

Chemical Constraints on Organic Cations in the Interstellar Medium[†]

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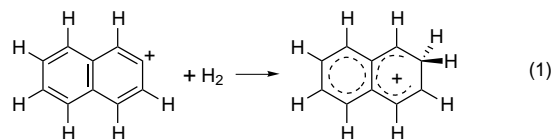
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The diffuse interstellar bands, first detected more than 70 years ago, are visible absorption features observed throughout the interstellar medium; the origin of these bands remains unknown.¹ The ionized polycyclic aromatic hydrocarbons (PAHs) have been implicated as potential carriers of these bands^{2–4} as well as important components of interstellar clouds. Dehydrogenated PAH derivatives may also be important in interstellar environments where ionization fields are strong.⁵ Nevertheless, there have been few studies^{6–8} of the chemical reactivity of these PAH ions especially regarding their stability in the interstellar medium where, with the exception of molecular hydrogen, the dominant species are atomic;⁹ quantitative studies of ion–atom reactions are difficult. In this paper we report studies of the reactions of the prototypical PAH cations $C_{10}H_8^+$, $C_{10}H_7^+$, and $C_{10}H_6^+$ with the major interstellar neutral species, including H_2 and H, N, and O atoms. The closed shell $C_{10}H_7^+$ ion is relatively unreactive with atoms but readily associates with H_2 and other molecules.¹⁰ In contrast, the radical ions ($C_{10}H_8^+$ and $C_{10}H_6^+$) are unreactive with molecular reagents, but exhibit novel reactions with the atomic reagents. These studies suggest that, although previous spectroscopic studies have focused on the parent radical cations,^{11–13} the protonated ions are likely to be the dominant forms of PAH cations in the interstellar medium.

The experiments were carried out in a tandem flowing afterglow-selected ion flow tube (FA-SIFT),¹⁴ which is ideally suited to the study of ion–atom reactions. The $C_{10}H_8^+$ ion is formed by Penning ionization of naphthalene with metastable argon atoms which are generated in a cold cathode discharge;¹⁵ this relatively gentle ionization process¹⁶ cleanly generates the parent cation of naphthalene. The dehydrogenated ions, $C_{10}H_7^+$

and $C_{10}H_6^+$, are formed by chemical ionization of naphthalene with helium ions that are produced by electron impact ionization. Kinetic studies demonstrate that these ions exist in both cyclic and acyclic forms.¹⁷ The reactant ions are extracted from the source region, mass-selected, and injected into the reaction flow tube where they are thermalized by collisions with helium. Molecular reactants are added through a manifold of inlets, and kinetics are measured as a function of reaction distance. Atomic hydrogen is generated by passing ultra-high-purity H_2 through a microwave discharge tube; calibration reactions are used to measure the hydrogen atom density,^{18–20} and indicate that dissociation ratios are about 30%. Atomic nitrogen is formed by passing N_2 through the microwave discharge, and atomic oxygen is formed by titration of atomic nitrogen with nitric oxide:^{21,22} $N + NO \rightarrow N_2 + O$. Dissociation ratios of N_2 are about 2%. Small corrections to the rate constants are made to account for wall recombination and mixing of the atomic reagents.²³ Studies of the reactions of PAH cations with molecular reagents were also carried out with a dual-cell, 3-T, Fourier transform-ion cyclotron resonance instrument (Extrel FTMS 2001).²⁴ $C_{10}H_7^+$ was formed both by electron impact on bromonaphthalene and by a displacement reaction of SiF_3^+ with fluoronaphthalene.²⁵

The reaction rate constants and product distributions are summarized in Table 1. While $C_{10}H_8^+$ and $C_{10}H_6^+$ are unreactive with the molecular hydrogen, $C_{10}H_7^+$ reacts readily by association. The reaction with H_2 generates protonated naphthalene with a rate constant of $5.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at 0.5 Torr of helium pressure:



Kinetic studies as a function of helium pressure indicate that the accessible pressure regime in the FA-SIFT lies in the

(16) It is particularly important to use a gentle ionization process when forming small PAH cations such as $C_{10}H_8^+$. For example, when using He^+ rather than Ar metastables as an ionization agent, the reactivities of $C_6H_6^+$ and $C_{10}H_8^+$ toward nitrogen atoms were found to be ~80% and ~65% lower, respectively; this suggests the formation of ring-opened isomeric ions when employing He^+ ionization.

(17) When $C_{10}H_7^+$ is produced with He^+ as the precursor, two isomers are formed in comparable amounts; one is reactive, and the other is almost unreactive. When Ar^+ is used to produce ions, the reactive isomer represents ~75% of the $C_{10}H_7^+$ signal; therefore, we assign the reactive isomer to the cyclic structure and the relatively unreactive isomer to the acyclic structure, following Ausloos' procedure in the case of dehydrogenated benzene cation: Ausloos, P.; Lias, S. G.; Buckley, T. J.; Rogers, E. E. *Int. J. Mass Spectrom. Ion Processes* **1989**, 92, 65–77. When $C_{10}H_6^+$ is produced with He^+ as the precursor, about 60% of the ions are reactive and about 40% show low reactivity.

(18) Petrie, S.; Javahery, G.; Bohme, D. K. *J. Am. Chem. Soc.* **1992**, 114, 9205–9206.

(19) Scott, G. B. I.; Fairley, D. A.; Freeman, C. G.; McEwan, M. J.; Adams, N. G.; Babcock, L. M. *J. Phys. Chem.* **1997**, 101, 4973–4978.

(20) Tosi, P.; Ianotta, S.; Bassi, D.; Villinger, H.; Dobler, W.; Lindinger, W. *J. Chem. Phys.* **1984**, 80, 1905–1906.

(21) Schiff, H. I. *Ann. Geophys.* **1964**, 20, 86.

(22) Setser, D. W. In *Reactive Intermediates in the Gas Phase*; Academic Press: New York, 1979; p 10.

(23) The atoms are not instantaneously and homogeneously mixed in the reaction flow tube. The mixing distance (which depends both on the shape of the inlet and the flow rates) is deduced by performing experiments at two different inlet positions (50 and 70 cm from the detection end). The loss of oxygen atoms on the flow tube walls can be important and strongly depends on the surface conditions. This effect can be accounted for by performing experiments which vary the atom–wall collision frequencies. The flow of oxygen atoms also alters the ion transmission of the sampling orifice in the molybdenum plate at the detection end, thus giving an artificial lowering of the ion count rate as the NO titration proceeds. Therefore, we monitor the ratio of the reactant and product ions as an indicator of the progress of the reaction. The masses of the reactant and product ions are similar, and no evidence for mass discrimination was found.

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(1) Tielens A. G. G. M.; Snow T. P., Eds. *The Diffuse Interstellar Bands*; Kluwer Academic Press: Dordrecht, 1995.

(2) Crawford, M. K.; Tielens, A. G. G. M.; Allamandola, L. J. *Astrophys. J.* **1985**, 293, L45.

(3) Van der Zwet, G.; Allamandola, L. J. *Astron. Astrophys.* **1985**, 146, 76.

(4) Léger, A.; d'Hendecourt, L. *Astron. Astrophys.* **1985**, 146, 81.

(5) Allamandola, L. J.; Tielens, A. G. G. M.; Barker, J. R. *The Astrophys. Suppl. Ser.* **1989**, 71, 733–775.

(6) Bohme, D. K. *Chem. Rev.* **1992**, 92, 1487–1508.

(7) Feng, W. Y.; Lifshitz, C. *Int. J. Mass Spectrom. Ion Processes* **1996**, 152, 157–168.

(8) Nourse, B. D.; Cox, K. A.; Cooks, R. G. *Organic Mass Spectrom.* **1992**, 27, 453–462.

(9) For example, the major species (and their relative abundances) in ζ Ophiuchi, a representative diffuse cloud: H (0.36), H_2 (0.32), O (3.3×10^{-4}), C and C^+ (1.3×10^{-4}), and N (7.7×10^{-5}). Diplas, A.; Savage, B. D. *Astrophys. J.* **1994**, 427, 274–287. Snow, T. P.; Witt, A. N. *Astrophys. J. Lett.* **1996**, 468, L65–68.

(10) Association reactions of $C_{10}H_7^+$ with CO, H_2O , and NH_3 are observed in both FA-SIFT and FTMS experiments. Le Page, V.; Keheyan, Y.; Bierbaum, V. M.; Snow, T. P. In preparation.

(11) Salama, F.; Allamandola, L. J. *Nature* **1992**, 358, 42

(12) Salama, F.; Allamandola, L. J. *Astrophys. J.* **1992**, 395, 401

(13) Léger, A.; d'Hendecourt, L.; Défourneau, D. *Astron. Astrophys.* **1995**, 293, L53

(14) Van Doren, J. M.; Barlow, S. E.; DePuy, C. H.; Bierbaum, V. M. *Int. J. Mass Spectrom. Ion Processes* **1991**, 109, 305–325.

(15) Howorka, F. *J. Chem. Phys.* **1978**, 68, 804.

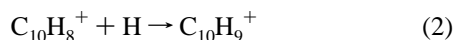
Table 1. Rate Coefficients and Products for the Reactions of $C_{10}H_n^+$ ($n = 6, 7, 8, 9$)

ionic reactant	neutral reactant	ionic products (branching ratio)	rate coeff ^a ($cm^3 s^{-1}$)
$C_{10}H_9^+$	H ₂		no reaction ^b
	H		$<1 \times 10^{-11}$
$C_{10}H_8^+$	H ₂		no reaction ^b
	H	$C_{10}H_9^+$ (1.0)	1.9×10^{-10}
	O	$C_9H_8^+$ (0.55) ^c $C_{10}H_8O^+$ (0.45) ^c	1.0×10^{-10}
	N	$C_9H_7^+$ (0.3) ^c $C_{10}H_8N^+$ (0.7) ^c	2.3×10^{-11}
$C_{10}H_7^+$	H ₂	$C_{10}H_9^+$ (1.0)	5.2×10^{-11} ^d 2.2×10^{-11} ^e
	H	$C_{10}H_8^+$ (1.0)	$<5 \times 10^{-11}$ ^f
	O		$<2 \times 10^{-11}$ ^f
	N		$<1 \times 10^{-11}$ ^f
$C_{10}H_6^+$	H ₂		no reaction ^b
	H	$C_{10}H_7^+$ (1.0)	$\sim 2 \times 10^{-10}$ ^f

^a Represents reactivity of the cyclic reactant ion, unless otherwise specified. Estimated total error: $\pm 15\%$ for reactions of H₂, $\pm 20\%$ for reactions of O atoms, and $\pm 30\%$ for reactions of N atoms and H atoms. (The error bars for reactions of O atoms are smaller than those for reactions of N atoms because more experimental measurements were made and small corrections for wall effects were included.) ^b No products observed; $k < 5 \times 10^{-13} cm^3 s^{-1}$. ^c Estimated error: $\pm 10\%$. ^d FA-SIFT experiment; includes three-body association. The linear isomer is not reactive with H₂ ($k < 5 \times 10^{-13} cm^3 s^{-1}$). ^e FTMS experiment; represents radiative association. ^f Reactivity due to both cyclic and acyclic reactant ions.

transition region between termolecular and saturated kinetics. Measurement of the rate constant for this reaction using the FTMS instrument yields a radiative association rate constant of $2.2 \times 10^{-11} cm^3 s^{-1}$ at 5×10^{-8} Torr and 300 K; the rate constant at 100 K, typical of diffuse clouds, is expected to be an order of magnitude larger.^{26–29} This relatively large radiative rate constant reflects the high stability and moderate molecular complexity³⁰ of the $C_{10}H_9^+$ ion and indicates that this association process will be important in the interstellar medium.

In contrast to its high reactivity with molecular reactants, $C_{10}H_7^+$ is relatively unreactive with atoms. The radical cations $C_{10}H_8^+$ and $C_{10}H_6^+$, however, exhibit facile reactions with the atomic reagents. Reaction of the naphthalene parent cation with hydrogen atoms proceeds exclusively by adduct formation with a rate constant of $1.9 \times 10^{-10} cm^3 s^{-1}$.



Comparison of this value with that for the corresponding

(24) di Petris, G.; Occhiucci, G.; Pepi, F. *Int. J. Mass Spectrom. Ion Processes* **1994**, *136*, 155–166.

(25) Grandinetti, F.; Occhiucci, G.; Ursini, O.; di Petris, G.; Speranza, M. *Int. J. Mass Spectrom. Ion Processes* **1993**, *124*, 21–36

(26) Bates, D. R.; Herbst, E. *Rate Coefficients in Astrochemistry*; Millar, T. J., Williams, D. A., Eds.; Kluwer Academic Publishers: Dordrecht, 1988; pp 17–40.

(27) Adams, N.; Smith, D. *Reactions of small transient species*; Fontijn, A., Clyne, M. A. A., Eds.; Academic Press: London, 1983; pp 311–386.

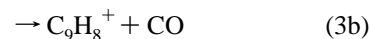
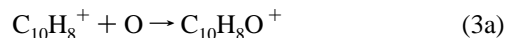
(28) Rowe, B. R. *Rate Coefficients in Astrochemistry*; Millar, T. J., Williams, D. A., Eds.; Kluwer Academic Publishers: Dordrecht, 1988; pp 135–152.

(29) Smith, M. A. *Unimolecular and bimolecular ion–molecule reaction dynamics*; Ng, C. Y., Baer, T., Powis, I., Eds.; Wiley: Chichester, 1994; pp 183–252.

(30) Dunbar, R. C. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 423–443.

reaction¹⁹ of $C_6H_6^+$ suggests that reactivity with H is not strongly dependent on the size of the ion; thus this association may continue to be important for larger PAHs in the interstellar medium. Protonated naphthalene, $C_{10}H_9^+$, does not react rapidly with H or H₂.³¹

Reactions of $C_{10}H_8^+$ with O and N atoms proceed by both addition and a novel bimolecular pathway:



The removal of a carbon atom from the aromatic framework of the naphthalene cation (eq 3b) is a remarkable process, but it is sufficiently exothermic³² to form the indene radical cation or the radical cations of propynylbenzene or vinyltoluene as products.³³ The reaction of $C_{10}H_8^+ + O$ occurs with a rate constant of $1.0 \times 10^{-10} cm^3 s^{-1}$ at 0.5 Torr of helium pressure, and the bimolecular channel accounts for about 55% of the overall reactivity. Similarly, the reaction of the nitrogen atom (eq 4b) extracts a CH group to form HCN;³⁴ this channel accounts for about 30% of the measured rate constant of $2.3 \times 10^{-11} cm^3 s^{-1}$. Secondary addition reactions and decarbonylation reactions are evident for the oxygen atom where the primary product ions have retained radical character. These secondary processes are essentially absent for nitrogen atoms since the initial association leads to loss of radical character.

These studies represent the first investigation of the reactions of polycyclic aromatic hydrocarbon cations with hydrogen, oxygen, and nitrogen atoms, major components of the interstellar medium. The rapid addition of hydrogen atom to the radical cations $C_{10}H_8^+$ and $C_{10}H_6^+$, as well as the efficient radiative association of $C_{10}H_7^+$ with molecular hydrogen, indicates that protonated naphthalene, $C_{10}H_9^+$, will be readily formed from its precursor ions in the interstellar medium. Reaction of $C_{10}H_8^+$ with oxygen and nitrogen atoms proceeds by both associative and novel abstraction processes. Further studies of the chemistry of larger PAH cations are warranted.

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(31) For these studies, $C_{10}H_9^+$ is produced in the source flow tube by the rapid, mildly exothermic (1.3 eV) proton transfer reaction $C_{10}H_8 + H_3O^+ \rightarrow C_{10}H_9^+ + H_2O$.

(32) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(33) Although all three channels are exothermic, we favor the formation of indene cation as the main product, not only for its lower heat of formation but also because the barrier for ring-opening may prevent formation of the radical cations of propynylbenzene or vinyltoluene.

(34) Either HCN or HNC can be produced in this reaction. However, *ab initio* calculations for $C_6H_6^+ + N$ favor the addition of nitrogen to carbon rather than insertion of nitrogen into a carbon–hydrogen bond; thus, the assignment of the neutral product as HCN is preferred.