A Computational Study of the Mechanisms for the Incorporation of a Nitrogen Atom into Polycyclic Aromatic Hydrocarbons in the Titan Haze

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Current photochemical models of Titan, Saturn’s largest satellite, include chemical reactions producing molecules composed of up to six carbon atoms and then extrapolate straight to aerosols, such as tholins. Laboratory evidence suggests that polycyclic aromatic hydrocarbons containing nitrogen atoms are formed during simulations of Titan’s atmosphere. This paper presents preliminary work on reactions that produce nitrogenated aromatic molecules containing up to 12 nonhydrogen atoms. These species would help bridge the gap between the small molecules and the aerosols in Titan’s stratosphere. We have determined the barriers and reaction energies for the incorporation of nitrogen into the rings of polycyclic aromatic hydrocarbons. The presence of a nitrogen atom increases the barrier heights relative to the pure hydrocarbon species to about 15 kcal/mol. Nitrogen in the ring promotes the formation of additional hydrocarbon rings by lowering the ring closing barrier to about 4 kcal/mol. Inclusion of these species in photochemical models of Titan is indicated.

Key Words: Titan; stratospheric chemistry; aromatics.

1. INTRODUCTION

Ground-based optical observations cannot penetrate Titan’s thick stratospheric haze to analyze the lower atmosphere. Therefore, before Voyager 1’s 1980 flyby of Titan, Saturn’s largest satellite, the extent of our knowledge of its atmosphere was a detection of methane, CH₄ (Kuiper 1944), and the identification of nitrogen as a major constituent (Allen et al. 1980). Not surprisingly, the chemical models of its atmosphere were limited to very simple hydrocarbons. Voyager’s observations dramatically changed this view, indicating a dense layer of smog produced by ongoing charged particle photochemistry and ultraviolet (UV) radiation in Titan’s stratosphere. Current knowledge suggests that Titan has a dense N₂ and CH₄ atmosphere, rich in complex organics (McKay and Toon 1992). Observations of the stratosphere yield a suite of hydrocarbon and nitrile emission features, plus a broad molecular signature for hydrogen. These observations indicate that after CH₄, the three most abundant equatorial species are ethane, C₂H₆, acetylene, C₂H₂, and propane, C₃H₈ (Kunde et al. 1981, Samuelson et al. 1997).

Laboratory simulations have shown that solid organic materials (tholins) form when gas mixtures with the composition of Titan’s atmosphere are irradiated with UV light or an electric discharge is passed through them (Khare et al. 1984a, McKay 1996, and Coll et al. 1999). Khare et al. (1984a) showed that the optical properties of this solid residue had a remarkable match with those of the Titan haze. In subsequent work, Sagan et al. (1993) showed that this solid material generated in the laboratory simulations contained about 6% of polycyclic aromatic hydrocarbons (PAHs). In recent work, Khare et al. (2001 submitted for publication) showed that the aromatic C–C and C–H stretching frequencies associated with PAHs appear shortly after the simulations begin, thus suggesting rapid formation of aromatic molecules. Thermal decomposition (Khare et al. 1984b) of the solid residue showed several aromatic molecules and many of these contained nitrogen atoms. Coll et al. (1999) found benzene as a pyrolysis product, but did not detect multiple ring aromatics; however, it is possible that the larger rings decomposed and were not observed under the conditions of their experiment (Coll et al. 1998). McKay (1996) found that while the amount of nitrogen contained in the solids varied from experiment to experiment, the solids always contained sizable amounts of nitrogen.

It has been suggested (see, for example, Clarke and Ferris 1997) that small molecules such as C₂H₂, HC₃N, and others...
form photopolymers, which condense to form the tholins. However, the organic solids obtained in the laboratory simulations of these processes do not match the optical properties of Titan as well as those obtained by Khare et al. (1984a). Unfortunately, the PAHs and photopolymers have not been observed in Titan’s atmosphere, possibly due to their rapid incorporation into the tholins and the thick obscuring haze that blocks out emission from the lower atmosphere. Since the PAHs are much more stable than linear chains and since the smaller molecules are currently included in the models (Yung et al. 1984, Toublane et al. 1995, and Lara et al. 1994), the PAHs could be an important missing link in the modeling of Titan’s atmosphere and the formation of the tholins.

It is known that acetylene and diacetylene (C₄H₂) can be excited using the available photons on Titan to produce long-lived excited states that can react with other hydrocarbons to produce larger species (Zelikoff and Aschenbrand 1956, Okabe 1981 and 1983, Seki and Okabe 1993, Zwier and Allen 1996, Frost et al. 1996). The photon energies are sufficiently large that, in addition to electronic excitation, acetylene (C₂H₂) can be dissociated into C₂H + H. Irion and Kompa (1982) have argued that benzene is formed from radical reactions involving C₂H and not from the excited state of C₂H₂. Clark and Ferris (1996) find that cyanoacetylene is photochemically converted into 1,3,5-tricyanobenzene, probably by way of a radical intermediate, while other ring products form from excited state reactions. Since the concentrations of both the aromatic species and excited states of acetylene and diacetylene are expected to be small, the growth of multiple rings probably does not occur by this mechanism. The aromatics are also strong absorbers in the UV and have long-lived excited states. Thus the reaction of excited states of the aromatics with the high concentration of small molecules, such as acetylene, are potentially important synthesis routes. However, as a first step we consider the more computationally tractable radical reactions. That is, we consider the reactions of radicals formed photochemically, but not the reactions of excited electronic states.

The mechanism for the formation of benzene by radical reactions seems well established (Miller and Melius 1992, Wang and Frenklach 1997, and Walch 1995). Since the mechanism is known and Coll et al. (1999) observed benzene in their simulations of Titan, we consider the formation of additional aromatic rings. In combustion, the radicals are formed by the rupture of bonds due to the thermal energy, which is clearly not the case on Titan. There is ample energy, coming from light, cosmic rays, Saturn magnetospheric proton or electrons, or interplanetary electrons (Sagan and Thompson 1984) to break a C–H bond and form radicals. In addition, hydrogen atoms are formed by the decomposition of CH₄ and H and C₂H are formed from the decomposition of C₂H₂. Either H or C₂H can abstract an aromatic hydrogen and begin the radical reactions. Two mechanisms have been proposed for the formation of the second and higher rings in pure hydrocarbons; the Frenklach (Wang and Frenklach 1997, Wang and Frenklach 1994, and Appel et al. 2000) and the Bittner–Howard (1981) mechanisms. The Frenklach mechanism is based on hydrogen loss from the aromatic ring followed by the addition of two acetylene molecules to the ring at adjacent sites and subsequent closure to form the additional ring. The Bittner–Howard mechanism involves the addition of one acetylene molecule to the ring followed by a second addition of C₂H₂ to the first acetylene and final closure to form the additional ring. We have computed (Bauschlicher and Ricca 2000) the reaction barriers for the Frenklach and Bittner–Howard mechanisms. Both of these mechanisms have a maximum barrier of about 11 kcal/mol for the H abstraction step, but we suggested that the Bittner–Howard mechanism offered some advantages at lower temperatures. We note that a third mechanism based on the reaction of C₅H₅ rings has also been proposed (Marinov et al. 1998).

Wong et al. (2000) modeled the chemistry of Jupiter using radical reactions and found that benzene and larger rings were formed. They found that energetic particles, which lead to ion processes that formed H atoms, were necessary for the formation of aromatics. They also found that temperatures higher than those on Titan were required for efficient multiple ring formation. Due to the much higher H₂ concentration on Jupiter, it is not clear if these conclusions apply to Titan; however, the work of Wong et al. supports the idea that radical reactions are important in the growth of polycyclic aromatics. It would be interesting to see if the addition of the Bittner–Howard mechanism to Wong’s model lowered the temperature at which the multiple rings formed.

Laboratory simulations of Titan’s atmosphere (Sagan et al. 1993) have shown that PAH molecules are in the tholins and that the tholins contain sizable amounts of nitrogen. As with soot on Earth, we speculate that in addition to PAHs being trapped in the tholins, PAH molecule addition could be an important tholin growth mechanism. Since the Titan atmosphere contains HCN, HCN addition to the PAHs could be the mechanism by which the nitrogen inclusion occurs. These reactions have not been investigated previously, and in this manuscript we extend the PAH radical growth mechanisms to include HCN reactions. We note that future work should include photochemically driven, excited state reactions and ion reactions.

2. COMPUTATIONAL METHODS

The molecular geometries were optimized and the harmonic frequencies were computed using the B3LYP (Stephens et al. 1994) hybrid (Becke 1993) functional in conjunction with the 6-31G* basis sets (Frisch et al. 1984). The frequencies confirmed that we have either minima or transition states. We computed the zero-point energy as one half the sum of the B3LYP harmonic frequencies. We note that the basis set used in this work is larger than in our previous study (Bauschlicher and Ricca 2000). For the pure hydrocarbon species we expect the change in the basis set to have only a small (± 2 kcal/mol) effect on the results. However, we have used a larger basis set because the current species contains nitrogen as well as carbon and hydrogen. The B3LYP
calculations were performed using the Gaussian 98 computer code (Frisch et al. 1998).

3. RESULTS AND DISCUSSION

Figure 1 summarizes the results of a mechanism which adds the HCN before the C2H2. The first step is the loss of a hydrogen atom. We show that this is occurring by hydrogen abstraction by H, but the loss of an H could also arise from H abstraction by C2H or, as noted in the Introduction, the energy to break the bond can come from light, cosmic rays, Saturn magnetospheric proton or electrons, or interplanetary electrons. The hydrogen abstraction is endothermic by 5.8 kcal/mol. Using the smaller basis set, we found (Bauschlicher and Ricca 2000) that this process has a barrier of 11.52 kcal/mol and is endothermic by 6.90 kcal/mol. Since the reaction is about 1 kcal/mol less endothermic with the bigger basis set, we would not be surprised if the barrier was also about 1 kcal/mol smaller. The next step, reaction (2), adds the HCN to the radical site; this reaction is exothermic and has only a small barrier. The third step adds a C2H2 to the radical site at the nitrogen. This step is exothermic and has a barrier of 13.9 kcal/mol, or about 2–3 kcal/mol larger than the barrier for the hydrogen abstraction step. For the case with only C2H2 additions, this step has a barrier of 4.2 kcal/mol. Thus the presence of a nitrogen atom increases the barrier by about 10 kcal/mol. The ring closing is exothermic and has a small barrier; see reaction (4). The hydrogen at the site of the ring closing is very weakly bound and is easily lost.

In Fig. 2 we show the results for the case where the HCN adds after the C2H2. The barrier for the HCN addition is small as found for reaction (2). However, the ring closing (reaction (8)) has a higher barrier than found for reaction (4) or for the case of only C2H2 additions.

In Fig. 3 the results for the Frenklach-like mechanism are presented. Reaction (9) is the loss of a hydrogen, which is relatively weakly bound. If this hydrogen loss is associated with a hydrogen abstraction reaction it is an exothermic process. Reaction (10) is a hydrogen abstraction, and we suspect that it has a barrier of about 11 kcal/mol as found previously. Reaction (11) adds an HCN and is exothermic with a small barrier as found for reactions (2) and (7). The ring closing reaction first involves a 180-degree rotation about the C–C bond that brings the N sufficiently close to the C2H group to allow the intramolecular reaction to occur. The rotation costs 1.5 kcal/mol, which is small relative to the activation barrier of 9.7 kcal/mol. Thus the highest barrier in the Frenklach-like mechanism is associated with the hydrogen abstraction of the ring hydrogens. That is, the maximum barrier is the same for the cases with and without nitrogen. However, as discussed previously (Bauschlicher and Ricca 2000), the disadvantage of the Frenklach-like mechanism is that two specific ring hydrogens must be abstracted for a ring to form, and this could be a slow process for a very large PAH molecule.

A comparison of the present results, which lead to a product with nitrogen in the ring, with those obtained previously for the species without nitrogen, shows that the presence of a nitrogen atom increases the largest barrier in the reaction mechanism. If the mechanism involves a hydrogen abstraction, the largest barrier increases from about 11 kcal/mol for the pure hydrocarbon case (for both the Bittner–Howard and Frenklach mechanisms) to about 15 kcal/mol in the nitrogen case. If the aromatic C–H bonds are not broken by H abstraction, the change is from about 5 or 7 kcal/mol (Frenklach and Bittner–Howard, respectively) to
15 kcal/mol in the nitrogen case. At the temperatures on Titan (about 170 K) an increase of the barrier from 7 to 15 kcal/mol results in a dramatic reduction (more than $10^{10}$ coming from the $e^{-B/RT}$ factor in the Arrhenius rate expression, where $B$ is the barrier) in the reaction rate. However, the aromatic systems are strong UV absorbers and efficiently convert this energy into vibrational energy (see for example Allamandola et al. 1989). It is possible that vibrational energy makes these reactions possible even at 170 K.

In Fig. 4 we consider a mechanism that leads to a CN side group. This is accomplished by adding cyanoacetylene, HC$_3$N, which is known to exist in the atmosphere of Titan, instead of C$_2$H$_2$. This process, shown in reactions (13)–(16), leads to a second ring with barriers very similar to the pure hydrocarbon case. If an H atom reacted with the carbon of the cyano side group, the formation of another ring could occur following the mechanism shown in Fig. 1. Attack of the CN by a radical such as HC$_2$ could also lead to the CN being incorporated into a ring. The barriers for this reaction are sufficiently low that the reaction is possible at 170 K. Thus there is at least one radical mechanism that can form CN side groups. This is consistent with Clark and Ferris (1996), who noted that the photochemistry of HC$_3$N probably involved both a radical and excited state ring growth mechanisms. In addition, ion process could also lead to ring formation; therefore the chemistry on Titan could be a very complex mixture of radical, excited state, and ion processes.

Since reactions that lead to a nitrogen atom in a ring have barriers only slightly larger than those for the pure hydrocarbon case, the obvious question is, does the presence of the nitrogen in the ring affect the growth of additional rings? We consider two different cases in Figs. 5 and 6. Starting from pyridine, the weakest C–H bond is at a position ortho to the nitrogen. The
loss of the H is only endothermic by 0.5 kcal/mol in a hydrogen abstraction reaction; see reaction (17). The Bittner–Howard-like reaction mechanism, shown in reactions (18) to (21), has a maximum barrier of 4.8 kcal/mol for the ring closing (reaction (20)). This is about 3 kcal/mol smaller than the maximum barrier for the pure hydrocarbon case or for the case of CN side group (reactions (13) to (16)). That is, the nitrogen in the ring promotes the formation of the next ring. However, this effect, like the effect of including the nitrogen in the ring growth process, is relatively small, about 3 kcal/mol. These reaction barriers are sufficiently low that such reactions should be possible even at 170 K. Thus even if the synthesis of the nitrogen in the ring is not occurring by a radical mechanism (reactions (1)–(8)), the subsequent ring growth, like the all hydrocarbon case, may occur by a radical mechanism.

In Fig. 6, we consider a second growth mechanism. Reaction (22) is very similar to reaction (18), and the change in orientation of the C2H2 slightly increases the barrier and decreases the exothermicity. The addition of the second C2H2 has a slightly larger barrier due to the change in orientation of the first C2H2, while the ring closing has a slightly smaller barrier—compare reactions (23) and (24) with reactions (19) and (20). Unlike the mechanisms shown in Figs. 1 and 2, a loss of a hydrogen atom does not seem likely for the product of reaction (24), either a hydrogen atom will react with the radical, as shown in reaction (25), or the radical could be the point where the formation of the next ring initiates.

4. CONCLUSIONS

All the mechanisms involving the addition of HCN and C2H2 to a pure aromatic ring to form an additional ring have barriers lower than 15 kcal/mol. Such a barrier of 15 kcal/mol is probably too high to allow reactions to occur in the atmosphere of Titan unless the reaction rates are enhanced by vibrational energy of the aromatic molecule. The presence of a nitrogen atom in the aromatic ring promotes the formation of an additional ring. The addition of cyanoacetylene and acetylene to form aromatic nitriles has barriers very similar to the pure hydrocarbon case with a maximum barrier smaller than 8 kcal/mol. The barriers of these reactions, and those for the pure hydrocarbon synthesis, are sufficiently low that they could occur in the atmosphere of Titan. We suspect that the chemistry on Titan is a complex mixture of radical reactions of the type studied here, excited state, and ion chemistry. We conclude that polyaromatic and nitrogenated polyaromatic molecules should be included in photochemical models, especially in the tholin formation. While we have considered the reactions of radicals formed by photochemistry, we have not considered photochemically driven, excited state reactions nor have we considered ion chemistry; we are currently extending this work to consider these additional mechanisms.

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REFERENCES


