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HYDROGENATION OF CARBON-CLUSTER CATIONS WITH MOLECULAR HYDROGEN: IMPLICATIONS FOR THE GROWTH OF CARBON-CLUSTER MOLECULES

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ABSTRACT

Experimental results are reviewed for the hydrogenation and deuteration of carbon-cluster cations in the gas phase. Emphasis is given to reactivity measurements performed with Fourier transform ion-cyclotron resonance (FTICR) spectrometry for large cluster ions derived from graphite and diamond by laser vaporization, and reactivity measurements performed with selected-ion flow tube (SIFT) mass spectrometry for small cluster ions derived from benzene by electron impact. New SIFT measurements are presented for reactivities of small cluster ions primarily produced from acyclic hydrocarbon molecules by electron impact. Attention is given to the insight provided by these reactivity measurements into the influence of the morphology of carbon-cluster cations on the efficiency of their hydrogenation and deuteration and on the growth of carbon-cluster molecules as it is perceived to occur in interstellar chemistry.

INTRODUCTION

Carbon atoms can aggregate or "cluster" as covalently bonded molecules with chain, ring, saucer and even polyhedral structures. The geometric constraints on these structures arise from the directional nature of the C—C bonding (which is often multiple, in contrast to many other atoms) so that studies of the chemistry of homonuclear carbon clusters provide a unique opportunity to investigate the influence of geometric constraints on chemical reactivity. Some insight into the influence of morphology on reactivity has been provided by the seminal research of Smalley and co-workers [1] which indicates a remarkable range of reactivity for the chemistry of neutral carbon clusters. However, this reactivity has been difficult to quantify since the neutral clusters are difficult to monitor directly in the laboratory. In contrast, ionized carbon clusters can be detected directly with a mass spectrometer and their reactions can be investigated quantitatively with techniques currently available for the study of ion/molecule reactions. Reactivities of carbon-cluster ions have already been measured with several molecules including H_2

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[2], D_2 [3,4], CH_4 [4,5] CO [2,6], O_2 [3], C_2H_2 [5], C_2H_4 [5], C_6H_{12} (cyclohexane) [7], C_2N_2 [4], and HCN [8]. Here we focus on the hydrogenation (and deuteration) of carbon-cluster ions by reactions with molecular hydrogen (and deuterium) to see how this molecule explores the active sites on a carbon-cluster ion and, in so doing, reveals its grander morphology.

Another incentive for the study of the hydrogenation of carbon-cluster ions by molecular hydrogen comes from interstellar chemistry with the discovery of long-chain carbon molecules in interstellar and circumstellar environments. In interstellar gas clouds of low optical depth in which carbon is mostly ionized, growth of carbon-cluster molecules in the gas phase can be perceived to proceed in a manner similar to that originally proposed by Suzuki [9] in which hydrogenation of carbon-cluster ions facilitates neutralization. The overall scheme can be summarized by the sequence of radiative association, hydrogenation and neutralization reactions

$$C_n + C^+ \longrightarrow C_{n+1}^+ + h\nu \tag{1}$$

$$C_{n+1}^+ + H_2 \longrightarrow C_{n+1}H^+ + H \tag{2a}$$

$$\longrightarrow C_{n+1}H_2^+ + h\nu \tag{2b}$$

$$C_{n+1}H^+ + e \longrightarrow C_{n+1} + H \tag{3}$$

The final neutralization [step (3)] will compete with the secondary hydrogenation reaction

$$C_{n+1}H^+ + H_2 \longrightarrow C_{n+1}H_2^+ + H \tag{4a}$$

$$\longrightarrow C_{n+1}H_3^+ + h\nu \tag{4b}$$

The hydrogenation steps (2a) and (4a) correspond to H-atom transfer leading to the formation of a new covalent C—H bond in the carbon-cluster ion, while steps (2b) and (4b) correspond to the dissociative addition (or chemisorption) of molecular hydrogen. The latter two steps result in the covalent addition of two hydrogen atoms as opposed to the electrostatic addition of H_2, which would result in a very weak electostatic interaction without dissociation of the reactant H_2 molecule. At the low pressures of interstellar environments, the gas-phase addition reactions (2b) and (4b) must proceed by radiative association in which the adduct ion stabilizes by the emission of radiation, while in laboratory environments at moderate pressures, stabilization by collision with another molecule is also possible.

Recent experimental evidence indicates that dissociative addition of molecular hydrogen to carbon-cluster ions may also be achieved through the formation of bimolecular products at the expense of the carbon content of the carbon-cluster ion. For example, McElvany et al. [3] have observed that the reaction

$$C_n^+ + D_2 \longrightarrow C_{n-3}D_2^+ + C_3 \qquad (5)$$

competes with D-atom transfer for even values of n ($n = 6, 8$). The driving force for this channel appears to be the relatively high stability of the C_3 molecule.

Clearly, the importance of the overall ionic-growth scheme for neutral carbon-cluster molecules is critically dependent on the efficiencies of the intermediate hydrogenation steps (2) and (5). These efficiencies need to be known to judge the merits of this scheme. Other questions also need to be answered to assess completely the role of hydrogenation. How efficient are the secondary hydrogenation reactions which compete with neutralization by electron-ion recombination? How effective are reactions of type (5) in the preferential formation of carbon clusters of a specific size? Is there a limit to the size of carbon-cluster ions which can be hydrogenated, and therefore a limit to the growth of carbon-cluster molecules in this fashion?

Here we provide a review and assessment of the efficiencies of the hydrogenation and deuteration reactions of carbon-cluster ions with molecular hydrogen and deuterium which have been determined experimentally, and report new data for the reactions of several of the smaller carbonaceous ions. The earlier measurements of the hydrogenation and deuteration of carbon-cluster ions were performed primarily with the selected-ion flow tube (SIFT) technique for smaller clusters derived by electron impact from the cyclic benzene molecule and with a Fourier transform ion cyclotron resonance (FTICR) spectrometer for larger cluster ions derived by laser vaporization from graphite or diamond. The new measurements reported here were done with a SIFT apparatus and emphasis was placed on reactions of small cluster ions derived from linear parent molecules.

Formation of carbon-cluster ions in the laboratory

Gas-phase carbon-cluster cations have been formed from a variety of carbonaceous materials. Early mass-spectrometric studies showed that C_2^+ and C_3^+ could be produced by electron ionization of the corresponding neutral molecules derived from the sublimation of graphite [10]. In the pioneering mass-spectrometric experiments of Furstenau and Hillenkamp [11], carbon-cluster ions with n up to 28 were detected in the microplasma produced by the interaction of UV laser light with thin carbon foils. Rohlfing et al. [12] were able to derive carbon-cluster ions with n from 1 to 190 from the laser vaporization of graphite in combination with supersonic jet expansion and ionization downstream. More recently, carbon-cluster ions have been derived directly from a plasma generated by laser vaporization of graphite or diamond [3,13] as well as polynuclear aromatic hydrocarbons, coal and soot [14–16]. Laser-desorption Fourier transform mass spectra of benzene soot samples have indicated a series of even-numbered aggregate cations extending beyond C_{600}^+ [15]!

Dissociative electron-impact ionization of suitable gas molecules, either acyclic or cyclic, has provided a practical method for generating smaller cluster ions. For example, benzene vapor has been used as a parent for carbon-cluster ions with $n = 4$–6 [2]. A recent report of the production of C_7^+ and C_{10}^+ by dissociative electron-impact ionization of octachloropentafulvalene and octachloronaphthalene illustrates a general method for producing C_n^+ species by exhaustive halogen elimination from perhalo-conjugated hydrocarbons [17]. Large carbon-cluster cations have also been observed in hydrocarbon flames where they are believed to be produced directly from polyaromatic particles in the same mass range or from single soot particle layers rather than from small carbon chains [18].

Structures and energetics of carbon-cluster ions

Broadly speaking, theory and experiment suggest that carbon clusters experience two stages of geometric closure as the number of carbon atoms increases. The first stage of closure, from a chain to a ring, occurs near $n = 10$, while the second stage, from a layer to a polyhedral structure, occurs near $n = 40$. Graphitic structures may become important above $n = 24$ [19]. Kroto has presented a set of empirical chemical and geodesic rules which suggest enhanced stabilities (and closed-cage structures) from $n = 24$, 32, 36, 50, 60, and 70, relative to near neighbors [20]. The formation of C_{60} and C_{70} clusters can be regarded as an intermediate step in the growth of microcluster carbon into bulk carbon phases [19].

LCAO-X alpha calculations suggest that the general trends in stability for carbon-cluster cations is similar to that for the neutral clusters [13]. One finds no change in the case of linear clusters: chains with an odd number of atoms are more stable than those with an even number of atoms. A slight shift is seen for cyclic clusters but both the ionic and neutral rings show a "four-periodicity" in stability: neutral clusters with $n = 6$, 10, 14, etc. have enhanced stabilities, but cationic clusters show enhanced stabilities at $n = 7$, 11, 15, etc. [13,19]. The cross-over in stability from linear to cyclic structures appears at $n = 7$ [13]. The MNDO calculations by McElvany et al. [3] suggest a cross-over closer to $n = 10$ but their experiments also provide evidence for the existence of two structural isomers for C_7^+. More recently, Parent and McElvany [8] have reported experimental evidence for two structural isomers of C_8^+ and C_9^+.

The first and only direct experimental evidence for the geometrical structure of a carbon-cluster ion has come from the remarkable Coulomb explosion experiments of Faibis et al. [21], which indicate a bent and possibly cyclic structure for the ground state of C_3^+, in contrast to the theoretical predictions of a linear structure [3,13].

EXPERIMENTAL

The new measurements reported here were performed with the selected-ion flow tube (SIFT) apparatus in the Ion Chemistry Laboratory at York University [22,23]. The carbon-cluster cations were generated in an axial ionizer (Extranuclear Model 0413) by electron impact on a suitable parent molecule. Cyanogen was chosen as a parent gas for C_2^+, methylacetylene for C_3^+, diacetylene for C_3^+ and C_4^+, *n*-butane for C_4^+, and *n*-pentane for C_5^+. The electron energy was usually held in the range from 40 to 60 eV. With *n*-butane and *n*-pentane, higher energies of 100–110 eV were found to be more appropriate. Attempts were also made to derive carbon-cluster cations by electron impact on a graphite rod placed along the axis of the ionizer. C_n^+ ions from $n = 3$ to $n = 10$ were achieved with 100 eV electrons at a tungsten filament current of 20 mA. However, this method in general did not provide sufficient intensities and stabilities to be practical.

The buffer gas was helium which was passed through zeolite traps (a 50:50 mixture of Union Carbide molecular sieves 4A and 13X) cooled to liquid nitrogen temperatures to remove traces of water vapor. The diacetylene was synthesized by the alkaline hydrolysis of 1,4-dichlorobut-2-yne [24] and was stored at dry-ice temperatures to avoid polymerization. The deuterium (C.P. Grade, Matheson) had a minimum isotopic purity of 99.5%. All measurements were taken at an ambient temperature of 296 ± 2 K and a total helium pressure of ca. 0.35 Torr.

RESULTS

Tables 1 and 2 summarize experimental results reported for the hydrogenation and deuteration of carbon-cluster ions. They include the results of the new SIFT measurements with small cluster ions discussed below. In these latter measurements, rate constants for the primary reactions were derived from the semi-logarithmic decay of the primary ion, while those for secondary reactions were derived by curve fitting the product ion profile to the integrated rate expressions.

C_2^+

The reaction of C_2^+ with hydrogen has been studied previously, both at the low pressures in an ICR cell [25] and at the moderate pressures which prevail

TABLE 1

Summary of experimental results for the hydrogenation and deuteration of carbon-cluster ions C_n^+

n	Products	Product distribution	k_{exp} [a]	Source [b]	Ref.
2	$C_2D^+ + D$	1.0	8.0	EI (cyanogen)	This work
		1.0	11	EI (C_2H_2, C_2N_2)	29
	$C_2H^+ + H$	1.0	12	EI (cyanogen)	This work
		1.0	14	EI (C_2H_4)	26
		1.0	11.2	EI (C_2H_2)	25
3	$C_3D^+ + D$	1.00	1.5	LVGD	3
		0.95	1.3	EI (HC_2CH_3, graphite)	This work
	$C_3H^+ + H$	1.0	3.0	EI (HC_2CH_3)	33
		0.95	1.8	EI (C_4H_2)	This work
4	$C_4D^+ + D$	1.00	3.2	LVGD	3
	$C_4H^+ + H$	1.0	0.96 (4.1)	EI (benzene)	2
			(7)	EI (n-C_4H_{10})	31
		1.0	1.6	EI (C_4H_2)	This work
5	$C_5D^+ + D$	1.00	4.5	LVGD	3
		1.0	5	EI (n-pentane)	This work
	$C_5H^+ + H$	1.0	6.2 (7.3)	EI (benzene)	2
6	$C_6D^+ + D$	0.85	1.35	LVGD	3
	$C_3D_2^+ + C_3$	0.15			
	$C_6H^+ + H$	0.20	2.7 (3.5)	EI (benzene)	2
	$C_6H_2^+$	0.80			
7	$C_7D^+ + D$	1.00	1.9	LVGD	3
8	$C_8D^+ + D$	0.75	0.063	LVGD	3
	$C_5D_2^+ + C_3$	0.25			
9	$C_9D^+ + D$	1.00	0.41	LVGD	3
10–19	No reaction		< 0.002	LVGD	3

[a] Measured rate constant in units of $10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$. Values in parentheses refer to 80 K.

[b] EI = electron impact; LVGD = laser vaporization of graphite or diamond.

in a SIFT apparatus [26]. Exclusive H-atom transfer as indicated by the reaction

$$C_2^+ + H_2 \rightarrow C_2H^+ + H \tag{6}$$

was observed to occur under both operating conditions, and rate constants of $(1.12 \pm 10\%) \times 10^{-9}$ and $(1.40 \pm 20\%) \times 10^{-9}\,cm^3\,molecule^{-1}\,s^{-1}$, respectively, have been reported [25,26]. The rate constant of $(1.2 \pm 30\%) \times$

TABLE 2

Summary of experimental results for the hydrogenation of C_nH^+ and deuteration of C_nD^+ ions

n	Products	Product distribution	k_{exp} [a]	Source [b]	Ref.
2	$C_2D_2^+ + D$	0.80	11	From $C_2^+ + D_2$	This work
	$C_2D_3^+$	0.20			
	$C_2H_2^+ + H$	1.0	17	EI (C_2H_4)	26
		1.0	7.8	EI (C_2H_2)	25
3	$C_3D_2^+ + D$	1.00	0.09	LVGD	3
	$C_3H_3^+$	1.0	0.21	EI (propylene), $C^+ + HC_2CN$	22
4	$C_4D_2^+ + D$	1.00	0.80	LVGD	3
	$C_4H_2^+ + H$	1.0	1.5 (3.2)	EI (benzene)	2
		1.0	1.8	EI (diacetylene)	This work
5			< 0.002	LVGD	3
			< 0.0010	EI (1,4 pentadiyne)	32
			< 0.02	($C_5^+ + D_2$)	This work
6	$C_6D_2^+ + D$	1.00	0.0095	LVGD	3
	$C_6H_2^+ + H$	1.0	0.013	EI (benzene)	2
			(< 0.001)		
7			< 0.002	LVGD	3
8	$C_8D_2^+ + D$	1.00	> 0.063	LVGD	3
9			< 0.002	LVGD	3

[a] Measured rate constant in units of 10^{-10} cm^3 molecule^{-1} s^{-1}. Values in parentheses refer to 80 K.

[b] EI = electron impact; LVGD = laser vaporization of graphite or diamond.

10^{-9} cm^3 molecule^{-1} s^{-1} obtained here is in good agreement. For the analogous D-atom transfer reaction with deuterium, we can report a rate constant of 8.0×10^{-10} cm^3 molecule^{-1} s^{-1}. The apparent isotope effect on the rate constant can be attributed entirely to the difference in the collision rate constants. The experimental value for the ratio of reaction rate constants, $k(H_2)/k(D_2)$, is 1.5 and it compares favourably, within experimental error, with the value of 1.37 predicted by the average quadrupole orientation (AQO) theory [27] for the corresponding ratio of collision rate constants. In the calculation of collision rate constants, the polarizabilities and quadrupole moments were taken to be 0.819 (0.809) $\times 10^{-24}$ A^3 and 0.637 (0.63) esu cm^2 for H_2 (D_2) [28]. The individual reaction efficiencies, expressed as the ratio of the reaction to the collision rate constant, are 0.75 and 0.71, respectively.

The bimolecular D-atom transfer reaction between C_2^+ and D_2 has been observed previously in a FTICR experiment at about 350 K [29]. The reported rate constant of 1.1×10^{-9} cm^3 molecule^{-1} s^{-1} is about 40% higher than the value obtained in this study. In the FTICR experiment, the C_2^+ was produced either from C_2N_2 or from small hydrocarbon molecules by electron impact between 20 and 70 eV. Systematic studies of charge transfer/energy-bracketing reactions with Xe and Kr indicated that the C_2^+ produced from C_2N_2 was a long-lived excited-state ion and that a mixture of C_2^+ states was produced when C_2^+ was formed from small hydrocarbon molecules. However, the rate constant for the reaction with D_2 was observed to be independent of the nature of the source gas used and therefore the extent of excitation of the C_2^+ ions. In our study, a separate measurement of the charge-transfer reaction between Xe and C_2^+, produced from C_2N_2 by electron impact, indicated two components of C_2^+ with different reactivities, a reactive component (80%, $k = 4.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) and an unreactive component (20%, $k < 5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}), in contrast to the FTICR result. However, the decays observed in C_2^+/D_2 SIFT experiments indicated similar reactivities for these two components towards D_2. This latter observation is consistent with the FTICR results.

The hydrogenation reactions of C_2H^+ and $C_2H_2^+$ have been observed previously with the ICR [25,30] and SIFT [26] techniques in separate measurements in which C_2H^+ and $C_2H_2^+$ were derived by the electron ionization of acetylene and ethylene, respectively. The earlier ICR study had shown that H-atom transfer occurs with C_2H^+ but not with $C_2H_2^+$ unless at least one quantum of excess vibrational energy is present in this ion [30]. In the SIFT experiments the C_2H^+ and $C_2H_2^+$ ions were injected into helium buffer gas at ca. 0.4 Torr and hydrogenation was reported to occur by the reactions

$$C_2H^+ + H_2 \longrightarrow C_2H_2^+ + H \tag{7}$$

$$C_2H_2^+ + H_2 \longrightarrow C_2H_3^+ + H \tag{8a}$$

$$\longrightarrow C_2H_4^+ \tag{8b}$$

The H-atom transfer reaction (8a) is endothermic by 1 kcal mol^{-1} for ground-state populations [30]. Smith and Adams have attributed the appearance of $C_2H_3^+$ in their experiments entirely to the reaction of the Boltzmann population of the first vibrationally excited state. Under their conditions of ca. 0.4 Torr of helium, about 50% of the $C_2H_2^+$ generated by electron impact from ethylene was reported to react by addition of molecular hydrogen. The C_2H^+ was reported to react only by hydrogen-atom transfer with a specific rate of 1.7×10^{-9} cm^3 molecule^{-1} s^{-1}, which is larger than the ICR value of $0.78 \pm 0.05 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}.

In the study reported here, sequential hydrogenation and deuteration of C_2^+ was observed. Figure 1 presents data for the sequential deuteration. Some differences are apparent in the product distributions when the C_2D^+ and $C_2D_2^+$ are produced by chemical reaction rather than by electron impact on ethylene, as was the case in the experiments of Smith and Adams [26]. The data in Fig. 1 clearly show that $C_2D_2^+$ and $C_2D_3^+$ ions are both produced directly from C_2D^+ in helium at 0.35 Torr (1.15×10^{16} atoms cm^{-3}) in the proportions

$$C_2D^+ + D_2 \xrightarrow{0.80} C_2D_2^+ + D \qquad (9a)$$

$$\xrightarrow{0.20} C_2D_3^+ \qquad (9b)$$

Furthermore, an analysis of the data indicates that the $C_2D_2^+$ produced by chemical reaction reacts with D_2 primarily by addition of molecular deuterium and not noticeably by D-atom transfer. The addition reaction has an effective bimolecular rate constant of 1.4×10^{-11} cm^3 molecule^{-1} s^{-1}. $C_2D_3^+$ was observed to be unreactive, $k < 8.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

C_3^+

The reaction of C_3^+ (derived from methylacetylene) with hydrogen has been measured previously in a SIFT apparatus by Herbst et al. [31] who reported that the reaction at 298 K (in helium buffer gas at a few tenths of a Torr) proceeds exclusively by H-atom transfer with a specific rate of 3.0×10^{-10} cm^3 molecule^{-1} s^{-1}. Here we report the results of a re-investigation of this reaction with both hydrogen and deuterium. For the reaction of C_3^+ (derived from diacetylene) with hydrogen we observed a specific rate of 1.8×10^{-10} cm^3 molecule^{-1} s^{-1} at 296 K, a somewhat lower value. The reaction with deuterium was investigated with C_3^+ derived from methylacetylene and graphite and was found to be slower, $k = 1.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, and in good agreement with the deuterium result obtained with the FTICR laser-vaporization technique [3] (see Table 1). The apparent isotope effect on

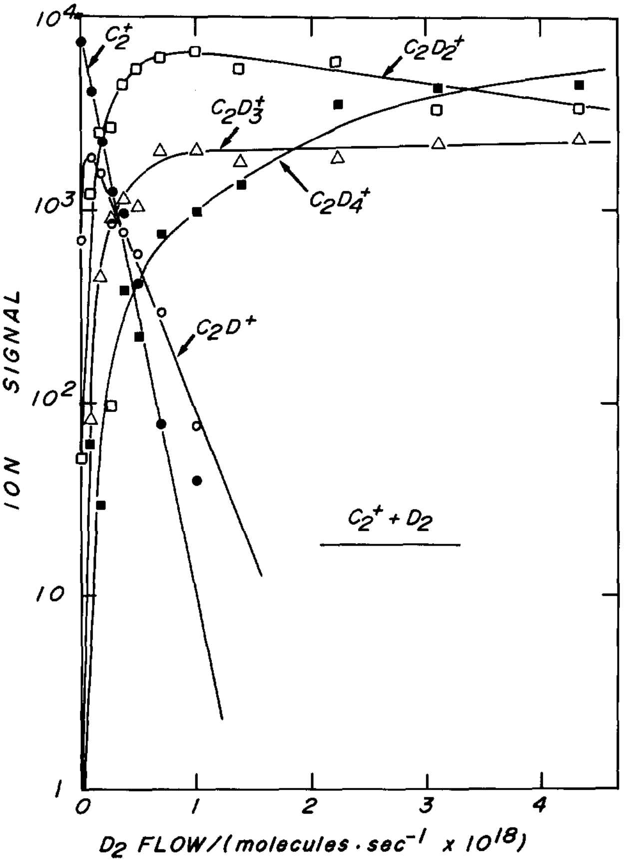


Fig. 1. Observations of the deuteration of C_2^+ in helium buffer gas at a total pressure of 0.35 Torr and helium density of 1.15×10^{16} atoms cm^{-3}. $T = 295$ K, $\bar{v} = 7.8 \times 10^3$ cm s^{-1}, and $L = 46$ cm. The C_2^+ is generated by electron impact at 55 eV from cyanogen.

the reaction rate constants, $k(H_2)/k(D_2) = 1.38$, can again be attributed to the difference in the collision rate constants for which a ratio of 1.39 is predicted by the AQO theory [27]. The reaction efficiencies, which are 0.11 and 0.12 for the hydrogenation and deuteration reactions, respectively, show no isotope effect.

Both $C_3H_3^+$ ($C_3D_3^+$) and $C_3H_2^+$ ($C_3D_2^+$) were observed as product ions. A product analysis of the data indicates that the former ion is produced exclusively by the reaction of C_3H^+ (C_3D^+) while the latter ion is produced by the reaction of C_3^+. We have shown previously that C_3H^+ produces $C_3H_3^+$ in a termolecular addition reaction with hydrogen when C_3H^+ is generated by electron impact of propylene [22]. An analysis of this reaction in the present experiments, in which C_3H^+ is generated by chemical reaction from C_3^+, indicates an apparent bimolecular rate constant of 1.5×10^{-10} cm^3 molecule^{-1} s^{-1} at 0.346 Torr of helium (1.13×10^{16} atoms cm^{-3}), which is in good agreement with the value obtained in the earlier electron ionization study of this reaction. For the reaction of C_3^+ with D_2 we can report the following branching ratio at 0.345 Torr of helium.

$$C_3^+ + D_2 \xrightarrow{0.95} C_3D^+ + D \tag{10a}$$

$$\xrightarrow{0.05} C_3D_2^+ \tag{10b}$$

A similar ratio was obtained with hydrogen. The $C_3H_3^+$ ($C_3D_3^+$) and $C_3H_2^+$ ($C_3D_2^+$) ions were found to be unreactive towards hydrogen (deuterium), $k < 10^{-12}$ cm^3 molecule^{-1} s^{-1}, in agreement with previous reports [31].

C_4^+

The H and D-atom transfer reactions of C_4^+ with H_2 and D_2, respectively, have been characterized separately with the SIFT [2] and FTICR [3] techniques, respectively. The FTICR result for the rate constant is about four times greater than the SIFT result when account is taken of the differences in the reduced mass of the reacting systems. Giles et al. [2] have suggested that this discrepancy may be due to the presence of vibrationally excited ions at the very low pressures of the FTICR experiments. Their SIFT experiments indicated the presence of vibrational excitation when C_4^+ is produced from benzene vapor by electron impact. The C_4^+ produced in this manner showed a reduced reactivity when the excitation was removed by quenching collisions with nitrogen. In our SIFT experiments, C_4^+ was derived from diacetylene. There was no substantial evidence for vibrational excitation as more than a decade of linearity was observed in the decay of the C_4^+ signal. The rate constant of 1.6×10^{-10} cm^3 molecule^{-1} s^{-1} is only slightly larger than the earlier SIFT result. There was no evidence for the direct formation of $C_4H_2^+$ by association.

We can also report agreement with the latest SIFT result of Giles et al. [2] for the H-atom transfer reaction of C_4H^+ with H_2 (see Table 2) and the failure of $C_4H_2^+$ to react with H_2. Again it should be noted that the $C_4H_n^+$ ions were produced from benzene by electron impact in the experiments of Giles et al. [2], whereas they are produced in our experiments from C_4^+ by sequential H-atom transfer.

C_5^+

Deuterium-atom transfer was observed to proceed with C_5^+ derived from *n*-pentane with D_2 addition contributing less than 1% to the total reaction.

Our rate constant obtained for this reaction, within experimental uncertainty, agrees with that reported for the reaction of C_5^+ produced from laser vaporization of graphite or diamond [3]. It also agrees with the value, when corrected for the reduced-mass difference, reported by Giles et al. for the reaction of hydrogen with C_5^+ derived from benzene by electron impact [2]. The C_5D^+ ion produced by the chemical reaction of C_5^+ with D_2 did not react further, $k < 2 \times 10^{-12}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ in agreement with the observations of McElvany et al. [3]. Giles et al. [2] have previously shown that C_5H^+ derived from benzene does not react with H_2, while Bohme et al. [32] have reported this non-reaction for C_5H^+ produced by electron impact on 1,4-pentadiyne.

DISCUSSION

Experimental results

Measurements have now been reported for hydrogen (or deuterium) reactions with carbon-cluster ions, C_n^+, having values of n up to 19. In these experiments the cluster ions were produced in several different ways from a variety of carbonaceous material: from solid graphite and diamond to benzene to linear chain-like hydrocarbon molecules, but no obvious dependence on the source material or mode of production is manifested by the experimental results, suggesting that the cluster ions have lost all memory of their birth. The agreement between the different measurements is generally within experimental error. H-atom (or D-atom) transfer is the predominant reaction channel which is observed. Significant molecular addition has been seen only with C_3^+ and C_6^+ and only in the collision-dominated SIFT experiments. Dissociative addition with concomitant elimination of a C_3 molecule has been observed for C_6^+ and C_8^+ only in the collisionless FTICR experiments. It seems that the elimination of C_3 proceeds through a complex which is sufficiently long-lived under SIFT conditions to be stabilized prior to decomposition [2]. Only the FTICR experiments have provided results for cluster ions C_n^+ with values of n beyond 6. These results show a strikingly abrupt decrease (by more than a factor of 200) in the reactivity towards molecular deuterium for values of n between 9 and 10. Also, for the specific value of $n = 7$, the FTICR experiments with D_2 suggest the existence of both a reactive and non-reactive isomer.

Above $n = 2$, the reactivity of the carbon-cluster ions tends to decrease non-monatonically as n increases, with the odd cluster ions being more reactive. Possibly the reactivity of C_3^+ is abnormally low in this pattern of reactivity. C_2^+ reacts with a rate close to the collision rate. Within experimental error, there is no significant chemical isotope effect for $n = 2, 3, 5$ and 6 when hydrogen is replaced by deuterium. The magnitude of the isotope effect for

$n = 4$ is uncertain since the rate constants for the reactions with H_2 and D_2 were measured separately with different techniques under conditions leading to questionable degrees of vibrational excitation of the C_4^+ ion [2].

The product C_nH^+ ions add a second H atom in reactions with H_2, but apparently only for even values of n. H-atom transfer has been observed for $n = 2$, 4 and 6, while D-atom transfer has been reported for $n = 2$, 4, 6 and 8. Again, within experimental error, there is no obvious chemical isotope effect for 2, 4 and 6. The slow D-atom transfer reaction with C_3D^+ observed in the FTICR experiments may have been driven by kinetic or internal energy in the reactants. A re-investigation of this reaction by Herbst et al. [33] suggests that it has a slight activation energy. Except for the reaction with C_2H^+, which proceeds essentially at the collision rate, the hydrogenation (deuteration) reactions of the higher even cluster ions C_nH^+ which were observed are very inefficient. They proceed at well below 1 in 10 collisions and, with the exception of C_8D^+, with an efficiency lower than that for the hydrogenation of the bare carbon-cluster ion.

The higher reactivities observed for C_n^+ ions with odd values of n and C_nH^+ ions with even values of n is curious, but not unique to reactions with H_2 and D_2. The odd/even patterns of reactivity have been noted by Parent and McElvany [8] who have formulated for reactions with carbon-cluster ions of the type C_n^+ and C_nX^+ the empirical rule that, irrespective of the neutral reactant, odd n ions will be more reactive than even n ions for an odd-electron series, and vice versa for an even-electron series. The rule can be explained using the Hückel theory [8]. Briefly, as even-electron ions, C_nH^+ ions have filled HOMOs for odd n and half-filled HOMOs for even n. The latter group of ions should therefore be more reactive. The odd-electron C_n^+ ions are open-shell species for both even and odd values of n. The odd n ions, with three electrons in the HOMO, can complete their HOMO and so are more reactive than the even n ions in the series.

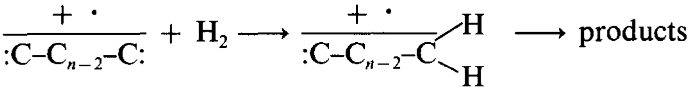
The laboratory investigations also have shown that further hydrogenation of the $C_nH_2^+$ ions by H-atom or D-atom transfer does not proceed at a measurable rate for even or odd values of n. Apparently hydrogenation stops after the carbon-cluster ion has accommodated two H atoms. Why should this be so?

Energetics

In sequential hydrogenation, both reaction endothermicity and kinetic barriers can lead to "bottlenecks" which may stop the hydrogenation prior to full saturation. Little is known about the enthalpies of formation of unhydrogenated or hydrogenated carbon-cluster ions in their various structural forms. Predictions of enthalpy changes for hydrogenation reactions become problematic already for $n = 3$. Kinetic effects which may arise, for example, from energy barriers or steric effects, also become impossible to predict quantitatively. However, useful insight is provided by the MNDO calculations of McElvany et al. [3], which have produced heats of formation for carbon-cluster ions of the type C_n^+ (linear with bond lengths optimized), C_nH^+ (linear) and $C_nH_2^+$ (linear with C—H bonds at opposite ends of the cluster ion) with $n = 3$–9. H-atom transfer was found to be exothermic for all C_n^+ ions when the C—H bond is formed at a terminal C atom, and more so by about 35–40 kcal mol^{-1} for odd values of n. Calculations on C_nH^+ structures in which the C—H bond formed is not at the terminal C atom indicate that the formation of C_nH^+ is endothermic. The calculations also show that further hydrogenation is exothermic by about 40 kcal mol^{-1} for even values of n when the C—H bonds are formed at opposite ends of the linear cluster ion and at most 10 kcal mol^{-1} exothermic for odd values of n. Actually, the uncertainty in the calculated values allows for the possibility of these latter reactions being slightly endothermic so that their inefficiency may be attributed to overall endothermicity (in the absence of information on possible energy barriers).

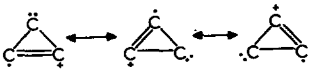
Mechanism

The enthalpy changes calculated by McElvany et al. [3] are remarkably consistent with the trends in reactivity observed for the reactions of C_n^+ and C_nH^+. They add strength to the proposal that the small cluster ions ($n < 10$) are linear chains with a pair of non-bonding electrons (carbene character) at each end and a charge and radical site delocalized over the length of the chain, and that such chains form a collision complex with H_2 in which two new C—H bonds are formed as shown in the reaction [3,6,19,22]



(11)

The collision complex may fragment by loss of H or C_3 or be collisionally stabilized. All three channels have been observed. Loss of C_3, which has been observed with C_6^+ and C_8^+, appears to be thermodynamically more favorable when carbon-cluster products with odd values of n are formed. Addition of H_2 has been observed only with C_3^+ and C_6^+. With an increase in the number of internal C atoms, the charge will be more delocalized so that we can expect a general decrease in reaction rate as n increases. An absence of carbene character in cyclic structures would account for the much lower reactivity for clusters with n beyond 9 which are predicted by theory to be more stable as rings rather than chains. But the extent of carbene character of cyclic carbon-cluster ions remains to be explored. For example, for C_3^+ we can envisage the interesting structure



in which the carbene and radical sites and the charge are completely delocalized about the ring. The Coulomb explosion experiments suggest that such a structure may have stability [21] and such a structure could also account for what might be construed as an abnormally low reactivity for C_3^+.

An analogous situation should apply to the secondary reactions of C_nH^+ ions with H_2 except that only one carbene site at one end of the chain is available in this case. Fragmentation by loss of H may be thermodynamically allowed only for even values of n and loss of C_3H from $HC_3H_2^+$ appears to be energetically less favorable than loss of C_3 from $C_3H_2^+$. Dissociative addition of H_2 has been observed only with C_2H^+ and C_3H^+.

Implications for interstellar chemistry

The observed fall-off in the reactivity of carbon-cluster ions towards hydrogen for increasing values of n which abruptly becomes immeasurably small at $n = 10$ has important implications for the carbon-cluster growth scheme described by reactions (1)–(4). The results suggest that there is an early limit to growth in this fashion, at least at a temperature of 298 K. Reaction (2) already becomes a bottleneck at $n = 10$. But what about the efficiency of hydrogenation at the much lower temperatures of interstellar clouds?

Only a few measurements are available for H-atom transfer to carbon-cluster ions at temperatures lower than 298 K. Giles et al. [2] have reported SIFT measurements at 80 and 210 K for the reactions of C_n^+ with H_2 for $n = 4$–6. For these three reactions, the rate constant was found to increase with decreasing temperature approximately as T^{-1}. Such a temperature dependence suggests that the rates of these three reactions may approach the collision limit at the low temperatures of interstellar clouds [2]. This is an important result since it implies a maximum efficiency for the carbon-cluster growth scheme for values of n up to 6. No measurements are available for the temperature dependence of the rate constants for values of n between 6 and 9 and in the critical regime just beyond 9. Clearly such measurements would be extremely valuable for assessing the probability of further growth to larger carbon clusters in these environments. But it does appear that the modified Suzuki scheme is effective only in producing chains of carbon possibly with up to 9 atoms. Consequently, neutralization mechanisms other than reactions (2) and (3) must be found to produce large carbon-cluster molecules if sequential radiative association reactions of type (1) are effective in building up carbon-cluster ions with n beyond 9.

The interesting competing channel (5) observed in the FTICR experiments for the C_6^+ and C_8^+ cluster ions, if it persists down to the low temperatures of interstellar clouds, will "drain" some of the growth preferentially toward the odd-n cluster molecules C_3 and also C_3H and C_5H.

CONCLUSIONS

(1) Gas-phase measurements of reactions of polycarbon and hydrocarbon ions with molecular hydrogen or deuterium have shown that the hydrogenation of carbon-cluster ions with less than 20 C atoms is restricted to the sequential addition of at most two H atoms and the dissociative addition of at most one hydrogen molecule at 298 K.

(2) Only acyclic chain structures appear to have active sites for C—H bonding or the dissociative addition (chemisorption) of molecular hydrogen, and these are present only at the two ends of the chain. This means that these ions never become co-ordinatively saturated because they quickly use up the active sites suited for C—H bonding or dissociative addition.

(3) Active sites for hydrogenation appear to be missing in cyclic ring structures of carbon atoms, and presumably also surfaces and spheres, so that the morphologies of these structures are not expected to promote C—H bond formation or the dissociative addition (or chemisorption) of molecular hydrogen.

(4) Dissociative addition reactions accompanied by the elimination of C_3 cluster molecules can present stumbling blocks towards growth and favor formation of smaller carbon-cluster molecules with odd values of n.

(5) The modified Suzuki scheme for the growth of neutral carbon clusters described by reactions (1)–(4) is not effective beyond $n = 9$ at 298 K. The hydrogenation step (2) steadily decreases with an odd/even reactivity pattern as n increases, and becomes very inefficient beyond $n = 9$. There is a limit to growth in this fashion at 298 K. Whether a similar limit applies at the low temperatures of interstellar clouds remains an open question but the laboratory observations do suggest efficient formation of carbon-chain molecules with n up to 6 and possibly 9 carbon atoms. Beyond $n = 9$ the formation of chain, ring, saucer or polyhedral structures of carbon atoms by successive radiative association of C^+, if it does occur, would require a mechanism for the neutralization of C_n^+ different from that initiated by hydrogenation.

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