Laboratory measurements of gas-phase reactions of polyatomic carbon ions $C_n^+ (n = 1–6)$ and $C_nH^+ (n = 2–5)$ with carbon monoxide

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The selected-ion flow tube (SIFT) technique has been employed in the study of reactions of carbon monoxide with the polyatomic carbon cations C_n^+ ($n = 1 - 6$) and C_nH^+ ($n = 2–5$) at 296 ± 2 K in helium buffer gas at ~0.34 Torr and 1.1×10^{16} atoms cm^{-3}. The polyatomic carbon cations were generated by electron impact on a suitable parent molecule. Carbon monoxide was observed to add rapidly to C_n^+ ($n = 2–6$) twice in succession to form polyatomic carbon monoxide and dioxide cations, and once to C_nH^+ to form polyatomic carbon monoxide cations. Further additions did not occur with measurable specific rates. This remarkable behavior is attributed to double bond formation at the terminal carbon atoms of the polyatomic carbon cations. The specific rate for the addition of CO was observed to vary with the size of the polyatomic carbon cation, increasing to a maximum for reactions with five atoms in the reacting ion. This trend is attributed to an increase in the lifetime of the intermediate addition complex.

I. INTRODUCTION

Polyatomic carbon ions have recently become of interest in models of the chemistry of interstellar gas clouds. Mechanisms for the formation of these ions in partially ionized interstellar carbon regions have been proposed, as have reactions of these ions which may lead to the synthesis of neutral polyatomic carbon molecules.[1-3] However, corroborative experimental evidence for these reactions has not been available. This situation is now beginning to change. Very recently, experimental studies have been reported of the reactivity of polyatomic carbon ions C_n^+ ($n = 3–19$) towards hydrogen and oxygen.[4] Here, we report the results of laboratory measurements of reactions of polyatomic carbon ions (with up to six carbon atoms) with carbon monoxide. Carbon monoxide is the second most abundant molecule in dense intersellar clouds and so is an obvious choice as a neutral reagent. But reactions with carbon monoxide are also of interest for a more fundmental reason, in that they provide a means to interrogate the electronic nature of the polyatomic carbon ions.

Consideration of the Lewis structures of carbon-chain cations indicates that such polyatomic carbon ions may have carbene character at both terminal carbons. For example, the tetracarbon-chain cation has the following resonance forms:

$$\begin{gathered} :\mathrm{C{=}C{=}C{=}C}^{\cdot +} \leftrightarrow {}^{+\cdot}\mathrm{C{=}C{=}C{=}C}: \leftrightarrow :\mathrm{C{=}C{=}C}^{\cdot}\text{–}\mathrm{C}:^{+} \leftrightarrow \\ :\mathrm{C{=}C}^{+}\text{–}\mathrm{C}^{\cdot}\mathrm{{=}C}: \leftrightarrow :\mathrm{C}^{+}\text{–}\mathrm{C}^{\cdot}\mathrm{{=}C{=}C}: \leftrightarrow :\mathrm{C{=}C}^{\cdot}\text{–}\mathrm{C}^{+}\mathrm{{=}C}:. \end{gathered} \tag{1}$$

It may be noted that the ionic charge and radical electron are delocalized in this ion. The unbonded electron pair on each of the two terminal carbon atoms should be available for bonding with a similarly unbonded electron pair on a donor molecule as, e.g., the electron pair on the carbon atom of carbon monoxide. The occurrence of such bonding, therefore, may be explored with measurements of the kinetics of association reactions between polyatomic carbon ions and carbon monoxide, especially if bimolecular reaction channels do not compete.[5]

The recombination energy of polyatomic carbon ions is less than the ionization energy of CO so that charge–transfer is not a competing channel for their reactions with CO at room temperature. Other bimolecular reaction channels also seem unlikely given the high C–O bond strength. This means that the association of polyatomic carbon ions and carbon monoxide can be expected to proceed exclusively to form adduct ions. With an unbonded electron pair available at both terminal carbon atoms, carbon-chain cations should add carbon monoxide twice according to reactions (2) and (3):

$$\overset{+\cdot}{\overline{:\mathrm{C}\text{–}\mathrm{C}_{n-2}\text{–}\mathrm{C}:}} + :\mathrm{CO} \rightarrow \overset{+\cdot}{\overline{:\mathrm{C}\text{–}\mathrm{C}_{n-2}\text{–}\mathrm{C{=}C{=}O}}}, \tag{2}$$

$$\overset{+\cdot}{\overline{:\mathrm{C}\text{–}\mathrm{C}_{n-2}\text{–}\mathrm{C{=}C{=}O}}} + :\mathrm{CO} \rightarrow \overset{+\cdot}{\overline{\mathrm{O{=}C{=}C}\text{–}\mathrm{C}_{n+2}\text{–}\mathrm{C{=}C{=}O}}}. \tag{3}$$

In contrast, when one end of the polyatomic carbon ion is already occupied, as is the case with C_nH^+, only one molecule of CO is expected to add according to reaction (4):

$$:\mathrm{C}_n\mathrm{H}^+ + :\mathrm{CO} \rightarrow \mathrm{C}_{n+1}\mathrm{HO}^+. \tag{4}$$

Further additions of CO sequential to reactions (3) and (4) are not expected to lead to the formation of coordinate bonds.

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In the laboratory investigation reported here, the addition reactions of types (2)–(4) are studied at moderate pressures in helium buffer gas and room temperature, and are expected to proceed primarily in a termolecular fashion with collisional stabilization by the bath gas molecules. In the interstellar environment, where the pressure is much lower, such association reactions must proceed by radiative stabilization.

II. EXPERIMENTAL

The measurements were performed with the selected-ion flow tube (SIFT) apparatus in the Ion Chemistry Laboratory.[6,7] The polyatomic carbon cations were generated in an axial ionizer (Extranuclear, Model 0413) by electron impact on a suitable parent molecule. Cyanogen was chosen as the parent gas for C^+ and C_2^+, acetylene for C_2H^+, allene and methylacetylene for C_3^+, diacetylene for C_3^+, C_3H^+, C_4^+, and C_4H^+, *n*-butane for C_4^+, *n*-pentane for C_5^+, 1,4-pentadiyne for C_5^+ and C_5H^+, and dicyanodiactetylene for C_5^+ and C_6^+. The electron energy was usually held in the range from 30–80 eV. The buffer gas was helium which was passed through zeolite traps (a 50:50 mixture of Union Carbide molecule sieves 4A and 13X) cooled to liquid nitrogen temperature to remove traces of water vapor. The purity of the carbon monoxide was 99.5 mol % (Matheson, C.P. Grade). All measurements were made at an ambient temperature of 296 ± 2 K.

III. RESULTS

The results of the rate constant measurements are summarized in Table I. Rate constants for the primary reactions were derived in the usual manner[8] while those for secondary reactions were derived by curve fitting the ion product profiles to the integrated rate expressions.

A. C^+

Atomic carbon ions were derived from cyanogen by impact with 40 eV electrons. The selected C^+ ions were observed not to react with CO, $k \leqslant 5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, and no C_2O^+ was seen to be produced.

B. C_2^+

C_2^+ ions were generated by electron impact from cyanogen, selected, and allowed to thermalize in helium buffer gas. Separate experiments with xenon as the neutral reactant indicated that the C_2^+ produced in this fashion has two components of distinctly different reactivity towards xenon. About 80% of the selected C_2^+ was observed to react with xenon by charge–transfer, $k = 4.7 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, while the remaining 20% was totally unreactive, $k \leqslant 3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The rate constant for the charge–transfer reaction was determined from the initial curvature in the C_2^+ decay using the method of Glosik *et al.*[9] The fraction of C_2^+ ions reactive towards xenon and the rate constant for charge–transfer appeared to be independent of the energy of the ionizing electrons within the range from 32–80 eV.

TABLE I. Summary of rate constants (in units of 10^{-10} cm^3 molecule^{-1} s^{-1}) measured at 296 ± 2 K for association reactions of C_n^+, $C_{n+1}O^+$, $C_{n+2}O_2^+$, C_nH^+, and $C_{n+1}HO^+$ with CO.[a]

n	C_n^+	$C_{n+1}O^+$	$C_{n+2}O_2^+$	C_nH^+	$C_{n+1}HO^+$
1	⩽0.005	0.20	⩽0.005		
2	0.074	0.40	⩽0.002	1.0	⩽0.002
3	0.20	3.0	⩽0.002	0.32	⩽0.002
4	2.9	1.0	⩽0.006	2.5	⩽0.002
5	8 ± 4	1.3	⩽0.002	1.0	⩽0.002
6	2 ± 1				

[a] Effective bimolecular rate constants are reported. The measurements were made in helium buffer gas at a total pressure ~0.34 Torr and a density of 1.1×10^{16} atoms cm^{-3}. Unless indicated otherwise, the accuracy of the rate constants is estimated to be ± 30%.

Insight into the identity of the two components of C_2^+ has been provided recently from experiments using Fourier transform ion cyclotron resonance spectrometry in which C_2^+ was derived by electron impact from C_2N_2 and C_2H_2.[10] At the low pressures of these experiments 100% of the C_2^+ ions derived from cyanogen was found to charge–transfer with xenon with a rate constant of $(1.0 \pm 0.2) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, while the C_2^+ derived from C_2H_2 showed two components of different reactivity towards xenon. An analysis of the products observed for the two components reacting with methane, together with the application of spin correlation rules, has suggested that the reactive component of C_2^+ is the electronically excited $^2\Pi_u$ state.[10]

Our SIFT experiments for the reaction of C_2^+ with CO were performed at electron energies of 35 and 52 eV. The reactivity of both components of C_2^+ was explored by performing experiments with and without the addition of xenon upstream in the flow tube to quench the reactive component of C_2^+. No difference was observed in the reactivity of the two components toward CO. With both components only the addition reaction (5) was observed:

$$C_2^+ + CO \rightarrow C_3O^+ \tag{5}$$

and the rate constant was 7.4×10^{-12} cm^3 molecule^{-1} s^{-1} at 0.35 Torr and 1.2×10^{16} helium atoms cm^{-3}. The product C_3O^+ was observed to add a second molecule of CO according to reaction (6):

$$C_3O^+ + CO \rightarrow C_4O_2^+, \tag{6}$$

with a rate constant of 4.0×10^{-11} cm^3 molecule^{-1} s^{-1} which was determined from a fit to the C_3O^+ profile. The $C_4O_2^+$ did not add a third molecule of CO, $k \leqslant 2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

We can also report the observation of the addition reaction (7):

$$C_2O^+ + CO \rightarrow C_3O_2^+. \tag{7}$$

C_2O^+ was present in the reaction region, most probably due to the reaction of C_2^+ with the water vapor impurity present in the helium buffer gas. Reaction (7) was observed to proceed with an apparent bimolecular rate constant of 2.0×10^{-11} cm^3 molecule^{-1} s^{-1} at the same conditions as those for reactions (5) and (6). The $C_3O_2^+$ did not add another CO molecule, $k \leqslant 5 \times 10^{-13}$ cm^3 molecule^{-1} cm^3.

C. C_3^+

The C_3^+ ion was generated by electron impact in allene, methyl acetylene, or diacetylene diluted with helium (15%). Two molecules of CO were observed to add sequentially as indicated by reactions (8) and (9):

$$C_3^+ + CO \rightarrow C_4O^+, \tag{8}$$

$$C_4O^+ + CO \rightarrow C_5O_2^+. \tag{9}$$

The ion signal of the intermediate C_4O^+ was obscured by the presence of the adduct HC_4O^+ formed from CO and C_3H^+ which is present as a result of the reaction of C_3^+ with water impurities. Computer fits to the decay of C_3^+ and the rise in $C_5O_2^+$ provided apparent bimolecular rate constants of $(0.20 \pm 0.06) \times 10^{-10}$ and $(3.0 \pm 1.0) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, respectively, for reactions (8) and (9). The $C_5O_2^+$ product did not react further, $k \leqslant 2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. There was no evidence for an unreactive component to C_3^+.

D. C_4^+

The C_4^+ ion was derived from diacetylene diluted in helium (15%) by electron impact at 52 eV. Two additions of CO were observed as indicated in reactions (10) and (11):

$$C_4^+ + CO \rightarrow C_5O^+, \tag{10}$$

$$C_5O^+ + CO \rightarrow C_6O_2^+. \tag{11}$$

The apparent bimolecular rate constants for the two steps were determined to be 2.9×10^{-10} and 1.0×10^{-10} cm^{-3} molecule^{-1} s^{-1}, respectively, at 0.34 Torr and 1.1×10^{16} helium atoms cm^{-3}. There was no evidence for the addition of a third molecule of CO for which we can report an upper limit to the rate constant of 6×10^{-13} cm^3 molecule^{-1} s^{-1}. Typical results are shown in Fig. 1. There was some evidence for a very minor ($\leqslant 0.5\%$) unreactive component of the initial signal at $m/z = 48$.

E. C_5^+

Several gases were tried as parents for C_5^+ including 1,4-pentadiyne, dicyanodiacetylene, and *n*-pentane. *n*-pentane was found to be most suitable but the C_5^+ signals were low in intensity and the data were scattered. Nevertheless, it was clear that two molecules of CO again added sequentially to the reactant ion as indicated by reactions (12) and (13):

$$C_5^+ + CO \rightarrow C_6O^+, \tag{12}$$

$$C_6O^+ + CO \rightarrow C_7O_2^+. \tag{13}$$

The decay of the signal observed at $m/z = 60$ appeared to have a lower slope at high flows of CO. This was attributed to the presence of C_5H^+ which reacts more slowly with CO and was taken into account in the derivation of the rate constant for reaction (12). The rate constant for reaction (13) was derived from a fit to the rise in the $C_7O_2^+$ signal. The behavior of the signal of the intermediate C_6O^+ was obscured by the presence of C_6HO^+ formed from C_5H^+. The $C_7O_2^+$ was observed not to add another CO molecule, $k \leqslant 2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

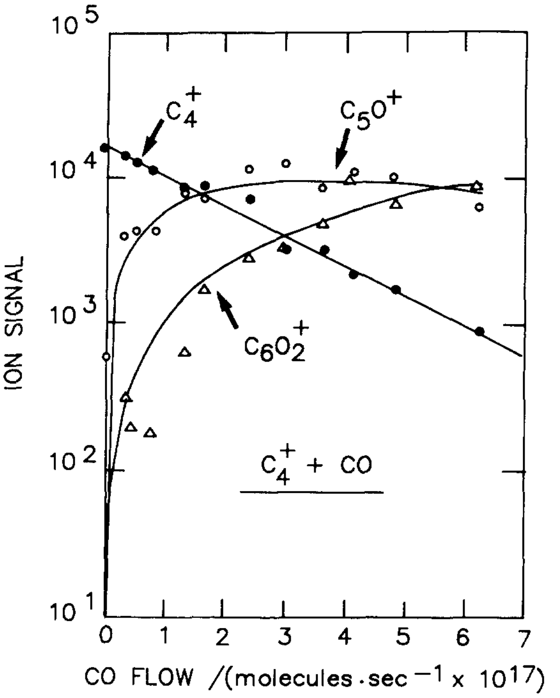

FIG. 1. Observations of the association reactions initiated by C_4^+ in carbon monoxide and helium buffer gas at a total pressure of 0.344 Torr and helium density of 1.12×10^{16} atoms cm^{-3}. $T = 297$ K, $\bar{v} = 5.3 \times 10^3$ cm s^{-1}, and $L = 46$ cm. The C_4^+ is generated by electron impact at 52 eV in a 15% mixture of diacetylene in helium. The solid curves represent a computer fit with effective bimolecular rate constants of 2.9×10^{-10} and 1.0×10^{-10} cm^3 molecule s^{-1} for the association of the first and second molecule of CO, respectively. No further association of CO was observed.

F. C_6^+

Both dicyanodiacetylene and *n*-hexane were used as source gases for C_6^+ but substantial amounts of this ion were difficult to generate. It was possible to determine an effective bimolecular rate constant for the addition of one molecule of CO according to reaction (14):

$$C_6^+ + CO \rightarrow C_7O^+. \tag{14}$$

The rate constant was found to be $(2 \pm 1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Some $C_8O_2^+$ was observed as a secondary product formed from the addition of a second molecule of CO but not in sufficient amounts to determine the kinetics of its formation and further reaction. Some C_4O^+ was observed as a primary product, but its formation could be attributed to the reaction of C_3^+ initially present.

G. C_nH^+

The experiments with C_2H^+ (acetylene), C_3H^+ (diacetylene), C_4H^+ (diacetylene), and C_5H^+(1,4-pentadiyne) were straightforward. Here, the source gas is indicated in parentheses. In each case, only the addition of one CO molecule was observed as indicated in reaction (15). The addition proceeded rapidly, $k \geqslant 3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}:

$$C_nH^+ + CO \rightarrow C_{n+1}HO^+. \tag{15}$$

The association of a second molecule of CO did not occur and had a specific rate with an upper limit of 2×10^{-13}

cm^3 molecule^{-1} s^{-1}. We have reported previously results obtained with C_3H^+ derived from propylene.[7]

IV. DISCUSSION

With the exception of the specific rate for the reaction with C^+, the effective bimolecular specific rates which have been measured in this study for the addition of CO molecules are generally high, $k \geqslant 7.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, in helium at 0.34 Torr and 1.1×10^{16} atoms cm^{-3}. Such large effective bimolecular rate constants in association reactions are indicative of the formation of strongly bound adducts in which covalent bonding is likely to occur, rather than the formation of weakly bound adducts in which electrostatic bonding prevails.[11-13] Ion/molecule addition reactions with CO which have been measured and in which covalent bonding in unlikely have effective bimolecular rate constants at similar helium pressures and a similar temperature which are much lower. For example, the reactions of Ca^+,[14] HCO^+,[15] CH_2O^+,[15] and CH_3O^+[16] have effective bimolecular rate constants reported to be $\leqslant 4 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 300 K. Other addition reactions which have been investigated with CO in which covalent bonding is more likely, show effective bimolecular rate constants which are moderately large as, e.g., with N_3^+ ($\sim 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1})[17] and CH_2^+ and CH_3^+ ($\sim 1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}).[18,19] For these latter reactions covalently bound adducts of the type $^+N{=}N{-}N{=}C{=}O$, $(H_2C{=}C{=}O)^+$, and $CH_3{-}C^+{=}O$ are possible.

Semiempirical quantum chemical calculations have shown that carbon cluster ions with n up to 9 have linear electronic ground states.[20,21] Furthermore, the charge appears to be delocalized by resonance throughout the length of the cluster in both even and odd cluster ions with the largest charge density residing on the terminal carbon atoms. We have proposed previously that the terminal carbon atoms have carbene character so that coordination may occur in association reactions of these cluster ions with CO which has an available unbonded electron pair on the carbon atom.[5,22] The sequential addition of just two CO molecules to C_n^+ can, therefore, be rationalized in terms of the direct formation of double bonds at the two terminal carbon atoms as shown in reactions (2) and (3). The exothermicities for addition reactions of this type are high as can be seen in Table II. The available enthalpies of formation indicate a range in exothermicity for the addition of one molecule of CO from 87–116 kcal mol^{-1} and that for the addition of the second molecule of CO from 82–96 kcal mol^{-1}. With the C_nH^+ ions carbene character is present only at one terminal carbon so that only one double bond is expected to form and only one CO molecule expected to add, just as is observed.

Figure 2 displays the observed trend in the effective bimolecular specific rate of the association reaction (2) with the number of carbon atoms in the reacting cluster ion. The specific rate is seen to increase with n until it apparently reaches a maximum at $n = 5$. Similar trends appear to exist for the reactions (3) and (4) when n is taken to be the total number of atoms rather than the number of carbon atoms in the reacting cluster ions which in these cases are heteroatomic. One possible exception is the reaction of C_2H^+ with CO which has a rate constant which is high compared to that for the reaction of C_3H^+ with CO. Theories for association reactions indicate that the specific rate of association is enhanced by a long lifetime for the intermediate association complex which, in turn, is determined by the energy of association and the number of atoms in the association complex.[11,12] The energy of association for the association complex in reactions of type (2) and (3) is close in value to the reaction exothermicity. Table II shows that the exothermicities of reactions of types (2) and (3) are all quite large and about equal, and for the reactions of type (2) actually decrease slightly as n increases. The observed increase in the specific rate of association should therefore be attributed primarily to an increase in the lifetime of the intermediate association complex which is expected from the increase in its number of atoms.

It is interesting to compare the results for the reactions of polyatomic carbon ions with CO to those reported recently for reactions with O_2 since the carbene end of a polyatomic carbon ion also can form a double bond with an oxygen atom.[4] Indeed, C_nO^+ was the major product ion observed for the reactions of C_n^+ with O_2 for $n = 3$–9.[4] The formation of a double bond with the carbene end of the polyatomic carbon ion in this case would be accompanied by the elimination of an oxygen atom. Other minor products observed for the reactions of C_n^+ with O_2 correspond to scission of the

TABLE II. Available thermochemical information for standard enthalpies of formation[a] and reaction (in kcal mol^{-1}) at 298 K.

n	C_n^+	$C_{n+1}O^+$	ΔH [reaction (2)]	$OC_{n+2}O^+$	ΔH [reaction (3)]
1	431[b]			199	
2	475[b]	333	−116	211	−96
3	473 (480)[b]	347	−100	232	−89
4	487	365	−96	247	−92
5	502	381	−95	273	−82
6	517	404	−87	289	−89

[a] Unless indicated otherwise, all enthalpies of formation are MNDO values calculated in Ref. 4.

[b] From J. L. Franklin, J. D. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, Natl. Stand. Ref. Data Ser. 26, 41 (1969).

[c] The enthalpy of formation of CO has been taken from the reference in footnote b to be −26.4 kcal mol^{-1} at 298 K.

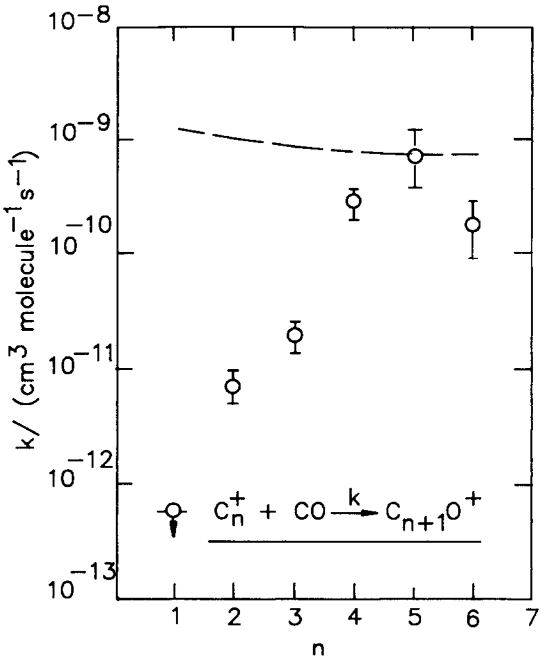

FIG. 2. Variation in the effective bimolecular rate constant measured for the addition of one molecule of CO to C_n^+ as a function of cluster size. The buffer gas is helium at a total pressure of 0.34 Torr and density of 1.1×10^{16} atoms cm^{-3}. $T = 296 \pm 2$ K. The dashed curve represents the variation in the collision rate constant.

carbon chain accompanied by the formation of neutral products which may involve C=O double bonds, viz. CO_2 and C_2O_2.[4]

The pressure dependence of the observed association reactions was not investigated in this study, but at the operating pressures of the helium buffer gas they are likely to be dominated by collisional stabilization. In interstellar gas clouds these association reactions would have to proceed by radiative stabilization. As is the case for collisional association, the efficiency of radiative association is thought to be enhanced by a high association energy and a large number of atoms in the association complex.[23] The high binding energy of CO towards C_n^+ and $C_{n+1}O^+$ indicated in Table I, and probably also towards C_nH^+, is, therefore, favorable for radiative association reactions involving these polyatomic carbon ions in interstellar clouds, particularly as the number of atoms in the association complex becomes large. Neutralization of the adduct ions $C_{n+1}O^+$ and $C_{n+1}HO^+$ by charge-transfer and proton-transfer, respectively, would then lead to the formation of polycarbon monoxide molecules, while neutralization of the adduct ions $C_{n+2}O_2^+$ by charge-transfer would yield polycarbon dioxide molecules. Polycarbon dioxide molecules have not yet been identified in the interstellar medium, and tricarbon monoxide is the largest polyatomic monoxide molecule which has been observed to date.[24]

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