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Original Investigations

A Theoretical Study on the Photodissociation of C_3O_2

Yoshihiro Osamura and Kichisuke Nishimoto

Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan

Shinichi Yamabe

Department of Chemistry, Nara University of Education, Takabatake-cho, Nara 630, Japan

Tsutomu Minato

Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

The photodecomposition of C_3O_2 into C_2O and CO is studied with the *ab initio* MO calculation. It is found that, starting from the second excited state of C_3O_2 (Δ_u), the ground-state C_2O (triplet) is yielded through the bent dissociation. The stable structure of the excited triplet state of C_3O_2 as an intermediate is also demonstrated.

Key words: Photodissociation – Carbon suboxide – Carbonylcarbene

1. Introduction

Carbon suboxide C_3O_2 is one of cumulene-type molecules and shows various interesting physico-chemical behaviors [1]. Especially the photolysis of C_3O_2 in the presence of olefin results in a simple insertion of a carbon atom [2]; i.e. the overall reaction is

$$C_3O_2 + C_2H_4 \xrightarrow{h\nu} C_3H_4 + 2\,CO \tag{1}$$

This reaction is thought to be accompanied with the intermediacy of the C_2O molecule:

$$O{=}C{=}\overset{*}{C}{=}C{=}O \xrightarrow{h\nu} \overset{*}{C}{=}C{=}O + C{=}O \tag{2}$$

$$\overset{*}{C}{=}C{=}O + CH_2{=}CH_2 \longrightarrow CH_2{=}\overset{*}{C}{=}CH_2 + C{=}O \tag{3}$$

When C_3O_2 is labelled in the central position ($=C^*=$), the inserted atom is found in the central atom of allene. The possibility of the existence of atomic carbon as an intermediate can be excluded, because the decomposition of C_3O_2 into 2 CO and C (^3P) requires a very large amount of energy [3]. While the initial photochemical step is the decomposition of C_3O_2 into CO and carbonylcarbene C_2O as

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is shown in Eq. (2), it is not yet clarified how this reaction is brought about. In order to investigate theoretically the mechanism of this decomposition, the electronic structure of C_3O_2 and C_2O and the minimum-energy path of the reaction represented by Eq. (2) are studied with the *ab initio* MO calculation. The SCF MO's are obtained with the STO-3G minimal basis set using the Gaussian 70 program package [4]. The excited states of these species are calculated within the singly excited configuration interaction (SECI) method and the generalized restricted Hartree–Fock (GRHF) method [5][1].

2. Electronic States of C_3O_2

Let us consider the molecular structure of C_3O_2 in the ground state. Whereas Weimann and Christoffersen [6] found theoretically that the bent structure of this molecule is stable, other experimental [7, 8] and theoretical [9, 10] results suggested that the linear structure ($D_{\infty h}$ symmetry) is more favorable than the bent one. Our calculation supports the latter result. In our calculation, the equilibrium structure is found to have $R_{CC} = 1.261$ Å and $R_{CO} = 1.180$ Å. This result is in good agreement with experimental geometry ($R_{CC} = 1.28$ Å, $R_{CO} = 1.16$ Å) [11].

Since π orbitals of the $D_{\infty h}$-symmetry C_3O_2 are all doubly degenerate, its excited states are somewhat complicated. In the left hand side of Fig. 1, the energy levels

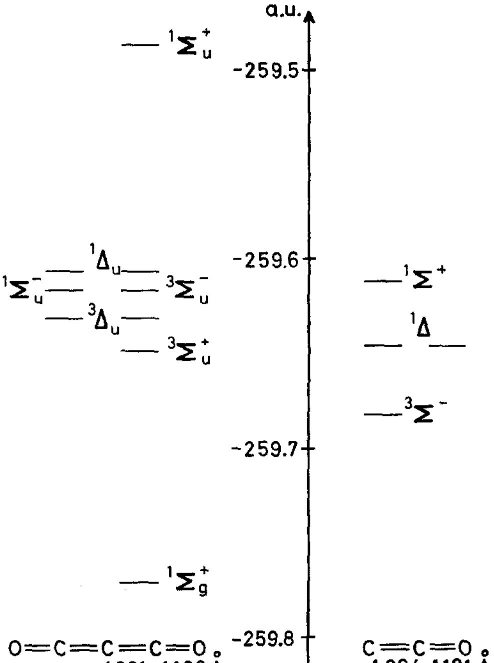

Fig. 1. Low-lying state energies of C_3O_2 and C_2O calculated by SECI method in the equilibrium geometries of their ground states. Energies in the right side are the sum of that of C_2O and the ground-state energy of CO (−111.2257 a.u.)

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[1] The GRHF program was coded by S. Iwata and K. Morokuma for the Rochester Version of Gaussian 70.

of low-lying states calculated by SECI are given. The several low-lying excited states are approximately expressed as follows;

$$^{3,1}\Phi_{\Sigma_u^+} = \frac{1}{\sqrt{2}}(^{3,1}\phi_1 + {}^{3,1}\phi_3), \tag{4}$$

$$^{3,1}\Phi_{\Delta_u} = \begin{cases} \dfrac{1}{\sqrt{2}}(^{3,1}\phi_2 + {}^{3,1}\phi_4) & (5) \\[2ex] \dfrac{1}{\sqrt{2}}(^{3,1}\phi_1 - {}^{3,1}\phi_3), & (6) \end{cases}$$

$$^{3,1}\Phi_{\Sigma_u^-} = \frac{1}{\sqrt{2}}(^{3,1}\phi_2 - {}^{3,1}\phi_4), \tag{7}$$

where

$$\begin{aligned} ^{3,1}\phi_1 &= |\cdots(\pi_{3x})^1(\pi_{3y})^2(\pi_{4x})^1|\cdot{}^{3,1}\sigma, \\ ^{3,1}\phi_2 &= |\cdots(\pi_{3x})^1(\pi_{3y})^2(\pi_{4y})^1|\cdot{}^{3,1}\sigma, \\ ^{3,1}\phi_3 &= |\cdots(\pi_{3x})^2(\pi_{3y})^1(\pi_{4y})^1|\cdot{}^{3,1}\sigma, \\ ^{3,1}\phi_4 &= |\cdots(\pi_{3x})^2(\pi_{3y})^1(\pi_{4x})^1|\cdot{}^{3,1}\sigma, \\ ^{3,1}\sigma &= \frac{1}{\sqrt{2}}(\alpha\beta \pm \beta\alpha). \end{aligned}$$

Before discussing the decomposition of C_3O_2, it is of interest to examine the relation between its geometrical deformation in low-lying states and the change of the state energy. There, geometrical parameters (the C_1—C_2 bond distance R, the C_1—C_2—C_3 bond angle θ, and the C_2—C_1—O_1 angle ϕ) are varied independently and Fig. 2 gives the results for some low-lying states. The numbering of atoms is as follows:

—003—

The enlargement of R makes both the ground and excited states unstabilized significantly. Thus, the elongation of the C—C bond preserving the linear structure would be unfavorable to cause the dissociation in any low-lying state.

While the decrease of θ in the ground state of C_3O_2 reveals a relatively slow energy ascent, that in three excited states has a rather sharp ascent as is shown in the middle of Fig. 2. This flat energy curve in the ground state arises from the fact that the central carbon atom has the large negative charge which relaxes the destabilization during the C—C—C bending distortion according to the Walsh rule [12]. Such facile bending is related to the very low frequency found in the IR and Raman spectra [7, 8, 13].

Variation of bond angle ϕ exhibited in the right of Fig. 2 makes the ground state extremely unstable. On the other hand, the excited states give very flat energy curves. This result in the excited states indicates that C—C—O angle distortion is more important than the C—C—C distortion to initiate the photodecomposition.

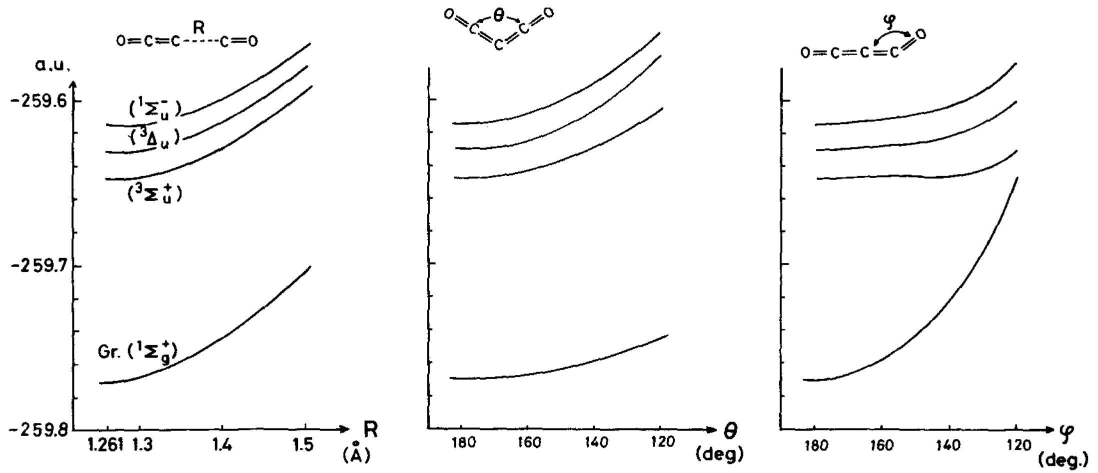

Fig. 2. Energy curves of ground and several excited states for *R*, *θ* and *ϕ* variation with respect to the equilibrium geometry of C_3O_2 given in its ground state

However, the simultaneous variation of two ϕ's ($\sphericalangle$CCO) in both sides brings about the appreciable destabilization because of the annihilation of two double bonds through the $D_{\infty h} \rightarrow C_{2h}$ distortion.

3. Electronic States of C_2O

As a result of the photodecomposition of C_3O_2, the ground-state CO is yielded. The other product, carbonylcarbene C_2O, is triplet in its ground state and its structure is linear [14] with two electrons of parallel spin occupying doubly degenerate π orbitals. The existence of C_2O is suggested primarily by Williamson and Bayes [15]. Thomson and Wishart [16] carried out an MO calculation of C_2O using a larger basis set. Their result for an optimized geometry of C_2O in the ground state ($^3\Sigma^-$) is $R_{CC} = 1.365$ Å and $R_{CO} = 1.122$ Å. Our calculation using the GRHF method gives $R_{CC} = 1.364$ Å and $R_{CO} = 1.181$ Å. Comparison of the geometry between C_2O and the fragmental part of C_3O_2 indicates that an extension of the C_2—C_3 bond occurs and the C_3—O_2 bond is almost constant during the reaction $C_3O_2 \rightarrow C_2O + CO$.

In the right side of Fig. 1, the energy levels of C_2O are given. This result is obtained by an SECI calculation. The lowest $^1\Delta$ states lie by ca. 1 eV above $^3\Sigma^-$, one of which has a major configuration, $|\cdots(\pi_{1x})^2(\pi_{1y})^2(\pi_{2x})^1(\pi_{2y})^1|$.

4. Discussion of the Photodecomposition of C_3O_2

Low-lying states of C_3O_2 are Σ and Δ states as are described in Fig. 1. These states are constructed from the two different electron configurations. In the left side of Fig. 3, schematic assignment of twelve pi electrons and C_1—C_2 bonding two σ

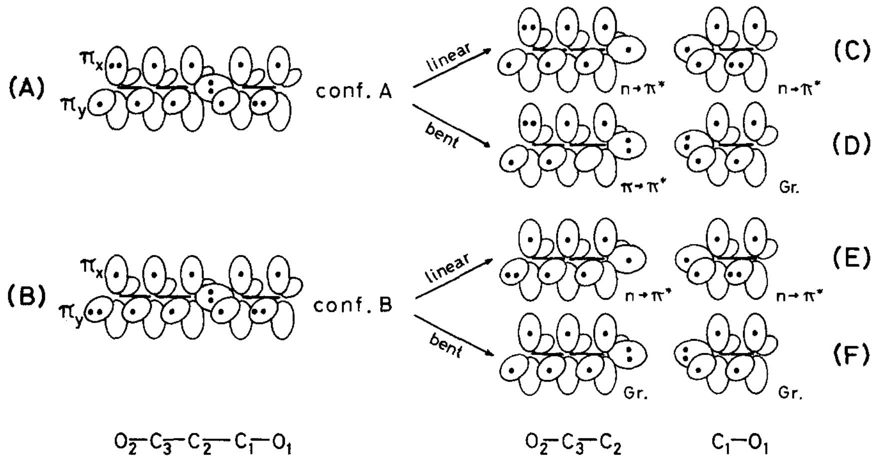

Fig. 3. Schematic description of the electron assignment to π_x, π_y and σ orbitals of C_3O_2, C_2O and CO

electrons is shown. In the ground state of C_3O_2, 6 of 10 pi orbitals are doubly occupied. Six electrons are in one pi orbital (π_x) and the residual 6 electrons are in the other pi orbitals (π_y), see Fig. 3(A). This assignment of electrons is defined as configuration A and holds also for excited Σ^+ states.

The other assignment, configuration B, is composed of mainly by $\pi_x \rightarrow \pi_y$ (or $\pi_y \rightarrow \pi_x$) excitation with 5 electrons in π_x (or π_y) orbitals and 7 electrons in π_y (or π_x) orbitals (Fig. 3(B)). This configuration contributes to the Δ state and the Σ^- state of high-lying energy. Considering this occupation of electrons, it is a matter of interest to examine how they behave themselves to form the electronic structure of the product in the dissociation process. As is examined in the energy curve of R dependence of Fig. 2, the linear fragmentation of $C_3O_2 \rightarrow C_2O + CO$ is unfavorable. This is explained schematically as follows. In both configurations A and B, two σ radicals would be produced by linear C—C bond cleavage, because the number of electrons in each symmetry orbital σ, π_x and π_y must be conserved. It is considered that the configurations of these σ radicals correspond to the excitation from σ to π orbitals in both the C_2O and CO molecules (Fig. 3(C) and (E)). Therefore, linear decomposition of C_3O_2 is expected to give energetically higher states.

Once the linear dissociation is unfavorable, the bending distortion of C_3O_2 should be introduced in order to avoid the high energy barrier imposed by the restriction of σ, π_x and π_y symmetries. The relaxation of the distinction between σ and π_y (or π_x) (i.e. $C_{\infty h} \rightarrow C_s$) may give the effective orbital mixing to make the reacting system stabilized. That is, electrons can be redistributed, through the σ–π_y mixing, for the more likely electronic structure of the product than that in the separation of σ and π_y. Through $C_{\infty h} \rightarrow C_s$ deformation, doubly degenerate π_x and π_y orbitals split to π (π_x) and σ-type ($\sigma + \pi_y$) orbitals.

Since the number of electrons in each π and σ-type orbital must be conserved by bending dissociation, in the configuration A ((A) → (D) in Fig. 3), 6 electrons in the π_y orbitals and 2 σ electrons would be rearranged to 4 electrons in CO and 4 in the C_2O molecule. Then, CO can be settled down at the ground-state configuration with two (σ-type) lone-pair electrons. On the other hand, there are two probable ways for 4 electrons to be assigned to C_2O. One is the combination of 3 electrons in π_y orbitals and 1 electron in a σ lone-pair orbital. The other one is that of 2 electrons in the π_y orbital and 2 electrons in the σ lone-pair orbital (Fig. 3(D)). It is considered that this configuration corresponds to a Δ state in the C_2O molecule. These two electron configurations belong to excited states of C_2O regardless of whichever is more stable.

In configuration B ((B) → (F) in Fig. 3), 9 electrons which consist originally of $7(\pi_y)$ plus $2(\sigma)$ in C_3O_2 are rearranged, through σ–π_y mixing, to C_2O and CO. These 9 electrons are distributed to the ground-state of CO(4) and C_2O(5). Thus, C_2O molecules can fall into the ground-state triplet configuration with 3 electrons in π_y orbital and 2 electrons in σ lone-pair orbital. Main contributor of the bending mode to cause the (B) → (F) dissociation is expected to be the angle $\phi(\sphericalangle C_2C_1O_1)$ as is shown in Fig. 2.

The combination of the intuitive discussion given in Fig. 3 and the excitation energy shown in Fig. 1 substantiates the fact that photolyzing at 3000 and at 2500 Å produces two different intermediates which are thought to be C_2O ($^3\Sigma$) and C_2O ($^1\Delta$), respectively [15].

5. Minimum Energy Path from C_3O_2 to C_2O and CO

The previous simple model indicates that the most probable photodissociation of C_3O_2 may occur at the $^{1,3}\Delta_u$ state with configuration B of the lowest energy and the reaction does not take place by the linear separation but needs the bending deformation.

Since the ground state of the C_2O molecule is a triplet, the decomposition conceivably occurs from an excited triplet state of C_3O_2. To obtain this reaction path starting from the $^3\Delta_u$ state of C_3O_2, a GRHF calculation is carried out. In the left side of Fig. 4, four geometrical parameters $\{r, r', \theta$ and $\phi\}$ to be optimized at a given R are shown. The results of the minimum energy path are displayed in Table 1 and in Fig. 4 as a snapshot. Fig. 5 shows the potential energy curve along this minimum energy path.

It is noteworthy, in Fig. 5, that the energy valley appears at $R \simeq 1.5$ Å which corresponds to the distance of the C—C single bond. Therefore, the stable structure of triplet C_3O_2 originating from the $^3\Delta_u$ state is expected to exist in the course of

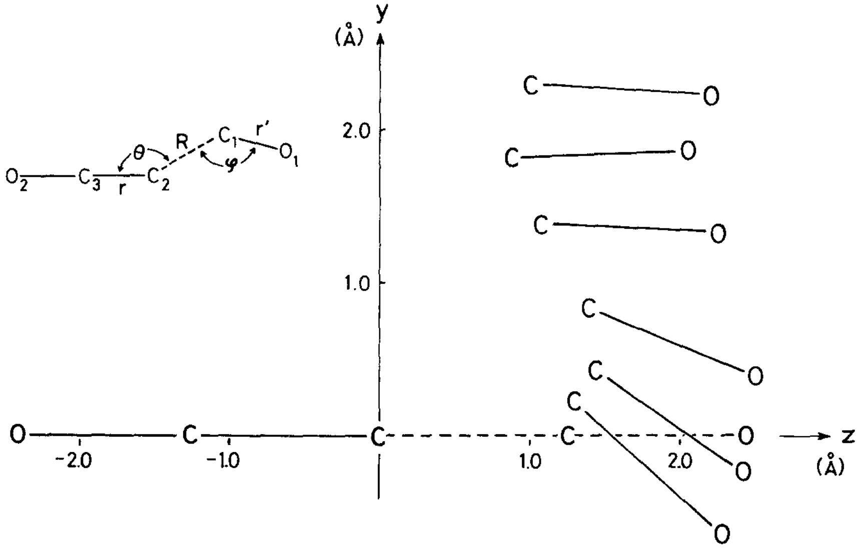

Fig. 4. Optimized path for the decomposition of C_3O_2 ($^3\Delta_u$). At the left shoulder the optimized geometrical parameters are given

Table 1. Geometries and energies along the minimum energy path of the photodissociation starting from $^3\Delta_u$ of C_3O_2 calculated by the GRHF method. Geometrical parameters are defined in Fig. 4

R (Å)	θ (deg)	ϕ (deg)	r (Å)	r' (Å)	Total energy (a.u.)
1.3	170	138	1.26	1.18	−259.6599
1.5	164	130	1.25	1.20	−259.6807
1.75	128	125	1.307	1.174	−259.6541
2.0	116	119	1.358	1.154	−259.6571
2.25	114	114	1.362	1.149	−259.6675
2.5	114	111	1.363	1.147	−259.6740
∞	–	–	1.364	1.145	−259.6755

the dissociation. Judging from the result of Fig. 2, large ϕ variation enhances the loss of the one-planed π bond in the excited states to yield the above mentioned excited-state structure. In order to get over the activation barrier, the subsequent break of the C—C single bond is needed and is caused by large θ variation. This geometrical change is important to the formation of a σ lone-pair orbital in C_2O. As R increases, bond angle θ changes from 180° to 120° owing to the fact that minus charge is piled up on the central carbon atom.

A reaction path from the $^1\Sigma_u^-$ state of C_3O_2 to the $^1\Delta$ state of C_2O, although not calculated here, would be almost like this triplet reaction path. Though the $^3\Delta_u$ state is, by nature, the second excited state of the $D_{\infty h}$ C_3O_2, its state energy is lowered significantly through such a deformation.

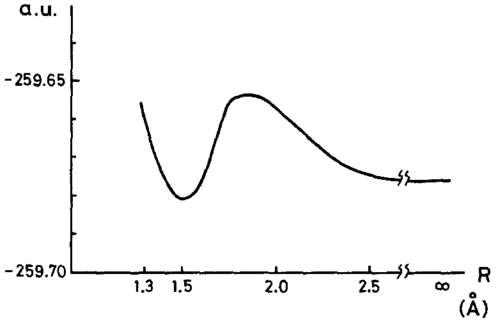

Fig. 5. Potential energy curve along the decomposition path: $C_3O_2(^3\Delta_u) \rightarrow C_2O(^3\Sigma^-) + CO$. Since the C_3O_2 molecule in the initial stage of the reaction has nearly linear structure with possibly almost degenerate states, the one-configuration description imposed by the employment of the GRHF method must be checked by the CI wave function. But the energy lowering by the CI calculation is found to be about 0.0035 a.u. (at most), which shows that the overall potential curve shown in Fig. 5 is almost invariant even with a more accurate wave function

6. Concluding Remark

The photodecomposition of C_3O_2 into C_2O and CO is calculated to occur at the second excited state Δ_u of C_3O_2, and the reaction path is the non-linear elimination of CO. The explanation for this is given reasonably by the discussion of the σ–π mixing. The calculation confirms the orientation predicted qualitatively.

The C_2O molecule which is produced by the decomposition of C_3O_2 is a reactive intermediate and may react with olefin to form allene. Theoretical analysis of the reaction in Eq. (3) will be provided in a forthcoming paper.

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