Laboratory Anion Chemistry: Implications for the DIBs, and a Potential Formation Mechanism for a Known Interstellar Molecule

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Abstract

Due to recent interest in molecular anions as possible interstellar species, we have carried out several laboratory studies of anion chemistry. The reactions of the series C_n^- and C_nH^- with H and H_2 were studied to address the viability of such species in the diffuse interstellar medium and to address their ability to be carriers of the DIBs. These same molecules were also reacted with N and O to show possible heteroatomic products. C_mN^- was a particularly stable product from the reaction of $C_n^- + N$. C_3N^- was further reacted with H to study chemistry that could produce HC3N, a known interstellar species. The reactions were done in a flowing afterglow selected ion flow tube apparatus (FA-SIFT). The anions were generated in an electron impact or cold cathode discharge source and the anion of interest was then selected by a quadrupole mass filter. The selected ion was then reacted with the atomic or molecular species in the flow tube and products were detected by another quadrupole. While the C_n^- species do not appear to be viable DIB carriers, their possible presence could provide a mechanism for the formation of known heteratomic neutral molecules detected in the ISM.

1. Introduction

The reactions of negative-ions with atoms have historically received little attention, in part due to the limited and unusual environments in which such reactions would have significance. The first anion-atom studies provided insight into the ion chemistry of the lower ionosphere (Fehsenfeld *et al.* 1966). More recently, it has been suggested that there may be negative ions in the interstellar medium (ISM), where it is known that atomic species are abundant. Specifically, some carbon chain species have been cited as possible carriers of some of the unidentified visible absorption features known as the diffuse interstellar bands (DIB)(Fulara *et al.* 1993; Tulej *et al.* 1998). Some neutral carbon chain species, C_n (n = 2,3,5), HC_n (n = 2-8), and C_nH_2 (n = 2,3,4,6), have been positively identified in the ISM by radio techniques, but the presence of their negative ion counterparts remains undetermined (Thaddeus *et al.* 1998; Blanksby *et al.* 1999). The most abundant atomic species in the ISM is H atom, followed by N and O atoms. Recently, the reactions of organic cations, including small hydrocarbons (McEwan *et al.* 1999; Scott *et al.* 1998; Scott *et al.* 1999; Scott *et al.* 1999; Scott *et al.* 2000) and polycyclic aromatic hydrocarbons (LePage *et al.* 1997, 1999a, 1999b; Snow *et al.* 1998) with H, N, and O atoms have been investigated to elucidate the chemistry of planetary atmospheres and the ISM. Also detected in the ISM by radio astronomy are heteroatomic species containing carbon and either N or O (C_nO (n = 1,2,3), C_nN (n = 1,3,4), and HC_nN (n = 1,2,3,5,7,9,11)). In some regions of the ISM, it is possible that reactions of carbon chain anions serve as precursors to these species. In the present work, we report the results of FA-SIFT experiments that explored the reactivity of C_n^- (n = 2,4-7) and HC_n^- (n = 2,4,6,(7)) with H, N and O and describe and addition to the Langevin theory that accounts for this unique case.

2. Experimental Procedures

The experiments were carried out using a FA-SIFT apparatus that has been discussed in detail elsewhere (Van Doren et $al.$ 1987). The C_2^- and HC_n^- species were generated using electron impact on acetylene and the C_n^- (n > 2) were generated using a cold cathode discharge source (Leopold et $al.$). Atomic hydrogen was produced using a thermal dissociator on H_2 (Barckholtz et $al.$). Atomic nitrogen was produced using a microwave discharge on N_2 and oxygen atoms were produced as a product of the quantitative reaction of NO with N.

3. Chemical Results

The rate constants and efficiencies for the reactions of H, N and O with C_n^- are reported in Tables 1, 2, and 3 and reactions with HC_n^- are reported Table 4. H atom reacts quickly and the reaction is primarily associative detachment, producing neutrals of the form $C_n H$ and $C_n H_2$. O atom reacts quickly and produces CO and C_{n-1}^- or HC_n^- as well as $C_n O^-$ and H for reactions with HC_n^-. N atom reacts more slowly with C_n^- and produces $C_n N^-$ where n is odd as well as C_{n-1}^- with CN. The rapid reaction of these species with H atom suggests the carbon chain anions are unlikely carriers of the unidentified DIBs. Of interest, though, is the number of neutral species produced in these reactions that have been detected in the ISM by radio astronomy. Specifically, CO, CN, HCCN, HCCH, C_3, C_5, $C_6 H_2$, and $C_n H$ where n is 2,4,5,6,7 and 8 are generated in these reactions and are neutrals detected in the ISM through radio astronomy. In the O atom reactions, it was found that the reaction was rapid, and in the case of $C_5^- + O$, the efficiency of the reaction, which is defined as the reaction rate constant (k_{exp}) divided by the theoretical collisional rate constant as predicted by Langevin theory (k_L), was greater than 1. This gave rise to new considerations in the potential that describes the collision.

Table 1. Reactions of C_n^- with H atom

(C_n^-)	k_{exp} $(cm^3/sec$ x $10^{-10})$	k_{exp}/k_L	k_{exp}/k_{ODPI}
2	7.7 (±0.9)	0.39	0.32
4	6.2 (±1.9)	0.32	0.25
5	6.2 (±0.9)	0.32	0.25
6	6.1 (±1.0)	0.32	0.22
7	6.9 (±0.6)	0.36	0.25
8	7.3 (±1.3)	0.38	0.25
9	7.2 (±1.6)	0.37	nodata
10	7.5 (±0.8)	0.39	nodata

Table 2. Reactions of C_n^- and $C_n H^-$ with N atom

(C_n^-)	k_{exp} $(cm^3/sec$ x $10^{-10})$	k_{exp}/k_L	k_{exp}/k_{ODPI}
2	2.3 (±0.4)	0.28	0.24
4	2.0 (±0.7)	0.27	0.22
5	2.7 (±0.5)	0.37	0.30
6	1.5 (±0.4)	0.21	0.15
7	2.2 (±0.4)	0.31	0.22

Table 4. Reactions of C_n^- with H atom

n $(C_n H^-)$	Atom	k_{exp} $(cm^3/sec$ x $10^{-10})$	k_{exp}/k_L	k_{exp}/k_{ODPI}
2	H	16 (±3)	0.82	0.72
	N	0.5 (±0.2)	0.06	0.05
	O	6.2 (±1.7)	0.93	0.82
4	H	8.3 (±2.1)	0.43	0.35
	N	~0.06	0.008	0.007
	O	5.3 (±0.2)	0.88	0.72
6	H	5.0 (±0.7)	0.26	0.18
	N	~0.1	0.02	0.01
	O	5.4 (±0.3)	0.93	0.65
7	H	7.4 (±1.3)	0.39	nodata

Table 3. Reactions of C_n^- and $C_n H^-$ with O atom

(C_n^-)	k_{exp} $(cm^3/sec$ x $10^{-10})$	k_{exp}/k_L	k_{exp}/k_{ODPI}
2	5.8 (±1.3)	0.84	0.70
4	5.6 (±0.7)	0.92	0.73
5	6.4 (±1.0)	1.09	0.86
6	4.7 (±0.7)	0.80	0.56
7	5.3 (±0.5)	0.92	0.65

4. Theoretical Adjustment to the Langevin Rate

In 1905, Langevin first described the potential between an ion and a polarizable neutral (Langevin 1905). The potential had two parts, a centrifugal part based on the relative collisional energy (E) and the impact parameter (b) and an attractive part based on the polarizability of the neutral (α_n). From this potential, Langevin derived a rate constant that depended exclusively on α_n. The potential took the form:

$$V_L(r) = E\frac{b^2}{r^2} - \frac{1}{2}\frac{\alpha_n e^2}{r^4}$$

This theory works well to describe the rate of collision in most ion-neutral cases, but in a few cases, significant deviation can be observed. The modification of the theory due to a permanent dipole has been described in detail (Hsieh and Castleman 1981) and has been parameterized for easy use by experimentalists (Su and Bowers 1973; Su and Chesnavich 1982). In our case, the deviation comes not from the non-point nature of the neutral, but from the non-point nature of the ion. These carbon chain anion-atom systems have two major factors that contribute to this deviation. First, the negative ions have large, diffuse electronic clouds and are Π-conjugated molecules that facilitate movement of the electrons within the molecule and specifically along the axis of the molecule. Second, the atoms have relatively low polarizabilities. This effectively lowers the Langevin rate constant making a deviation due to the ionic polarizability more apparent. Due to these factors, terms need to be added to the existing Langevin potential. The new terms are added in the following fashion:

$$V_{eff}(r) = V_L + V_\alpha$$

where V_α is the potential term that arises from the induced dipole-induced dipole interaction between the ion and the neutral. The effect of this potential term is studied in two forms. The first is assuming the ion is a point-polarizable ion (PPI) such that the orientation of the ion with respect to the neutral is not considered. The first form of this potential term, where EA is the electron binding energy of the ion, IP is the ionization potential of the neutral and α_{ion} is the polarizability of the ion, is (Karplus and Porter 1970):

$$V_{PPI} = -\frac{3}{2}\left(\frac{EA \times IP}{EA + IP}\right)\frac{\alpha_{ion}\alpha_n}{r^6}$$

The second form was an orientation dependent polarizable ion (ODPI) where the axis of the molecule creates an angle with the approach vector of the neutral, as shown in figure 1. Here, where $\alpha_{parallel}$ and $\alpha_{perpendicular}$ are with respect to the long axis of the molecule, the potential takes the form:

$$V_{ODPI}(r) = -\frac{3}{2}\left(\frac{EA \times IP}{EA + IP}\right)\frac{(\alpha_{parallel}\cos\theta + \alpha_{perpendicular}\sin\theta)\alpha_n}{r^6}$$

Using calculated values for the polarizabilities of the ions, the rate constants are derived in a similar fashion as the original theory. The results are listed in Table 5 and show significant deviation in the rate constant as chain length increases as well as a significantly larger effect generated by ODPI over PPI in this case. Calculations were also done for the benzene cation and significant deviation was seen there as well, suggesting that large PAH cations collisions would be affected by the additional potential term.
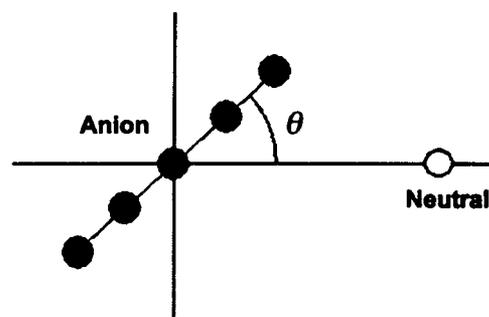
Fig. 1.— C_5^- has some orientation with respect to the approaching atom. This orientation is specified by the angle θ

Table 5. Deviations of k_{PPI} and k_{ODPI} from k_L - C_n^- + O

n (C_n^-)	%Deviation (PPI from Langevin)	%Deviation (ODPI from Langevin)
2	20.43	21.15
4	19.22	25.72
5	19.50	26.36
6	29.77	39.64
7	30.88	41.26
8	36.67	48.76

5. Future Work

Current modeling suggests that larger PAH cations would be likely candidates for the unidentified DIB carriers. We plan to study the reaction of PAH cations (carbon number 30 - 60) with H atom to address the viability of these species in the ISM.

Acknowledgments

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