Communication

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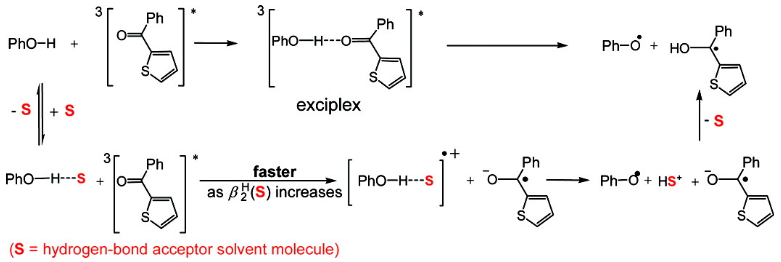

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Kinetic Solvent Effects on the Reaction of an Aromatic Ketone π,π^* Triplet with Phenol. Rate-Retarding and Rate-Accelerating Effects of Hydrogen-Bond Acceptor Solvents

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In a seminal study, Scaiano and co-workers[1] reported that the quenching by phenols of two ketone triplets, n,π^* benzophenone and π,π^* 4-methoxypropiophenone, gave phenoxyl and ketyl radicals efficiently (eqs 1 and 2). For phenol, $k_2/10^8$ M^{-1} s^{-1}

$$\mathrm{ArCOR} \xrightarrow{h\nu} \xrightarrow{\mathrm{ISC}} {}^3[\mathrm{ArCOR}]^* \tag{1}$$

$$\mathrm{PhOH} + {}^3[\mathrm{ArCOR}]^* \rightarrow \mathrm{PhO}^\bullet + \mathrm{Ar}\dot{\mathrm{C}}(\mathrm{OH})\mathrm{R} \tag{2}$$

values for these n,π^* and π,π^* ketones were, respectively, 13 and 49 in benzene and 0.8 and 1.1 in wet acetonitrile. The lower rates in wet acetonitrile were attributed to formation of a PhOH···solvent hydrogen bond (HB).[1] Carbonyls with lowest π,π^* triplets were known to abstract H-atoms from hydrocarbons much more slowly than carbonyls having similar excitation energies with lowest n,π^* triplets, and Wagner et al.[2] had postulated that the π,π^* triplets abstracted hydrogen predominantly via their thermally populated, higher energy nπ^* states. Later, Leigh et al.[3] proposed that reactions of phenols with π,π^* carbonyl triplets involved an intermediate HB exciplex that gave phenoxyl and ketyl radicals by Electron Transfer Proton Transfer (ETPT) (eq 3).[4]

$$\mathrm{PhOH} + {}^3[\mathrm{ArCOR}]^* \rightleftharpoons {}^3[\mathrm{Ar(R)C{=}O\cdots HOPh}]^* \rightarrow$$
$${}^3[\mathrm{Ar(R)}\dot{\mathrm{C}}-\bar{\mathrm{O}}\cdots\mathrm{H}\overset{\bullet +}{\mathrm{O}}\mathrm{Ph}] \rightarrow \mathrm{Ar}\dot{\mathrm{C}}(\mathrm{OH})\mathrm{R} + {}^\bullet\mathrm{OPh} \tag{3}$$

Kinetics of the bimolecular reactions of triplet ketones with phenols have usually been measured in a single solvent, there being only a few reports of measurements in two[1,5] and three[6] solvents. This is unfortunate because a *systematic* study of kinetic solvent effects (KSEs) for any H-atom abstraction,[7] eq 4

$$\mathrm{XH} + \mathrm{Y}^\bullet \rightarrow \mathrm{X}^\bullet + \mathrm{YH} \tag{4}$$

can provide important insights into the reaction mechanism(s).[8] Observed KSEs can be quantitatively accounted for by assuming that *only* the (often small) equilibrium fraction (eq 5)

$$\mathrm{XH} + \mathrm{S} \xrightleftharpoons{K^{\mathrm{S}}_{\mathrm{XH/S}}} \mathrm{XH\cdots S} \tag{5}$$

of XH molecules that are not making a HB to a HB acceptor (HBA) solvent molecule, S, can react with $\mathrm{Y}^\bullet$ (eq 4), with a rate constant $k^0_{\mathrm{XH/Y}^\bullet}$ that is equal to the experimental rate constant in a non-HBA solvent, such as with an alkane. The experimental rate constant for H-abstraction[7] in S, $k^{\mathrm{S}}_{\mathrm{XH/Y}^\bullet}$, is given by eq I,[8,9]

$$k^{\mathrm{S}}_{\mathrm{XH/Y}\bullet} = k^0_{\mathrm{XH/Y}\bullet}/(1 + K^{\mathrm{S}}_{\mathrm{XH/S}}[\mathrm{S}]) \tag{I}$$

which also indicates that the ratio of experimental rate constants in any pair of solvents will be independent of the reactivity of $\mathrm{Y}^\bullet$.[8] This independence has been verified many times.[8,9] Such KSEs can be *quantitatively* described by eq II,[8,9] where α_2^{H} and β_2^{H} are the Abraham et al.'s[10,11] thermodynamically based constants representing, respectively, the relative HB donor (HBD) ability of solute XH in CCl$_4$ [range = 0.00 (alkanes) to ~1.0 (strong organic acids)][10] and the relative HB acceptor (HBA) ability of solute S in CCl$_4$ [range = 0.00 (alkanes) to 1.00 (hexamethylphosphortriamide)].[11]

$$\log(k^{\mathrm{S}}_{\mathrm{XH/Y}\bullet}/\mathrm{M}^{-1}\,\mathrm{s}^{-1}) = \log(k^0_{\mathrm{XH/Y}\bullet}/\mathrm{M}^{-1}\,\mathrm{s}^{-1}) - 8.3\,\alpha_2^{\mathrm{H}}\,\beta_2^{\mathrm{H}} \tag{II}$$

Equation II correlates KSEs for H-abstractions[7] by a variety of $\mathrm{Y}^\bullet$ radicals from hydrocarbons, aniline, *tert*-butyl hydroperoxide, and numerous phenols[8,9] (and other substrates).[12] However, in ionizing solvents (e.g., methanol), ionizable substrates (e.g., phenol) react with electron-deficient radicals more rapidly than eq II would predict.[8] This is due to fast electron transfer to $\mathrm{Y}^\bullet$ from the (generally low) concentration of X^- anion present in equilibrium with XH (eq 6). This Sequential Proton Loss Electron Transfer

$$\mathrm{XH} + \mathrm{Y}^\bullet \rightleftharpoons \mathrm{H}^+ + \mathrm{X}^- + \mathrm{Y}^\bullet \rightarrow \mathrm{H}^+ + \mathrm{X}^\bullet + \mathrm{Y}^- \tag{6}$$

(SPLET)[8,13] occurs in parallel with the "normal" H-abstraction[7] (eq 4). SPLET can usually be completely suppressed by the addition of low concentrations of acetic acid.[8,13]

The quenching of the π,π^* triplet ketone, 2-benzoylthiophene (**^{3}BT***), by a variety of substrates has been previously studied by laser flash photolysis (LFP).[5a,6a] It was concluded that the phenol + **^{3}BT*** reaction involved a HB exciplex and gave the phenoxyl ($\mathrm{PhO}^\bullet$) and BT ketyl ($\mathrm{BTH}^\bullet$) radicals by a (concerted) ETPT mechanism with a quantum yield close to unity.[6a] Herein, we address the question: Are the KSEs for this PhOH + **^{3}BT*** HB exciplex reaction correctly described by eq II?

A pulsed Nd:YAG laser (λ_{exc}= 355 nm, 10 ns pulse, energy 15−17 mJ) was employed with [BT] chosen to give an absorbance of 0.35 ([BT] = 1.9−2.5 mM). The solvents (Table 1) were of the highest purity available and were used as received. LFP of deaerated solutions of BT gives the **^{3}BT*** absorption (maxima at 350 and 600 nm). The **^{3}BT*** decay was accelerated by the addition of PhOH (in a dose-dependent manner) with the appearance of absorbancies due to the ketyl ($\mathrm{BTH}^\bullet$, $\lambda_{\max}$ = 350 and 580 nm) and $\mathrm{PhO}^\bullet$ ($\lambda_{\max}$ = 380 and 410 nm) radicals, both being formed with a high efficiency (Supporting Information). A plot of the logarithms of the rate constants for **^{3}BT*** quenching by phenol, k_q (Table 1), in the solvents against the solvents' β_2^{H} values shows an excellent linear correlation provided the point for solvent **2** is ignored (as it should be[14] Figure 1, solid line). The slope of this line is −3.9, which is significantly lower than the slope calculated from eq II and phenol's α_2^{H} value of 0.59[9] [i.e., −8.3 × 0.59 = −4.9 (Figure 1, dashed

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Table 1. Rate Constants for Quenching of ^{3}**BT*** by Phenol in Various Solvents with β_2^H Values for the Solvents

no.	solvent	$\beta_2^{H\ a}$	$k_q/10^8\ M^{-1}\ s^{-1}$
1	n-C_8H_{18}	0.00	105 ± 5
2	CH_2Cl_2	0.05	23[b]
3	PhH	0.14	28 ± 3
4	$PhCH_3$	0.14	35 ± 2
5	$PhOCH_3$	0.26	11.3 ± 0.5
6	CH_3CN	0.44	1.4[b]
7	$CH_3C(O)OC_2H_5$	0.45	2.3 ± 0.2
8	1,4-dioxane	0.47[c]	1.9 ± 0.1
9	tetrahydrofuran	0.51	0.62 ± 0.05
10	$(C_2H_5O)_3PO$	0.77	0.13 ± 0.04

[a] From ref 11. [b] Value of k_q from ref 6a. [c] From ref 13b.

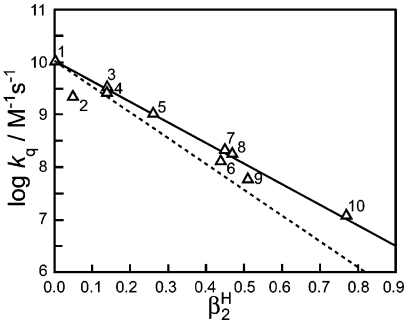

Figure 1. Logarithm of k_q for the reaction of ^{3}**BT*** with phenol in various solvents (numbered as in Table 1) versus the solvents' β_2^H values. Solvent **2** was not included in constructing the solid correlation line[14] (slope −3.9). The dashed line has the predicted (eq II) slope of −4.9; see text.

line)]. That is, the magnitudes of the HBA solvents' suppression of the rate are less than those for all free radical + phenol H-atom abstraction[7] reactions examined to date. This would be the case if the ^{3}**BT*** + PhOH reaction had a significant SPLET component.[8,13] However, this appears improbable for two reasons: (i) even for reactions where a SPLET mechanism is strongly favored, it does not occur in dioxane (**8**);[13b] and (ii) the addition of 10 mM acetic acid to THF and triethyl phosphate produced a very small increase in k_q (Supporting Information) rather than the decrease expected if the SPLET mechanism occurred.[15]

We propose that the slope of the solid line in Figure 1 (−3.9) is lower than predicted (−4.9) because, in HBA solvents, the ^{3}**BT*** + PhOH reaction occurs by two mechanisms, ***A*** and ***B***. ***A*** involves Leigh's[3] exciplex process with HB formation between ^{3}**BT*** and only those PhOH molecules that are *not* H-bonded to a solvent molecule and for which a plot of log $k_{\boldsymbol{A}}$ versus β_2^H would fit eq II (slope −4.9). The contribution of mechanism ***B*** increases as the HBA activity of the solvent increases. It must involve PhOH molecules that are H-bonded to solvent molecules and does not occur in the non-HBA solvent, octane. This mechanism could involve either all, or some subset, of PhOH•••S species. We suggest that ***B*** occurs by electron transfer to ^{3}**BT*** from (reactive) PhOH•••S followed by, or concerted with, proton transfer from the resulting highly acidic phenol radical cation, $(PhOH)^{\bullet+}$, to the S to which it is already H-bonded. The stronger this H-bond, the more facile the ***B*** mechanism will be. The overall KSE is described by eq III. We predict that KSEs for quenching of ^{3}**BT*** by other phenols will also be described by this equation.

$$\begin{aligned}\log(k^S_A + k^S_B) &= \log k^0_A - 8.3 \times \{1-(1-3.9/4.9)\}\ \alpha_2^H\beta_2^H \\ &= \log k^0_{\boldsymbol{A}} - 6.6\ \alpha_2^H\beta_2^H = \log k^S_q \qquad \text{(III)}\end{aligned}$$

In our review of KSEs on H-atom abstractions from phenols,[8] the (formally trimolecular) ETPT mechanism, ***B***, in which the electron and proton go to *different acceptors*, was described as an unidentified fourth possible mechanism for intermolecular H-abstractions from phenols by strongly oxidizing radicals and nonradicals. Unimolecular (i.e., intramolecular) examples of this mechanism are known in chemistry and biology,[8] but the only intermolecular example of phenol oxidation by this mechanism that we are aware of involved an added solute as the proton acceptor[16] and hence is not, strictly speaking, a KSE.

In conclusion, a fourth mechanism, ***B***, for H-atom abstraction from phenol in PhOH•••S HB complexes has been identified and quantified. Although the mechanism ***B*** rate increased with the solvents' HBA strength (β_2^H), the overall rate decreased as β_2^H increased. Nevertheless, the exciting possibility remains of "inverse" KSEs where the rates of H-atom abstraction from a HBD actually increase as the solvents become stronger HBAs.

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Supporting Information Available: Transient absorption spectra and kinetic data for quenching of ^{3}**BT*** by pnenol in different solvents. This material is available free of charge via Internet at http://pubs.acs.org.

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(4) The photoreduction of benzophenone by aliphatic amines had previously been suggested to proceed via amine triplet ketone charge-transfer complexes (exciplexes) which favored subsequent H-abstraction reactions. See: (a) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc*. **1981**, *103*, 1048−1054. (b) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1980**, *102*, 1419−1421.

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(7) H-abstraction is used to refer to two, nonexclusive, mechanisms:[8] (i) transfer of a proton and one of its bonding electrons (hydrogen atom transfer, HAT); (ii) transfer of a proton with an accompanying electron from a nonbonding orbital (proton-coupled electron transfer, PCET).

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(14) The β_2^H value for CH_2Cl_2 is too small. In a full paper, we will show that β_2^H for CH_2Cl_2 should be revised upwards to 0.15, a value that puts log k_q in **2** essentially on the solid correlation line shown in Figure 1.

(15) In the only previous example of acetic acid increasing the rate of an ArOH/$Y^\bullet$ reaction,[13c] acceleration was attributed to the excellent anion solvating abilities of the acid enhancing ArOH ionization and, hence, the contribution of SPLET to the measured rate.

(16) The quenching of triplet C_{60} by phenols is accelerated by added pyridine (Pyr) bases.[17] This was attributed to a trimolecular transition state ET from PhOH•••Pyr to $^3C_{60}$ concerted with PT to the H-bonded base.[17]

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