J. Org. Chem. **1990**, *55*, 5595-5601 **5595**

The Role of Substituents on Carbodication Stability

Richard M. Pagni,*,† Winn Peebles,† Robert C. Haddon,‡ and Sigma V. Chichester‡

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600, and AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Received May 31, 1990

The exchange reactions of a series of phenalenyl cations, **2a,c**, **6a–d**, **7**, and **8**, were examined in CF_3SO_3D by ^1H NMR spectroscopy. For ions **6a–c** with amino substituents, competing protonation of the substituents was observed. Exchange reactions at C-2 of ions **2a** and **8** were especially rapid. Exchange at C-5 for a series of 1,9-disubstituted phenalenyl cations was quantitatively correlated with σ_p^+ values for the substituents. The correlation equation can be used to predict the reactivity at C-5 for other phenalenyl cations. The role of the number, nature, and location of the substituents in affecting the rate is noted. The results of the experiments are consistent with a mechanism in which the ions are protonated to form carbodications, which are species of current research interest.

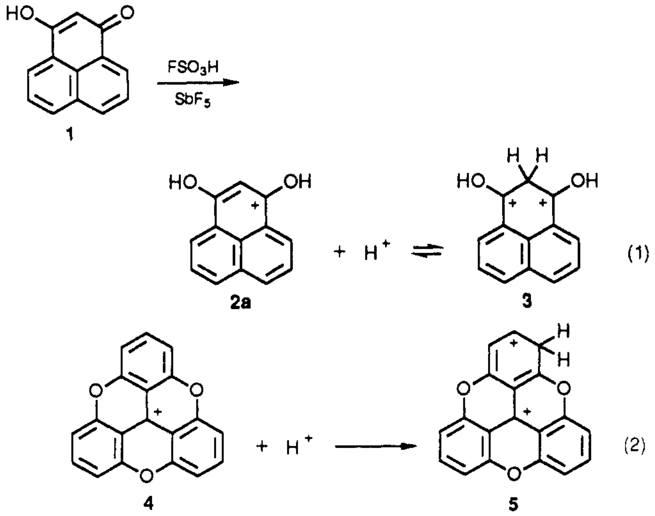
Introduction

The synthesis and characterization of multiply charged organic cations, both in solution and in the gas phase, is a topic of current interest.[1] Part of the fascination with this area is to see if species that differ only in charge vary in structure. Theoretical studies on ion structure and stability have been invaluable[2] because charged ions are often difficult to prepare in solution and, when prepared in the gas phase, difficult to characterize.

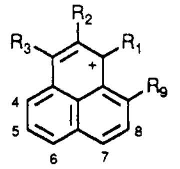
Multiply charged cations will in general be more difficult to prepare because of their large heats of formation, but the same technology used to prepare cations with unit charge still might be viable. One of these methods involves protonation. Protonation of an uncharged species will, of course, generate a carbocation, protonation of a carbocation will yield a carbodication, and so forth. One would expect this to become increasingly difficult, however, because of charge repulsion due to Coulomb's Law. In fact, the reverse reactions should be favored because fragmentation separates the positive charges. This is the basis of the exciting new technique of Coulomb explosion.[3]

Some years ago we discovered that certain carbodications are easily prepared by protonation of the corresponding carbocations.[4] 1,3-Dihydroxyphenalenyl cation (**2a**) yields, for example, carbodication **3** in 100% magic acid (1:1 FSO_3H–SbF_5)/liquid SO_2 at −80 °C. In fact the carbodication is the predominant species at equilibrium under these conditions. On the other hand, ion **4** yielded dication **5** irreversibly under similar conditions. Clearly the strength of the acid ($H_0 \approx -17$[5]), and the presence of cation-stabilizing hydroxyl groups in **2a** and oxygen atoms in **4** contributed significantly to these results.

Direct observation of carbodications by ^1H or ^{13}C NMR spectroscopy, as was done for the two prior examples, was not always possible. In these cases it was still possible to learn much about the dications by the position and rate of deuterium exchange for the monocation in the weaker CF_3SO_3D ($H_0 = -14.1$ for CF_3SO_3H[5]).[4a,b] Ion **2a**, for example, underwent a very rapid exchange at position 2 and a much slower exchange at positions 5 and 8. Thus, two carbodications of widely differing stability exist in this system.



The phenalenyl ring system has proven to be an ideal system in which to investigate the phenomenon of cation protonation. There are several reasons for this: The ion precursors are easy to prepare; the ring system contains an extensive π-system in which to delocalize one or more positive charges; the ring system, even when substituted, yields interpretable NMR spectra; and, it is possible to place a variety of substituents at various positions onto the ring. Many of these factors came into play in the study of the deuterium exchange in hydroxy-substituted phenalenyl cations (**2a–d**) in CF_3SO_3D.[6] It was found that the number and position of the substituents profoundly influenced the position and rate of exchange. The details of this work will be discussed at a later moment in this paper.



2a: $R_1 = R_3 = OH$; $R_2 = R_9 = H$
b: $R_1 = R_2 = OH$; $R_3 = R_9 = H$
c: $R_1 = R_9 = OH$; $R_2 = R_3 = H$
d: $R_1 = OH$; $R_2 = R_3 = R_9 = H$
e: $R_1 = R_2 = R_3 = R_4 = H$

---

† University of Tennessee.

‡ AT&T Bell Laboratories.

(1) (a) Prakash, G. K. S.; Rawdah, T. N.; Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 390. (b) Pagni, R. M. *Tetrahedron* **1984**, *40*, 4161. (c) Koch, W.; Maquin, F.; Stahl, D.; Schwarz, H. *Chimia* **1985**, *39*, 376.

(2) (a) Lammertsma, K.; Schleyer, P. v. R.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1321. (b) Radom, L.; Gill, P. M. W. *J. Am. Chem. Soc.* **1988**, *110*, 5311. (c) Wong, M. W. *J. Am. Chem. Soc.* **1989**, *111*, 1156. (d) Lammertsma, K.; Güner, O. F.; Thibodeaux, A. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1989**, *111*, 8995.

(3) Vager, Z.; Naamen, R.; Kanter, E. P. *Science* **1989**, *244*, 426.

(4) (a) Pagni, R. M.; Smith, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 506. (b) Smith, R. J.; Pagni, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 4769.

(5) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley: New York, 1985.

(6) (a) Pagni, R. M.; Smith, R. J.; Moore, T.; Burnett, M. N. *Isr. J. Chem.* **1980**, *20*, 308. (b) Smith, R. J.; Moore Miller T.; Pagni, R. M. *J. Org. Chem.* **1982**, *47*, 4181.

0022-3263/90/1955-5595$02.50/0

Table I. ^1H NMR Spectral Data for Phenalenyl Cations in CF_3SO_3H[a]

ion	H-2	H-3	H-4	H-5	H-6	H-7	H-9	H-10
6a	8.05	8.84	8.68	8.22	8.68	8.84	8.05	-
6b	7.97	8.89	8.75	8.25	8.75	8.89	7.97	-
6c	see text and Figure 1							
6d	7.79	8.93	8.78[b]	8.19	8.81[b]	8.61	8.21	-
7	8.78	9.14	9.06	8.58	9.06	9.14	8.78	-
8	7.06	-	-	7.83	8.82	8.82	7.83	-
2a	6.89	-	9.09	8.09	8.74	8.74	8.09	9.09
2c	7.54	8.72	8.58	7.94	8.58	8.72	7.54	-

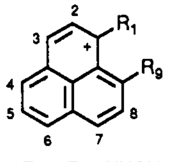
(columns H-2 to H-10 under: chemical shift of)

[a] Internal standard Me_4N^+ (δ 3.10). [b] The assignments for H-4 and H-6 may be reversed.

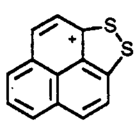
If the protonation of cations is to become a viable, general method for the preparation of carbodications, much more needs to be known about the factors that not only make the reaction possible, but also facile. To this end we report below an extensive study of the protonation of additional substituted phenalenyl cations in CF_3SO_4H(D).[7]

Results and Discussion

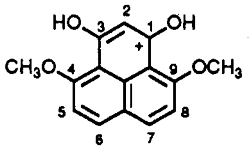
The ions **6a–d**, **7**, and **8** were chosen for study because of their availability and varied substituents, which occur mainly at the one and nine positions. Ion **8**, on the other hand, has four activating substituents at position 1, 3, 4, and 9. Ions **2a** and **2c** were also reexamined so that a better comparison of the behavior of the present ions can be made to those reported in our earlier work.[4,6] A solution of **7** was prepared by dissolution of the corresponding tetrafluoroborate salt in acid. Solutions of the other ions were prepared by protonation of the corresponding ketone, thione or imine.[8] Prior work has shown that protonation of phenalenones in CF_3SO_3H(D) is essentially irreversible and quantitative.[6b] Protonation of 9-aminophenalenone has been shown by Solodař and Kochkin to occur exclusively on the carbonyl oxygen.[9] The evidence here is that in all cases protonation occurs quantitatively at the site that gives the phenalenyl cation.



6a: $R_1 = R_9 = NHCH_3$
b: $R_1 = R_9 = NH_2$
c: $R_1 = OH$; $R_9 = NH_2$
d: $R_1 = OH$; $R_9 = SH$



7



8

The ^1H NMR spectral data of the ions are presented in Table I. The assignments are straightforward and based on the effect of charge on chemical shift, splitting patterns, extensive decoupling experiments, and comparison to the spectra of known ions. In the case of the unsymmetrical **6d**, the assignments of H-2 and H-8 were based on a comparison to the spectra of ions **2c** and **7** and neutral thiophenols and phenols; the assignments of H-3 and H-7 then follow from the assignments of H-2 and H-8. The assignments of H-4 and H-6 remain unclear, however.

The 9-amino-1-hydroxyphenalenyl cation (**6c**) is interesting because its ^1H NMR spectrum at 200 MHz (Figure 1) clearly shows the presence of more than one species. This was confirmed by the ^{13}C NMR spectrum of the solution which showed 26 resonances; a single phenalenyl cation will yield only 13 resonances. The ^1H NMR spectrum is due to a 1:1 mixture of the cation **6c** and a dication **6c′** formed by protonation of the nitrogen atom of **6c**. Solodař and Kochkin have come to the same conclusion about this system by UV/vis spectroscopy.[9] It was possible to assign unequivocally the somewhat overlapping resonances to all 14 hydrogens of the two ions by methods described above. The assignments are shown above the resonances seen in Figure 1. It is clear from Figure 1 and eq 3 that ion **6c** shows accidental degeneracy of H-2 and H-8, H-3 and H-7, and H-4 and H-6. If one wants to observe deuterium exchange at C-2 and C-8 in ion **6c**, one must do this indirectly by examining the apparent exchange at C-2 and C-8 in ion **6c′**, which one can reasonably assume not to exchange in CF_3SO_3D.

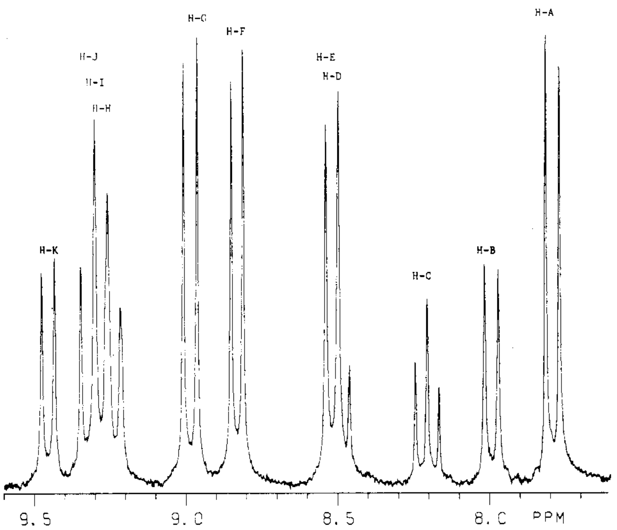
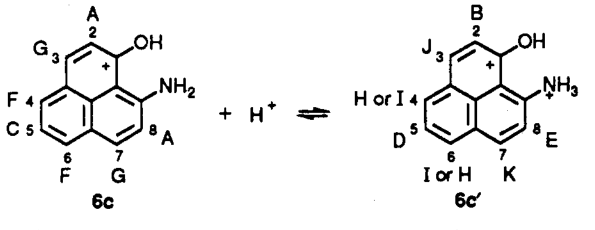


Figure 1. ^1H NMR spectrum of **6c** ⇌ **6c′**.



(3)

Because **6c** actually exists as an equilibrium mixture of a monocation and a nitrogen-protonated dication, it is reasonable to ask if the other ions in Table I, particularly **6a** and **6b**, and those studied earlier,[4,6] do not behave similarly. Except for **6c**, which was just described, and **6a** and **6b**, which will be described below, there is no evidence that the ions exist in an equilibrium similar to that in eq 3. For **6a**, except for a perturbation in the doublet at lowest field, the aryl hydrogen chemical shifts are, surprisingly, consistent with a single ion alone. This turns

---

(7) Some of this work has appeared in communication form: Peebles, W.; Pagni, R. M.; Haddon, R. C. *Tetrahedron Lett.* **1989**, 2727.

(8) The precursor to **6c** exists in an amino ketone–hydroxy imine equilibrium in organic solvents. Likewise, the precursor to **6d** exists in a thiol ketone–hydroxy thione equilibrium in neutral solvents.

(9) Solodař, S. L.; Kochkin, V. A. *J. Org. Chem. U.S.S.R* **1982**, *18*, 1096.

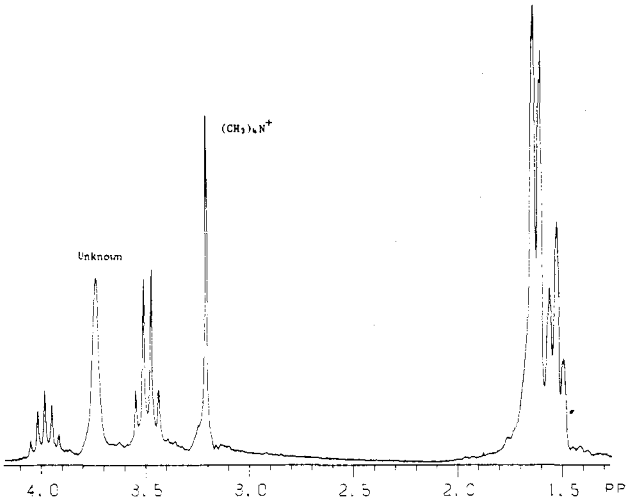
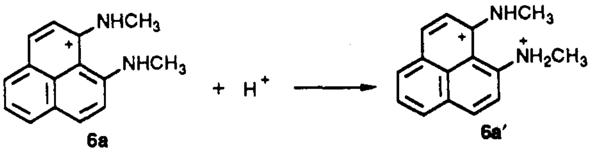


Figure 2. ^{1}H NMR spectrum of **6a** ⇌ **6a′** in the NH and CH_3 regions.

out to be due to a fortuitous overlap of the aryl peaks of **6a** and the dication **6a′** at 200 MHz, however. The NH and CH_3 regions of the proton spectrum (Figure 2) clearly show evidence of two species. The methyl region, for example, consists of a lower field doublet due to $NHCH_3$ and an upfield triplet due to $^+NH_2CH_3$. Spin decoupling shows the doublet to be coupled to the apparent quintet at δ 4.00, which is due to the overlap of slightly nonequivalent $NHCH_3$ quartets. The methyl triplet is coupled to the quartet at δ 3.50, which is assigned to $^+NH_2CH_3$. Consideration of these facts and peak integrations suggests that the solution contains a 1:5 mixture of ions **6a** and **6a′**.[10,11]

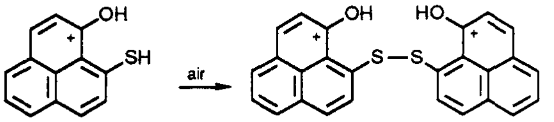


6a **6a′** (4)

Ion **6b** showed no evidence whatsoever for two cations in its ^{1}H NMR spectrum but, because of the behavior of **6a** and **6c** in CF_3SO_3H, this cannot be the case. Based on substituents on ions **6a** and **6c** and the equilibrium constants for eqs 3 and 4, a reasonable equilibrium ratio of **6b** and its nitrogen-protonated dication **6b′** is 1:3. Experiments to be described later are also consistent with this ratio.

Because the exchange rates in CF_3SO_3D are measured by observing changes in peak integrations and multiplicities of aryl hydrogens in the monocations, how can one obtain the desired information for **6a** and **6b** when the chemical shifts for their aryl hydrogens exactly match those of the dications **6a′** and **6b′**, respectively? It is easy to show (Appendix 1) that this situation causes no problem and that one can obtain the desired information from the observed peaks in the normal manner.

The exchange reactions were treated as irreversible and pseudo-first-order because the reactions are run with a large excess of CF_3SO_3D. Except for cation **7** whose exchange was particularly slow, all the ions exchanged only at the central C-H position of each six-membered ring. This is entirely consistent with the electrophilic addition of D^+ to form a σ-complex having two charges stabilized by the substituents located at the corner position of the rings. Addition of the D^+ to the corner position would not yield such stabilization. Ion **7** also underwent exchange at positions 4 and 6, in addition to the expected exchange at positions 2, 5, and 8. The unusual exchange likely occurred through a species other than the cation. Ion **2b**, which also reacted at a very slow rate and at unexpected positions, undoubtedly behaved similarly.[6] Ion **7** was unusual in one other respect. In the presence of air it underwent an irreversible reaction to form an ion tentatively assigned to the interesting disulfur-bridged dication **6**. The air oxidation of thiols to form disulfides is, of course, a well-known reaction. This air oxidation complicated the analysis of the exchange behavior of **7** in CF_3SO_3D but caused no problem when the exchange experiment was run on a degassed sample.



7 **9** (5)

For most of the phenalenyl ions it was not necessary to correct the kinetics data, but for **6a**, **6b**, and **6c** it was because of the competing protonation of the nitrogen atom. The behavior of these systems can be represented as:

$$PHD^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PH^+ + D^+ \tag{6}$$

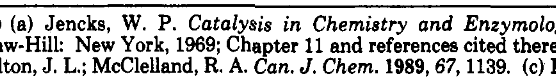
$$PH^+ + D^+ \xrightarrow{k_2} PD^+ + H^+ \tag{7}$$

where PH^+ and PD^+ are the monocations before and after exchange and PHD^{2+} is the nitrogen-protonated dication. This system should not be confused with a preequilibrium scheme in which PH^+ would be treated as a transient with a small steady-state concentration, which is certainly not true here. In the present case, where k_1 and $k_{-1} \gg k_2$, the following equation is true:

$$k_{\text{obs}} = k_2 \frac{[PH^+]_0}{[PH^+]_0 + [PHD^{2+}]_0} \tag{8}$$

where $[PH^+]_0$ and $[PHD^{2+}]_0$ are the initial concentrations of PH^+ and PHD^+ which are known from the NMR studies in CF_3SO_3H. In other words, $k_{\text{obs}} = k_2$ times the fraction of the phenalenyl ions in the monocation state. Equation 8 has previously been used by other researchers in many circumstances and guises,[12] but its derivation has always been intuitive. Because chemical systems which mimic eqs 6 and 7 are common, a mathematical proof of the validity of eq 8 is presented in Appendix 2.

Even the k_2's could be corrected further because the rate constants are pseudo-first-order. Furthermore, if one imposes a mechanism onto eq 7, e.g., eq 9, a further correction to yield the desired k_3 is required. Because these corrections are essentially the same for all the ions studied (Appendix 2, part 3), they have not been applied here.



$$PH^+ + D^+ \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} P{<}^{H}_{D}\,{}^{2+} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} PD^+ + H^+ \tag{9}$$

---

[10] The observed relative integrations of the quintet, quartet, doublet, and triplet (going from low to high field) were 10:15:50:27. The best fit of these data was for a 1:5 mixture of **6a** to **6a′** in which relative integrations of 12:14:38:27 are expected. Other admixtures of **6a** anf **6a′** yielded poorer fits.

[11] The broad singlet at δ 3.7 is attributed to an unknown species. There is no evidence to believe that this peak is associated with the **6a**–**6a′** system.

(12) (a) Jencks, W. P. *Catalysis in Chemistry and Enzymology*; McGraw-Hill: New York, 1969; Chapter 11 and references cited therein. (b) Bolton, J. L.; McClelland, R. A. *Can. J. Chem.* **1989**, *67*, 1139. (c) For a different approach, see: Ritchie, C. D *Physical Organic Chemistry*, 2nd ed.; Marcel Dekker: New York, 1990; p 43.

Table II. Exchange Half-lives of Phenalenyl Cations in CF_3SO_3D[a]

	substituents				$\tau_{1/2}$[b] of			total $\tau_{1/2}$[b]
substrate	R_1	R_3	R_4	R_9	H-2	H-5	H-8	(H-2, H-5 + H-8)
6a	$NHCH_3$			$NHCH_3$	0.058	0.32	0.058	0.027
6b	NH_2			NH_2	0.26	0.70	0.26	0.11
6c	OH			NH_2	6.5	2.0	0.25	0.21
2c	OH			OH	1.3	4.0	1.3	0.56
6d	OH			SH	2.5	15	6.0	1.6
7[c]	-S-S- bridge at C-1 and C-9				7.0	no exchange	7.0	3.5
8	OH	OCH_3	OCH_3	OH	<0.02 s (25 °C)[d]	53 min (25 °C)[e]	53 min (25 °C)[e]	<0.02 s
2a	OH	OH			90 s (25 °C)[e]	9.0	9.0	90 s

[a] At 60 °C unless noted otherwise. [b] In days unless noted otherwise. [c] Exchange at C-4 and C-6 also occurs, with $\tau_{1/2}$ = 7.2 days at each position. [d] Estimated value. [e] Experiments were run entirely in the probe of the NMR spectrometer.

Table III. Correlation of Rate of Exchange at C-5 and Substituent Constants for 1,9-Disubstituted Phenalenyl Cations

substrate	log $\tau_{1/2}$(H-5)	$\Sigma\sigma_p^+$ (substituents)[a]
6a	−0.495	−3.0 (NHMe, NHMe)[b]
6b	−0.155	−2.6 (NH_2, NH_2)
6c	+0.301	−2.22 (OH, NH_2)
2c	+0.602	−1.84 (OH, OH)
6d	1.176	−0.98 (OH, SH)[c]
7	(1.965)	−0.12 (-SS-)[d]

[a] $\sigma_p^+(NHCH_3) = -1.5$, $\sigma_p^+(NH_2) = -1.3$, $\sigma_p^+(OH) = -0.92$, $\sigma_p^+(SH) = -0.06$. [b] $\sigma_p^+(NHMe) = {}^1/_2[\sigma_p^+(NH_2) + \sigma_p^+(NMe_2)]$, $\sigma_p^+(NMe_2) = -1.7$. [c] σ_p^+(SH) was taken equal to σ_p^+(SMe). [d] Value calculated from the correlation. $\sigma_p^+(\text{-SS-}) = 2\sigma_p^+(SH)$.

The results of the experiments are reported in Table II as half-lives of exchange of H-2, H-5, and H-8. Total half-lives of exchange at the three sites can be computed (Appendix 3) and are also reported in Table I. The total half-lives of exchange, as well as the individual half-lives, are in qualitative agreement with expectations based on the nature of the substituents and their number. 1,3-Dihydroxyphenalenyl cation (**2a**) is notable in that it exchanges much more rapidly than any other disubstituted ion, even those with more activating amino groups. Phenalenyl cation **8** reacts even more rapidly than **2a**[13] because it not only has the structural features of **2a** but also two additional activating substituents. The distance between the site of exchange and the substituent is an especially important factor in determining the ease of exchange. Carbon 2 (C-2) in both **2a** and **8**, for example, is flanked by two hydroxyl groups. With the exception of cation **6c**, the other five 1,9-substituted phenalenyl cations exchange more rapidly at C-2 and C-8, the sites adjacent to the substituents, than at C-5 which is more remote from the substituents. The behavior of the unsymmetrical cations, **6c** and **6d**, was also interesting because, at the sites next to the substituents, exchange occurred more rapidly next to the more activating group, NH_2 (versus OH) for **6c** and OH (versus SH) for **6d**. When identical groups are attached to the phenalenyl cation, the location of the groups is also important. **2a** exchanges much more rapidly (at C-2) than **2c**, even though they both contain two hydroxyl groups at activating positions. The 1,2-dihydroxyphenalenyl cation **2b** is the least reactive of the three dihydroxyl ions because one of the substituents is at a deactivating position (C-2).[6b]

Because the proton resonances of the equilibrating **6c** and **6c′** do not overlap severely in CF_3SO_3H, it was possible to observe exchange in both ions, even though exchange actually only occurs in the monocation **6c**. As expected, H-5 in both ions exchanged at identical rates. It was not possible, however, to compare directly the exchange rates of H-2 and H-8 because the two hydrogen have identical chemical shifts in ion **6c**. The apparent $\tau_{1/2}$ for H-2 and H-8 for **6c** is 1.25 days, whereas $\tau_{1/2}$ for H-2 = 6.5 days and $\tau_{1/2}$ for H-8 = 0.25 days as measured from cation **6c′**. It can be shown (Appendix 4) that the two sets of values measured in the two cations are in reasonable agreement.

$$\begin{tikzcd} \mathbf{6c} \arrow[r, shift left, "\text{fast}"] \arrow[dr, "\text{slow}"'] & \mathbf{6c'} \arrow[l, shift left] \arrow[d, "\times"] & \text{(measure exchange at C-2 and C-8 in this ion)} \quad (10) \\ & \text{exchange} & \end{tikzcd}$$

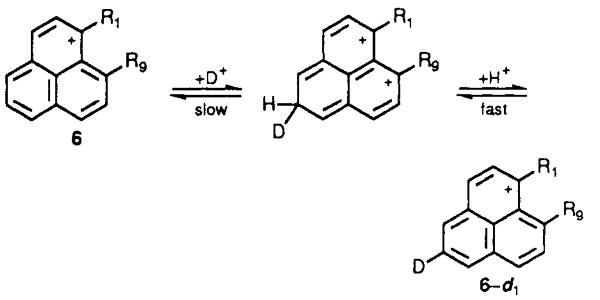
An excellent quantitative correlation of rate and substituent effect was also obtained; this is consistent with a mechanism in which there is a build up of charge in the rate-determining step (eq 11). Only phenalenyl cations with substituents at the 1- and 9-positions were used, whose substituents then were correlated with the rate of exchange at C-5 only. This site was chosen because it is equidistant to the two substituents. σ_p^+ values were used for the substituent constants because an increase of one positive charge in going from reactant to intermediate in the rate-determining step is expected (eq 11). The correlation attempted was log $\tau_{1/2}$(H-5) versus $\Sigma\sigma_p^+$, where $\Sigma\sigma_p^+$ is the sum of the two substituent constants. The data are collected in Table III. The correlation yielded the equation log $\tau_{1/2}(\text{H-5}) = 0.836\Sigma\sigma_p^+ + 2.065$, with a correlation coefficient of 0.993. Because $\tau_{1/2}$ and k, the rate constant for exchange, are inversely related, the slope of the equation yields $\rho = -0.836$.[14] A negative slope is expected in a reaction involving a build up of positive charge, but the electron demand of the substituents is not very large. This can be attributed to the fact that (1) the phenalenyl ions possess two, rather than the normal one, substituents; (2) the positive charges are more extensively delocalized than in benzene derivatives; and (3) the substituents on the phenalenyl cations are more removed from the reaction center than they are on benzene.

Several other things are worth noting about the correlation. First, ion **7** undergoes exchange at C-5 at a rate too slow to measure. This is understandable because the correlation equation predicts the $\tau_{1/2}$ (H-5) for **7** to be 92 days. Second, ion **2d** with a single substituent (OH) at C-1

---

[13] Because of the facile exchange with protons in CF_3SO_3H, H-2 is severely broadened in the ^1H NMR spectrum of **8**. The $\tau_{1/2}$(H-2) reported in Table II was estimated by comparison to the $\tau_{1/2}$ values for H-5 and H-8 in **8** with those for the H-2, H-5, and H-8 in **2a**. The 2,2′,2″,6,6′,6″-hexamethoxytriphenylmethyl cation shows even more rapid exchange in CF_3SO_3H.[4a]

[14] It is easy to show that ρ will be the same if the pseudo-first-order rate constants are corrected for $[D^+]$ and a mechanism such as that of eq 11 imposed on the data.



(11)

is predicted to have a half-life of exchange of about 20 days at C-5,[15] while the unsubstituted phenalenyl cation **2e** should have a half-life of exchange of a little less than 39 days at the same position.[16] These predictions are in good agreement with our prior work.[6] Lastly, the correlation equation nicely accounts for the behavior of **6b**. Recall that the rate data for this ion had to be corrected because the ion is presumed to be in equilibrium with an undetected nitrogen-protonated dication **6b′**; the monocation and dication were assumed to be present in a 1:3 ratio. Had this estimate not been essentially correct, the correction would have been poorer.

Conclusion

The behavior of a large number of phenalenyl cations in CF_3SO_3H and other stronger acids has been examined in the present and earlier reports. The rate of exchange in CF_3SO_3D is not only determined by the nature and number of substituents but also, and perhaps most importantly, by the location of the groups. Several of the ions, notably the amino-substituted and the tetrasubstituted ones, exchange fast enough in CF_3SO_3D that the corresponding dications should be detectable by ^1H NMR spectroscopy in still stronger acids, as was the case with the 1,3-dihydroxyphenalenyl cation (**2a**). One should be able to use the equilibrium mixtures of mono- and dications as indicators in acidity function measurements in the highly acidic regime where there are presently few reliable values.

Experimental Section

Trifluoromethanesulfonic acid (CF_3SO_3H) was purified by distillation before use. CF_3SO_3D was prepared from CF_3SO_3H as previously described.[17] 3-Hydroxyphenalenone, the precursor to **2a**, was prepared by the method of Eistert et al.,[18] and 9-hydroxyphenalenone, the precursor to **2c**, was prepared by the method of Haddon et al.[19] 9-Mercaptophenalenone, 9-aminophenalenimine, and 9-(*N*-methylamino)-1-(methylimino)phenalene, the precursors to **6d**, **6b**, and **6a**, respectively, were prepared by the methods of Franz and co-workers.[20] 3-Hydroxy-4,9-dimethoxyphenalenone[21] and 9-aminophenalenone,[22] the precursors to **8** and **6c**, were synthesized by the procedures of Haddon and co-workers. Phenaleno[1,9-*cd*]dithiolium hexafluorophosphate, the source of **7**, was also prepared by a method developed by Haddon.[19]

Solutions of the ions in CF_3SO_3H and CF_3SO_3D were prepared as described in an earlier study[6b] and were ordinarily not degassed. When degassed samples were required, the degassing was accomplished by several freeze–pump–thaw cycles on a vacuum line. ^1H NMR spectra were obtained at 200 MHz. The tetramethylammonium ion was used internally as the chemical shift standard (δ 3.10). Peak integrations for the samples were compared to those for the tetramethylammonium ion peak. Because spectra could be obtained with just a few pulses and then stored, it was possible to monitor reactions having very short half-lives.

Appendix 1

In Appendix 2, it is shown that for

$$\mathrm{PHD^{2+}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{PH^+} + \mathrm{D^+} \tag{1}$$

$$\text{and} \quad \mathrm{PH^+} + \mathrm{D^+} \xrightarrow{k_2} \mathrm{PD^+} + \mathrm{H^+}, \tag{2}$$

$$[\mathrm{PHD^{2+}}] = [\mathrm{PHD^{2+}}]_0 e^{r_1 t} \tag{3}$$

$$\text{and} \quad [\mathrm{PH^+}] = [\mathrm{PH^+}]_0 e^{r_1 t}, \tag{4}$$

$$\text{where} \quad r_1 = -\frac{[\mathrm{PH^+}]_0}{[\mathrm{PH^+}]_0 + [\mathrm{PHD^{2+}}]_0} k_2 \tag{5}$$

If the ^1H NMR signals for PH^+ and PHD^{2+} fortuitously merge, it follows that

$$([\mathrm{PHD^{2+}}] + [\mathrm{PH^+}]) = ([\mathrm{PHD^{2+}}]_0 + [\mathrm{PH^+}]_0) e^{r_1 t} \tag{6}$$

In other words, one can derive r_1 even when one cannot detect PHD^{2+} and PH^+ individually.

Appendix 2

Part 1. Consider the reaction of phenalenyl cation PH^+, either by the reversible protonation of a heteroatom to form PHD^{2+} or onto the ring to give ultimately the deuterated phenalenyl cation PD^+

$$\mathrm{PHD^{2+}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{PH^+} + \mathrm{D^+} \tag{1}$$

$$\mathrm{PH^+} + \mathrm{D^+} \xrightarrow{k_2} \mathrm{PD^+} + \mathrm{H^+} \tag{2}$$

Because the interconversion of PHD^{2+} and PH^+ is fast, $k_2 \ll k_1$ and k_{-1}, where k_2 and k_{-1} are pseudo-first-order rate constants. Also, because of the large excess of D^+, reaction 2 is essentially irreversible. Thus,

$$\frac{d[\mathrm{PHD^{2+}}]}{dt} = -k_1[\mathrm{PHD^{2+}}] + k_{-1}[\mathrm{PH^+}] \tag{3}$$

and

$$\frac{d[\mathrm{PH^+}]}{dt} = k_1[\mathrm{PHD^{2+}}] - (k_{-1} + k_2)[\mathrm{PH^+}] \tag{4}$$

This is a set of first-order differential equations[23] whose solution is of the form

$$[\mathrm{PHD^{2+}}] = A_1 e^{r_1 t} + A_2 e^{r_2 t} \tag{5}$$

and

$$[\mathrm{PH^+}] = B_1 e^{r_1 t} + B_2 e^{r_2 t} \tag{6}$$

where

$$r_{1,2} = \frac{(-k_1 + k_{-1} + k_2) \pm [(k_1 + k_{-1} + k_2)^2 - 4k_1k_2]^{1/2}}{2} \tag{7}$$

If $[\mathrm{PHD^{2+}}] = [\mathrm{PHD^{2+}}]_0$ and $[\mathrm{PH^+}] = [\mathrm{PH^+}]_0$ at $t = 0$,

---

[15] For **2d**, $\Sigma\sigma^+ = -0.92 + 0 = -0.92$.

[16] For **2e**, $\Sigma\sigma^+ = 0$. $\tau_{1/2}$ has been statistically corrected.

[17] Smith, R. J.; Pagni, R. M. *J. Org. Chem.* **1981**, *46*, 4307.

[18] Eistert, B.; Eifler, W.; Goth H. *Chem. Ber.* **1968**, *101*, 2162.

[19] Haddon, R. C.; Wudl, F.; Kaplan, M. L.; Marshall, J. H.; Cais, R. E.; Bramwell, F. B. *J. Am. Chem. Soc.* **1978**, *100*, 7629.

[20] Franz, K. D.; Martin, R. L. *Tetrahedron* **1978**, *34*, 2147.

[21] Haddon, R. C.; Hirani, A. M.; Kroloff, N. J.; Marshall, J. H. *J. Org. Chem.* **1983**, *48*, 2115.

[22] Haddon, R. C.; Chichester, S. V.; Mayo, S. L. *Synthesis* **1985**, 639.

[23] Martin, W. T.; Reissner, E. *Elementary Differential Equations*; Addison-Wesley: Reading, MA, 1961.

$$A_1 = (k_1(k_{-1} + k_2 + r_1)[\mathrm{PHD}^{2+}]_0 - (k_{-1} + k_2 + r_1)(k_{-1} + k_2 + r_2)[\mathrm{PH}^+]_0)/k_1(r_1 - r_2) \quad (8)$$

$$A_2 = [\mathrm{PHD}^{2+}]_0 - A_1 \quad (9)$$

$$B_1 = \frac{k_1}{k_{-1} + k_2 + r_1} A_1 \quad (10)$$

$$\text{and} \qquad B_2 = \frac{k_1}{k_{-1} + k_2 + r_2} A_2 \quad (11)$$

Equations 5 and 6 are not useful in their present form, but can be greatly simplified because $k_1, k_{-1} \gg k_2$. When these inequalities are applied, r_1 and r_2 simplify to

$$r_2(-\text{root}) \approx -(k_1 + k_{-1}) \quad (12)$$

and

$$r_1(+\text{root}) \approx -\frac{[\mathrm{PH}^+]_0}{[\mathrm{PH}^+]_0 + [\mathrm{PHD}^{2+}]_0} k_2 \quad (13)$$

The derivation of eq 13 is found in part 2 below. Because $k_1 + k_{-1}$ is large and k_2 is small, e^{r_2t} decays very rapidly and e^{r_1t} slowly. Furthermore, $A_1 \approx [\mathrm{PHD_0}^{2+}]$, which yields $A_2 \approx 0$, and $B_1 \approx [\mathrm{PH}^+]_0$, which yields $B_2 \approx 0$. Therefore,

$$[\mathrm{PHD}^{2+}] = [\mathrm{PHD}^{2+}]_0 \exp\left[-\left(\frac{[\mathrm{PH}^+]_0}{[\mathrm{PH}^+]_0 + [\mathrm{PHD}^{2+}]_0}\right)k_2t\right] \quad (14)$$

and

$$[\mathrm{PH}^+] = [\mathrm{PH}^+]_0 \exp\left[-\left(\frac{[\mathrm{PH}^+]_0}{[\mathrm{PH}^+]_0 + [\mathrm{PHD}^{2+}]_0}\right)k_2t\right] \quad (15)$$

Part 2. The equation in part 1 that yields r_1 and r_2 is

$$r^2 + (k_1 + k_{-1} + k_2)r + k_1k_2 = 0 \quad (1)$$

Because $k_1, k_{-1} \gg k_2$

$$k_1 + k_{-1} = k_1\left(\frac{[\mathrm{PHD}^{2+}]_0 + [\mathrm{PH}^+]_0}{[\mathrm{PH}^+]_0}\right) \quad (2)$$

If one lets $([\mathrm{PHD}^{2+}]_0 + [\mathrm{PH}^+]_0)/[\mathrm{PH}^+]_0 = R$ and $r' = r/k_2$,

$$k_2^2r'^2 + (Rk_1 + k_2)k_2r' + k_1k_2 = 0 \quad (3)$$

If one divides eq 3 by k_2^2 and lets $k_1/k_2 = A$, one gets

$$r'^2 + (RA + 1)r' + A = 0 \quad (4)$$

The solution to eq 4 is

$$r' = \frac{-(RA + 1)^2 \pm [(RA + 1)^2 - 4A]^{1/2}}{2} \quad (5)$$

Equation 5 is equivalent to eq 7, part 1. One can also solve eq 4 for A:

$$A = \frac{-r'(r' + 1)}{r'R + 1} \quad (6)$$

From this equation it can be seen that when $A = \infty$, $r' = -1/R$ or $-\infty$, and when $A = 0$, $r' = 0$ or -1. It is easy to see that for r_1'(+root of eq 5), $r_1' = 0$ when $A = 0$ and $r' = -1/R$ when $A = \infty$. Also for r_2'(−root of equation 5), $r_2' = -1$ when $A = 0$ and $r_2' = -\infty$ when $A = \infty$. Because the −root (r_2' and thus r_2) has been eliminated from eqs 3 and 4 of part 1, and because $k_1 \gg k_2$, i.e. $A = k_1/k_2$ is large, only the following need concern us:

$$r_1' = r_1/k_2 \rightarrow -1/R \text{ as } A \rightarrow \infty \quad (7)$$

$$\text{or} \qquad r_1 \rightarrow -(1/R)k_2 = -\left(\frac{[\mathrm{PH}^+]_0}{[\mathrm{PH}^+]_0 + [\mathrm{PHD}^{2+}]_0}\right)k_2 \text{ as } k_1/k_2 \rightarrow \infty \quad (8)$$

Therefore,

$$r_1 \approx -\left(\frac{[\mathrm{PH}^+]_0}{[\mathrm{PH}^+]_0 + [\mathrm{PHD}^{2+}]_0}\right)k_2 \text{ when } k_1, k_{-1} \ll k_2 \quad (9)$$

This solution can also be shown to be true empirically. When $k_1 = 10k_2$ and $[\mathrm{PH}^+]_0/([\mathrm{PH}^+]_0 + [\mathrm{PHD}^{2+}]_0) = {}^1/_6$, for example, the difference between the exact and approximate values of r_1 is only 1.4%. The error goes down as k_1/k_2 becomes larger. Note also that when $[\mathrm{PHD}^{2+}]_0 = 0$, r_1 becomes $-k_2$, as is expected. When $[\mathrm{PH}^+]_0$ is small, $r_1 = -Kk_2$ as is expected ($K = [\mathrm{PH}^+]_0/[\mathrm{PHD}^{2+}]$).

Part 3. The measured k_2, k_2(obs), is more appropriately expressed as

$$k_2(\text{obs}) = \left(\frac{[\mathrm{PH}^+]_0}{[\mathrm{PH}^+]_0 + [\mathrm{PHD}^{2+}]_0}\right)k_{\mathrm{EAS}} \quad (1)$$

where k_{EAS} is the corrected observed rate constant. k_{EAS} is still phenomenological. An expanded version of $\mathrm{PH}^+ + \mathrm{D}^+ \rightarrow \mathrm{PD}^+ + \mathrm{H}^+$ would include a σ complex:

$$\mathrm{PH}^+ + \mathrm{D}^+ \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{PHD}'^{2+} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{PD}^+ + \mathrm{H}^+ \quad (2)$$

where PHD'^{2+} is the σ complex (the prime is used to distinguish this dication from the one which is formed by protonation of a heteroatom). Because the reaction is essentially irreversible, k_{-4} can be ignored. Thus,

$$\frac{\mathrm{d}[\mathrm{PH}^+]}{\mathrm{d}t} = -k_3[\mathrm{D}^+][\mathrm{PH}^+] + k_{-3}[\mathrm{PHD}'^{2+}] \quad (2)$$

and

$$\frac{\mathrm{d}[\mathrm{PHD}'^{2+}]}{\mathrm{d}t} = k_3[\mathrm{D}^+][\mathrm{PH}^+] - (k_{-3} + k_4)[\mathrm{PHD}'^{2+}] \quad (3)$$

One may apply the steady-state approximation to eq 3 and apply the results to eq 2. This yields

$$\frac{\mathrm{d}[\mathrm{PH}^+]}{\mathrm{d}t} = -k_3\left(\frac{k_4}{k_{-3} + k_4}\right)[\mathrm{D}^+][\mathrm{PH}^+] \quad (4)$$

Therefore,

$$k_{\mathrm{EAS}} = k_3\left(\frac{k_4}{k_{-3} + k_4}\right)[\mathrm{D}^+] \quad (5)$$

$k_4/(k_{-3} + k_4)$, which represents the fraction PHD'^{2+} going on to PD^+, contains an isotope effect because k_4 represents breaking a C–H bond and k_{-3} breaking a C–D bond. Therefore, $k_4/(k_{-3} + k_4) < 1$ because $k_4/k_{-3} > 1$. For example, if $k_4/k_{-3} = 5.0$, $k_4/(k_{-3} + k_4) = 0.83$. In principle one can derive k_3 from k_{EAS}, but this was not done because $[\mathrm{D}^+]$ is constant from experiment to experiment and $k_4/(k_{-3} + k_4)$ is approximately constant throughout the series of compounds. Furthermore, the exact value of $k_4/(k_{-3} + k_4)$ is not known.

Appendix 3

One can derive the overall half-life of exchange (τ) from the individual half-lives τ_1, τ_2, τ_3, etc. If the overall rate constant for exchange is $k = k_1 + k_2 + k_3 + \ldots$, it follows that

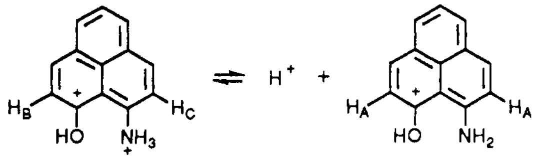
$$k = \frac{\ln 2}{\tau_1} + \frac{\ln 2}{\tau_2} + \frac{\ln 2}{\tau_3} + \ldots \qquad (1)$$

But $\tau = k/\ln 2$. Therefore

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \frac{1}{\tau_3} + \ldots \qquad (2)$$

Appendix 4

For ion **6c**, the question arises as to whether the rates of exchange at H_1 (H_B) and H_9 (H_C) as measured in the nitrogen-protonated dication correspond to the rates of exchange at the same positions in the monocation. The problem arises because H_1 and H_9 (H_A) in the monocation have identical chemical shifts. It follows that the exchange at H_A, H_B, and H_C is governed by the equations



$$H_B = H_{B_0}e^{-k_Bt} \qquad (1)$$

$$H_C = H_{C_0}e^{-k_Ct} \qquad (2)$$

$$\text{and} \qquad H_A = H_B + H_C = H_{B_0}e^{-k_Bt} + H_{C_0}e^{-k_Ct} \qquad (3)$$

But $H_{C_0} = H_{B_0}$ and $H_{A_0} = 2\ H_{B_0}$, therefore

$$H_A = \frac{H_{A_0}}{2}\ (e^{-k_Bt} + e^{-k_Ct}) \qquad (4)$$

Experiments showed $k_B = \ln 2/6.5d = 0.11d^{-1}$ and $k_C = \ln 2/0.25d = 2.8d^{-1}$. Thus,

$$H_A = \frac{H_{A_0}}{2}\ (e^{-0.11t} + e^{-2.8t}) \qquad (5)$$

But $H_A = {}^1/_2 H_{A_0}$ when $t = \tau_{1/2}$.

$$\text{Therefore, } \tfrac{1}{2}H_{A_0} = \tfrac{1}{2}H_{A_0}(e^{-0.11\tau_{1/2}} + e^{-2.8\tau_{1/2}}) \qquad (6)$$

This equation is true when $\tau_{1/2} = 0.87$ days. This is in reasonable agreement with the experimental value of 1.2 days.

Photochemical Cycloaddition Reactions of Cyanoacetylene and Dicyanoacetylene

James P. Ferris* and Jean Claude Guillemin

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180-3590

Received January 31, 1990

Photolysis of cyanoacetylene with 185- or 206-nm light yields 1,3,5-tricyanobenzene while 254-nm radiation yields a mixture of tetracyanocyclooctatetraenes, 1,2,4- and 1,3,5-tricyanobenzene. A polymer of cyanoacetylene is the major photoproduct. 1,3,5-Tricarbomethoxybenzene was the only photoproduct identified from the irradiation of methyl propiolate at 254 nm. Mono-, di-, and tricyanobenzenes are formed by irradiation of mixtures of acetylene and cyanoacetylene at 185, 206, and 254 nm along with trace amounts of cyclooctatetraenes. No photoadducts were detected on photolysis of mixtures of cyanoacetylene and CO or HCN. The tetracyanocyclooctatetraene structures were established by UV, MS, and NMR analyses. The ^{1}H NMR of the product mixture exhibited a singlet at δ 7.028 consistent with either **1** or **2** and two singlets at δ 6.85 and 6.91 assigned to **3**. Photolysis of mixtures of dicyanoacetylene and acetylene with either 185- or 206-nm light yielded 1,2-dicyanobenzene and (*E,Z*)-1-buten-3-yne-1,4-dicarbonitrile. These products were also obtained using 254-nm light along with a mixture of tetracyanocyclooctatetraenes. The same three singlets were observed in this product mixture as were observed in the tetracyanocyclooctatetraenes obtained from cyanoacetylene. From this observation it was concluded that the δ 7.02 signal is due to **2** and not **1**. The photolysis of cyanoacetylene and dicyanoacetylene in the presence of ethylene with 185-nm light yields 1-cyanocyclobutene and 1,2-dicyanocyclobutene, respectively. 2-Cyanobutadiene and 2,3-dicyanobutadiene are the photoproducts with 254-nm light. Reaction pathways are proposed to explain these findings.

Cyanoacetylene and dicyanoacetylene have a central role in many cosmochemical processes as indicated by their presence in the interstellar medium,[1] the atmosphere of Titan,[2,3] and the proposed role of cyanoacetylene in the formation of pyrimidines and some amino acids on the primitive Earth.[4-6] Cyanoacetylene and dicyanoacetylene are subjected to ultraviolet radiation in each of these environments, which may result in their conversion to more complex organic compounds. The layer of particulates in the atmosphere of Titan is probably due to the photolysis of aerosols which contain cyanocarbon compounds mixed with hydrocarbons such as acetylene and ethylene.[7,8] Photolysis of these aerosols may yield higher molecular weight compounds and polymers. One of the photochemical reactions of cyanoacetylene is dissociation to radicals with light of 193 nm (eqs 1, 2).[9] Some of these radicals may initiate the reaction of methane on Titan (eqs 3, 4).[10]

---

[1] Mann, A. P. C.; Williams, D. A. *Nature* **1980**, *283*, 721–725.

[2] Kunde, V. G.; Aikin, A. C.; Hanel, R. A.; Jennings, D. E.; Maguire, W. C.; Samuelson, R. E. *Nature* **1981**, *292*, 686–688.

[3] Yung, Y. *Icarus* **1987**, *72*, 468–472.

[4] Ferris, J. P.; Sanchez, R. A.; Orgel, L. E. *J. Mol. Biol.* **1968**, *33*, 693–704.

[5] Ferris, J. P.; Zamek, O. S.; Altbuch, A. M.; Freiman, H. *J. Mol. Evol.* **1974**, *3*, 301–309.

[6] Sanchez, R. A.; Ferris, J. P.; Orgel, L. E. *Science* **1966**, *154*, 784–785.

[7] Sagan, C.; Thompson, W. R. *Icarus* **1984**, *59*, 133–161.

[8] Ferris, J. P. *Org. Photochem.* **1987**, *8*, 1–65.

[9] Halpern, J. B.; Miller, G. E.: Okabe, H.; Nottingham, W. *J. Photochem. Photobiol. A* **1988**, *42*, 63–72.

[10] Yung, Y. L.; Allen, M.; Pinto, J. P. *Astrophys. J. Suppl. Ser.* **1984**, *55*, 465–506.

0022-3263/90/1955-5601$02.50/0