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ARTICLES

Reducing Power of Photogenerated α-Hydroxy Radicals. Proton-Coupled Electron Transfer

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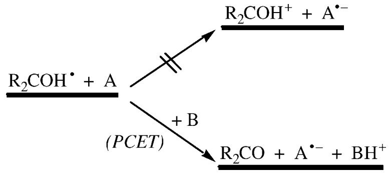
Proton-coupled electron transfer (PCET) has been reported in a number of systems. The oxidation product of a disubstituted α-hydroxy radical is a protonated ketone. In a case where electron transfer from such a radical to an electron acceptor is energetically unfavorable, it was of interest to probe whether electron transfer would occur if coupled with proton transfer to an added base. Through an experimental design based on fragmentation of benzopinacol radical cation, diphenylketyl radical ($Ph_2COH^\bullet$, $E^{ox} = -0.25$ V vs SCE) was photochemically generated as the only radical intermediate in a moderately polar solvent (1,2-dichlorethane). Direct electron transfer to 1,2,4,5-tetracyanobenzene (TCB, $E^{red} = -0.65$ V vs SCE) is endothermic by 0.4 eV and does not occur. In the presence of pyridine derivatives, however, PCET does, indeed, take place. In these termolecular reactions the electron is transferred to one molecule and the proton to another. Detailed kinetic studies by laser flash photolysis showed that a hydrogen-bonded complex between the ketyl radical and the pyridine base is formed, which then reacts with TCB, leading to $TCB^{\bullet-}$, benzophenone, and the protonated base. In these experiments, two $TCB^{\bullet-}$ are formed per absorbed photon in a very clean reaction. The equilibrium constants for complex formation decrease with decreasing pK_a of the base (∼18, 6, and 2 M^{-1} for 2,6-lutidine, 3-chloropyridine, and 2-chloropyridine, respectively). When the driving force for the overall reaction is ∼0.2−0.4 eV, the PCET rate constant reaches 1.5×10^9 M^{-1} s^{-1}, which is one-fifth of the diffusion-controlled limit in dichloroethane. However, as the reaction becomes nearly isoenergetic, the PCET rate constant drops by a factor of 4. The deuterium isotope effect of ∼3.2 for the PCET reaction with 2-chloropyridine as base is consistent with a concurrent electron/proton transfer.

Introduction

The reducing power of a radical depends strongly on the stability of the cation formed upon electron transfer from the radical to an electron acceptor. With increasing stability of the cation, the oxidation potential of the radical decreases and the reducing power of the radical increases.[1] Thus, the presence of a heteroatom at the α-position increases the reducing power of a radical. In the case of an oxygen atom, the oxidation product is an oxonium salt and, in the case of a nitrogen atom, it is an iminium salt. For example, whereas the oxidation potential of $PhCH_2^\bullet$ is +0.73 V, that of $MeOCH_2^\bullet$ is −0.24, and that of $Me_2NCH_2^\bullet$ is −1.03 V vs SCE.[1b]

In the case of an α-hydroxy radical ($R_2COH^\bullet$), the resultant oxidation product upon electron transfer to an acceptor is a protonated ketone (R_2COH^+). Because the ketone is a poor base, proton transfer from a protonated ketone to a strong base could become a highly exothermic process. Thus, the question was, if electron transfer from an α-hydroxy radical to a particular acceptor (A) is energetically unfavorable, would the electron transfer take place *if* coupled with a proton transfer to an added base (B) such that the overall process becomes energetically favorable, Scheme 1.

SCHEME 1



Several photochemical examples of proton-coupled electron transfer (PCET) reactions have been reported, and it is an area of current interest from both experimental and theoretical points of view.[2] These reports include reactions of organometallic compounds,[3] and those of biological systems,[4] with an emphasis on designs to provide preformed structures with optimum geometry for proton transfer. PCET was also demonstrated in an organic system in which triplet-excited C_{60} reacts with a ground-state hydroquinone/base complex.[5] We discuss here another type of PCET in which the reactant is a free radical. This termolecular acceptor/radical/base process further illustrates the diversity of PCET and helps to define the scope of these processes. In addition, the ability to modulate the reducing power of a free radical through extrinsic means, i.e., without changing the chemical structure of the radical, could play a role in extending the utility of these intermediates.[6]

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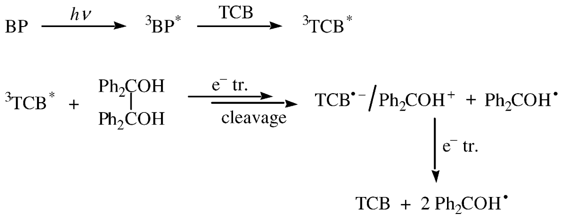
SCHEME 2



Experimental Design

Diphenyl ketyl radical ($Ph_2COH^•$) is a well-characterized species that can readily be studied by laser flash photolysis. The oxidation potential of this radical in acetonitrile has been reported recently to be −0.25 V vs SCE.[1c] With 1,2,4,5-tetracyanobenzene (TCB) as an electron acceptor, which has a reduction potential of −0.65 V vs SCE,[7a] electron transfer from $Ph_2COH^•$ would be endothermic by ~0.4 eV and, thus, quite unfavorable. In addition, $TCB^{•-}$ has a well-defined absorption band in the visible range that can be monitored in the presence of the ketyl radical.[7b] The challenge was to devise a scheme to generate the ketyl radical at a high enough rate to permit investigation of the follow-up reactions. The ketyl radical can be generated through hydrogen atom abstraction by triplet-excited benzophenone from a number of hydrogen atom donors such as alkyl benzenes.[8] Unfortunately, these reactions tend to be slower than 10^7 M^{-1} s^{-1}. Although hydrogen atom abstraction from ethers is somewhat faster,[8] two different α-oxy radicals would be produced, potentially complicating the kinetics.

We chose another approach to generate the ketyl radical as the only intermediate in the presence of TCB, Scheme 2. Excitation of benzophenone leads, via fast intersystem crossing, to triplet benzophenone ($^3BP^*$, $E_T = 68.6$ kcal/mol).[9] Triplet energy transfer from $^3BP^*$ to TCB ($E_T = 64.8$ kcal/mol or 2.81 eV)[9] leads to $^3TCB^*$. As mentioned above, TCB has a reduction potential of −0.65 V vs SCE; its triplet state can thus oxidize a molecule with oxidation potential of ≤2.1 V. Benzopinacol, with an estimated oxidation potential of ~2.1 V, would therefore undergo electron-transfer reaction with $^3TCB^*$, leading to the radical cation of benzopinacol, which is known to undergo fast cleavage to Ph_2COH^+ and $Ph_2COH^•$.[10] The cation Ph_2COH^+ will be formed in cage with $TCB^{•-}$. In 1,2-dichloroethane (DCE), the solvent used in this study, the rate constant for out-of-cage separation of an ion pair is $\sim 4 \times 10^8$ s^{-1}.[11] Electron transfer from $TCB^{•-}$ to Ph_2COH^+ is expected from the above discussion to be exothermic by ~0.4 eV and could, therefore, occur much faster than separation. Accordingly, two ketyl radicals could be formed per triplet benzophenone and would be the only radicals present, Scheme 2.

Reaction Intermediates and Primary Rate Constants

The objective of this work is to probe the proton-coupled electron transfer in the reaction of the ketyl radical with TCB in the presence of an added base (B). Four transient species are involved in the reaction, and they all can be monitored by flash photolysis. These are triplet benzophenone ($^3BP^*$), triplet TCB ($^3TCB^*$), the ketyl radical ($Ph_2COH^•$), and finally, reduced TCB ($TCB^{•-}$), a product of PCET. In accordance with Scheme 2, each $^3BP^*$ leads to a $^3TCB^*$, which, in turn, leads to two $Ph_2COH^•$. In the presence of a base, if proton-coupled electron transfer occurs, the two ketyl radicals would lead to two $TCB^{•-}$. From the relative intensities of the absorption bands of the individual species, together with their independently determined extinction coefficients, the validity of the scheme can, therefore, be verified.

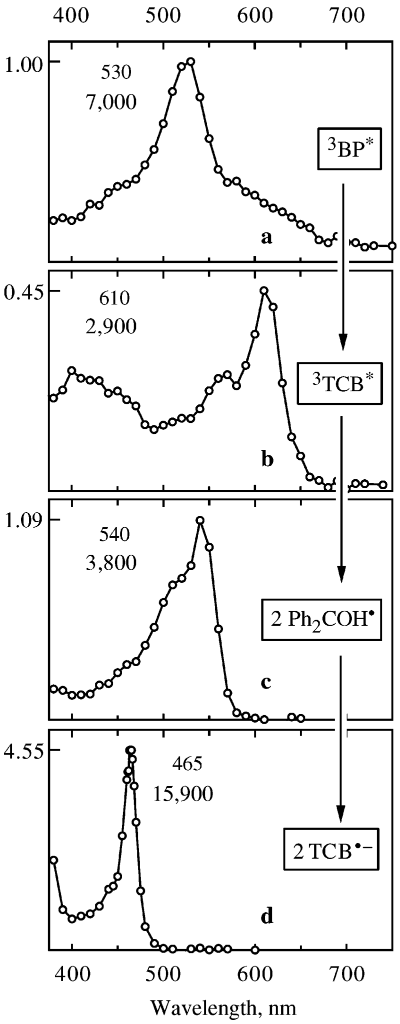


Figure 1. Absorption spectra following 355 nm excitation in 1,2-dichloroethane of (a) benzophenone (0.006 M) and those upon *successive* addition of (b) 1,2,4,5-tetracyanobenzene, (c) benzopinacol, and (d) lutidine (all at 0.02 M). The spectra were obtained from measurements delayed by 100−200 ns (a and b) or by 1−1.5 μs (c and d) after the pulse. The relative intensities of the spectra, corrected for laser power and for a minor decay (<5%) during the delay time, are given on the vertical axes. The extinction coefficients of the different species (based on a value of 7000 for $^3BP^*$) at their absorption maxima are shown.

In a nanosecond laser flash photolysis experiment (355 nm excitation), the transient absorption spectrum of a solution containing benzophenone (0.006 M) and TCB (0.02 M) in 1,2-dichloroethane (DCE) was compared to one with no TCB (Figure 1). Based on an extinction coefficient of 7000 for $^3BP^*$ at λ_{max} of 530 nm[12] (Figure 1a), an extinction coefficient of 2900 can be deduced for $^3TCB^*$ at its λ_{max} of 610 nm (Figure 1b). When benzopinacol (0.02 M) is added to the solution of BP and TCB, a spectrum identifiable with the ketyl radical is obtained (Figure 1c). Importantly, the optical density at 540 nm, the λ_{max} of the ketyl radical, is 1.09 times that of $^3BP^*$ at its λ_{max} (Figure 1a). The reported extinction coefficient of $Ph_2COH^•$ is nearly one-half that of $^3BP^*$.[12] Thus, within experimental error, two ketyl radicals are formed per $^3BP^*$. This indicates that, although several steps are involved, (1) energy transfer, (2) electron transfer, (3) fragmentation of a radical cation, followed by (4) a second electron transfer (Scheme 2), the reactions seem to be quite clean and proceed with essentially unit efficiency. In the absence of other additives, the ketyl radical, as expected, decays slowly by second-order coupling to reconstitute the pinacol. In other words, despite several steps, under these conditions, no net reaction takes place.

The rate constant for triplet energy transfer from ^{3}BP* to TCB, k_1, determined from the decay of ^{3}BP* absorption and from the growth of ^{3}TCB* as a function of [TCB], was found to be 3.6×10^9 M^{-1} s^{-1}. This rate constant is approximately one-half the diffusion-controlled limit in DCE, which is reasonable for a triplet energy transfer reaction with ~4 kcal/mol exothermicity.[13] The rate constant of the reaction of ^{3}TCB* with benzopinacol, k_2, was similarly determined from the decay of ^{3}TCB* and from the growth of $Ph_2COH^\bullet$ at different concentrations of the pinacol. A rate constant of 6.8×10^8 M^{-1} s^{-1} was measured for this reaction, with the cleavage of the pinacol radical cation and the in-cage electron transfer from $TCB^{\bullet-}$ to Ph_2COH^+ being too fast to be time resolved.[10] The rate constant k_2, being only one-tenth of the diffusion-controlled limit, is within the expected range because of the small driving force for electron transfer from benzopinacol to ^{3}TCB*. For the purpose of probing a subsequent proton-coupled electron-transfer reaction, this process at moderate pinacol concentrations (0.01 or 0.02 M) will be faster than the follow-up reactions of the ketyl radical. It is worth noting that, under our experimental conditions, no direct reaction between ^{3}BP* and benzopinacol could be detected.

Effect of Base: Proton-Coupled Electron Transfer

Having shown that the diphenylketyl radical can be generated in the presence of TCB with no subsequent reaction between them, we then studied the effect of an added base. To ensure that proton-coupled electron transfer would be possible in these reactions, it was important to choose a base such that the overall reaction would be exothermic.

$$Ph_2COH^\bullet + TCB + B \rightarrow Ph_2CO + TCB^{\bullet-} + BH^+$$

As discussed above, the electron transfer *alone* is endothermic by ~0.4 eV. From the difference between the pK_a of benzophenone and that of the base, the driving force for the proton-transfer step can be estimated. The pK_a in acetonitrile of benzophenone is nearly 0,[1c] whereas that of lutidine is ~14.[14] Thus, the pair benzophenone + protonated lutidine is estimated to be 0.8 eV lower in energy than protonated benzophenone + lutidine. That is, the reducing power of the ketyl radical should increase by ~0.8 eV, *if* the electron transfer is coupled with proton transfer to a base such as lutidine. Thus, the overall reaction (combined electron and proton transfer) would be rendered exothermic by ~0.4 eV rather than endothermic by ~0.4 eV in the absence of a base. If the difference between the pK_a's of benzophenone and lutidine in DCE is not much different from that in acetonitrile, the estimated change in driving force should be similar.

Indeed, addition of lutidine (0.02 M) to a DCE solution containing benzophenone, TCB, and benzopinacol yields $TCB^{\bullet-}$, identified by a characteristic spectrum (see the Experimental Section) with a λ_{max} at 465 nm, Figure 1d. Comparing the intensity of the $TCB^{\bullet-}$ signal to that of ^{3}BP* and of $Ph_2COH^\bullet$, together with the independently determined extinction coefficients of theses species, reveals that each ketyl leads to the formation of $TCB^{\bullet-}$ with unit efficiency.

As discussed below, the addition of lutidine does *not* lead to any detectable deprotonation of the ketyl radical to form a benzophenone radical anion. Thus, the reducing species is the diphenyl ketyl radical, and proton-coupled electron transfer does take place, representing a dramatic increase in the reducing power of the ketyl radical. The question now is the mechanism by which this ternary reaction takes place, which is likely to involve the formation of at least one complex between two of the reactants (radical, acceptor, and base) that subsequently reacts with the third species.

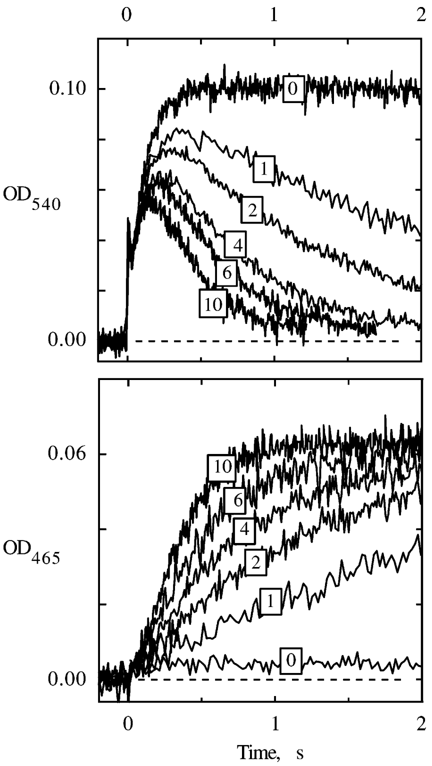


Figure 2. Top: Growth and decay of the diphenylketyl radical ($Ph_2COH^\bullet$) monitored at 540 nm in the absence and presence of varying concentrations of lutidine (given in mM by the labels). Bottom: Growth of tetracyanobenzene radical anion ($TCB^{\bullet-}$) monitored at 465 nm at the same varying concentrations of lutidine as above. The laser power for the 465 nm experiment was ~6 times less than that used for the one at 540 nm.

Reaction Kinetics

At low laser power, where the ketyl radical concentration is low, and in the absence of a base, the decay of the radical (via coupling) monitored at 540 nm is barely noticeable on a 2 μs scale (Figure 2). The decay rate of $Ph_2COH^\bullet$ increases with increasing concentration of added lutidine and is concurrent with the grow-in signal of $TCB^{\bullet-}$ at 465 nm (Figure 1d). As shown in Figure 2 and from data fitting, the growth rates of $TCB^{\bullet-}$ are equal to the decay rates of $Ph_2COH^\bullet$.

The decay rates of the ketyl radical for several sets of measurements at constant [TCB] and varying [lutidine], as well as at constant [lutidine] and varying [TCB], are shown in Figure 3. These data were obtained by fitting the transient absorption at 540 nm to a two-exponential rise and fall.[15] Under the reaction conditions used in these experiments, the rise represented interception of ^{3}TCB* by benzopinacol, and the fall represented the decay of the ketyl radical. The concentration of benzopinacol was kept at either 0.01 or 0.02 M in order to ensure that the rate of formation of the ketyl radical remains greater than its decay rate. This condition usually leads to higher accuracy in evaluation of the decay rate. At low concentration of either the acceptor or the base, the rate increases in proportion to the concentration of the varying reactant. At higher concentrations of either reactant, however, the rate increases more slowly, suggesting formation of a binary complex that is subsequently intercepted by the third reactant.

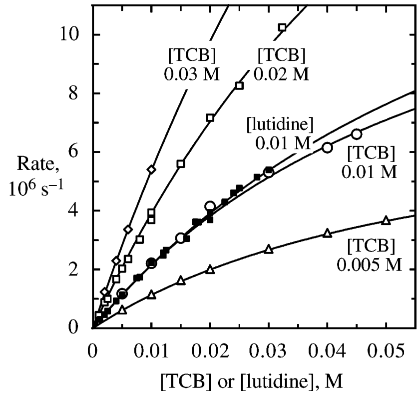
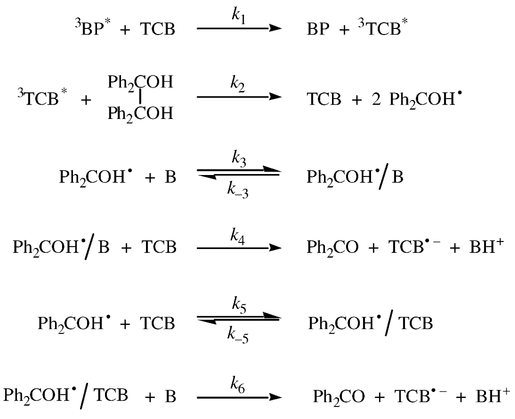


Figure 3. Decay rate (in 10^6 s^{-1}) of the ketyl radical as a function of the concentration of added lutidine at fixed TCB concentrations of 0.005, 0.01, 0.02, and 0.03 M (open symbols) and as a function of TCB concentration at a fixed lutidine concentration of 0.01 M (solid squares). The curves are the calculated rates based on fixed values for $k_3 = k_5 = 8 \times 10^9$ M^{-1} s^{-1}, the diffusion-controlled rate constant, and the fitting parameters $k_4 = k_6 = 1.0 \times 10^9$ M^{-1} s^{-1}, $K_3 = 15.9$ M^{-1}, and $K_5 = 11.9$ M^{-1} (see Scheme 3 and text for details).

SCHEME 3



$$^3\mathrm{BP}^* + \mathrm{TCB} \xrightarrow{k_1} \mathrm{BP} + {}^3\mathrm{TCB}^*$$

$$^3\mathrm{TCB}^* + \begin{matrix}\mathrm{Ph_2COH} \\ | \\ \mathrm{Ph_2COH}\end{matrix} \xrightarrow{k_2} \mathrm{TCB} + 2\ \mathrm{Ph_2COH}^\bullet$$

$$\mathrm{Ph_2COH}^\bullet + \mathrm{B} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{Ph_2COH}^\bullet/\mathrm{B}$$

$$\mathrm{Ph_2COH}^\bullet/\mathrm{B} + \mathrm{TCB} \xrightarrow{k_4} \mathrm{Ph_2CO} + \mathrm{TCB}^{\bullet -} + \mathrm{BH}^+$$

$$\mathrm{Ph_2COH}^\bullet + \mathrm{TCB} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \mathrm{Ph_2COH}^\bullet/\mathrm{TCB}$$

$$\mathrm{Ph_2COH}^\bullet/\mathrm{TCB} + \mathrm{B} \xrightarrow{k_6} \mathrm{Ph_2CO} + \mathrm{TCB}^{\bullet -} + \mathrm{BH}^+$$

As shown in Figure 3, the tendency to level off is very similar for the two sets of data where either [TCB] was varied, and the lutidine concentration was fixed at 0.01 M or vice versa. This similarity suggests one of two possibilities. (1) The ketyl radical forms complexes both with the base and with TCB, and the two equilibrium constants are of similar magnitude. At sufficiently high base or TCB concentrations, the rate would level off as most of the ketyl radical is complexed. (2) Alternatively, the reaction proceeds via a single complex, where the rate constant for complex formation is very similar to the rate constant for the follow-up PCET reaction (see, further, below) (Scheme 3).

Stabilization of a complex between $\mathrm{Ph_2COH^\bullet}$ and lutidine (equilibrium constant K_3) would be through hydrogen bonding. Changes in the spectrum of the ketyl radical[16] in the presence of lutidine are consistent with the formation of such a hydrogen-bonded complex. The absorption spectrum of the complex is slightly red shifted from that of the free ketyl radical, Figure 4, similar to the spectra of hydrogen-bonded ketyl radical/amine complexes.[17] This modest spectral change shows also that lutidine is not a strong enough base to deprotonate the ketyl radical to give benzophenone radical anion, $\mathrm{BP}^{\bullet -}$, which has a distinctly different absorption spectrum; see the Experimental Section.

From the change in intensity at 570 nm as a function of lutidine concentration, an equilibrium constant for the complex formation between the ketyl radical and lutidine, K_3, of ~18 M^{-1} was obtained, Figure 5.[18] A reaction of this complex with TCB, k_4, leading to $\mathrm{TCB}^{\bullet -}$, protonated lutidine, and benzophenone would be formally a PCET.

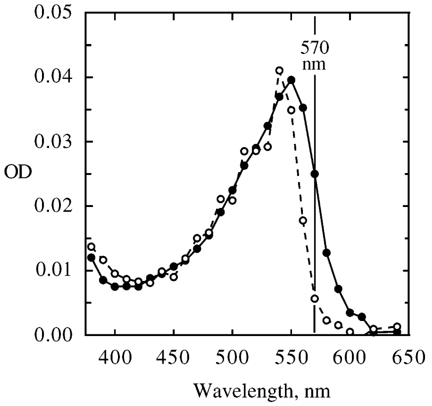


Figure 4. (---) Absorption spectrum of diphenylketyl radical obtained from 355 nm excitation of benzophenone in dichloroethane in the presence of 0.75 M butylbenzene. (—) Corresponding spectrum in the presence of 0.43 M lutidine. With an association constant, K_3, of ~18 M^{-1} for complex formation between the ketyl radical and lutidine, the latter spectrum corresponds to a mixture of ~87% complex and ~13% free ketyl radical. No absorption was detectable at $\lambda > 650$ nm, where any $\mathrm{BP}^{\bullet -}$ ($\lambda_{\max} = 690$ nm) would have shown a strong absorption.

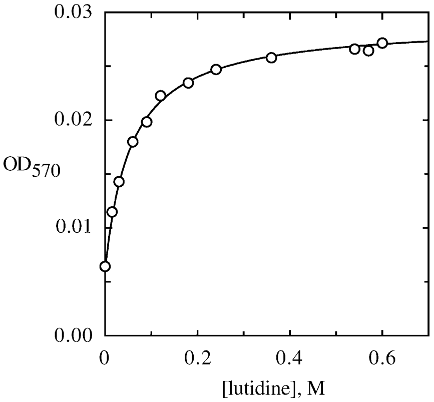


Figure 5. Optical density at 570 nm of photolytically generated diphenylketyl radical as a function of lutidine concentration. The spectral change is due to complex formation between the ketyl radical and lutidine and is strongest at 570 nm, where the extinction coefficient ratio is ~4.8 (see Figure 4). The curve is calculated for an equilibrium constant of 18 M^{-1}.

It is conceivable that the ketyl radical, $\mathrm{Ph_2COH^\bullet}$, could also form a charge-transfer (CT) complex with TCB (equilibrium constant K_5). We did not detect any change in the spectrum of the ketyl radical as a function of [TCB]. On this basis alone such a complex should not be ruled out, however, because its absorption would peak in the IR, considering, as mentioned above, that the energy gap between the neutral components and the pair with complete charge transfer is only 0.4 eV. In turn, if formed, such a complex would react with the base in a PCET process, k_6, to generate the same products.

We also investigated the possibility of complex formation between TCB and lutidine. A weak CT absorption can be detected between these reactants in DCE. The equilibrium constant for this complex formation, however, is too small to affect the reaction kinetics. From the nearly linear change in optical density of the CT absorption in the ~340−380 nm range with increasing lutidine concentrations up to 2 M, an equilibrium constant of less than 0.2 M^{-1} can be estimated. The equilibrium constants for complex formation between TCB and weaker bases (see below) are still lower than that with lutidine.

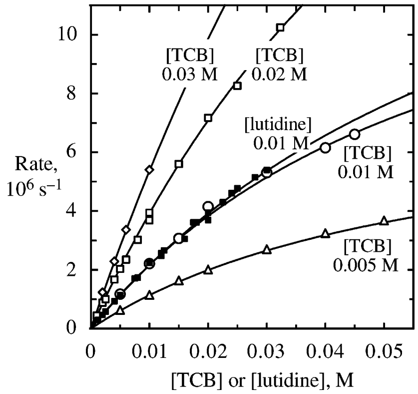


Figure 6. Same data as in Figure 3 with curves calculated on the assumption that only the base forms a complex with the ketyl radical, using the fitting parameters: $k_3 = 1.86 \times 10^9$ M^{-1} s^{-1}, $k_4 = 1.53 \times 10^9$ M^{-1} s^{-1}, and $K_3 = 18.6$ M^{-1} (see text for details).

Thus, either only the ketyl radical/lutidine complex, which is spectroscopically detected, is involved in the kinetic scheme or, in addition, a ketyl radical/TCB complex (which, if formed, would be difficult to detect) is also involved. Because the free and the base-complexed ketyl radical have similar absorption at 540 nm, the optical density at this wavelength is a measure of the total concentration of the radical.

The different sets of data mentioned above, in which the concentration of one of the reactants (TCB or lutidine) was varied and the other was kept constant, were first analyzed assuming that both complexes are formed at the diffusion-controlled limit, i.e., $k_3 = k_5 = 8 \times 10^9$ M^{-1} s^{-1}.[19] To decrease the number of fitting parameters, the rate constants of the two proton-coupled electron-transfer reactions, k_4 and k_6, were assumed to be equal. Under these assumptions, the best fit to the data was obtained for $K_3 = 15.9$ M^{-1}, $K_5 = 11.9$ M^{-1}, and $k_4 = k_6 = 1.0 \times 10^9$ M^{-1} s^{-1}, Figure 3. The value of K_3, 15.9 M^{-1}, is reasonably close to the spectroscopically determined value of ~18 M^{-1}.

Alternatively, the data were fitted assuming that only the $Ph_2COH^•$/lutidine complex is formed. In this fitting procedure the rate constant for complex formation k_3 was included as a floating parameter. An equally good fit was obtained with $k_3 = 1.86 \times 10^9$ M^{-1} s^{-1}, $K_3 = 18.6$ M^{-1}, and $k_4 = 1.53 \times 10^9$ M^{-1} s^{-1}, Figure 6. Again, the computed K_3 of 18.6 M^{-1} is close to the independently determined value of ~18 M^{-1}.

To distinguish between these two alternative schemes, we replaced lutidine by another base, 3-chloropyridine (pK_a ~10, in acetonitrile).[14] If a $Ph_2COH^•$/TCB complex is in fact involved in these reactions, the equilibrium constant for its formation, K_5, being independent of base, should be equal in the two experiments.

The decay rates, as expected for a poorer base, are smaller than those obtained for the lutidine experiment, and the tendency to level off is less pronounced, Figure 7. The 3-chloropyridine data show, however, a trend similar to that with lutidine. The curvature in the plot of the rate of ketyl radical decay vs [TCB] at 0.01 M 3-chloropyridine is very similar to that of the plot vs [3-chloropyridine] at 0.01 M TCB, Figure 7. This behavior is again compatible with the two alternative explanations discussed above for the lutidine experiment.

Fitting the 3-chloropyridine data under the same two-complex assumptions used above for the lutidine experiment gave the following parameters: $K_3 = 5.2$ M^{-1}, $K_5 = 4.4$ M^{-1}, and $k_4 = k_6 = 9.1 \times 10^8$ M^{-1} s^{-1}. The equilibrium constant K_3 obtained from this analysis is comparable to the value of ~6 obtained independently from the spectral change of the ketyl radical as a function of [3-chloropyridine]. These analyses provide good fits for the data with each base and yield values for the equilibrium constants K_3 that are not very different from those determined independently. However, significantly different values of the equilibrium constant, K_5, were obtained from fitting of the two sets of data (11.9 and 4.4 M^{-1}). Therefore, although the data with each base can be explained in terms of complexes of the ketyl radical with both the base and TCB, these apparent successes must be regarded as accidental.

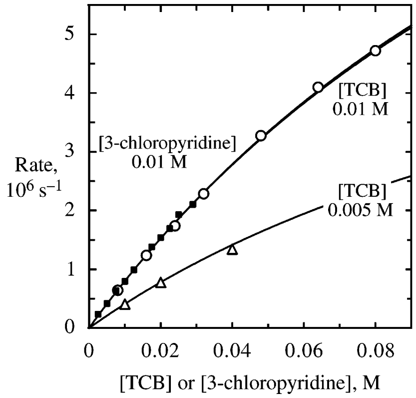


Figure 7. Decay rate (in 10^6 s^{-1}) of diphenylketyl radical as a function of the concentration of added 3-chloropyridine at fixed TCB concentrations of 0.005 and 0.01 M (open symbols) and as a function of TCB concentration at a fixed 3-chloropyridine concentration of 0.01 M (solid squares). The curves are the calculated rates based on the fitting parameters $k_3 = 1.55 \times 10^9$ M^{-1} s^{-1}, $k_4 = 1.51 \times 10^9$ M^{-1} s^{-1}, and $K_3 = 5.9$ M^{-1} (see text for details). Because of the very close values of k_3 and k_4, the two curves at fixed concentrations of 0.01 M are almost indistinguishable (see text).

Limiting the fitting of the 3-chloropyridine data to the ketyl/base complex as discussed above for the lutidine data gave the following parameters: $k_3 = 1.55 \times 10^9$ M^{-1} s^{-1}, $K_3 = 5.9$ M^{-1}, and $k_4 = 1.51 \times 10^9$ M^{-1} s^{-1} (Figure 7). Again, the value of the equilibrium constant obtained from this fitting procedure is quite similar to that determined spectroscopically (~6 M^{-1}). Thus, both sets of data can be explained in terms of a hydrogen-bonded complex between the ketyl radical and the base, followed by a PCET reaction with the acceptor, TCB. The agreement between the spectroscopically determined equilibrium constants for both bases and those derived from the fitting of the kinetic data provides strong support for this mechanism.

Despite the ~0.2−0.25 eV difference in driving force between the reactions with lutidine and with 3-chloropyridine (Δp$K_a \approx 4$), the PCET rate constant, k_4, in *both* cases is ~1.5×10^9 M^{-1} s^{-1}. The fact that these values are very similar but below the diffusion-controlled rate constant (8×10^9 M^{-1} s^{-1}) may indicate that a restricted geometry is required for the PCET reaction to take place. The electron transfer would be faster if TCB were closer to the ketyl radical, but the generated ion pair ($TCB^{•-}$ and pyridinium derivative) would be more stable if TCB were closer to the base. Thus, the PCET reaction might be favored only at a limited, optimum configuration within the termolecular intermediate. Alternatively, the reaction with 2,6-lutidine, which has a larger driving force, might be slower due to steric hindrance from the two *o*-methyl groups.

Beyond a certain point, the rate constant for PCET, k_4, is expected to decrease with decreasing driving force for the reaction, which is controlled by the pK_a of the base. 2-Chloropyridine seems to be the weakest base (pK_a ~7 in acetonitrile)[14] that we can use to induce the reaction at a rate that can be measured in our flash photolysis experiment. The dependence

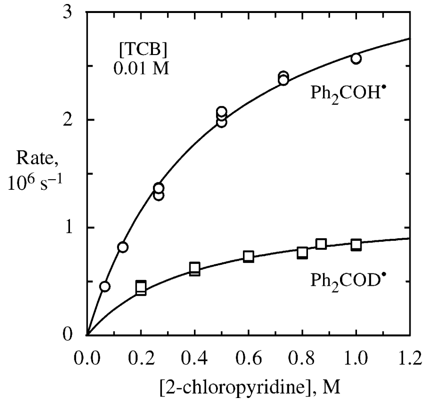


Figure 8. Decay rate (in 10^6 s^{-1}) of diphenylketyl radical as a function of the concentration of added 2-chloropyridine at fixed TCB concentrations of 0.01 M (○). The curve is the calculated rates based on the fitting parameters $K_3 = 2.2$ M^{-1} and $k_4 = 3.8 \times 10^8$ M^{-1} s^{-1}. The corresponding fitting parameters for decay rates of the deuterated ketyl radical (□) are $K_3 = 2.5$ M^{-1} and $k_4 = 1.2 \times 10^8$ M^{-1} s^{-1}.

TABLE 1: Rate Constants (k_3) and Equilibrium Constants (K_3) for Complex Formation between Diphenyl Ketyl Radical and Different Pyridine Derivatives and Rate Constants (k_4) for Proton-Coupled Electron Transfer

base (B)	k_3 (10^9 M^{-1} s^{-1})	K_3 (M^{-1})	k_4 (10^9 M^{-1} s^{-1})
2,6-lutidine	1.86	18.6	1.53
3-chloropyridine	1.55	5.9	1.51
2-chloropyridine		2.2	0.38

of the reaction rate on [2-chloropyridine] is shown in Figure 8, which shows a much clearer leveling-off than with the other bases. This is due to a significant decrease in k_4, which allows the experiment to be carried out at such high concentrations of the base that a substantial fraction of the radical is hydrogen-bonded to the base. Because of a decrease in k_4 relative to k_3, only the equilibrium constant K_3 and the rate constant for the PCET reaction, k_4, can be determined from the data. The best fit was obtained for K_3 of 2.2 M^{-1} and k_4 of 3.8 × 10^8 M^{-1} s^{-1}. The equilibrium constant for complex formation between the ketyl radical and 2-chloropyridine obtained from the change in absorption spectrum of the radical is less accurate in this case, because of a smaller difference in the spectrum between the free and the hydrogen-bonded radical. The value estimated from the spectral change for K_3, 2−3 M^{-1}, however, brackets the kinetically determined equilibrium constant of 2.2 M^{-1}, providing additional support for the mechanism. Considering the uncertainties about the pK_a values in dichloroethane, the PCET reaction with 2-chloropyridine (p$Ka \approx 7$) is likely to be isoenergetic within ~0.1 eV. Thus, the 4-fold drop in PCET rate constant relative to those with the stronger bases, i.e., bases with larger driving force, is quite reasonable.

The kinetic data for the different bases are summarized in Table 1.[20] The error margin for the rate constants is likely to be ~10%.

$$Ph_2COH^{•} + B \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Ph_2COH^{•}/B \xrightarrow[k_4]{+TCB} Ph_2CO + TCB^{•-} + BH^+$$

(equilibrium const K_3)

Deuterium Isotope Effect

In the reactions discussed in this work, no electron transfer from the ketyl radical to the acceptor takes place in the absence of a base, and no proton transfer from the ketyl radical to the base takes place in the absence of an acceptor. The coupled electron/proton transfer proceeds, however, at rates approaching the diffusion-controlled limit. In principle, these processes could be concerted or the electron transfer could precede a fast proton transfer. For the latter to be the case, hydrogen bonding of the ketyl radical to a pyridine base would have to lower the oxidation potential of the ketyl radical to the extent that electron transfer to TCB becomes energetically feasible. It is unlikely that hydrogen bonding would lower the oxidation potential of the ketyl radical by the ~0.4 V that is needed to allow for a fast electron transfer. Nevertheless, independent support for concurrent electron/proton transfer was sought.

In a PCET reaction in which the proton transfer is concurrent with the electron transfer, a deuterium isotope effect would be expected. An example of such an isotope effect is given in ref 5a. The present reaction with 2-chloropyridine as base proceeds at a rate constant k_4 that is considerably lower than the diffusion-controlled limit and seemed, therefore, to be well suited to test for an isotope effect. Replacing the OH group of the ketyl radical by OD was achieved by carrying out the reaction using benzopinacol-d_2. As shown in Figure 8, deuteration does indeed lower the reaction rate by a substantial amount. Fitting the data as described above gives an equilibrium constant K_3 of 2.5 M^{-1} and a rate constant for the PCET step, k_4, of 1.2 × 10^8 M^{-1} s^{-1}. The equilibrium constants K_3 for the OD and OH compounds are similar,[21] whereas the PCET rate constants yield a deuterium isotope effect k_4^H/k_4^D of ~3.2. The large isotope effect is in agreement with a concurrent, but not a sequential, electron/proton-transfer reaction.

Concluding Remarks

The PCET described in this work represents a termolecular reaction in which a photogenerated free radical transfers the electron to one molecule and the proton to another. With rare exception,[5a] in most reported PCET reactions, both the electron and the proton are transferred to the same molecule.

Through a careful experimental design, diphenyl ketyl radicals are formed in a fast reaction that allows the kinetics of the PCET to be reliably studied. All the available data can be explained in terms of complex formation between the ketyl radical and a base, followed by a PCET reaction with the acceptor, TCB. If at all formed, a ketyl radical/TCB complex is likely to play only a minor role. The lack of any detectable perturbation of the ketyl radical absorption by added TCB further diminishes the likelihood that a ketyl radical/TCB complex is involved in the PCET reaction. Even the tendency of the PCET rate to level off at high concentrations of TCB is consistent with the mechanism in which only the base forms a complex with the ketyl radical.

It is interesting that the analyses can provide values for the rate constant of complex formation (k_3) that are not directly measured and are not readily determinable by other techniques. In the present range of concentrations and rate constants, the decay rate of the ketyl radical is governed by both k_3 and k_4. The reason is discussed further in the Kinetic Analysis part of the Experimental Section.

The fact that the equilibrium constant K_3 decreases from lutidine through 3-chloropyridine to 2-chloropyridine is expected on the basis of pK_a. The fact that k_3 and k_4 are of similar magnitude in the cases of both lutidine and 3-chloropyridine must be accidental. If the reduction potential of the acceptor became more negative, k_4 would begin to decrease, whereas k_3, being independent of the acceptor, will not be affected. The data for 2-chloropyridine suggest that k_4 decreases faster than k_3 as the basicity of the pyridine derivative decreases.

The lower reaction rates with 3-chloropyridine relative to those with lutidine seem to be entirely due to a smaller equilibrium constant for complex formation and not due to differences in the PCET reaction. Using 2-chloropyridine as a base, a deuterium isotope effect k_4^H/k_4^D of ~3.2 for the PCET reaction was obtained, which supports a concurrent electron/proton-transfer mechanism.

Experimental Section

Materials and General Techniques. Tetracyanobenzene, TCB (Aldrich), was recrystallized from chloroform before use. Benzophenone and benzopinacol (Aldrich) were used without further purification. 1,2-Dichloroethane (EM Science) was stored over sodium carbonate to remove traces of hydrochloric acid. The pyridine bases 2,6-lutidine, 2-chloropyridine, and 3-chloropyridine (Aldrich) were passed through neutral alumina shortly before use.

Benzopinacol-d_2 was prepared by dissolving 1 g of the undeuterated compound in dichloroethane (~5 mL), adding methanol-d_4 (~4 mL), evaporating the solvents, and repeating the procedure once.

Laser Flash Photolysis. The samples were contained in a 1 × 1 × 4 cm quartz cell and were excited at right angles to the monitoring beam. The excitation source was an OPOTEK Q-switched Nd:YAG laser system. For 355 nm excitation, the frequency-tripled output from an OPOTEK Vibrant Q-switched Nd:YAG laser system (pulse width 4 ns, 2−8 mJ) was used. The excitation pulses were attenuated, when necessary, using neutral density filters. The analyzing beam from a pulsed Oriel 150-W xenon lamp (model 66007) was collected and focused on the entrance slit (2 nm) of an Instrument S. A. H-20 monochromator. A Hamamatsu R-446 photomultiplier tube (PMT) in a custom housing (Products for Research) was attached to the exit slit of the monochromator. A computer-controlled Stanford Research Systems high voltage power supply (model PS310) was used with the PMT. The signals from the PMT were digitized using a Tektronix TDS 620 oscilloscope and transferred to a PC, via a GPIB interface, for data storage and processing. A Quantum Composer pulse generator (Model 9318) provided TTL trigger pulses to control the timing for the laser, lamp, and oscilloscope.

The kinetic experiments were carried out at constant concentrations of benzophenone (0.006 M) and of benzopinacol (0.01 or 0.02 M). The concentration of one of the reactants (TCB or the base) was kept constant and that of the other was varied. All samples were freshly prepared and were thoroughly purged with argon prior to and during irradiation.

Reaction Stoichiometry and Relative Extinction Coefficients. The reaction stoichiometry was confirmed from relative optical densities (corrected for differences in laser power) and independently determined extinction coefficients. Following 355 nm excitation, transient spectra (Figure 1) were measured from a DCE solution of benzophenone (0.006 M) and from those to which successively TCB, then benzopinacol, and, finally, lutidine (each at 0.02 M) were added. The optical density (0.66, due to BP absorption) at the excitation wavelength (355 nm) was essentially unaffected by the successive addition of the other reactants. The relative intensities at the respective λ_{max} of the different species in these four samples, ^{3}BP*, ^{3}TCB*, $Ph_2COH^\bullet$, and $TCB^{\bullet-}$, were 1.0:0.45:1.09:4.55, Figure 1. The optical density ratio of 1.0:1.09 due to absorption by ^{3}BP* and $Ph_2COH^\bullet$ yields an extinction coefficient of 3800 for $Ph_2COH^\bullet$, on the assumption that 2 ketyl radicals are formed per ^{3}BP* and based on $\epsilon(^3BP^*)$ ~7000.[12] The extinction coefficient of 3800 for $Ph_2COH^\bullet$ is the same as the value we obtained via an independent route; see below. Similarly, the ratio of 1.0:4.55 for absorption by ^{3}BP* and by $TCB^{\bullet-}$ yields an $\epsilon(TCB^{\bullet-})$ of 15 900 (assuming 2 $TCB^{\bullet-}$ are formed per ^{3}BP*) that compares well with an independently determined value of ~15 000; see below.

Extinction Coefficient of Diphenylketyl Radical. Diphenylketyl radical was generated in DCE by hydrogen atom abstraction by ^{3}BP* from toluene. Solutions of BP alone and of BP with toluene (1.5 M) were matched for absorbance (0.8) at the excitation wavelength (355 nm). The solutions were thoroughly purged with argon, and the absorptions of ^{3}BP* and $Ph_2COH^\bullet$ were monitored at 530 and 540 nm, respectively. Based on the measured optical density ratio of 1:0.54 and on the value of $\epsilon(^3BP^*)$ of 7000,[12] $\epsilon(Ph_2COH^\bullet)$ of 3800 is obtained. This extinction coefficient is comparable to literature values of 3500 ± 200, obtained under varied conditions,[12] consistent with formation of the ketyl radical with unit efficiency.

Extinction Coefficient of Tetracyanobenzene Radical Anion. The extinction coefficient of tetracyanobenzene radical anion ($TCB^{\bullet-}$) was determined using triplet benzophenone (^{3}BP*) as a reference. Laser excitation (355 nm) of benzophenone (0.008 M) in the presence of TCB (0.01 M) in argon-purged acetonitrile generates ^{3}TCB* (λ_{max} ~ 610 nm). Reaction of ^{3}TCB* with an electron donor leads to a triplet radical ion pair, which is assumed to dissociate in such a polar solvent into free radical ions with unit efficiency. The ratio of the optical density at 463 nm (λ_{max} of $TCB^{\bullet-}$ in acetonitrile) from such an experiment to that at 530 nm (λ_{max} of ^{3}BP*) from an irradiated solution containing only BP corresponds to the ratio of the extinction coefficients of these intermediates at their respective λ_{max}. Based on an extinction coefficient of 7000 for ^{3}BP*, an extinction coefficient in acetonitrile of 15 400 or 14 600 was obtained for $TCB^{\bullet-}$, using 1,2,4-trimethylbenzene or *o*-xylene as electron donor, respectively.[22]

Complexes of Diphenylketyl Radical with Bases. In these experiments, the ketyl radical was formed via hydrogen atom abstraction by ^{3}BP*. Laser excitation (355 nm) of BP (0.006 M) in argon-purged DCE containing 0.75 or 1.5 M butylbenzene generates the ketyl radical.[23] The spectra in the absence and in the presence of different concentrations of the pyridines were recorded after ~1 or 0.5 μs, respectively, to avoid contribution from ^{3}BP* absorption. Because the ketyl radical decayed slightly, but at a varied rate, on the time scale of the experiment (up to 8 μs), the signal intensity was extrapolated to time zero. The decay rate was slightly higher in the absence of base and gradually decreased with increasing concentration of added pyridines, resulting in a larger correction for the spectrum in the absence of base. In these experiments, the relative intensities and not the absolute values are the important parameters. Correction for the intensity ratio in the absence and at the highest concentration of base was <15%. Similar corrections were made to the optical densities used to determine the equilibrium constants for TCB/base complexes (see, for example, Figure 5).

The transient spectrum following laser excitation (355 nm) of benzophenone (0.006 M) in the presence of 1,2,4,5-tetramethoxybenzene (0.04 M) in DCE showed a sharp band at 450 nm (tetramethoxybenzene$^{\bullet+}$) and a broad band at 690 nm ($BP^{\bullet-}$). From the intensity (extrapolated to zero time) relative to ^{3}BP*, the extinction coefficient of $BP^{\bullet-}$ at 690 nm is estimated to be ~7500 (or higher), based on whether the triplet geminate radical ion pair is formed with unit efficiency (or less). The absorption spectrum is similar to that reported for $BP^{\bullet-}$ in acetonitrile.[24] The lack of any detectable absorption at $\lambda > 640$ nm in the spectra of the ketyl radical in the presence of lutidine or the chloropyridines (Figure 4) indicates that $BP^{\bullet-}$, if at all present in equilibrium with the ketyl radical/base complex, contributes <2% to the observed decay rates of the ketyl absorption.

Decay Rates of Diphenylketyl Radical. Because of differences in rate constants and the choice of concentrations for the experiments, the decay of $^3BP^*$ and the formation of $^3TCB^*$ occur at a rate that is at least six times higher than the decay rate of the ketyl radical. By excluding the very early part in the transient decay (the spike due to $^3BP^*$, near $t = 0$ in Figure 2), the rise and fall of the absorption due to the ketyl radical monitored at 540 nm were analyzed as the sum of two exponentials. Within the concentration range used in these experiments, the rise corresponds to the formation of the ketyl radical through interception of $^3TCB^*$ by benzopinacol. The rate of this process is given by k_2[benzopinacol], $k_2 = 6.8 \times 10^8$ M^{-1} s^{-1}, and benzopinacol was used at either 0.01 or 0.02 M. The resulting rate of growth of the ketyl absorption was taken as a fixed parameter, and the decay rates that were obtained from the fitting procedure were used in the kinetic analyses.

The observed decay kinetics in the deuterated pinacol experiment are somewhat complicated by a contribution from undeuterated material, formed through D/H reexchange with environmental moisture during sample preparation. As a result, the decay of the ketyl radical consists of two components: one fast, due to the decay of the undeuterated radical, and one slow, due to the decay of the deuterated radical. The ratio of the two components was approximately 1:2, respectively. The fast decay rate was used as a fixed parameter, determined from the experiment with undeuterated pinacol.

Kinetic Analysis. If no complex is formed with TCB, the decay rate of the ketyl absorption (decay constant, λ) is the smaller root of a quadratic secular equation,[25]

$$\lambda^2 - (p + q + k_{-3})\,\lambda + pq = 0 \qquad (1)$$

The other root is considerably larger than the time constants used for the biexponential fit where $p = k_3$ [B] and $q = k_4$ [TCB]. This expression is symmetric in the quantities k_3 [B] and k_4 [TCB]. Thus, if k_3 and k_4 happen to be equal (or approximately equal) the decay rate will have exactly the same (or approximately the same) quantitative dependency on [B] *and on* [TCB], even though only one of these reactants actually forms a complex with the ketyl radical. The tendency toward leveling-off as a function of either concentration can be viewed as a consequence of a competition between complex formation and PCET for the step that limits the rate of formation of the final products ($TCB^{\bullet-}$, BH^+, and benzophenone,).

If both TCB and the base form complexes with the ketyl radical, the decay constant for decay of the ketyl absorption is the smallest root of a cubic secular equation, for which an analytical expression is well-known.[26]

A least-squares procedure was used to fit the measured decay rates to a set of rate constants according to Scheme 3. Data at higher concentrations of base or TCB were given greater weight because they better define the tendency of the decay rates to level off. The Levenberg−Marquardt algorithm provided by IGOR was used to optimize the fit.[27] For every case, it was verified that the smallest decay constant corresponded to decay of the ketyl radical and the next smallest corresponded to interception of TCB* to form the ketyl radical, as had been assumed in fitting the transient absorption traces to a biexponential form.

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0.80 V vs SCE, respectively). The rate constants with these quenchers are 7.7, 8.2, and 8.1 × 10^9 M^{-1} s^{-1}, respectively.

(20) Potential complication from a hydrogen-bonded complex between the pinacol and the pyridine base that could affect the kinetics can be ruled out by the absence of a fast $TCB^{\bullet-}$ formation that would be concomitant with the decay of $^3TCB^*$.

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