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Mechanism of [2 + 2] Cycloaddition and Related Reactions between Electron Donors and Electron Acceptors. Perepoxide Quasi-Intermediate and Its Roles in the Reactions of $^1\Delta_g$ Molecular Oxygen with Olefins

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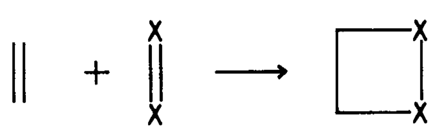
Received October 29, 1973

Abstract: An attempt has been made by means of the semiempirical SCF CNDO/2 method and the CI-perturbation procedure to elucidate the mechanism of stereoselective thermal [2 + 2] cycloaddition reactions between electron donors and electron acceptors. An ambiguous intervention of a perepoxide structure to be termed "quasi"-intermediate manifested itself on the CNDO/2 potential energy surface for the addition of $^1\Delta_g$ molecular oxygen to ethylene. The role of the quasi-intermediate has been discussed. In the light of the [2 + 2] cycloaddition mechanism, "ene" and [6 + 2] cycloaddition mechanisms have been discussed also.

An application of the frontier electron theory to Diels–Alder reactions was an indispensable prologue to progress in the theory of cycloaddition reactions.[1] The symmetry properties of frontier orbitals, the highest occupied (HO) molecular orbital (MO) of an electron-donating partner and the lowest unoccupied (LU) MO of an electron-accepting partner, were pointed out to be important. The symmetry rule was found afterward by Woodward and Hoffmann[2] to cover other sorts of chemical reactions and has been elevated to a brilliant and elegant stereoselection rule. A simple symmetry argument predicts that a thermal [2 + 2] cycloaddition reaction (eq 1) is the opposite to a thermal [4 + 2] cycloaddition reaction (eq 2) in the stereochemical course. Nevertheless, we know, some chemical species, e.g., $^1\Delta_g$ molecular oxygen,[3] benzyne,[4] tetracyanoethylene,[5] azodicarboxylic ester,[6] ketene,[7] ketenimmonium cation,[8] and chlorosulfonyl isocyanate,[9] undergo both [2 + 2] and [4 + 2] cycloaddition reactions with high stereospecificity.[10-15]



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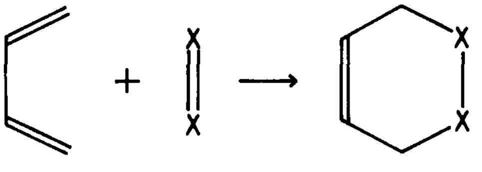
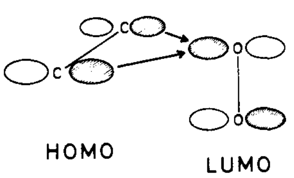


(2)

In our previous paper, we pointed out the possibility of a novel [2 + 2] cycloaddition mechanism from a consideration of orbital interaction in the reaction of $^1\Delta_g$ molecular oxygen[16] and successively disclosed a common feature between singlet oxygen and benzyne as [2 + 2] cycloaddends by means of an HOMO–LUMO overlap analysis.[17] Both reagents have the LUMO's at low energy levels; they are powerful electron acceptors. These chemical species provide the LUMO rather than the HOMO for the significant orbital interaction with olefins. The interaction works most effectively at the nuclear arrangement in which two nucleophilic centers of the donor and one electrophilic atom of the acceptor form an isosceles triangle with the other reacting atom of the acceptor tailing out of the trigonal plane (1 and



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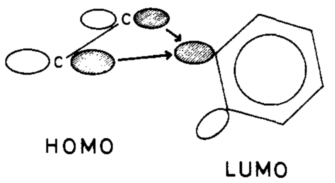

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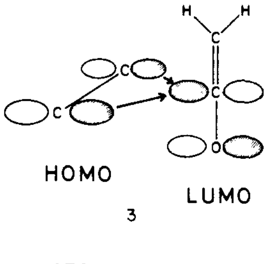

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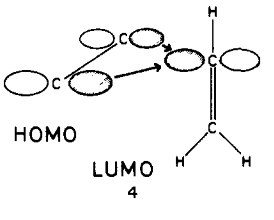

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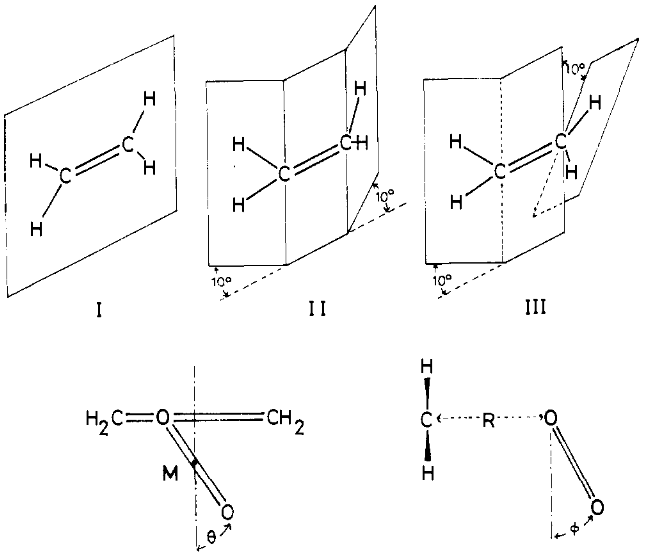
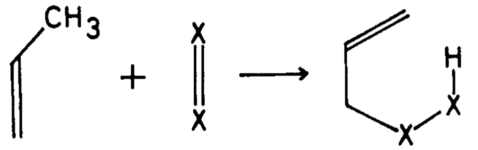


Figure 1. Models and parameters employed for calculating the potential energy surface of interacting singlet oxygen and ethylene.

2).[18] Nearly at the same time Sustmann et al.[19] found a similar characteristic in the reaction of ketene with ethylene by the SCF perturbation MO methods (**3**). Also in the case of vinyl cation interacting with ethylene and acetylene, the leading influence of the HOMO-LUMO interaction has been recognized (**4**).[20]

Our present purpose is to explore the reaction path after the initial stage. In addition we will refer to the mechanisms of ene reactions (eq 3) and of the [6 + 2] cycloaddition reactions (eq 4). Most of the chemical species cited above undergo both types of reactions. The ene reactions have been found with singlet oxygen,[3b,21] benzyne,[22] tetracyanoethylene,[5b] azodicarboxylic ester,[14] and chlorosulfonyl isocyanate,[23] while not yet with ketene and ketenimmonium ion. The [6 + 2] cycloadduct has been proposed as the intermediate in the reaction of singlet oxygen with cycloheptatriene.[24] With benzyne,[25] azodicarboxylic ester,[26] chlorosulfonyl isocyanate,[27] the [6 + 2] cycloadducts have been detected, in some cases, as the major products.



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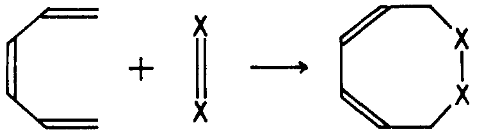

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A Typical Potential Energy Surface. The potential energy surface for transforming the initial perepoxide structure into the four-membered dioxetane structure were investigated by semiempirical SCF CNDO/2 calculations.[28] The effects of the geometrical changes of ethylene on the essential features of the potential energy surface were examined. Three models were used for this purpose (Figure 1). One is ethylene itself (model I). Model II was used to estimate the effect of the bending of methylene moieties; both methylene planes bend backward by 10°. In model III, the methylene group attacked by the cyclic member oxygen at the initial stage bends backward (10°) while the other methylene rotates (10°) to accept the tail oxygen. The parameters R, θ, and ϕ are used to define the intermolecular arrangement (Figure 1). The distance R is the intermolecular one between the ethylene plane and the attacking oxygen atom. The angle θ represents the rotation of O_2 from the perepoxide-like structure with both oxygen atoms in the bisecting plane of ethylene ($\theta = 0°$) to the four-membered ring structure ($\theta = 90°$). The parameter ϕ denotes the angular displacement from the parallel alignment ($\phi = 0°$) of ethylene and singlet oxygen. The C-C and the O-O bond lengths were fixed to those of ethylene and $^1\Delta_g$ molecular oxygen. The energy surfaces for each model (I, II, III) with the definite ϕ were drawn with the parameters, θ and R. The angle θ is assumed to determine the position of the middle point of O-O bond (M). The point M ascends in the bisecting plane of ethylene proportionately with the rotation angle $\theta = 0°$ (perepoxide) to $\theta = 90°$ (dioxetane).

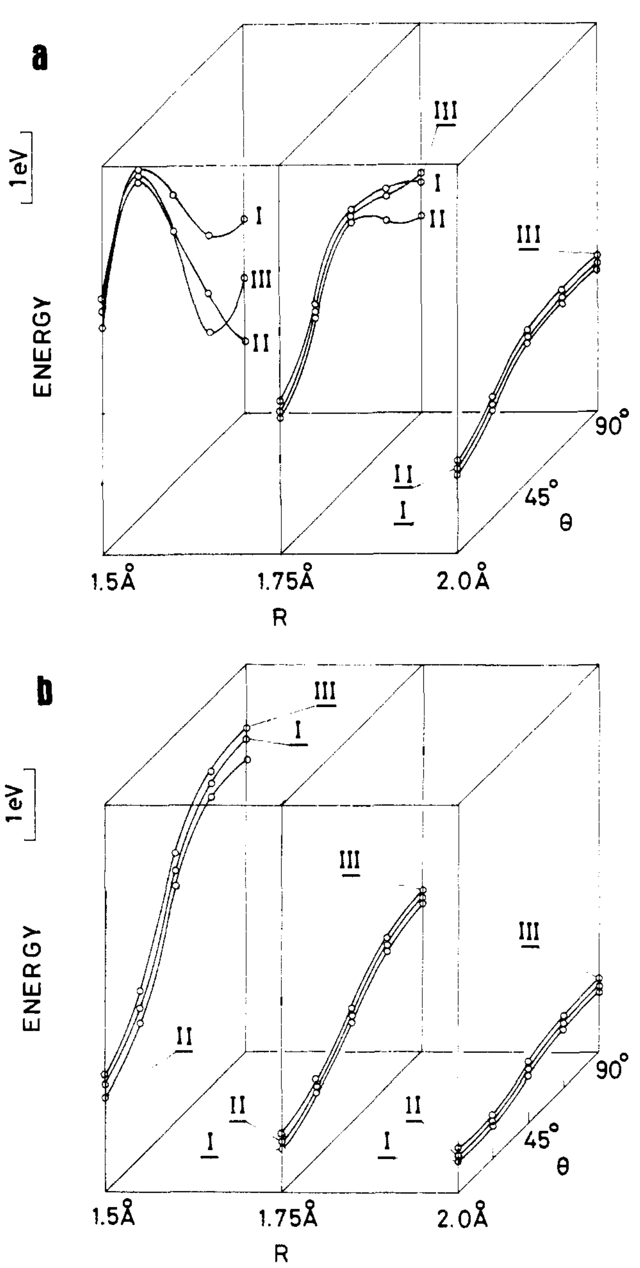

Figure 2. Typical potential energy surfaces for the addition of singlet oxygen with ethylene: (a) $\phi = 0°$; (b) $\phi = 22.5°$.

The potential energy surfaces for $\phi = 0°$ confirm the relative stability of the perepoxide structure at $R = 1.75$ and $R = 2.0$ Å (Figure 2a). At $R = 1.5$ Å, the four-membered ring structure is more stable. The perepoxide valley is further deepened on the energy surface for $\phi = 22.5°$ (Figure 2b). The essential features have been found to be indepen-

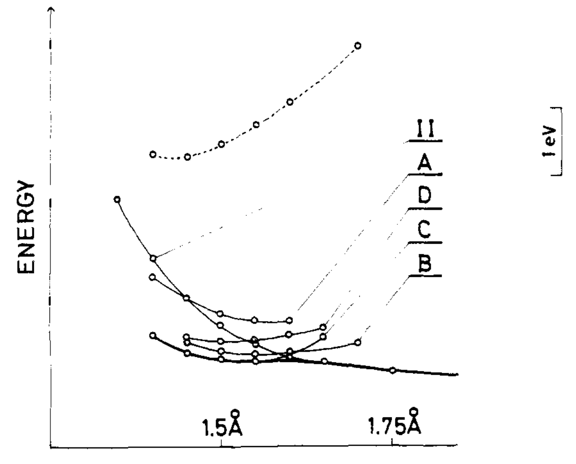

Figure 3. Potential energy curves in the perepoxide section or in the section $\theta = 0°$: (A) EO, $\phi = 11.25°$; (B) EO, $\phi = 22.5°$; (C) EO, $\phi = 33.75°$; (D) EO, $\phi = 45°$. EO and III are defined in the text.

dent of the ethylene part of the model. Suppose that the typical potential energy surfaces are superimposed qualitatively. Then it does not appear that any trajectory from the perepoxide valley to the dioxetane basin is directly downhill. More or less additional activation energy may be required when the system leaves the valley. However high the transformation barrier may be, if the locus of the molecular trajectory for the perepoxide structure ascends constantly along the reaction coordinate and is possible to associate with the path down to dioxetane, we could assign the term "concerted" to the reaction in the sense that the reaction path is not intercepted by any intermediate species. On the other hand, we would be compelled to declare that a two-step mechanism occurs, however low the barrier may be, if a local energy minimum exists on the perepoxide valley. The alternative of the one or the other mechanism depends solely on the presence or the absence of a perepoxide intermediate.

On the Perepoxide Intermediate. We subsequently examined the probability of a perepoxide intermediate in the [2 + 2] addition reaction of singlet oxygen with ethylene or investigated the potential energy curve on the perepoxide valley, i.e., in the $\theta = 0°$ section. If it exists as a stable species, the nuclear arrangement of the ethylenic part is expected to resemble that of ethylene oxide (model EO). The angle ϕ found in Figure 2 to affect the potential energy surface considerably is employed as the parameter. The energy estimation was carried out with the O–O bond length unchanged (lengthening this bond has been found to destabilize the system drastically—see the dotted line in Figure 3 for the model with the bond length of hydrogen peroxide).

The composite potential energy curve (bold line in Figure 3) based on the CNDO/2 calculations for $\phi = 11.25°$ (A), $\phi = 22.50°$ (B), $\phi = 33.75°$ (C), $\phi = 45.0°$ (D) shows the existence of a level or an extremely easy ascent on the perepoxide valley. If any energy minimum exists, it is very shallow. As far as our statements are based on the potential curve, we may say, perepoxide itself cannot be isolated by any means in the [2 + 2] addition reaction. In such a sense the perepoxide structure cannot be a genuine intermediate.[29] However, if the flat region on the surface is high, some kinetic or dynamic effects could happen to be observed as if the perepoxide intermediate intervened actually. This property is an attribute of the true intermediate. Such partial but not complete fulfilment of the conditions for reaction intermediate recommends the designation "quasi"-intermediate.

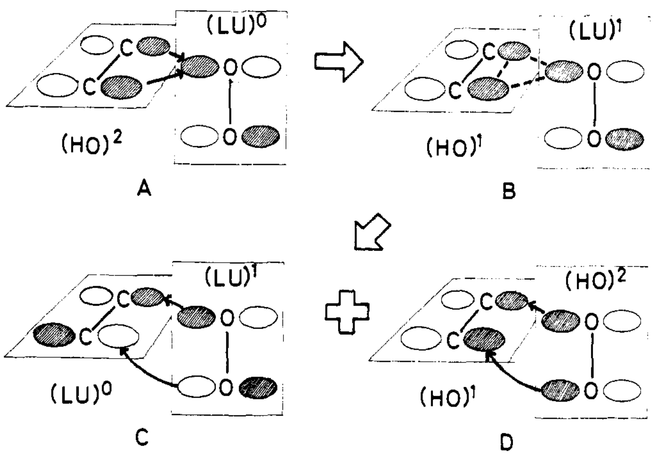

Figure 4. Schematic representation of the changes in the important mode of orbital interaction and in the intermolecular arrangement.

Discussion

We think it proper to imagine a mechanism where the reacting system, having stepped into the perepoxide valley at the outset, wanders without locating a stable chemical species until it finds its way over the dioxetane product. The [2 + 2] cycloaddition reaction of a singlet oxygen with ethylene is likely to occupy an intermediate position in the concerted-nonconcerted spectrum, rather than either extreme. Hays and Hoffmann,[30] investigated the potential energy surface for the addition of benzyne to ethylene by the extended Hückel MO method to find a similar feature, or a valley with a cul-de-sac at the end to which **2** structure corresponds. If the system were not endowed with some peculiarity, it would loiter on the valley only to dissociate into the original components. It is necessary to refer to what is the special nature of these species, in order to comprehend the mechanism of [2 + 2] cycloaddition reactions between donors and acceptors.

The geometry (**1**), nominated for the most probable, causes the most effective charge transfer from the HOMO of ethylene to the LUMO of singlet oxygen (A in Figure 4). With closer proximity of the molecular components, the electronic state contains the transferred configuration to a greater extent. The electronic structure can be schematically represented by one in which an electron of the ethylene HOMO is transferred into the oxygen LUMO (B in Figure 4).[31] The LUMO of the oxygen having partial electron is favored by its orbital symmetry to participate in a cyclic interaction with the LUMO of ethylene (C in Figure 4). The HOMO of ethylene having released partial electron can enter into the cyclic interaction with the HOMO* [32] of the oxygen (D in Figure 4), although this interaction appreciably occurs even at the perepoxide structure on account of favorable symmetry. Both modes of interaction, especially, the LUMO–LUMO interaction, may contribute to the stabilization during the perepoxide → dioxetane transformation process. The following HOMO–HOMO and LUMO–LUMO interaction become strong as the preceding HOMO–LUMO interaction increases the occupancy of the acceptor LUMO and decreases the occupancy of the donor HOMO. Accordingly, both interactions operate efficiently for the system with distinct donor-acceptor relationship. The importance of such as the following orbital interaction between donors and acceptors was first pointed out by one of the present authors (K.F.) in connection with "symmetry-forbidden" 1,2-cis addition of electrophiles to olefins.[33] Recently Epiotis[34] also recognized the significance of the following interaction in the donor-acceptor cycloaddition reactions.[35] Naturally as is expected, the change in the or-

Table I. The Coefficients[a] of the Zero Configuration[b] and the HOMO → LUMO Electron-Transferred Configuration for (i) Perepoxide Structure, (ii) Dioxetane Structure, and (iii) Perepoxide-Type Ethylenes

	Zero configuration	Electron-transferred configuration
(i)	0.987	0.137
(ii)	0.996	0.000
(iii)	0.970	0.114

[a] The coefficients of the other configurations are negligibly small ($\simeq 10^{-2}$). [b] The electron configuration where the interacting combined system has the original electron configurations in both isolated subsystems.[36]

bital interaction along the reaction coordinate accompanies the geometrical change of intermolecular arrangement; the suprafacial–suprafacial interaction is not always favored throughout from the beginning to the end.

In passing, we calculated the weights of each electron configuration in the combined systems, a perepoxide structure, a suprafacial–suprafacial approach of singlet oxygen and ethylene, and ethylene–ethylene system for the comparison with the perepoxide structure. The calculations were made by means of the CI-perturbation method.[36] The results are summarized in Table I. The mixing of the HOMO → LUMO transferred configuration is prominent in the perepoxide structure, the coefficient being 0.137. For the interacting ethylene molecules, situated so as to compare with the perepoxide structure, the coefficient was evaluated 0.114. This value is smaller than that with singlet oxygen. The comparison was made for the models composed of interacting molecules separated at the same distance $R = 3.0$ Å. If we make allowance for the covalent bond radii 0.772 and 0.66 Å for carbon and oxygen,[37] the coefficient for the ethylene–ethylene system should have been estimated for more separated ethylenes, and we could have obtained a still smaller value than 0.114. It follows that thermal ethylene dimerization is less favored by the preceding and the following interactions as compared with singlet oxygen–ethylene system, even if the dimerization process were initiated by the perepoxide-type arrangement (this may not be true).

The perepoxide-like structure seems to play dual roles as the junction between the reactant system and the product system, being at an intermediate point on the reaction coordinate. The path leading to it is a symmetry-allowed concerted process. In addition, the perepoxide structure breeds the driving force for the forthcoming transformation into dioxetane.

A second, extensively studied singlet oxygen reaction is the so-called "ene" reaction in which oxygen adds to alkylated olefins involving hydrogen abstraction and double bond shift to produce an allylic hydroperoxide (eq 3). It is not likely that both the C═C double bond and the allylic C–H bond equivalently contribute at the outset of the reaction. The HOMO of alkyl olefins, the frontier orbital toward electrophile, is localized on the π bond. It is expected that a perepoxide-like arrangement is most stabilized by the same HOMO–LUMO interaction as with ethylene. The electron transfer from the HOMO reduces the bonding property of π and σ-CH bonds and mitigates the π-type antibonding property between them. This is inferred from the sign relation of the HOMO. The resultant lengthening of the original π bond and C–H bond and the concurrent strengthening of the hyperconjugation between them allows the interacting system to constitute the six-membered transient state. It is probable that the interaction between the unoccupied orbital of olefin localized on the C–H bond on account of the lengthening and the LUMO of singlet oxygen having accepted partial electron works appreciably in the process from the perepoxide-like structure to the six-membered transient state. The significant role of the perepoxide-like structure is clearly supported by the small deuterium-isotope effects in the ene reactions of singlet oxygen (k_H/k_D = 1.1–2.4 for 1-methylcyclohexene[38] and 1.4–1.6 for 2,3-dimethyl-2-butene[39]).[40]

We may have nothing novel to add on the normal [4 + 2] cycloaddition reactions and the related endo perepoxide formation processes with aromatic hydrocarbons.[11] A suprafacial–suprafacial concerted mechanism is favored. The genuine [6_s + 2_s] cycloaddition reaction is improbable on account of the phase imcompatibility between the symmetric HOMO of triene and the antisymmetric LUMO of singlet oxygen. There is, however, left the possibility that apparent [6_s + 2_s] additions may occur through such a meandering process as has been proposed for the [2 + 2] cycloaddition reaction. A terminal double bond of the triene is expected to play the role which the ethylenic double bond does in the [2 + 2] cycloaddition reaction. In fact the photooxygenation of cycloheptatriene in methanol solution containing methylene blue, followed by hydrogenation over PdC,[27] has been found to give a mixture, of which the components are considered to be derived from the [4 + 2] and [6 + 2] cycloadducts and the allylic hydroperoxide.

The mechanisms proposed for singlet oxygen are taken as covering most of [2 + 2] cycloaddition reactions between donors and acceptors. However, the preference of two-centric interaction between a reaction center of donor and a reaction center of acceptor may be expected in case of extremely polar π-bond of donor; the electrophilic center of acceptor with the larger LUMO amplitude preferentially interacts with a nucleophilic atom of donor with the larger HOMO amplitude. In fact 1,4-dipolar species have been detected or trapped.[41] In these cases the three-centric interaction structure plays a less important role in the reaction mechanism. Another remark should be made for the reactions of acceptors with conjugative moieties delocalizing incipient lone-pair electrons on the tail atom at the three-center structure. These acceptors give rise to the additional stabilization. For example, electron-withdrawing substituents e.g., CN groups, attached to the tail atom is predicted to stabilize "quasi"-intermediate so excessively that it may be a true intermediate. The observed color on mixing electron-donating olefin with tetracyanoethylene, which fades out as the reaction proceeds, may be ascribable to a charge-transfer complex.[42]

We do not think that we can now propose a convincing whole mechanism of [2 + 2] cycloaddition reactions of cumulative double bonds, e.g., ketene and chlorosulfonyl isocyanate, with olefins. The electronic cause of determining the regioselectivity remains open to question. Further investigations are necessary in order to refer in detail to such mechanisms.

Acknowledgment. One of the authors (S.I.) is grateful to Dr. H. Fujimoto and Mr. S. Yamabe for the availability of the calculation programs used in this study. We acknowledge the use of the FACOM 230·60 computer generously provided by the Data Processing Center of Kyoto University.

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