Reaction mechanism of the C_nO (n=2~9) productions in the C_3O_2 discharge

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A series of carbon monoxides C_nO ($n = 2 \sim 9$) had been simultaneously synthesized by creating an electrical discharge in a sample of tricarbon dioxide C_3O_2. To investigate the reaction mechanism, the relative abundance of the C_nO products was calculated. The fact that the relative abundance of both C_nO ($n = 2 \sim 9$) and C_mO^+ ($m = 2 \sim 5$) were similar and that carbon carbenes :C were the only chemically active species in the reactions means they were formed by the carbon insertion reactions.

1. Introduction

Carbon insertion is a "humorous" reaction: gaseous carbon atoms of the :C, :CCO or C_3O_2 species (carbon carbenes) "jump" into previously existing CC bonds without cleavage of the overall molecular structure and without the significant occurrence of side reactions[1]. More than ten years ago, Ogata *et al*. resumed the carbon insertion reaction into CC bond, intrigued by Endo's development of the pulsed-discharge-nozzle FTMW spectrometer. As was expected, the rotational spectrum (Fig.1) of a series of carbon monoxides C_nO ($n = 2 \sim 9$) was simultaneously observed in the discharge of C_3O_2. We report here the relative distribution of the C_nO products and the reaction mechanisms.

2. Results and Discussions

2.1 Relative abundances of C_nO produced by the C_3O_2 discharge

We have calculated the relative abundances of C_nO products from their rotational intensities[2] by taking into account the rotational partition functions and the magnitude of electric dipole moments to which the rotational intensities were proportional. The rotational

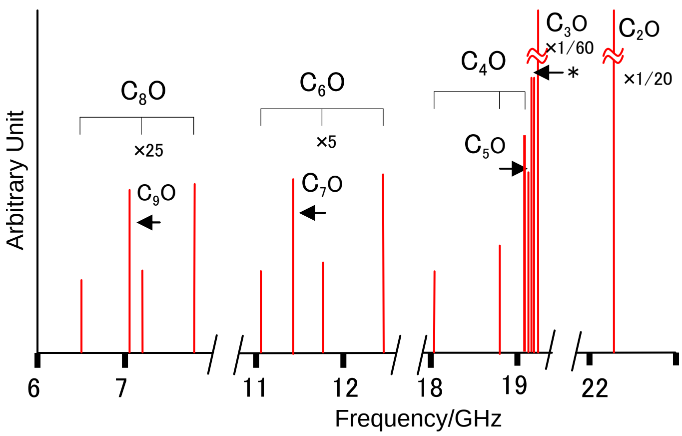

Fig. 1. Rotational spectrum of C_nO (n=2~9) exhibit triplet spectrum for even n and singlet for odd n. The vertical scales for n = 2, 3, 4 and 5, 6 and 7, and 8 and 9 are factored by 1/20, 1/60, 1, 5, 25, respectively. The lines marked * are C_3O for the ^{13}C species.

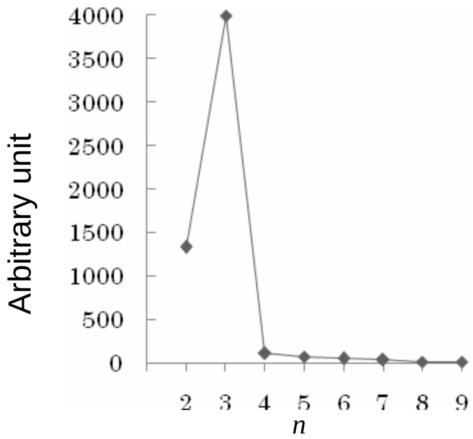

Fig. 2. Relative abundances of C_nO (n=2~9) produced by the discharge of C_3O_2.

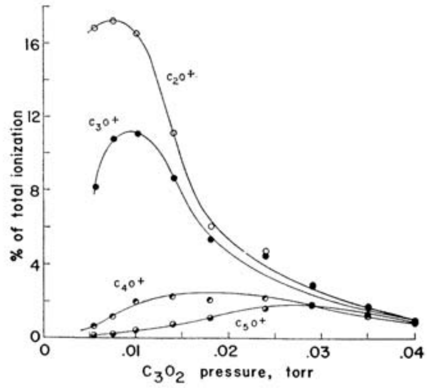

Fig. 3. Pressure dependence of relative abundances of C_mO^+ ions formed from electron impact in C_3O_2 [3]. Stepwise insertions of a carbon atom lengthened the carbon chains.

temperature of C_nO (n=2~9) was determined to be 3 K from the J-dependence of the rotational intensities of C_7O and C_9O, and the electric dipole moments were determined from *ab initio* MO calculations of ub3lyp/6-31g(d) level as 1.19, 1.95, 2.31, 3.10, 3.32, 4.13, 4.29, and 5.14 D for C_nO (n = 2 ~ 9), respectively. The relative abundances of the corresponding C_nO for n from 2 to 9 (Fig.2) were found to decrease monotonically with n as 1336, 3988, 115, 81, 58, 42, 19, and 15, respectively, except for C_2O which was further involved in the carbon insertion reactions by :CCO→ :C + CO. These relative abundances are similar to a series of C_nO^+ (n=2~5) produced by the reactions of the C_nO^+ ion with neutral C_3O_2 [3] (Fig. 3).

2.2 Reaction mechanism

NIST Chemistry WebBook shows the electron-impact mass spectrum of C_3O_2.[4] The main fragment ions are :CCO, :C and CO. The :CCO fragment can undergo further elimination of CO to produce :C. The C_2 and C_3 species (m/z = 24 and 36, respectively) may be formed from :C fragments, by :C + :C $\rightarrow$ C_2 and :C + C_2 $\rightarrow$ C_3, and are not involved in the carbon insertion reaction. Thus, it can be seen that carbon carbenes :C are, in practical terms, the only active species in the decomposition system of tricarbon dioxide. The fact that the relative abundances of the C_nO species (Fig. 2) resemble those of the C_nO^+ ions (Fig. 3), and that the chemically active species in the reaction system were carbon carbenes implies that only the carbon chains in C_nO were lengthened by progressive carbon-carbene insertions.

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