Utility of Acid–Base Behavior of Excited States of Organic Molecules

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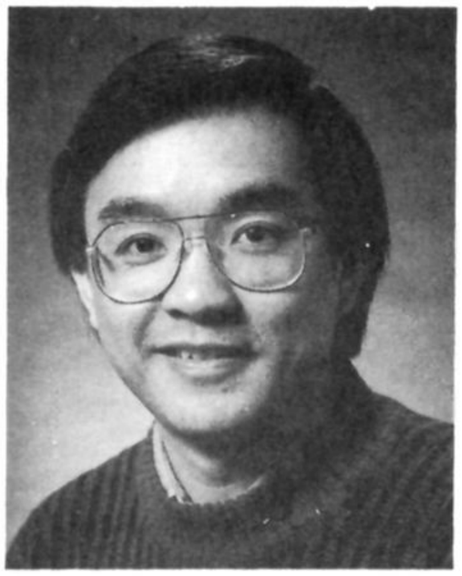
Contents

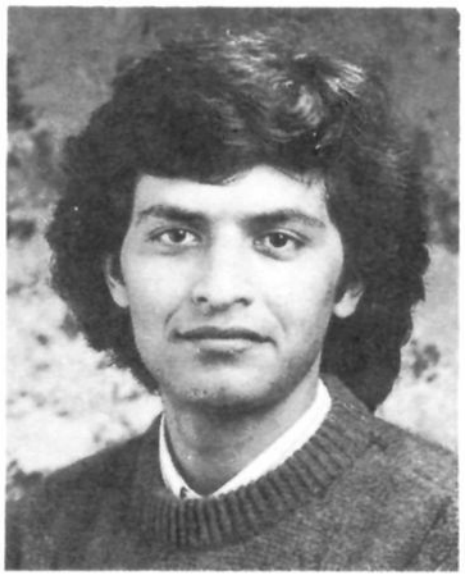
I. Introduction

Since the pioneering work of Förster[1] and Weller,[2] the study of acid–base chemistry of electronically excited states has blossomed into a mature field with several reviews of the subject appearing during the period 1970–1990.[3] These reviews summarize much that is known with respect to reversible proton transfer processes of excited states. The subject is now introduced in all modern organic photochemistry textbooks. This review is not an update of the general field of acid–base chemistry of organic excited states: Ireland and Wyatt's review[3a] still remains an authoritative source. Such an effort would be a substantial one as many new studies have since appeared. Instead this review will focus on the *utility* of excited state acid–base chemistry: how a change in acidity/basicity of a molecule in the excited state can result in new chemistry, including new examples of excited-state acid–base phenomena. Also discussed are examples of the use of "pH jump" experiments for the study of chemical phenomena. The vast majority of the papers in the field of acid–base chemistry of excited states that have appeared since the Ireland and Wyatt[3a] review is concerned with reversible prototropic phenomena. These in general will not be reviewed in this work.

The *utility* of excited-state acid–base chemistry was briefly discussed at the end Ireland and Wyatt's review[3a] as relatively few examples were known at the time. The notion that one can utilize the change in acidity or basicity of a molecule in the excited state to initiate new chemistry is naturally appealing to chemists. As many chemical reactions may be understood in terms of simple Brønsted acid–base chemistry, this is hardly surprising. However, this area has seen extensive development only during the last decade. This appears to be an opportune time for a review to evaluate the progress of this field. Because of the limited number of examples reported, it is difficult to generalize many of the reactions. Such is often the case for many types of photochemical reactions and is ascribed to the high selectivity of reactivity of excited states. In any case, care must be exercised in ascribing a photochemical mechanism as the result of a change in acid–base property of the reactive excited state.



Peter Wan was born in Hong Kong in 1956. After a short period living in Wales, U.K., he immigrated to Canada in 1968 and obtained the B.Sc. (1979) and Ph.D. (1983; with Keith Yates) degrees from the University of Toronto. After spending a postdoctoral year with Nicholas Turro at Columbia University on an NSERC postdoctoral fellowship, he joined the faculty at the University of Victoria in 1984 as an NSERC University Research Fellow and Assistant Professor, where he is currently Associate Professor of Chemistry. Mechanistic organic photochemistry is the research interest of Wan's group. He has made contributions to the understanding of acid–base catalysis of organic photochemical reactions including uncovering several new types of mechanisms. He is a member of the photochemistry editorial board of the *Journal of Photochemistry and Photobiology*.



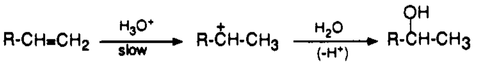
Deepak Shukla was born in India in 1962 and is currently a graduate student at the University of Victoria. After obtaining his B.Sc. (Delhi) and M.Sc. (IIT, Kanpur) degrees he spent a period working in Dr. S. Chandrasekhar's laboratory before joining Wan's group in 1989 to pursue his Ph.D. degree. His Ph.D. thesis is concerned with the photogeneration and chemistry of carbanions and carbocations.

Acid–base catalysis of photochemical reactions, first reviewed by Wubbels,[4] is related to the topic of this review. Observation of acid or base catalysis of a photochemical reaction does not necessarily imply that the excited state responsible for reaction possessed enhanced basicity or acidity since the catalysis may occur in a secondary step.[4] However, it is clear that an excited state with enhanced acidity or basicity would be prone to undergo base- or acid-catalyzed reactions, respectively. Such types of catalysis will fall into the mandate of this review. Photochemical reactions that generate strong acids (or bases), as observed for example in the photochemistry of onium salts, have important applications in industry.[5] In general, these photochemical reactions are not the direct result of enhanced acidity (or basicity) of the electronically excited state responsible for the chemistry. These types of photoreactions have been adequately discussed elsewhere[5] and will not be addressed here.

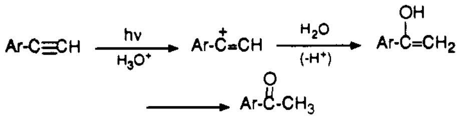
II. Carbon Bases

A. Alkenes and Alkynes

Neutral carbon of organic compounds is inherently a very weak base due to the lack of nonbonding electrons. However, the π-system of alkenes, alkynes, and aromatic systems are potential basic sites due to the availability of π-electrons. Thus electrophilic attack of a π-system by proton may be viewed as an acid–base reaction. In general, such a reaction is carried out in aqueous acid resulting in overall hydration of the π-system (eq 1). In addition, rates are generally slow for most substrates unless moderate to strong acids are used.[6] Wooldridge and Roberts[7a] first reported the facile photohydration of arylacetylenes to the corresponding ketones (in an overall Markovnikov sense) in aqueous solution in the presence of dilute acid but under conditions in which there was no competing thermal hydration (eq 2). The mechanism of the photohydration was believed to proceed via initial protonation of the alkyne, to give a vinyl cation, analogous to the ground-state mechanism. The facile protonation of the excited state was rationalized as being due to the enhanced basicity of the alkyne moiety in the excited state, more specifically as a result of extensive charge migration from the benzene ring to the alkyne. The photoadditions of methanol[7b] and acetic acid[7c] to diphenylacetylene may be rationalized in a similar manner. Roberts et al.[7d] have also reported ortho neighboring-group participation by an amide group in the photohydration of alkynes and cyano groups although the number of examples studied did not allow for detailed mechanistic interpretation.

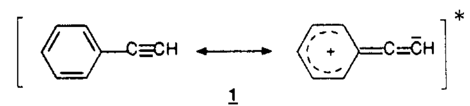


$$\mathrm{R\text{-}CH{=}CH_2} \xrightarrow[\text{slow}]{\mathrm{H_3O^+}} \mathrm{R\text{-}\overset{+}{C}H\text{-}CH_3} \xrightarrow[\mathrm{(-H^+)}]{\mathrm{H_2O}} \mathrm{R\text{-}\overset{OH}{C}H\text{-}CH_3} \quad (1)$$



$$\mathrm{Ar\text{-}C{\equiv}CH} \xrightarrow[\mathrm{H_3O^+}]{h\nu} \mathrm{Ar\text{-}\overset{+}{C}{=}CH} \xrightarrow[\mathrm{(-H^+)}]{\mathrm{H_2O}} \mathrm{Ar\text{-}\overset{OH}{C}{=}CH_2} \longrightarrow \mathrm{Ar\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3} \quad (2)$$

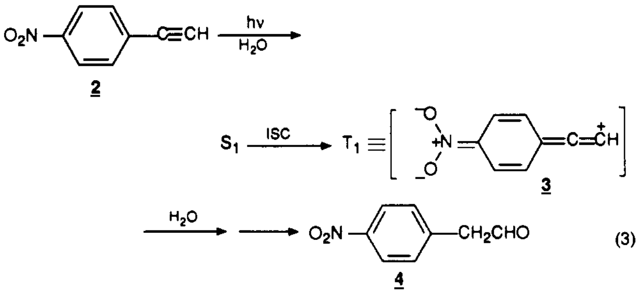
Yates and co-workers[8a–k] have carried out systematic mechanistic investigations of the photohydration of aryl alkynes, alkenes, and allenes. This was driven in part by the idea of utilizing the apparent enhanced basicity of these moieties to carry out what are otherwise difficult transformations in the ground state. Simple substituted aryl alkynes and alkenes were shown to undergo acid-catalyzed photohydration to give the corresponding Markovnikov addition products.[8a,b] Quantum yields for photohydration were acid dependent and reached significant values at moderate acidity ($\Phi > 0.2$). The fluorescence emissions of the reactive compounds were quenched with increasing acidity, in a complementary manner with respect to the plots of product quantum yields with acidity. In addition, fluorescence lifetimes were found to decrease with increasing acidity. These observations support the notion that the primary photochemical step is protonation of S_1, which is believed to be substantially polarized, as shown by 1 for the parent phenylacetylene. Excited-state dipole measurements of some of these compounds have been measured[8k] and were found to be in the range 4–6 D (for styrene, 2-vinylnapthalene, and 2-napthylacetylene), adding support for the viability of such highly polarized structures in S_1.



1

Rates of photoprotonation of S_1 were estimated from fluorescence data (both steady-state and lifetime measurements) and product quantum yields and were found to be in the range $(0.2–6) \times 10^7\ M^{-1}\ s^{-1}$. The ground-state protonation rate constants for these same compounds are in the range $10^{-5}–10^{-7}\ M^{-1}\ s^{-1}$.[6] Thus the excited state is approximately $10^{11}–10^{14}$ times more reactive with respect to protonation. Moreover, the sigmoid behavior of the fluorescence quenching and product quantum yield data suggests that the pK_{BH^+} of these substrates is in the range 0 to –2, indicating that these compounds are vastly more basic than their corresponding ground-state species, which have estimated $pK_{BH^+} \approx -10$.[9] Simple arylallenes were shown to react in an analogous fashion but with lower quantum yields.[8d] Recent laser flash photolysis studies of the photoprotonation of selected styryl substrates by McClelland and co-workers[8l–n] have confirmed the formation of intermediate carbocations in these photohydrations. In these flash photolysis studies, use of acidic but weakly nucleophilic media such as 2,2,2-trifluoroethanol (TFE) or TFE–H_2O are essential since the photogenerated benzylic carbocations have lifetimes that are generally too short to be followed by conventional nanosecond laser systems if photogenerated in wholly aqueous solution. The direct observation of transient benzylic carbocations in these photoprotonations confirms the validity of the photohydration mechanism proposed above by Yates and co-workers.[8a–k]

Nitro-substituted phenyl alkynes, alkenes, and allenes react via the triplet state, giving rise to overall anti-Markovnikov hydration products.[8a,b,d] For example, *p*-nitrophenylacetylene (2) gave *p*-nitrophenylacetaldehyde (4) exclusively. (The corresponding Markovnikov product is *p*-nitrophenylacetone, which was not observed.) The presence of the nitrophenyl moiety results in a new type of mechanism for photohydration. The observation of anti-Markovnikov



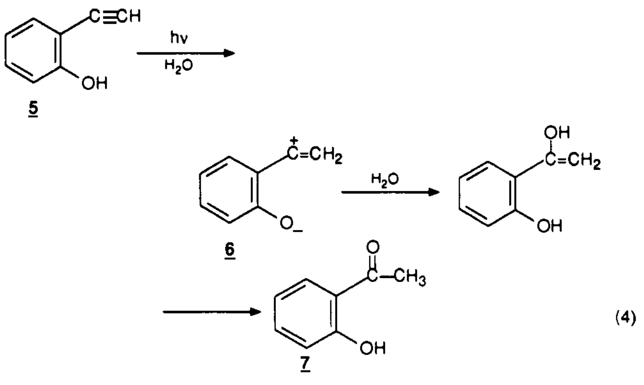
(3)

products indicates that the reactive triplet state is highly polarized, but in the reverse manner (e.g., **3**) as observed for the non-nitro-substituted compounds. The reversed polarization facilitates nucleophilic attack by water at the terminal carbon of the alkyne, alkene, or allene group, resulting in overall anti-Markovnikov hydration. This mode of hydration is not observed in the ground state for any of the styryl substrates studied.

General acid catalysis of photoprotonation of selected aryl alkynes and alkenes has been shown to operate.[8c,e] Studies of the photoprotonation in various buffers gave rates of photoprotonation from general acids such as H_3PO_4 and H_3BO_3. Brønsted plots gave α values in the range 0.14–0.18, suggesting early transition states in these protonations as compared to the ground-state reaction, which typically have $\alpha > 0.5$,[6] indicative of late transition states.

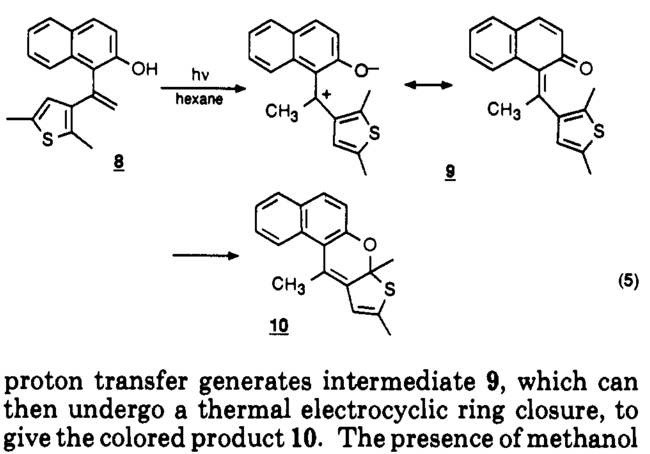
The area of excited-state intramolecular proton (hydrogen) transfer was reviewed in 1977 by Klöpffer[3d] and is an area of active current research.[10a–h] The vast majority of these systems results in no net chemical change with the transferred proton (hydrogen) returning to the donor site at very fast rates. Many of these systems result in the formation of transient phototautomers.[10i–k] In these reactions, it is often difficult (or impossible) to prove that the reaction proceeds via proton transfer. Whether the distinction is necessary or not is a moot point. The interest in these reactions stems primarily from their very fast rates. Those examples where no net chemistry is observed will be considered to be outside the mandate of this review. A recent paper by Chou and Kasha and co-workers[10h] demonstrates the dramatic effect of added water to the intramolecular double proton transfer of 7-azaindole. The 7-azaindole phototautomer is observable (green fluorescence at 530 nm) only upon addition of small amounts of water to ethyl ether and *p*-dioxane solutions of the compound. In liquid water, however, the compound fails to give observable amounts of the phototautomer. The authors argue that in low concentrations of water, 7-azaindole exists as the monohydrate, which can catalyze the double proton transfer. In wholly aqueous solution, the molecule exists as the polyhydrate which is argued to inhibit solvent reorganization necessary for the phototautomerization. The observation of water catalysis in this case suggests that protons are in fact being transferred since a double transfer of hydrogen atom to and from water would be expected to have a high activation barrier. The enhancing effect of hydroxylic solvents on the rate of excited state intramolecular proton transfer has been noted by other workers,[10j] again suggesting that many of these photoinduced intramolecular transfers do indeed involve proton.

In the present context of photohydration, Yates and co-workers[8g,h] have utilized the known enhanced acidity of the phenolic proton in S_1 to intramolecularly catalyze the photohydration of aryl alkynes and alkenes. For example, the photohydration of *o*-hydroxyphenylacetylene (**5**) to give ketone **7** was found to be much more efficient than simple arylacetylenes in the pH 7–1 region and did not display the usual enhancement by external acid. Above pH 7, the photohydration efficiency decreases rapidly and is associated with formation of the ground-state phenolate ion ($pK_a = 8.6$). The mechanism is believed to involve an intramolecular proton transfer from the phenolate to the alkyne moiety, to generate the transient zwitterionic species **6**, which can revert back to substrate or is trapped by water, leading to ketone **7** (eq 4). The photobehavior of *o*-hydroxystyrenes is similar. A rate constant for intramolecular proton transfer of α-methyl-*o*-hydroxystyrene has been estimated to be $8 \times 10^9\ s^{-1}$. Since the bimolecular rate constants for photoprotonation of these compounds by proton are in the range $(0.2–6) \times 10^7\ M^{-1}\ s^{-1}$, proton transfer from solvent in the pH 7–1 region would not be competitive with the intramolecular pathway.



(4)

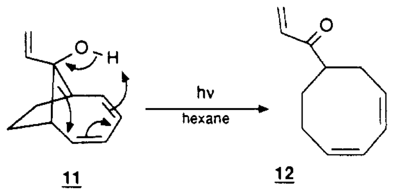
Another example[11] of the high efficiency of intramolecular proton transfer from phenol to alkene is in the photochromic reaction of the 2-naphthol derivative **8**, which on photolysis ($\lambda_{ex} = 334$ nm) in hexane gave the colored product **10** ($\lambda_{max} = 385$ nm) with high quantum yield ($\Phi = 0.2$) (eq 5). In this reaction, intramolecular proton transfer generates intermediate **9**, which can then undergo a thermal electrocyclic ring closure, to give the colored product **10**. The presence of methanol retards the photochromic reaction and is most probably due to the addition of methanol to **9**, to give a colorless methanol adduct. However, full characterization of the proposed methanol adduct would have provided added support for the intermediacy of **9**. The high quantum



(5)

efficiency in hexane indicates that intramolecular proton (hydrogen) transfer of this kind does not require any assistance from solvent.

The intramolecular photorearrangement of bicyclic diene 11 to give dienone **12** (eq 6) has been reported by Miesen et al.[12] Although the details of the reaction have not been fully delineated, it is possible to view the transformation as involving initial proton transfer to the photoexcited diene unit which has enhanced basicity. The subsequent rearrangement of electrons ensures that a product is formed irreversibily. Photolysis of the substrate with a deuterium label at the hydroxyl group gave a product with deuterium at the expected vinyl position, consistent with an intramolecular process. Further studies, particularly in hydroxylic solvents, would be required to show that initial proton transfer to the diene moiety is indeed the primary photochemical step.



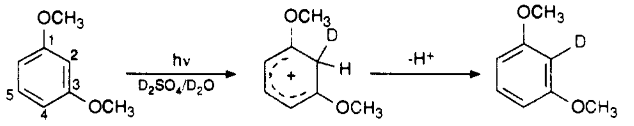
11 12 (6)

B. Aromatic Systems

The protonation followed by deprotonation of aromatic systems is the simplest of all electrophilic aromatic substitution reactions. This acid–base reaction may be followed by deuterium or tritium labeling studies. Aromatic π-systems in the ground state are very weak bases: an estimated pK_{BH^+} for highly activated compounds such as 1,3,5-trimethoxybenzene is approximately −6 (H_0 acidity scale).[9] Reports of the facile *photo*protonation of aromatic compounds have appeared since 1963,[13a,i] although the first systematic mechanistic investigations were not carried out until much later. Several reports show that deuterium exchange takes place when aromatic compounds such as toluene and anisole are irradiated in deuterated acids such as CF_3CO_2D although little quantitative data were measured in most cases.[13] Mason and Smith[13e] using Förster cycle calculations[3] estimated that the pK_{BH^+} of several simple aromatic compounds (benzene, toluene, and naphthalene) to be in the range +5 to +10, indicating that they become much stronger bases in S_1. However, no isotope (deuterium or tritium) exchange was observed and the authors concluded that prototropic equilibrium is not established during the lifetime of the excited state. In a related study, Smith[13f] showed that the fluorescence emissions of anisole and the three isomeric dimethoxybenzenes were all quenched significantly in moderately concentrated H_2SO_4. For example, the fluorescence intensity of 1,3-dimethoxybenzene was half-quenched at $H_0 = +0.47$, suggesting that this compound is vastly more basic in S_1 than in the ground state. Since no hydrogen exchange was observed, Smith[13f] concluded that prototropic equilibrium was not attained and that the fluorescence quenching phenomenon was due to a proton-induced radiationless deactivation process but with no exchange.

More recent studies by Wan and co-workers[14a,b] have shown conclusively that the fluorescence quenching by acid of dimethoxybenzenes and related compounds is accompanied by proton/deuteron exchange when the photolyses are carried out in D_2SO_4/D_2O solution. The sigmoid behavior in the fluorescence quenching plots displayed a mirror-image relationship with plots of quantum yields for proton exchange vs acidity, supporting the notion that these substrates are indeed vastly more basic in S_1 ($pK_{BH^+}* \sim -1$ to +0.5) than in the ground state ($pK_{BH^+} \sim -6$).[9]

The regioselectivity of photoprotonation and associated chemistry of the three isomeric dimethoxybenzenes and related compounds has also been investigated.[14a,b] For example, it has been shown that photolysis of 1,3-dimethoxybenzene in 10% D_2SO_4/D_2O resulted in deuterium exchange exclusively at the 2-position when taken to low conversions (eq 7). The photoreaction is acid catalyzed with measurable quantum efficiencies at acidities greater than ~pH 2. Much stronger acids are required to effect thermal exchange, which is known to take place predominantly at the 4-position, with a lesser amount at the 2-position.[15] McClelland and co-workers[14c,d] have also shown that many of these same substrates can be photoprotonated in 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) with concurrent detection of the expected intermediate cyclohexadienyl cations by laser flash photolysis. For example, laser flash photolysis (248 nm) of 1,3-dimethoxybenzene and several derivatives in HFP resulted in a single transient (λ_{max} 395–460 nm; decay rates ~10^2–10^4 s^{-1}) which is consistent with exclusive photoprotonation at the 2-position.



(7)

The regioselectivity of the observed photoprotonation may be rationalized with simple HMO theory in a qualitative way.[14b] Using standard HMO parameters for oxygen, calculations gave five HMO's that are bonding and three antibonding. With the assumption that each oxygen will utilize two valence electrons in the π-system, all five bonding HMO's are occupied. Considering only the HOMO and LUMO (Ψ_5 and Ψ_6, respectively), it is clear that promotion of an electron from Ψ_5 to Ψ_6 will result in a decrease of electron density at carbons 3 and 4 and at oxygen and an increase at carbons 2 and 5 (Figure 1). In fact, HMO results predict that C5 should be more basic than C2 in the excited state. Facile photoprotonation of position 2 has already been demonstrated and there is evidence to suggest[14b] that position 5 is also photoprotonated when the reaction is taken to high conversion, indicating that the photoprotonation rate at this site is much lower (less basic) than at the 2-position. The intrinsic reactivity of the C2 position is probably much higher since this site is significantly more sterically congested than C5 in 1,3-dimethoxybenzene. Thus simple HMO theory has its limitations for excited states, which was not unexpected. However, the correct qualitative predictions make it useful for quick calculations.

Simple HMO calculations to predict the direction in change of electron density of dimethoxybenzenes in the excited state have also been made by Smith,[13f] the

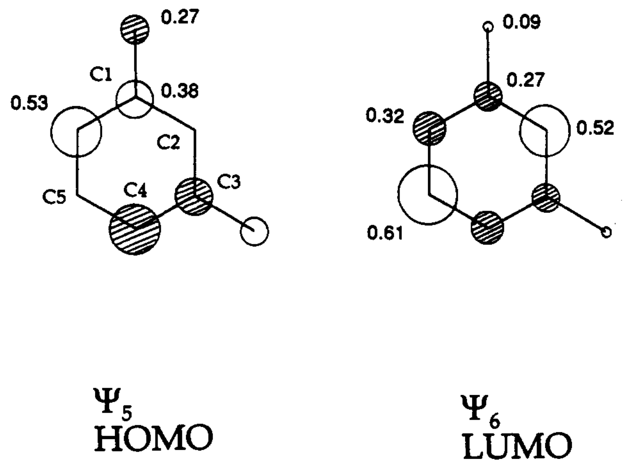
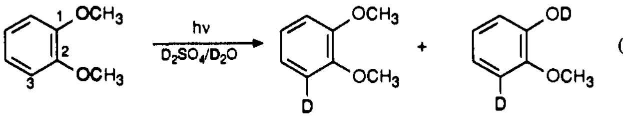


Figure 1. Hückel molecular orbitals Ψ_5 (HOMO) and Ψ_6 (LUMO) of 1,3-dimethoxybenzene (shaded orbitals indicate positive sign of HMO coefficient; numerals indicate absolute magnitude).

results of which corroborate the above findings. In addition, Zimmerman and Sandel[55] first noted that HMO calculations could be used to rationalize the activating effects of a methoxy group on benzene rings in the excited state. Their results showed ortho and meta activation.

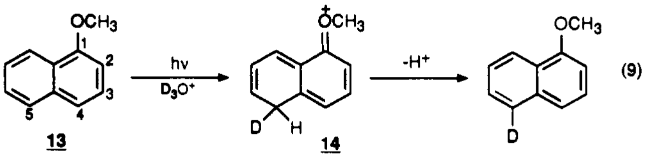
The photochemistry of 1,2-dimethoxybenzene and derivatives in aqueous acid results in proton exchange at the 3-position as well as *ipso* substitution of one of the methoxy (alkoxy) groups (eq 8), both of which are



(8)

primary photoproducts and catalyzed by acid.[14a,b] The mechanism of the *ipso* substitution involves attack of solvent water and loss of the methoxy group, as shown by O-18 labeling studies. Recent studies[14b] have now shown that the cyclohexadienyl cations formed in the photoprotonation of 1,2-dialkoxybenzenes are susceptible to nucleophilic attack by water (hence overall *ipso* substitution). Since thermally generated dialkoxy-substituted cyclohexadienyl cations are not known to undergo *ipso* substitution, it is likely that the photogenerated species differs significantly in structure from the thermally accessible one, as already shown for the 1,3-isomers. Note also that the site of deuterium exchange is meta to the site of *ipso* substitution (eq 8). Such a product is believed to require formation of a non-Kekulé intermediate in the reaction mechanism.

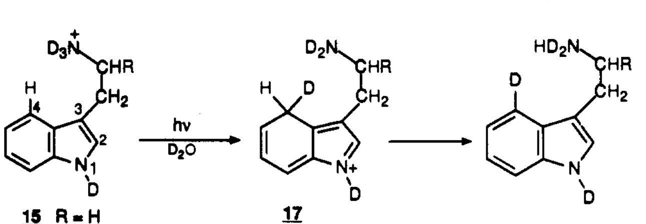
Stevens and Strickler[16a] have studied the excited state H–D exchange of naphthalene in aqueous H_2SO_4. Exchange quantum yields of α-deuterionaphthalene were in the range 0.00019–0.033 over the 30–64% H_2SO_4 used. In contrast to the situation in the ground state,[16b] the β-isomer was found to be more reactive than the α-isomer. Fluorescence quenching by H_2SO_4 was interpreted as being due to protonation of S_1. These results indicate that simple unactivated aromatic compounds are not efficiently photoprotonated thus requiring the use of strong acids to effect observable reaction. The use of strong acids introduces the possibility of competing thermal exchange, making such studies problematic. Shizuka and Tobita[17a,b] reported that 1-methoxynaphthalene (**13**) undergoes observable excited state H–D exchange at much lower acidity (Φ = 0.24 in 4:1 D_2O–CH_3CN with 0.1 M D_3O^+). The exchange was regioselective at the 5-position, as determined by analysis of the product by ^{1}H NMR (eq 9).



(9)

However, 2-methoxynaphthalene was unreactive under similar conditions. Fluorescence quenching by acid was observed only for the reactive compound and the resulting k_q was used to estimate a deuteration rate constant of 1.1 × 10^8 M^{-1} s^{-1} for **13**. McClelland and co-workers[14c] have recently demonstrated that the photoprotonation of **13** can also be achieved in HFP. Using laser flash photolysis, a transient with λ_{max} = 550 nm has been assigned as the cyclohexadienyl cation **14** obtained by protonation of **13** at C5.

With regard to photochemical proton exchange of heteroaromatic systems, only indole derivatives have been extensively studied.[17c–f,18] Interest in these systems stems from ongoing studies aimed at understanding the photophysical and photochemical behavior of tryptophan in aqueous solution. Whereas the parent indole does not undergo regioselective proton exchange on photolysis in deuterated solvents,[17f,18] tryptamine (**15**) and tryptophan (**16**) and derivatives have been shown to undergo regioselective H–D exchange at C4 (eq 10).[17c–f,18] The quantum yields for exchange in 9:1



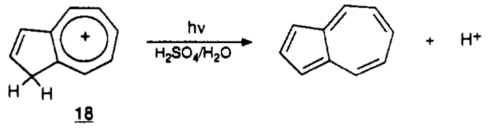
(10)

MeOD–D_2O are 0.26 and 0.16 for **15** and **16**, respectively. The mechanism of reaction is believed to involve intramolecular proton transfer from the side-chain ammonium group to generate intermediate cation **17**. This internal proton-transfer quenching mechanism of S_1 is believed to be one of the major pathways for nonradiative decay of these compounds. The rates of internal quenching were estimated from lifetime measurements and are 0.91 × 10^8 and 1.8 × 10^8 s^{-1} for **15** and **16**, respectively. Cozens et al.[18] have carried out laser flash photolysis studies of these indole derivatives in TFE and observed transients assignable to cyclohexadienyl-type cations **17** with λ_{max} = 350 and 420 nm and 300–500-ns lifetimes.

Pincock and co-workers[19] have developed two acidity scales (in 20% EtOH–80% aqueous H_2SO_4 and in wholly aqueous $HClO_4$) for fluorescence quenching by acid observed for many aromatic compounds. This was carried out to linearize quenching plots in the strong acid region, where the titratable proton concentration used does not give linear Stern–Volmer plots. The indicator used was 1-cyanonaphthalene for which fluorescence quenching is observable beginning at pH 1. In addition, its ground-state basicity is very low and hence will not be protonated thermally even in strong acid. The fluorescence quenching of a variety of aromatic chromophores by acid was successfully treated using the developed excited-state acidity functions, although the mechanism of quenching was not delineated with the exception of selected compounds where the reaction mechanism in acid was already understood.

III. Carbon Acids

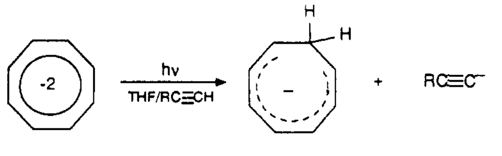
Carbanions are ubiquitous and important intermediates in organic chemistry. They play a central role in organic synthesis due to their facility in forming C–C bonds. Carbanions are generally made via deprotonation of the corresponding carbon acid precursor by the action of a base of appropriate strength. Until recently, however, excited-state carbon acids have not been reported in the literature although a number of research groups have made earlier attempts at their photogeneration.[20] Förster cycle calculations show that fluorene and related compounds should be vastly more acidic in S_1, with excited-state pK_a's ≈ -8 to -12.[20] However, photochemical excitation of fluorene and other hydrocarbons with a benzyl moiety in D_2O failed to result in proton exchange. An early work of Grellmann et al.[21] showed that azulenium cations were much more acidic in S_1 than in the ground state (eq 11).



(11)

Thus photolysis of azulenium cation **18** in strong acid resulted in formation of transient azulene formed via deprotonation, as detected by flash photolysis experiments. However, C–H deprotonation here does not lead to a carbanion, and in the present context, the azulenium cation is not strictly an excited-state carbon acid.

Deprotonation rates from C–H acids in the ground state are typically slow because of the lack of hydrogen bonding to solvent and the substantial geometrical and solvation changes generally required on deprotonation of carbon acids.[9b,22] If true for electronically excited states as well, such intrinsically slow rates would not compete favorably with the fast rates of decay generally available for S_1. It would appear that only under ideal conditions would C–H deprotonation from a neutral precursor be observable photochemically. Interestingly, two examples of the facile *protonation* of electronically excited carbanions have been reported.[23] In both of these examples, an aromatic anion (the cyclooctatetraene dianion and the cyclononatetraene anion) is protonated on electronic excitation in a medium where it would not be protonated in the ground state (eq 12).



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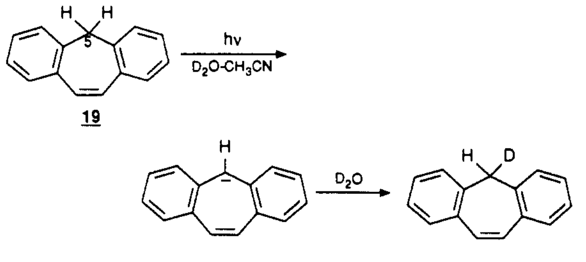
The reaction was followed by analysis of the products (photochemical and thermal) arising from the protonated derivative. These results show that aromatic anions are more basic in S_1 than in the ground state. One may interpret this as evidence that ground-state aromatic (4n + 2) systems are not favored in the excited state. Looking at the reverse reaction (i.e., photochemical deprotonation of a carbon acid to form the carbanion), it has already been shown that fluorene does not undergo deprotonation on photochemical excitation. However, deprotonation of fluorene would generate a 4n + 2 ground-state anion. Perhaps what is required is a precursor hydrocarbon which generates a 4n anion on deprotonation. This is indeed the necessary condition (vide infra).

The first example of an excited-state carbon acid was reported by Wan and co-workers[24a,d] who showed that photolysis of suberene (**19**) in D_2O–CH_3CN resulted in exchange of the benzylic proton with deuteron (Φ = 0.030). The reaction could be followed by 250 MHz ^1H, ^2H, or ^{13}C NMR, which showed conclusively that exchange took place almost exclusively (>98%) at C5, with a residual (1–2%) exchange taking place at the vinyl carbons. Photolysis of 5,5-dideuteriosuberene in H_2O–CH_3CN resulted in exchange of the deuteron at the 5-position with proton from solvent (Φ = 0.035). The proposed mechanism of reaction involves as a primary step C–H bond heterolysis with water acting as the general base, to generate the intermediate suberenyl anion, which is reprotonated almost exclusively at the 5-position (eq 13). Reprotonation at the vinyl position would give a tautomer which on rearrangement (1,5-sigmatropic shift) regenerates the substrate. Consistent with the carbanion mechanism is the observation that fluorescence emission is quenched efficiently by H_2O in CH_3CN solution ($k_q = 1.68 \times 10^8$ M^{-1} s^{-1}) and that use of 5,5-dideuteriosuberene gave a primary isotope effect for fluorescence quenching of $(k_H/k_D)_q = 2.8$. Moreover, the fluorescence emission of **19** in aqueous solution was found to increase on increasing the acidity below pH ≈ 0, suggesting an excited state p$K_a \approx -1$, compared to the estimated ground state p$K_a \approx 31$–38. Additional support for this mechanism is the recent observation of base catalysis of exchange by primary amines.[24e]



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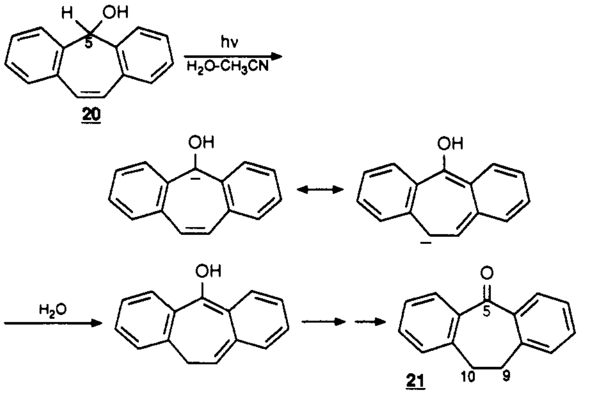
Since related compounds such as fluorene and diphenylmethane were shown to be totally unreactive, Wan and co-workers[24a,d] proposed that the photogeneration of a 4n anion is a necessary requirement for observation of carbon acid behavior in S_1. Thus xanthene and thioxanthene, both of which are isoelectronic with suberene (**19**), have been shown to undergo benzylic proton exchange on excitation in D_2O in the presence of primary amines as bases.[24f] The base-catalyzed photoketonization[24b] of 5-suberenol (**20**) to dibenzosuberone **21** operates through a carbanion mechanism (eq 14). The benzylic proton of **20** becomes very acidic in S_1, perhaps rivaling the acidity of the hydroxyl group, although such a relative acidity measurement cannot be made easily since it is not known to what extent the hydroxyl proton exchanges while the substrate is electronically excited. Strong evidence for a carbanion mechanism is the isolation of 5-deuterio-5-suberenol and dibenzosuberone **21** in which each of the 9- and 10-positions is monodeuterated on photolysis in D_2O solution. Fluorescence quenching of **20** by H_2O in CH_3CN solution gave $k_q = 1.2 \times 10^8\ M^{-1}\ s^{-1}$ and again a substantial primary isotope effect was observed for k_q when 5-deuterio-5-suberenol was used ($(k_H/k_D)_q$ = 2.9).



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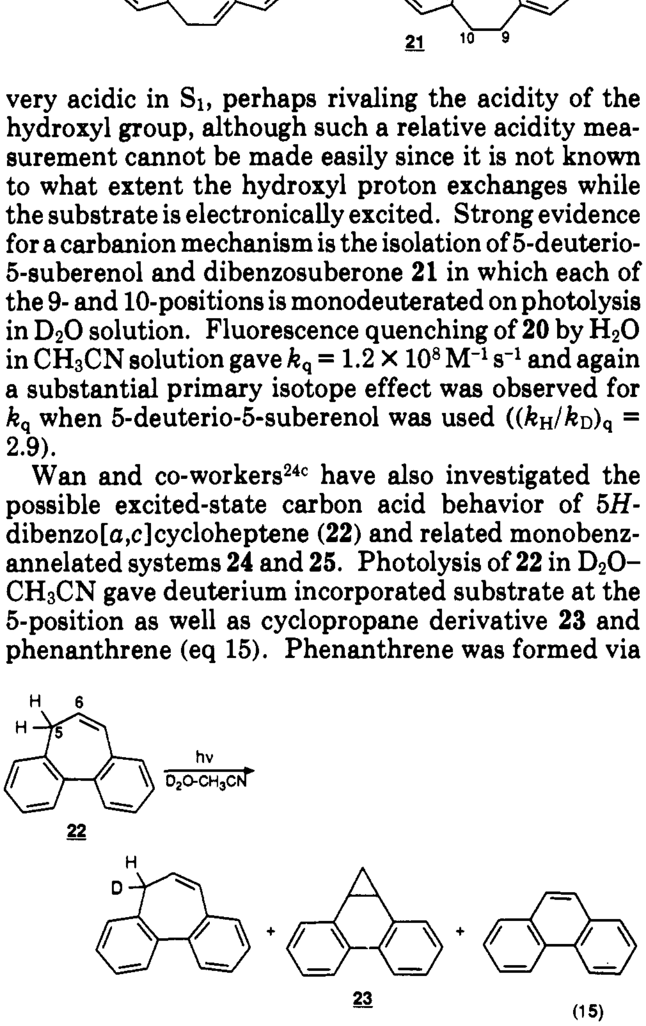
Wan and co-workers[24c] have also investigated the possible excited-state carbon acid behavior of 5*H*-dibenzo[*a*,*c*]cycloheptene (**22**) and related monobenzannelated systems **24** and **25**. Photolysis of **22** in D_2O–CH_3CN gave deuterium incorporated substrate at the 5-position as well as cyclopropane derivative **23** and phenanthrene (eq 15). Phenanthrene was formed via secondary photolysis of **23**. The mechanism of formation of **23** was shown to arise via a true di-π-methane rearrangement from the triplet state and a 1,7-hydrogen shift followed by electrocyclic ring closure from the singlet state. Carbanion formation via C–H bond heterolysis at the 5-position was shown to be a singlet-state pathway with its efficiency highly dependent on the H_2O concentration (k_q for fluorescence quenching by H_2O was $2.05 \times 10^8\ M^{-1}\ s^{-1}$). Derivatives **24** and **25** showed no evidence for carbon acid behavior; instead these compounds reacted exclusively via a very efficient ($\Phi \approx 0.9$) photorearrangement to give **26**, the mechanism[25] of which has been shown to occur via initial 1,7-hydrogen shift followed by electrocyclic ring closure (i.e., not a true di-π-methane mechanism). It appears that carbon acid behavior cannot compete with the highly efficient molecular rearrangement of these more flexible compounds although they possess the correct incipient 8π-electron carbanion system.



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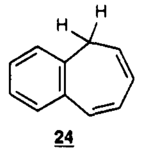
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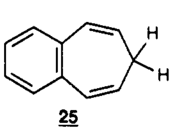
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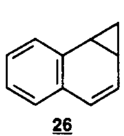
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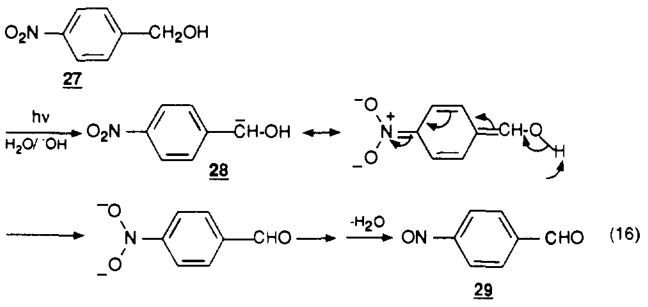
It seems reasonable that the measured k_q's for fluorescence quenching by H_2O of those compounds displaying excited-state carbon acid behavior are equatable to the rates of C–H bond ionization by H_2O acting as the base (i.e., k_H). Since these are the first such rate measurements for this process, it is difficult to comment on the exact magnitude at this time. Suffice it to say that k_H is below the diffusion-controlled rate (hence there is the possibility of enhancing the rate) but is much larger than rates observed in the ground state. However, unlike the situation in the ground state, most hydrocarbons do not have measurable k_H (i.e., $k_H < 10^5\ M^{-1}\ s^{-1}$) in the excited state since only selected systems show observable reaction.

The results reported show that there is an enhanced driving force for the photogeneration of cyclically conjugated 8π (4n) carbanions from an excited-state precursor, compared to 4n + 2 systems or those which do not give rise to a cyclically conjugated intermediate. The study of photodecarboxylation of several dibenzannelated acetic acids also support this notion.[26] In addition, the study of photosolvolysis of several dibenzannelated systems (in which carbocations are intermediates) again indicate a strong preference for intermediates of 4n (4π) electrons.[27] Although the reactions investigated are not pericyclic reactions in the traditional sense, Woodward–Hoffmann[28] and the Dewar–Zimmerman[29] rules work nicely in predicting the outcome. That is, there appears to be an inherent stabilizing effect of a 4n array of electrons of these compounds (whether negatively or positively charged) on the excited-state surface, analogous to the well-known aromatic stabilization associated with 4n + 2 systems in the ground state, where the concept of aromaticity has more solid basis. Since one cannot use the same criteria of aromaticity—which are well known in the ground state—for excited-state species because of their intrinsically short lifetimes, one encounters a dilemma in trying to offer a simple explanation for the enhanced reactivity observed in these studies. It is clear, however, that 4n systems appear to have a special inherent stability which is manifested in the ease of photodeprotonation of suberene (**19**) and related compounds[24] and the photosolvolysis of 9-fluorenol derivatives.[27] If one assumes that the increased *photo*reactivity of the 4n systems implies a lower activation barrier on the S_1 surface, the extension of the Hammond postulate would indicate that the excited state of 4n charged intermediates are indeed more stabilized than their 4n + 2 counterparts. This interpretation is based on the following assumptions: (i) applicability of the Hammond postulate to the S_1 surface and (ii) adiabaticity of the C–H bond cleavage step. There is no reason to doubt the former but evidence for an adiabatic first step is at present not available. In any case, the phenomenon of enhanced photoreactivity of incipient

4n vs 4n + 2 systems in ionic reactions is intriguing and worth additional studies.

In addition to the above reports of excited-state carbon acids, three other examples have been reported although demonstration of deuterium exchange was lacking in all of them.[30a,b,31] A theoretical study of the deprotonation of acetylene in its excited states has also been carried out[32] as well as general theoretical analysis of excited-state proton transfers including carbon acids.[33] Of the initial three reports, one is concerned with the excited-state acid–base behavior of 1- and 2-naphthylamines in basic media.[30a] On the basis of only fluorescence emission data (both steady state and lifetime measurements) it was proposed that in very strong base ($H_- > 14$), aryl-H ionization at the 4-position occurred from the amide anion, to give a dianion, all on the excited-state surface. This proposal is extraordinary if proven to be true. However, the conclusions should be taken with some caution since no isotope exchange experiments on carbon were carried out. In addition, the spectral assignments were made with little reference to model systems. Another[30b] reports the fluorescence quenching observed for fluorene on increasing the basicity of the medium above pH 12 and is attributed to fluorenyl anion formation from excited-state fluorene. Again, deuterium exchange was not demonstrated. On the basis of the results of Wan and co-workers,[24a,d] it appears unlikely that carbon acid behavior is observable for fluorene, even in basic medium.

Wan and Yates and co-workers[31] have proposed that the photochemistry observed for *m*- and *p*-nitrobenzyl alcohols and related compounds may be rationalized by proposing that the primary photochemical event is benzylic C–H bond heterolysis from the triplet excited state, to generate a delocalized anion, which subsequently reacts to give the observed redox-type products. For *p*-nitrobenzyl alcohol (**27**), the initially generated carbanion **28** reacts via an overall simple redox reaction to give *p*-nitrosobenzaldehyde (**29**) (eq 16). The reaction is catalyzed by hydroxide ion consistent with a carbanion mechanism. However, photolysis in $D_2O/^-OD$ resulted in no observable deuterium incorporation in substrate **27**, indicating that every photogenerated carbanion leads to product. A significant α-deuterium (at the benzylic position) isotope effect ($\Phi_H/\Phi_D > 4$) was observed which is indicative of abstraction of these protons in the product forming step. The mechanism of reaction for *m*-nitrobenzyl alcohol is similar to that proposed for **27**, that is, initial formation of an α-hydroxy-*m*-nitrobenzyl carbanion **30**. However, simple redox chemistry was not observed. Instead, two products, *m*-nitrobenzaldehyde (**31**) and 3,3′-azoxybenzaldehyde (**32**) were isolated. Wan and Yates[31c] originally proposed that the reaction mechanism for the meta isomer took a route essentially identical to that proposed for **28**, which required the formation of a non-Kekulé intermediate. However, direct evidence for through-conjugation between meta positions was not readily available. The current understanding[31d] of the reaction mechanism of this reaction involves electron transfer from photogenerated carbanion **30** to substrate, to generate the corresponding radical, which on loss of a proton gives *m*-nitrobenzaldehyde radical anion. Subsequent transfer of another electron to substrate gives observed **31**. Alternatively, further reduction of *m*-nitrobenzaldehyde radical anion would be expected to give **32**, which has been confirmed by independent reaction of **31** with photogenerated reducing sources.[31d]



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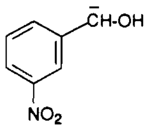

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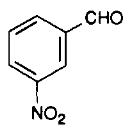

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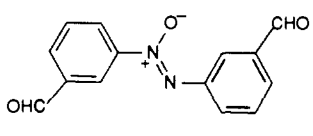

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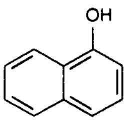
IV. Oxygen Acids

It is now well established that phenols and naphthols and their derivatives are considerably more acidic in S_1 than in the ground state.[3] Much of the earlier studies of excited-state proton transfer (ESPT) of these compounds were mainly concerned with the measurement of their excited state pK_a's. Since the singlet-state lifetimes of most of phenols and naphthols are very short, the dynamics of ESPT could not be studied very well by steady-state techniques. The advent of picosecond laser spectroscopy has enabled precise measurements of various kinetic parameters of these ESPT reactions as well as providing new insights into the understanding of these photoprototropic equilibria.[34–36] For example, on the basis of simple Förster cycle analyses, the excited singlet state acidity of 1-naphthol (**33**) and 2-naphthol (**34**) were found to be essentially identical (p$K_a^* \approx 2.8$).[3a] However, using picosecond spectroscopy, 1-naphthol (**33**) has been shown to be much more acidic (p$K_a^* = 0.4$) than 2-naphthol (**34**).[35] Also, it has been noted that in contrast to 2-naphthol (**34**), the fluorescence emission from 1-naphthol (**33**) is either absent or very weak in aqueous solution.[2,35,36a,b] Webb et al.[35] have shown that an important deactivational pathway operating only for 1-naphthol (**33**) is photoprotonation of the 5- and 8-positions, resulting in deuterium incorporation at these positions on photolysis in acidic D_2O, with a quantum yield of 0.11. These photoprotonations are presumed to proceed via intermediate phototautomers, e.g., **35**, but these have not been directly observed. The enhanced basicity at the 5- and 8-positions of **33** would have been expected on the basis of what has been reported for deuterium incorporation of 1-methoxynaphthalene (**13**).[17a,b]



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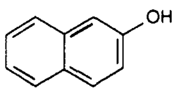

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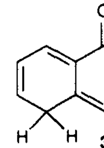

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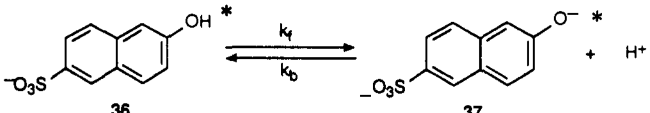
Tolbert and Haubrich[37] have found that the excited-state acidity of 2-naphthol can be enhanced by up to 4 pK_a units with substitution of the 5- or 8-positions with a cyano group. This effect is attributed to lowering of the more acidic ^1L_a state on substitution with an electron-withdrawing group. The availability of these more acidic naphthols allow ESPT reactions to be carried out in nonaqueous environments.

The first examples of utilizing the enhanced acidity of excited-state naphthols to induce a transient pH change ("pH jump") were reported by Clark et al.[38] and Gutman et al.[39a] in 1979. In this method, the enhanced acidity of excited singlet state naphthols is used to provide a means for a transient increase in local proton concentration, which results in a rapid lowering of the pH. Clark et al.[38] showed that pulsed laser excitation of an aqueous solution (pH 7) of 2-hydroxynaphthene-6-sulfonate (**36**) at 266 nm resulted in rapid establishment of excited-state acid–base equilibrium (k_f = 1.02 × 10^9 s^{-1}; k_b = 9 × 10^{10} s^{-1}) (eq 17). The authors calculated that the H_3O^+ concentration increased by $>10^{-4}$ M during the excited-state lifetime ($\tau \approx 10$ ns) of **36**. Thus, the solution which initially had a pH of 7 before excitation was rapidly modulated on laser excitation, to pH < 4 on a time scale given by the proton-transfer rate.



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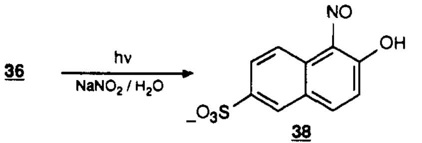
(17)

Gutman et al.[39a,b] have directly measured the change in pH obtained by laser excitation of naphthols, by reaction of the dissociated protons with a pH indicator present in solution. Thus, laser excitation (347.2 nm) of an aqueous solution of 2-hydroxynaphthene-3,6-disulfonate and bromocresol green resulted in the rapid decrease in the absorbance of the basic form of the indicator. The increase in proton concentration as determined by the kinetic analysis was approximately 10^{-5}–10^{-4} M above the prepulse level. A similar increase in the concentration of discharged protons was measured by following the rate of reprotonation of the naphtholate after its decay to the ground state.[39c,d] The pH jump technique has now been used to probe the microenvironments of biological systems[34,39e,g] as well as local structures of electrolyte solutions.[39f]

For a transient *increase* in pH, photoexcited acridine and 6-methoxyquinoline have been employed.[40a,b] The basicity of the nitrogen of heterocyclic aromatic compounds is known to increase in S_1.[3,40c] Thus excited-state intramolecular proton transfer between nitrogen heterocycles and phenolic hydroxyl groups has been extensively studied.[3,40c] In the present applications,[40a,b] photoexcited acridine and quinoline abstract proton from water, producing hydroxide ion. Kinetic studies of the reaction were carried out in the presence of metal cations[40a] and in various solvents,[40b] the latter studies being used to probe the effect of solvent structure on proton transfer.

The use of the enhanced acidity of phenols and naphthols in their excited states to initiate chemical reactions is an attractive concept. Mansueto and Wight[41] have reported the polymerization of amorphous formaldehyde initiated by excited-state proton transfer from 2-nitrophenol (pK_a = 9.1; pK_a* = −0.6). Thus laser photolysis (308 nm) of crystalline formaldehyde doped with 2-nitrophenol (20:1 CH_2O–2-nitrophenol) at 77 K resulted in the formation of polyoxymethylene ($\Phi < 0.05$; chain length ~ 10). According to the authors, this is the first example of a solid-state chain reaction initiated by proton transfer from an electronically excited dopant molecule. If correct, this report demonstrates that it is possible to utilize the enhanced photoacidity of phenols within a solid for the purpose of inducing an irreversible chemical reaction. The results presented do not rule out the possibility of irreversible photogeneration of acid on photolysis of *o*-nitrophenol. In general, nitroaromatic compounds have very short singlet-state lifetimes and it is doubtful that *o*-nitrophenol will be sufficiently long-lived in S_1 to transfer a proton to reactant. Photoexcited nitro groups are also known to abstract hydrogen atoms, which in the present case could induce the observed polymerization. Experiments using nitroaromatic compounds incapable of releasing proton would have been informative. In addition, the authors do not present evidence for quantitative recovery of starting material in order to show that irreversible photochemistry of *o*-nitrophenol did not occur.

Saeva and Olin[42] reported the photonitrosation of **36** and 1- and 2-naphthols in neutral aqueous solution in the presence of sodium nitrite. Thus, photolysis of **36** in the presence of sodium nitrite (pH 7) gave 1-nitroso-2-hydroxynaphthene-6-sulfonate (**38**) ($\Phi \approx 10^{-4}$) (eq 18).



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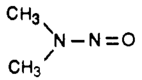
The authors suggested that the reaction mechanism involves formation of nitrous acid as the nitrosating agent, which is formed from reaction of nitrite ions with dissociated protons from the excited singlet state of **36**. However, this proposal has been disputed on several grounds including the argument that the experiments used photon intensities which are too low to cause any significant changes in proton concentration.[43]

Chow et al.[44] have reported the photonitrosation of naphthols, anthrols, and 9-phenanthrol in the presence of *N*-nitrosodimethylamine (**39**) in various solvents. For example, photolysis of 1-naphthol (**33**) in the presence of **39** gave 1,4-naphthoquinone monooxime (**40**) and dimethylamine. The proposed mechanism of reaction involves initial formation of an exciplex between photoexcited **33** and **39**. ESPT from **33** to **39** takes place within the exciplex. This is followed by energy migration from the naphtholate moiety to protonated **39** within the exciplex, followed by its decomposition,



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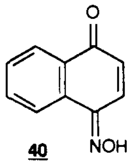

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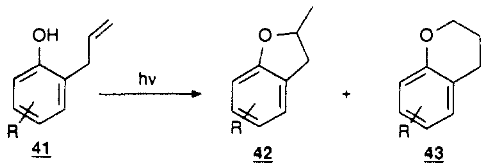
to give 1-naphtholate, dimethylamino radical cation, and nitric oxide. Geminate electron transfer between 1-naphtholate and dimethylamino radical cation leads to 1-naphthyloxy radical and dimethylamine. Radical coupling of 1-naphthyloxy radical with nitric oxide leads to **40**. In independent studies, Chow and co-workers[45] have shown that nitrosoamines such as **39** require proton association as well as electronic excitation for it to undergo homolytic cleavage to yield ammonium radicals and nitric oxide. The requirement of ESPT in the reaction mechanism was based on the observation that general bases such as water and triethylamine quenched the photonitrosation.[44b]

o-Allylphenols (41) have been shown to undergo photocyclization in a variety of solvents to yield a mixture of furanyl 42 and pyranyl ethers 43[46a-d] (eq 19). A reaction mechanism has been proposed in which



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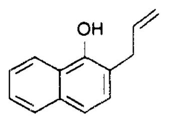
ESPT from the excited phenol to the alkene takes place, to generate isomeric carbocation intermediates, which subsequently cyclizes to the observed products (eq 19). The problem with this initially appealing mechanism is that the alkene moiety is a very weak base (this chromophore is not photoexcited in the reaction). Although phenols are much more acidic in S_1 ($pK_a \approx 3$) than in the ground state, this change in acidity is still insufficient to protonate the alkene. A recent study[46e] of 41 (R = H) and related compounds in "cold" water and ammonia clusters (in the gas phase) showed no evidence for excited-state intramolecular proton transfer. However, it is not clear whether this lack of reaction is intrinsic to the compounds or to the clusters.

An alternative mechanism for the reaction which involves initial electron transfer between the phenol and alkene moieties has been proposed.[47] The initially formed radical–ion pair reacts via proton transfer, leading to isomeric biradicals, which subsequently couples to give the observed products. Structurally related *o*-allylanilines react in a similar fashion, and an electron-transfer mechanism is widely accepted for these compounds.[47a]

In related work, Chow et al.[48] have reported that 1-allyl-2-naphthol (44) and 2-allyl-1-naphthol (45)



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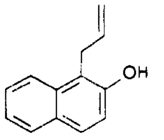

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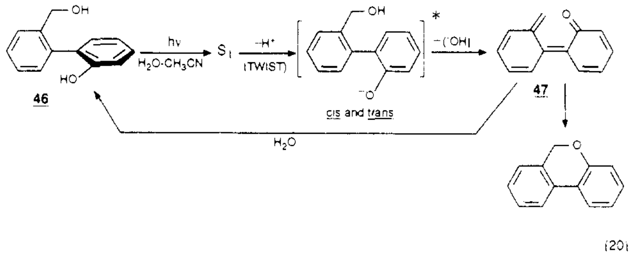
undergo a similar photocyclization reaction to give the corresponding dihydrofuranyl and pyranyl ethers. It has been shown that the reaction is via the singlet excited state and that proton transfer from the naphthol is necessary for cyclization. The proposed mechanism is believed to involve initial intramolecular proton transfer to the alkene via two isomeric hydrogen-bonded complexes. Again, the same argument against this intramolecular ESPT mechanism as discussed above could be made.

Huang et al.[49] have reported the photocyclization of 2-(2′-hydroxyphenyl)benzyl alcohol (**46**) and derivatives in aqueous solution to give dibenzopyrans. The mechanism of reaction is of interest for two reasons: (i) the requirement of a phenol moiety in which its excited-state ionization is required for reaction at pH < 10 and (ii) the substantial change in geometry that takes place on going from substrate (which is highly twisted) to product (which is essentially planar). Shown in eq 20



(20)

is the proposed mechanism for the reaction at pH < 10. The primary photochemical step is believed to involve a very fast twisting of the biphenyl to a more planar geometry which is probably concerted with deprotonation of the phenol moiety. This is followed by a dehydroxylation step, to generate the biphenyl-*o*-quinonemethide intermediate 47, which is facilitated by the electron-rich phenolate ion and increased electronic communication through the biphenyl ring system. Subsequent electrocyclic ring closure gives the observed dibenzopyran. The presence of methanol in the solvent results in the trapping of 47, to give the corresponding methyl ether product. Otherwise, trapping by water gives back substrate. Excitation of **46** at pH > 10 results in substantially higher quantum yields for product formation. Under these conditions, only the phenolate ion of **46** is excited. This suggests that at pH < 10, the dissociated proton from the phenol moiety does not act as a catalyzing acid for the subsequent dehydroxylation step and that it is the electron-donating power of the phenolate ion and the more planar biphenyl ring system that are responsible for the driving force of the dehydroxylation step.

V. Photodissociation of Arylmethyl Alcohols

A. Benzyl Systems

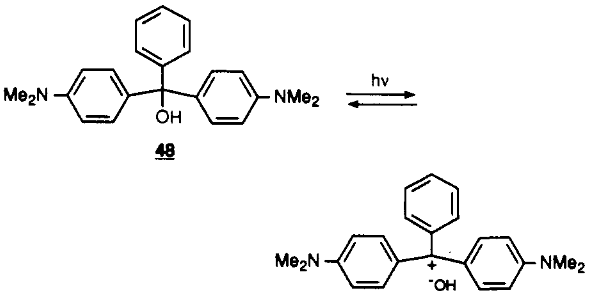
The acid-catalyzed solvolysis of arylmethyl alcohols (ROH) to give arylmethyl cation (R^+) and water (eq 21) may be viewed as an acid–base reaction, with the substrate alcohol functioning as a pseudobase and the arylmethyl cation as a pseudoacid. Ionizations of this

$$\underset{(ROH)}{ArCH_2OH} + H^+ \rightleftharpoons \underset{(R^+)}{ArCH_2^+} + H_2O \qquad (21)$$

kind in the ground state generally require strong acid with diaryl or triarylmethyl systems being extensively studied as the reaction serves as an indicator of the relative stability of the corresponding carbocations.[9a,50] Thus pK_{R^+} values (for the reverse direction shown in eq 21) using the H_R acidity function[51] have been measured for a variety of substrates and are generally < −3 except for heavily stabilized cations such as the

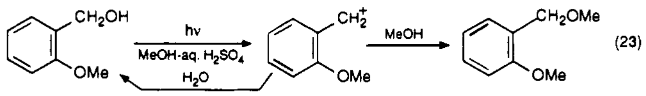
4,4′,4″-trihydroxytriphenylmethyl cation, which have $pK_{R^+} > 0$.[9a,50] Since the electronically excited states of ROH and R^+ of these substrates are readily accessible, it is of interest to consider how the equilibrium of eq 21 is affected in the excited singlet state. Feldman and Thame[52] were the first to address this point. Since all arylmethyl carbocations R^+ absorb at much longer wavelength than the precursor alcohol ROH, the 0,0 energy of R^+ will always be less than the that of ROH. It is easy to see using the Förster cycle that R^+ should be a much weaker pseudoacid in S_1 than in S_0. Conversely, ROH should ionize much more readily in S_1 than in S_0. Assuming identical entropies of reaction in the ground and excited states, Feldman and Thame[52] calculated the $pK_{R^+}{}^*$ of several dibenzannelated diarylmethyl alcohols (e.g., 9-phenylxanthen-9-ol) to be in the 22–25 range. In contrast, their known ground-state pK_{R^+}'s are in the +0.1 to −3.7 range. This implies that ROH should dissociate readily when photochemically excited whereas the ground-state process requires strong acid. However, the authors were not able to obtain direct evidence for excited-state ionization and concluded that the intrinsically short lifetimes of excited-states precluded such reaction for most substrates.

Leucohydroxides are well-known photochromic molecules which on photoexcitation dissociates into a highly stabilized and colored triarylmethyl cation and hydroxide ion[53] (eq 22). Presumably equilibrium in the excited state is not attained in these dissociations, and the facile cleavage of these compounds is due to a low-lying dissociative potential energy surface which leads to ground state ionic products. Thus the adiabaticity of these photodissociations has never been demonstrated. Irie[53a] irradiated 48 in aqueous solution and observed an increase in pH which returned to its original value on removal of light. The direction of this pH jump is in the opposite direction as those observed using naphthols and related compounds (vide supra). Manring and Peters[53b] have studied the photodissociation dynamics of 48 using picosecond laser flash photolysis. In CH_3CN a transient assignable to the cation (λ_{max} = 610 nm) was observable 2 ns after the laser pulse. No such species was observable in cyclohexane.



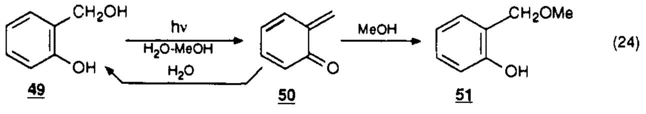
(22)

Turro and Wan[54a] first demonstrated that simple methoxy and dimethoxy-substituted benzyl alcohols undergo efficient photodissociation in dilute aqueous H_2SO_4, to form the corresponding benzyl cation, which can be trapped by added MeOH in the solvent, under conditions where no ground-state dissociation occurred (eq 23). Unlike the leucohydroxides, the arylmethyl cation intermediates in these ionizations are not exceptionally stabilized: they are most likely formed initially on the excited-state surface and hence may be truly regarded as excited-state ionizations with a corresponding $pK_{R^+}{}^*$ value. Corroborating this view of the reaction mechanism is the observation that the fluorescence emissions of these compounds were quenched by added acid concurrent with acid catalysis of methyl ether formation, indicative of proton assistance of the ionization. The fluorescence quenching plots were sigmoid with half quenching efficiencies in the pH 1.5 to 0.5 acidity range for the reactive compounds suggesting that these arylmethanols have vastly more positive pK_{R^+} in S_1 than in S_0. Additional studies reporting quantum yields and rate constants for these and other reactive systems have subsequently been published.[54b,c] The most reactive system discovered so far in this series of compounds is 2,6-dimethoxybenzyl alcohol, which has a quantum yield of nearly unity for carbocation formation in neutral solution. In 1:1 $MeOH–H_2O$ (pH 7), the quantum yield formation of the methyl ether is 0.31. Unlike other compounds, the photoionization of this substrate does not require acid catalysis. An examination of the relative reactivity of the methoxy and dimethoxy-substituted benzyl alcohols studied to date[54] indicate a reactivity trend that essentially parallels that initially observed for the photosolvolysis of methoxybenzyl acetates first reported by Zimmerman and Sandel,[55] who first proposed and quantified the idea of meta activation. The present studies provide the first quantitative measure (based on rate measurements) of relative reactivity of all three methoxy isomers in addition to demonstrating that hydroxide ion can be an excellent leaving group in photochemical reactions. It has been noted[54c] that predictions from Förster-cycle calculations for these substrates should be taken with caution since it appears that excited-state equilibrium is never achieved in these reactions; kinetic factors probably play the major role in determining actual relative reactivity in these photochemical dissociations.



(23)

The photodissociation efficiency of *o*-hydroxybenzyl alcohol (49) was found to be significantly higher than that of 2-methoxybenzyl alcohol and is believed to be the result of intramolecular catalysis by the phenolic group (eq 24). In this substrate, the known enhanced acidity of the phenol in S_1 is used to assist the departure of the hydroxide ion, resulting in an overall photodehydration reaction, to generate *o*-quinonemethide 50, which subsequently reacts with methanol to give 51.[54b,56a] A photocondensation reaction resulting in the formation of phenol–formaldehyde type oligomers was observed when the photolysis was carried out at high pH in the absence of MeOH.[56a] Using triarylmethanol derivatives, Hamai and Kokubun[56b,c] have shown that heavily stabilized derivatives of 50 with long lifetimes may be photogenerated in hexane.

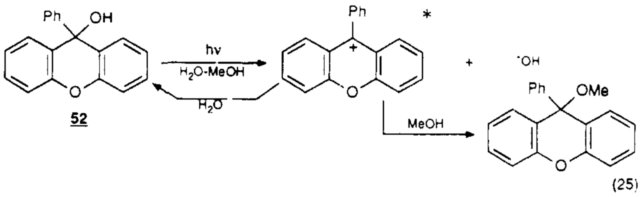


(24)

The photoionization of simple arylmethanols such as pyrenyl and 2-naphthylmethanol has also been reported.[57] All of these substrates require the assistance of acid to effect reaction and are much less reactive than methoxy-substituted benzyl alcohols.

B. Dibenzannelated Systems

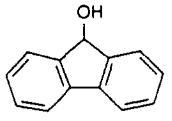
Although Feldman and Thame[52] were not able to demonstrate conclusively the generality of photoionization (to the corresponding carbocation and hydroxide ion) of several dibenzannelated alcohols, Wan et al.[58a] have reported the efficient photodehydroxylation of 9-phenylxanthen-9-ol (52) (eq 25). In the presence of methanol as cosolvent, the corresponding methyl ether was isolated in high yields. Moreover, they demonstrated using steady-state fluorescence emission studies that the cation was generated adiabatically, showing that ionization was indeed taking place (at least in part) on the excited state surface. Recent laser flash photolysis studies by McClelland et al.,[58b] Das and Minto,[58c] and Okuyama et al.[58d] have confirmed that the primary photochemical step in this reaction is loss of hydroxide ion, with substantial quantum yields that are highly solvent dependent and that at least part of the dehydroxylation step is adiabatic. Results of the laser flash photolysis study by Okuyama et al.[58d] showed that the decay of photogenerated 9-(*p*-methoxyphenyl)-9-xanthenylium cation exhibited biphasic first-order decay. The rapid decay is ascribed as being due to ion pair recombination with the slower decay being due to recombination of the cation with solvent. A related benzopyranol derivative has also been reported to undergo efficient photodehydroxylation to give a carbocation intermediate.[58e]



(25)

Wan et al.[27,59] have also reported the efficient photodehydroxylation of 9-fluorenol and derivatives. Photolysis of the parent 9-fluorenol (53) in aqueous alcohol[27,59a] gave the corresponding alkyl ethers in high yield. Under similar conditions, none of the related compounds 55–57 reacted. The authors proposed that the primary photochemical step is C–OH bond heterolysis to generate the 9-fluorenyl cation (54) as the primary intermediate. This cation is antiaromatic in the ground state due to the 4π (4n) electrons in the internal conjugated cyclic array and is exceptionally difficult to generate under thermal conditions. Its ease of photogeneration and the lack of photoreactivity of 57 is consistent with an enhanced driving force for the photogeneration of 4n systems in the excited state discussed earlier. The enhanced reactivity which appears to be inherent in 9-fluorenol systems has now been further demonstrated in studies of a variety of 9-fluorenol derivatives such as 58.[59b,c] Interestingly, the photodehydroxylation of 58 was found to be acid catalyzed, adding further support for an ionic mechanism.

Recent laser flash photolysis by Mecklenburg and Hilinski[60a] and McClelland et al.[60b] have confirmed the intermediacy of 54 in the photolysis of 53 in aqueous solution. A transient at 515 nm with a lifetime < 20 ps in H_2O–MeOH was observed and assigned to 54 by Mecklenburg and Hilinski.[60a] McClelland et al.[8m,60b,c] were able to extend the lifetime of this highly reactive cation to ≥ 30 μs in the very non-nucleophilic but highly ionizing solvent HFP and also in TFE. In addition, the chemistry observed for photogenerated 9-fluorenyl cations[8m,60c] is consistent with a highly destabilized (ground-state *antiaromatic*) species. However, no evidence was obtained in any of these studies which would indicate that the heterolysis step is adiabatic, as required on the basis of the rationalization of the reaction offered by Krogh and Wan.[27] These simple photoheterolysis pathways for the generation of carbocations—in which the precursor alcohol may be viewed as a very strong pseudobase in the excited state—open up a variety of studies of structure–reactivity of ionic mechanisms and especially how ground- and excited-state reaction surfaces are related.



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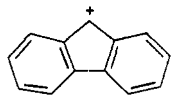

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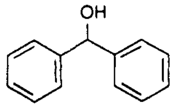

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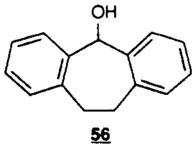

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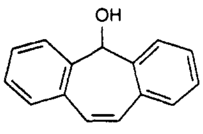

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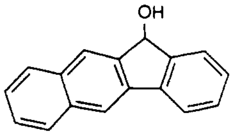

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VI. Summary

The utility of acid–base chemistry of electronically excited states has been amply demonstrated since the review of Ireland and Wyatt.[3a] It is anticipated that the use of laser flash photolysis in these investigations will continue to provide new insights into mechanistic details never available before. Studies concerning the dynamics of intramolecular proton transfer and phenol–naphthol–hydroxypyrene photodeprotonation still dominate the literature in this area. With the discovery of excited-state carbon acids, the relatively facile photodissociation of arylmethyl alcohols and new results in the study of photoprotonation of aromatic substrates, the scope and utility of excited state acid–base chemistry have been increased significantly during the last few years and suggest that other new examples and insights await discovery in this emerging field.

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