Do H atoms stick to PAH cations in the interstellar medium?

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Abstract. Recent experimental work has shown that under relatively high density conditions, selected PAH cations associate efficiently with H atoms to form protonated PAH ions. If such association reactions occur efficiently under low density conditions, the protonated PAH ions can be considered as candidate molecular species in diffuse interstellar clouds. The high density and low density processes are not the same, however, since at high density association proceeds by collisional stabilization while at low density it proceeds by radiative stabilization. In this paper, we show using theoretical techniques that for the cation $C_6H_6^+$, the laboratory results do not prove that the association with H is efficient at low densities, whereas for $C_{10}H_8^+$ and most probably larger PAH cations, the radiative association with H is very efficient. For these latter cations, the competitive H-atom transfer channels (e.g. $H + C_{10}H_8^+ \rightarrow C_{10}H_7^+ + H_2$), which can lead to catalytic formation of H_2 by regeneration of the PAH cations, are probably not important.

Key words: molecular processes – ISM: molecules – ISM: clouds – ISM: abundances

1. Introduction

The PAH hypothesis (Allamandola et al. 1985, 1989; Léger & Puget 1984; Puget & Léger 1989) has stimulated astrochemists to understand the physics and chemistry of aromatic molecules under interstellar conditions (see, e.g. Jochims et al. 1994). Recent experimental studies of assorted reactions of the PAH cations $C_6H_6^+$ (benzene), $C_{10}H_8^+$ (naphthalene), and $C_{16}H_{10}^+$ (pyrene) with the atoms H, O, and N using the selected ion flow tube (SIFT) technique (Bohme 1992; Petrie et al. 1992; Le Page et al. 1997; Snow et al. 1998; Scott et al. 1997) have shown that association channels, in which the PAH cation and the atom stick together, are prominent, especially for reactions with atomic hydrogen, a prevalent if not dominant form of hydrogen in diffuse interstellar clouds. Rapid association reactions with H might lead to observable quantities of protonated PAH's in such sources. Under the conditions of the experiments, however, the protonated PAH cationic product is stabilized by colli-

sions with the bath gas helium rather than via the slower radiative mechanism, which dominates only at gas densities typically $\leq 10^{12}\,cm^{-3}$. The experimental results do not therefore pertain directly to the interstellar medium and have to be approached in a cautious manner (Bates & Herbst 1988). In this paper, we look in detail at two of the recently studied association reactions:
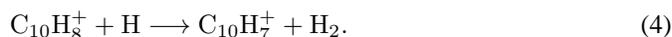
$$C_6H_6^+ + H \longrightarrow C_6H_7^+ \tag{1}$$

and

$$C_{10}H_8^+ + H \longrightarrow C_{10}H_9^+ \tag{2}$$

so as to determine the rate coefficients for association via the radiative mechanism. In the laboratory both these processes have only been studied in the collisional regime. The processes must compete with normal exothermic reactions; i.e.,

$$C_6H_6^+ + H \longrightarrow C_6H_5^+ + H_2 \tag{3}$$

and

$$C_{10}H_8^+ + H \longrightarrow C_{10}H_7^+ + H_2. \tag{4}$$

Reaction (3) has a measured branching fraction of 0.35 (Scott et al. 1997) under SIFT conditions ([He] $\approx 10^{16}\,cm^{-3}$) at 300 K, while reaction (4) has not been detected but is known to be slightly exothermic (Ho et al. 1995). Cassam-Chenaï et al. (1994) have suggested that reactions of the type exemplified by (3) and (4) may well constitute an important formation mechanism for interstellar molecular hydrogen. Assuming that the deprotonated ionic products of these reactions can then associate with H atoms, the formation of interstellar H_2 in this manner can be regarded as catalytic.

Since the association reactions

$$C_6H_5^+ + H_2 \longrightarrow C_6H_7^+ \tag{5}$$

and

$$C_{10}H_7^+ + H_2 \longrightarrow C_{10}H_9^+ \tag{6}$$

are known to occur, the latter under low density conditions (Scott et al. 1997; LePage et al. 1997; Snow et al. 1998), it is likely that there are no activation energy barriers in the exit channels of reactions (3) and (4). The potential surfaces for the reactions

between $C_6H_6^+$ and H and between $C_{10}H_8^+$ and H then appear as shown in Fig. 1, where the potential minimum refers to the collision complex, which is stabilized in the association channels.

At the simplest level of theory, the effective binary rate coefficient (cm^3 s^{-1}) k_{eff} for association in the presence of a competitive exothermic channel is given by the expression (Herbst 1985a,b; Bates & Herbst 1988; Klippenstein et al. 1996; Herbst 1996)

$$k_{eff} = \frac{k_1(k_r + k_c[He])}{k_{-1} + k_{-2} + k_r + k_c[He]} \tag{7}$$

where k_1 (cm^3 s^{-1}) is the collisional rate coefficient for complex formation, k_{-1} and k_{-2} are the unimolecular rate coefficients (s^{-1}) for complex dissociation into reactants and exothermic products, respectively, and k_r and k_c are the unimolecular and bimolecular rate coefficients for radiative and collisional stabilization of the complex, respectively. The form of the expression for k_{eff} derives from the assumption that the complex is at steady state (Bates & Herbst 1988) and that the exothermic products are formed from the complex and not via a "parallel" process which avoids the complex (Gerlich & Horning 1992.) In this formulation, all of the rate coefficients in expression (7) are thermal averages, while k_r and k_c represent rate coefficients for complex stabilization via one "strong" process which removes sufficient energy. Stabilization via successive processes in which only a fraction of the needed energy is lost is not considered explicitly. For systems without exothermic channels, $k_r \approx 10^2$ s^{-1} and $k_c \approx 10^{-10}$ cm^3 s^{-1} (Bates & Herbst 1988). The radiative stabilization rate coefficient is typically estimated by considering vibrational emission in a microcanonical or canonical model via harmonic oscillator selection rules and using measured and/or calculated absorption coefficients (Herbst & Dunbar 1991, Klippenstein et al. 1996). The collisional stabilization rate coefficient is determined mainly by comparing the efficiency of various bath gases. These values can be significantly lower if exothermic channels exist such that complex stabilization requires considerable amounts of energy (see Fig. 1).

Unless the complex dissociation rate coefficients k_{-1} and k_{-2} are extraordinarily small, a logarithmic plot of k_{eff} vs [He] shows a horizontal line at low densities corresponding to the radiative association limit, a linear plot at densities above $\approx 10^{12}$ cm^{-3} corresponding to the three-body regime, and a near-saturated to saturated regime at still higher densities, where the effective rate coefficient for association approaches the collisional value k_1. The value of k_1 is typically given for non-polar neutral reactants by the Langevin approximation (Herbst 1996), in which all collision partners that surmount a centrifugal barrier depending on centrifugal and long-range ion-induced dipole forces proceed to form a complex. This assumption, which is generally successful for ion-molecule reactions, is less successful for ion-atom processes, in which collisional rate coefficients can be up to 10 times smaller than the Langevin value (see, e.g., Scott et al. 1997; Snow et al. 1998). Although differing explanations for such low rate coefficients exist, such as effi-
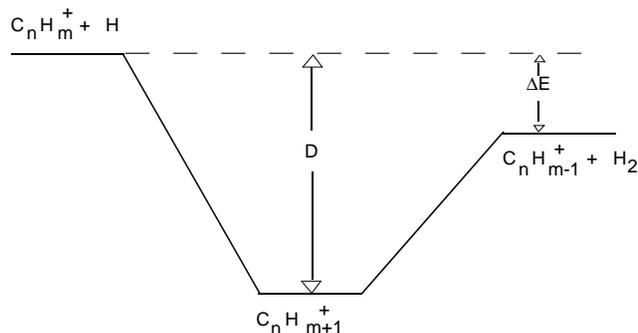

Fig. 1. The potential surface for association of PAH cations with atomic hydrogen in the presence of a competitive exothermic channel in which a hydrogen atom transfers from the PAH to form molecular hydrogen. The symbol D represents the dissociation energy of the complex into reactants while the symbol ΔE represents the reaction exoergicity. ΔE is 0.69 eV for reaction (3) and is uncertain for reaction (4) – see text.

ciencies less than unity for complex formation (Truhlar 1975, Gerlich et al. 1980, Herbst 1982), and small potential barriers (Giles et al. 1989, Sorgenfrei & Gerlich 1994), a reasonable general explanation is that the long-range forces are weaker than in the Langevin approximation. Such an explanation has been advanced, for example, by Klippenstein (1997) for the case of H + $C_6H_5^+$. For such processes, saturation will occur at values below $k_{eff} = 10^{-9}$ cm^3 s^{-1}, as appears to happen for reaction (1) (Petrie et al. 1992).

For systems with very long-lived complexes ($k_r \geq k_{-1}, k_{-2}$) it is possible that k_{eff} has little dependence on density at all and remains at or near k_1. Such complexes are associated with both large dissociation energies and/or large numbers of vibrational degrees of freedom.

Even at the simple level of theory depicted above, it is difficult to infer the low pressure radiative rate coefficient for association from measurements at higher densities. With the SIFT apparatus, the experiment often lies in a near saturated regime ([He] $\approx 10^{16}$ cm^{-3}). Under such conditions one can only determine lower limits to the three-body and radiative association rate coefficients. These lower limits can be orders of magnitude too low (McEwan et al. 1999).

A closer look at the physics of the collision makes the estimation of the low pressure association rate from SIFT data even more difficult. Expression (7) for k_{eff} is oversimplified in several aspects. First, complex stabilization in the presence of a strongly exothermic channel undoubtedly requires more than one collision and possibly more than one photon to achieve stabilization. Secondly, the rate coefficients in expression (7) are functions of energy and angular momentum, not independently averaged thermal entities, and sums over these parameters relevant to the details of the collision and the temperature of the system must be undertaken. The net result of these complications is that determination of the radiative association rate coefficient in the absence of direct experimental data at the temperature desired is best obtained by a detailed theoretical approach. This approach can be tested in part by determining if it can reproduce the SIFT data. In this paper, we utilize the phase space

method (Chesnavich & Bowers 1982; Herbst 1985a,b, 1996; Bates & Herbst 1988; Klippenstein et al. 1996) to calculate the radiative association rate coefficients for reactions (1)-(2). Still more detailed methods based on potentials such as shown in Fig. 1 have been developed (Gilbert & Smith 1990; Wardlaw & Marcus 1986; Klippenstein 1991; Klippenstein et al. 1996) but these are more computationally intensive and are most needed for the higher density regimes.

To further complicate matters, the potential can be more complex than shown in Fig. 1. For example, small barriers might be present along the path (e.g. Sorgenfrei & Gerlich 1994; Giles et al. 1989) or alternative pathways can exist for exothermic products (Gerlich & Horning 1992). Although there are no indications that either of these possibilities need be considered here (we have searched for a possible barrier), our state of knowledge of the potential energy surfaces is insufficient to rule them out totally.

2. Phase space approach and quantum chemical calculations

In the phase space approach, the rate coefficients for complex dissociation are regarded as functions of angular momenum J and total energy E. In addition, the complex formation rate coefficient k_1 is dependent on the quantum states of the reactants. Thus, in the limit of "strong" relaxation, Eq. (7) refers to the effective association rate coefficient for reactants in specific angular momentum states colliding with a specific energy to form a complex of specific energy and angular momentum. The complex dissociation rate coefficients $k_{-1}(J, E)$ and $k_{-2}(J, E)$ are determined from microscopic reversibility (Herbst 1985b). A thermal association rate coefficient must be obtained via summation over the appropriate angular momentum and energy distributions. Complex formation for systems with non-polar neutral reactants is generally assumed to proceed via the Langevin approximation (Herbst 1996), which determines the range of angular momentum values of the complex. This assumption must be modified for the reactions studied here because the bulk of the experimental evidence indicates that complex formation occurs at lower rates. Such evidence includes total (association + H-atom transfer) rate coefficients that are much smaller than Langevin (see, e.g., Scott et al. 1997; Snow et al. 1998) as well as strong evidence for the saturation of reaction (1) at a value considerably less than the Langevin value (Petrie et al. 1992). As discussed in the previous section, we have chosen to assume that the discrepancy is due to a weaker long-range potential surface than is assumed in the Langevin formulation (see, e.g., Klippenstein 1997) rather than to relax the assumption that the probability of complex formation is unity (Truhlar 1975, Gerlich et al. 1980, Herbst 1982). We have therefore scaled the polarizability of H, which governs the long-range ion-induced dipole potential, by a scaling factor $f_H = 0.060$. A weaker long-range attraction results in fewer partial waves and a lower cutoff for the maximum impact parameter or angular momentum.

Since more than one "weak" inelastic collision or more than one infrared photon is generally needed to stabilize the complex

with respect to the exothermic products (an amount of energy exceeding ΔE in Fig. 1 must be shed), relation (7) is no longer valid and must be replaced by a more complex expression where the rate coefficients k_r and k_c reflect the branching between total relaxation and partial relaxation followed by dissociation into exothermic products. The simplest way to take this effect into account is the so-called "step ladder" method, in which a grid of complex vibrational energy levels with fixed spacing δ_{grid} exists from the initial energy of reactants to the energy at which stabilization occurs (Holbrook et al. 1996). Collisions and spontaneous emission of radiation then permit the complex to relax sequentially from one level to the next lower one. At each intermediate level, the possibility of complex dissociation into exothermic products must also be considered. For example, the reduced radiative stabilization rate coefficient in the low pressure limit, k_r', reflecting the existence of n intermediate complex levels, is given by the expression:

$$k_r' = k_r \times \prod_{i=1}^{n} \frac{k_r}{k_{i,-2} + k_r} \tag{8}$$

where we have assumed that k_r has no energy dependence and that the complex in intermediate level i can only dissociate into products. A similar expression holds for collisional stabilization in the three-body limit. (More advanced treatments of collisional stabilization also contain inelastic collisions in which the complex actually gains energy – see Holbrook et al. 1996)

The energy spacing between the complex grid levels should correspond to the average amount of energy lost in an inelastic collision or radiation of an infrared photon; here we choose 0.05 eV and 0.18 eV as standard spacings for inelastic collisions and radiative emission respectively. The first number is somewhat greater than kT at 300 K, while the second is an average energy for harmonic oscillator transitions in hydrocarbons (Herbst & Dunbar 1991). These values can be varied to determine their effect on the effective rate coefficient for association. Holbrook et al. (1996) give examples from previous calculations in which spacings of 0.003–0.09 eV are utilized for inelastic collisions at room temperature. For the case of radiation, we also consider the possibility of overtone and combination bands which are energetic enough to allow complex stabilization with one photon (so that the unaltered Eq. 7 is valid in the low pressure domain), but at an emission rate $k_r \approx 1\,\mathrm{s}^{-1}$, which is 1–2 orders of magnitude below the harmonic value (Herbst & Dunbar 1991). For collisional stabilization by He, an energy-independent rate coefficient k_c for stepwise deactivation of $3 \times 10^{-10}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$ is utilized.

The phase space approach requires knowledge of the energetics and rotational constants of reactants, intermediate complex, and products, plus the vibrational frequencies of the complex and exothermic products. The necessary information is listed in Table 1 and derives from various sources. The relative energies are experimental (Lias et al. 1988; Ho et al. 1995), while the harmonic frequencies and rotational constants are theoretical in origin. We have used the Gaussian 94 suite of programs (Frisch et al. 1995) to obtain the vibrational frequencies and rotational constants of $C_6H_7^+$ and $C_{10}H_9^+$, as well as the

Table 1. Energies, harmonic frequencies, and rotational constants of complex and product PAH ions

Molecule	Relative Energy[a] (eV)	Harmonic frequencies[b] (cm^{-1})	Rotational constants[c] (cm^{-1})
$C_6H_6^+$	0.00	$f_H \alpha_H = 0.04\,Å^3$	0.193^d
			0.179
			0.0931
			$g_e/\sigma = 1/6^e$
$C_6H_7^+$	-3.53	174, 318, 370, 591, 597, 658	0.181
		805, 854, 922, 985, 998, 1005	0.177
		1018, 1046, 1054, 1161, 1179, 1241	0.091
		1243, 1334, 1392, 1461, 1509, 1578	$g_e/\sigma = 1/2$
		1628, 1677, 3003, 3022, 3240, 3251	
		3252, 3276, 3277	
$C_6H_5^+$	-0.69	260, 346, 349, 401, 453, 628^f	0.226^g
		650, 769, 849, 861, 862, 939	0.180
		974, 1043, 1063, 1107, 1177, 1257	0.100
		1288, 1429, 1461, 1747, 3075, 3078	$g_e/\sigma = 1/2$
		3112, 3125, 3128	
$C_{10}H_8^+$	0.00	$f_H \alpha_H = 0.04\,Å^3$	0.106
			0.041
			0.030
			$g_e/\sigma = 1/4$
$C_{10}H_9^+$	-2.98	140, 185, 291, 382, 408, 473	0.101
		531, 534, 540, 654, 729, 792	0.040
		833, 855, 883, 904, 975, 1000	0.029
		1006, 1083, 1102, 1125, 1126, 1148	$g_e/\sigma = 1$
		1168, 1249, 1267, 1286, 1315, 1316	
		1366, 1407, 1473, 1506, 1526, 1556	
		1592, 1611, 1671, 1719, 1789, 1828	
		3166, 3189, 3385, 3390, 3392, 3395	
		3407, 3410, 3419	
$C_{10}H_7^+$	-0.01^h	149, 191, 301, 312, 379, 427^i	0.115^j
		463, 501, 536, 612, 657, 706	0.041
		718, 731, 751, 839, 852, 868	0.030
		888, 973, 981, 991, 1025, 1028	$g_e/\sigma = 1$
		1085, 1106, 1149, 1171, 1213, 1244	
		1274, 1315, 1382, 1436, 1447, 1533	
		1602, 1702, 3017, 3027, 3031, 3037	
		3042, 3045, 3064	

[a] experimental values with respect to reactants $PAH^+ + H$; the non-zero energies are for the protonated complex and for the deprotonated ion + H_2 exothermic products

[b] harmonic frequencies shown above have not been scaled for the case of $C_6H_7^+$ and $C_{10}H_9^+$; in the phase space calculations, scaling factors of 0.95 have been used for the former species and 0.89 for the latter. Vibrational frequencies are not needed for reactants.

[c] Rotational constants have been calculated at assorted levels

[d] Klippenstein (1997)

[e] electronic degeneracy divided by symmetry number

[f] Klippenstein (1997)

[g] Klippenstein (1997)

[h] an alternative possibility is -0.27 eV. See text for a discussion of the uncertainty.

[i] Klippenstein (1997)

[j] Klippenstein (1997)

Table 2. Phase space results for $C_6H_6^+ + H$

T(K)	Density (cm^{-3})	Exit Channel	δ_{grid} (eV)	k_{eff} (cm^3 s^{-1})	k_{exo} (cm^3 s^{-1})
300	$1\ 10^{16}$	loose ($f_{H_2} = 1.00$)	0.05	$5.5\ 10^{-11}$	$4.6\ 10^{-10}$
300	$1\ 10^{16}$	loose ($f_{H_2} = 0.0125$)	0.05	$3.5\ 10^{-10}$	$1.7\ 10^{-10}$
300	$1\ 10^{16}$	loose ($f_{H_2} = 0.00125$)	0.03	$4.2\ 10^{-10}$	$9.3\ 10^{-11}$
300	$1\ 10^{16}$	tight	0.05	$3.3\ 10^{-10}$	$1.8\ 10^{-10}$
300	$1\ 10^{04}$	loose ($f_{H_2} = 1.00$)	0.18	$1.4\ 10^{-16}$	$5.2\ 10^{-10}$
300	$1\ 10^{04}$	loose ($f_{H_2} = 0.0125$)	0.18	$1.1\ 10^{-15}$	$5.2\ 10^{-10}$
300	$1\ 10^{04}$	loose ($f_{H_2} = 0.00125$)	0.18	$3.3\ 10^{-15}$	$5.2\ 10^{-10}$
300	$1\ 10^{04}$	tight	0.18	$4.1\ 10^{-16}$	$5.2\ 10^{-10}$
50	$1\ 10^{04}$	loose ($f_{H_2} = 1.00$)	0.18	$2.0\ 10^{-16}$	$5.6\ 10^{-10}$
50	$1\ 10^{04}$	loose ($f_{H_2} = 0.0125$)	0.18	$1.5\ 10^{-15}$	$5.6\ 10^{-10}$
50	$1\ 10^{04}$	loose ($f_{H_2} = 0.00125$)	0.18	$4.8\ 10^{-15}$	$5.6\ 10^{-10}$

rotational constants of $C_{10}H_8^+$. The MP2 level of theory was utilized for $C_6H_7^+$ while the HF/6–31G* level was used for $C_{10}H_8^+$ and $C_{10}H_9^+$. Supplementing our calculations, previous theoretical results from Klippenstein (1997) are listed in Table 1 for assorted species.

Although the phase space result for k_{eff} is typically averaged over thermal distributions of reactant rotational and translational motions, here we have simplified the procedure by using the most probable rotational level of the PAH cationic reactant only. This simplification is needed because of the many populated thermal rotational levels of the PAH cations due to their small rotational constants. The spherical top approximation has been employed, in which the one rotational constant is assumed to be the geometric mean of the three calculated constants A, B, C. Restrictions of rotational levels due to nuclear spin effects have been handled by the symmetry number method.

Complex dissociation into exothermic products occurs, except for the lowest intermediate levels of the grid, with considerable energy above that of the products. It is known that the phase space approach can overestimate the dissociation rate in this instance (Khundkar et al. 1987). In addition to the use of the phase space method (often called a "loose transition state" method in the chemical literature), we have therefore also calculated the dissociation rate for the $C_6H_7^+$ complex, which possesses large amounts of energy, using an RRKM approach (also referred to as a "tight transition state" method; Herbst 1985a). The "tight" transition state is defined along the exit channel of the potential surface (Fig. 1) for best agreement between theory and experiment – see below.

3. Results

Tables 2 and 3 contain, respectively, our computed rate results for $C_6H_6^+ + H$ and $C_{10}H_8^+ + H$. In both tables, rate coefficients are listed for association (k_{eff}) and exothermic reaction (k_{exo}) at two gas densities – 10^{16} cm^{-3}, which corresponds to the SIFT operating condition of 0.3 torr pressure at 300 K, and 10^4 cm^{-3}, which corresponds to the low density (interstellar) limit. The results for each set of reactants are discussed separately.

3.1. $C_6H_6^+ + H$

Using the phase space method with a scaling factor f_{H_2} of unity for the product channel and a grid size of 0.05 eV, we calculate at the SIFT operating density and 300 K that the effective rate coefficient for association is about 10% of the overall rate coefficient of 5×10^{-10} cm^3 s^{-1}. The experimental results of Scott et al. (1997) show a somewhat lower total rate coefficient of 2.1×10^{-10} cm^3 s^{-1} with a branching fraction for association of 65%. The disagreement regarding the total rate coefficient can be reduced by weakening the entrance channel long-range potential by adopting a still lower scaling factor f_H of 0.015. We choose not to further reduce the scaling factor here since the disagreement is not large.

To improve the adequate agreement between theory and experiment regarding the branching fractions, we can pursue two approaches. First, we can introduce a scaling factor of less than unity for the long-range potential on the exit channel. If the long-range potential is weaker, the range of angular momenta is lower, and fewer rotational states of the products are allowed. A scaling factor implies that the backward association reaction will saturate with a rate coefficient below the Langevin value. Such saturation has been seen for the analogous association of $C_{10}H_7^+ + H_2$ (Snow et al. 1998). With a scaling factor $f_{H_2} = 0.0125$, and the grid size maintained the same, the branching fraction leading to association grows to 67%, which is in perfect agreement with experiment. One can lower the scaling factor still further and maintain the correct branching fraction for association by reducing the grid size, so as to require more stabilizing collisions. A second approach is to utilize the "tight" transition state approach to dissociation; locating the transition state at that point in the exit channel potential where it is 2.30 eV greater than the potential minimum leads to a branching fraction for association of 65%. We have additionally assumed that the transition state parameters are similar to those of the complex with the exception that one mode of vibration must be removed.

When the assorted theoretical models are used for low density (radiative) association, we find that the rate coefficient at 300 K is quite small and that there is little if any temperature dependence. At 300 K, we obtain values for k_{ra} in the range $1.4 \times 10^{-16} - 3.3 \times 10^{-15}$ cm^3 s^{-1}. The 50 K values listed in Table 2 are only slightly larger, making this process totally unimportant in the interstellar medium. The basic reason why radiative association is so inefficient is that the $C_6H_7^+$ complex does not have enough degrees of freedom to live long enough to radiate away its excess energy before dissociating into products.

3.2. $C_{10}H_8^+ + H$

Unlike the situation for the benzene cation, the association between the naphthalene ion and atomic hydrogen is calculated to be efficient at all densities. The exothermicity of the reaction to form $C_{10}H_7^+ + H_2$ is uncertain in that there are two widely divergent values - 0.013 eV and 0.273 eV, with the lower of the two values the more probable (Ho et al. 1995). One would expect that with the higher exothermicity, stabilization of the complex

Table 3. Phase space results for $C_{10}H_8^+ + H$

T(K)	Density (cm^{-3})	Exit Channel	δ_{grid} (eV)	ΔE (eV)	k_{eff} (cm^3 s^{-1})	k_{exo} (cm^3 s^{-1})
300	$1\,10^{16}$	loose ($f_{H_2} = 1.00$)	0.05	0.273	$5.2\,10^{-10}$	$5.5\,10^{-14}$
300	$1\,10^{16}$	loose ($f_{H_2} = 0.0125$)	0.05	0.273	$5.2\,10^{-10}$	$5.5\,10^{-14}$
300	$1\,10^{16}$	loose ($f_{H_2} = 1.00$)	0.05	0.013	$5.2\,10^{-10}$	$4.0\,10^{-15}$
300	$1\,10^{16}$	loose ($f_{H_2} = 1.00$)	0.02	0.013	$5.2\,10^{-10}$	$3.1\,10^{-14}$
300	$1\,10^{04}$	loose ($f_{H_2} = 1.00$)	0.18	0.273	$5.0\,10^{-10}$	$2.2\,10^{-11}$
300	$1\,10^{04}$	loose ($f_{H_2} = 0.0125$)	0.18	0.273	$5.2\,10^{-10}$	$2.8\,10^{-12}$
300	$1\,10^{04}$	loose ($f_{H_2} = 1.00$)	0.18	0.013	$5.2\,10^{-10}$	$8.7\,10^{-16}$
50	$1\,10^{04}$	loose ($f_{H_2} = 1.00$)	0.18	0.273	$5.6\,10^{-10}$	$2.1\,10^{-13}$
50	$1\,10^{04}$	loose ($f_{H_2} = 1.00$)	0.18	0.013	$5.6\,10^{-10}$	$2.4\,10^{-16}$

would be more difficult. Still, as can be seen in Table 3, the computed value for k_{eff} is essentially equal to the total rate coefficient at both high and low density, and at both temperatures studied -300 K and 50 K, whether or not the high or the low exothermicity is used, and whatever the scaling factor used for the exit channel potential. The main reason for this is the large size of the complex ion; its many degrees of freedom allow energy to be spread out sufficiently that dissociation via a single mode is unlikely on a short time scale. A second reason is that the exothermicity of reaction, even if the larger of the two values is chosen, is significantly smaller than in the benzene ion case. The calculated size of the rate coefficient for exothermic product formation is small; the reaction is probably observable only under low density conditions if the larger exothermicity value is the correct one. As in the case of $C_6H_6^+ + H$, the computed total rate coefficient for association plus reaction is a factor of a few larger than the measured one (Snow et al. 1998; Le Page et al. 1997).

4. Discussion

The determination of radiative association rate coefficients from high density, saturated SIFT data is not facile, especially when competitive exothermic channels exist. Despite the fact that both $C_6H_6^+ + H$ and $C_{10}H_8^+ + H$ associate with rate coefficients near the collisional value at high densities, we calculate that the two systems are quite different at low densities, where the dominant mechanism for stabilization of the complex ion is radiative rather than collisional. Under these conditions, the association $C_6H_6^+ + H \to C_6H_7^+$ occurs with a very low rate coefficient while the association $C_{10}H_8^+ + H \to C_{10}H_9^+$ occurs at the collisional rate coefficient.

There are a variety of uncertainties in the theoretical approach we have utilized, which make low density experimental confirmation crucial (see, e.g. Gerlich & Horning 1992 or Sorgenfrei & Gerlich 1994 for a discussion of such experiments on other systems). First, insufficient details are available concerning the potential surfaces for the two systems studied to rule out unusual problems such as small potential barriers and multiple reaction pathways. Secondly, the complex stabilization rate coefficients k_r and k_c are rather uncertain, as is the proper ladder

size for collisional deactivation of the complex. Serendipitously, low density association experiments involving atomic hydrogen are planned (Gerlich, private communication).

In diffuse interstellar clouds, where atomic hydrogen is especially abundant, the formation of the protonated naphthalene ion $C_{10}H_9^+$ is predicted to occur readily if the naphthalene cation is itself present. The formation of the protonated benzene ion $C_6H_7^+$ is unlikely even if the benzene cation is present. Protonated benzene can be formed efficiently in dense interstellar clouds via the exceedingly efficient association of $C_6H_5^+$ with H_2; the precursor ion is itself formed from Diels-Alder type reactions (McEwan et al. 1999). It is likely that addition of atomic hydrogen to more complex PAH cations follows the example of the naphthalene cation rather than the benzene cation mainly because of the increase in the number of degrees of freedom of the system. Interestingly, this analysis, which concurs with the view of Snow et al. (1998), would rule out a catalytic-type chemistry for the formation of H_2 on PAH cations as formulated by Cassam-Chenaï et al. (1994).

Finally, the efficiency of any further hydrogenation of protonated PAH cations via association with H atoms to yield even more saturated forms; e.g.,

$$C_6H_7^+ + H \longrightarrow C_6H_8^+ \qquad (9)$$

is probably low under interstellar conditions since the measured rate coefficients at high density are rather small and uncertain (Bohme 1992; Le Page et al. 1997; Snow et al. 1998). A theoretical determination of the radiative association rate coefficient of the above reaction (and the analogous one involving $C_{10}H_9^+$) should probably await suitable potential surfaces since, with present information, it is unclear why the measured rate coefficients are so small.

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