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The effect of N-heteroatoms and CH_3 substituents on dissociative electron–ion recombination of protonated single six membered ring compounds at room temperature

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ABSTRACT

Electron–ion dissociative recombination rate constants have been determined for protonated single six-membered hydrocarbon rings with varying N-atom substitution in the rings and varying degrees of methyl substitutions to the rings. The species studied have been protonated forms of the xylenes (C_8H_{10}; with configurations o, m, and p), the picolines (C_6H_7N; with methyl substitutions located at 2, 3, and 4), mesitylene (C_9H_{12}) and 2, 5-lutidine (C_7H_9N). By operating at high reactant vapor pressures, ternary association has been made to dominate over recombination to create proton bound dimers and the rate constants of these species have been determined. The studies were made at room temperature in a flowing afterglow with a Langmuir probe to determine the reduction in electron density as a function of distance along the flow tube. All of the data except for mesitylene showed a consistent trend with the numbers of N-atom substitutions and CH_3 attached to the rings. For the protonated species, the rate constants increase with the number of nitrogens and decreased with number of CH_3 substituents attached to the ring. For proton bound dimers, the rate constants increase with both, the number of N-atoms and number of CH_3 substituents. For the xylene and picoline isomer's the measurements showed that the rate constants were independent of isomeric form, and thus, it is not necessary to study all isomeric forms. The relevance of these studies to the ionosphere of Titan is discussed.

1. Introduction

Recently, single six membered ring compounds have been detected in the atmosphere of Titan, a planetary satellite of Saturn, by the highly successful Cassini spacecraft [1]. Masses in the range 1–99 amu have been detected by the on board positive ion-neutral mass spectrometer (INMS) [2], positive ion masses up to 350 amu by the Cassini Plasma Spectrometer (CAPS), Ion Beam Spectrometer (IBS), and negative ions 50–8000 amu by the CAPS Electron Spectrometer (ELS) [3]. Within these masses are the six membered rings C_6H_6 (benzene), $C_5H_5N^+$ (ionized pyridine), and $C_7H_9{}^+$ (protonated toluene). Double rings of naphthalene, anthracene and anthracene dimers have been identified with the IBS [3] and polycyclic aromatic hydrocarbons (PAH's) with the ELS. Since the atmosphere of Titan is composed of ~98% nitrogen [4], it is considered that there may be a great deal of N substitution in the rings. The next most abundant species in this atmosphere is methane (CH_4; ~2% [4]), and it can be concluded that the rings present within the Titan atmosphere may have many methyl (CH_3) substitutions. All of these ion species are likely to have different recombination rate constant's and, thus, a body of rate constants needs to be measured to expose any trends within the nitrogen or methyl substituted (CH_3) ring species.

These data will be beneficial to the models which have been produced by Vuitton et al. [5] and Cravens et al. [1]. Both models show a body of hydrocarbon ion chemistry with cyanides present within the Titan atmosphere. With this in mind, the recombination reactions of protonated and proton bound dimers of benzene (C_6H_6), toluene ($C_6H_5CH_3$), pyridine (C_5H_5N) and pyrimidine ($C_4H_4N_2$) have been previously studied and their rate constants determined [6]. More recently, the recombination rate constants for protonated 4-picoline (C_6H_7N), cyclohexane (C_6H_{12}), 1,4 dioxane ($C_4H_8O_2$), furan (C_4H_4O), pyrrole (C_4H_5N), 1-methylpyrrole (C_5H_7N), thiophene (C_4H_4S) and pyrrolidine (C_4H_9N) have also been determined [7]. With more than one substituent in or on the ring, isomeric forms are possible and this has been investigated for all of the isomeric forms of protonated xylenes (C_8H_{10}; with configurations o, m, and p) and the picolines (C_6H_7N; with a methyl substitution located at 2, 3, and 4). The proton bound dimers have also been studied, as well as mesitylene (C_9H_{12}) and 2, 5-lutidine (C_7H_9N) recombination rate constants [7]. Rate constants for the xylenes and picolines, only varied a little with isomeric form and therefore it is not necessary to study all isomeric forms. This was fortunate since the increasing

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substituents also corresponds to decreasing vapor pressure which makes it more difficult to introduce the reactant vapor into the reaction vessel. In addition, in these previous studies, only species with few N atoms and CH_3 substituents have been investigated, and the purpose of the present study is to extend this to larger numbers of substituents to look for trends in the recombination rate constants.

2. Experimental

The recombination rate constants, α_e, were determined in a flowing afterglow using a Langmuir probe operating within the orbital limited region. This apparatus has been described in detail previously and only features relevant to the present studies are described here [8]. By measuring the decrease in electron density, $[e]$, as a function of distance, z, along the flow tube and utilizing Eq. (1)

$$\frac{1}{[e]_z} - \frac{1}{[e]_0} = \frac{z\alpha_e}{V_p} \qquad (1)$$

where V_p is the plasma flow velocity, $[e]_z$ is the measured electron density and $[e]_0$ is the upstream electron density, the recombination rate constant can be determined. The flowing afterglow uses a helium (Airgas UHP He) flow which is ionized upstream in a microwave cavity and allowed to flow to a downstream mass spectrometer under the action of a roots blower pump. Sequential additions of Ar, H_2 and reactant vapors, RV, to the flow convert the plasmas from $He^+/He_2^+/e$, to Ar^+/e, H_3^+/e, and RVH^+/e with the final step being the proton transfer from H_3^+ to RV as seen in Eq. (2).

$$H_3^+ + RV \rightarrow RVH^+ + H_2 \qquad (2)$$

This protonated monomer then recombines with the electrons.

$$RVH^+ + e \rightarrow \text{products} \qquad (3)$$

However, the addition of larger concentrations of RV allows association

$$RVH^+ + RV + He \rightarrow (RV)_2H^+ + He \qquad (4)$$

to dominate over recombination (2) generating the dimer $(RV)_2H^+$ which then recombines [9]. Plots of recombination rate constant, α_e, versus RV concentration, [RV], then reveals regions where $H_3^+ + e$, $RVH^+ + e$ and $(RV)_2\ H^+ + e$ dominate the flow as seen in the plots shown in Fig. 1 for 2, 3, and 4, picolines. It can be seen that, for 4-picoline, there are well defined plateaus showing the recombination rate constants for RVH^+ and $(RV)_2H^+$. Here the α_e for RVH^+ and $(RV)_2H^+$ can be read directly from the plot, as previously discussed [6]. As the recombination moves to 3-picoline and then to 2-picoline, the plateaus become less distinct and the chemical model in Eq. (5) has to be used to fit the data to determine the recombination rate constants [7].

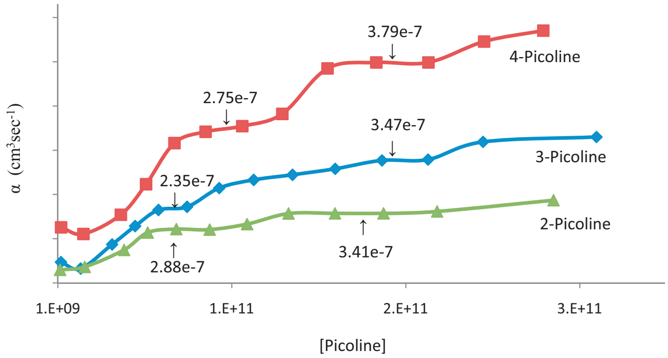

Fig. 1. Plot of 2, 3, and 4 picoline rate constant (α_e) verse reactant vapor concentration. The plateaus are well defined for 4-picoline but less so for 2 and 3 picoline. Note: the plots are vertically offset from each other for viewing ease, but the rates of the protonated form and the proton bound dimer are labeled on each curve.

$$\underset{\alpha_3\downarrow e}{H_3^+} \underset{H_2,k_{-2}}{\overset{RV,k_2}{\rightleftharpoons}} \underset{\alpha_M\downarrow e}{RVH^+} \underset{k_{d,He}}{\overset{RV,He,k_a}{\rightleftharpoons}} \underset{\alpha_{D\downarrow e}}{(RV)_2H^+} \qquad (5)$$

Rate constants determined in this way, are accurate to within ±15% for the monomer systems with the dimers less accurate (±20%) because of the fitting procedures. For cross comparison of the isomeric forms, only the relative errors are important, and these have a random error of ±5%, this was determined from a series of studies of N_2H^+ recombination under the same experimental conditions [10]. The kinetic data for all of the systems studied are given in Table 1. The purities of the species indicated were 2-picoline (sigma, 98%), 3-picoline (Sigma, ≥99.5%), 4-picoline (Sigma, 99%), o-xylene (EMD, >98%), m-xylene (Sigma, 99%), p-xylene (Fisher, 99.9%), mesitylene (Sigma, ≥99%) and 2,5-lutidine (Sigma, 95%). Since the RV's are liquid at room temperature, they were freeze-pump-thawed several times before use to remove any dissolved gases. The neat vapor was then used to make a 0.5–1% mixture in helium (National Welders UPC He). It was always ensured that the vapor was in a concentration substantially less than the saturated vapor pressure to prevent the vapor from condensing substantially on the flow tube walls. This enabled constant concentrations of these sticky vapors to be introduced into the flow tube. Also included in Table 1 are data previously obtained from the literature [6,7]. Note that where a plateau for $(RV)_2H^+$ is not obtained (i.e., a sufficiently large [RV] could not be introduced into the flow tube)

Table 1
Recombination rate constants, α_e ($cm^3\ s^{-1}$), indicated for the protonated species (RVH^+) and their proton bound dimers ($(RV)_2H^+$) together with relevant data from previous studies reported in the literature [6,7]. These species contain various combinations of CH_3 substituents attached to the rings and N-atoms substituted in to the rings.

CH_3	Compound	Monomer	Dimer	*N*	Compound	Monomer	Dimer
CH_3							
0	Benzene[a]	8.0(−7)[b]	5.0(−7)	0	Benzene[a]	8.0(−7)	5.0(−7)
1	Toluene[a]	3.8(−7)	1.25(−6)	1	Pyridine[a]	8.5(−7)	6.0(−7)
2=	o-Xylene	2.8(−7)	1.2(−6)	2	Pyrimidine[a]	1.35(−6)	7.0(−7)
2=	m-Xylene	2.7(−7)	2.55(−6)				
2=	p-Xylene	2.15(−7)	1.7(−6)				
3	Mesitylene	7.0(−7)	2.5(−6)				
CH_3;N							
1, 0	Toluene[a]	3.8(−7)	1.25(−6)				
1; 1=	2, picoline	2.88(−7)	3.4(−7)				
1; 1=	3, picoline	2.42(−7)	3.5(−7)				
1; 1=	4, picoline	2.85(−7)	3.8(−7)				
2; 1	Lutidine	5.5(−7)	N/A				

[a] Data from the literature [5,6].

[b] (−7) means × 10^{-7}.

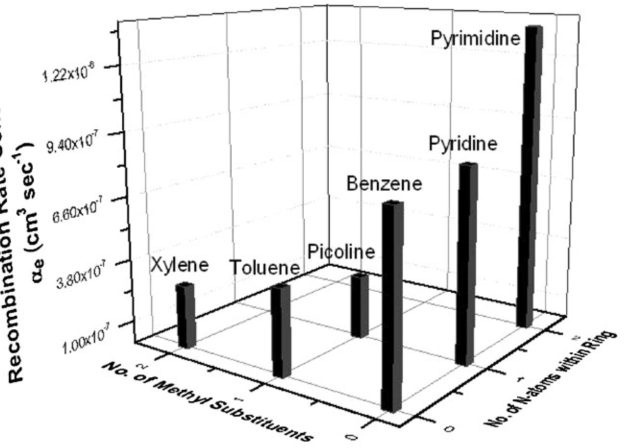

Fig. 2. A plot of the rate coefficients, α_e, (cm^3 s^{-1}) for a series of recombining protonated single six membered ring compounds as a function of the number of CH_3 substituents and N-atoms in the rings. 2,5-Lutidine and mesitylene were also studied and show increasing values and are included in Table 1, but are omitted from this figure for clarity.

only approximate values of $\alpha_e((RV)_2H^+)$could be obtained through modeling.

3. Results and discussion

A great deal of information can be obtained from a study of Table 1.

For the species with CH_3 substituents attached to the single six membered rings, the RVH^+ rate constants decrease with increasing numbers of CH_3 groups and increase with increasing numbers of N-atoms. The isomeric forms of xylene all had essentially the same α_e, as did the isomers of picoline indicating that, for species of this complexity, any isomer could be used for determining α_e. Note that mesitylene was not consistent with the trend for other protonated aromatic rings that have substituted CH_3 groups. This may be due to its low vapor pressure and the difficulties associated with making a mix in such cases. However, protonated lutidine did conform to the overall trend. These trends can be seen more clearly from the plots in Figs. 2 and 3 for the protonated monomers, RVH^+, and the proton bound dimers, $(RV)_2H^+$, respectively. It is interesting to note that the CH_3 substituents and N-atoms generally showed opposing trends. This behavior is surprising since the CH_3 substituents and N-atoms both provide electrons to the ring.

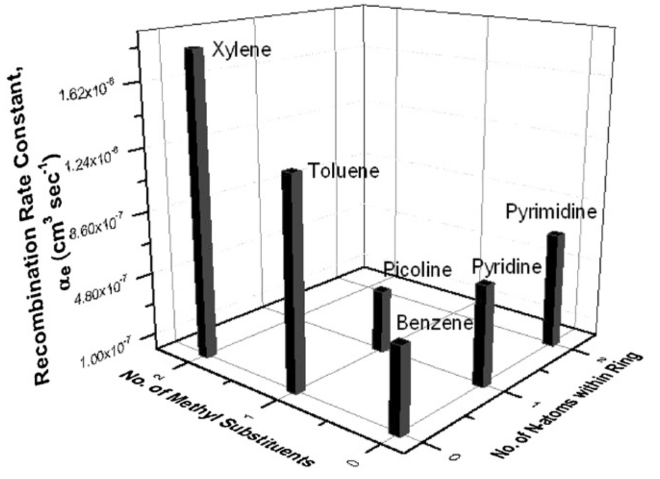

Fig. 3. A plot of the recombining proton bound dimer rate constants, α_e, (cm^3 s^{-1}) for a series of proton bound dimers of single six membered ring compounds as a function of the number of CH_3 substituents and N-atoms in the rings. Mesitylene shows an increasing value and is included in Table 1. However it is omitted here for clarity.

4. Conclusions

The rate constants for a series of recombination's of single six membered ring compounds with CH_3 substituents and N-atoms substituted in the ring show some degree of consistency. The trends in reactivity are, thus, well established and the data can be included in the chemical models of the Titan atmosphere with confidence. From Fig. 2 for the monomers, it is evident that the α_e get larger with increasing numbers of N-atoms in the ring, but smaller with increasing number of methyl substituents. For the dimers, the situation is very different with α_e being larger and increasing with the number of CH_3 substituents. This trend does not continue for mesitylene, which has three CH_3 groups symmetrically arranged in the molecule. With increasing numbers of N-atoms in the ring, the α_e, increases, but the values are smaller than for the monomers. Again the trends are clearer from the plot, as can be seen from Fig. 3. Note that no $\alpha_e((RV)_2H^+)$ was available for lutidine because an RV high enough could not be introduced into the flow tube to make the dimer dominant. These studies are important due to the Titan atmosphere consisting of ~98%, N_2 and there are likely to be significant numbers of N-heteroatoms in the rings and, thus, larger recombination rate constants. Also since the monomer α_e decrease with increasing number of CH_3 substituents, these species have more time to associate to form dimers which then recombine more rapidly with the increasing numbers of CH_3 substituents. These trends should prove useful in chemical models of the Titan atmosphere to allow for the more accurate representation of the ionization balance. Note that within these data, the xylene and the picoline isomers show very little variation. No theoretical calculations have been made for species of this complexity. Such calculations are necessary to fully understand the reaction mechanism which occurs. However, these data may prove critically important to the Titan ionosphere where ring compounds have been detected including one with an N-heteroatom in the ring (pyridine) and one with a CH_3 attached to the ring (toluene). It is likely that, since N_2 and CH_4 are the most abundant species in the Titan atmosphere, the species in this study should be included in the chemical models. Extrapolation of the data to larger numbers of N-atoms and CH_3 groups can now be done with some confidence, and these species could also reasonably be included in the models. Obviously, recombination rate data need to be obtained for the larger species, including those with more than one ring. Also, association reactions of these species with the abundant ions (CH_3^+, $C_3H_3^+$, $C_2H_5^+$, etc.) need to be investigated to confirm the suggested reaction paths to larger species [6]. The products of these reactions could be compared with the observations of masses up to 350 amu detected in the CAPS/IBS experiments on Cassini. From the recombination and association data, limited chemical models could be created such as that given below (Fig. 4).

This shows parallel routes to naphthalene, due to the associations of species such as CH_3^+ and $C_3H_3^+$ with single ring hydrocarbons followed by recombination. For example, previously discussed CH_3^+ associates with benzene to produce toluene after recombination [6]. This toluene then can associate with $C_3H_3^+$ [11], both the cyclic and linear species, which after recombination could produce naphthalene. Alternately, toluene could associate with CH_3^+ followed by recombination to build up the molecules size by CH_2. Similar sequential association/recombination with CH_3^+ could lead to the build up to naphthalene. Such mechanisms with other hydrocarbon ions could rapidly generate multi-ring PAH's, which needs to be investigated.

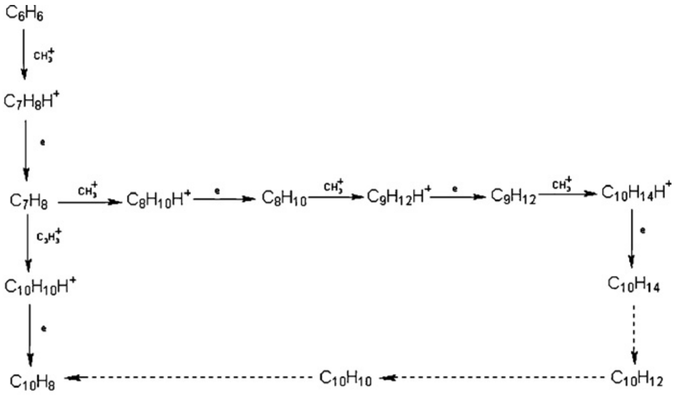

Fig. 4. Possible parallel routes to the production of naphthalene through interactions of benzene with ions present within the Titan atmosphere. The association of $C_3H_3^+$ with toluene followed by recombination rapidly results in the production of naphthalene. The production of naphthalene can alternatively be achieved by a series of association reactions with CH_3^+ followed by recombination. Note that the association reaction pathway with CH_3^+ is hydrogen rich and the doted path represents the loss of these extra hydrogen's.

The study that has been carried out so far has concentrated on the least massive species. However, the Cassini data has shown that there are also more massive species [1], indicating that there are likely to be both aliphatic and aromatic compounds present with polymer forms and nitrile (CN) and amine (NH_2) group attached. These groups can be attached to carbon atoms in six-membered rings (as in the case of CH_3 groups) or at the end of carbon chains. The studies presented here need to be extended to include these groupings and to determine how the presence of these groupings effects the recombination rate constants and if the dependencies are similar to those for the CH_3 groups. In particular, what is the effect of the electron withdrawing power and how does this affect the association to form proton bound dimers, and affect the efficiency of ring closing.

As more side groups are added to the six membered rings, the species begin to more closely resemble thymine and cytosine, the nitrogenous base pairs of nucleic acids. With the recent discovery of non-terrestrial amino acids in the Atmahata Sitta [12] and Murchison [13] meteorites the roles which the interstellar production of organic compounds played in the origin of life on the early Earth is becoming increasing important. The data here, may help in the modeling of the interstellar production of amino acids and complex organic molecules which would have been deposited on the early Earth. There is a wealth of understanding to be gained from such studies and these situations all need to be investigated.

Acknowledgements

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