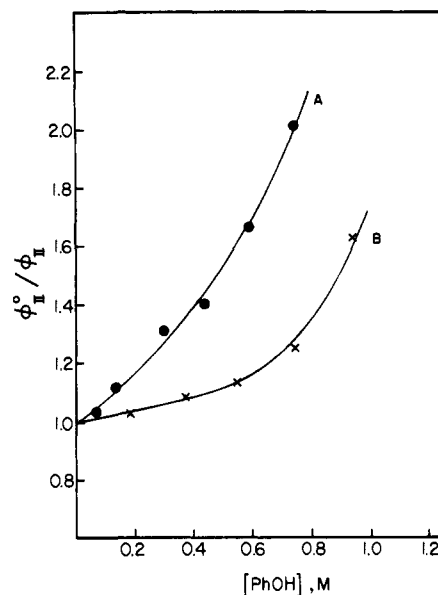


Figure 5. Plots according to eq 9 for the quenching of the photofragmentation of valerophenone by phenol in 9:1 acetonitrile–H₂O (●) and in 9:1 acetonitrile–D₂O (×).

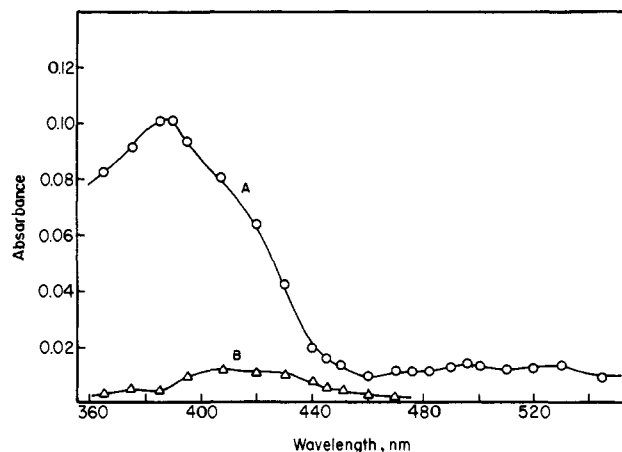


Figure 6. Transient spectra observed following laser irradiation of *p*-hydroxypropiofenone (0.20 M) in 9:1 acetonitrile–water: A, immediately after laser excitation; B, after 0.5 μs .

Table IV. Rate Constants for the Self-Quenching of *p*-Hydroxypropiofenone at 22 °C

solvent	k_{SQ}^a , $\text{M}^{-1} \text{ s}^{-1}$	solvent	k_{SQ}^a , $\text{M}^{-1} \text{ s}^{-1}$
acetonitrile–water (9:1)	6.3×10^7	methanol- <i>d</i> ₄	1.3×10^7
acetonitrile–D ₂ O (9:1)	1.4×10^7	benzene	5.9×10^8
methanol	2.8×10^7		

^a Obtained by monitoring T–T absorptions at 395 nm.

for triplet decay vs. the concentration of **3** (Figure 7). A summary of the rate constants is given in Table IV.

We also carried out some triplet quenching experiments with *p*-hydroxypropiofenone with sorbic acid as a quencher. The quenching rate constants obtained are $7.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in 1:9 water–acetonitrile and $7.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in 1:9 D₂O–acetonitrile. The fast and isotope insensitive rates confirm our transient assignment (Figure 6A) as the triplet state.

(e) Solvent and Isotope Effect. The rates of reactions of carbonyl triplets with several phenols were also examined in 9:1 acetonitrile–water and 9:1 acetonitrile–D₂O. The results are given in Table V. As expected, changing from benzene to wet aceto-

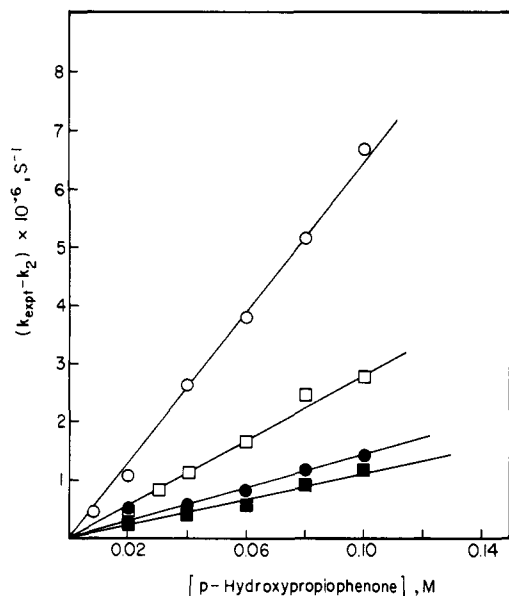


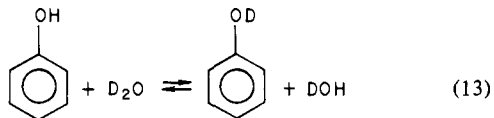
Figure 7. Self-quenching of *p*-hydroxypropiophenone triplet in 9:1 acetonitrile-water (O), 9:1 acetonitrile- D_2O (●), methanol (□), and methanol- d_4 (■).

Table V. Isotope Effects for the Interaction of Carbonyl Triplets with Phenols in Wet Acetonitrile at 22 °C

ketone	phenol	$k_H, M^{-1} s^{-1}$	k_H/k_D
benzophenone	phenol	8.0×10^7	1.2
	<i>p</i> -methoxyphenol	3.9×10^9	1.3
	hydroquinone	4.2×10^9	1.3
	<i>p</i> -iodophenol	1.8×10^8	1.4
	<i>p</i> -cyanophenol	2.1×10^7	1.2
<i>p</i> -methoxypropiophenone	phenol	1.1×10^8	3.9
	<i>p</i> -methoxyphenol	2.0×10^9	1.9
	hydroquinone	3.2×10^9	1.3
	<i>p</i> -iodophenol	1.9×10^8	2.8
	<i>p</i> -cyanophenol	2.9×10^7	3.4
valerophenone	phenol	1.1×10^8	3.8
	<i>p</i> -nitrophenol	3.2×10^9	0.95
<i>p</i> -Hydroxypropiophenone	<i>p</i> -hydroxypropiophenone	6.3×10^7	4.5

nitrile results in a pronounced decrease in the rate constants for the quenching of the carbonyl triplets as well as for the self-quenching of *p*-hydroxypropiophenone (Table IV). It is noted that the relative magnitude of the decrease in the quenching rate constants on changing solvent from a nonpolar to a polar hydrogen-bonding one is dependent not only on the nature of the carbonyl triplet (i.e., benzophenone < *p*-methoxypropiophenone) but also on the nature of the para substituent in the phenol (i.e., $OC_3 \ll I < H \ll CN$).

In acetonitrile- D_2O , fast $D \leftrightarrow H$ exchange (reaction 13) leads



to the formation of phenol- d_1 , and the rates obtained in this solvent should be attributed to deuterium rather than hydrogen abstraction. Figure 8 illustrates the kinetic plots leading to isotope effects of 3.9 (for phenol) and 2.8 (for *p*-iodophenol) in the case of *p*-methoxypropiophenone. Note that the isotope effects are significantly higher for *p*-methoxypropiophenone than for benzophenone (Table V).

(f) **Temperature Dependence.** The rate constants for the quenching of *p*-methoxypropiophenone and benzophenone triplets by phenol, *p*-methoxyphenol, and *p*-bromophenol have been determined in toluene in the temperature range -75 to $+22$ °C. Arrhenius plots are shown in Figures 9 and 10. The activation

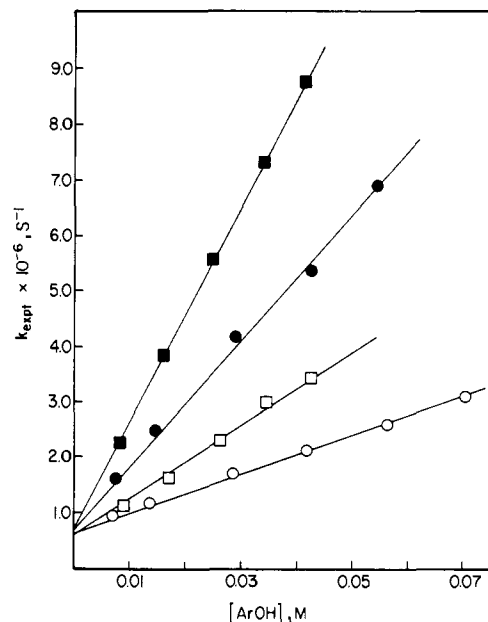


Figure 8. Isotope effects on *p*-methoxypropiophenone triplet quenching by phenol (●), phenol- d_1 (○), *p*-iodophenol (■), and *p*-iodophenol- d_1 (□) in wet acetonitrile according to eq 7.

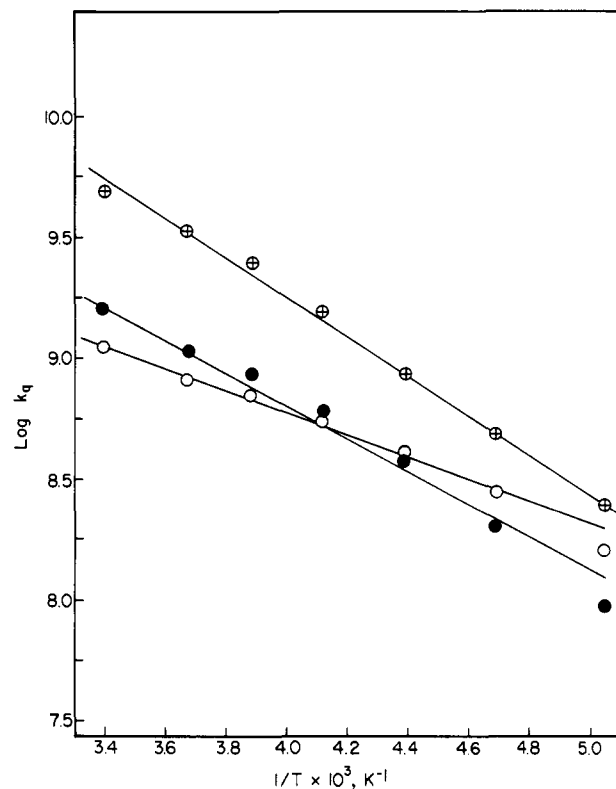


Figure 9. Arrhenius plots for the quenching of benzophenone triplet in toluene by *p*-methoxyphenol (⊕), phenol (○), and *p*-bromophenol (●).

parameters obtained from these plots are presented in Table VI. We note that these Arrhenius parameters correspond to *total quenching*, not just hydrogen abstraction.

Discussion

The results presented in this paper provide, for the first time, absolute rate constants for the reactions of aromatic carbonyl triplets with phenols. Of the ketones chosen for detailed investigation, benzophenone ($E_T = 68.6$ kcal/mol)³⁵ is well-known³⁶

(35) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973.

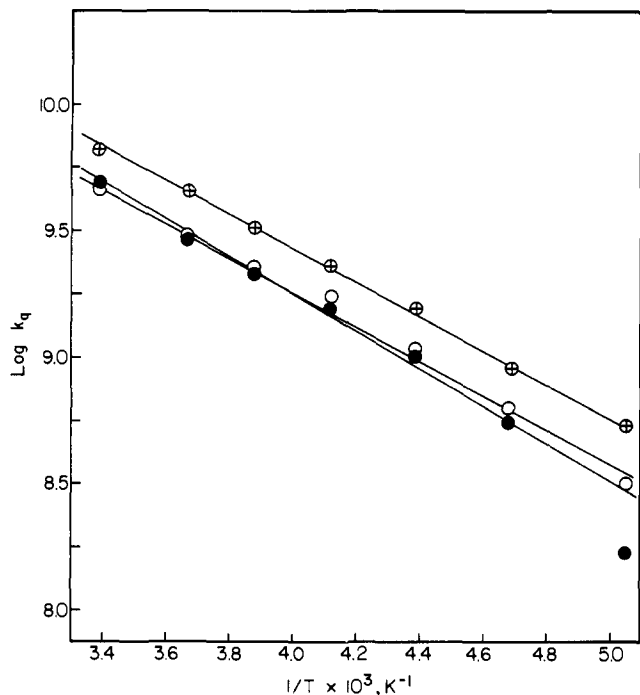


Figure 10. Arrhenius plots for the quenching of *p*-methoxypropiofenone triplet in toluene by *p*-methoxyphenol (⊕), phenol (○), and *p*-bromophenol (●).

for its lowest triplet state being of n, π^* character in nonpolar, polar, and hydrogen-bonding solvents. On the other hand, in analogy to various *p*-methoxy-substituted phenyl alkyl ketones^{37a,38} that have been extensively studied for spectroscopic and hydrogen abstraction properties, *p*-methoxypropiofenone ($E_T \approx 72$ kcal/mol) has the lowest triplet state of primarily π, π^* character. The lowest n, π^* triplet state in *p*-methoxyphenyl alkyl ketones^{37a} lies above, but close to, the lowest π, π^* triplet state (within 3–4 kcal/mol), the energy separation being strongly dependent on the nature of the solvent. The photoreactivity of *p*-methoxy ketone triplets toward hydrogen abstraction has been described³⁷ in terms of participation of equilibrium populations of upper n, π^* triplets (rather than in terms of vibronic mixing^{36a,39} of triplet n, π^* and π, π^*). A recent theoretical study⁴⁰ has shown that for ketones with the triplet π, π^* state lying below the triplet n, π^* state, in-plane hydrogen abstraction may take place as a result of the crossing of the zero-order reaction profiles of the two states.

Surprisingly, we find that in benzene the rate constants for the quenching of *p*-methoxypropiofenone triplet by phenols are higher than those for benzophenone triplet (Table I). The difference between the rate constants for the two ketones becomes smaller in wet acetonitrile (Table V). When considered in view of the fact that the photoreactivity of an n, π^* carbonyl triplet in hydrogen abstraction from $-C-H$ site is far greater than that of a π, π^* triplet (*p*-methoxyacetophenone is 10–100 times less reactive than benzophenone toward alcohols and hydrocarbons), our results indicate that the mechanism of reactions of carbonyl triplets with phenols is different from those with hydrocarbons or alcohols containing $-C-H$ group.³

(36) (a) Yang, N. C.; Dusenbery R. L. *Mol. Photochem.* **1969**, *1*, 159–71. (b) Dym, S.; Hochstrasser, R. M. *J. Chem. Phys.* **1969**, *51*, 2458–68. (c) Lutz, H.; Duval, M.-C.; Breheret, E.; Lindqvist, L. *J. Phys. Chem.* **1972**, *76*, 821–2.

(37) (a) Wagner, P. J.; Kempainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604–14. (b) Wagner, P. J.; Nakahira, T. *Ibid.* **1973**, *95*, 8474–5.

(38) (a) Yang, N.; McClure, D.; Murov, S.; Hauser, J.; Dusenbery, R. *J. Am. Chem. Soc.* **1967**, *89*, 5466–68. (b) Kearns, D.; Case, W. *Ibid.* **1968**, *90*, 5087–97.

(39) Yang, N. C.; Dusenbery, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 5899–900.

(40) Chandra, A. K. *J. Photochem.* **1979**, *11*, 347–60.

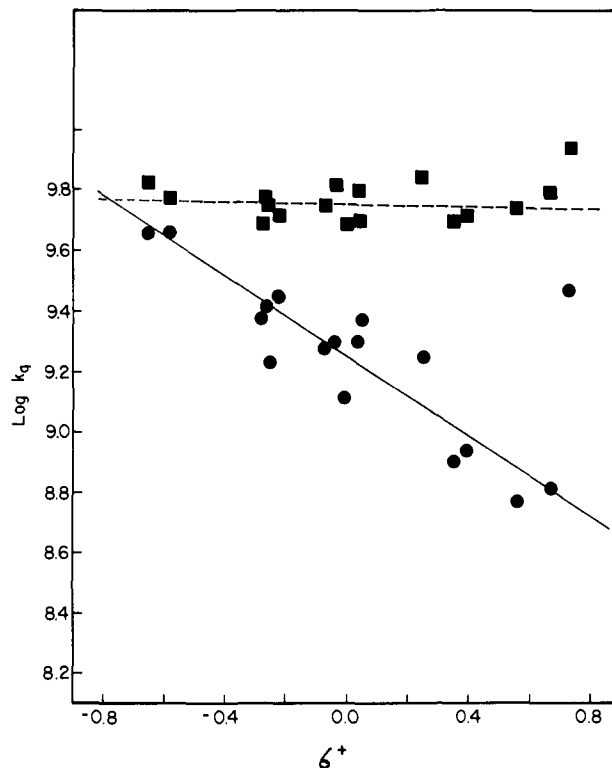


Figure 11. Hammett plots for the quenching of benzophenone (●) and *p*-methoxypropiofenone (■) triplet by phenols in benzene.

The lowest triplet state of phenol is located at 81.7 kcal/mol,⁴¹ it appears unlikely that phenol would quench the carbonyl triplets efficiently by energy transfer. This is supported by the inefficiency of the quenching by anisole ($E_T = 80.8$ kcal/mol).³⁵ Quenching studies with substituted anisoles (Table III), with the exception of *p*-nitroanisole, lead to the same conclusion; i.e., the contribution of electronic energy transfer to the quenching processes by phenols is negligible. In the case of *p*-nitrophenol, the quenching appears to take place exclusively by energy transfer. This conclusion is based on (a) lack of formation of ketyl radicals, (b) lack of kinetic isotope effect, and (c) similarity of the quenching rate constants for *p*-nitrophenol and *p*-nitroanisole. Apparently, substitution by a nitro group lowers the triplet energy enough⁴² to render energy transfer from the ketone triplets energetically favorable.

Our results indicate that, at least in certain cases, it can be unequivocally established that “physical” quenching (reaction 5) is an important mode of interaction: e.g., at low temperatures or in the presence of heavy atoms.⁴³

The Hammett plot (Figure 11) for the rate constants of the reactions of benzophenone triplet with various para and meta substituted phenols in benzene leads to $\rho = -0.65$. This value is lower in magnitude than that obtained for biacetyl in benzene ($\rho = -1.15$).⁷ The negative value does however establish the electrophilic character of the benzophenone triplet. By contrast, the Hammett plot (Figure 11) for *p*-methoxypropiofenone in benzene shows virtually no dependence of the rates of quenching with the nature of the substituents ($\rho \approx -0.02$). The effect is, at least partially, the result of almost diffusion-controlled rates which renders the process insensitive to substituent effects. In wet acetonitrile the reactions are slower and as a result show more selectivity. From the data in Table V, it is clear that the ρ values

(41) McClure, D. S. *J. Am. Chem. Phys.* **1949**, *17*, 905–13.

(42) The phosphorescence origin of various nitroaromatics, including nitrobenzene, is found to lie in the 18 000–21 000-cm⁻¹ range: McGlynn, S. P.; Azumi, T.; Kinoshita, M. “Molecular Spectroscopy of the Triplet State”; Prentice Hall: Englewood Cliffs, NJ, 1969.

(43) Wagner and Puchalski have recently shown that in the acetophenone-1-phenylethanol system only about 50% of the quenching events lead to radical formation: Wagner, P. J., Puchalski, A. E. *J. Am. Chem. Soc.* **1980**, *102*, 7138–7140.

Table VI. Activation Parameters for the Quenching of Carbonyl Triplets by Phenols in Toluene

ketone	phenol	activation energy, kcal/mol	$\log A$, $M^{-1} s^{-1}$
benzophenone	<i>p</i> -methoxyphenol	3.7	12.51
	phenol	2.1	10.59
	<i>p</i> -bromophenol	3.1	11.49
<i>p</i> -methoxypropiofenone	<i>p</i> -methoxyphenol	3.1	12.11
	phenol	3.1	11.96
	<i>p</i> -bromophenol	3.4	12.20

for both ketones would be more negative in wet acetonitrile than in benzene. This is also expected in terms of increased importance of polar structures in the transition state in polar solvents. The large difference in reactivity between benzene and wet acetonitrile solvents reflects the importance of hydrogen bonding at the reactive site in the latter. The phenols containing substituents with large σ values form stronger hydrogen bonds with the polar solvent and are therefore expected to show more pronounced solvent dependence.

The isotope effect observed in the case of phenol is 1.2 for benzophenone, 3.9 for *p*-methoxypropiofenone, 3.8 for valerophenone, and 4.5 for the self-quenching in *p*-hydroxypropiofenone. The values of k_H/k_D for phenol and other systems are summarized in Tables IV and V. The rather large isotope effect in the cases of *p*-hydroxy- and *p*-methoxypropiofenone clearly indicates that hydrogen transfer takes place during the quenching processes involving π, π^* triplets and phenols. Again, to our surprise, we find that benzophenone shows relatively low isotope effects in its reactions with various phenols. Benzophenone appears to react by a complex mechanism involving a transition state where hydrogen transfer is not as developed as in the case of *p*-methoxy- and *p*-hydroxypropiofenone.

In a way the magnitude of the isotope effects for *p*-methoxypropiofenone reacting with phenol and for the self-quenching of *p*-hydroxypropiofenone should be regarded as the unusual ones, since reactions as fast as the ones observed here tend to show very low isotope effect⁴⁴ and this is in fact predicted by theoretical models.⁴⁵

The activation energies for the interaction of benzophenone triplets with phenols are of similar magnitude to those reported for the quenching of benzophenone triplets by hydrocarbons and alcohols.^{19a,46} The larger values for the rate constants for phenols are primarily the result of less stringent entropic requirements, as indicated by the higher preexponential factors (see Table VI). Steel et al.^{47,48} have examined the temperature dependence of the photoreduction for acetophenone and substituted acetophenones and observed that the activation energy becomes higher as the nature of the lowest triplet increases in π, π^* character. In our case we find that both ketones interact with comparable activation energies, perhaps reflecting the rather more complex nature of the process in the case of phenols.

On the basis of the results obtained in the present study, a tentative mechanism involving charge-transfer interactions may be proposed for the quenching reactions of aromatic ketone triplets by phenols. Two different explanations can be proposed to explain the origin of the inefficiency observed at low temperatures, in the presence of heavy atoms and perhaps even at room temperature. One possibility would require the intermediacy of an exciplex which may either lead to the final products (reaction 3) or undergo reversal to the reagents in the ground state. The latter process

is a radiationless transition between two states of different multiplicity and hence should be favored by the presence of heavy atoms; such an effect is actually observed in our studies (e.g., *p*-iodophenol).⁴⁹ Until quite recently we would have been happy to propose this mechanism. However, the recent studies by Wagner⁴³ and by Cohen⁵⁰ cast some doubts on the generality of mechanisms of this type. The second possibility would involve efficient hydrogen abstraction followed by different degrees of cage recombination depending on temperature and substitution.⁵¹ Our evidence is not sufficient to conclusively rule out either mechanism.

The importance of charge transfer seems evident, whether through the intermediacy of an exciplex or in the form of polar contributions in the transition state; however, these effects are not reflected by the solvent dependence of the rate constants. This is the result of the engagement of the phenolic O-H group in hydrogen bonding; this seems to outweigh the effect due to the stabilization of polar configurations by the solvent.

Our study provides definitive evidence for the efficient formation of phenoxy radicals in the quenching of carbonyl triplets by phenols, therefore supporting the earlier suggestions⁶⁻⁸ that the reaction is reversible as a result of radical disproportionation which regenerates the reagents. At the same time, we have shown that a nonnegligible fraction of the primary quenching events also regenerate the reagents. Surprisingly an n, π^* triplet (benzophenone) shows very low isotope effects, while π, π^* triplets lead to large k_H/k_D ratios. These observations cannot be understood with conventional models in which the carbonyl triplet is viewed as an alkoxy radical when the n, π^* character predominates. Perhaps conventional interpretations should be widely questioned, since recent results from other laboratories suggest that the so-called "inefficient" photoreduction by amines⁵⁰ produces radicals with nearly quantitative yields, while, by contrast, the "efficient" photoreduction by alcohols does not.⁴³ In this respect our results probably raise more questions than they answer; awareness of the complexities of these reactions is perhaps the first step toward understanding these processes.

Experimental Section

Materials. Benzophenone (Fluka) was recrystallized twice from ethanol; *p*-methoxypropiofenone (Aldrich), valerophenone (Aldrich), and isovalerophenone (Pfaltz and Bauer) were distilled under vacuum, and *p*-hydroxypropiofenone (Aldrich) was sublimed under vacuum. All solvents were Aldrich Gold Label and were used as received.

Substituted phenols were usually recrystallized, sublimed, or distilled as necessary; they were available from Eastman (*p*-bromophenol), K&K (*p*-fluorophenol), and Baker (phenol) and the rest from Aldrich.

Methanol- d_4 and deuterium oxide were products from Aldrich and Columbia Organic Chemical Co., respectively.

Sample Preparation. Freshly prepared solutions were used in all experiments. Kinetic measurements were carried out on 1-mL samples contained in Suprasil cells made of rectangular tubing (3 × 7 mm i.d.). All experiments were carried out under oxygen-free conditions; the samples were deaerated by bubbling oxygen-free argon. The concentrations of the ketones were in the 0.01–0.005 M range for most of the quenching studies.

Spectral data regarding transients were obtained by using a flow system to avoid excessive exposure to the laser beam. The optical path in the flow system was also 3 mm. The solution flowing into the cell was deaerated by bubbling helium constantly through the stock solution prior and during the experiment.

Laser Photolysis Instrument. Our facility makes use of a Molelectron UV-400 nitrogen laser for excitation. The monitoring system consists of a pulsed Eimac UV-150 xenon lamp. The detection arrangement uses a B&L high-intensity monochromator and an RCA-4840 photomultiplier tube, the signal from which is terminated into 93 Ω and into a Tektronix R7912 transient digitizer; this unit is in turn interphased to a PDP 11/55

(44) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 5399. Griller, D.; Howard, J. A.; Marriott, P.; Scaiano, J. C. *Ibid.* **1981**, *103*, 619–623.

(45) Johnston, H. S. "Gas Phase Reaction Rate theory"; Ronald Press: New York, 1966; Chapter 13.

(46) The values reported by Topp^{19a} also correspond to total quenching, not solely to hydrogen abstraction.

(47) Berger, M.; McAlpine, E.; Steel, C. *J. Am. Chem. Soc.* **1978**, *100*, 5147–51.

(48) The comment on Topp's work⁴⁶ also applies to Steel's data.⁴⁷

(49) The alternative explanation that the efficient quenching by halo-phenols is the result of C–X bond cleavage seems highly unlikely, since haloisoles are considerable less reactive than the corresponding phenols (see Table III).

(50) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1980**, *102*, 1419–1421.

(51) It should be noted that oxygen centered radicals tend to show fast relaxation times.

multiuser computer which controls the experiment, averages the data from several laser shots, and processes the information.

Irradiation and Product Analysis. The irradiation of valerophenone and isovalerophenone was carried out in matched Pyrex tubes (9-mm o.d.) in a Rayonet reactor fitted with a merry-go-round and 14 RPR-3500 lamps. The concentrations of the ketones were in the 0.15–0.10 M

range. The irradiated samples were analyzed for acetophenone by VPC on an Apiezon L column (5 ft) at 135 °C, using a Beckman GC-5 instrument equipped with flame ionization detectors.

Acknowledgment. We are grateful to Professor P. J. Wagner for the communication of unpublished results.

Reaction of *tert*-Butoxy Radicals with Phenols. Comparison with the Reactions of Carbonyl Triplets

P. K. Das, M. V. Encinas, S. Steenken, and J. C. Scaiano*¹

Contribution from the Radiation Laboratory,² University of Notre Dame, Notre Dame, Indiana 46556. Received November 12, 1980

Abstract: *Tert*-butoxy radicals generated in the photodecomposition of di-*tert*-butyl peroxide react efficiently with phenols to yield the corresponding phenoxy radicals. Typical rate constants in benzene at 22 °C are 3.3×10^8 and 1.6×10^9 M⁻¹ s⁻¹ for phenol and *p*-methoxyphenol, respectively. The process is considerably slower in polar solvents; e.g., when pyridine is used as cosolvent, the rate constant for phenol drops to 4.7×10^6 M⁻¹ s⁻¹ as a result of strong hydrogen bonding which decreases the reactivity of the phenolic O–H group. Isotope effects (H/D) are typically in the 3–5 range.

The hydrogen abstraction reactions of alkoxy radicals have been a subject of considerable interest. Many extensive studies based on competition techniques by Walling,³ Ingold,⁴ Zavitsas,⁵ and their co-workers have resulted in a vast amount of data regarding the relative rates of hydrogen abstraction reactions of *tert*-butoxy radical with various substrates. Recently, absolute rates of reactions of *tert*-butoxy radical with a large number of organic substrates^{6–8} have been reported. Rate constants have been determined^{6,7} by nanosecond laser flash photolysis by using di-*tert*-butyl peroxide as the photochemical source of *tert*-butoxy radicals and monitoring the formation of the ketyl radical resulting from hydrogen abstraction by *tert*-butoxy radical from diphenylmethanol (in competition with the reaction with another substrate).

In contrast to the numerous studies concerning the reactions of alkoxy radicals with various substrates including hydrocarbons, aldehydes, ethers, and alcohols, their reaction with phenols has drawn little attention. The kinetics and mechanisms of the reactions of *tert*-butoxy radical with phenols at 122 °C have been examined by Ingold^{9,10} using competition techniques, but no absolute rates have been reported.

The similarity between the behavior of n,π^* carbonyl triplets and alkoxy radicals toward hydrogen abstraction has been emphasized in several studies.^{11–13} In addition to the similarity of the electronic configurations of n,π^* triplets and alkoxy radicals,

Table I. Kinetic Data for the Reactions of Para-Substituted Phenols with *tert*-Butoxy Radical and Spectral Data for Phenoxy Radicals in 1:2 Benzene-Di-*tert*-butyl Peroxide at 22 °C

para substituent	λ_{\max}^a , nm	ϵ_{\max}^b	highest concn, ^c mM	k_3^d , M ⁻¹ s ⁻¹
H	400	0.64	42	3.3×10^8
OH	398	1.3	5	3.2×10^9
OC ₂ H ₅	404	1.4	21	1.7×10^9
OCH ₃	403	1.5	21	1.6×10^9
C(CH ₃) ₃	404	1.0	31	5.6×10^8
C ₂ H ₅	404	0.91	33	5.3×10^8
CH ₃	404	0.91	17	5.5×10^8
C ₆ H ₅	502	0.80	33	5.3×10^8
F	392	0.54	40	3.8×10^8
Cl	412	0.86	29	2.9×10^8
Br	421	1.4	32	2.4×10^8
I	463	1.8	42	3.4×10^8
CN	443	0.51	22	9.7×10^7
NO ₂				$<1 \times 10^6$

^a ± 3 nm; this is the wavelength maximum in the spectral region, 355–650 nm. ^b $\pm 20\%$; relative to ϵ_{\max} of Ph₂COH, monitored at 545 nm. ^c This is the highest concentration of phenol used to measure k_{exptl} (eq 4). ^d Estimated error, $\pm 20\%$.

the thermochemistry of abstractions by both species is virtually identical, as a result of the close values of triplet excitation energies and double-bond contributions to the C=O bond.¹⁴

tert-butoxy radicals react with phenols producing phenoxy radicals which can be directly monitored by their spectral absorptions. In this paper, we report the results of an investigation of the kinetics of the hydrogen abstraction reactions from various phenols by *tert*-butoxy radical generated by laser photolysis. We also present a comparison between the behavior of carbonyl triplets and *tert*-butoxy radical as far as their hydrogen abstraction reactions with phenols are concerned.

Results

(a) Kinetics. The photodecomposition of di-*tert*-butyl peroxide by pulses from a nitrogen laser (337.1 nm, 8 ns, ~ 3 mJ) was used as a source of *tert*-butoxy radical. In the presence of a hydrogen donor, e.g., phenol, the radical abstracts a hydrogen atom, a

(1) To whom correspondence should be addressed at the Division of Chemistry, National Research Council, Ottawa, Canada, K1A 0R6.

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