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MECHANISM OF THERMAL 2+2 CYCLOADDITION REACTIONS BETWEEN ELECTRON-DONORS AND ELECTRON-ACCEPTORS

REACTIONS OF HETERONUCLEAR CYCLOADDENDS, C=O GROUPS

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Abstract—The 2 + 2 cycloaddition and "ene" mechanisms previously proposed for electron-accepting homonuclear cycloaddends have been found to hold for heteronuclear ones. Only a difference recognized between them consists in the relative stability of intermediate species. We think the proposed mechanism including its variations can cover thermal 2 + 2 cycloaddition reactions between donors and acceptors and "ene" reactions.

With surprising facility carbon dioxide[1]† and carbonyl compounds[2] react with electron-donating ethylene derivatives even at low temperature (Scheme 1). The corresponding reactions have been observed with isoelectronic molecular system, i.e., nitroso compounds.[3] Usually oxetane formation from C–C multiple bonds and CO moiety is associated with excited-state reactions.[4] The facile occurrence of the thermal 2+2 cycloaddition is intriguing on account of the symmetry-forbiddenness of suprafacial, suprafacial bond formation process and the transition-state strain of the symmetry-allowed suprafacial, antarafacial cycloaddition.[5]

The thermal 2 + 2 cycloaddition mechanism has long been at issue in theoretical and experimental spheres of organic chemistry. Woodward and Hoffmann, in discussing stereospecific combination of ketenes with olefins, noted the special role of carbonyl π^* orbital in setting the stage for and in being coalescent with the $2_s + 2_a$ cycloaddition reaction.[5] In fact the predominant role of ketene carbonyl π^* orbital[6] as well as vacant p-orbital in the model reaction between vinyl cation with olefins[7] have been ascertained by molecular orbital (MO) methods. Nearly at that time we suggested that the 2 + 2 cycloaddition of $^1\Delta_g$ molecular oxygen may begin with cyclic 3-centered interaction between nucleophilic ethylene p-orbitals and one of electrophilic atomic orbital lobes of the oxygen.[8] The preference of such an intermolecular arrangement was found to consist in the most effective operation of particular orbital interaction between the highest occupied MO (HOMO) of electron-donating ethylene and the lowest unoccupied MO (LUMO) of electron-accepting oxygen. The argument was also found to hold for the benzyne reaction,[9] which is compatible with the total reaction path by the extended Hückel (EH) MO calculation.[10] On the EH potential energy surface an ambiguous situation manifested itself, which corresponds neither to a local energy dip for a true intermediate nor to an ascending slope leading directly to the transition state but to an energy valley at a relatively low altitude with a *cul-de-sac* at the end.[10] The same peculiarity to be termed *quasi*-intermediate have been also observed on the CNDO potential energy surface for the singlet oxygen reaction.[11]

This paper is intended to report the results of our investigation on the 2 + 2 cycloaddition mechanism of heteronuclear cycloaddends, C=O groups, especially the intermolecular disposition of reactants at the initiation stage (Chapter I) and the property of "intermediate" (Chapter II).

I. *Initial stage*

Methods of calculations. The interaction energies ΔW of ethylene–carbon dioxide and ethylene–formaldehyde systems are calculated by the perturbation method[12] previously developed on the basis of semi-empirical self-consistent field (SCF) MO's including all overlap integrals and valence electrons.[13] The total interaction energy ΔW is in turn factorized into four energy terms due to delocalization (D), polarization (Π), Coulombic interaction (E_Q) and electron-exchange (E_K) as follows;

$$\Delta W = -D - \Pi + E_Q + E_K.$$

The delocalization term D symbolizes the stabiliza-

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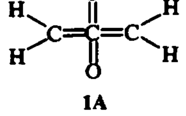
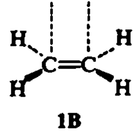
†The 2 + 2 cycloadduct itself has not been detected as yet but the intermediary intervention was suggested on the basis of the detailed investigation of the successive elementary reactions.

tion energy due to electron-transfer from the occupied MO's of one reactant to unoccupied MO's of the other. This term, especially its component corresponding to the interaction between the HOMO of electron-donating partner and the LUMO of accepting one, is generally know to contribute most to stabilizing the weakly interacting system. It is usually E_K term for neutral closed-shell molecules that copes with the stabilizing effect of delocalization term to result in destabilizing to a considerable degree. The exchange energy stems from the intermolecular interaction between the occupied orbitals. The polarization energy Π represents the stabilization brought by promoting electrons from ground-state configuration to excited-state one within the individual molecule under the influence of the other approaching molecule. The Coulombic energy E_Q is owing to the interaction of net charge. The last two terms are usually too small to dominate the mechanism of chemical reactions involving neither highly polarizable reactants nor charged species.

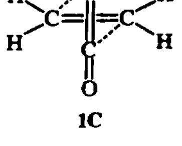
Examined models for reaction paths. At the outset our attention is concentrated on comparing the 3-center interaction model already found necessary for the HOMO of ethylene and the LUMO of electron-accepting species, $^1\Delta_g$ molecular oxygen,[8] benzyne[9] and ketene,[10] to interact with each other most effectively, with symmetry-allowed $2_s + 2_a$ and symmetry-forbidden $2_s + 2_s$ processes. Thus the interaction energy of carbon dioxide with ethylene is calculated for the models **1A**, **1B** and **1C** for 3-center interaction process, $2_s + 2_s$ and $2_s + 2_a$ processes, respectively. In the nuclear configuration **1A**, CO_2 molecule is situated on the bisecting plane of ethylene with C atom of CO_2 vertically by 3·0 A above the C=C bond of ethylene. For the $2_s + 2_s$ model IB, the carbon and an oxygen of CO_2 occupy the symmetrical positions with respect to reflection in the bisecting plane, and the other model **1C** takes the tetrahedral shape with the two carbons of ethylene and the carbon and one of the oxygen atoms of CO_2 at each corner. The corresponding models (**2A**, **2B** and **2C**) are chosen for the ethylene–formaldehyde system.



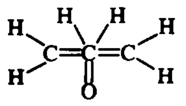
1A



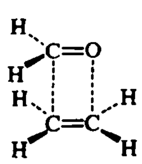
1B



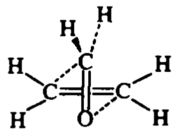
1C



2A



2B



2B

In order to confirm or make up the results of the perturbation calculations, the total energies of both combined systems are computed by the CNDO method.[14] The parallel and the orthogonal arrangements are examined as the function of the parameter R representing the degree of parallel displacement of CO_2 and CH_2O along each C–O bond line. The C_2H_4–CO_2 orthogonal arrangement including both 3-center model and $2_s + 2_a$ process are examined through the deviation R from the geometry with the highest ordered symmetry (C_{2v}) corresponding to 3-center model (**3**). The other typical $2_s + 2_s$ process is shown by R = half the C=O bond length of the parallel alignment, R similarly defined as the deviation from the highly symmetrical nuclear configuration (**4**). For the CH_2O–C_2H_4 system, the analogous parametrization and modeling hold for 3-center interaction (**5**) and $2_s + 2_s$ processs (**6**), while the $2_s + 2_a$ (**7**) process disposing each reactant in the vertical planes does not correspond to any translational variations of **5**. The relevant nuclear disposition is obtained by the rotation of CH_2O about C–O bond by 90° following the parallel displacement along the bond axis of the 3-center model.

RESULTS AND DISCUSSIONS

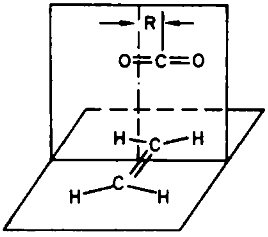
Total interaction energy ΔW shown in Tables 1 and 2 suggests the favorableness of the 3-center interaction models in both cases of carbon dioxide and formaldehyde. Scrutinizing the interaction energy by partioning it into E_Q, E_K, D and Π terms, we can see the serious differences of the 3-center model from the others among the delocalization terms as well as the Coulombic term, although the latter is of minor effect. In turn we will narrow down the consideration of orbital interaction into the arguments of charge-transfer interaction in order to extract the essential cause of the preference of the 3-center interaction model. From the evaluated stabilization energy between each pair of the occupied–unoccupied MO's it can be concluded that the favorableness of the 3-center model is attributed primarily to the effective operation of the interaction of the π-bonding orbital, i.e., the

Table 1. The interaction energy of C_2H_4–CO_2 system (eV)

	3-centered interaction	$2_s + 2_s$	$2_s + 2_a$
D	0·081 (0·052)	0·061 (0·028)	0·063 (0·033)
E_K	0·257	0·276	0·274
E_Q	−0·063	−0·050	−0·048
Π	0·003	0·008	0·003

Table 2. The interaction energy of C_2H_4–CH_2O system (eV)

	3-centered interaction	$2_s + 2_s$	$2_s + 2_a$
D	0·118 (0·078)	0·064 (0·027)	0·049 (0·000)
E_K	0·464	0·449	1·171
E_Q	−0·030	0·005	0·000
Π	0·013	0·037	0·037



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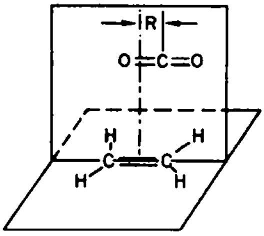

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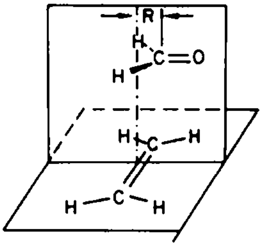

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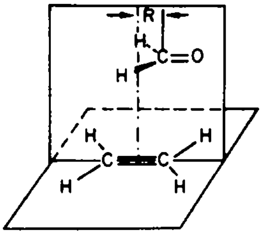
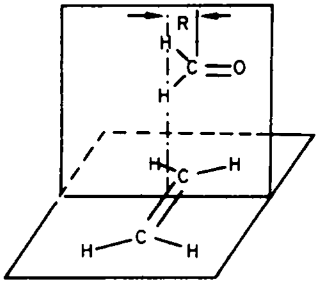


6

HOMO of electron-donating ethylene with π*-antibonding orbital, i.e., the LUMO of electron-accepting C=O bonds. The stabilization energy owing to the particular orbital interaction listed in parenthesis amounts to 64% and 66% of total delocalization energy for carbon dioxide and for formaldehyde, respectively. Accordingly, to put it strongly, the nuclear disposition at the initial stage are governed by the HOMO–LUMO interaction, which is most favored by the intermolecular arrangements schematically represented by the illustrations 8 and 9. Meanwhile we will be concerned with the other term responsible for stabilizing the 3-center interaction model. The E_Q term is in these cases composed probably of the attraction between negatively charged carbons of ethylene and positively charged carbon of CO moiety and the repulstion between the ones and the O atom. The preference of the 3-center model is considered to consist partly in such molecular arrangement as may favor the net charge interaction.



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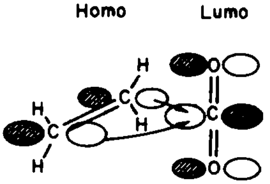

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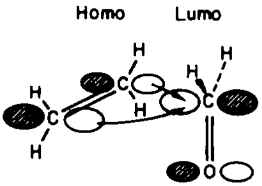


9

A noticeable and noteworthy characteristic of E_K terms is that the exchange repulsion for $2_s + 2_a$ process (7) of ethylene–formaldehyde system is overwhelmingly large. The abnormal E_K value may be considered to result from the repulsive interaction of the proximal C–H σ-orbitals of formaldehyde with the occupied orbitals of ethylene. The effect of the repulsive exchange interaction may constitute a serious steric obstacle to $2_s + 2_a$ approach as well as the transition-state strain indispensable for the effective orbital overlap.

We need not refer to the polarization term in particular so far as the reasoning for the favorableness of 3-center geometry is a matter of our primary concern. The estimated values of Π term are too small to exert a considerable influence on probable nuclear arrangement at the initial state.

As a result of perturbation calculations, we may say, the thermal 2 + 2 cycloaddition reactions between electron-donating olefins and electron-accepting carbon dioxide and certain CO compounds begin with the cyclic interaction of the nucleophilic centers of the donors with an electrophilic one of the acceptors (**1A**, **2A**), rather than with the corresponding rectangular $2_s + 2_s$ (**1B**, **2B**) or tetrahedral $2_s + 2_a$ (**1C**, **2C**) approaches. These conclusions are entirely the same as those with the 2 + 2 cycloaddition reactions of $^1\Delta_g$ molecular oxygen.[8] It is also pointed out in the preceding note,[9] though on the basis of a simple HOMO–LUMO overlap analysis, that the benzyne reaction is likely to be initiated by the similar mechanism. The most probable geometry predicated by the overlap analysis is compatible with those at 2·75 ~ 2·50 A on the reaction path obtained by EH study of Hayes and Hoffmann.[10]

Before definite conclusion it is necessary to rule out the other potential candidates overlooked, in order to justifying our choices of the models. Systematic CNDO calculations on the models described in the preceding section confirm the adequacy of each 3-center interaction model, although in case of ethylene–formaldehyde system the most stable configuration is a little (by about 0·2 A) shifted from the ideal model (Figs 1 and 2).

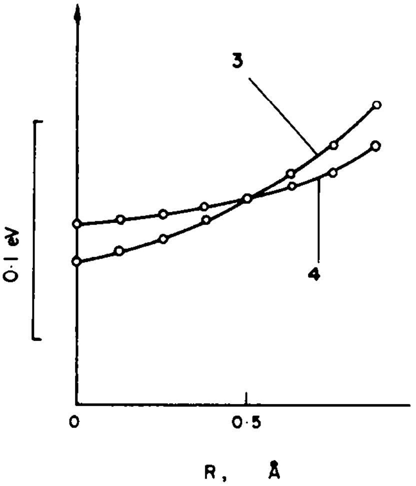


Fig 1. CNDO energy curve for C_2H_4–CO_2 system.

II. *Cyclic 3-center structure into 4-membered product*

Typical potential energy surface. In this chapter we will describe the results of CNDO calculations on typical potential surfaces for transforming the initial-stage arrangement into the 4-membered structure. In our calculations two degrees of angular freedom, i.e., the rotation of methylene moiety about C=C bond (Φ) and the retirement of it in the opposite direction of the approaching CO compounds (Θ) are allowed for an ethylene part while further two parameters θ and ϕ are used for denoting the angular displacements of formaldehyde molecule from the symmetrical disposition with respect to the reflection in the bisecting plane of ethylene, and the deformation from the parallel alignment including the hybrid change of the CO carbon. The other freedom R corresponds to the distance between the reactants. The parametrization is illustrated in Fig 3. The C–C and C–O bond lengths were fixed to those of ethylene and formaldehyde. The potential energy surfaces were drawn for several combinations of Θ, Φ and ϕ using the parameters θ and R. The angle θ is assumed to determine the middle point of C–O bond (M). The point M ascends in the bisecting plane of ethylene proportionally to the rotation angle θ=0 (3-center model) to θ = 90 (oxetane).

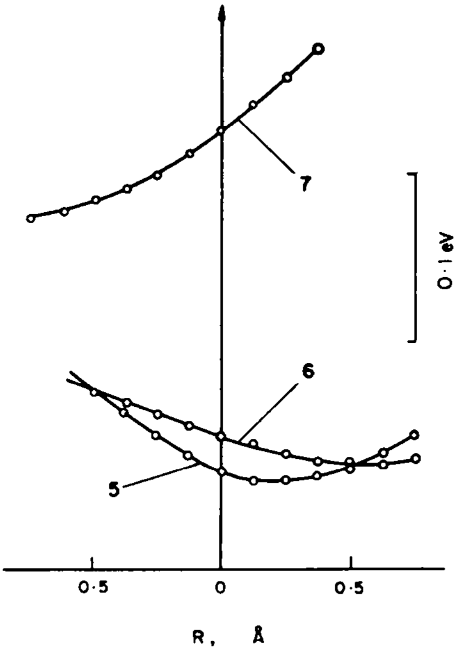


Fig 2. CNDO energy curve for C_2H_4–CH_2O system.

Typical potential energy surfaces for three ethylene part models A(Θ = 0, Φ = 0 at both carbons), B (Θ = 10, Φ = 0 at both carbons) and C (Θ = 10, Φ = 0 at one and Θ = 0, Φ = 10 at the other) are visualized in the 3-dimensional coordinate (Fig 4). Models B and C are employed to estimate the

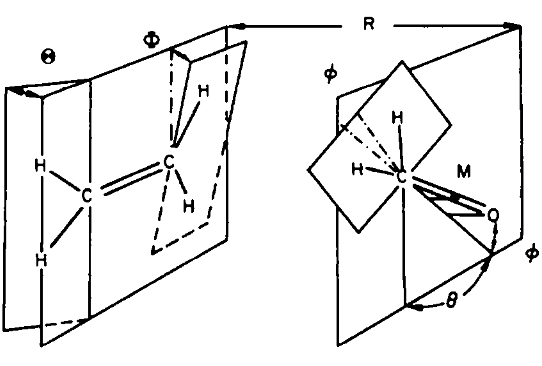


Fig 3. Parametrization for computing CNDO potential energy surfaces for transformation of 3-center structure into 2 + 2 cycloadduct.

molecular deformation effects stemming from the structural transformation into possible product and from an expected assisting twist of ethylene about C–C bond in response to the deviation of electrophilic entity from the symmetrical disposition, respectively. We have however found that such geometrical changes cause no significant effects on the undulation of the surface. For the approach of formaldehyde with the ground-state geometry unchanged ($\phi = 0$) the 3-center model ($\theta = 0$) is shown in Fig 4 to be more stable at each R than the comparable rotational models with parameter θ (Fig 4A). The preference of the 3-center model is still marked in a series of potential energy surfaces for re-hybridization model of formaldehyde ($\phi = 11{\cdot}25$) (Fig 4B). Furthermore a considerable deep hollow on the surfaces should be noted, which may suggest the existence of intermediate species.

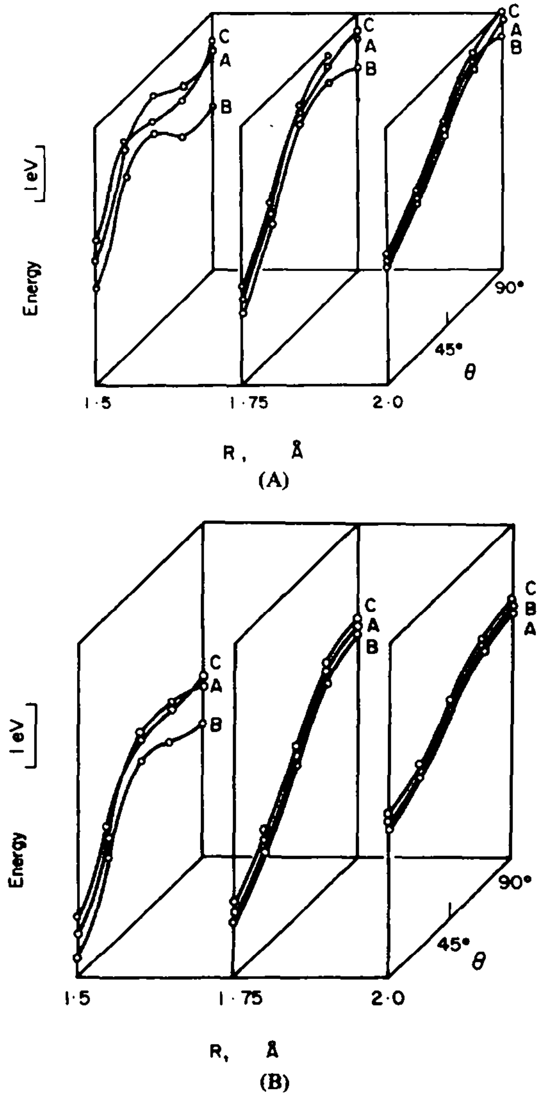
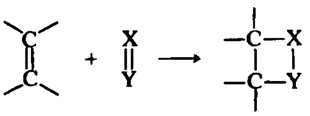


Fig 4. Potential energy surfaces for transformation of 3-center structure into 2 + 2 cycloadduct: (A) for ϕ = 0 CH_2O model and (B) for $\phi = 11{\cdot}25$ CH_2O model. The symbols A, B, and C in figures stand for corresponding ethylene part models defined in the text.

DISCUSSIONS

With some certainty we can now imagine the stereochemical path of the thermal 2 + 2 cycloaddition reaction between C=O bond with mono-olefin. The cyclic 3-center structure most probable for the intermolecular arrangement at the initiation step of the reaction may hold even at still shorter intermolecular distance R. The interacting ethylene–formaldehyde system appears to locate a place for steady life before it in turn falls onto the 2 + 2 cycloadduct basin. The features are the same in essentials as the preceding findings with strongly electron-demanding homonuclear two electrons/two orbitals system, ${}^1\Delta_g$ molecular oxygen and benzyne.[8,9,12,13]

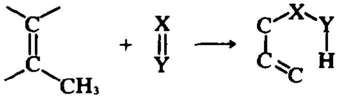


SCHEME 1.

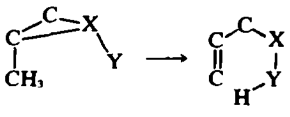
Only a considerable difference between heteronuclear C=O and the homonuclear oxygen and benzyne cycloaddends is recognized in the relative stability of the 3-center structure: the CNDO potential energy surface for the heteronuclear addends is found to be equipped with a local minimum suggesting a genuine intermediate of cyclic 3-membered species while a flattened region, of which the embodiment to be termed *quasi*-intermediate is instead located in the EH energy surface for benzyne cycloaddition[10] and in the CNDO surface for the singlet oxygen reaction.[11] Insofar as the CNDO potential energy surface for ethylene–formaldehyde system is concerned, the 2 + 2 cycloaddition reactions of heteronuclear CO moiety may be intercepted by such an intermediate. With rough approximation of CNDO procedure in mind, we must keep ourselves from insisting the intermediary intervention of genuine intermediate strongly. However, even if any local energy minimum for a true intermediate does not exist on the actual potential energy surface, it would be likely that the metastable state involving the cyclic 3-center structure may exert the effects on kinetics as if it were a genuine intermediate, since the residence time of molecular trajectory is expected to be long enough on the region flattened in such case.

The similarities of the heteronuclear C=O group to the homonuclear cycloaddends in the working HOMO–LUMO interactions at the initial state, and therefore, in the forthcoming leading orbital interaction[11] necessarily prepared by the foregoing HOMO–LUMO interaction would recommend one to design some experiments intended to ascertain the stereochemical behaviors of the substrate olefin in 2 + 2 cycloaddition reaction of heteronuclear moiety. We are informed of the stereoselectively retentive pattern of electron-donating olefin configuration in the reactins of homonuclear cycloaddends; $^1\Delta_g$ molecular oxygen,[15] benzyne,[16] tetracyanoethylene,[17] azodicarboxylic diester[18] ketene[20] and keteneimmonium cation[21] and in those of heteronuclear accumulated double bond, i.e., chlorosulfonyl isocyanate,[19] but no stereochemical experiments with heteronuclear isolated double bonds have not been attempted as yet.

It would be appropriate to refer to the mechanism of the "ene" reaction (Scheme 2) observed with formaldehyde, trichloroacetaldehyde, carbonyl dicyanide, diethylmesoxalate and methyl pyruvate,[22] as well as perfluorocyclobutanone.[2b] We don't think that alkyl substituents from which a hydrogen is abstracted perturb the essential features of the potential energy surface obtained for unsubstituted ethylene. We believe the "ene" reaction as well as 2 + 2 cycloaddition reaction involving heteronuclear electron-accepting double bond occurs via the corresponding cyclic 3-center intermediate. The prediction on the "ene" mechanism for heteronuclear electron-acceptors is strongly encouraged by the thermal reactions of the alkyl substituted 3-membered dipolar species, e.g., aziridine N-oxide[23] and episulfoxide[24] systems which rearrange at relatively low temperature to give allylic compounds corresponding to the "ene" reaction products (Scheme 3). Furthermore the observed reactivity order of various carbonyl compounds in "ene" reactions is compatible with our arguments for the important role of the cyclic 3-membered structure. Remembering that the stabilization due to the charge-transfer interaction between the HOMO of electron-donating olefin and the LUMO of electron-accepting cycloaddends contributes overwhelmingly to the choice of the 3-membered ring geometry and assuming the similar mechanism for "ene" reaction, we expect the more electrophilic the acceptor carbonyl is, the more readily the "ene" reaction takes place. In fact perfluorocyclobutanone[2b] and carbonyl dicyanide[22] react with propene and methylacetylene and with 1,2-dimethylstyrene at room temperature and 25°, while for the reactions of formaldehyde with methylenecyclopentane and methylenecyclohexane were carried out at 200°.[22]



SCHEME 2.



X—Y=S—O, HN—O

SCHEME 3.

Isoelectronic function of CO group, nitroso compounds have been known to undergo thermal 2 + 2 cycloaddition reaction with mono-olefin at relatively low temperature or below room temperature.[3] The reaction path is expected to be similar to that of CO group. The 4 + 2 cycloadducts is common to both functional groups.[2b,25] But the 6 + 2 cycloadduct has been detected in the reactions of nitroso species with triene[26] while any reactions of carbonyl moiety with conjugate triene has not yet been attempted (to our knowledge). "Ene" reactions of carbonyl bond have been observed extensively[22] while not yet for nitroso compound. The question, whether these differences in chemical behaviors between carbonyl and nitroso groups may consist in any intrinsic property or not, requires further experimental efforts in the future.

CONCLUSION

From our results of perturbation calculations supplemented by the CNDO calculations, it is now concluded that a primary origin of the facile proceeding of thermal 2 + 2 cycloaddition reactions of C=C bond activated by electron-donating substituents with carbon dioxide and with CO moiety bearing electron-withdrawing substituents may consist in the appropriate outset free from the transition-state strain inevitable for symmetry-allowed $2_s + 2_a$ process and from the orbital-symmetry restriction of $2_s + 2_s$ process. The advantage of the cyclic 3-center interaction is taken by the reacting system in which each reaction partner takes charge of the clear-cut separate parts; one is an electron-acceptor, the other being an acceptor. If not so, the interacting combined system cannot enjoy a sufficient stabilization due to one-way charge-transfer interaction between the HOMO of the donor and the LUMO of the acceptor, on account of the large separation between interacting orbital energy levels, for the delocalization energy is inversely proportional to the gap.

The leading features of thermal 2 + 2 cycloaddition reactions of heteronuclear C=O bonds are in excellent agreement with those highly electron-demanding homonuclear cycloaddends, $^1\Delta_g$ molecular oxygen, benzyne, as well as, expectedly of tetracyanoethylene and azodicarboxylic diester. We believe that the mechanism of orbital interaction previously proposed for homonuclear 2 + 2 cycloaddends may obtain with most thermal 2 + 2 cycloaddition reactions of two electrons/two orbitals systems between donors and accepotrs. The interaction of bidentate HOMO of donors exclusively with an atomic orbital lobe of the acceptor LUMO not only sets the initial stage but also plays an indispensable role in preparing the motivity for the subsequent transformation into 2 + 2 cycloadducts. The resultant electron-accepted "LUMO" and electron-released "HOMO" are favored by orbital symmetry to interact in turn with the original LUMO of donor and the HOMO of acceptor in suprafacial, suprafacial manner, respectively. The orbital interaction may facilitate a rotation of cyclic 3-center structure to final products. It should be noted that the CNDO calculations show the difference between homo- and hetero-nuclear cycloaddends in relative stability of "intermediate species". We may say, it is likely that the intermediate may be trapped in the reactions of heteronuclear cycloaddends while not in the reactions of homonuclear addends on the other hand.

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