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Low-Temperature Rate Coefficients for the Reaction of Ethynyl Radical (C_2H) with Benzene

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The reaction of the C_2H radical with benzene is studied at low temperature using a pulsed Laval nozzle apparatus. The C_2H radical is prepared by 193-nm photolysis of acetylene, and the C_2H concentration is monitored using $CH(A^2\Delta)$ chemiluminescence from the $C_2H + O_2$ reaction. Measurements at very low photolysis energy are performed using CF_3C_2H as the C_2H precursor to study the influence of benzene photodissociation on the rate coefficient. Rate coefficients are obtained over a temperature range between 105 and 298 K. The average rate coefficient is found to be five times greater than the estimated value presently used in the photochemical modeling of Titan's atmosphere. The reaction exhibits a slight negative temperature dependence which can be fitted to the expression $k(\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) = 3.28(\pm 1.0) \times 10^{-10}\ (T/298)^{-0.18(\pm 0.18)}$. The results show that this reaction has no barrier and may play an important role in the formation of large molecules and aerosols at low temperature. Our results are consistent with the formation of a short lifetime intermediate that decomposes to give the final products.

1. Introduction

Benzene (C_6H_6) is the first aromatic compound that has been detected in the interstellar medium and in planetary atmospheres. ISO (Infrared Space Observatory) observations report the presence of benzene in carbon-rich stars,[1] Jupiter, and Saturn.[2] Recently, Coustenis et al.[3] found evidence for the presence of benzene in Titan's atmosphere. They inferred a constant mean mole fraction of 4×10^{-10} and point out that aromatic chemistry may hold considerable significance in Titan's atmospheric chemistry. In a study about benzene formation in Titan, Wilson et al.[4] conclude that the primary mechanism for the production of benzene on Titan involves the recombination of propargyl (C_3H_3) radicals. This model is able to reproduce the Coustenis et al.[3] benzene density.

At low temperature (interstellar media, planetary atmospheres) as well as at high temperature (circumstellar envelopes), the chemistry of benzene, through reactions with little or no activation barriers, is assumed to be involved in the chemical pathways for polycyclic aromatic hydrocarbon (PAH) formation. PAHs are cited[5−7] to be present in planetary atmospheres such as Jupiter, Saturn, and their moons, especially Titan, where PAHs are thought[6] to be one of the ways for the production of Titan's haze, which hides the moon's surface from direct Earth observations. Information about the chemistry that leads to PAH formation is needed to be able to interpret the new data collected by instruments such as the mass spectrometer and aerosol collector on board the European Space Agency's Huygens probe.[8]

There is a wealth of high-temperature studies concerning the mechanism of formation of these large molecules using complex chemical schemes,[9−12] but only a few low-temperature mechanisms were considered.[4,13,14] It has been shown that the extrapolation of high-temperature mechanisms to low temperatures is not always relevant.[16] In one of the most recent modeling studies of Titan's atmosphere, Wilson and Atreya[17] clearly highlight the need for further study of aromatic mechanisms at lower temperatures applicable for the planetary atmosphere. The most recent work about benzene chemistry for Titan's atmosphere was performed by Lebonnois.[14] He compares two different complex chemical schemes for the formation of PAHs and aerosols in Titan and Jupiter. The most likely scheme includes the reaction of benzene with ethynyl radical. Again, the author points out the lack of data for likely reactions at temperatures relevant to the planetary atmospheres, especially for the title reaction. So far, the C_2H + benzene kinetic rate coefficient used in the atmospheric models is an estimation by Wang and Frenklach[15] and the same value is used at high or low temperature. The accuracy of these models down to Titan-like temperatures (90 K) is based on the validity of the kinetics data used in the chemical scheme. Experimental measurements of these key reaction properties and, in particular, kinetic rate coefficients are needed.

The ethynyl radical is an important chemical species in planetary atmospheres. It is formed by photodissociation of acetylene by solar radiation.[18−20] Low temperature kinetics and product formation of reactions of this radical with hydrocarbons or nitrogen-containing species have been studied previously,[21−24] but no measurement of C_2H rate coefficients with aromatic compounds has been performed.

In this paper, we present the measurement of the rate coefficient of the reaction of the C_2H radical with benzene between 105 and 298 K. Experiments are performed in a pulsed Laval nozzle apparatus using pulsed laser photolysis to produce C_2H, and chemiluminescence of the $CH(A^2\Delta)$ radical produced from the $C_2H + O_2$ reaction is used to follow the C_2H concentration. In this system, the influence of laser photolysis of benzene on the absolute uncertainties is also studied and rate coefficients with an uncertainty of around 30% can be inferred. The reaction shows no entrance barrier, and the rate coefficient

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is close to the classical gas kinetic rate coefficient. The implication of these results in the modeling of planetary atmospheres and the possible product formation are discussed.

2. Experimental Section

The kinetics data are obtained with a pulsed Laval nozzle expansion apparatus using pulsed laser photolysis and chemiluminescence. A detailed description of the experiment has been given previously,[25] and only a brief overview will be presented here. The Laval nozzle is mounted on a movable reservoir inside a vacuum chamber, which is pumped by a mechanical pump (pumping speed ≈ 60 L/s). Low temperatures (165 and 105 K) are obtained by supersonic expansion of the gas through low Mach number (*Ma*) $Ma = 2$ and 3 Laval nozzles, respectively. All the nozzles were characterized by impact pressure measurement, and the temperature of the supersonic expansion was determined by recording the laser-induced fluorescence rotational spectrum of the OH A−X electronic transition.[22] The gas admitted into the chamber through the Laval nozzle block is mainly nitrogen, with small amounts of acetylene and oxygen and the other reactants. The gases are mixed prior to the pulsed valve injection in a 150 mL stainless steel cylinder. The supersonic expansion is formed by opening two solenoid valves in the pre-expansion chamber for ∼5 ms. The expansion through the Laval nozzle results in a collimated supersonic gas flow, which has uniform density and temperature distributions. The pressure in the main chamber is adjusted to obtain the best collimation of the flow. Four milliseconds after the valves are opened, a uniform initial concentration of the C_2H radical is produced, coaxially in the flow, by 193-nm photolysis of acetylene using an unfocused beam of an excimer laser. Typical photolysis fluences inside the vacuum chamber are ∼10 mJ/cm^2 in an approximately 10-ns pulse, which is three times lower than the photolysis fluences used in previous studies[25] (see section 3).

The C_2H concentration along the length of the flow is monitored using the chemiluminescence tracer method[26] by adding oxygen to the gas flow. In this method, the concentration of C_2H is followed in time by observing $CH(A^2\Delta) \rightarrow (X^2\Pi)$ chemiluminescence produced by the $C_2H + O_2$ reaction. The chemiluminescence signal is detected 12 cm downstream of the nozzle using a photomultiplier tube with a filter (10-nm bandpass centered around 430 nm) and recorded using a multichannel scaler in a photon-counting regime. Typically, a radical decay profile is obtained by accumulating signal from 4000 to 6000 photolysis laser pulses. The experiment is run at a 10-Hz repetition rate. Time delays for the opening of the pulsed valves, the pulsing of the excimer laser, and the multichannel scalar trigger are generated using a multiple channel digital delay generator. The total gas density is calculated using the measured main chamber pressure (which is equal to the pressure in the supersonic expansion) and the temperature of the expansion.

The benzene is injected into the flow by bubbling a clean flow of nitrogen into liquid benzene (Aldrich). The bubbler is a glass volume of 150 mL. The nitrogen is injected directly into the liquid through a glass tube and a frit. An additional volume of 500 mL is added after the bubbler to allow the good mixing of the nitrogen with the benzene vapor. The total gas flow rate in the bubbler is fixed at 6 SCCM (standard cm^3 per minute). The benzene density is altered by changing the total pressure in the bubbler with a needle valve placed after the additional volume. Then the benzene density is measured in a 457-mm path length cell by measuring the benzene absorption at 193 nm. The ratio of benzene and nitrogen in the absorption cell is measured by plotting the natural logarithm of the transmitted laser intensity after the cell as a function of the total pressure in the absorption cell. This ratio remains the same after the supersonic expansion. The benzene density in the supersonic flow is calculated from this ratio using the total gas density in the supersonic expansion (the total density is typically $(2.4 \pm 0.2) \times 10^{16}$ cm^{-3} for the $Ma = 3$ nozzle and $(4.7 \pm 0.7) \times 10^{16}$ cm^{-3} for the $Ma = 2$ nozzle) and the flow rates of the carrier gas. The uncertainty in the benzene density in the supersonic flow is the largest source of error and is discussed in section 3.

The purities of gases are as follows: N_2, 99.999%; C_2H_2, 99.6%; O_2, 99.998%. Since acetylene is stabilized by acetone, it is purified further by passing it through an activated carbon filter. For low laser energy experiments, to test the effect of benzene dissociation on the kinetics, we have used CF_3C_2H as the precursor rather than acetylene. Previous experiments[21] have shown that the photodissociation of trifluoropropyne is more efficient by a factor of 2. For room temperature measurements, the gas mixture is continuously flowed into the main chamber through a special gas inlet port, bypassing the Laval nozzle block and the pulsed valves.

3. Results

Rate coefficients are determined under pseudo-first-order conditions assuming that the concentration of C_2H radical is much smaller than the reagent concentration. Under these conditions, the kinetics of C_2H removal can be expressed as

$$-\mathrm{d}[C_2H]/\mathrm{d}t = [C_2H](k[C_6H_6] + k_{O_2}[O_2] + k_{C_2H_2}[C_2H_2]) = k_{obs}[C_2H] \quad (1)$$

$$[C_2H] = [C_2H]_0 \exp[-k_{obs}t] \quad (2)$$

where k_{O_2} and $k_{C_2H_2}$ are the rate coefficients for the reaction of ethynyl radical with, respectively, O_2 and acetylene. $[C_2H]_0$ is the initial ethynyl radical concentration. The bimolecular rate coefficient k for the reaction of C_2H with benzene is determined by plotting the observed first-order decay rate constant, k_{obs}, vs the reagent concentration $[C_6H_6]$ while the concentration of the other reactant remains constant. As already mentioned, the C_2H decay is followed by measuring the chemiluminescence from the electronically excited $CH(A^2\Delta)$. The $CH(A^2\Delta)$ lifetime in collision free conditions is much shorter than the reactive lifetime of C_2H in the supersonic flow. In a quasi-steady-state approximation for the $CH(A^2\Delta)$ concentration, the chemiluminescence emission intensity is directly proportional to the instantaneous C_2H concentration. Details of the 193-nm photolysis of C_2H_2 to create an initial concentration of C_2H and the chemiluminescence tracer method are discussed previously.[27] A typical decay trace of the chemiluminescence signal is shown in Figure 1. The experimental chemiluminescence traces are fitted by single exponential decays using a nonlinear least-squares fitting program employing the Levenburg−Marquadt algorithm. The observed single-exponential decay confirms that the experiment is done under pseudo-first-order conditions. Fitting is done starting at 15-μs delay after the photolysis laser pulse to avoid interference from the scattered laser light and emission produced by the photolysis pulse. This delay time also allows time for the quenching by nitrogen molecules of the anticipated excited C_2H radicals generated by the 193-nm photolysis of acetylene. At room temperature, the rate coefficient for the quenching of excited C_2H by nitrogen molecules is equal to 8×10^{-11} cm^3 molecule^{-1} s^{-1}.[28] By assumption that this

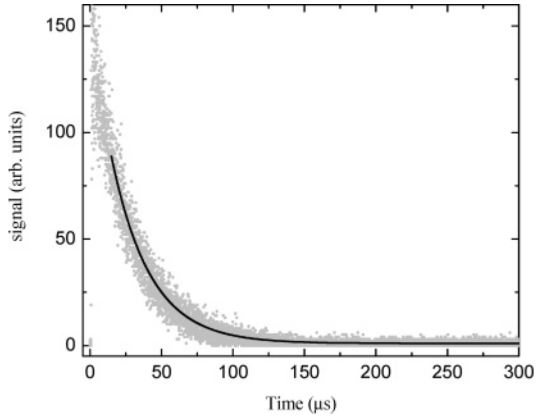

Figure 1. CH A−X 0−0 chemiluminescence vs time at 105 K in the presence of benzene. The chemiluminescence is proportional to the C_2H concentration under the conditions of the experiment. The full line is the exponential fitting of the signal.

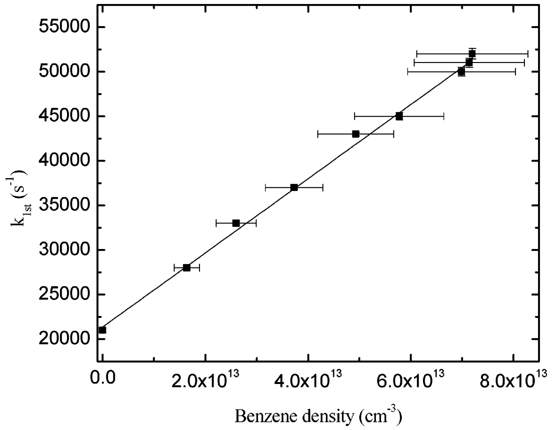

Figure 2. Plot of the first-order decay rate constant vs the reactant concentration. The straight line is a least-squares fit to the experiment points. The error bars on the experimental points are the standard deviations from the least-squares fitting plus the calculated uncertainty for the benzene density.

TABLE 1: Rate Coefficients for the C_2H + Benzene Reaction Obtained with the Pulsed Laval Nozzle Apparatus

T (K)	total density (10^{16} cm^{-3})	benzene density range (10^{12} cm^{-3})	rate coefficient[a] (10^{-11} cm^3 s^{-1})
105	2.4	16−72	41.6 ± 13
165	4.7	27−88	32.6 ± 10
298	6.7	17−74	34.6 ± 10
298	2.5	20−84	38.0 ± 11

[a] The error bars are reported as 30% of the measured rate coefficient.

value does not decrease dramatically at low temperature, the characteristic time for the quenching of excited C_2H by nitrogen in our flow is less than 1 μs. The measurements are repeated for different reactant concentrations. The plot of k_{obs} vs the reactant concentration is a straight line whose slope is the rate constant k for the studied reaction, at the temperature and density of the flow as shown in Figure 2. A 15% uncertainty in the benzene density is inferred from the uncertainty of the absorption cell pressure and absorption strength measurements. The measured pseudo-first-order rate coefficient at zero reactant density is due to reaction of C_2H with the other reactants (C_2H_2 and O_2) and also to the radical diffusion out of the irradiation zone. The results for the title reaction are shown in Table 1 along with the measurement uncertainties for each set of runs, which are reported as 30% of our measurement, as discussed further. Each measurement has been performed three times. The rate constants shown in Table 1 are the average of these measurements.

At 193 nm, the cross section for single-photon photodissociation of benzene is known to be significant.[29] We have to take into account, therefore, the destruction of benzene in the flow by the 193-nm photolysis pulse. Berman et al.[30] have studied the reaction of CH radical with benzene above room temperature using 266-nm photolysis of bromoform to generate CH. They compare their results to an earlier experiment (Butler et al.)[31] where the CH radical was obtained by photolysis of bromoform at 193 nm. At 266 nm, Berman et al.[30] measured a rate constant six times larger than the one measured by Butler et al. and they assume that the discrepancy comes from benzene dissociation. As mentioned above, we have used a very low laser fluence to reduce the benzene photodissociation and also used CF_3C_2H instead of acetylene to further reduce the photolysis energy. At room temperature the value of the benzene photodissociation cross section is 2.20×10^{-17} cm^3. If we consider the highest fluence used in our experiment, the amount of photodissociated benzene (assuming the branching ratio is equal to 1) is 20% of the total benzene density. This amount is less than 10% at the lowest laser fluence. For the $Ma = 3$ nozzle, we have performed the measurement of the rate constant for three different laser energies. Decreasing or increasing the photolysis pulse energy by 50%, respectively, increases and decreases the value of the rate constant by only 10%. Our rate coefficient is already close to the gas kinetic limit based on the hard-spheres approximation and cannot be much larger than these results. In addition, even if C_2H reacts similarly fast with the benzene photolysis products, at the low laser fluence used, the amount of dissociated benzene remains lower than 10% of the total benzene density. However, 193 nm is not a convenient wavelength for studies involving aromatic compounds, and therefore we indicate that the measured rate coefficients are approximate values. Because of photolysis phenomena and the experimental uncertainty in the temperature, the uncertainty of the mean rate coefficients is greater than in previous studies.[22] The averaged rate coefficient should be taken with a total uncertainty of ±30%.

At low temperature, our nozzles do not allow a study as a function of the total density. However at room temperature, the total pressure can be adjusted easily by changing the pumping capacity. We have measured the rate coefficient for two different nitrogen total pressures. As shown in Table 1, changing the flow pressure has a negligible effect on the reaction kinetics of the title reaction. The final results are presented in Figure 3 with the estimated point by Wang and Frenklach.[15] Our measurements are five times larger than the Wang and Frenklach estimation. Within the experimental uncertainty, we can fit our results by the expression $k(\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) = 3.28(\pm1.0) \times 10^{-10}\ (T/298)^{-0.18(\pm0.18)}$.

4. Discussion

The present work is the only experimental study of the reaction kinetics of the C_2H radical with benzene. No direct information about the products of the reaction can be inferred from this experiment, and up to now, there are no theoretical studies of the reaction of the C_2H radical with aromatic hydrocarbon molecules. Here, we discuss the possible mechanism for the reaction of ethynyl radical with benzene. Then we present the implication of the observed large rate coefficient on low temperature chemistry for planetary atmospheres, especially for Titan.

4.1. Reaction Mechanism and Temperature Dependence. It is commonly accepted that reactions of carbon-containing

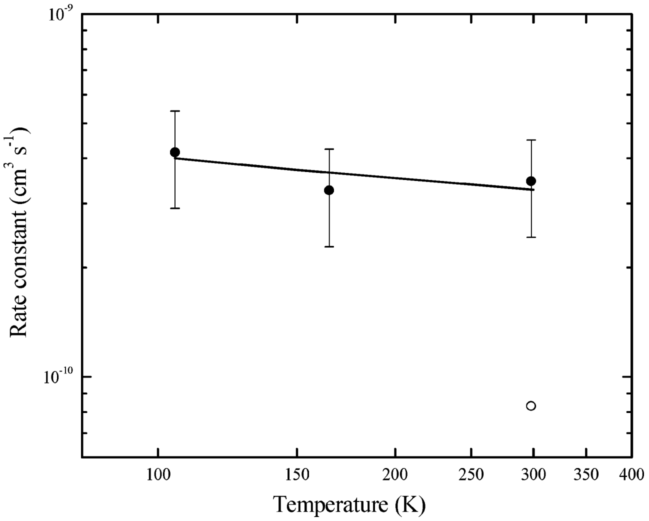

Figure 3. Rate coefficient for the reaction of C_2H with benzene at different temperatures. The full circles are our results, and the open circle is the estimation by Wang and Frenklach.[15] The line is a fit of our experimental data k(cm^3 molecule^{-1} s^{-1}) = 3.28(±1.0) × 10^{-10} $(T/298)^{-0.18(\pm0.18)}$. Error bars are 30% of the measured rate coefficient as discussed in the text.

radicals (C, CH, $^1CH_2$, CN)[31,32−36] with unsaturated hydrocarbons proceed via the formation of an initial intermediate. This intermediate, which is formed without any activation energy, is expected to have a very short lifetime[31] and to decompose to give the substitution products. Kaiser et al.[32] have performed a crossed beam experiment of the reaction of atomic $C(^3P_j)$ with benzene. They inferred from their measurement that the reaction of C atoms with aromatic compounds leads to ring expansion. Nevertheless, Bergeat and Loison[33] have studied the C reaction with benzene and are in disagreement with the conclusion of Kaiser et al.[32] The H production ratio measured by Bergeat and Loison[33] is not consistent with the substitution process, which suggests that the reaction of carbon atoms with benzene follows a much more complex reaction path than the simple addition−elimination mechanism leading to an H atom plus a species derived by carbon−hydrogen exchange. Recently, Goulay et al.[37] have measured the rate coefficient of the CH radical with a PAH, anthracene. They conclude that the reaction is barrierless and would lead to the formation of cyclopropa[*b*]anthracene ($C_{15}H_{10}$). The first step of the reaction is the formation of a three-carbon-atom ring. Our results for the reaction of C_2H with benzene show a large rate coefficient at all temperatures. There is a slight negative dependence with temperature and no dependence with the total pressure up to 1 Torr. This behavior of the rate coefficient is similar to previous results obtained for reactions of the C_2H radical with unsaturated hydrocarbons—excluding the chemistry of nitrogen-containing species—which can be explained by the formation of a C_8H_7 complex that decomposes to give the final products.

It is also very interesting to compare the mechanisms of the studied reaction with the mechanism of the CN radical + benzene reaction. C_2H and CN are isoelectronic and both have a strong dipole moment. However it is important to keep in mind that the difference in the dipole orientation can lead to differences for the attack of the aromatic system by the radical. Balucani et al.[36] present a crossed beam experiment and electronic structure calculations for the reaction of the CN radical with benzene. The calculated potential energy surface shows no barrier in the entrance channel. On the basis of this calculation and on their observations, they inferred that the major product of the reaction is cyanobenzene (C_7H_5N). The entrance channel is thought to be the CN attack on the π electron system of the benzene to form a carbon−carbon σ bond. The intermediate 1-cyano-cyclohexadienyl radical gives cyanobenzene and an H atom. The exit channel is not barrierless, but the activation energy remains well below the energy of the reactants. The large rate coefficient at low temperature for the reaction of ethynyl with benzene is consistent with a barrierless attack of the aromatic ring by the radical leading to the formation of the 1-ethynyl-cyclohexadienyl radical, stabilized by electron delocalization. One of the possible evolutions of this radical is the rupture of the C−H bond to give phenylacetylene and an H atom as expected by Wang and Frenklach.[12] This reaction has an exothermicity of 35.31 kJ mol^{-1}. Nevertheless, it is clear that our experiment is not sufficient to make a conclusion about the reaction mechanism.

The rate constant for the studied reaction increases slightly as the temperature is lowered. The experimentally measured temperature dependence of the rate constant can be compared with predictions of a model where the rate constant is determined by the capture of the reactants by long-range attractive electrostatic forces.[38] As benzene does not have any dipole moment, the interaction between the C_2H radical and the aromatic ring should be considered to be close to a dipole−quadrupole interaction. However, some studies by Phillips[39] have shown that the attractive dispersion interaction must be taken into account in order to reproduce experimental data. Stoecklin et al.[38] also suggest that the dispersion contribution to the rate coefficient is likely to predominate at temperatures above 10 K. The formula given by Stoecklin et al.[38] for the electrostatic interaction leads to a rate coefficient of 1.28 × 10^{-10} cm^3 s^{-1}, which is constant with temperature. By use of the Stoecklin et al.[38] analytical formula for the dispersion contribution, the theoretical global rate coefficient k_{th} for the reaction of C_2H with benzene in our temperature range can be approximated by the expression

$$k_{th} = 5.81 \times 10^{-10}\left(\frac{T}{298}\right)^{1/6} + 1.28 \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \quad (3)$$

Our measurements are only 1.75 times lower than the average value of this calculated rate coefficient within our temperature range. The measured rate coefficient exhibits a very weak negative temperature dependence, which disagrees with eq 3. However, these analytical formulas were established for diatomic molecules and the author outlines the nonapplicability of this formula for large molecules, and two previous measurements of the rate coefficients of dipolar radicals with aromatic molecules[37,40] have shown temperature dependences that are not always consistent with dipole−quadrupole or dispersion interactions. Thus, the interaction between a dipolar radical and an aromatic compound must be the subject of further specific theoretical work. Furthermore, between 100 and 300 K, the rate coefficient should increase by only 15% due to the dispersion interaction. Our error bars are too large to make any conclusion considering the temperature dependence. The absolute value of the rate coefficient and the weak temperature dependence suggest that the reaction of the ethynyl radical with benzene is driven by a capture process.

4.2. Implication for Titan's Atmosphere. The understanding of the complex chemistry that leads to the formation of large molecules and particles in outer planetary atmospheres has been a critical challenge during the past decade. Currently, the photochemical model of Titan's atmosphere includes reaction of the C_2H radical with hydrocarbons, but only with fewer than four carbon atoms. As models become more elaborate, large hydrocarbons (4 or greater carbon atoms) will be added to the chemical scheme. Diacetylene and benzene are among those that are likely to be important.

In Titan, we assume that the mechanism of the formation of PAHs is the same as at high temperatures, involving the reaction of ethynyl radical with benzene.[6,15] Once the closure of the first aromatic ring has occurred, leading to the establishment of the benzene molecule or its hydrogen-abstracted radical equivalent, phenyl (C_6H_5), the propagation of PAH formation is promoted through the attachment of ethynyl radical onto benzene or acetylene onto phenyl

$$C_2H + C_6H_6 \rightarrow PAH \tag{R1}$$

$$C_2H_2 + C_6H_5 \rightarrow PAH \tag{R2}$$

This mechanism, known as the HACA (H-abstraction/C_2H_2-addition) sequence, may proceed through continued H abstraction followed by acetylene addition[15] or though continued acetylene addition to close the second ring.[41] Reactions R1 and R2 and also the phenyl radical addition on benzene

$$C_6H_5 + C_6H_6 \rightarrow PAH \tag{R3}$$

are considered as the first steps to form PAHs. The rate coefficients of those three reactions are given from Wang and Frenklach,[15] Yu et al.,[42] and Park et al.[43] for a minimum temperature varying from 300 to 500 K with the temperature range extending up to 2500 K. The rate coefficient for reaction R1 has been estimated[30] to be 8.3×10^{-11} cm^3 molecule^{-1} s^{-1} and is supposed to be constant with the temperature. We have shown that this value is too small by at least a factor of 5. A higher value closer to the gas kinetic rate coefficient must be used in atmospheric models. Moreover, Kaiser et al.[32] suggest that for Titan-like temperatures the reaction of C atoms with benzene may be more efficient than reaction R2 for the formation of large hydrocarbons. Our results point out the importance of the C_2H radical reaction with aromatic compounds for the formation of aerosols even at low temperatures. The contribution of the title reaction to the phenylacetylene reaction rate flux must be reviewed. The HACA mechanism must be adapted to temperatures relevant to the planetary atmospheres by updating rate coefficients of key reactions such as the title reaction. The reaction of the phenyl radical with acetylene is known to be slower and could play a weaker role in the formation of aerosols in Titan, depending on the relative abundances of each species.

The detection of the products of reactions, which will soon be available in our experiment, will add important information regarding the PAH formation at low temperature. The photochemistry models will be more relevant, and this will lead to a better understanding of the chemistry in Titan's atmosphere. It is also important to include, into the models, the chemistry of nitrogen containing species. There is evidence that nitrogen is involved in the formation of large molecules,[44−46] and more studies including this species must be performed at the same time as radical hydrocarbon experiments.

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