Table I. 1s Orbital Energies (au) for the α and β Positions of Pyrrole, Indole, and Cyclopentadiene

	C_α	C_β
pyrrole	−11.0387	−10.992
indole	−11.0646	−10.998
cyclopentadiene	−11.0104	−11.013

One can conclude, therefore, that these approaches must be included in the first category indicated above (kinetically controlled processes).

Obviously, among the procedures to be included in the second category, the simplest one would be, in principle, to evaluate the energy of the different protonated forms. However, this magnitude is basis-set dependent, and only if one employs a very large basis set, including polarization and correlation effects,[11] can one have some confidence on the reliability of the energy obtained. Unfortunately, for molecules as big as pyrrole and indole, such calculations are unfeasible. A possible alternative would be to obtain a linear correlation between the calculated protonation energy (ΔE_p), defined as the energy difference between the protonated and the nonprotonated forms, and the measured gas-phase proton affinity. Since we aim at comparing C_α vs. C_β protonation of the compounds under study, we have selected for this purpose a set of compounds–benzene (**1**), naphthalene (**2**), azulene (**3**), and cyclopentadiene (**4**)–that are carbon basis and whose gas-phase PA's have been measured with high accuracy.[12] To have confidence on the goodness of the corresponding linear relationship, the calculated protonation energy was obtained using INDO fully optimized geometries, conveniently scaled as indicated elsewhere.[9] All ab initio calculations were performed using a STO-3G minimal basis set.

The linear correlation obtained (see Figure 1) obeys the equation

$$PA = -0.572\Delta E_p + 52.5 \qquad r^2 = 0.999$$
$$\sigma_{PA} = 0.5 \text{ kcal/mol} \tag{1}$$

When eq 1 is used to predict the gas-phase PA's of pyrrole, for α and β protonation, the values obtained are 208.9 with and 205.2 kcal/mol, respectively. The first value is identical with the experimental one,[12a,c] and the second one is only a little smaller than the lower limit proposed by Houriet et al.,[4] from thermodynamic data obtained in a ion cyclotron double-resonance experiment.

The values obtained for indole (202.1 kcal/mol for α protonation and 207.1 kcal/mol for β protonation) indicate that, in contrast with pyrrole, in this particular case the β-protonated form is more stable than the α-protonated one.

If one considers now the C_{1s} orbital energies of the α and β positions (see Table I), it is evident that, in pyrrole, C_β is the most basic center and therefore the one that should undergo protonation in a process where conditions favor a kinetic control. This theoretical result is in agreement with the conclusion of Angelini et al.[6a,c] who have shown, by means of a kinetic analysis of gas-phase electrophilic substitutions of pyrrole by CH_3-F-CH_3^+, HeT^+, and t-$C_4H_9^+$ ions, that formation of the β-substituted compound predominates under all experimental conditions. Besides, the subsequent isomerization of the resulting excited intermediates to the thermodynamically more stable α-protonated form proposed by these authors is also in agreement with our previous discussion.

The values obtained for indole indicate also that the β position is the preferred protonation site from a kinetic point of view. Therefore one can conclude that (a) if the pyrrolic ring is either isolated or fused to a six-membered one protonation should take place on the β position and (b) in indole the corresponding protonated form is also the most stable one from a thermodynamic

point of view, while in pyrrole the α-protonated isomer is more stable than the β-protonated one. Consequently, in the latter case a subsequent isomerization involving a C_β–C_α proton shift might take place. The different behavior predicted for these two compounds is easily explained. In indole (and related systems) charge migrations between the six- and the five-membered rings[9,13] and polarizability effects[14] (both absent in pyrrole) contribute to extra stabilize the β-protonated form.

Finally, it must be noted that the other five-membered ring, cyclopentadiene, fits eq 1 very well when α protonation is assumed, indicating that, as in pyrrole, the α-protonated form is the most stable one. However, in contrast with pyrrole and indole, the kinetic protonation of cyclopentadiene must take place at C_α, which is the position that exhibits a higher 1s orbital energy (see Table I). This is a consequence of substituting an NH by a CH_2 group within the ring, which affects the charge distribution of the system. To confirm this point, we have obtained the charge distribution of this molecule using the YSP population analysis[15,16] which, as it has been shown elsewhere[17], reproduces well the inductive effects of alkyl substituents and is practically unsensitive[15] to the basis set used to expand the corresponding wave function. Our results indicate that, in contrast with pyrrole and indole, C_α in cyclopentadiene is not only the center with the higher intrinsic basicity but also the one that presents a higher electronic density.

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Intramolecular Exciplex Emission from Aqueous β-Cyclodextrin Solutions

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Cyclodextrins provide a unique environment for organic compounds in aqueous media and are known to promote a variety of organic reactions.[1,2] The complexing of two chromophores with cyclodextrins has been demonstrated by excimer emission with naphthalene or pyrene by both intermolecular and intramolecular probes.[3–7] Hamai recently reported the formation of an electron donor–acceptor complex consisting of 2-methoxynaphthalene, o-dicyanobenzene, and β-cyclodextrin in a molar ratio of 1:1:2 on the basis of its absorption and emission spectra and suggested

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Communications to the Editor

J. Am. Chem. Soc., Vol. 106, No. 2, 1984 423

Table I. λ_{max} and Quantum Yield for Exciplex Emission in Various Media

solvent	polarity $(f - (f'/2))^a$	λ_{max}^- (em)^b	ϕ(em)	τ(em), ns
n-pentane	0.0909	395	0.48	
diethyl ether	0.256	431		
methylene chloride	0.319	455		
2-propanol	0.370	489		
ethanol	0.380	498	0.012	5
β-cyclodextrin		500	0.0046	11
acetonitrile	0.393	516	0.014	7
methanol	0.393	521		

^{a} Where $(f - (f'/2)) = ((\epsilon - 1)/(2\epsilon + 1)) - ((n^2 - 1)/(4n^2 + 2))$; see ref 8. ^{b} λ_{max} emissions are corrected for instrument response.

that the cyclodextrin cavity has a polarity similar to that of dioxane.[6] Excited aromatic hydrocarbons readily form exciplexes with amines in nonpolar media, while undergoing electron transfer to yield radical ion pairs in polar media.[8-10] therefore, it seems surprising that no enhanced exciplex emission from aromatic hydrocarbon and amine systems has been reported in the presence of cyclodextrins in aqueous media.[11] We wish to report the first example of intramolecular exciplex emission in aqueous β-cyclodextrin solutions. Our results help to define both the stereochemical requirement and the environmental nature of β-cyclodextrin cavity in exciplex formation.

In aqueous solutions 1-α-naphthyl-3-(dimethylamino)propane (1) exhibits only naphthalene-like monomer emission (λ_{max} at 324,

1
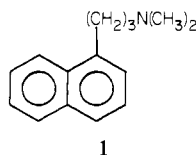
334, and 338 nm). In the presence of 0.01 M β-cyclodextrin a new broad emission is observed (λ_{max} at 500 nm), which has the same excitation spectrum as the 334-nm emission. This new emission is not observed in α- or γ-cyclodextrin solutions.

In organic solvents the λ_{max} of exciplex emission of **1** increases dramatically with solvent polarity, while the quantum yield of exciplex emission decreases (Table I). Both the λ_{max} and the quantum yield of exciplex emission in β-cyclodextrin solutions indicate that the exciplex of **1** experiences an environment with a polarity similar to ethanol.

In aqueous and β-cyclodextrin solutions the intensity of naphthalene-like emission of **1** (I_{fl}, 334 nm) decreases dramatically at high pH, because deprotonation of the amine increases its ability to quench naphthalene. A plot of I_{fl} vs. pH exhibits standard titration behavior with measured pK_a's of 9.4 and 8.9 for aqueous and 0.01 M β-cyclodextrin solutions, respectively (Figure 1). In β-cyclodextrin solutions the decrease in naphthalene-like emission with increasing pH is mirrored by a concomitant increase in the new longer wavelength emission (I_{ex}, 500 nm) with a pK_a of 8.8 (Figure 2). This new emission is assigned to the exciplex of **1** in the cyclodextrin cavity. At pH higher than 12 the intensity of exciplex emission decreases. This result is assigned to deprotonation of the hydroxyl groups of the cyclodextrin, which either decrease complexation of **1** or increases the polarity of the cavity.

The association of protonated **1** with β-cyclodextrin was measured by the increase in naphthalene-like emission with increasing cyclodextrin concentration. The result indicated the formation of a 1:1 complex with an association constant of 250 M^{-1} at pH at 6.3. The association constant for the unprotonated form of **1** was found to be 630 M^{-1} at pH 10.5 as measured by

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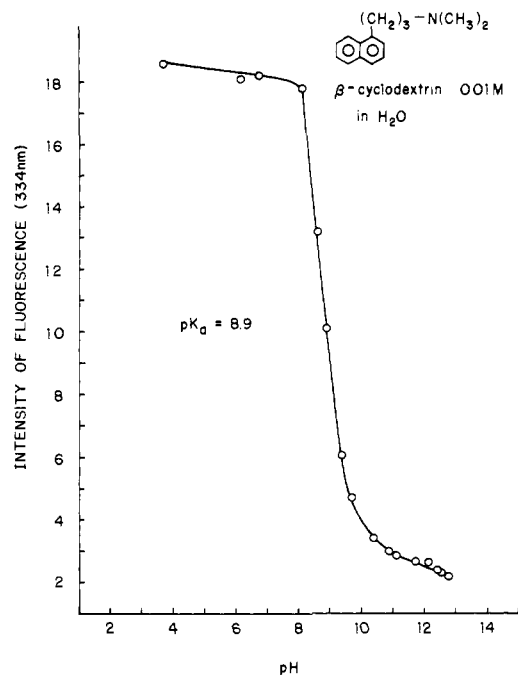
Figure 1. Plot of the relative intensity of the naphthalene-like fluorescence of **1** vs. pH in 0.01 M β-cyclodextrin solution.
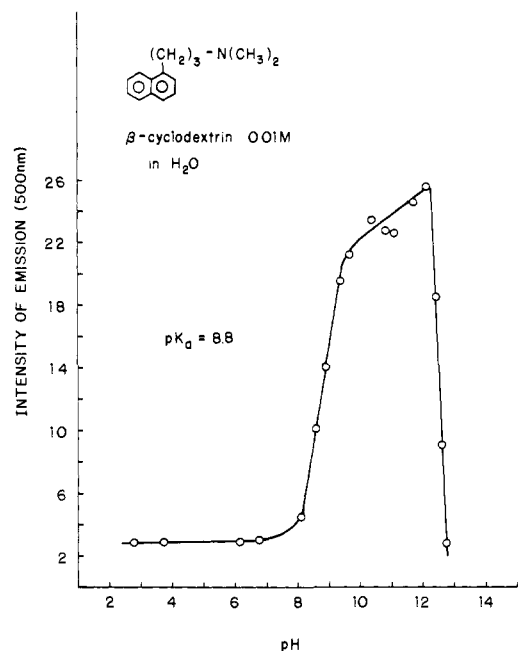
Figure 2. Plot of the relative intensity of exciplex emission of **1** vs. pH in 0.01 M β-cyclodextrin solution.

the increase in exciplex emission with increasing cyclodextrin concentration. The difference in the equilibrium constant between the protonated and unprotonated forms may be attributed to the increase in solubility of the protonated form in water as supported by the similarities of the pK_a of the amine in water with and without β-cyclodextrin.[12]

In aqueous solution two fluorescence lifetimes of 36 and 8 ns are observed for the naphthalene-like emission of the protonated and unprotonated forms of **1**, respectively. Upon complexation with β-cyclodextrin, the lifetime of unprotonated **1** increases from 8 ns to two lifetimes of approximately 10 and 16 ns. This increase in lifetime indicates that complexation to β-cyclodextrin decreases the rate of amine quenching of the naphthalene excited state. This conclusion is supported by the fact that the intensity of the

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naphthalene-like emission remains approximately constant with increasing cyclodextrin concentration. The observation of two lifetimes is probably due to two complexes of different geometry. The exciplex lifetimes are 5, 7, and 11 ns for ethanol, acetonitrile, and β-cyclodextrin solutions, respectively (Table I).

The data support a model where **1** forms an emissive 1:1 complex with β-cyclodextrin in water. Surprisingly, the β-cyclodextrin cavity for exciplex has a polarity similar to that of ethanol, considerably higher than anticipated. The results suggest that the intramolecular exciplex of **1** formed must be situated near the top of the β-cyclodextrin cavity in the proximity of OH groups, an environment considerably different from that of excimers. Exciplexes, which possess intrinsic charge-transfer character, are more polar than excimers. Their formation is governed by a delicate balance between their stabilization and dissociation to ion pairs by the polar environment.

The failure to observe intramolecular exciplex emission of **1** in α-cyclodextrin and in γ-cyclodextrin may be attributed to steric factors. The former possesses too small a cavity for association with **1**, while the latter possesses too large a cavity, where polar water molecules may enter freely to cause the dissociation of the exciplex to ion pairs. The effect of cyclodextrins on other intramolecular exciplex systems is being investigated.

Formation of Thermalized Singlet Silylene in the Reactions of Recoiling Silicon Atoms[†]

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The 1966 suggestion that silylene (SiH_2) is formed in the gas-phase reactions of high-energy recoiling silicon atoms[1] has been successful in accounting qualitatively for many of the chemically stable end products detected in these "hot atom" experiments.[1-7] Since studies of thermally generated silylene had led to an estimate of 1.2 for the relative reactivity of silane and butadiene toward *singlet silylene* at 385 °C, it was disconcerting to find that silane was 9 times as reactive as butadiene toward a common intermediate, X, formed from recoiling silicon atoms in ternary mixtures of phosphine,[8] silane, and butadiene.[9]

[†] This paper is dedicated to Professor William von Eggers Doering whose inspiration fuels so much of chemistry.

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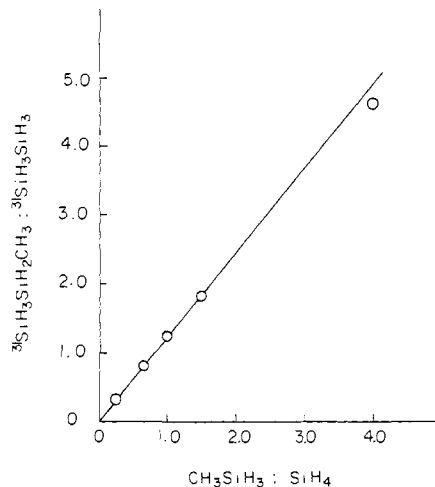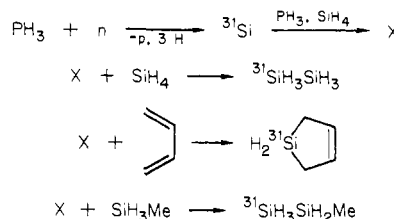

Figure 1. Ratio of disilane products $^{31}SiH_3SiH_2CH_3$:$^{31}SiH_3SiH_3$ as a function of substrate ratio CH_3SiH_3:SiH_4 in the reactions of recoiling ^{31}Si atoms in mixtures of 500 torr PH_3 and 500 torr CH_3SiH_3 + SiH_4.
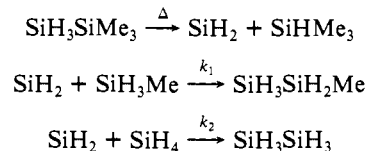
Scheme I

Scheme I includes the reaction of X with methylsilane, since competition experiments have now been undertaken with ternary mixtures of phosphine, silane, and methylsilane to answer the question: is X really ground-state singlet silylene? The SiH_3Me, SiH_4 substrate pair was chosen for recoil experiments because its relative reactivity toward thermally generated SiH_2 had been measured.[10]

When the yield ratios of $^{31}SiH_3SiH_2Me$ and $^{31}SiH_3SiH_3$, the products expected from Si–H insertion by nucleogenic $^{31}SiH_2$, are plotted against the substrate ratios as in Figure 1,[11] their slopes are the relative reactivity of methylsilane and silane toward whatever intermediates X give rise to these "silylene products". The observed ratio 1.32 ± 0.04 is in good agreement with the ratios k_1:k_2 measured by Paquin and Ring at high temperatures (Scheme II) but is too large to be reconciled with their differential activation parameters.[10]

Scheme II

$$SiH_3SiMe_3 \xrightarrow{\Delta} SiH_2 + SiHMe_3$$

$$SiH_2 + SiH_3Me \xrightarrow{k_1} SiH_3SiH_2Me$$

$$SiH_2 + SiH_4 \xrightarrow{k_2} SiH_3SiH_3$$

The reactivity ratios k_1:k_2 found by Paquin and Ring to vary from 1.30 at 287 °C to 0.967 ± 0.05 at 246 °C could be extrapolated to 0.044 at 25 °C.

We have varied the recoil reaction parameters, and the resulting data have led to several conclusions: (1) From 27 to 202 °C the reactivity ratio is constant within experimental error. (2) The presence of a 7-fold excess of argon or a $12^1/_2$-fold excess of ethane, both inert moderators, also leaves the reactivity ratio unchanged. Hence intermediate X carries little, if any, excess kinetic or vibrational energy.[12]   (3) Xenon, an inert "spin

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(11) The combined absolute yields of $^{31}SiH_3SiH_2Me$ and $^{31}SiH_3SiH_3$ totaled 40–50% at room temperature in mixtures containing 500 torr PH_3 and 500 torr SiH_3Me + SiH_4.