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The Simplest Linear-Carbon-Chain Growth by Atomic-Carbon Addition and Ring Opening Reactions

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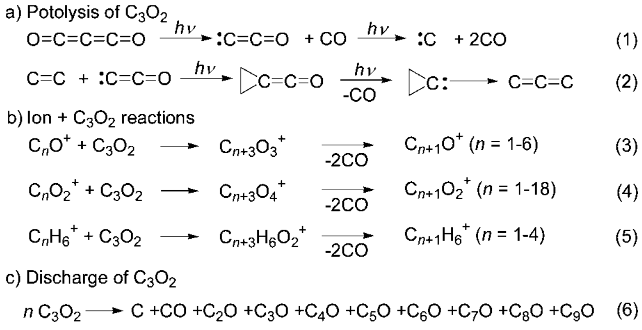
The formation mechanism of linear-carbon-chain molecules, C_nO ($n = 2 - 9$), synthesized in the discharge of C_3O_2 has been investigated on the basis of detailed analyses of previously obtained FTMW spectroscopic data. The relative abundances of the C_nO products determined from their rotational spectrum intensities agree with those for the C_nO^+ ions. The active chemicals in the reaction system include :C and :CCO only, and the observed products exclusively consist of C_nO, leading to a likely formation mechanism of the atomic-carbon addition and ring opening reaction. This formation mechanism is simple and efficient, and it is applicable not only to linear-carbon-chains but also to a wide range of carbon processes, in particular, to ultra low temperature or incomplete combustion conditions.

1. Introduction

The gas phase carbon growth reaction is one of the most fundamental reactions, and it is involved in a wide range of chemical processes such as combustion, CVD, electrical discharge, photolysis, pyrolysis, laser ablation, and molecular formation in interstellar space. The simplest reaction occurs when atomic carbon adds and then the intermediate undergoes a ring opening reaction (ACAROR), wherein the atomic carbon, :C, or its precursors, :CCO and C_3O_2, jump into the CC bond without cleaving the overall structure and hence do not produce a side-product, as summarized below:



Allene formation in the photolysis of C_3O_2 and ethene was discovered by Bayes[1] (eqs 1 and 2). We have applied this reaction to the preparation of many allene derivatives.[2] High-pressure[3] and ion-trap mass spectroscopies[4] have revealed that the linear-carbon-chain ions C_nO^+ ($n = 1- 6$), $C_nO_2^+$ ($n = 1-18$), and $C_nH_6^+$ ($n = 1-4$) can be formed by stepwise monocarbon insertions into the CC bond (eqs 3−5). The C_3O_2 molecule is, in this way, a good candidate to demonstrate the self-addition of :C into the CC bond and ring opening, because it contains both the :CCO precursor and the CC bond. Intrigued by this molecule, we simultaneously synthesized a series of carbon monoxides C_nO ($n = 2-9$) by creating an electrical discharge in a sample of tricarbon dioxide C_3O_2 (eq 6).[5] The products were identified by their observed Fourier transform microwave (FTMW) spectra shown in Figure 1.

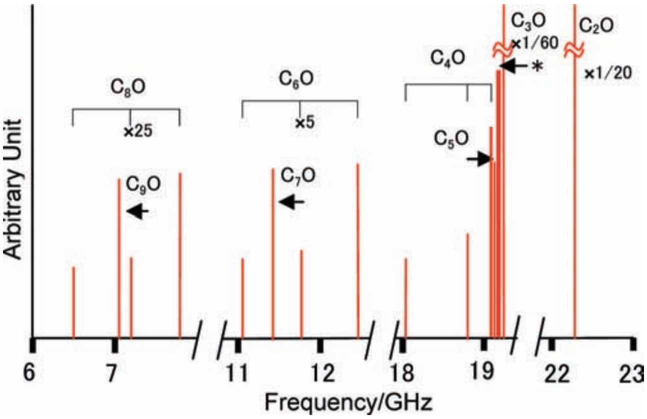


Figure 1. The rotational spectra of C_nO ($n = 2$~9) exhibit a triplet spectrum for even n and a singlet for odd n. The vertical scales for n = 2; 3; 4 and 5; 6 and 7; and 8 and 9 are factored by 1/20; 1/60; 1; 5; and 25; respectively. The lines marked * are C_3O for the ^{13}C species.

In this paper, we clarify the formation mechanism of the C_nO molecules and apply it to the development of more general linear-carbon-chain molecules.

2. Methods

A series of linear carbon monoxide molecules C_nO ($n = 2-9$) was synthesized by creating an electrical discharge in a sample of tricarbon dioxide C_3O_2 diluted in Ar. The sample of tricarbon dioxide was synthesized by the dehydration of malonic acid with phosphorus pentaoxide and purified by repeated distillations under reduced pressure. The pulsed-discharge-nozzle Fourier-transform-microwave (PDN-FTMW) spectrometer and the observed FTMW spectrum of the C_nO products used for the analyses of their formation mechanism were reported previ-

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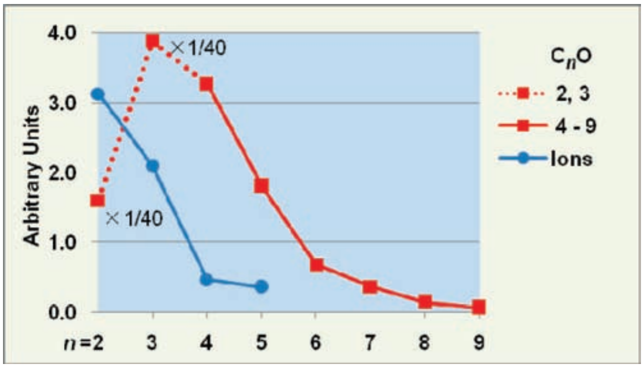

Figure 2. Relative abundances of C_nO molecules (the vertical scales for $n = 2$ and 3 are factored by 1/40) (■) and C_nO^+ ions (●).[3]

ously.[5] The relative abundances of the C_nO products were calculated from their relative intensities in the FTMW spectrum by taking into account the Boltzmann factors in the rotational states and the magnitude of the dipole moments. The dipole moments of the C_nO molecules were obtained from ab initio MO calculations of the B3LYP/6-31G(d) level. The detailed procedures are given in the Supporting Information.

The electron-impact mass spectrum of C_3O_2 was measured with a Shimadzu QP-5050 gas chromatograph−mass spectrometer (GC−MS) at Shizuoka University.

3. Results and Discussion

3.1. Formation Mechanism of the C_nO Molecules. At first glance, the observed rotational spectrum of the reaction products firmly convinced us that they must have been formed by the ACAROR, because almost all the observed spectra could be assigned to the C_nO ($n = 2-9$) molecules. We analyzed previous FTMW data to investigate the possible reaction mechanism.[5] We first determined the relative abundances of the C_nO products by using the intensities of the rotational spectra. The pairs of intensities for $n = 4$ and 5, 6 and 7, and 8 and 9 were close, which suggests the existence of a slight potential barrier to the formations of the $n = 4$, 6, and 8 species, and decreased successively by a factor of 5. The relative abundances for C_nO ($n = 2-9$) were calculated from their intensities by taking into account the population of energy states and the magnitude of the dipole moments. The details are provided in the Supporting Information, and the results are plotted in Figure 2. The relative abundance of C_2O was lower than that of C_3O, possibly due to further involvement in the carbon addition and ring opening reactions, similar to the case in interstellar space, where the fractional abundances to H_2 for C_2O and C_3O are 6×10^{-1},[6] and 1.4×10^{-10},[7] respectively. The calculated relative abundances for C_nO ($n = 3-9$) decreased with increasing n, which agrees with the abundances of C_nO^+ ions that are known to be lengthened by the stepwise mono carbon insertion of carbon atoms.[3]

The observed *m*/*e* (relative intensity) values for the mass spectrum of C_3O_2 were 68 (M^+, 73), 56 (3), 52 (5), 44 (7) 41 (9), 40 (100), 36 (4), 29 (4), 28 (26), 24 (15), 16 (3), and 12 (39), which agree with those of the NIST database.[8] Peaks 24 (15) and 36 (4), corresponding to C_2 and C_3 ions, respectively, appear to be formed by the reactions of :C, instead of by the direct fragmentation of C_3O_2, judging from the very small peak 16 (3) of the oxygen ion. C_2 was observed to be less competitive than :C in carbon addition and ring opening reactions due to energetic and kinetic factors. Therefore, the active chemicals in the reaction system were :C and :CCO only, and the ACAROR was the sole reaction that occurred. The C_nO molecules for $n =$ odd were singlet with an acetylene-type $^-C\equiv C-C\equiv O^+$, while those for $n =$ even were triplet with a cummulene-type:$C=C=C=C=O$.[5] Both species can react with :C via addition and ring opening with singlet−triplet intersystem crossing. The fact that the major observed products consisted of C_nO indicates that there was no cleavage of the overall structure, which is characteristic of the ACAROR.

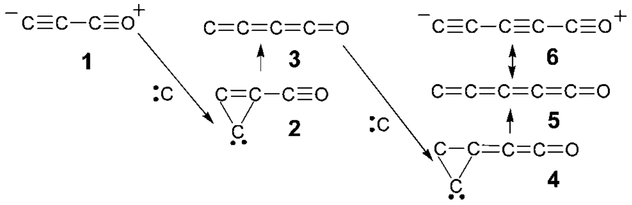

Figure 3. Proposed atomic-carbon addition and ring opening mechanism for the formation of C_nO molecules.

According to the above analyses, a likely reaction mechanism for the formation of C_nO molecules is, as we suggested in a previous paper,[5a] that, for a singlet C_nO molecule **1**, a carbon atom is added to the acetylene-type C′C bond to form cyclopropenylidene **2**. The carbene−carbon in the three-member ring further attacks the $C=C$ bond to open the strained-ring and then finally reaches the cummulene-type triplet molecule **3**. On the other hand, a carbon atom is added to the $C=C$ double bond for the triplet C_nO molecule **3** and then, via **4** and **5**, reaches the acetylene-type singlet molecule **6**. The processes in Figure 3 are repeated for longer C_nO molecules.

Acetylene-type structures $^-C\equiv C-(C\equiv C)_n-C\equiv O^+$ for the C_nO with $n =$ odd in Figure 3 seem consistent for the singlet species, where all atoms have rare-gas electronic configurations. In reality, the observed bond lengths $r(C_{(5)}-C_{(4)}) = 1.2736$, $r(C_{(4)}-C_{(3)}) = 1.2947$, $r(C_{(3)}-C_{(2)}) = 1.2668$, $r(C_{(2)}-C_{(1)}) = 1.2765$, and $r(C_{(1)}-O) = 1.1562$ Å in $^-C_{(5)}\equiv C_{(4)}-C_{(3)}\equiv C_{(2)}-C_{(1)}\equiv O^+$ exhibit bond length alternations.[5a] However, the large charge separation implied by the structure seems energetically unrealistic. Accordingly, the observed structural formula of C_5O cannot be expressed by a single canonical structure but must be attributed to resonance among acetylene-type and cummulene-type structures, and the extent of the latter increases with an increasing number of carbon atoms. Consequently, the acetylene-type expression, $^-C\equiv C-C\equiv C-C\equiv O^+$, is used for a singlet species in this paper, although it may not represent the exact structure.

3.2. Formation Mechanism of the General Linear-Carbon-Chain Molecules. The formation mechanism described above can also be applied to other linear-carbon-chain molecules prepared in laboratories and interstellar space; these databases are available on the homepage of Okabayashi.[9] The noteworthy molecules among them are the cyclic carbenes (c-HC_3)−R and their strained-ring opened isomers l-H−$C=C=C$−R, which are assumed to be involved in the formation mechanisms and are actually detected, for example $HC\equiv CH \xrightarrow{:C}$ c-C_3H_2 → l-$HC=C=CH$ (not detected) $\xrightarrow{:C}$ $HC_4H$$\xrightarrow{:C}$ (c-HC_3)−C_2H → l-HC_5H (not detected) $\xrightarrow{:C}$ HC_6H $\xrightarrow{:C}$ (c-HC_3)−C_4H; and also $HC\equiv C-CN$ $\xrightarrow{:C}$ (c-HC_3)−CN → l-HC_4N $\xrightarrow{:C}$ HC_5N $\xrightarrow{:C}$ (c-HC_3)−C_3N → l-HC_6N $\xrightarrow{:C}$ C_7N, where c and l indicate cyclic and linear, respectively. They are indicative of linear-carbon chain growth by atomic-carbon additions as well as ring openings. The only exception is (c-HC_3)$=C=C$, which cannot be prepared by direct ACAROR (see Figure 4); however, it can be formed by isomerization from (c-HC_3)$-C\equiv CH$. Thus, almost all molecules in Okabayashi's database are prepared by

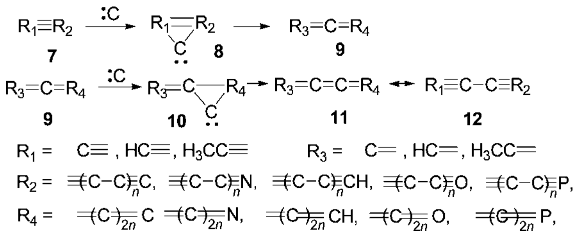

Figure 4. Formation mechanism for general linear-carbon-chain molecules detected in laboratories.

the ACAROR mechanism, as shown in Figure 4. A singlet molecule **7** reacts with a carbon atom to form **8** and **9**, whereas triplet **9**, via **10** and **11**, reaches **12**.

Many theoretical and experimental results supporting our formation mechanism are available. In the simplest case of $R_1 = R_2 = CH$ depicted in Figure 4, the theoretical investigations by Takahashi and Yamashita[10] and Ochsenfeld et al.[11a] and the crossed-beam reactions by Kaiser and co-workers[11b] have shown that the neutral−neutral reaction $C(^3P) + HC{\equiv}CH\ (^1\Sigma_g^+) \rightarrow$ l-C_3H_2 (propargylene **7**) occurs through the singlet−triplet crossing and via isomerization of c-C_3H_2 (cyclopropenylidene **6**). The formation enthalpies, $\Delta H^0_f(0\ K)$, for [$C + C_2H_2$ **5**], c-C_3H_2 **6**, and l-C_3H_2 **7** are 941, 725.5, and 533.1 kJ mol^{-1}, respectively.[11b] For C_3H_2, the c-C_3H_2 was detected because the potential barrier from the cyclic to the linear isomer was reasonably high.

In addition, the carbon oxide species C_2O, C_3O, C_4O, C_5O, and $C_{6/7}O$ have been observed by Kaiser et al.[12] in the radiation-induced reaction of carbon monoxide ice at 10 K, for which they proposed the following reaction model. A carbon atom is produced by the reaction of the photoexcited carbon monoxide with a second neighboring carbon monoxide:

$$CO^*(X\ ^1\Sigma^+) + CO(X\ ^1\Sigma^+) \rightarrow CO_2(X\ ^1\Sigma^+) + C(^3P/^1D)$$

The major route of formation of the $C_{n+1}O$ ($n = 1-4$) species is by a carbon atom added across a double bond of the C_nO ($n = 1-4$) molecule, followed by a rearrangement or ring opening, where the energies of formation for $C_{n+1}O$ were more favored than those of C_nO:

$$C_nO(X\ ^1\Sigma^+/^3\Sigma^+) + C(^3P/^1D) \rightarrow C_{n+1}O(X\ ^3\Sigma^+/^1\Sigma^+)$$

A second possible pathway was the reaction of $C_2(X^1\Sigma^+)$ with a carbon monoxide molecule:

$$CO(X\ ^1\Sigma^+) + C_2(X\ ^1\Sigma_g^+) \rightarrow C_3O(X\ ^1\Sigma^+)$$

Unfortunately, they were unable to observe anything that elucidated the kinetics of this pathway.[12]

It is commonly thought that atomic carbon exists primarily in a relatively diffuse part of the molecular cloud in space, where dense cores are not yet formed. Long carbon chains can be found in abundance, which suggests that they are formed by the ACAROR. Yamamoto et al. found that information concerning carbon-chain molecules has important implications for potentially redefining the star formation process.[13]

The ACAROR is a simple and efficient reaction with a low or zero activation energy and, hence, becomes overwhelmingly dominant in unfavorable conditions, such as ultra low temperatures[14] or incomplete combustion, as was demonstrated in linear-carbon-chain growth, cyclic-carbon-chain growth, fullerene growth from C_{60} to C_{70}, and soot formation and growth.[15]

4. Conclusions

1. The formation mechanism of linear-carbon-chain molecules has been investigated based on the detailed analyses of the FTMW spectroscopic data of C_nO ($n = 2-9$) produced by the electric discharge of C_3O_2.

2. The relative abundances of the C_nO products determined from their rotational spectrum intensities agree with those for the C_nO^+ ions. The active chemicals in the reaction system include :C and :CCO only, and the observed products consist exclusively of C_nO, leading to a likely formation mechanism of the atomic carbon addition and ring opening reaction (ACAROR). Almost all the linear carbon chains so far detected in laboratories or in space can be explained with the ACAROR.

3. A remarkable feature of the ACAROR is that it is simple and efficient, involving only an atomic carbon :C jump into the CC bond with a low or no activation energy and without cleaving the overall structure, and therefore, it does not produce a side-product.

4. The ACAROR mechanism is applicable not only to linear carbon chains but also to a wide range of carbon processes, in particular, to ultra low temperature or incomplete combustion conditions.

Acknowledgment. We thank Professor Y. Endo and Y. Oshima for useful discussions.

Supporting Information Available: Analyss of the population of energy states, the fractions of the C_nO molecules in the *J* rotational state, and table/figure of the relative abundances of C_nO and C_nO^+. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Bayes, K. D. J. *Am. Chem. Soc.* **1962**, *84*, 4077–4080.

(2) (a) Ogata. *The Reports of the Faculty of Liberal Arts*; Shizuoka University (Sciences): 1982; Vol. 18, pp 29−36. (b) Ogata, T.; Yoshikawa, M.; Fujii, K. *Chem. Lett.* **1985**, 1797–1798. (c) Ogata, T.; Ando, B. *J. Mol. Spectrosc.* **1986**, *118*, 70–75. (d) Ogata, T.; Fujii, K.; Yoshikawa, M.; Hirota, F. *J. Am. Chem. Soc.* **1987**, *109*, 7639–7641. (e) Ogata, T. J. *Mol. Spectrosc.* **1990**, *139*, 253–258. (f) Ogata, T. *J. Phys. Chem.* **1992**, *96*, 2089–2091.

(3) Schildcrout, S. M.; Franklin, J. L. *J. Am. Chem. Soc.* **1970**, *92*, 251–253.

(4) Bortolini, O.; Pandolfo, L.; Tomaselli, C.; Traldi, P. *Int. J. Mass Spectrom.* **1999**, *190/19*, 171–179.

(5) (a) Ogata, T.; Ohshima, Y.; Endo, Y. *J. Am. Chem. Soc.* **1995**, *117*, 3593–3598. (b) Ohshima, Y.; Endo, Y.; Ogata, T. *J. Chem. Phys.* **1995**, *102*, 1493–1500.

(6) Ohishi, M.; Ishikawa, S.; Yamada, C.; Kanamori, H.; Irvine, W. M.; Brown, R. D.; Godfrey, P. D.; Kaifu, N.; Suzuki, H. *Astrophys. J. Lett.* **1991**, *380*, L39–L42.

(7) Brown, R. D.; Godfrey, P. D.; Cragg, D. M.; Rice, E. H. N.; Irvine, W. M.; Friberg, P.; Suzuki, H.; Ohishi, M.; Kaifu, N.; Morimoto, M. *Astrophys. J.* **1985**, *297*, 302–308.

(8) NIST Chemistry WebBook, http://webbook.nist.gov/chemistry/.

(9) Homepage of Prof. T. Okabayashi, http://www.ipc.shizuoka.ac.jp/∼sctokab/Okab.htm.

(10) Takahashi, J.; Yamashita, K. *J. Chem. Phys.* **1996**, *104*, 6613–6627.

(11) (a) Ochsenfeld, C.; Kaiser, R. I.; Lee, Y. T.; Suits, A. G. *J. Chem. Phys.* **1997**, *106*, 4141–4151. (b) Kaiser, R. I.; Ochsenfeld, C.; Head-Gordon, M.; Lee, Y. T.; Suits, A. G. *J. Chem. Phys.* **1997**, *106*, 1729–1741.

(12) Jamieson, C. S.; Mebel, A. A.; Kaiser, R. I. *Astrophys. J. Supp.* **2006**, *163*, 184–206.

(13) (a) Sakai, N.; Ikeda, M.; Morita, M.; Sakai, T.; Takano, S.; Osamura, Y.; Yamamoto, S. *Astrophys. J.* **2007**, *663*, 1174–1179. (b) Sakai, N.; Sakai, T.; Hirota, T.; Yamamoto, S. *Astrophys. J.* **2008**, *672*, 371–381.

(14) Smith, I. W. M.; Herbst, E.; Chang, Q. *Mon. Not. R. Astron. Soc.* **2004**, *350*, 323–330.

(15) (a) Ogata T., Mieno T, Tatamitani Y. Proceedings of the Carbon 2007 Conference, B083, Seattle, WA. (b) Ogata T., Shibi Y., Tatamitani Y. Mieno T. Proceedings of the Carbon 2008 Conference, P0469, Nagano, Japan.

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