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# Bimolecular Hydrogen Abstraction from Phenols by Aromatic Ketone Triplets[†]

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## ABSTRACT

**Absolute rate constants for hydrogen abstraction from 4-methylphenol (para-cresol) by the lowest triplet states of 24 aromatic ketones have been determined in acetonitrile solution at 23°C, and the results combined with previously reported data for roughly a dozen other compounds under identical conditions. The ketones studied include various ring-substituted benzophenones and acetophenones, α,α,α-trifluoroacetophenone and its 4-methoxy analog, 2-benzoylthiophene, 2-acetonaphthone, and various other polycyclic aromatic ketones such as fluorenone, xanthone and thioxanthone, and encompass n,π*, π,π*(CT) and arenoid π,π* lowest triplets with (triplet) reduction potentials ($E^*_{\mathrm{red}}$) varying from about −10 to −38 kcal mol$^{-1}$. The 4-methylphenoxyl radical is observed as the product of triplet quenching in almost every case, along with the corresponding hemipinacol radical in most instances. Hammett plots for the acetophenones and benzophenones are quite different, but plots of log $k_Q$ *vs* $E^*_{\mathrm{red}}$ reveal a common behavior for most of the compounds studied. The results are consistent with reaction via two mechanisms: a simple electron-transfer mechanism, which applies to the n,π* triplet ketones and those π,π* triplets that possess particularly low reduction potentials, and a coupled electron-/proton-transfer mechanism involving the intermediacy of a hydrogen-bonded exciplex, which applies to the π,π* ketone triplets. Ketones with lowest charge-transfer π,π* states exhibit rate constants that vary only slightly with triplet reduction potential over the full range investigated; this is due to the compensating effect of substituents on triplet state basicity and reduction potential, which both play a role in quenching by the hydrogen-bonded exciplex mechanism. Ketones with arenoid π,π* states exhibit the fall-off in rate constant that is typical of photoinduced electron transfer reactions, but it occurs at a much higher potential than would be normally expected due to the effects of hydrogen-bonding on the rate of electron-transfer within the exciplex.**

## INTRODUCTION

Hydrogen abstraction is arguably the best known and most extensively studied photochemical reaction of aromatic ketones (1–3). Three primary mechanistic classes have been recognized: "pure" alkoxyl-radical-like abstractions such as those from alkanes or alcohols (4,5); electron transfer–initiated abstractions such as those involving tertiary amines, in which the hydrogen atom is transferred as a proton between fully-formed ketyl radical anion/donor radical cation pairs (6–9), and charge-transfer (CT) assisted abstractions such as those from alkylbenzenes, in which only partial ionization occurs (10,11). As is well known, the n,π* triplet is the reactive state in aliphatic or benzylic hydrogen abstractions, and ketones with lowest π,π* triplet states react predominantly via the higher energy n,π* state, populated thermally from the lower energy state (3,12). The configuration of the lowest triplet state is believed to be less important in electron transfer–mediated reactions, and thus for most amine donors, for example, rate constants are determined primarily by the thermodynamics of electron transfer (3) (*cf* [13], however). The mechanism for CT-assisted hydrogen abstraction from alkylbenzenes is believed to involve the initial formation of an exciplex, held together by interactions between the electron-deficient n-orbital of the ketone and a π-MO of the H-donor, which results in a slight increase in acidity of the transferring hydrogen and facilitates its transfer. Rate constants for ketone triplet quenching via this mechanism correlate with both the arene ionization potential and the triplet reduction potential of the ketone (10).

Aromatic ketones abstract hydrogen from phenols at rates that are substantially faster than those from substituted toluenes, as might be expected on the basis of the lower ionization potential and bond dissociation energy of phenol compared to those of toluene (14). Nevertheless, the characteristics of the process are fundamentally different for the two hydrogen donors; in particular, the reaction with phenols is *faster* for ketones with lowest charge-transfer π,π*("π,π*[CT]") triplets than for those with lowest n,π* triplet states (14,15). Early work by Scaiano and coworkers (14) defined several fundamental differences between the reactivities of benzophenone (n,π*) and 4-methoxypropiophenone (π,π*[CT]) triplets toward phenols in nonaqueous solvents, including the effects of polar substituents on the phenol (appreciable for the first, but not for the second), isotope effects (appreciable for the second, but not for the first), and temperature (roughly the same for both).

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[†] This paper is part of a special issue dedicated to Professor J. C. (Tito) Scaiano on the occasion of his 60th birthday.

*Abbreviations:* 4MP, 4-methylphenol; MeCN, acetonitrile; $E_T$, triplet energy; $E$(A/A), half-wave reduction potential; $E^*_{\mathrm{red}}$, triplet reduction potential; CT, charge transfer; $\Delta G_{\mathrm{et}}$, free energy of electron transfer; T-T, triplet–triplet.

Those researchers also showed that protic solvents have a rate-retarding effect in both cases, which has been suggested to be the result of hydrogen bonding between the solvent and both the phenol (16) and the excited ketone (17). Recent work by Canonica and coworkers (18) demonstrates that in aqueous media the differences in reactivity between ketones of different lowest triplet configuration disappears, and the reaction proceeds via a simple electron-transfer/proton-transfer mechanism.

Some time ago, we proposed a mechanism for the π,π*(CT) process that involves the intermediacy of a hydrogen-bonded exciplex between the phenol and ketone triplet, in which net hydrogen-atom abstraction occurs in the form of coupled electron/proton transfer (16). The hydrogen-bonding interaction was proposed to reduce the threshold for electron transfer from phenol to triplet ketone, because the partially protonated triplet is more easily reduced by the partially ionized phenol. Such a process would be expected to be more favorable in lowest π,π*(CT) triplet ketones because of the enhanced basicity of this triplet configuration compared to that of the n,π* state. Linschitz and coworkers (19) proposed a similar mechanism in their comprehensive study of the quenching of fluorenone (π,π*) triplets by phenols and other hydrogen donors in aprotic solvents.

Our earlier study revealed that the lowest (n,π*) triplet states of both donor- and acceptor-substituted benzophenone derivatives react with 4-methylphenol (4MP) at rates faster than benzophenone itself, resulting in a V-shaped Hammett plot (16). The enhanced reactivity of donor-substituted derivatives relative to the parent was proposed to result from vibronic mixing of the higher-lying π,π*(CT) triplet with the lowest (n,π*) state, the extent of which increases as the $(n,\pi^*)^3 - (\pi,\pi^*[CT])^3$ energy gap is reduced, coupled with increasing basicity of the π,π* state as the electron-donating power of the substituent(s) increases. Acceptor-substituted derivatives were proposed to react at increased rates relative to benzophenone due to reaction via the CT exciplex-mediated mechanism that is common to benzylic hydrogen donors (10,11), which presumably merges with a sequential electron-/proton-transfer mechanism in ketones with particularly low triplet reduction potentials.

Although phenolic hydrogen abstraction by aromatic carbonyl compounds has continued to be of interest in recent years (18–29), there have been no studies reported that probe the trends in the kinetics of the reaction in nonaqueous solvents as a function of the structural and electronic properties of the ketone in an extensive and systematic way. Accordingly, in the present paper we report the results of a survey of the absolute rate constants for reaction of the lowest triplet states of nearly 40 aromatic ketones with a single phenol (*para*-methylphenol) in acetonitrile (MeCN) solution at room temperature. The specific ketones studied in this work are shown in Scheme 1; the list includes several for which rate constants have been reported previously (16,22,24), but most are reported here for the first time. The list includes various substituted acetophenones, benzophenones, and several bicyclic and tricyclic ketones, with lowest triplet states of n,π*, π,π* and π,π*(CT) configuration, and with triplet state reduction potentials that vary between about −38 and −10 kcal $mol^{-1}$.

## MATERIALS AND METHODS

MeCN (reagent grade) was used as received from Caledon Laboratories (Georgetown, ON, Canada). Most ketones were obtained from Sigma-Aldrich (Milwaukee, WI) or Lancaster Synthesis (Windham, NH), and were each recrystallized from an appropriate solvent or vacuum-distilled. 4-Methoxy-4′-methylbenzophenone (**3**) (30), 4-thiomethoxybenzophenone (**9**) (31), and 4-dimethylaminoacetophenone (**15**) (32) were prepared and purified according to literature procedures, whereas 4-methoxy-α,α,α-trifluoroacetophenone (**34**) was a generous gift from Professor P. J. Wagner. 4MP (Caledon) and phenol (Sigma-Aldrich) were vacuum-distilled, 4-cyanophenol (Sigma-Aldrich) was recrystallized from water and dried in air and 4-methoxyphenol (Sigma-Aldrich) was recrystallized from benzene.

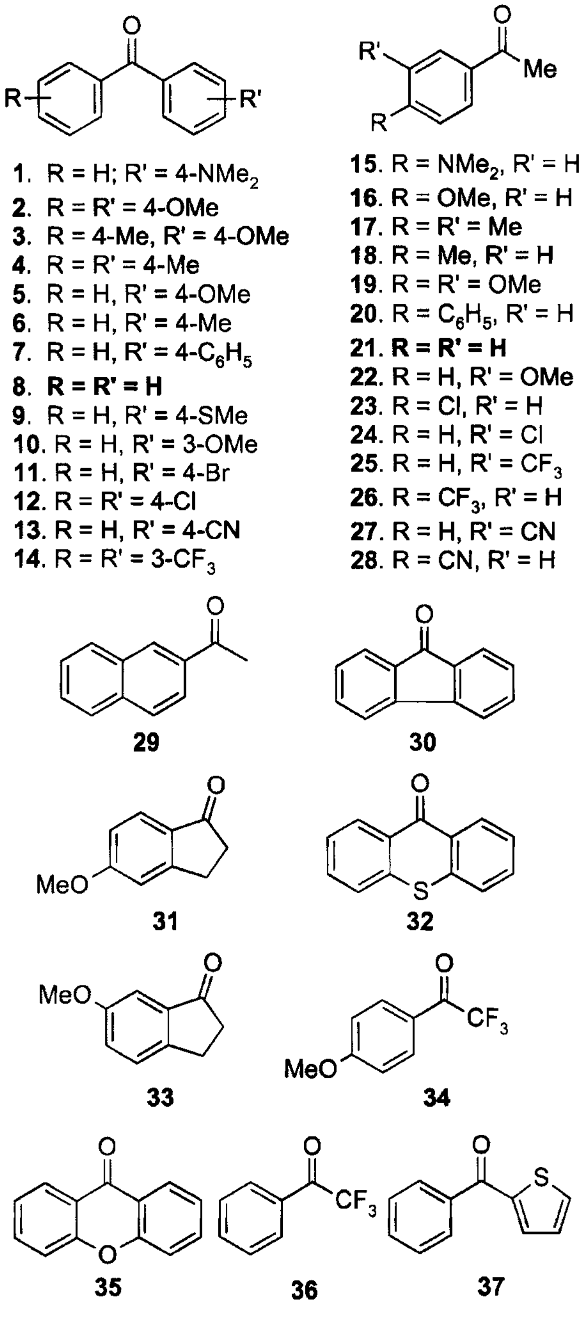
Nanosecond laser flash photolysis experiments were carried out at room temperature on deaerated MeCN solutions of the ketones (0.01–0.05 *M*) and employed the pulses from a Lumonics TE-861M excimer laser (Kanata, ON, Canada) filled with $N_2$/He mixtures (337 nm, 6 ns, ~4 mJ) and a microcomputer-controlled detection system, as previously described (33,34). Samples were contained in custom-built cells fabricated from 3 × 7 mm or 7 × 7 mm rectangular Suprasil quartz tubing (Vitro-Dynamics, Rockaway, NJ), sealed with rubber septa and at concentrations required to produce absorbances between 0.2 to 0.9 at the laser wavelength. Each solution was deaerated with argon or dry nitrogen until constant lifetimes were achieved. When necessary, the laser intensity was attenuated with neutral density filters at low concentrations of added 4MP to reduce second-order contributions to the triplet decays due to triplet–triplet annihilation. Quenchers were added as aliquots of standard solutions.

## RESULTS

Triplet–triplet (T-T) absorption spectra were determined for each ketone over several time windows after the laser pulse, and generally agreed well with previously reported spectra in the numerous cases where they were available (35,36). For those that have not been previously reported, the triplet assignments were confirmed by quenching with 1,3-cyclohexadiene or oxygen, which afforded rate constants on the order of $\sim 1 \times 10^{10}\ M^{-1}\ s^{-1}$ in every case. The lifetimes varied between ~1 and 50 μs in deoxygenated MeCN solution under the conditions of our experiments, depending on the ketone and the rigor with which the samples were deoxygenated prior to the experiment.

In each case, addition of 4MP to the solutions caused a shortening of the triplet lifetime in proportion to the concentration of added reagent. For most of the ketones studied, transient absorption spectra were also recorded in the presence of sufficient 4MP to reduce the lifetime of the ketone triplet to ~10% or less of its value in the absence of the phenol; these revealed the formation of weak, much longer-lived absorptions due to the 4-methylphenoxyl radical ($\lambda_{max}$ = 405 nm) and the corresponding hemipinacol radical in almost every case. Examples of typical behavior are shown in Fig. 1 for 4-bromobenzophenone (**11**) and 4-trifluoromethylacetophenone (**26**) in the presence of 4MP. The intensities of the phenoxyl radical absorptions produced under these conditions varied by less than a factor of two for most of the ketones studied. The exceptions were 4-dimethylaminobenzophenone (**1**), 4-dimethylaminoacetophenone (**15**), 3-trifluoromethylacetophenone (**25**) and 3-cyanoacetophenone (**27**), for which the phenoxyl radical absorptions were significantly weaker than typical values (**15**, **25**, and **27**) or barely detectable at all (**1**); in the latter case, transient absorptions in this region of the spectrum were dominated by that assignable to the corresponding hemipinacol radical (37). Figure 2 shows transient absorption spectra recorded for the 4-dimethylamino-substituted ketones **1** and **15** in the presence of phenol (*vide infra*) and 4MP, respectively.

Pseudo-first-order rate constants for triplet decay ($k_{decay}$) were measured in the presence of various concentrations of added 4MP, monitoring the T-T absorptions at wavelengths chosen to minimize



Scheme 1.

contributions from the radical products; those ketones with T-T absorption maxima below 350 nm were monitored at 360 nm. With some of the acetophenones, overlap between the decaying triplet absorptions and longer-lived radical product absorptions could not be avoided, so triplet decay constants were determined by fitting the decays to first order kinetics using the appropriate (nonzero) residual absorption value due to the radical product(s) as the infinity level. Absolute rate constants for triplet quenching were then obtained in the usual way, from plots of $k_{decay}$ *vs* 4MP concentration according to (Eq. 1); these plots were linear over at least a factor of 10 in $k_{decay}$ in every case. The rate constants obtained are presented in Tables 1–3, along with Hammett substituent constants for the substituted benzophenones and acetophenones, and the T-T and hemipinacol radical absorption maxima.

$$k_{decay} = k_0 + k_Q[Q] \qquad (1)$$

Tables 1–3 also contain the triplet energies ($E_T$), half-wave reduction potentials ($E[A^-/A]$), and triplet reduction potentials ($E^*_{red} = E_T - E[A^-/A]$) for each of the ketones studied in this work except **1**, for which no data are available. The triplet energies and reduction potentials for **2**, **4**, **8**, **12** and **13** in the benzophenone series and all the acetophenones except **15**, **19**, **20** and **22** are from a single source measured under standardized conditions (10), and can thus be considered to have the greatest degree of internal consistency. Those for the others are from a variety of sources (see the Tables for specific references), and thus the uncertainties in the derived $E^*_{red}$ values for these ketones are somewhat higher. The triplet energies are derived from phosphorescence emission spectra recorded in polar glasses (methyltetrahydrofuran [MTHF]), 4:1 ethanol:methanol, or 5:5:2 ether:isopentane:ethanol (EPA) at 77K, while reported reduction potentials have been corrected when necessary to the SCE reference electrode in MeCN solution. (Reversible) half-wave reduction potentials for benzophenones **1**, **3**, **10** and **11**, which have evidently not been reported, were estimated from a plot of $-E(A^-/A)$ *vs* $\Sigma\sigma$ for the other compounds in the series (30).

Absolute rate constants were also measured for quenching of the triplet state of **1** by phenol, 4-cyanophenol and 4-methoxyphenol in MeCN solution at 23°C. The values obtained were identical within experimental error: (2.41 ± 0.15), (2.28 ± 0.05) and (2.42 ± 0.12) $\times 10^9\ M^{-1}\ s^{-1}$, respectively.

## DISCUSSION

Figure 3 shows Hammett plots of the rate constants for quenching of the triplet states of the substituted benzophenones and acetophenones by 4MP in MeCN solution. Of the 14 benzophenones included in the plot for that series of compounds, data for nine of them were already available from earlier studies (16,22,24). The five new compounds studied in the present work were chosen with specific reasons in mind. 4-Dimethylaminobenzophenone (**1**) and 4-methylthiobenzophenone (**9**) both possess lowest $\pi,\pi^*$(CT) triplet states in polar solvents (31,39), and consequently exhibit much lower reactivity toward carbon-based hydrogen donors than is the case with the other ($n,\pi^*$ triplet) benzophenones in the series (3). In contrast, the triplet states of these two compounds are both quenched quite rapidly by 4MP, consistent with the earlier conclusion that the $\pi,\pi^*$(CT) triplet states of aromatic ketones are intrinsically more reactive than $n,\pi^*$ triplets toward phenolic hydrogen donors (14,16). 4-Phenylbenzophenone (**7**) was chosen to provide a comparison between the reactivity of an arenoid $\pi,\pi^*$ triplet benzophenone and those with lowest $n,\pi^*$ or $\pi,\pi^*$(CT) triplet states. It is the least reactive derivative in the series, though only modestly less reactive than benzophenone itself, in sharp contrast to the situation with carbon-based hydrogen donors (3). To a first approximation, its ~10-fold lower reactivity compared to that of **9** illustrates the difference in reactivity between arenoid $\pi,\pi^*$ and $\pi,\pi^*$(CT) ketone triplets toward phenolic hydrogen donors. 3,3′-Bis(trifluoromethyl)benzophenone (**14**), a lowest $n,\pi^*$ triplet (30), was chosen with the intention of extending the range in triplet reduction potential to somewhat more negative values. As more or less expected, this compound exhibits similar reactivity to the slightly less easily reduced 4-cyano derivative (**13**). Finally, 4-methoxy-4′-methylbenzophenone (**3**) was added to the list in

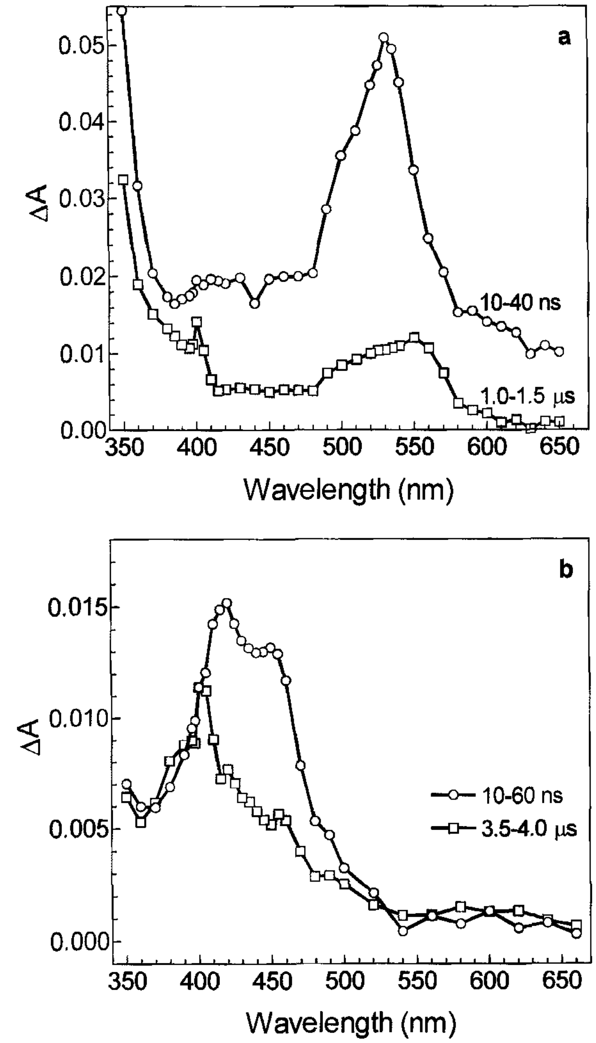


**Figure 1.** Transient absorption spectra recorded by 337-nm laser flash photolysis of deoxygenated solutions of (a) 4-bromobenzophenone (**11**; 3.8 m*M*) and (b) 4-trifluoromethylacetophenone (**26**; 68 m*M*) in MeCN in the presence of 4–6 m*M* 4MP.

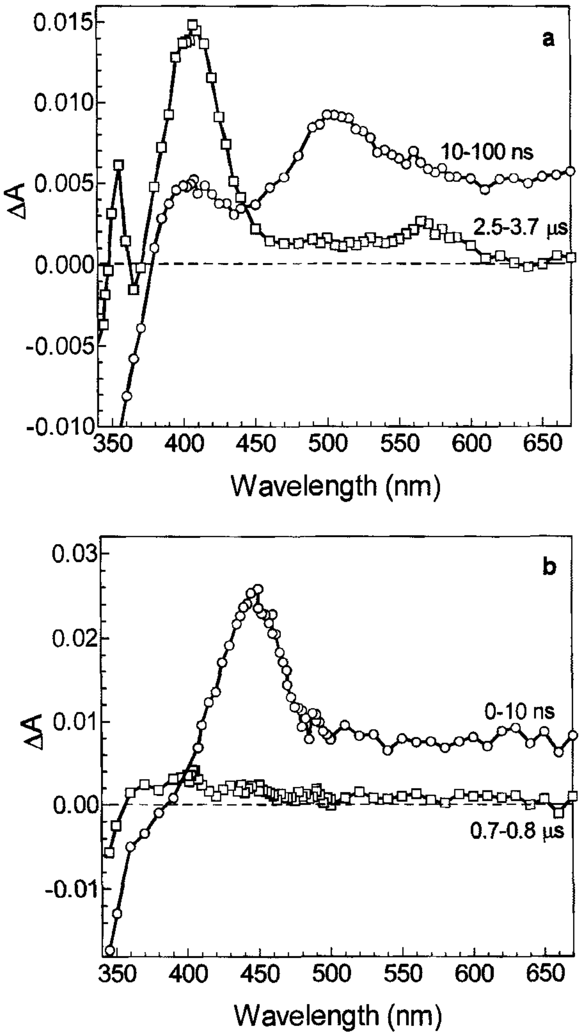


**Figure 2.** Transient absorption spectra recorded by 337-nm laser flash photolysis of deoxygenated MeCN solutions of (a) 4-dimethylaminobenzophenone (**1**; 0.1 m*M*) + phenol (0.8 m*M*); and (b) 4-dimethylaminoacetophenone (**15**; 0.1 m*M*) + 4MP (9.9 m*M*).

order to provide an additional example of a donor-substituted benzophenone n,π* triplet. Its behavior is unexceptional, as it is quenched by 4MP at a rate intermediate between the 4,4′ dimethoxy- and 4,4′-dimethyl-derivatives (**2** and **4**, respectively).

The plot for the benzophenone derivatives (Fig. 3a) extends the range in Hammett σ-constants covered in our original treatment by ~40%, and with three exceptions, the new data fit well with the previously established trend (16). The three exceptions are 4-phenyl- and 4-thiomethoxybenzophenone (**7** and **9**, respectively), which were discussed above, and 3-methoxybenzophenone (**10**). The latter compound, which possesses a lowest n,π* triplet state (24), reacts some three times faster than would be predicted on the basis of the Hammett σ-value and the trend established by the other compounds included in the plot.

The form of the Hammett plot for the acetophenones is much different than that exhibited by the benzophenones. Most of these compounds possess lowest π,π*(CT) triplet states, and hence quenching by 4MP proceeds rapidly and with rate constants that are almost independent of substituent for most compounds in the series. Only four of these compounds possess lowest n,π* triplet states—the parent ketone (**21**) and the meta-cyano (**27**), meta-trifluoromethyl (**25**) and para-trifluoromethyl (**26**) derivatives (12, 50). Interestingly, only **25** and **26** exhibit significantly reduced reactivity compared to the others. As in the benzophenone series, the para-phenyl derivative (**20**) exhibits the lowest reactivity of all, with a rate constant that is roughly two orders of magnitude lower than that typical of the π,π*(CT) triplet acetophenones in the series. Least squares analysis of the data, excluding those for **20** and the n,π* triplet ketones, affords a Hammett ρ-value of +0.34 ± 0.07 ($r^2 = 0.657$), indicating that the enhanced reactivity of the carbonyl π,π*(CT) triplet state compared to that of the n,π* state depends very little on the strength of the polar substituent, as defined by its Hammett σ-value.

A more revealing perspective is provided by plots of $\log(k_Q/M^{-1}\ s^{-1})$ *vs* triplet reduction potential ($E^*_{red}$), which are shown in Figs. 4a and 4b for the substituted benzophenones and acetophenones studied in this work, respectively. The position of the point for 4-dimethylaminoacetophenone (**15**; $k_Q \sim 6 \times 10^8\ M^{-1}\ s^{-1}$) is uncertain because neither a triplet energy nor reduction potential appear to be available; its $E^*_{red}$ value can be safely assumed to be significantly higher (*i.e.* more positive) than that of **1** ($E^*_{red}$ =

**Table 1.** Substituted benzophenones studied, their Hammett substituent constants, triplet energies, reduction potentials, T-T and hemipinacol radical absorption maxima (MeCN) and absolute rate constants for triplet quenching by *para*-methylphenol in MeCN at 23°C.

| Ketone | $\sum\sigma$* | $E_T$† | $-E(A^-/A)$‡ | $-E^*_{red}$§ | $\lambda_{max}^{T\text{-}T}$(nm) | $\lambda_{max}^{rad}$ (nm) | $k_Q/10^9\ M^{-1}\ s^{-1}$ |
|---|---|---|---|---|---|---|---|
| 1 4-NMe$_2$ | −0.83 | 63.5‖ | 49.3¶ | 14.2 | 510 | 405 | 2.1 ± 0.2 |
| 2 4,4′-(OMe)$_2$ | −0.54 | 69.4 | 46.5 | 22.9 | 545 | 555 | 2.4 ± 0.3# |
| 3 4-Me-4′-OMe | −0.44 | 69.2¶ | 45.8¶ | 23.4 | 530 | 560 | 1.28 ± 0.08 |
| 4 4,4′-(Me)$_2$ | −0.34 | 69.1 | 45.0 | 24.1 | 525 | — | 1.07 ± 0.05# |
| 5 4-OMe | −0.27 | 69.0**,†† | 45.0‡‡ | 24.0 | 520 | 550 | 1.17 ± 0.07# |
| 6 4-Me | −0.17 | 69.2**,†† | 43.8†† | 25.4 | 525 | — | 0.58 ± 0.05# |
| 7 4-Ph | −0.01 | 60.7‡‡ | 39.4§§ | 21.3 | 540 | — | 0.15 ± 0.04 |
| 8 H | 0.00 | 69.2 | 42.1 | 27.1 | 520 | 550 | 0.30 ± 0.01# |
| 9 4-SMe | 0.00 | 64.0**,‖‖ | 42.4‖‖ | 21.6 | 533 | 575 | 1.27 ± 0.13 |
| 10 3-OMe | 0.12 | 68.4**,¶¶ | 41.7¶ | 26.7 | ~560 | 545 | 2.01 ± 0.15¶¶ |
| 11 4-Br | 0.23 | 69.7¶¶ | 40.6¶ | 29.1 | 525 | 550 | 0.86 ± 0.12# |
| 12 4,4′-(Cl)$_2$ | 0.46 | 68.6 | 38.5 | 30.1 | 545 | — | 2.1 ± 0.2# |
| 13 4-CN | 0.66 | 66.8 | 32.7 | 34.1 | 545 | — | 3.9 ± 0.2# |
| 14 3,3′-(CF$_3$)$_2$ | 0.86 | 69.1**,†† | 36.0†† | 33.1 | 545 | — | 3.33 ± 0.19 |

* From (38). † 0,0 Band in kcal mol$^{-1}$; 2-MeTHF solvent; from (10) unless otherwise noted. ‡ Half-wave reduction potential *vs* SCE in MeCN, in kcal mol$^{-1}$; from (10) unless otherwise noted. § $E_T - E(A^-/A)$ in kcal mol$^{-1}$. ‖ From (39). ¶ Interpolated from data in (30). # From (16). ** From (35). †† From (30). ‡‡ From (40). §§ From (31). ‖‖ From (24). ¶¶ From (41).

−14.1 kcal mol$^{-1}$), probably on the order of about −10 kcal mol$^{-1}$. The data in the two plots are divided into two groups: those (designated by solid symbols) for which the $E^*_{red}$ values are derived from a single source (10) and thus have the highest level of internal consistency, and those (designated by open symbols) that are derived from a variety of sources and thus have higher uncertainties. The plots show that contrary to what might be implied by the Hammett behavior, the two series of compounds in fact behave quite analogously. They both exhibit V-shaped log $k_Q$ *vs* $-E^*_{red}$ profiles, with minimum rate constants on the order of ~3 × 10$^8$ $M^{-1}$ s$^{-1}$ at $E^*_{red}$ values of about −27 for the benzophenones and −29 kcal mol$^{-1}$ for the acetophenones. For both series, the quenching rate constants increase and level off as $E^*_{red}$ is either increased or decreased from these values; the limiting values of $k_Q$ are ~6 × 10$^9$ $M^{-1}$ s$^{-1}$ on the low reduction potential side and 0.6–2 × 10$^9$ $M^{-1}$ s$^{-1}$ on the high side. The form of the plots is consistent with two distinct quenching mechanisms: one whose rate constant depends on triplet reduction potential, which can be associated with reaction via the n,π* state, and one for which no such dependence is apparent. We associate the latter with reaction via the π,π*(CT) triplet state. The overall form of the plots can thus be interpreted as the result of superposition of these two quite different sets of behavior, with those ketones displaying n,π* triplet reactivity located to the left of the minima in the plots, and those that react via the π,π*(CT) triplet mechanism situated to the right. Interestingly, the minima in the two plots of Fig. 4 appear to occur at slightly different values of $E^*_{red}$, with that for the acetophenones occurring ~2 kcal mol$^{-1}$ lower than that for the benzophenones. Unfortunately, this is on the edge of our range of uncertainties in the $E^*_{red}$ values employed for the analysis, so little can be made of the difference.

For reaction via the n,π* mechanism, the dependence of the rate constant on triplet reduction potential is qualitatively analogous to that for benzylic hydrogen abstractions, for which reaction is believed to be initiated by the formation of an n-type exciplex (51) in which charge flows from the arene (donor) into the half-filled

**Table 2.** Substituted acetophenones studied, their Hammett substituent constants, triplet energies, reduction potentials, T-T absorption maxima (MeCN) and absolute rate constants for triplet quenching by *para*-methylphenol in MeCN at 23°C.

| Ketone | $\sum\sigma$* | $E_T$† | $-E(A^-/A)$‡ | $-E^*_{red}$§ | $\lambda_{max}^{T\text{-}T}$(nm) | $\lambda_{max}^{rad}$ (nm) | $k_Q/10^9\ M^{-1}\ s^{-1}$ |
|---|---|---|---|---|---|---|---|
| 15 4-NMe$_2$ | −0.83 | — | — | — | 445 | Not detected | 0.58 ± 0.03 |
| 16 4-OMe | −0.27 | 70.1 | 51.4 | 18.7 | 380 | — | 1.24 ± 0.03‖ |
| 17 3,4-(Me)$_2$ | −0.24 | 70.3 | 50.7 | 19.6 | 350 | 390 | 1.11 ± 0.08 |
| 18 4-Me | −0.17 | 72.2 | 50.4 | 21.8 | 331¶ | — | 1.13 ± 0.07 |
| 19 3,4-(OMe)$_2$ | −0.15 | 67.3‖ | 45.0# | 22.3 | 375 | — | 0.59 ± 0.04‖ |
| 20 4-Ph | −0.01 | 60.8¶ | 40.4** | 20.4 | 420 | 445 | 0.0156 ± 0.0005 |
| 21 H | 0.00 | 73.5 | 49.3 | 24.2 | 335¶ | 390 | 1.09 ± 0.07 |
| 22 3-OMe | 0.12 | 72.4¶ | 45.7†† | 26.7 | 380 | — | 1.32 ± 0.04 |
| 23 4-Cl | 0.23 | 71.7 | 48.3 | 23.4 | 349 | 385 | 1.23 ± 0.06 |
| 24 3-Cl | 0.37 | 68.8 | 38.4 | 30.4 | <350 | 425 | 1.14 ± 0.18 |
| 25 3-CF$_3$ | 0.43 | 73.0 | 43.8 | 29.2 | 418 | 430 | 0.25 ± 0.03 |
| 26 4-CF$_3$ | 0.54 | 71.7 | 41.7 | 30.0 | 425 | 455 | 0.53 ± 0.05 |
| 27 3-CN | 0.56 | 73.0 | 40.3 | 32.7 | 420 | ~425 | 3.0 ± 0.4 |
| 28 4-CN | 0.66 | 69.2 | 36.4 | 32.8 | <350 | 500 | 2.4 ± 0.4 |

* From (38). † 0,0 Band in kcal/mol; 2-MeTHF solvent; from (10) unless otherwise noted. ‡ Half-wave reduction potential *vs* SCE in kcal/mol; MeCN solvent; from (10) unless otherwise noted. § $E_T - E(A^-/A)$ in kcal/mol. ‖ From (16). ¶ From (35). # N,N-dimethylformamide/0.1 *M* tetrabutylammonium perchlorate *vs* ferrocene/ferrocenium, corrected (+0.464 V *vs* SCE) for ferrocene in DMF; D.D.M. Wayner, personal communication. ** Estimated from data from (42). †† MeCN/0.1 *M* tetraethylammonium perchlorate *vs* ferrocene/ferrocenium, corrected (+0.449 V *vs* SCE) for ferrocene in MeCN; M.S. Workentin, personal communication.

**Table 3.** Other ketones studied, their triplet energies, reduction potentials, T-T absorption maxima (MeCN) and absolute rate constants for triplet quenching by *para*-methylphenol in MeCN at 23°C.

| Ketone | $E_T$* | $-E(A^-/A)$† | $-E^*_{red}$‡ | $\lambda^{T\text{-}T}$ (nm) | $\lambda^{rad}$ (nm) | $k_Q/10^9\ M^{-1}\ s^{-1}$ |
|---|---|---|---|---|---|---|
| 29 2-Acetonaphthone | 59.5§ | 39.7‖ | 19.8 | 425 | — | $0.0034 \pm 0.0004$ |
| 30 Fluorenone | 50.3¶# | 29.7** | 20.6 | 421 | 390, 510 | $0.097 \pm 0.003$ |
| 31 5-Methoxy-1-indanone | 73.4†† | 50.7‡‡ | 22.7 | 383 | 380 | $1.74 \pm 0.13^k$ |
| 32 Thioxanthone | 63.6‖‖ | 38.5¶¶ | 25.1 | 625 | 490 | $2.96 \pm 0.06$ |
| 33 6-Methoxy-1-indanone | 71.4††,§§ | 46.2‡‡ | 25.2 | 383 | 360 | $2.18 \pm 0.11^k$ |
| 34 4-Methoxy-α,α,α-trifluoroacetophenone | 65.9 | 37.5 | 28.4 | 420 | 390, 460 (w) | $1.98 \pm 0.09$ |
| 35 Xanthone | 74.1¶¶,## | 39.9¶¶ | 34.2 | 620 | 500 | $3.75 \pm 0.09$ |
| 36 α,α,α-Trifluoroacetophenone | 69.9 | 31.9 | 38.0 | <350 | — | $8.1 \pm 0.3$ |
| 37 2-Benzoylthiophene | 63.2*** | 41.5††† | 24.3 | 600 | — | $0.37 \pm 0.03$ |

* 0,0 Band in kcal/mol; 2-MeTHF solvent; from (10) unless otherwise noted. † Half-wave reduction potential *vs* SCE in kcal/mol; MeCN solvent; from (10) unless otherwise noted. ‡ $E_T - E(A^-/A)$ in kcal/mol. § From (35). ‖ From (43). ¶ In 5:2:2 EPA (ethanol:isopentane:diethyl ether) at 77K. # From (44). ** From (45). †† 4:1 EtOH:MeOH at 77K. ‡‡ MeCN/0.1 *M* tetraethylammonium perchlorate *vs* ferrocene/ferrocenium, corrected (+0.449 V *vs* SCE) for ferrocene in MeCN; M.S. Workentin, private communication. §§ From (24). ‖‖ From (46). ¶¶ From (47). ## From (48). *** From (49). ††† From (26).

n-orbital of the ketone (10). The rate constants for quenching via this mechanism depend as well on the oxidation potential of the hydrogen donor; this is known to be true for the quenching of benzophenone triplets by both substituted toluenes (10,11,52) and substituted phenols (14). Clearly, this mechanism can be expected to merge into a discrete electron-transfer mechanism as the triplet reduction potential is reduced to the point at which electron transfer becomes exergonic (*i.e.* $\Delta G_{et} < 0$). The rate constants for quenching of acetophenone and benzophenone n,π* triplets by toluene or para-xylene exhibit essentially identical dependences on triplet reduction potential (10), unlike the situation with 4MP for which the data (using the same set of $E^*_{red}$ values) are suggestive of a small difference in reactivity between the two series of ketones.

We believe that a simple electron transfer mechanism best fits the trends exhibited by the n,π* triplet ketones. Canonica and coworkers (18) reported compelling evidence for electron transfer in their study of the quenching of benzophenone (**8**), 3-methoxyacetophenone (**22**) and 2-acetonaphthone (**29**) triplets by substituted phenols in aqueous solution, for which there is little dependence of the rate constant for reaction on the nature of the lowest carbonyl triplet state. The situation is clearly expected to be quite different in protic solvents, in which the solvent is by far the dominant hydrogen bond donor and acceptor for both the excited ketone and the phenolic donor, and the hydrogen-bonded exciplex mechanism specific to π,π* triplet reactivity thus cannot operate. Interestingly, Canonica *et al.* (18) observed a significant enhancement in reactivity for benzophenone relative to the acetophenone derivative at common $\Delta G_{et}$ values, and showed that it results from a larger solvent reorganization energy term in the case of the acetophenone, perhaps due to somewhat greater localization of charge in the ketyl radical anion.

The rate constants for phenolic quenching via the π,π*(CT) mechanism, on the other hand, depend on neither the triplet reduction potential of the ketone nor the oxidation potential of the phenol, at least in an overall sense. The lack of dependence on the oxidation potential of the phenol was demonstrated previously for 4-methoxypropiophenone in benzene (14); 4-dimethylaminobenzophenone (**1**) in MeCN behaves similarly, as shown by the nearly identical rate constants with which its triplet state is quenched by phenol and the 4-methyl, 4-methoxy- and 4-cyano derivatives. This is an expected manifestation of the hydrogen-bonded exciplex

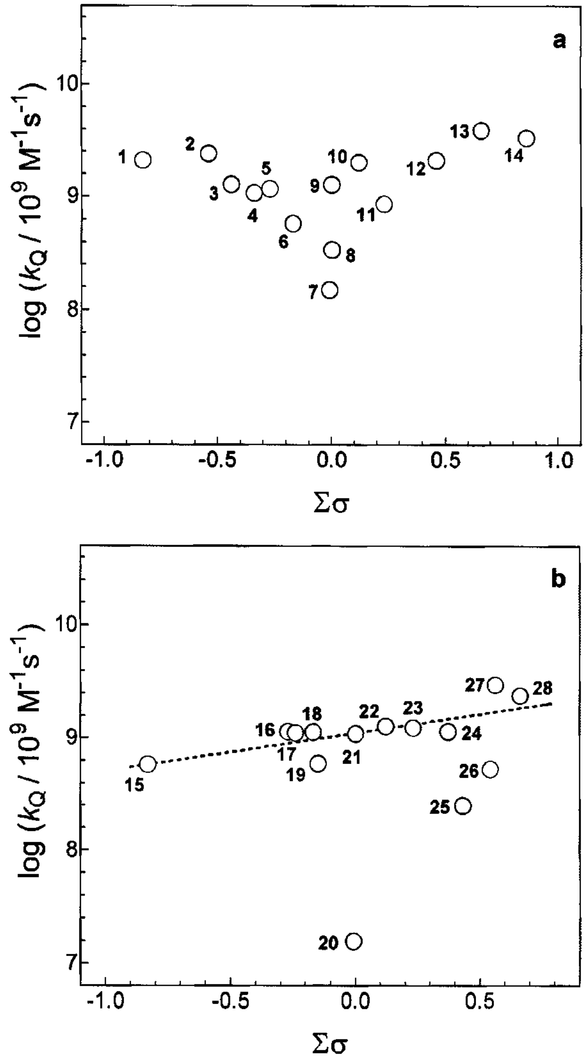


**Figure 3.** Plots of log $k_Q$ *versus* Hammett substituent constants (Σσ), for the quenching of substituted benzophenone (a) and acetophenone (b) triplets by 4MP in deoxygenated MeCN solution at 23°C.

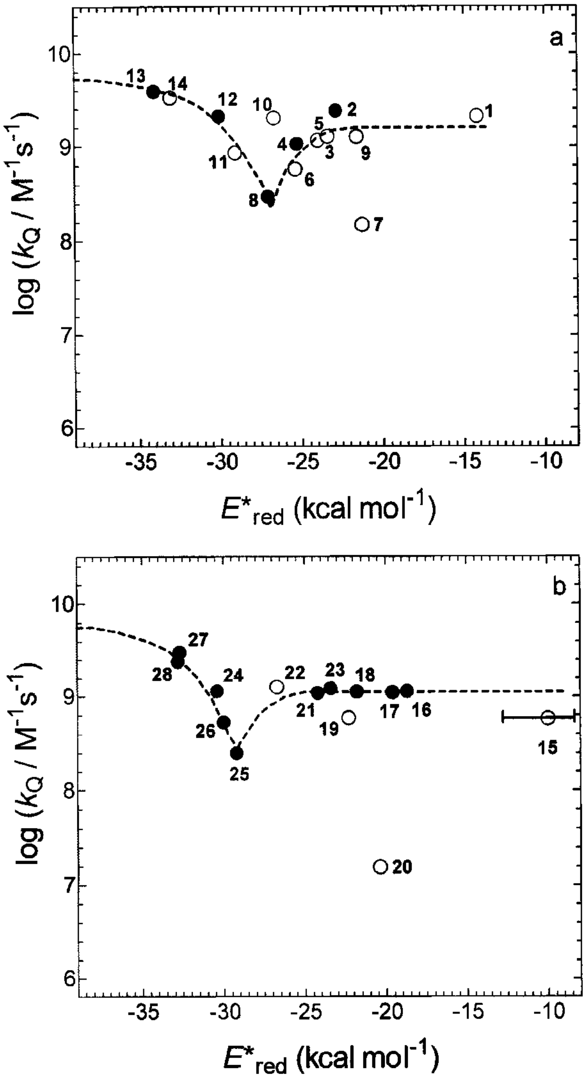


**Figure 4.** Plots of log $k_Q$ *versus* triplet state reduction potential ($E^*_{\rm red}$), for the quenching of substituted benzophenone (a) and acetophenone (b) triplets by 4MP in deoxygenated MeCN solution at 23°C. The solid points in the plots indicate those ketones for which the $E^*_{\rm red}$ values are from a single source (10) and thus have the highest degree of internal consistency. The curves drawn through the points are meant to accentuate the qualitative trends in the data and are not quantitatively meaningful.

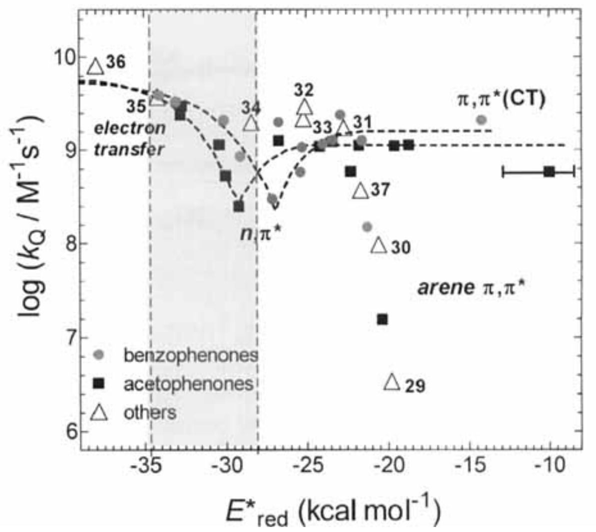


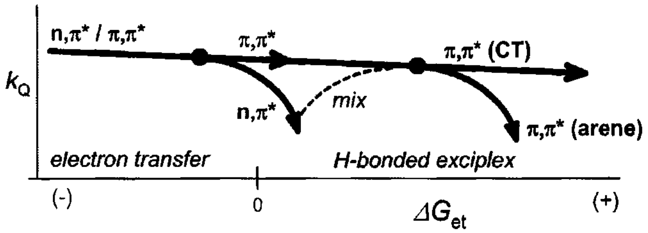
**Figure 5.** Plots of log $k_Q$ *versus* triplet state reduction potential ($E^*_{\rm red}$) for the quenching of **1–14** and **16–37** by 4MP in deoxygenated MeCN solution at 23°C. The shaded area between −28.1 and −34.6 kcal mol$^{-1}$ represents the range of uncertainty in the (thermodynamic) half-wave oxidation potential of 4MP.

mechanism for phenolic hydrogen abstraction, in which net H-atom transfer proceeds in the form of coupled electron-/proton-transfer. A relatively weak overall dependence of log $k_Q$ on $E^*_{\rm red}$ of the ketone is expected because the rate constant should depend on both the reduction potential *and* the basicity of the π,π*(CT) triplet state, and these vary with substituent in opposing fashion. Substituents that increase the basicity of the π,π*(CT) triplet state and hence make exciplex formation more favorable also have the effect of raising the reduction potential of the ketone, which slows down the rate of intramolecular electron transfer within the H-bonded exciplex; one balances the other out, resulting in little net effect on the overall rate constant as a function of substituent.

A similar interplay between hydrogen-bond acidity and oxidation potential holds for the phenolic donor, resulting in little or no net variation of the rate constant for reaction of a given π,π*(CT) triplet ketone with substituents on the phenol. The two plots of Fig. 4 can thus be understood as the superposition of two separate dependencies: one characteristic of photoinduced electron transfer, to which reaction via the n,π* triplet state is confined, and one characteristic of the π,π*(CT) triplet state, for which there is at most only a slight net dependence on $E^*_{\rm red}$. The reactivity of the n,π* state drops with increasing $E^*_{\rm red}$, but reaches a minimum level and then recovers as mixing with the higher lying π,π*(CT) triplet state increases. Reactivity levels off again when the latter becomes the lower energy triplet state.

Figure 5 summarizes the variation in log($k_Q$/$M^{-1}$ s$^{-1}$) with $E^*_{\rm red}$ for all the ketones studied in this work, illustrating how the data for the other ketones that have been examined (*i.e.* **29–37**) compare to those for the acetophenones and benzophenones. The shaded area in the plot defines our uncertainty in pinpointing the $E^*_{\rm red}$ value below which electron transfer is exergonic; electrochemical oxidation of 4MP and other phenols in nonaqueous solvents is irreversible (19,53,54) and so a value of the standard oxidation potential is not available. We have thus indicated in the plot a range of possible values, which extends from the reported peak potential for (irreversible) oxidation of the compound ($E_0$ = +1.20 eV *vs* SCE in MeCN) (54) to the value extrapolated from a plot of the standard oxidation potentials of substituted anisoles, toluenes and anilines *vs* $\sigma^+$ ($E_0 \sim +1.50$ V *vs* SCE in MeCN) (16,53).

Ketones **29–37** all possess lowest π,π* triplet states, and most can be arranged qualitatively into two general groups: one for which the lowest triplet is of arenoid π,π* type (2-acetonaphthone [**29**] and fluorenone [**30**]; **7** and **20** also fall into this class) and one in which the carbonyl group is contained in a benzannelated ring and the lowest triplet is of π,π*(CT) type (5- and 6-methoxyindanone [**31** and **33**, respectively], thioxanthone [**32**], and xanthone [**35**]). The ketones in the latter group are all quenched rapidly by 4MP, with rate constants on the order of 2–4 × $10^9$ $M^{-1}$ s$^{-1}$. The arenoid π,π* triplets (**7**, **20**, **29** and **30**) are much less reactive, exhibiting rate constants that vary between 3.4 × $10^6$ and 1.5 × $10^8$ $M^{-1}$ s$^{-1}$; the value for **29** ($k$ = 3.4 × $10^6$ $M^{-1}$ s$^{-1}$) is roughly 20 times *lower* than that reported by Canonica and coworkers (*18*) in aqueous solution. The trend in the rate constants for these compounds appears to



**Scheme 2.**

define yet a third correlation with $E^*_{red}$, exhibiting a precipitous decline at $E^*_{red} \sim -21$ kcal mol$^{-1}$, a potential some 6–8 kcal mol$^{-1}$ higher than those at which the n,π* ketones exhibit an analogous (but ultimately arrested) decline in rate constant. The behavior is consistent with the merging of the electron transfer and H-bonded exciplex mechanism discussed earlier, and essentially defines a subset of the behavior exhibited by the π,π*(CT) triplet ketones. The drop-off in rate constant is presumably caused by the fact that variations in arene substituent do not result in significant changes in the basicity of the triplet state, in contrast to the effects of polar substituents. The extensive study reported by Linschitz and coworkers (19) on the quenching of triplet fluorenone by phenols attests to the importance of hydrogen bonding in this particular case, and as Fig. 5 shows, its reactivity falls into line with the biphenylyl and naphthyl ketones studied here. In essence, intervention of the hydrogen-bonded exciplex mechanism extends the reactivity of arenoid π,π* ketones considerably beyond the point at which simple electron transfer becomes endergonic. 2-Benzoylthiophene (**37**) also appears to fall within this group; its lowest (π,π*) triplet state is associated primarily with the thienoyl group (49) rather than the benzoyl. Its reactivity toward phenolic hydrogen donors, both intermolecular and intramolecular, has recently been studied in detail by Perez-Prieto and coworkers (26,27,55). The rate constant reported here for reaction with 4MP is roughly two-fold higher than that reported for its reaction with the parent phenol under similar conditions (26).

As for the two remaining (π,π*) ketones studied, α,α,α-trifluoromethylacetophenone (**36**) and the 4-methoxy analog (**34**), the first is exceptional in that it possesses a sufficiently low reduction potential that reaction by electron transfer is unavoidable; as expected, it is significantly more reactive than any of the other ketones studied, exhibiting a rate constant of *ca* $8 \times 10^9$ $M^{-1}$ s$^{-1}$. Quenching yields the corresponding radicals in good yield, and affords no evidence for the formation of the ketyl radical anion. The same is true of **34**, whose higher triplet reduction potential results in a four-fold decrease in reactivity compared to that of the parent. The reactivity of this compound is similar to those of the benzo- and acetophenone π,π*(CT) triplets, but it also appears to fall within the trend suggested by the rate constants for the arenoid π,π* triplets.

## SUMMARY AND CONCLUSIONS

Scheme 2 illustrates in a qualitative way the dependence of the rate constants for quenching of aromatic ketone triplets by phenols on the thermodynamics of electron transfer and the nature of the lowest triplet state, as delineated by the reactivity of the 37 aromatic ketones considered in this work toward 4MP in MeCN solution.

The rate constant is at a maximum and is independent of the nature of the lowest triplet state when $\Delta G_{et} < 0$; in this regime, reaction is initiated by electron-transfer to produce the corresponding radical ion pair, which then undergoes (ultra)fast proton transfer to yield the corresponding radicals. Presumably, in this regime the fundamental difference between ketones of different lowest triplet state configurations is confined to the structure of the exciplex whose formation precedes the electron transfer event; π,π* triplets are significantly more basic than n,π* triplets, and thus can participate in hydrogen bonding with the phenolic donor whereas n,π* triplets cannot. Such an interaction enhances the efficiency of electron transfer within the excited complex, but this is irrelevant when the free energy for electron transfer in its absence, as calculated from standard redox potentials for the ketone and phenol, is already negative.

The difference in the structures of the exciplexes formed by n,π* and π,π* triplet ketones is felt only as $\Delta G_{et}$ approaches zero; the reactivity of the n,π* state begins to drop, while that of the π,π* state remains essentially unchanged due to the accelerating effect of hydrogen bonding on the rate of intraexciplex electron transfer. The interaction serves to make the ketone triplet a better electron acceptor by moving electron density to the phenol, which takes on increased phenoxide ion character and is hence more easily oxidized than it is in uncomplexed form. This provides an extra window of reactivity, whose width is determined by the hydrogen bond basicity of the ketone triplet and the acidity of the phenol, and by the thermodynamics of electron transfer within the hydrogen-bonded exciplex. Substituents that increase the basicity of the triplet or the acidity of the phenol have the opposite effect on the intraexciplex electron transfer rate. The corollary is not necessarily true; this results in a second demarcation of π,π* reactivity, between those ketones bearing polar (electron-donating) substituents, which imbue charge-transfer character to the π,π* triplet state, and those ketones bearing neutral arene substituents, for which the character of the π,π* triplet is essentially that of the arene substituent. Arenoid π,π* triplets thus experience a fall-off in rate constant, whereas π,π*(CT) triplets do not because of a much smaller compensating effect of substituents on hydrogen bond basicity. Nevertheless, the intermediacy of the hydrogen-bonded exciplex in the quenching of arenoid π,π* triplet ketones provides 4-MP with 5–10 kcal mol$^{-1}$ greater overall reducing power, compared to the situation with n,π* triplet ketones. In protic solvents, in which hydrogen-bonding interactions between the excited ketone and phenol are precluded, electron transfer is left as the only remaining operable mechanism for the reaction, and the dependence on triplet state configuration disappears (18).

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