

## Measurements of $\text{C}_3\text{H}^+ 3$ , $\text{C}_5\text{H}^+ 3$ , $\text{C}_6\text{H}^+ 6$ , $\text{C}_7\text{H}^+ 5$ , and $\text{C}_{10}\text{H}^+ 8$ dissociative recombination rate coefficients

H. Abouelaziz, J. C. Gomet, D. Pasquero, B. R. Rowe, and J. B. A. Mitchell

Citation: *The Journal of Chemical Physics* **99**, 237 (1993); doi: 10.1063/1.465801

View online: <http://dx.doi.org/10.1063/1.465801>

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# Measurements of $C_3H_3^+$ , $C_5H_3^+$ , $C_6H_6^+$ , $C_7H_5^+$ , and $C_{10}H_8^+$ dissociative recombination rate coefficients

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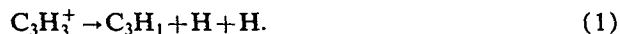
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(Received 13 November 1992; accepted 5 March 1993)

The rate coefficients  $\alpha$  for the dissociative recombination (DR) of the aromatic cyclic ions  $C_6H_6^+$  and  $C_{10}H_8^+$  have been measured in a flowing afterglow experiment at room temperature using  $Xe^+$  and  $Kr^+$  as precursor ions.  $C^+$  was also used as a precursor ion and this allowed the DR rate coefficients for  $C_3H_3^+$ ,  $C_5H_3^+$ , and  $C_7H_5^+$  to be determined. The values obtained (in units of  $10^{-6} \text{ cm}^3 \text{ s}^{-1}$ ) at 300 K are, respectively,  $\alpha(C_3H_3^+) = 0.7$ ,  $\alpha(C_5H_3^+) = 0.9$ ,  $\alpha(C_6H_6^+) = 1.0$ ,  $\alpha(C_7H_5^+) = 0.7$ ,  $\alpha(C_{10}H_8^+) = 0.3$  with an uncertainty estimated to be  $\sim 30\%$ . A discussion is given concerning the relationship between the DR rate and the structural complexity of the ions.

## I. INTRODUCTION

The presence of aromatic and polycyclic aromatic hydrocarbon (PAH) ions in flames is well documented<sup>1,2</sup> and considerable attention has been given to understanding their role in soot formation in fuel rich combustion. Recently, there has been much speculation concerning the presence of such species in interstellar space. The small cyclic radicals  $C_3H$  and  $C_3H_2$  have been identified by Yamamoto *et al.*<sup>3</sup> and by Thaddeus *et al.*<sup>4</sup> and the formation of these species has been attributed to the dissociative recombination of the propenyl ion



For many years, the observation of cyclic species in interstellar clouds had proved elusive and it had been proposed that this was because the dissociative recombination (DR) process (1) is so energetic that it tended to lead to rupture of the carbon ring in cyclic compounds, thus producing aliphatic species.<sup>5</sup>

Another longstanding enigma in interstellar astrophysics has been the identity of the species giving rise to the "diffuse interstellar bands." These features which appear in the infrared absorption spectrum of numerous astrophysical objects have eluded definitive interpretation for over 50 years. In more recent times, a series of diffuse infrared emission bands were discovered.<sup>6</sup> There is now considerable evidence to suggest that these emission features are due to emission of infrared radiation by ionized PAH molecules<sup>7</sup> in space. Arguments have also been made that PAH molecules are responsible for the diffuse interstellar bands<sup>8</sup> although there are some problems concerning the mechanisms for producing specific PAH's.<sup>9</sup> Attempts at modeling the ion chemistry of PAH compounds in interstellar clouds have been made<sup>10</sup> and one of the significant processes that must be included in such models is the neutralization of PAH ions by electron recombination. Up until this time, there has been a complete absence of information concerning the rate for PAH ion-electron

recombination. Indeed, the entire field of complex ion-electron recombination is an open subject.<sup>11</sup>

This paper describes a series of experiments in which the flowing afterglow Langmuir probe-mass spectrometer (FALP-MS) apparatus at the Université de Rennes has been used to measure rate coefficients for the dissociative recombination of aromatic and PAH ions at room temperature.

## II. EXPERIMENTAL METHOD

The FALP-MS apparatus is illustrated in Fig. 1 and has been discussed in detail elsewhere.<sup>12</sup> It employs a movable Langmuir probe which is used to measure the electron density as a function of distance along the flow tube. It also incorporates, however, a movable mass spectrometer and this is used to monitor the density of individual ions along the tube. This arrangement allows the rate coefficients for the recombination of individual ions in mixed ion plasmas to be measured and greatly extends the capabilities of the flowing afterglow method.

Helium buffer gas, dried by passage through a liquid nitrogen trap, is introduced at a flow rate of 24  $\ell/\text{min}$  through the entry port  $G_1$  into a 4 cm diam Pyrex tube. Gas flow is established along the tube by means of a roots pump. A microwave discharge in this tube produces a helium plasma that contains He,  $He^+$ ,  $He_2^+$ , metastable helium atoms,  $He^m$ , and electrons. A second gas such as xenon, krypton, or carbon monoxide is injected through the entry port  $G_2$  and converts the helium plasma into one containing  $Xe^+$ ,  $Kr^+$  or  $C^+$  ions, respectively, via ion-molecule and charge-exchange reactions.

A second reactant gas, in this case benzene or naphthalene vapor, is introduced at the entry port  $G_3$  consisting of eight axially arranged hypodermic needles. This gas reacts with the ions produced at  $G_2$  to produce the particular ions,  $M^+$ , that are to be studied.

Suppose that  $M^+$  can undergo recombination with electrons

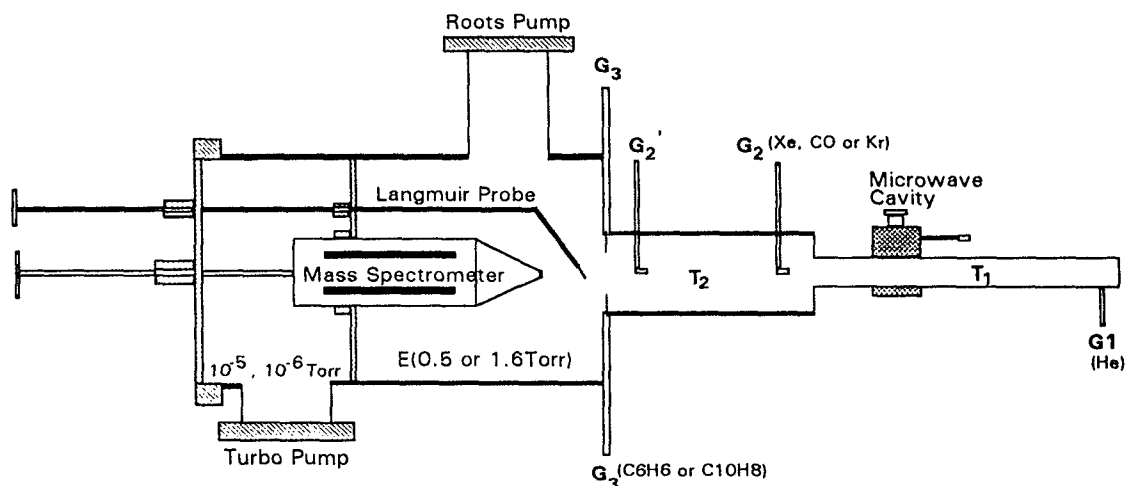


FIG. 1. New flowing afterglow apparatus at the University of Rennes (FALP-MS).



and can also undergo ion–molecule reaction with an impurity gas, X,



We can designate the rate coefficient of reaction (2) as  $\alpha$  and that of reaction (3) as  $k$ . One can write down the equation for the change in the concentration of  $M^+$  along the tube as

$$\frac{d[M^+]}{dt} = v \frac{d[M^+]}{dz} = -\alpha[M^+]n_e - k[M^+][X], \quad (1)$$

where  $z$  is the distance along the tube. One can integrate Eq. (1) from some starting position,  $z_0$  to some position  $z$ , thus,

$$v \ln \frac{[M^+]_z}{[M^+]_{z_0}} = -\alpha \int_{z_0}^z n_e dz - k[X](z - z_0), \quad (2)$$

where  $v$  is the flow velocity along the tube,  $n_e$  is the electron density, and  $[M^+]_z$  is the density of  $M^+$  at a distance  $z$ . It has been determined in other experiments that ambipolar diffusion is negligible in this apparatus. If the density of impurities  $[X]$  is very low or if  $k$  is very small, then one can determine  $\alpha$  by measuring the ratio

$$\ln \frac{[M^+]_z}{[M^+]_{z_0}} \text{ vs } \frac{1}{v} \int_{z_0}^z n_e dz$$

for different  $z$  values along the tube. This should yield a straight line plot with slope  $\alpha$ . An alternative method of determining  $\alpha$  is to measure the same ratio at a fixed position while the electron density  $n_e$  is varied by altering the position of the microwave cavity and by varying the microwave power. The concentration of impurity gas  $[X]$  will be independent of  $n_e$  and so the determination of  $\alpha$  will not be affected even if impurities are present. In practice, both methods are used and good agreement has generally been found between the values measured in each case.

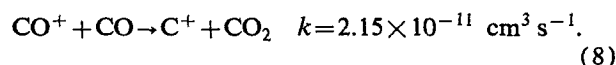
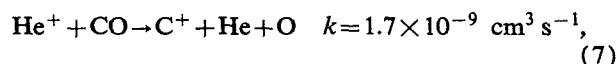
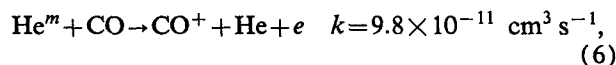
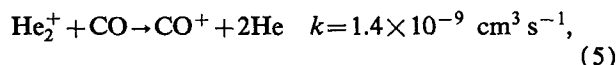
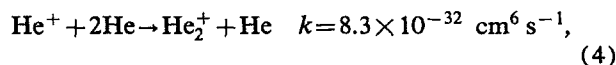
This particular set of experiments was complicated by the low vapor pressures of the reactant gases used, namely benzene and naphthalene vapors. In subsequent studies that will focus on heavier species with even lower vapor pressures, it will be necessary to heat the entry port through which the reactant gas is introduced.

A second complication arose due to the rapid coating of the Langmuir probe surface with deposited carbon. In order to minimize the effects of this disturbance, the probe was thermally cleaned before every measurement by the passage of an electric current of 1 mA.

### III. EXPERIMENTAL RESULTS

#### A. $C^+$ precursor ion

The reaction between  $C^+$  ions and  $C_6H_6$  have been measured elsewhere<sup>13</sup> and the rate coefficient and product branching ratios are known.  $C^+$  was selected therefore for use in the benzene experiment. It was produced by the injection of  $100 \text{ cm}^3 \text{ min}^{-1}$  of CO through the entry port  $G_2$  resulting in the following reactions with the helium plasma:



The rate coefficients for ion–molecule reactions, quoted in this paper, have been taken from Ref. 13 unless otherwise stated.

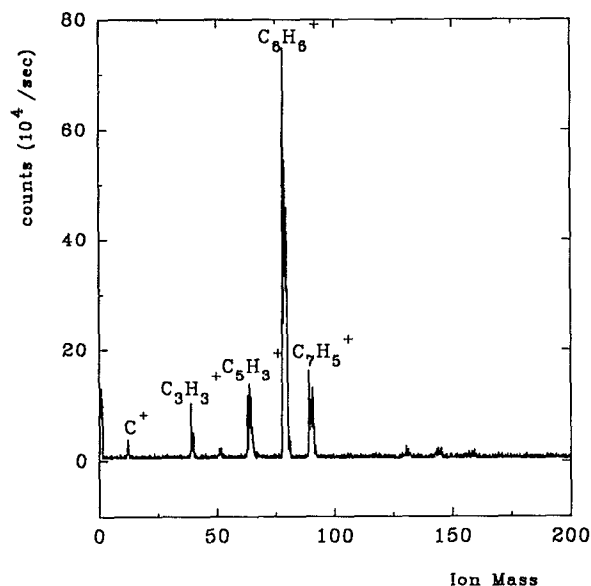
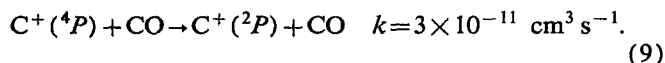


FIG. 2. Typical mass spectrum taken during the measurements at 5 cm of  $G_3$ .

It is important to ensure that the carbon ions are all in their ground  $^2P$  state since the first excited state,  $^4P$ , has sufficient internal energy (16.4 eV) to break the benzene ring. Reactions (7) and (8) are not sufficiently exothermic to produce  $C^+$  in the excited  $^4P$  state. Interaction with atomic carbon could produce this state but the flow rate of CO is kept sufficiently high to ensure that any  $C^+ (^4P)$  formed would rapidly be converted to the ground  $^2P$  via the reaction



A mass spectrum, taken close to the entry port  $G_3$  showed that  $C^+$  was the only ion present in the discharge at this point.

Benzene vapor was introduced further downstream at  $G_3$  at a rate of  $10 \text{ cm}^3 \text{ min}^{-1}$ . The  $C^+$  ions react with the benzene to give the following products:<sup>14</sup>

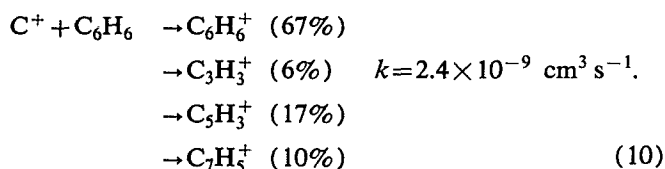


Figure 2 shows the mass spectrum taken in the reaction zone, downstream from  $G_3$ . It can be seen that  $C_6H_6^+$  comprises 70% of the total in good agreement with Ref. 14. Also it is seen that only the ions produced by reaction (10) were found. Since the pressure in the apparatus is rather low (0.5 Torr), cluster formation via three-body association reactions is very inefficient and so no dimer ions were found.

It can be seen from Fig. 2 that a  $C^+$  ion peak appears in the mass spectrum. The recombination of  $C^+$  ions with electrons is a very slow process and the only process lead-

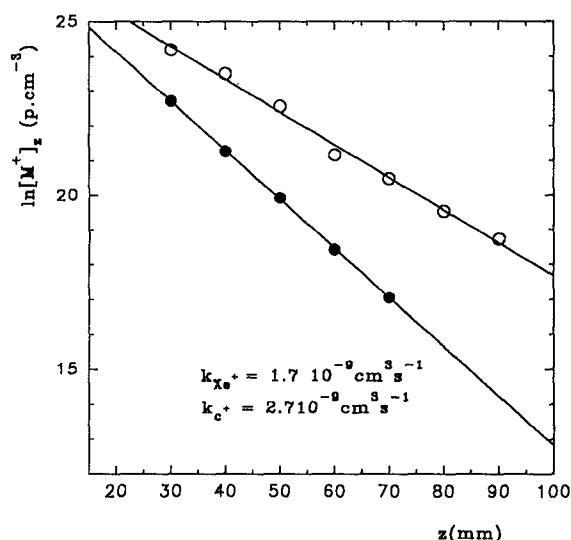


FIG. 3. Plots of decay of  $C^+$  and  $Xe^+$  along the flow tube as a function of mass spectrometer and Langmuir probe position.

ing to the demise of  $C^+$  is reaction (10). One can write the equation for the change of  $C^+$  concentration thus,

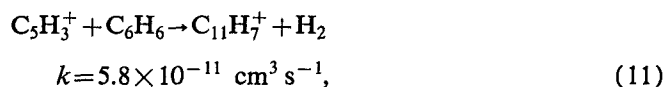
$$\frac{d[C^+]}{dt} = v \frac{d[C^+]}{dz} = -k_{C^+}[C^+][C_6H_6]. \quad (3)$$

Integrating with respect to  $z$  yields

$$\ln \frac{[C^+]_z}{[C^+]_{z_0}} = -\frac{k_{C^+}}{v} [C_6H_6] (z - z_0). \quad (4)$$

If the flow rate of benzene is kept constant, a plot of  $\ln[C^+]_z/[C^+]_{z_0}$  vs  $z$  is linear with a slope of  $-(k_{C^+}/v)[C_6H_6]$ . Using this analysis and our data (Fig. 3), we were able to determine a value of  $k_{C^+}$  of  $2.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  in good agreement with Ref. 14.

The only ion-molecule reaction that would involve any of the molecular ions in the interaction region is



but the characteristic time  $(k[C_6H_6])^{-1}$  for this reaction (2600  $\mu\text{s}$ ) is long compared with the lifetime of the ions in the apparatus (560  $\mu\text{s}$ ) and so can be neglected.

Figures 4, 5, 6, and 7 show plots of

$$\ln \frac{[M^+]_z}{[M^+]_{z_0}} \text{ vs } \frac{1}{v} \int_{z_0}^z n_e dz$$

for the ions produced from the  $C^+-C_6H_6$  reaction and from these the (300 K) recombination rate coefficients have been determined. These are listed in Table I.

The uncertainty concerning these results arose from three factors. The velocity of the plasma flow was measured by using the Langmuir probe and pulse modulating the microwave discharge. The accuracy of such a technique was found to be very good, around 3%. The second contribution came from the calculation of the integral of the electron density. It was actually the uncertainty in the

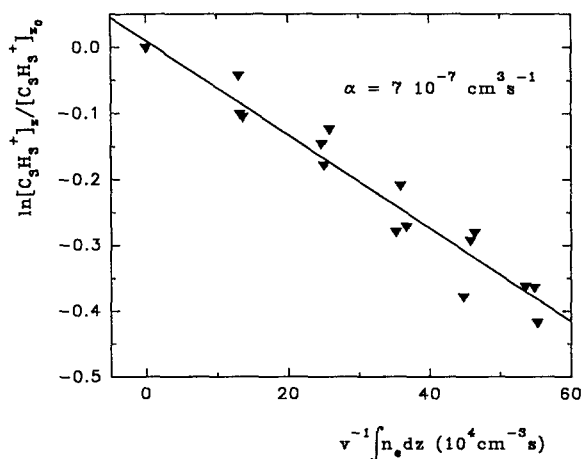


FIG. 4. Plots of decay of  $C_3H_3^+$  along the flow tube as a function of integrated electron density. Variation of  $n_e$  due to decreasing density along the flow.

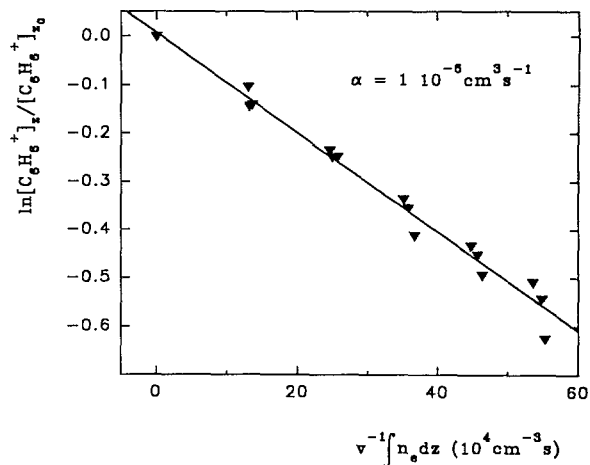


FIG. 6. Plots of decay of  $C_3H_3^+$  along the flow tube as a function of integrated electron density. Variation of  $n_e$  due to decreasing density along the flow.

electron density itself. As the reproducibility of Langmuir probe measurements was generally very good and the probe length was also well defined, an uncertainty of 8% was acceptable there. The last contribution to the uncertainty in  $\alpha$  resulted from the determination of the ion density along the flow axis. This required the knowledge of the electron density and the intensities of the whole ions that are present in the mass spectrum. By averaging over several mass spectra, it was possible to obtain a very low error (3%) in the different peak intensities. It is known however that the sensitivity of the mass spectrometer can easily change within the observed mass range due to mass discrimination effects. In order to minimize this problem, the resolution of the mass spectrometer was decreased until the ratios of the peak intensities were unchanged by a further decrease. Although the mass discrimination effects are always difficult to evaluate, we estimated a maximal addi-

tional error of  $\sim 15\%$ . Summing up, the total uncertainty was found to be 30%.

The only previous measurement for the recombination of one of these ions was that of Graham and Goodings<sup>15</sup> for  $C_3H_3^+$ . They obtained a value of  $1 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  at 2000 K. Although the rate coefficient for DR is usually thought to vary as  $T^{-1/2}$ , merged beams studies by McGowan *et al.*<sup>16</sup> have shown that rates for polyatomic species usually display a faster decrease with temperature above 1000 K. Thus a  $T^{-1}$  variation might be more appropriate for these ions. Such a variation would produce good agreement between the results of Graham and Goodings and the present measurements.

Further discussion of these results will be reserved for later.

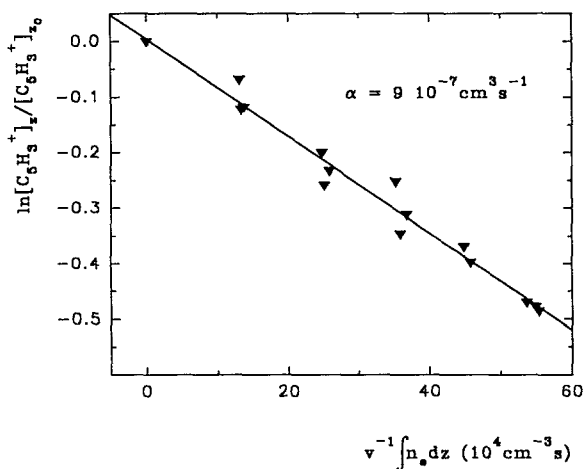


FIG. 5. Plots of decay of  $C_6H_6^+$  along the flow tube as a function of integrated electron density. Variation of  $n_e$  due to decreasing density along the flow.

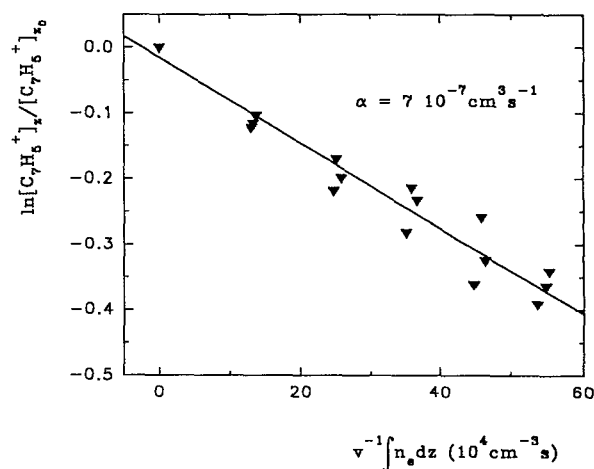


FIG. 7. Plots of decay of  $C_7H_7^+$  along the flow tube as a function of integrated electron density. Variation of  $n_e$  due to decreasing density along the flow.

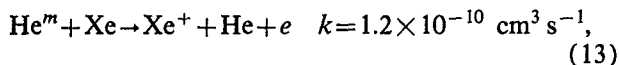
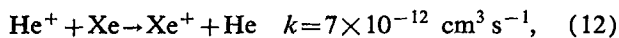
TABLE I. Measured dissociative recombination rate coefficients of  $C_3H_3^+$ ,  $C_3H_3^+$ ,  $C_6H_6^+$ ,  $C_7H_5^+$ , and  $C_{10}H_8^+$  at 300 K.

Formula	Species	$\alpha \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ measured
$C_3H_3^+$	Cyclopropenyl ion	$7 \pm 2$
$C_3H_3^+$	Unknown	$9 \pm 3$
$C_6H_6^+$	Benzene ion	$10 \pm 3$
$C_7H_5^+$	Unknown	$7 \pm 2$
$C_{10}H_8^+$	Naphthalene ion	$3 \pm 1$

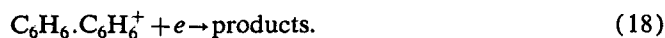
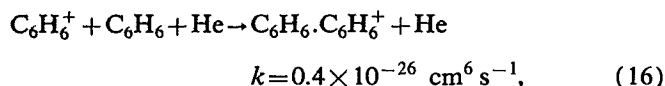
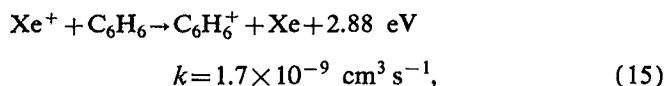
## B. $Xe^+$ precursor ion

$Xe^+$  has an ionization potential of 12.13 eV and reacts with benzene to produce only one ion,  $C_6H_6^+$ , via a charge exchange process. We have measured the rate for the  $Xe^+ - C_6H_6$  reaction, using the method described above and find a rate of  $1.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  (see Fig. 3).

$Xe^+$  is formed via the reactions



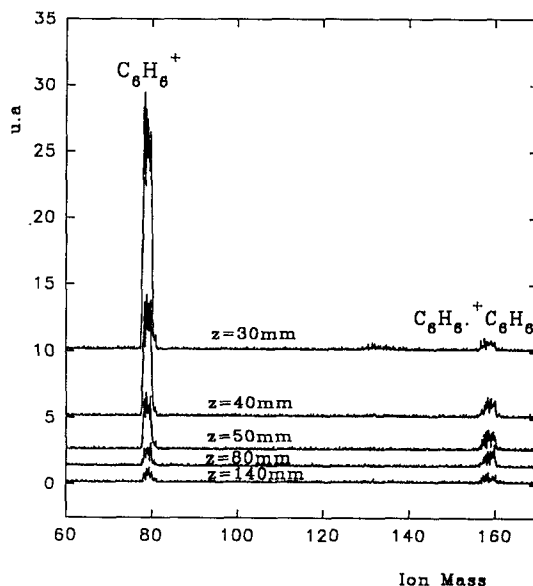
The first two reactions are slow and in order to produce sufficient  $Xe^+$ , the pressure in the flow tube was raised to 1.6 Torr so that reaction (14) dominated. Benzene vapor was injected at  $G_3$  giving rise to the following reactions:



The mass spectrum downstream from  $G_3$ , measured using  $Xe^+$  and  $C_6H_6$  is shown in Fig. 8 and it can be seen that the dimer ion is a significant species. Reaction (16) is very fast and the characteristic time for dimer formation at 1.6 Torr is  $225 \mu\text{s}$  which is short compared with the ion lifetime in the apparatus of  $1540 \mu\text{s}$ . This means that reaction (16) represents a loss mechanism for  $C_6H_6^+$  and so must be taken into account when measuring the recombination coefficient. This is accomplished by using the technique described above where the ratio of

$$\ln \frac{[C_6H_6^+]_z}{[C_6H_6^+]_{z_0}} \text{ vs } \frac{1}{v} \int_{z_0}^z n_e dz$$

is measured at a single  $z$  value while the electron density is varied. This was found to yield a value of  $\alpha(C_6H_6^+) = 1 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$  in good agreement with that obtained using  $C^+$  as the precursor ion. The alternative technique

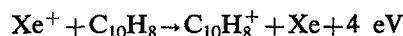
FIG. 8. Mass spectra of  $C_6H_6^+$  and  $C_6H_6^+ \cdot C_6H_6$  (aggregate) at different separations between the mass spectrometer and the entry port  $G_3$ .

where the measurements are taken at different  $z$  values was found to yield a larger rate due to the influence of reaction (16).

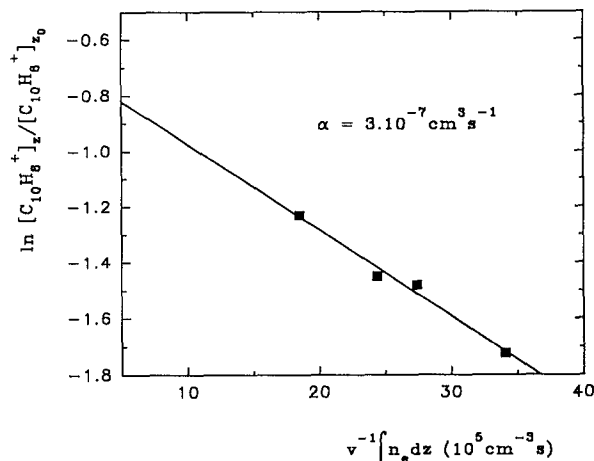
The experiment was repeated with  $Kr^+$  as the precursor ion and again a value of  $1 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$  was found.

## C. Naphthalene ion recombination

The ionization potential of naphthalene is 8.12 eV and  $Xe^+$  was chosen to be the precursor ion as the reaction



is not sufficiently exothermic to break the naphthalene ring structure. The experiment was performed as in the benzene case and Fig. 9 shows the plot of

FIG. 9. Plot of decay of  $C_{10}H_8^+$  at fixed distance as a function of integrated electron density.  $n_e$  varied by changes in the discharge power and cavity position.

$$\ln \frac{[C_{10}H_8^+]_z}{[C_{10}H_8^+]_{z_0}} \text{ vs } \frac{1}{v} \int_{z_0}^z n_e dz$$

taken at one  $z$  value for a variety of electron densities. Again there was evidence of clustering in the plasma and so the other method of varying the  $z$  position was not employed.

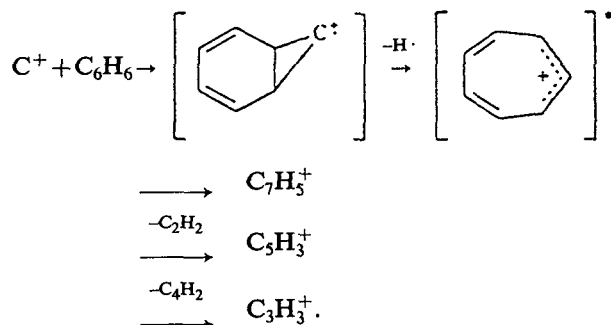
The result of this measurement is given in Table I.

#### IV. DISCUSSION

There are several questions concerning this study that cannot be satisfactorily answered. The first concerns the state of excitation of the ions. These complex ions have many different vibrational and rotational modes and it is not possible to say that the ions are definitely in their ground states. Eventually, it is planned to incorporate an infrared laser system into the experiment which will allow absorption spectra of the reacting ions to be observed. Excited vibrational states will appear as "hot-bands" in such spectra and this system will permit a much better characterization of the ions to be performed.

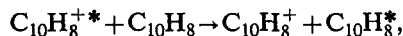
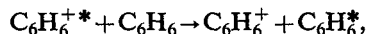
A second question concerns the isomeric form of the ions and in particular whether or not the ions are in their cyclic form. In this instance, perhaps, a better answer can be given. For the  $C_3H_3^+$  ion, the cyclopropenyl form of the molecule is more stable than the linear propargylium form by more than 1 eV and so is likely to dominate the plasma.<sup>17</sup> Similarly the very stable aromatic structure of benzene is likely to be preserved in  $C_6H_6^+$  which is formed through charge-exchange reactions. The  $C^+ - C_6H_6$  reaction is exothermic by only 2 eV which is insufficient to break the benzene ring. This requires at least 2.8 eV. For the case of  $Xe^+$ , the exothermicity is 2.88 eV, so the reaction is essentially thermoneutral for ring-breaking. For  $Kr^+$ , the reaction is exothermic by 4.75 eV, however, the recombination rate measured for  $C_6H_6^+$  produced from  $Kr^+$  is the same as that for  $C_6H_6^+$  produced from  $C^+$  and  $Xe^+$  suggesting that the structures are the same.

Smith and DeCorpo<sup>18</sup> have proposed that  $C_7H_5^+$ ,  $C_5H_3^+$ , and  $C_3H_3^+$ , are formed via an attack on a  $C=C$  bond in benzene by the  $C^+$  ion to form the seven carbon, tropylium structure, thus



Thus  $C_7H_5^+$  is likely to have a seven carbon ring structure. As mentioned above,  $C_3H_3^+$  is likely to favor the cyclopropenyl ring structure and probably,  $C_5H_3^+$  will favor the five-carbon cyclopentadienyl structure.

In the case of naphthalene, there can be little doubt that the ion will retain some form of ring structure, most likely similar to that of the parent. It has to be noticed that for benzene and naphthalene ions the following processes:



are probably extremely efficient in cooling down the internal excitation and preserving the structure since it is known that near resonant exothermic charge exchange is usually a fast process.<sup>19</sup> This conclusion is supported by the fact that the value of  $\alpha(C_6H_6^+)$  does not change with the nature of the precursor ion.

However, it must be realized that the above discussion involves considerable speculation and formal identification of the ionic structures will require the application of spectroscopic techniques to the measurement.

Turning to the actual values for the rate coefficients, it is clear from Table I that there is no obvious relationship between the values of the rates and ion complexity. In a recent paper, Bates<sup>20</sup> has argued that the dissociative recombination rate for a polyatomic ion can be estimated from the typical rate for the recombination of a diatomic molecule ( $10^{-7} \text{ cm}^3 \text{ s}^{-1}$ ) times the number of bonds that can be broken.

Since neutral molecules have even numbers of electrons, their molecular ions have odd numbers and are thus less stable. In a system that is unsaturated or that has a ring structure, the odd electron is delocalized and this tends to enhance its stability. When such a molecular ion captures an electron, it is difficult for the sudden localization of the energy, required to break a bond, to occur. Indeed, in the recombination process, it is perhaps more likely that the energy will be absorbed in a variety of vibrational modes that will eventually decay via the emission of radiation. The overall rate of a recombination process is both determined by the probability of electron capture, and by the efficiency with which the system can disperse the recombination energy. For a given ion, a process in which the energy is first stored is likely to display a smaller recombination rate than one which immediately leads to the ejection of an atom or radical. An analogy to this occurs in electron impact dissociation where it is found that the rate of decomposition is lower for unsaturated or aromatic molecular ions than for systems containing only saturated bonds.<sup>21</sup> On the other hand, as the size of the ions increases, the stabilization by dispersion of energy through a variety of modes could become extremely efficient compared to autoionization. In such a case, the rate would be limited essentially by a kind of capture process. However, a simple formula as given by Bates,<sup>20</sup> obviously does not apply to the case of massive ions which charges are delocalized.

It is our intention to extend this study to larger polycyclic aromatic species and to branched aromatics. One might expect that the rates for the latter might be larger than for unbranched aromatics as it should be easier to cast

off the side chain and that the rates for PAH ions might increase with size as the energy delocalization would be more efficient.

## ACKNOWLEDGMENTS

This work was made possible by the financial support of GRD Physico-Chimie des Molécules et des Grains Interstellaires and Dynamique des Réactions Moléculaires and by a NATO collaborative grant. We would also thank A. Canosa for his help in the preparation of the manuscript.

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