Quenching Processes in Hydrogen-Bonded Pairs: Interactions of Excited Fluorenone with Alcohols and Phenols

László Biczók,[†] **Tibor Bérces,**[‡] **and Henry Linschitz*,**[‡]

Contribution from the Central Research Institute for Chemistry, Hungarian Academy of Sciences, P.O. Box 17, 1525 Budapest, Hungary, and Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254-9110

Abstract: In order to clarify mechanisms of excited state interactions in hydrogen-bonded pairs, we have studied the kinetics of dynamic quenching of singlet and triplet fluorenone by a series of alcohols, phenols, and related compounds, in which hydrogen-bonding power, redox potential, and acidity are systematically varied. In addition, effects of solvent basicity or polarity and deuteration help identify the role of hydrogen-bonding in physical or chemical quenching processes. Alcohols and weak acids, with high oxidation potentials, do not quench the triplet, but quench the singlet at rates which parallel hydrogen-bonding power. This is attributed to a physical mechanism, involving vibronic coupling to the ground state via the hydrogen bond. This is much stronger in the excited state than in the ground state, and provides efficient energy dissipation in the radiationless transition. Phenols, with hydrogen-bonding power comparable to that of the alcohols but with much lower oxidation potentials, quench both singlet and triplet by electron or H-atom transfer, depending on potentials, acidities, and solvent polarity, as shown by formation of anion or neutral fluorenone radicals from the triplet. Rates increase with both decreasing oxidation potential of the phenol and increasing acidity of the incipient cation radical. Quenching proceeds via a hydrogen-bonded complex and is facilitated by proton transfer contributions to the effective excited state redox potential.

Hydrogen bonding and solvent polarity are key factors in controlling pathways of energy dissipation following electronic excitation.[1−3] In molecules with $n\pi^*$ and $\pi\pi^*$ levels, these factors may function simply by varying the relative positions of the two types of levels,[4] thereby indirectly influencing the rates of transitions among singlets and triplets by virtue of El Sayed's rule.[3,5] Alternatively, solvent-moderated shifts of the levels may enhance or inhibit radiationless transitions to the ground state via the "proximity effect" discussed by Lim.[6]

Our concern here is with intermolecular hydrogen-bonding effects, particularly quenching, which involve more specific interactions.[7] A number of these effects may occur, which may be more-or-less closely related, differing in the extent and type of charge transfer at or across the bonding site. For example, the formation, or change in strength, of intermolecular hydrogen bonds following excitation may lead simply to new vibronic,

dissipative modes, which couple excited and ground states.[7b−11a] Such motion may be accompanied by various degrees of electron transfer which may be delocalized through the bond,[3,12−16] or lead to reversible proton displacements,[17,18] or to associated electron−proton movement resulting in reversible or irreversible H-atom transfer.[19−23] To further characterize, and perhaps more clearly distinguish among these processes, we examine in this paper the quenching of singlet and triplet fluorenone by hydrogen-bonded reagents (alcohols, acids, or phenols) of

[†] Hungarian Academy of Sciences.

[‡] Brandeis University.

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1997.

(1) A report of this work has been given earlier: Biczók, L.; Bérces, T.; Linschitz, H. *Abstracts*; XVI IUPAC Symposium on Photochemistry; University of Helsinki, Finland, July 1996, pp 131−132.

(2) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; Chapter 6.

(3) Mataga, N; Kubota, T. *Molecular Interactions and Electronic Spectra*; Dekker: New York, 1970; Chapters 7 and 8.

(4) Brealey, G. J.; Kasha, M. *J. Am. Chem. Soc* **1955**, *77*, 4462.

(5) El-Sayed, M. A. *J. Chem. Phys.* **1963**, *38*, 2834.

(6) Lim, E. C. *J. Phys. Chem.* **1986**, *90*, 6770.

(7) In this paper, we deal primarily with 1:1 intermolecular hydrogen-bonded pairs, formed in the excited state, as established by ground state absorption spectra and second-order quenching kinetics. The behavior of such systems has been much less studied[7d] than the first-order ultrafast phenomena in excited intramolecularly H-bonded molecules. Extensive references to these latter effects, such as proton or H-atom shifts, tautomerization, concerted multiple proton movement, etc., are given in: (a) *J. Phys. Chem.* **1991**, *95* (Michael Kasha Festschrift), 10215−10524. (b) Herbich, J.; Hung, C. Y.; Thummel, R. P.; Waluk, J. *J. Am. Chem. Soc.* **1996**, *118*, 3508. (c) Herek, J. L.; Pedersen, S.; Banares, L.; Zewail, A. H. *J. Chem. Phys.* **1992**, *97*, 9046. (d) Flom, S. R.; Barbara, P. F. *J. Phys. Chem.* **1985**, *89*, 4489.

(8) Inoue, H.; Hida, M.; Nakashima, N.; Yoshihara, K. *J. Phys. Chem.* **1982**, *86*, 3184.

(9) Lin, S.; Struve, W. *Photochem. Photobiol.* **1991**, *54*, 361.

(10) Schulman, S. G.; Liedke, P. Z. *Phys. Chem.* **1973**, *84*, 317.

(11) (a) Zaitsev, N. K.; Demyashkevich, A. B.; Kuzmin, M. G. *Khim. Vysok. Energ.* **1978**, *12*, 430; (b) **1979**, *13*, 331.

(12) Miyasaka, H.; Tabata, A.; Kamada, K.; Mataga, N. *J. Am. Chem. Soc.* **1993**, *115*, 7335 and extensive references therein.

(13) (a) Ikeda, N.; Miyasaka, H.; Okada, T.; Mataga, N. *J. Am. Chem. Soc.* **1983**, *105*, 5206. (b) Martin, M. M.; Ikeda, N.; Okada, T.; Mataga, N. *J. Phys. Chem.* **1982**, *86*, 4148. (c) Martin, M. M.; Miyasaka, H.; Karen, A.; Mataga, N. *J. Phys. Chem.* **1985**, *89*, 182.

(14) (a) Yamamoto, S.; Kikuchi, K.; Kokubun, N. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2950. (b) Kikuchi, K.; Watarai, H.; Koizumi, M. *Ibid.* **1973**, *46*, 749.

(15) Tanaka, H.; Nishimoto, K. *J. Phys. Chem.* **1984**, *88*, 1052.

(16) (a) Zhao, X. G.; Cukier, R. I. *J. Phys. Chem.* **1995**, *99*, 945. (b) Cukier, R. I. *Ibid.* **1995**, *99*, 16101.

(17) Hasselbacher, C. A.; Waxman, E.; Galati, L. T.; Contino, P. B.; Ross, J. B. A.; Laws, W. R. *J. Phys. Chem.* **1991**, *95*, 2995.

(18) (a) Tolbert, L. M.; Nesselroth, S. M. *J. Phys. Chem.* **1991**, *95*, 10331. (b) Miyasaka, H.; Wada, K.; Ojima, S.; Mataga, N. *Isr. J. Chem.* **1993**, *33*, 183. (c) Miyasaka, H.; Tabata, A.; Ojima, S.; Ikeda, N.; Mataga, N. *J. Phys. Chem.* **1993**, *97*, 8222.

(19) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(20) Belyaev, A. B.; Kuz'min, V. A.; Levin, P. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1988**, 1007.

(21) Leigh, W. J.; Lathioor, E. C.; St. Pierre, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 12339.

(22) Das, P. K.; Encinas, M. Y.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4154.

(23) (a) Turro, N. J.; Engel, R. *J. Am. Chem. Soc.* **1969**, *91*, 7113; *Mol. Photochem.* **1969**, *1*, 142, 235. (b) Turro, N. J.; Lee, T. *Mol. Photochem.* **1970**, *2*, 185.

varying bonding strength, redox potential, and acidity.[1] This permits evaluation of the relative importance and interaction of these factors in controlling the quenching mechanism.

Fluorenone is a particularly interesting molecule whose sensitive and specific responses to both solvent polarity and hydrogen-bonding make it useful for this study. Since its level assignments and energy-flow pathways have been the subject of much study and controversy it is helpful first to review briefly the essential observations and interpretations. On the basis of absorption spectrum shifts caused by substitution, by polar or hydrogen-bonding solvents,[24,25] or by oxime formation and other criteria,[26] the lowest excited singlet state, S_1 (23 000 cm^{-1}),[25] is identified as $\pi\pi^*$. In aprotic solvents, processes following excitation to S_1 are governed essentially by the dependence of intersystem transitions (ISC) on solvent polarity. In nonpolar media (hexane), fluorescence is extremely weak ($\varphi_F \approx 5 \times 10^{-4}$ [26,27]) and S_1 decays almost entirely by ISC[27] to the lowest triplet ($\pi\pi^*$, 17 600 cm^{-1}).[27,28] With increasing solvent polarity, the triplet yield decreases and both fluorescence and internal conversion (IC) increase. In acetonitrile, φ_F, φ_T, and φ_{IC} are respectively 0.034, 0.48, and 0.49.[27] This pattern is correlated with polarity-dependent shifts in the location of an intervening $n\pi^*$ state, either singlet[29,30] or triplet,[31] which facilitates ISC from S_1 to T_1.[4] However, in hydroxylic solvents, new effects appear. Despite the polarity of the solvent, fluorescence is again weak, short-lived,[32,33] and now sharply red-shifted,[28] the triplet yield falls, and IC becomes by far the most important dissipative process.[33] We have given rate constants for all processes originating in S_1 in nonpolar, polar, and hydroxylic solvents,[27,29,33] as well as for fluoro-, methoxy-, and amino-substituted fluorenones in aprotic solvents.[29b] Fujii et al. have recently proposed that S_1 is $n\pi^*$ in ethanol, in order to explain the low fluorescence yield compared to that found in aprotic polar media.[34] This assignment is entirely contrary to the effects of hydroxylic solvents on both the absorption and emission spectra, as outlined above, and cannot be correct. The low fluorescence yield in alcohols must clearly be attributed to quenching specifically associated with hydrogen bonding of the excited singlet, as further demonstrated here.

Additional interest in the fluorenone case derives from the fact that much of the work on quenching in hydrogen-bonded pairs has been done on systems such as aryl alcohols or amines,[10–19] in which the excited moiety, with enhanced acidity[35] or bonding power, is also the proton donor. The opposite situation, in which intermolecular bonding occurs to an excited proton acceptor, has been studied mainly in aza-aromatics[19,36] or quinones.[20,37–39] Thus, fluorenone in polar media provides a different type of acceptor system for study,

with a simple structure, a single bonding site, access to both S_1 and T_1 states, and established energy-flow pattern.[24–33] Its low-lying excited states limit interference by energy transfer to quenching agents. Evidently, the behavior of fluorenone in hydrogen-bonded situations bears also on general problems concerning charge and H-atom transfer in the photoreduction of ketones.[2,21–23,40–43]

In this paper, we demonstrate the full range of quenching interactions in hydrogen-bonded pairs, from a "pure" physical process (vibronically induced internal conversion) to quenching by electron transfer alone, and finally by coupled electron–proton transfer. It is shown that the strength of hydrogen-bonding to the excited fluorenone singlet is directly correlated with the efficiency of dynamic quenching by agents (alcohols and acids) of high ionization potential. Such binding is also important in quenching by phenols, where, in addition, we find evidence for significant charge transfer, dependent on redox potentials and associated with H-atom transfer. Recently Leigh and co-workers have studied in detail H-atom transfer reactions from *p*-cresol to a series of triplet benzophenones[21] and have drawn conclusions regarding phenol-ketone interactions similar to those based on our fluorenone quenching work. Closely related studies on radiationless energy dissipation in hydrogen-bonded aminofluorenones with charge transfer excited states[29b] have also been made by Moog et al.[44]

Experimental Section

Materials. Fluorenone (Fluka), 4-methoxy-, 4-nitro-, and 4-cyanophenol (Aldrich) were repeatedly recrystallized. Pyridine derivatives (Aldrich) were distilled; other chemicals (Aldrich) were best available grade and were used as received. Solvents were HPLC-grade (Aldrich). Solutions were purged with nitrogen before measurement.

Apparatus and Procedure. Fluorescence spectra were recorded on a home-built spectrofluorimeter, equipped with a Princeton Applied Research 1104 A/B photon counting system. Peak emissions in CH$_2$-Cl$_2$ and DMF were found at 514 nm, in agreement with earlier observations.[25,33] Fluorescence lifetimes at 514 nm were measured using an Applied Photophysics SP-3 time-correlated single-photon counting apparatus with a hydrogen lamp operated at 30 kHz. Data were analyzed by nonlinear-least squares deconvolution.

Triplet reactions were followed by flash photolysis with excitation at 351 nm from a Lambda-Physik LPX-100 excimer laser. Transient absorption and decay at the triplet peak, 435 nm,[27] was recorded on a Hitachi VC-6041 digital storage oscilloscope. Further details of instrumentation have been described.[29]

Equilibrium constants, K, for formation of 1:1 hydrogen-bonded complexes were calculated from the effects of added reagents on absorption spectra of fluorenone solutions, using the relationship given by Mataga and Tsuno (eq 1).[45]

$$[1 - A^0/A]_\lambda/C_0 = -K + (\epsilon_C/\epsilon)K(A^0/A) \qquad (1)$$

Here, ϵ_C and ϵ respectively denote the extinction coefficients of the complex and free molecule and A^0 and A are absorbances in absence

(24) Kuboyama, A. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1540.

(25) Liptay, W.; Weisenberger, H.; Tiemann, F.; Eberlein, W.; Konopka, G. *Z. Naturforsch.* **1968**, *23A*, 377.

(26) Yoshihara, K.; Kearns, D. R. *J. Chem. Phys.* **1966**, *45*, 1991.

(27) Andrews, L. J.; Deroulède, A.; Linschitz, H. *J. Phys. Chem.* **1978**, *82*, 2304 and references therein.

(28) Huggenberger, C.; Labhart, H. *Helv. Chim. Acta* **1978**, *61*, 250.

(29) (a) Biczók, L.; Bérces, T. *J. Phys. Chem.* **1988**, *92*, 3842. (b) Biczók, L.; Bérces, T.; Marta, F. *J. Phys. Chem.* **1993**, *97*, 8895.

(30) Kobayashi, T.; Nagakura, S. *Chem. Phys. Lett.* **1976**, *54*, 429.

(31) (a) Gastilovich, E. A.; Korol'kova, N. V.; Val'kova, G. A. *Zh. Fiz. Khim.* **1991**, *65*, 2881. (b) Gastilovich, E. A.; Konoplev, G. G.; Korol'kova, N. V.; Val'kova, G. A. *Zh. Fiz. Khim.* **1991**, *65*, 3240.

(32) Munroe, B. M.; Groff, R. P. *Tetrahedron Lett.* **1973**, *40*, 3955.

(33) Biczók, L.; Jicsinszky, L.; Linschitz, H. *J. Inclus. Phenom.* **1994**, *18*, 237.

(34) Fujii, T.; Sano, M.; Mishima, S.; Hiratsuka, H. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1833.

(35) Ireland, J. F.; Wyatt, P. A. H. *Adv. Phys. Org. Chem.* **1976**, *12*, 132.

(36) Shapovalov, V. L.; Demyashkevich, A. B.; Kuz'min, M. G. *Zh. Prikl. Spektros.* **1980**, *33*, 1111.

(37) Levin, P. P.; Kokrashvili, T. A.; Kuz'min, V. A. *Izv. Akad. Nauk SSSR* **1983**, 284.

(38) Petrushenko, K. B.; Vokin, A. I.; Turchaninov, V. K.; Gorshkov, A. G.; Frolov, Y. L. *Izv. Akad. Nauk SSSR* **1985**, 267.

(39) Amada, I.; Yamoji, M.; Sase, M.; Shizuka, H. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2751.

(40) Wagner, P. J.; Truman, R. J.; Puchalski, A. E.; Wake, R. *J. Am. Chem. Soc.* **1986**, *108*, 7727.

(41) Manring, L. E.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 6452.

(42) Miyasaka, H.; Kiri, M.; Morita, K.; Mataga, N.; Tanimoto, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1569.

(43) Cohen, S. G.; Parola, A.; Parsons, G. H. *Chem. Rev.* **1973**, *73*, 141.

(44) Moog, R. S.; Burozski, N. A.; Desai, M. M.; Good, W. R.; Silvers, C. D.; Thompson, P. A.; Simon, J. D. *J. Phys. Chem.* **1991**, *95*, 8466.

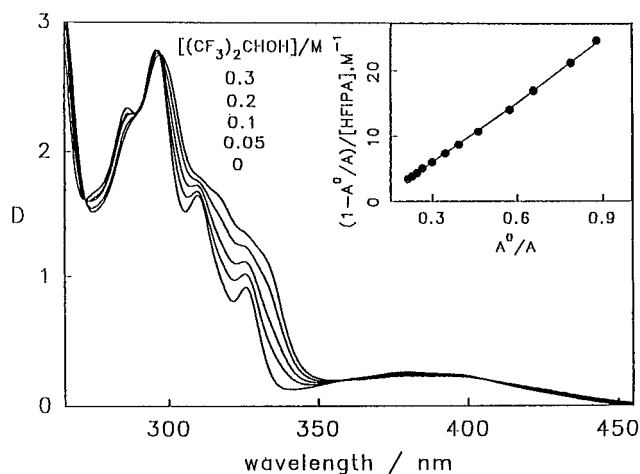(45) Mataga, N.; Tsuno, S. *Bull. Chem. Soc. Jpn.* **1957**, *30*, 368, 711.

Figure 1. Effect of addition of HFIP on absorption spectrum of fluorenone in methylene chloride. Insert: Plot of absorbance data at 336 nm, according to eq 1.

and presence of bonding agent, whose total concentration, C_0, is much greater than that of the substrate.

Cyclic voltammetric measurements on phenols in DMF were carried out vs SCE on a PAR-EGG Model 362 scanning potentiostat. Solutions contained 0.1 M tetrabutylammonium hexafluorophospate and 2 mM ferrocene as internal standard. At sweep speeds of 200 mV/s, oxidations were entirely irreversible, and potentials listed below are taken at three/fourths of the initial oxidative peak height.[46] Deuterium isotope effects on quenching by phenols were studied by comparing fluorescence or triplet lifetimes in phenol solutions equilibrated with CH_3OH or CH_3-OD. For singlet quenching, the methanols were added in 5-fold excess of the phenol concentration, and corrections were made for any quenching caused by methanols themselves. For the triplet, much higher methanol/phenol ratios (10−100) were used, since the alcohols influence only the triplet yields, not lifetimes. Measurements could be made with methanol at concentrations as high as 0.1 M in CH_2Cl_2 or 1.0 M in DMF. Spectra of long-lived transient products of triplet quenching at times after complete triplet decay were measured by flash photolysis (Nd-YAG laser, 355 nm) using low laser energies to avoid 2-photon processes. Data from ∼16 flashes at each of three independent runs were averaged for each system.

Results and Discussion

I. Hydrogen-Bonding in the Ground State. Figure 1 shows the effect of the strongly H-bonding alcohol, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) on the absorption spectrum of fluorenone in methylene chloride. The long wavelength band changes only slightly upon addition of HFIP, but a red-shift and increased absorption are marked in the 300−350 nm region. Isosbestic points appear at 272, 297, 358, and 405 nm, and application of eq 1 to the data at 336 nm gives a good line (Figure 1, insert). We conclude that fluorenone and HFIP form a 1:1 ground state complex in CH_2Cl_2 and, from the intercept of the plot of Figure 1, obtain $K = 3.5 \pm 0.4$ M^{-1}. Other alcohols are much less effective in influencing fluorenone absorption. The equilibrium constant for bonding with trifluoroethanol (TFE) in CH_2Cl_2 is $K = 0.7$ M^{-1}, while we can only estimate upper limits ($K < 0.6$ M^{-1}) for methanol or octanol. In DMF, none of the alcohols, even HFIP up to 1 M, caused any detectable change in fluorenone absorption, because of preferential bonding to the solvent.[47,48]

(46) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980.

(47) Abraham, M. H.; Duce, P. P.; Prior, D. V. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1355.

(48) Joesten, M. D.; Schaad, L. J. *Hydrogen Bonding*; Dekker: New York, 1974.
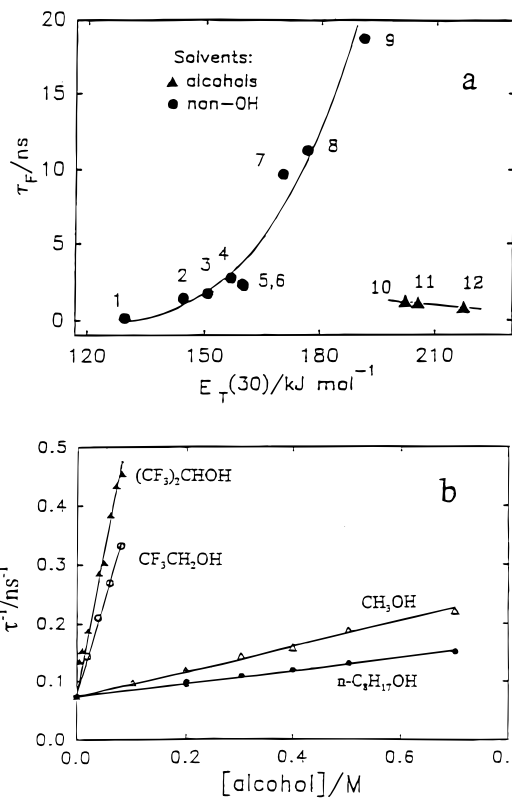

Figure 2. (a) Fluorescence lifetimes of fluorenone in hydroxylic (▲) and non-hydroxylic solvents (●) as function of $E_T(30)$ solvent polarity parameter: 1, methylcyclohexane; 2, diethyl ether; 3, dioxane; 4, tetrahydrofuran; 5, ethyl acetate; 6, dimethoxyethane; 7, dichloroethane; 8, acetone; 9, acetonitrile; 10, 1-octanol; 11, 1-pentanol; 12, ethanol (from ref 33, reprinted with kind permission of Kluwer Academic Publishers). (b) Quenching of fluorenone singlet by alcohols; reciprocal fluorescence lifetimes (ns^{-1}) vs alcohol concentration in methylene chloride.

Among the phenols in CH_2Cl_2, absorbance data at 336 nm also gave good lines according to eq 1 for 4-cyanophenol ($K = 10.7$ M^{-1}) and phenol itself ($K = 2.8$ M^{-1}). This order parallels their relative hydrogen-bonding power, as measured with respect to common acceptors[47,48] (see below). Substitution of electron-donating groups (methyl or methoxy) further decreased K.

II. Quenching by Alcohols. We have noted above different effects of aprotic and hydroxylic solvents on the fluorescence lifetime of fluorenone, indicating different solvent interaction mechanisms. These effects are compared in Figure 2A. When the solvatochromic index "$E_T(30)$" is taken as a measure of solvent polarity,[49] the lifetime increases smoothly with polarity for the aprotic sequence methylcyclohexane → acetonitrile. However, in alcohols, the lifetime is sharply decreased at comparable values of $E_T(30)$ and varies with this measure of polarity in the opposite way.[33,34]

This behavior is shown in more detail in Figure 2B. Plots of reciprocal fluorescence lifetimes vs quencher concentration are linear for several alcohols in CH_2Cl_2, at concentrations at which there is little or no hydrogen-bonding to ground state fluorenone. Fluorescence decay remains single exponential in all cases. Moreover, values of φ_0/φ, from steady state fluorescence measurements, match τ_0/τ ratios throughout the Stern−Volmer quenching range (Figure 3).[50] We conclude that

(49) Reichardt, C. *Solvent Effects in Organic Chemistry*, 2nd ed.; Verlag Chemie: Weinheim, Germany, 1988.

(50) In both kinetic and steady state fluorescence measurements, interference from the weak and sharply red-shifted emission from hydrogen-bonded excited fluorenone[28] is negligible.
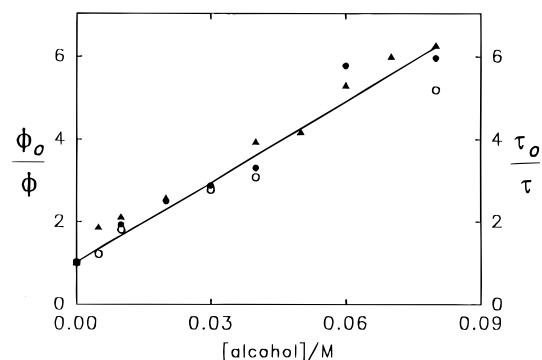
Figure 3. Dynamic quenching by HFIP in methylene chloride (internal conversion to the ground state): Stern–Volmer plots of fluorescence yield (●), reciprocal lifetime (▲), and triplet yield of fluorenone (○).

Table 1. Rate Constants for Quenching of Singlet Excited Fluorenone by Hydrogen-Bonding Agents in CH_2Cl_2 and DMF and Related Parameters

quencher	α^a	pK_a (DMSO)^b	IP (eV)^c	log $K_{HB}{}^d$	$10^8 k_q$ $(M^{-1} s^{-1})^e$ CH_2Cl_2	DMF
$(CF_3)_2CHOH$	1.96	17.85^f	11.94	2.83	46.0	2.8
C_6H_5COOH		11.0	9.47	2.07	20.0	0.88
CF_3CH_2OH	1.51	23.5	11.49	2.00	32.0	0.80
CH_3OH	0.93	29.0	10.85	1.48	2.1	0.3
CH_3OD					1.6	
1-octanol		9.89^g		1.20^g	1.1	<0.3
tert-butyl alcohol	0.68	32.2	9.97	0.78	0.8^h	

^{a} α measures hydrogen-bond donor acidity.[51] ^{b} In DMSO, ref 53. ^{c} Lias, S. G.; et al. *J. Phys. Chem. Ref. Data* **1988**, *17* (Supplement 1). ^{d} K_{HB} is equilibrium constant for H-bond formation with reference acceptor, N-methylpyrrolidinone, in 1,1,1-trichloroethane; ref 47. ^{e} From lifetime measurements. ^{f} Bordwell, F. G. Private communication. ^{g} For 1-hexanol. ^{h} From steady state measurements, ϕ_0/ϕ, with $\tau_0 = 13.8$ ns.

quenching of fluorenone by these alcohols in the observed concentration range is dynamic, not static.

The pathway of singlet depopulation resulting from these interactions is clearly identified by considering relative fluorescence and triplet yields. Laser flash photolysis measurements of triplet formation show that fluorescence quenching by added alcohols in CH_2Cl_2 is accompanied by a steady decrease in φ_T, to the limiting values observed in pure alcohols. Figure 3 illustrates the decrease in φ_T which parallels the shortening of fluorescence lifetime. Thus, as shown in studies on pure solvents,[33] the deactivation of the fluorenone singlet by alcohols occurs via induced IC, not enhanced ISC.

Table 1 summarizes rate constants for quenching of the singlet by various alcohols and benzoic acid, in CH_2Cl_2 and DMF, derived from linear Stern–Volmer plots of reciprocal fluorescence lifetimes or steady state intensities, as indicated. Listed also are values of log K_{HB}, where the K_{HB} values are equilibrium constants for H-bond formation between the given alcohols and a common reference receptor, N-methylpyrrolidinone in 1,1,1-trichloroethane.[47] A clear correlation is seen between the quenching rate constant and the relative H-bonding power of the alcohols as measured directly by the values of log K_{HB} or by the parameter, α, of the Kamlet–Taft scale.[51] The decrease in rate by roughly 1 order of magnitude in passing from CH_2Cl_2 to DMF likewise parallels this solvent-dependent decrease in hydrogen-bonding equilibria.[48] Since increasing solvent polarity favors both electron and proton transfer, but decreases both the strength and extent of hydrogen-bonding,[47,48] the observed decrease in rate indicates that the quenching reaction proceeds via a hydrogen-bonded intermediate.

No quenching of the triplet was observed ($k < 10^4$ M^{-1} s^{-1}) for any of the reagents in Table 1. The only effect of alcohols on the triplet is to decrease the initial yield, as shown in Figure 3.

Comparison of the rate constants in Table 1 with corresponding values of quencher IP or pK_a values provides information regarding the participation of electron or proton transfer in the quenching process.[52] We may assume, in accord with the well-known general oxidizing character of excited aryl ketones, whether $n\pi^*$ or $\pi\pi^*$,[2,21–23,40–43] that electron transfer will occur, if at all, toward excited fluorenone. It is expected then that quenching rates would increase with decreasing oxidation potential or, in lieu of this, IP of the quencher. This is contrary to what is observed (Table 1). HFIP, the most effective quencher and the strongest hydrogen-bonding agent, has at the same time the highest IP, and decreasing IP values are associated with decreasing k_q values throughout the alcohol series. We conclude that electron transfer, beyond what is inherent in the bond,[52] is not involved in the quenching mechanism. The redox potential barrier in these cases clearly precludes such a pathway. The results with benzoic acid (Table 1) similarly argue against extensive transfer of a proton[52] in the quenching process. Thus, while the pK_a of benzoic acid in DMSO is some 12 units smaller than that of trifluoroethanol, nevertheless,[53] they have closely matched hydrogen-bonding power (as measured with respect to the common reference acceptor N-methylpyrrolidinone[47]) and display very similar quenching constants. Attempts to study dynamic quenching by proton donors appreciably stronger than benzoic acid, such as trifluoroacetic acid ($pK_a = 3.45$ in DMSO[53]) were limited by the onset of ground state protonation and accompanying secondary photochemical reactions.[54] Thus, at least to the degree of acid strength and hydrogen-bonding power represented by benzoic acid, proton transfer as such is also not involved in quenching. It is clear that *the essential factor in quenching by the reagents listed in Table 1 is simply the strength of the hydrogen bond to excited fluorenone.* For methanol, whose quenching rate is well below the diffusion limit, it is possible to check for a deuterium isotope effect. We do observe a small but significant value, $k_H/k_D = 1.35 \pm 0.1$, indicating that the hydrogen bond is itself involved in the quenching process. As pointed out earlier in considerations of Franck–Condon factors,[7d] the vibronic mode associated with H-bonding in the excited state favors the radiationless electronic transition by virtue of its high frequency and anharmonic character, and the k_H/k_D ratio is in accord with this role.[56,57] Moreover, this further supports the view that the H-bond provides an "accepting" mode for dissipation of the excitation energy.[7d–9]

Such motion, strongly coupled to radiationless electronic transitions, will result directly from the difference in basicity or, in this case, hydrogen-bond accepting power between excited and ground states. For aryl ketones, excited states, whether singlet or triplet, are considerably more basic than the ground

(52) By such "charge transfer" we mean electron or proton displacements beyond that which contributes to the strength of an equilibrated hydrogen bond in a configuration which does not correspond to quenching (ref 3, Chapter 7; ref 48, Chapter 2). Unambiguous evidence for such extensive or complete charge transfer would evidently be the direct observation, at sufficiently short time resolution, of transient ion–radical[12,13] or protonated or deprotonated species[18] kinetically related to the quenching process.

(53) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

(54) These effects will be discussed elsewhere.

(55) Ireland, J. F.; Wyatt, P. A. H. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 161.

(56) (a) Siebrand, W.; Williams, D. F. *J. Chem. Phys.* **1968**, *49*, 1860. (b) Siebrand, W. *J. Chem. Phys.* **1967**, *46*, 440 and references therein.

(57) Avouris, P.; Gelbart, W. M.; El-Sayed, M. A. *Chem. Rev.* **1977**, *77*, 793.

(51) Kamlet, M. J.; Abboud, J. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.

Table 2. Rate Constants for Quenching of Singlet and Triplet Excited Fluorenone by Phenols and 1,2,4-Trimethoxybenzene:[a] Related Parameters and Isotope Effects[b]

phenol	pK_a $(PhOH^{\bullet+})$[c]	log K_{HB}[d]	$E_{1/2}^{(OX)}$ (V vs SCE)[e]	$10^8 k_q$ (M^{-1} s^{-1})[a] singlet CH$_2$Cl$_2$	singlet DMF	triplet CH$_2$Cl$_2$	triplet DMF
4-NO$_2$	−15.0	3.12	1.73	98.0	3.7		
4-CN	−13.0		1.62	64.0 (1.0)	2.8 (1.1)	1.3 (1.2)	0.01 (1.2)
4-H	−8.1	2.14	1.40[f]	73.0	9.1	4.5	0.02
4-MeO	−4.7	2.18	1.09[g]	91.0 (1.0)	46.0[l]	51.0 (1.0)	2.0 (1.2)
4-OH	−5.5		1.03[h]	j	52.0[k]	52.0	7.7
2,6-diMeO			1.06	67.0[k] (1.0)	43.0[k]	5.0 (1.3)	2.0 (1.2)
1,2,4-trimethoxy benzene			1.22[i]	97.0	55	m	m

[a] From fluorescence lifetime measurements, except where noted. [b] Values of (k_H/k_D) in parentheses; uncertainty ±0.1. [c] Cation radical pK_a values in DMSO: Bordwell, F. G.; Cheng, J. *J. Am. Chem. Soc.* **1991**, *113*, 1736. [d] Equilibrium constants for hydrogen bond formation with *N*-methylpyrrolidinone, in 1,1,1-trichloroethane (ref 47). [e] Measured in DMF (this work), see text. [f] Literature values (vs SCE in MeCN): 1.47 V (Barbou, N.; Feitelson, J. *J. Phys. Chem.* **1984**, *88*, 1065); 1.30 V (Legros, B.; Vandereecken, P.; Soumillion, J. *J. Phys. Chem.* **1991**, *95*, 4752). [g] 1.16 V, Legros, B.; et al. See footnote f). [h] 1.16 V (Barbou, N., see footnote f). [i] 1.12 V (Rehm, D. *Z. Naturforsch.* **1970**, *25A*, 1442. Murphy, S.; Schuster, G. B. *J. Phys. Chem.* **1995**, *99*, 511). [j] Low solubility. [k] Quenching constants from fluorescence yields. [l] From closely agreeing fluorescence yields and lifetimes. [m] No quenching (k_q < 10^5 M^{-1} s^{-1}).

states.[35] While data in this regard are lacking for fluorenone, this appears in the related case of xanthone ($\pi\pi^*$), with pK_a values for S$_0$, S$_1$, and T$_1$ of −4.1, 1.0, and 3.0, respectively.[55] An even larger increase in basicity on excitation occurs for anthrone with pK_a values for S$_0$ and S$_1$ of −5.0 and 6.15, respectively.[35] With respect to fluorenone itself, enhanced basicity of the singlet is indicated, first, by the increase in dipole moment by 2.2 D upon excitation, corresponding to charge transfer toward oxygen[25] and, second, by the single exponential fluorescence decay in presence of the alcohols, indicating no dissociation of the complex back to excited singlet. Thus, radiationless transition from the hydrogen-bonded excited to nonbonded ground state will be accompanied by sharp, complete dissociation of the bond and efficient dissipation of energy, trapping the system in the lower state. Energy made available might also be taken up by both the adjoining carbonyl bond (whose vibrational spacing (∼4 kcal) should not be greater than the energy of the original hydrogen bond) and the closely linked, low-frequency internal torsional and bending modes.[7c,18b,58] Moreover, in addition to the favorable FC factor of the H-bond mode, the radiationless transition to the ground state may be further assisted by two other effects. First, the large relative displacement of the H-bonded proton between the excited and ground states will lead to intersection of the potential surfaces along the proton displacement coordinate, particularly following oscillations set up in forming the bond itself. Second, efficient transition to the lower state may be favored by a possibly small angle between the surfaces along this coordinate.[59] This would result from a match, at the intersection configuration, between the steep slope of the repulsive ground state potential and that for the relatively tightly bound proton in the H-bonded excited state.

In support of this picture, the failure of any of the alcohols, even HFIP, to quench the low-lying triplet (17 600 cm^{-1}) despite the possible favorable effect of the Energy-Gap Law,[60] is reasonably explained by spin restrictions on the radiationless ISC to the ground state.

III. Quenching by Phenols. Table 2 lists rate constants for quenching of both singlet and triplet excited fluorenone by substituted phenols in CH$_2$Cl$_2$ and DMF, at concentrations at which no ground state complexation is observed. For the singlets, the ratios φ_0/φ again correspond to τ_0/τ, and decays are single exponential. Similarly, the pseudo-first-order rate constant for triplet decay increases linearly with quencher concentration.[61] We may safely take the quenching to be dynamic in all cases.

The phenols listed in Table 2 fall rather clearly into two groups, A and B, according to their behavior toward fluorenone singlet vs triplet and their response to solvent variation. Phenols of group A (*p*-NO$_2$, *p*-CN, and *p*-H), characterized by high oxidation potentials, H-bonding power, and acidity of their cation radicals (Table 2), quench singlet fluorenone at close to diffusion-controlled rates in CH$_2$Cl$_2$, but at much lower rates in DMF. (We focus attention on the acidity of the (incipient) cation radical rather than that of the phenol itself, since this seems more closely related to the detailed nature of a polarized H-bonded transition state which may appear in a reaction involving electron and proton transfers (see below).) As already pointed out, this solvent effect indicates that H-bonding interactions are involved in the quenching process. Similar inhibitory effects of polar, as well as H-bonding, solvents are seen in the quenching of excited biacetyl by phenols,[23] and traces of water also inhibit quenching of triplet benzophenone or *p*-methoxypropiophenone by phenols in acetonitrile.[22] We have also observed inhibition by pyridines in quenching of excited fluorenones by phenols.[62] (These latter effects will be discussed more fully elsewhere.)

Phenols in group B (*p*-MeO, *p*-OH, and 2,6-diMeO) with lower values of the above molecular parameters, quench the singlet at high rates in CH$_2$Cl$_2$, but at only slightly lower rates in DMF. The same high rate and slight drop (about 2-fold) in DMF is found also in quenching of the singlet by 1,2,4-trimethoxybenzene (TMOB). It is quite unlikely that this high rate can be due to H-atom abstraction by the rather low-lying $\pi\pi^*$ fluorenone singlet. We therefore attribute quenching of the singlet by easily oxidized TMOB to reversible electron transfer and the slight decrease in rate, for both TMOB and group B phenols simply to the increase in viscosity from 0.44 cp in CH$_2$Cl$_2$ to 0.92 cp in DMF. It is suggested also that electron transfer is the primary interaction in quenching of the singlet by group B phenols. In these cases, the absence of a large solvent effect when the rates are diffusion-limited leaves open the question whether a hydrogen-bonded transition state necessarily appears in this process.

(58) (a) Douhal, A.; Lahmani, F.; Zewail, A. H. *Chem. Phys.* **1996**, *207*, 477. (b) Herek, J. L.; Pedersen, S.; Banares, L; Zewail, A. H. *J. Chem. Phys.* **1992**, *97*, 9046.

(59) (a) Onuchic, J. N.; Wolynes, P. G. *J. Phys. Chem.* **1988**, *92*, 6495. (b) Zener, C. *Proc. R. Soc. London, Ser. A* **1932**, *137*, 696.

(60) (a) Englman, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 145. (b) Freed, K. F.; Jortner, J. *J. Chem. Phys.* **1970**, *52*, 6272.

(61) Linschitz, H.; Pekkarinen, L. *J. Am. Chem. Soc.* **1960**, *82*, 2411.

(62) Biczók, L.; Linschitz, H. *J. Phys. Chem.* **1995**, *99*, 1843.

Different behavior is observed in quenching of the triplet. Group B phenols quench the triplet at much higher rates than group A in CH_2Cl_2, but now the rates in DMF drop sharply for *both* groups. Moreover, the easily oxidized but sterically hindered 2,6-dimethoxyphenol quenches, in CH_2Cl_2, at a rate considerably lower than 4-methoxyphenol and shows a smaller relative solvent effect. These observations again implicate H-bonding in the quenching reaction. However, while group A phenols have generally similar H-bonding power as the fluorinated alcohols (Tables 1 and 2) and exhibit the same solvent effect in singlet quenching, they quench the triplet quite efficiently ($k_q \approx 10^8$ M^{-1} s^{-1}) while the alcohols do not ($k_q <$ 10^4 M^{-1} s^{-1}). Moreover, TMOB, which quenches the singlet at a nearly diffusion-controlled rate, does not quench the triplet ($k_q < 10^5$ M^{-1} s^{-1}) . This may be explained by the large singlet−triplet splitting in fluorenone which lowers by about 0.67 V the effective potential for reduction of the triplet by electron transfer alone. Thus, neither the H-bond mechanism, even for very strongly bonding reagents (HFIP), nor electron transfer at the redox level of TMOB (which is not subject to spin restriction) is sufficient by themselves to account for the efficient triplet quenching.

Particularly significant is the appearance of long-lived flash transients following triplet quenching by all the phenols, whether group A or B. Figure 4 displays spectra of such residual transients after quenching by 4-methoxyphenol (Figure 4a), phenol (Figure 4b), and 4-cyanophenol (Figure 4c), in CH_2Cl_2 and DMF solutions. We first note that the absorptions of phenoxy[63] and 4-methoxyphenoxy[64] radicals lie at 400−405 nm and of 4-cyanophenoxy[65] around 443 nm. Fluorenone anion radical absorbs in the 340−370 nm region and, in aprotic low-polarity media, in a broad band with maximum around 560 nm.[66,67] In hydrogen-bonding solvents, this band is gradually blue-shifted[67,68] and appears at 450 nm in ethanol[67] or water.[66] The neutral ketyl radical shows a slightly blue-shifted 340−370 nm band, which largely overlaps that of the anion and also absorbs weakly as far as 550 nm.[66,67] In Figure 4a, the absorptions at 540 nm as well as the slightly shifted bands at 350−370 nm show that 4-methoxyphenol reacts to form the fluorenone ketyl in CH_2Cl_2 and the anion radical in more polar DMF. The methoxyphenoxy radical appears around 410 nm in both solvents. The relative peak heights in the DMF case correspond roughly to the extinction coefficients given for these species.[64,66] Generally similar behavior is seen for phenol (Figure 4b), in which the broadened 450−550 nm band in DMF may perhaps indicate some hydrogen bonding of the fluorenone anion radical. The strongly acidic cation radicals presumably initially formed in DMF are expected to lose protons readily, giving the observed phenoxy radicals. Figure 4c, with bands close to 350 nm and at 440 nm, indicates that quenching by 4-cyanophenol produces the fluorenone ketyl and cyanophenoxy radicals in both CH_2Cl_2 and DMF. The radical yield is appreciably lower in CH_2Cl_2 than in DMF, and is also lower than that for the other phenols (Figure 4a,b), suggesting an efficient back-reaction in a more strongly H-bonded radical pair.

A more quantitative determination of radical yields is impeded by the quite low absorbance of these transients, the overlap of
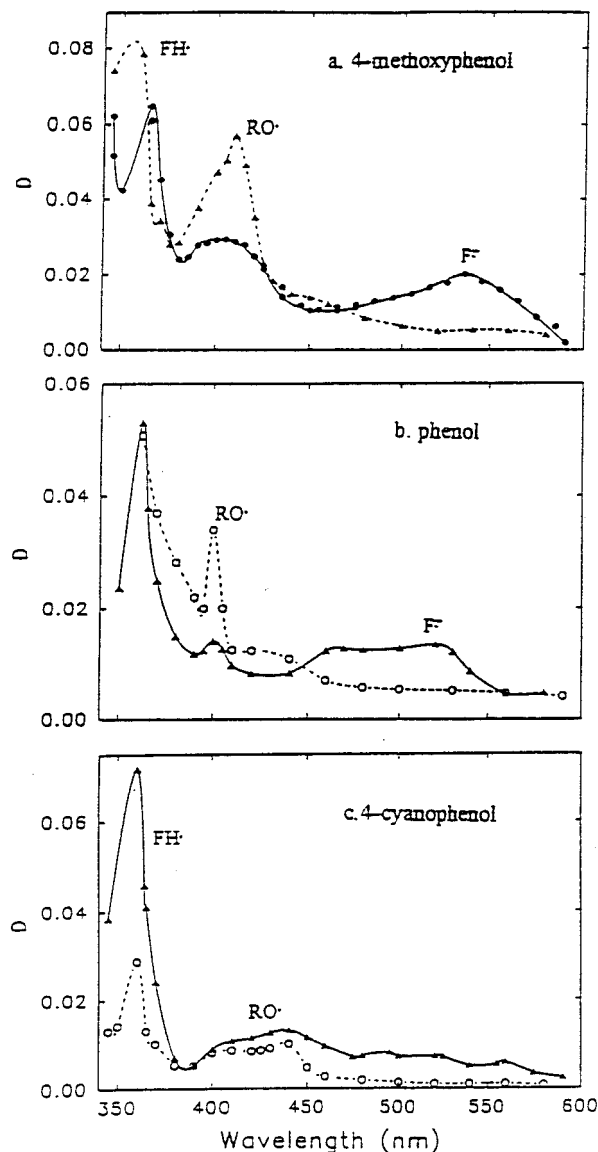

Figure 4. Spectra of long-lived transients following triplet quenching (t μs after flash) in CH_2Cl_2 ($\cdots$) or DMF ($-$), by the following: (a) 4-methoxyphenol (CH_2Cl_2, 0.4 mM, 2 μs; DMF, 4 mM, 15 μs); (b) phenol (CH_2Cl_2, 2.5 mM, 2 μs; DMF, 0.15 M, 5 μs); (c) 4-cyanophenol (CH_2Cl_2, 5 mM, 7 μs; DMF, 0.25 M, 10 μs).

their spectra (both with themselves and with parent fluorenone), and their sensitivity to solvent variation. However, it is evident that triplet fluorenone reacts within a hydrogen-bonded complex by electron transfer with easily oxidized phenols in polar solvents (DMF) and by H-atom transfer with all phenols studied in less polar media (CH_2Cl_2). Reversible H-atom transfer has been thoroughly established for other aryl ketones, both nπ* and $\pi\pi$*, by CIDNP,[69] CIDEP,[70] and flash photolysis.[22] Early studies by Turro and Lee have shown that triplet biacetyl also is quenched by phenols by reversible H-atom transfer.[23a] For the higher energy singlet, reduction will be easier than for the triplet, and we therefore assume that the same overall mechanism applies in this case also. While we do not observe transients following quenching of singlet fluorenone by these phenols, within the time resolution (~15 ns) of our flash apparatus, this is as expected, in view of the very fast back-reactions which

(63) Schuler, R. H.; Neta, P.; Zemel, H.; Fessenden, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 3825.

(64) Steenken, S.; Neta, P. *J. Phys. Chem.* **1982**, *86*, 3661.

(65) Das, P. K.; Encinas, S.; Steenken, S. Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4162.

(66) Hayon, E.; Ibata, T.; Lichtin, N. N.; Simic, M. *J. Phys. Chem.* **1972**, *76*, 2072.

(67) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, The Netherlands, 1988; pp 15, 299.

(68) Ichikawa, T.; Ueda, K.; Yoshida, H. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2695.

(69) (a) Rosenfeld, S. M.; Lawler, R. G.; Ward, H. R. *J. Am. Chem. Soc.* **1973**, *95*, 946. (b) Maurer, H. M.; Gardini, G. P.; Bargon, J. *J. Chem. Soc., Commun.* **1979**, 272. (c) Deboer, J. W. M.; Hutchinson, D. A.; Hawley, R.; Wan, J. K. S. *Chem. Phys.* **1979**, *43*, 81.

(70) Niizuma, S.; Kawata, H. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1627.

generally characterize formation of solvent-caged singlet radical or radical−ion pairs. Therefore, for quenching by these phenols, even for the most acidic, we must exclude the "pure" H-bonding mechanism, as indicated for quenching by alcohols, and consider only redox processes. In this regard, we also exclude "direct" H-atom abstraction, in view of the $\pi\pi^*$ character and low energy of the fluorenone triplets.[2] Indeed, we find that even such a powerful H-atom donor as tributylstannane quenches the triplet quite slowly ($k_q < 10^7$ M^{-1} s^{-1}) in benzene solution to form the ketyl radical.

Coupled electron−proton transfer is evidently needed to account for both the appearance of neutral product radicals in the triplet reaction[40,43] and for the observed quenching rates. Taking $E_{RED} = -1.275$ V vs SCE for fluorenone in DMF,[71] $E_{OX} = 1.62$ V for cyanophenol, and singlet energy = 2.81 eV, and assuming an initial charge separation of 7 Å, we obtain a $\Delta G°$ value close to zero for electron transfer.[19] For the triplet, with $E_T \approx 2.18$ eV, $\Delta G°$ is about $+0.6$ V in DMF and of comparable value in CH$_2$Cl$_2$, taking account of the Coulombic term.[19] These values are quite incompatible with the observed quenching rate, $k_q \approx 10^8$ M^{-1} s^{-1} (Table 2). The high efficiency of apparently endergonic electron transfer quenching reactions can of course be understood if proton transfer contributes to the process. For overall H-atom transfers, this may be evaluated by the difference in pK_a values of the acceptor and donor radicals, which ideally adds -60 mV per unit ΔpK_a to the $\Delta G°$ of the reaction.[19] The pK_a values of the phenol cation radicals in DMSO, as determined by Bordwell and Cheng (Table 2), are all strongly negative, far less than that of fluorenone ketyl whose pK_a in water equals 6.3.[66] In aprotic media, this value will increase even more due to loss of stabilization of the anion by hydration and H-bonding.[53] Thus, for *p*-cyanophenol in aprotic media, protonation associated with electron transfer, with Δp$K_a \geq 19$, would very substantially increase the driving force of reduction of excited fluorenone. The reorganization energy associated with these processes is presumably contributed in part by the solvent-dependent strength of the H-bond in the reaction complex, which moves the proton to a greater or lesser degree toward the fluorenone acceptor. In this regard, we note that the small but real isotope effect appears in quenching of the triplet by 4-methoxyphenol (Table 2), in DMF, even when the reaction corresponds to electron transfer, not H-atom transfer (Figure 4a).

In connection with these H-atom transfers from H-bonded phenols, we have shown earlier that coupled proton transfer may assist electron transfer even when charges move to *different* acceptors. For example, using triplet C$_{60}$ as substrate, addition of pyridines to phenols or naphthols in aprotic solution enables reduction by the H-bonded complex to occur, producing C$_{60}$ anions, neutral phenoxy or naphthoxy radicals, and the protonated base.[62,72] Moreover, cyclic voltammetry shows directly that the oxidation potentials of phenols and naphthols are reduced by H-bonding to pyridines, to an extent which increases with pyridine basicity.[72,73]

The cooperation between these two factors in quenching, proton and electron transfer, suggests that in a given series, one or the other would tend to be most important. The parameters and experimental results of Table 2 indicate that quenching by group A phenols would be most dependent on phenol or phenol cation radical acidity, while those of group B are favored by low oxidation potential. Since weakening one factor is compensated by strengthening of the other, a minimum might be seen in the intermediate region. The data in Table 2 do give some indication of this effect.

Leigh et al. have given a striking example of such a minimum, with similar interpretations, in their detailed study of quenching of a series of nπ^* benzophenone triplets by *p*-cresol in acetonitrile.[21] On the basis of Hammett plots, this is attributed to a switch in mechanism from initial electron to initial proton movement in the overall H-atom transfer, in response to the change in basicity of the several ketone triplets. Similarly, in comparing the quenching of triplet quinones and benzophenones by formate, the change in overall reaction from electron transfer (quinones) to H-atom transfer (ketones) has been associated with the greater base strength of the incipient ketone anion radical, which partially balances the lower reduction potential of the ketone triplet.[74] It is of interest that the solvent seems to be involved in the phenol−ketone reactions, even apart from its effect on H-bonding equilibria. Thus, Das et al. find simply a monotone negative slope in the Hammett plot for quenching nπ^* triplet benzophenone by a series of substituted phenols in benzene.[22] Mataga et al. have also proposed that H-bonding markedly lowers the redox potential barriers on the basis of effects on the IP and EA of the donor−acceptor pair. In this regard, they have observed the electron transfer intermediate in the excited aminopyrene−pyridine adduct,[12] whose formation is presumably associated with some proton displacement.[15] This is in contrast to the probably larger proton movements in the H-bonded complex of more acidic and less oxidizable hydroxy-pyrene with pyridine, in which one finds extremely fast internal conversion to the ground state.[18c] It is clear that the determination of the detailed dynamics of such interactions, including the relative phasing and amplitudes of electron and proton displacements in the H-bonded structure, as well as couplings with the ground state, remain fundamental problems for further study.

(71) Empis, J. M. A.; Herold, B. J. *J. Chem. Soc., Perkin Trans. 2* **1986**, 425.
(72) Gupta, N.; Linschitz, H.; Biczók, L. *Fullerene Sci. Tech.* **1997**, *5*, 343.
(73) Biczók, L.; Gupta, N.; Linschitz, H. Manuscript in preparation.
(74) Loeff, I.; Goldstein, S.; Treinin, A.; Linschitz, H. *J. Phys. Chem.* **1991**, *95*, 4423.