A Theoretical Study on the Paths of Photodissociation: Cyclopropanone → CO + C_2H_4

Shinichi Yamabe,*[1a] Tsutomu Minato,[1b] and Yoshihiro Osamura[1c]

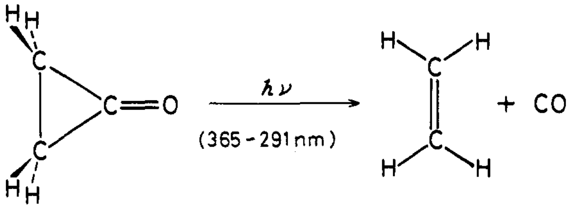
Contribution from the Department of Chemistry, Nara University of Education, Takabatake-cho, Nara 630, Japan, the Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan, and the Department of Chemistry, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan. *Received November 7, 1978*

Abstract: The state correlation diagram is examined for the least and nonleast ("bent-in-plane" and "bent-out-of-plane") motions of dissociation pathways of cyclopropanone in the excited states as well as in the ground state. For the pathways allowed by the symmetry ab initio calculations are made to explore the minimum-energy paths. For the lowest excited state of cyclopropanone two distinct dissociation paths are found to give different reaction mechanisms. The intermediacy of the biradical species in the bent-in-plane pathway is demonstrated.

I. Introduction

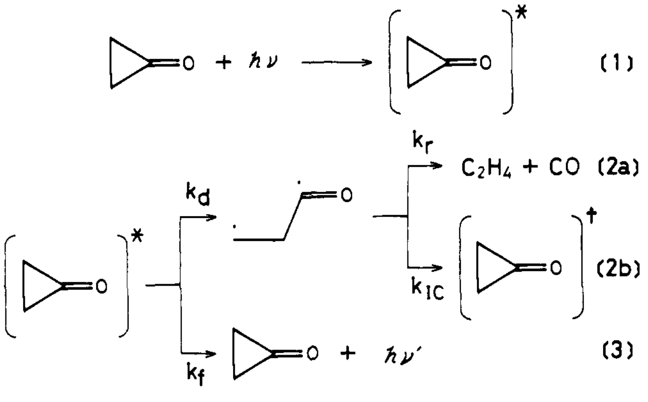
The simplest cyclic ketone, cyclopropanone (CP), has attracted considerable attention of organic and physical chemists for many years.[2] This parent molecule was synthesized primarily by Turro and Hammond[3] and by DeBoer and co-workers.[4] Its structure has been determined by microwave spectrsocopy[5] and by electron diffraction.[6] Many theoretical calculations have been made,[7] mainly placing stress on the question of its structural stability (e.g., the classical ring ketone or the oxyallyl). Thomas and his co-workers have studied rigorously the gas-phase photochemistry of CP and have suggested the mechanism shown in Scheme I for its photodissociation.[8] There, the k_{IC} is the rate constant to yield the vibrationally excited (electronically ground) state CP through the internal conversion (IC). They have also found that the thermal reaction of the gaseous CP gives only the polymerized product and that no volatile product is detected.

In view of the considerable interest in the reactivity of CP among experimentalists, a theoretical study on the mechanism of the photodissociation of CP seems desirable. In this work, an ab initio calculation of the dissociation path of CP in its several excited states as well as in its ground state is carried out.



Cyclopropanone (CP)

Scheme I



Our attention is focused on the intermediacy of the biradical shown in the above scheme.

II. A Consideration of the Reaction Path Based on the State Correlation Diagram

The least motion path of the decarbonylation, CP → CO + C_2H_4, is of C_{2v} symmetry, where the principal (z) axis is kept throughout the reaction. In Figure 1, the Hartree-Fock MO levels of CP and its dissociation products are shown according to the C_{2v} symmetry. The MO is calculated using the experimental geometry of CP[5] with the STO-3G minimal basis set.[9] The highest occupied (HO) MO of CP ($4b_1$) is the lone-pair orbital on the carbonyl oxygen and the lowest unoccupied (LU) MO of CP ($3b_2$) is the carbonyl π^* orbital. In ethylene, somewhat deformed, the HOMO ($9a_1$) is the π type and the LUMO ($4b_1$) is the π^* type. For carbon monoxide, the HOMO ($8a_1$) is the σ lone-pair orbital on the carbon atom and the doubly degenerate LUMOs ($5b_1$ and $3b_2$) are the π_x and $\pi_y(\bar{\pi})$ orbitals, respectively. Keeping in mind these MO levels, one can draw the state correlation diagram of the least motion path [(I) C_{2v}] shown in Figure 2. The number displayed at both edges of this figure denotes the way of assigning 30 electrons of the system to four symmetry orbitals (a_1, b_1, b_2, and a_2 MOs). Here it should be noted that the states of CP cannot be connected straightforwardly with those of the product belonging to the same symmetry, if their ways of electron assignment are different. Above the line representing the energy level of each state, a major configuration [e.g., ($4b_1 \rightarrow 3b_2$)] contributing to it is given. First of all, the $^1A_1$ ground states of CP and the product are connected via the avoided-crossing energy barrier, which says that the least motion path of the thermal decarbonylation of CP is symmetry forbidden and a non-least-motion path is required. Hoffmann and his co-workers have also pointed out this forbiddenness by their *orbital* correlation diagram.[7c] For low-lying excited states ($^{1,3}A_2$ and $^{1,3}B_2$) of CP, their energy curves are found here to have the avoided crossing and consequently the least motion pathways in these states are forbidden. For the $^{1,3}B_1$ state, the energy curves descend monotonically from CP to the product. This energy descent without the avoided-crossing barrier apparently renders the reaction of this state symmetry allowed. Thus, the photodissociation from the $^{1,3}B_1$ of CP takes place via the least motion path. However, the $^{1,3}B_1$ state locates at high energy compared with the wavelength (365-291 nm) used experimentally[8] and accordingly has a very short lifetime either because of the rapid IC to the lower states or because of the direct process to the product. Therefore, the probability of the dissociation from this state, even if allowed, would be minor.

Figure 2 is drawn only qualitatively in terms of the MO

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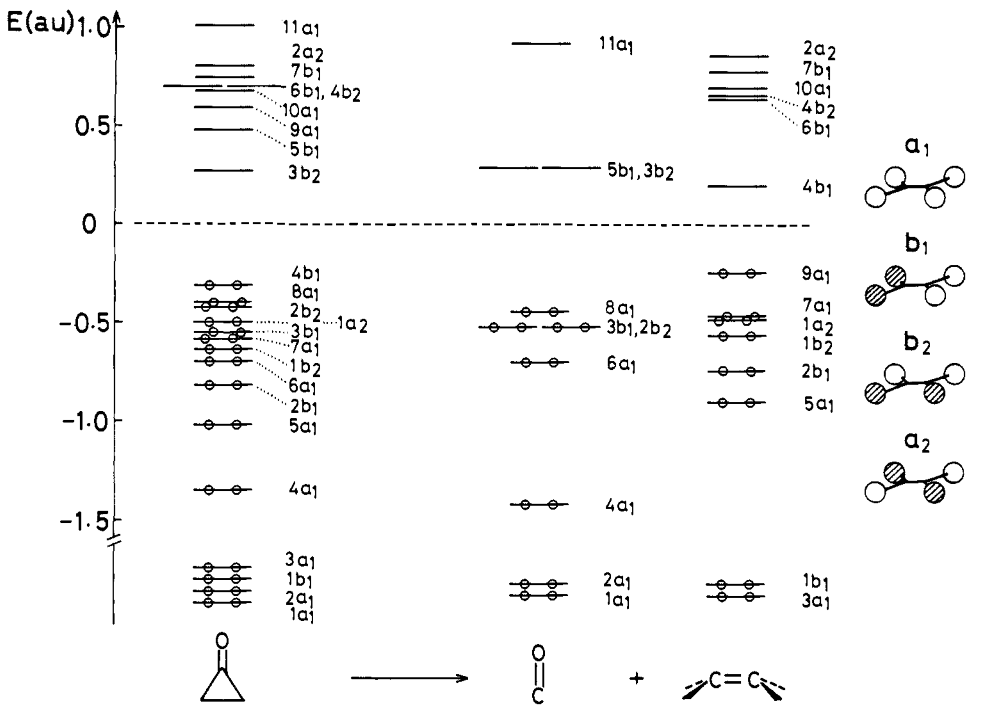


Figure 1. MO energy levels of cyclopropanone, CO, and ethylene according to the classification of the C_{2v} point group. In the right side, four types of symmetry orbitals are shown in terms of four hydrogen atoms of the ethylene site.

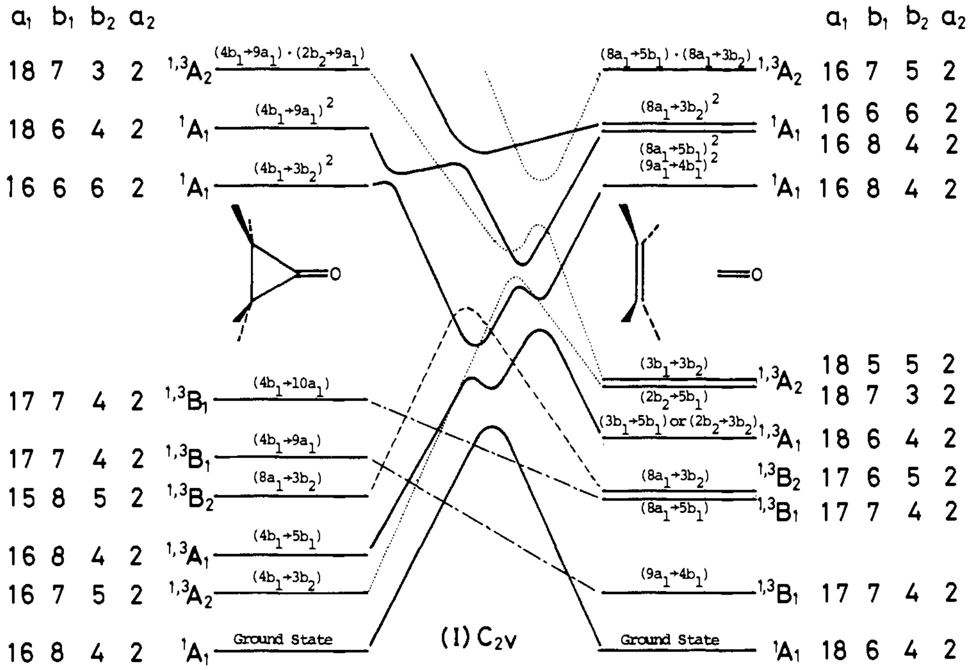


Figure 2. The state correlation diagram of the (I) C_{2v} fragmentation: CP → CO + C_2H_4. In both edges, 30 electrons of the system are assigned to four types of symmetry orbitals.

energy levels of Figure 1. For the later quantitative discussions, we need to obtain the state energy (E_T) more exactly and clarify the relationship between low-lying states. For this purpose, a multiconfiguration (MC) SCF calculation[10] with the STO-3G minimal basis set is carried out for some low-lying states. The motive for using the MCSCF wave function is that it is considered to be the best tool to follow the energy change systematically along the dissociation path, particularly around the point of the avoided crossing. This basis set is in accord with that used later in the geometry optimization so as to keep the energy scale uniform. Two technical simplifications are introduced. One is that only *R* (between carbonyl carbon and the middle point of the ethylenic C-C bond) is changed to describe the dissociation, other parts being frozen to experimental ones of CP.[5] The other is that, for the MCSCF wave function, only the major configurations of each state are adopted to represent the avoided crossing of the symmetry-forbidden separation. For instance, the $^{1,3}A_2$ energy curve is represented by three configurations [($4b_1$ → $3b_2$) of CP, ($2b_2$ → $5b_1$) and ($3b_1$ → $3b_2$) of the product]. In the allowed $^{1,3}B_1$ state, the generalized restricted Hartree-Fock (GRHF) orbital is used as the one-configuration wave function.[11] The calcu-

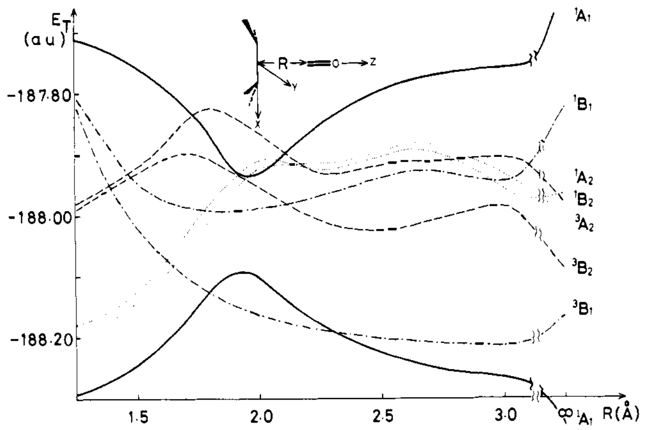


Figure 3. Quantitative description of the C_{2v} correlation diagram for some low-lying states. Each energy is calculated by the MCSCF wave function. The upper $^1A_1$ curve of this figure does not show such a complex avoided crossing (with double humps) as is predicted in Figure 2, because only two (closed-shell) configurations are adopted to represent the ground-state energy curve.

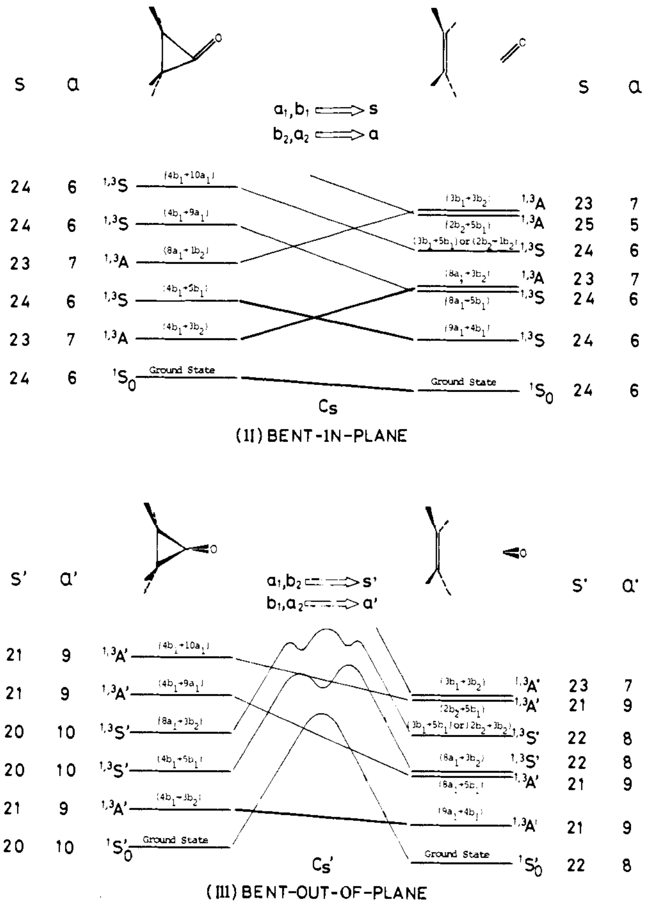


Figure 4. The state correlation diagram for (II) bent-in-plane path and (III) bent-out-of-plane path.

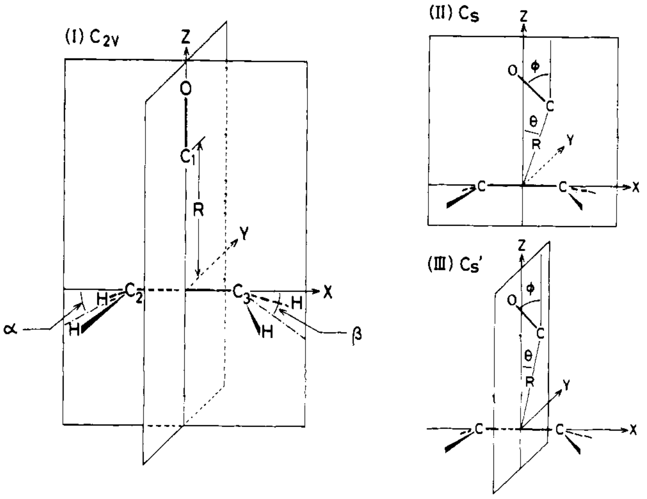


Figure 5. Definition of geometrical parameters to be optimized for obtaining the minimum-energy path.

lated result is exhibited in Figure 3. For this figure, the following explanation is given.

1. The energy curve of the $^1A_1$ ground state shows obviously a high barrier at $R \simeq 1.9$ Å, indicating that the C_{2v} path is symmetry forbidden and unfavorable.
2. The lowest excited state of CP, $^{1,3}A_2$, has a very low-lying position among various excited states. As R becomes larger, however, the state begins to climb the energy barrier due to the forbiddenness of the reaction.
3. The $^{1,3}B_2$ state of CP is situated relatively at high energy and also shows the energy barrier along the linear elimination.
4. The $^{1,3}B_1$ state gives the energy curve descending sharply in the range of $R = 1.3$–1.7 Å and has no energy barrier. The allowed path of this state is clearly demonstrated as R becomes larger.

Although in the strict sense the present MCSCF wave function with the STO-3G basis set is not necessarily sufficient to describe the accurate potential curve, it seems to give reasonable results both of the relative position of each state energy of CP and of the behavior of the avoided crossing for the symmetry-forbidden path. Thus, we may say that the essential feature of energy curves predicted qualitatively in Figure 2 is confirmed by the MCSCF calculation. Since the transition moment between the ground state ($^1A_1$) and the lowest excited state ($^1A_2$) is zero and the probability of staying at the $^1A_2$ state is great, the photodissociation starting from the $^{1,3}A_2$ state will dominate. Consequently, it is a matter of prime importance to consider the type of geometrical deformation which will switch forbiddenness of the $^{1,3}A_2$ state to allowedness.

In order for the dissociation to proceed easily, the C_{2v} symmetry imposed on the system should be relaxed. If the geometry is deformed in such a way as to remove one symmetry operation of C_{2v} (i.e., the reflection with respect to the mirror plane or the rotation), the symmetry of the system is reduced to C_2 or C_s. If the geometry of the system with the C_{2v} symmetry is deformed to that with the C_2 symmetry, the shape of the rectangle composed of four hydrogens in the ethylene site will be transformed into that of the parallelogram. This deformation causes the MO mixing of $a_1 + a_2 \rightarrow s$ (symmetric) and $b_1 + b_2 \rightarrow a$ (antisymmetric). Through this deformation, however, the essential feature of the correlation diagram is not so different as that in Figure 2. On the other hand, two ways of giving C_s symmetry to the system are possible. One is the dissociation of the (II) "bent-in-plane" keeping the (x-z) symmetry plane (C_s) and the other is that of the (III) "bent-out-of-plane" with the (y-z) symmetry plane (C_s'). The Cartesian coordinates are defined in Figure 3. In Figure 4 the state correlation diagram for these two C_s's is given. There, the ground-state dissociation becomes symmetry allowed in the (II) bent-in-plane path, whereas it is kept forbidden in the (III) bent-out-of-plane path. Thus, we can say that the thermal decarbonylation is initiated not through the concerted process [(I) and (III)] but through the scission of one C–C bond (II). In (II), the lowest excited state of CP ($^{1,3}A$) is connected in the

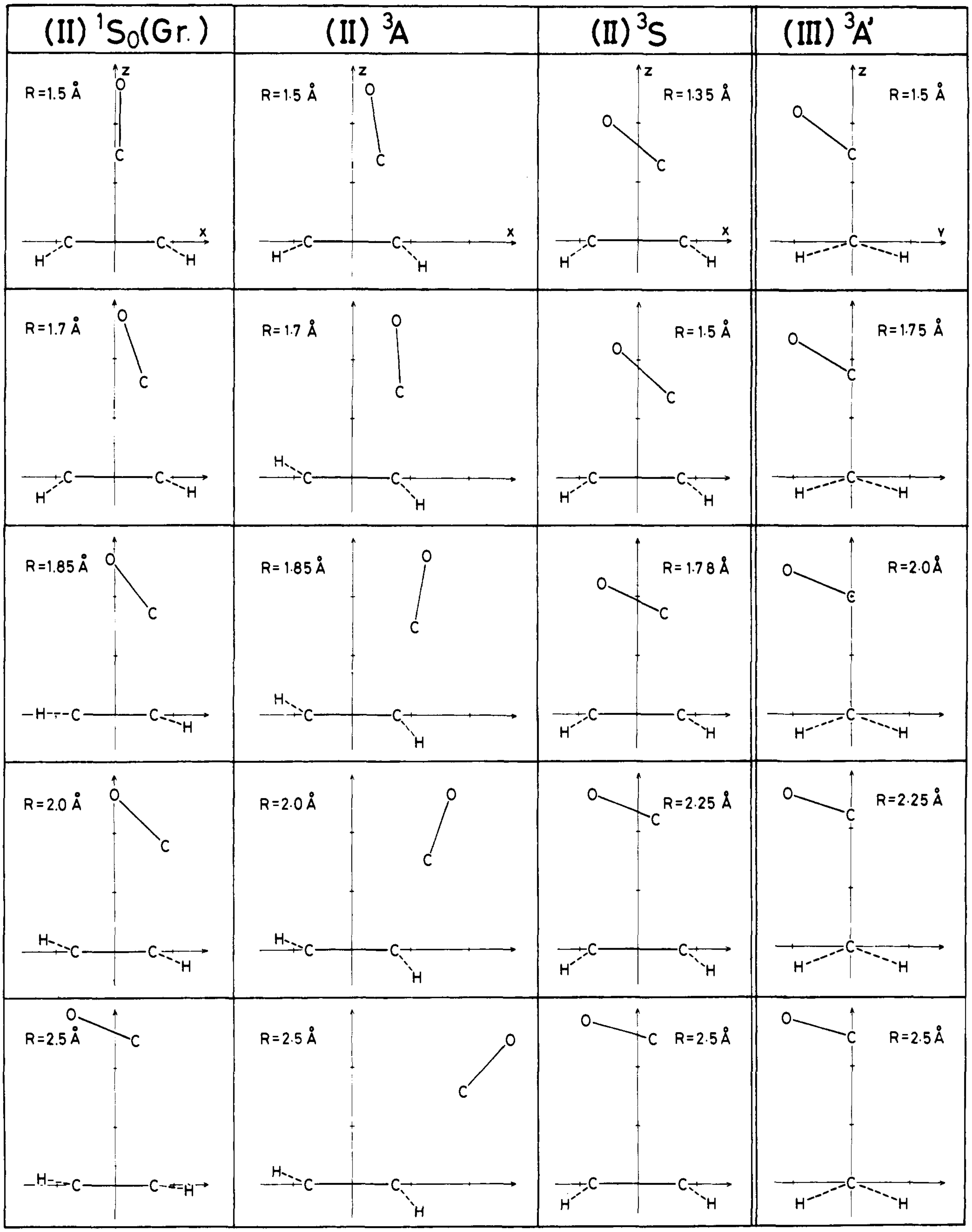


Figure 6. The snapshots of dissociation of CP along the calculated minimum-energy paths. Four paths follow the "allowed" states given by bold lines in Figure 4.

allowed manner with ^{1,3}A of the product which corresponds to the $(n,\bar{\pi}^*)^{1,3}$ CO and the ground-state C_2H_4. Since the energy of the $(n,\bar{\pi}^*)^{1,3}$ CO is in the high-energy position, the allowed line of ^{1,3}A will ascend toward the product site. In (III), the lowest excited state of CP (^{1,3}A$'$) is expected to go smoothly to the product [i.e., the ground-state CO and the $(\pi,\pi^*)^{1,3}$ state of C_2H_4]. Once these allowed processes indicated by bold lines are found by the $C_{2v} \rightarrow C_s$ (and C_s') deformation, their minimum-energy paths will be investigated in detail.

III. Method of Calculation

The minimum-energy paths of the allowed process introduced in Figure 4 are obtained by the optimization of five parameters (θ, ϕ, $r(C_2-C_3)$, α, and β) at a given R. These geometrical parameters are defined in Figure 5. For (III) C_s', the condition $\alpha = \beta$ is always held. While the usual Hartree-Fock MO is adopted to describe the ground-state dissociation, the wave function for each excited state is calculated by the GRHF method[11] with the STO-3G minimal basis set. The choice of this one-configuration wave function is thought to be a good approximation for each excited state, *except* in a special case.[12] Fortunately, this exceptional case is not dealt with in this work.

IV. The Result of the Optimized Path and the Potential Energy

On the basis of the discussion made by three correlation diagrams, four kinds of minimum-energy paths indicated by bold lines in Figure 4 are calculated. For the (II) bent-in-plane path, reactions in the $^1S_0$ (ground), ^3A (lowest excited), and ^3S (second excited) states are traced. For the (III) bent-out-of-plane path, the reaction in the sole symmetry-allowed state $^3A'$ is searched. In Figure 6 the snapshots of the optimized geometries are given.

In the (II) $^1S_0$, the ground (Gr)-state dissociation is shown and it is clearly exhibited that CO leaves the ethylene site, circumventing the least motion (symmetry-forbidden) path. It is also noteworthy that two hydrogens bonded to C_2 swing up to the $z > 0$ region at $R \simeq 2.0$ Å. This inversion of two hydrogens can be reasonably explained in terms of the charge distribution. In the elongated (i.e., weakened) $C_1 \cdots C_2$ bond, the charge is found to be substantially polarized ($C_1^{\delta+}$ and $C_2^{\delta-}$), which enhances the pyramidal configuration of the CH group on the C_2 atom. In this "zwitterionic intermediate", the upper ($z > 0$) pyramidal configuration appearing in the $^1S_0$ path is more favorable than the one below ($z < 0$), because the center of the charge density of the ethylenic π orbital escapes from the interacting region ($C_1 \cdots C_2$) to avoid the exchange repulsion against the carbonyl π density.

In the (II) ^3A, CO slides along the x axis to make two separated radical centers on C_1 and C_2. This behavior of CO corresponds to that appearing in the process of the Norrish type I with the cleavage of a bond α to the carbonyl.

In the (II) ^3S, the C-O bond is found to deviate substantially from the z axis even in the initial stage of the fragmentation. This is because the electronic charge on C_1 accumulated by the ($4b_1 \rightarrow 5b_1$) excitation enhances such geometrical deformation.

In the (III) $^3A'$, the C_1 atom of the leaving CO is always on the z axis and CO bends more and more as R becomes larger.[13] This bending motion along the dissociation is explainable according to the Walsh rule.[14] That is, through the ($4b_1 \rightarrow 3b_2$) excitation which contributes most significantly to the $^{1,3}A'$ (i.e., $^{1,3}A_2$) state, the electronic charge migrates from the p_x orbital of the carbonyl oxygen to the p_y orbital of the carbonyl carbon (C_1). Owing to the charge distribution on the y direction of C_1 accumulated by that excitation, the pyramidal geometry at this atom becomes more favorable than the original C_{2v} geometry. This enhances the motion of the bent-out-of-plane.

In Figure 7 the potential curves (E_T's) for the calculated paths (i.e., four allowed ones) corresponding to the snapshots of Figure 6 are given. For the (II) $^1S_0$, the obtained activation barrier becomes indeed lower than the avoided-crossing barrier exhibited in Figure 3, but still it (~80 kcal/mol) is too large to cause the facile thermal dissociation. This result corresponds to the experimental information that thermal reaction of CP yields only the polymerized product and it does not proceed homogeneously.[8]

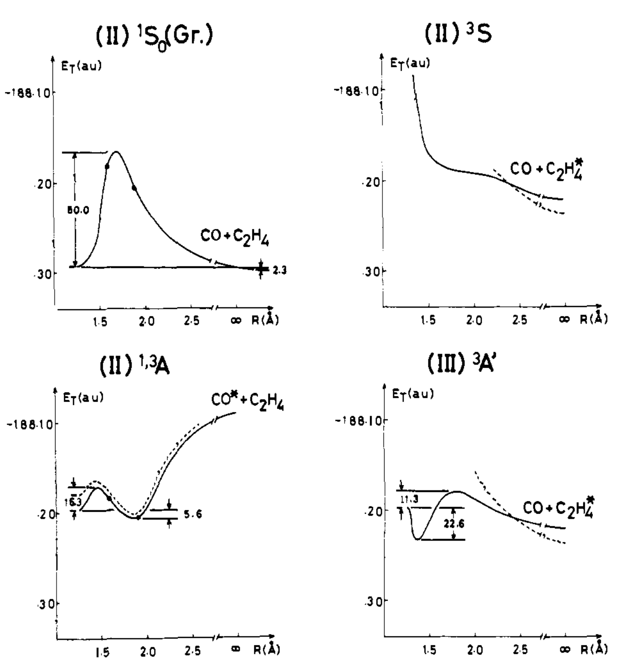


Figure 7. The energy curves corresponding to the optimized path shown in Figure 6. In (II) $^{1,3}A$, the broken curve of ^1A is calculated by the use of ^3A optimized geometry. In (II) ^3S and (III) $^3A'$, the broken descending line is obtained with the $(\pi,\pi^*)^3$ geometry of the twisted (locally D_{2d}) ethylene. Numbers without unit are in kcal/mol. The filled circles in (II) $^1S_0$ (Gr) and (II) $^{1,3}A$ indicate the crossing points of two energy curves.

The energy curve for the (II) $^{1,3}A$ connects the $^{1,3}A_2$ of CP with the $^{1,3}B_2$ of the $(n,\bar{\pi}^*)^{1,3}$ CO and the Gr C_2H_4. The full line is for triplet and the broken line is for singlet, respectively. While the state energy is predicted in Figure 3 to ascend monotonically toward the product site, the calculated curve is found to have a local minimum at $R \simeq 1.8$ Å. The appearance of this energy minimum indicates the possibility of the biradical intermediate. The further separation between CO and the ethylene site brings about the sharp increase in E_T, because the energy curve of $^{1,3}A$ approaches asymptotically to the energy of the $(n,\bar{\pi}^*)^{1,3}$ CO and the Gr C_2H_4. Here it is noteworthy that, when the energy curve of $^{1,3}A$ is superimposed on that of $^1S_0$, two crossing points of these curves are found. At these points, the geometries of the system in the $^{1,3}A$ and $^1S_0$ states are similar. Thus, we may say that the left crossing point ($R \simeq 1.6$ Å) gives the probability of the IC or isc (intersystem crossing) back to the unreactive electronically ground (but vibrationally excited) state of CP as is shown in eq 2b. Also, once the biradical intermediate is reached, the reaction is advanced further by transferring at $R \simeq 1.9$ Å to the ground-state dissociative process.

The energy curve of the (II) ^3S connects the second excited state $^3A_1$ with the $^3B_1$ of the Gr CO and the $(\pi,\pi^*)^3$ C_2H_4. The feature of this curve is almost like the predicted one in the correlation diagram and shows a sharp descent of the energy at $R \simeq 1.5$ Å. This dissociation of the (II) ^3S seems to proceed efficiently without the activation barrier. But the energy of the irradiation wavelength given experimentally (365-291 nm) is not enough to excite the Gr molecules of CP up to the ^1S state [originally $^1A_1$ of ($4b_1 \rightarrow 5b_1$) in Figure 2] and accordingly the probability of the photodissociation starting from the ^3S state would be small. The broken line at large R gives the energy of the system in which the bipyramidal geometry of the ethylene site is replaced by the twisted one (C_s symmetry broken). Whereas the bipyramidal structure of ethylene stays at a local energy minimum of the $(\pi,\pi^*)^3$ state, the twisted

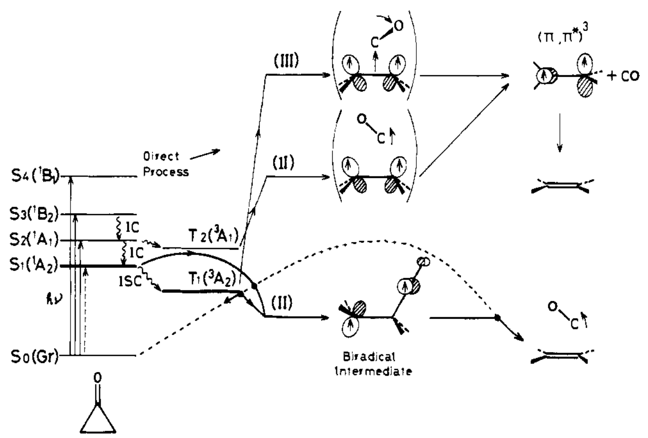


Figure 8. The mechanism of the photodissociation of cyclopropanone deduced from the present calculation.

geometry is most stable in its isolated (D_{2d}) state.[15] According to the present calculation, the reacting system with the twisted ethylene begins to be more stable, at $R \simeq 2.3$ Å, than that of the C_s optimized path.

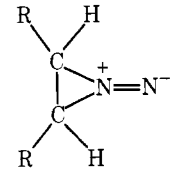
The energy curve of the (III) $^3A'$ connects the $^3A_2$ of CP with the $^3B_1$ of the Gr CO and the $(\pi,\pi^*)^3$ C_2H_4 in the bent-out-of-plane path. This result suggests the presence of the excited equilibrium structure of CP at $R \simeq 1.4$ Å from which the dissociation starts. The broken line for the twisted ethylene is the same as in the (II) ^3S. The dissociation process of the (II) ^1S and (III) $^1A'$ which gives the $(\pi,\pi^*)^1$ ethylene of high-lying energy is difficult to treat with the small basis set and is not traced in this work.

As a result of the energy optimization, two important pathways starting from the lowest excited state of CP are found to yield the product smoothly. One is the process of (II) $^{1,3}A$ → (biradical intermediate) → (II) $^1S_0$ and the other is that of (III) A′ via the excited equilibrium structure. Comparing the height of the activation barrier imposed on these two pathways in Figure 7, we may say that the reaction of the former route takes place with higher probability than that of the latter.

V. Concluding Remarks

In this study an ab initio calculation of the photodissociation of CP, based on the state correlation diagram, is presented. As a result of the energy optimization, various low-lying allowed paths are obtained. Since the present calculation is made with a small basis set (STO-3G, minimal), energetics shown in Figures 3 and 7 should be regarded as merely qualitative. In spite of this limitation, some important results for the photochemistry of CP are obtained and they are summarized schematically in Figure 8. In particular, two different pathways [(II) bent-in-plane and (III) bent-out-of-plane] starting from the $^{1,3}A_2$ state of CP would dominate. The dissociation of the former route is initiated by the scission of the C_1–C_2 bond α to the carbonyl and subsequently the biradical intermediate is formed. Through the IC or isc ($^{1,3}A \rightarrow {}^1S_0$), afterward, the ground-state CO and ethylene are yielded. In this route, the ethylene which does not undergo the twist motion of the CH_2 group during the reaction will be produced stereospecifically. The dissociation of the latter route is caused by the synchronous cleavage of the C_1–C_2 and C_1–C_3 bonds and then the ground-state CO and the $(\pi,\pi^*)^{1,3}$ ethylene are produced. After this, the ground-state ethylene is generated through isc. Since in the $(\pi,\pi^*)^{1,3}$ state of ethylene two planes composed of respective CH_2 groups are twisted perpendicularly, the ground-state ethylene would be obtained nonstereospecifically owing to the cis–trans isomerization.

When the activation energy of the $^{1,3}A$ curve is compared with that of the $^3A'$ curve in Figure 7, it is found that the former path is more favorable than the latter. This suggests that in the process of the photodecarbonylation of CP the ground-state ethylene is produced stereospecifically.[16] It is shown experimentally that the olefin is obtained stereospecifically in the deamination of aziridine derivatives via the intermediate i, of which the parent molecule is isoelectronic with CP.[17] This result of the stereochemistry would be related to the indication derived from the present calculation. Thus, the photodecarbonylation of CP is initiated predominantly from the lowest excited state, taking the bent-in-plane path, and the ground-state CO and C_2H_4 are yielded via the biradical intermediate.[18]



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(12) If a state of the higher energy belongs to the same symmetry as another state of the lower one, the energy of the former state should be obtained as the second root of the two-configuration CI matrix. This is needed to assure the orthogonality condition between the wave functions of two states. Therefore, the ^1S state in the (II) C_s path is not traced here together because its product is the $(\pi,\pi^*)^1$ C_2H_4 which is not manageable in the minimal basis set. However, if this state were followed by the GRHF method, it would yield a similar geometrical change to that of ^3S along the dissociation. This similarity is pointed out in the case of the dissociation of the $^{1,3}A'$ ketene in ref 13.
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(16) According to the referee's opinion, however, the (III) $^1A'$ path which is not dealt with here becomes important at the shorter λ_{irr} (= wavelength of irradiation, ~291 nm) to generate the $(\pi,\pi^*)^1$ C_2H_4. In this case, ethylene would be yielded nonstereospecifically. Thus, the investigation of the stereospecificity as a function of the λ_{irr} might be of experimental interest for the substituted CPs.
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(18) Based on this idea, we may interpret the effect of λ_{irr} on $\phi_{C_2H_4}/\phi_{CP}$ (ϕ = quantum yield) presented in Table III of ref 8. The shorter λ_{irr} which is sufficient to raise CP up to the energy curve of its excited states initiates the photodissociation easily ($\phi_{C_2H_4}/\phi_{CP} \rightarrow$ large). On the other hand, the longer λ_{irr} gives the ground-state product of polymerization *plus* ethylene ($\phi_{C_2H_4}/\phi_{CP} \rightarrow$ small but nonzero). This nonzero $\phi_{C_2H_4}$ by the longer λ_{irr} may be explained as follows. The successive irradiation of the longer λ_{irr}, although not enough for the vertical excitation, would happen to make CP jump up from the electronically ground (but vibrationally excited) state to the $^1A_2$ curve resulting in the formation of the biradical intermediate.

On Geometry Predictions for Conjugated Free Radicals Containing Three π Electrons Using ab Initio MO Theory

N. Colin Baird,* Rashmi R. Gupta, and Kathleen F. Taylor

Contribution from the Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7. *Received January 29, 1979*

Abstract: Restricted Hartree-Fock STO-3G calculations were performed for the π state of the conjugated free radicals **1-8**. For **1-4**, geometry optimizations without configuration interaction included yielded structures with bond lengths appropriate to one single and one double bond, whereas a single potential minimum with near-equal distances is obtained when CI is included. Thus the "doublet instability" problem known previously for allyl **1** apparently is the rule rather than the exception. Calculations including CI for **5-8** indicated that the delocalization energy calculated by MO methods (ab initio or semiempirical) for a radical ZXY can be grossly in error unless the relative energies of the structures $Z{=}X{-}\dot{Y}$ and $\dot{Z}{-}X{=}Y$ are predicted accurately.

Semiquantitative results for the geometry and rotational barriers of most closed-shell organic molecules can be obtained from ab initio molecular orbital theory at its current "standard" level—i.e., by employing a single-determinant wave function and expanding each MO in terms of a minimal (or "double ζ") basis set.[1] In contrast, MO calculations for free radicals, such as allyl **1**, are fraught with difficulties due mainly to the "doublet instability" problem;[2] corresponding problems occur also for open-shell states of molecules containing an even number of electrons. The problem basically is that calculations using restricted Hartree-Fock (RHF) theory for three-center, three π electron systems usually overestimate the stability of structures containing one short and one long bond (e.g., **1a** and **1b**) relative to those with intermediate bond lengths (e.g., **1c**). The case of the allyl radical **1** has received detailed attention by Paldus and Veillard, who showed that the problem is one of correlation energy and not of basis set size.[2] Recent calculations for triplet states are those for HCCN by Harrison et al.[3] and for trimethylenemethane by Davidson and Borden.[4]

$H_2C{=}C(H){-}\dot{C}H_2$ $H_2\dot{C}{-}C(H){=}CH_2$

1a **1b**

$\overset{\cdot}{\overline{H_2C{-}C(H){-}CH_2}}$

1c

In the present investigation, the predictions of ab initio RHF MO theory[5] both with and without configuration interaction for allyl **1**, for the free radicals **2-4**, **7**, and **8** isoelectronic with it, and for **5** and **6** are obtained to investigate further the doublet instability problem and to determine the delocalization energies of these systems. In the calculations, the minimal STO-3G basis set with standard molecular exponents[6] was used except where indicated. All results refer to the lowest π state only; the low-lying Σ states of **2-4**, **7**, and **8**, containing four π electrons with the unpaired electron in the σ framework, are discussed elsewhere.

For the radicals **1-4**, optimum heavy-atom bond lengths were determined separately in calculations without and with configuration interaction among all possible arrangements of the three electrons among three MOs (consistent with a net spin projection $M_S = +\frac{1}{2}$). We find that *two* potential minima with bonds of alternating length are predicted for **1**, **2**, and **3**, and that a single alternating-type minimum exists for **4**, in the single-determinant calculations (see Table I). In each case, however, such minima disappear and are replaced by a *single* structure of type **c**, with near-equal bond lengths between the conjugated atoms, when configuration interaction is included (see Table I). We conclude then that restricted open-shell MO theory will often predict (incorrectly) an "alternating" rather than a symmetrical structure for three π electrons, three π orbital networks and that CI among π-electron configurations is required to obtain meaningful results. Thus we suspect that the unsymmetrical structures predicted by single-determinant calculations for species such as NCO^+, NOC^+, NNC, CCN, and CCO (ref 7), for N_3 and $N_3{}^+$ (ref 8), and for HCC(H)O (ref 9) may be artifacts (but see the conclusions later regarding systems with different terminal groups).

$O{=}C(H){-}O\cdot$ $\cdot O{-}C(H){=}O$ $\overline{O{-}\dot{C}(H){-}O}$

2a **2b** **2c**

$HN{=}C(H){-}O\cdot$ $H\dot{N}{-}C(H){=}O$ $\overline{HN{-}\dot{C}(H){-}O}$

3a **3b** **3c**

$HN{=}N{-}O\cdot$ $H\dot{N}{-}N{=}O$ $\underset{\cdot}{\overline{HN{-}N{-}O}}$

4a **4b** **4c**

The role played by CI is illustrated best by the symmetrical-geometry allyl radical. Two-electron promotions allow for the correlation of the motion of the two electrons involved—for example, between the "spin-up" electron of the nonbonding MO and the "spin-down" electron of the bonding MO. Such correlation is important because these two electrons are predicted to be present simultaneously in the same p_π orbital (of a terminal atom) in 29% of the structures when the MOs are symmetric, if no CI is included. The participation by such unfavorable structures is reduced by about a factor of 2 by CI.

In RHF calculations *without* CI, the correlation between these two electrons can be achieved only if the molecule adopts "alternating" MOs, since this effectively localizes the non-

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