

Similarity Approach to Chemical Reactivity. Overlap Determinant Method in the Chemistry of Complex Reactions with Coarctate Transition States

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The overlap determinant method was applied to the study of various carbene reactions for which the name “complex” reactions was recently proposed. It has been shown that the method is able to deal correctly with these reactions even in situations where the existing classical technique of correlation diagrams fails. In addition to correctly predicting the allowedness and/or forbiddenness of these reactions, the complementary similarity approach provides a simple insight into the detailed mechanism of these processes.

INTRODUCTION

Some time ago we introduced a new simple method of the alternative reproduction of Woodward–Hoffmann rules¹ based on the analysis of nodal structure of the wave functions. The method, known as the overlap determinant method (ODM)² rapidly found a number of applications in various fields of pericyclic reactivity including all types of thermal, photochemical, and catalytic processes.^{3–5} The great advantage of this method is that it does not rely on molecular symmetry and that it can be used even in situations where the standard techniques of correlation diagrams are difficult to apply. Such is, e.g., the case with certain valence isomerizations, and the so-called “complex” reactions⁶ involving a number of carbene additions. These additions are predicted to be forbidden by the Woodward–Hoffmann rules,¹ and, in order to explain their occurrence, the asymmetric reaction path violating the forbiddenness of the concerted process had to be postulated.⁷ While this simple explanation is plausible from the qualitative point of view, the more recent spin coupled calculations⁸ suggest that the forbiddenness of the symmetric C_{2v} path is a result of the inadequate description of the singlet carbene structure at SCF level and disappears when more realistic description is used. Our aim in this study is to apply the overlap determinant method just to the above conflicting cases and to demonstrate that the method is able to deal with them correctly. Moreover, in addition to simple classification of these reactions in terms of allowedness and/or forbiddenness, the similarity approach closely tied with the overlap determinant method opens the possibility of detailed insight into the mechanism of these processes.^{9,10}

THEORETICAL

Since the principles of the overlap determinant method as well as of its subsequent generalizations are sufficiently described in the original literature,^{2,11} we consider it sufficient to recapitulate briefly the basic ideas of this approach to the extent necessary for the purpose of this study. The overlap determinant method is methodologically based on the formalism of the so-called mapping analysis¹² introduced by Trindle. This analysis is based on the comparison of the

nodal structure of the approximate wave functions of the reactant and the product of a given process. The nodal structure is quantitatively characterized by the value of overlap integral of the corresponding wave functions. For allowed reactions which are intuitively believed not to change the nodal structure the overlap is expected to be nonzero, while the more profound changes of the nodal structure in forbidden reactions result in the zero value of the overlap. The molecular orbitals describing the structure of both the reactant and the product and entering into the corresponding Slater determinants are described by the usual LCAO expansions in the basis of atomic orbitals

$$\Phi_R = |\varphi_1 \overline{\varphi_1} \varphi_2 \overline{\varphi_2} \cdots \varphi_n \overline{\varphi_n}| \quad (1a)$$

$$\Phi_P = |\psi'_1 \overline{\psi'_1} \psi'_2 \overline{\psi'_2} \cdots \psi'_n \overline{\psi'_n}| \quad (1b)$$

where

$$\varphi_i = \sum_{\mu} \rho_{\mu i} \chi_{\mu} \quad (2a)$$

$$\psi'_j = \sum_v \tau_{vj} \chi'_v \quad (2b)$$

The overlap, generally given by (3)

$$S_{RP} = \int \Phi_R \Phi_P d\tau \quad (3)$$

cannot be, however, calculated directly, since the atomic orbitals χ and χ' used as a basis for the LCAO expansion of molecular orbitals φ_i and ψ'_j are generally different. (This difference is formally denoted by a prime.) In order to overcome this problem Trindle proposed a rather complex numerical procedure¹² the basic idea of which is to express the primed orbitals in the basis of unprimed ones. The form of the transformation matrix τ , representing the operator of the topological identity, was determined from the condition of the maximization of a certain functional. As a consequence, the original method was numerically quite demanding and found no practical importance. The greatest advantage of ODM which is closely related to the above approach is that the tedious numerical construction of the transformation matrix τ was replaced by an extremely simple recipe allowing one to write down the form of this matrix

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without any calculations only on the basis of simple geometric considerations. Once this matrix (or its equivalent, the so-called assigning tables in overlap determinant method) is known, the whole next procedure is quite straightforward and consists in the transformation of the molecular orbitals of the product from the primed to unprimed basis and the subsequent calculation of the overlap integral S_{RP} .

$$\psi'_j = \sum_v \pi_{vj} \chi'_v \quad (4a)$$

$$\chi'_v = \sum_\mu \tau_{\mu v} \chi_\mu \quad (4b)$$

$$\psi_j = \sum_\mu \sum_v \pi_{vj} \tau_{\mu v} \chi_\mu \quad (4c)$$

If this overlap is nonzero, the reaction is allowed, while for the forbidden reactions the value of the overlap integral is zero. The above methodology was subsequently applied to various pericyclic reactions²⁻⁵ and in no case the method failed. This is why we attempt now to apply the formalism of the overlap determinant method to the above conflicting cases where the ordinary techniques like correlation diagrams or Dewar/Evans aromaticity rules meet with some difficulties.¹³

RESULTS AND DISCUSSION

Although the main goal of this study is to apply the ODM to "complex" carbene reactions, we consider it worthwhile to analyze first the addition of simple carbene CH_2 to ethene as a parent system for the whole class of these reactions. As a first example let us analyze therefore this reaction at the level of standard MO model. Within this model two valence electrons of carbene carbon are localized in a doubly occupied molecular orbital σ which can be, for convenience, regarded as resulting from the symmetric combination of two atomic basis functions χ_a and χ_b . On the basis of this result it is possible to write down the approximate wave functions describing the structure of the reactant (ethene + carbene) and the product (cyclopropane). These functions are given by

$$\Phi_R = |\pi \bar{\pi} \sigma \bar{\sigma}| \quad (5a)$$

$$\Phi_P = |\sigma'_1 \bar{\sigma}'_1 \sigma'_2 \bar{\sigma}'_2| \quad (5b)$$

where the individual molecular orbitals can be expressed in usual LCAO approximation.

$$\pi = \frac{1}{\sqrt{2}}(\chi_1 + \chi_2) \quad (6a)$$

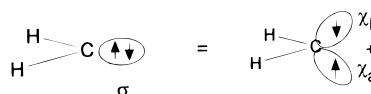
$$\bar{\pi} = \frac{1}{\sqrt{2}}(\chi_a + \chi_b) \quad (6b)$$

$$\sigma'_1 = \frac{1}{\sqrt{2}}(\chi'_1 + \chi'_a) \quad (6c)$$

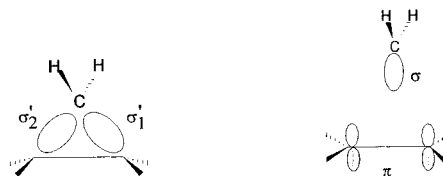
$$\sigma'_2 = \frac{1}{\sqrt{2}}(\chi'_2 + \chi'_b) \quad (6d)$$

In the case of concerted suprafacial attack, which is of our concern here, the assigning tables are extremely simple and

Scheme 1



Scheme 2



reduce the identity. The transformation of the product molecular orbitals from the primed to unprimed basis thus consists simply in omitting the primers in eqs 6c and 6d. On the basis of this transformation the overlap integral S_{RP} can be simply calculated, and its value is given by the value of the determinant whose elements are equal to the overlap integrals between the individual molecular orbitals of the reactant and the product, respectively.

$$S_{RP} = \begin{vmatrix} \int \pi \sigma_1 d\tau & \int \sigma \sigma_1 d\tau \\ \int \pi \sigma_2 d\tau & \int \sigma \sigma_2 d\tau \end{vmatrix}^2 \quad (7)$$

After substituting the actual values of the integrals

$$\int \pi \sigma_1 d\tau = \frac{1}{2} \int (\chi_1 + \chi_2)(\chi_1 + \chi_a) d\tau = \frac{1}{2} \quad (8a)$$

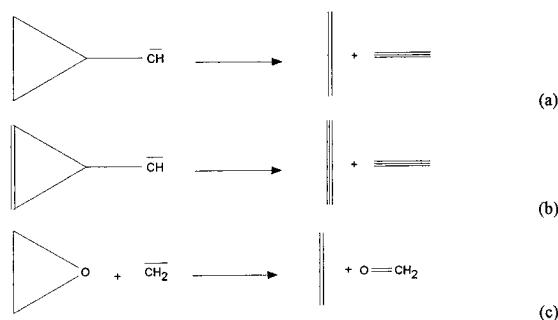
$$\int \sigma \sigma_1 d\tau = \frac{1}{2} \int (\chi_a + \chi_b)(\chi_a + \chi_1) d\tau = \frac{1}{2} \quad (8b)$$

$$\int \pi \sigma_2 d\tau = \frac{1}{2} \int (\chi_1 + \chi_2)(\chi_2 + \chi_b) d\tau = \frac{1}{2} \quad (8c)$$

$$\int \sigma \sigma_2 d\tau = \frac{1}{2} \int (\chi_a + \chi_b)(\chi_2 + \chi_b) d\tau = \frac{1}{2} \quad (8d)$$

the zero value of the determinant results indicating thus, in keeping with the prediction of the Woodward–Hoffmann rules, that the reactions should be forbidden. Such a conclusion is not, however, in harmony with the experiment since additions of this type are known to proceed readily. For that reason an explanation was proposed that the reaction does not follow the concerted synchronous path of C_{2v} symmetry, and actual calculations have indeed revealed that an asymmetric path with lower energy does exist.⁷ Some time ago the reaction was reconsidered again using much more realistic spin-coupled VB description,⁸ and surprisingly, the results of these calculations clearly demonstrated that the predicted forbiddenness of the reaction is apparently an artefact of the insufficient description of carbene structure at SCF level. When this structure is described more realistically, the energy barrier for a symmetric C_{2v} path is enormously reduced. The reaction thus becomes effectively allowed.⁸ While this change resulting from SC-VB carbene description would be very difficult to explain within the technique of correlation diagrams, the topological description of overlap determinant method is very easy to apply, and, as we shall see below, this application does indeed lead to the removal of the forbiddenness of the process. The reason for this removal lies in the change of the picture of the carbene structure resulting from the SC description. Within

Scheme 3



this approach two nonbonding electrons of carbene are no longer forced to enter the one doubly occupied molecular orbital but rather they remain in two singlet coupled orbitals closely resembling the two lobes of sp^3 hybridized carbon atoms (two remaining sp^3 orbitals enter the two CH bonds). Within the ODM this change in the carbene structure can be taken into account very simply, and the result is the modification of the approximate wave function which now can be written as

$$\Phi_R = \frac{1}{\sqrt{2}} \{ |\pi\bar{\pi}\chi_a\bar{\chi}_b| + |\pi\bar{\pi}\chi_b\bar{\chi}_a| \} \quad (9)$$

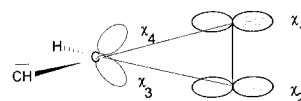
Taking into account that the wave function of the product is still sufficiently approximated by the one Slater determinant (5b) of the MO type, the overlap integral can straightforwardly be calculated and as can be seen its value is nonzero. [Here it is perhaps worth reminding that the overlap integral is not given in this case by the square of single overlap determinant but by the product of two determinants corresponding to electrons with α and β spins separately.]

$$S_{RP} = \sqrt{2} \begin{vmatrix} \int \pi\sigma_1 d\tau & \int \pi\sigma_2 d\tau \\ \int \chi_a\sigma_1 d\tau & \int \chi_a\sigma_2 d\tau \end{vmatrix}_\alpha \begin{vmatrix} \int \pi\sigma_1 d\tau & \int \pi\sigma_2 d\tau \\ \int \chi_b\sigma_1 d\tau & \int \chi_b\sigma_2 d\tau \end{vmatrix}_\beta \neq 0 \quad (10a)$$

This result is very interesting since it demonstrates that the forbiddenness of C_{2v} addition is indeed due to insufficient description of carbene at MO level and disappears when the more realistic correlated description is used. The success of Woodward–Hoffmann rules can thus clearly be attributed to the fact that a majority of “normal” molecules is usually well described by a set of doubly occupied molecular orbitals, but if, for whatever reason, such a picture is not precise enough, the difficulties can be expected, and the nodal structure of the wave function is to be analyzed by more sophisticated techniques like ODM.

In order to demonstrate the applicability of this method let us analyze, as a next example, also some other carbene reactions. A number of reactions of this type was recently analyzed by Herges,^{6,14} and it is because of specificity of their mechanisms that he proposed a name “complex” reactions for them.⁶ A typical example of such a type of processes is, e.g., the fragmentation of cyclopropylcarbene to ethene plus acetylene (a), the analogous fragmentation of cyclopropenylcarbene to two acetylenes (b), or the deoxygenation of oxirane by singlet carbene (c) (Scheme 3). The situation is relatively simple with the products which, because of their closed shell nature, are well approximated by a usual

Scheme 4



one-determinantal wave function composed of a set of doubly occupied molecular orbitals. A little bit more complex situation is, again, with the description of carbene species whose structure is better described by the spin-coupled theory. Taking into account the carbene structure suggested by this theory, the approximate wave function of, e.g., cyclopropylcarbene can be described as

$$\Phi_R = \frac{1}{\sqrt{2}} \{ |\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\chi_5\bar{\chi}_6| + |\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\chi_6\bar{\chi}_5| \} \quad (10)$$

where the molecular orbitals φ_1 and φ_2 describing the bonds in the cyclopropyl fragment are given by the ordinary LCAO expansions

$$\varphi_1 = \frac{1}{\sqrt{2}}(\chi_1 + \chi_4) \quad (11)$$

$$\varphi_2 = \frac{1}{\sqrt{2}}(\chi_2 + \chi_3) \quad (12)$$

and only the carbene electrons are described in a spin-coupled fashion as two singlet coupled orbitals χ_5 and χ_6 (Scheme 4). The product wave function is then simply given by a single Slater determinant (13)

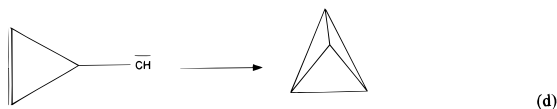
$$\Phi_P = |\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2\pi_3\bar{\pi}_3| \quad (13)$$

where the orbital π_1 is localized on the ethene and orbitals π_2 and π_3 on the ethyne fragment, respectively. On the basis of the wave functions (10 and 13) it is then possible to characterize the allowedness of the reaction (a) by the value of the corresponding overlap. Taking into account that for the symmetric suprafacial approach of both fragments the assigning tables have again the form the simple identity, it is possible to construct the overlap integral (14)

$$S_{RP} = \sqrt{2} \begin{vmatrix} \int \varphi_1\pi_1 d\tau & \int \varphi_1\pi_2 d\tau & \int \varphi_1\chi_5 d\tau \\ \int \varphi_2\pi_1 d\tau & \int \varphi_2\pi_2 d\tau & \int \varphi_2\pi_3 d\tau \\ \int \chi_5\pi_1 d\tau & \int \chi_5\pi_2 d\tau & \int \chi_5\pi_3 d\tau \end{vmatrix}_\alpha \begin{vmatrix} \int \varphi_1\pi_1 d\tau & \int \varphi_1\pi_2 d\tau & \int \varphi_1\chi_5 d\tau \\ \int \varphi_2\pi_1 d\tau & \int \varphi_2\pi_2 d\tau & \int \varphi_2\pi_3 d\tau \\ \int \chi_6\pi_1 d\tau & \int \chi_6\pi_2 d\tau & \int \chi_6\pi_3 d\tau \end{vmatrix}_\beta \neq 0 \quad (14)$$

Its nonzero value suggests that the reaction is allowed. Similarly it would be possible to analyze also the other examples of complex reactions (b) and (c), and the result in both cases is that the reactions are allowed. Here it is, however, interesting to remark that the allowedness of all these processes is not in this case conditioned by the more realistic SC description of the carbene moiety, but the same conclusions can be expected even from the use of standard correlation diagrams and, also, of the Herges's topological method.⁶ It would be, however, kept in mind that such a coincidence of the predictions based on spin-coupled ODM

and the MO based techniques is not valid generally and fails in other than $4n+2$ electron systems. In such cases, the correct description is only the one based on spin-coupled ODM. An interesting example seemingly contradicting this general rule is the reaction (d) in which the cyclopropenyl carbene was used as a precursor in a vain hope to get the tetrahedrane molecule. This reaction is topologically equivalent



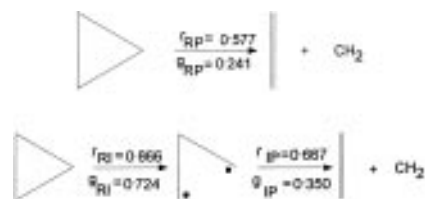
lent (isoconjugated) with the simple addition of singlet carbene to ethene, and it is thus possible to expect again the conflict of MO and spin-coupled predictions for it. While on the basis of correlation diagrams the forbiddenness can be expected, the more realistic spin-coupled overlap determinant method predicts it to be allowed. This conflict of two predictions is very interesting since the fact that reaction (d) was never observed seems to be rather consistent with the forbiddenness of the process. Such is not, however, the case, and the factor which overweighs the predicted electronic allowedness of the process at spin-coupled level is, like in $2_s + 2_a$ cycloadditions, the huge steric strain required to close the tetrahedrane cage.

Although the classification of "complex" carbene reactions is certainly an interesting and important feature of overlap determinant method, it is not the only result which the method is able to provide. Another, perhaps even more important, feature is that the method opens the possibility of a more detailed classification of the mechanisms of these reactions in terms of the relative ease of concerted and stepwise reaction paths. The basis of such a classification is the recently proposed similarity approach to chemical reactivity^{9,10} in terms of which the relative ease of concerted one-step and nonconcerted stepwise reaction mechanisms can be estimated. The basic quantity of this approach is the so-called topological similarity index.¹⁵ The importance of this quantity arises from its intuitive interpretation in terms of the so-called least-motion principle.¹⁶ According to this principle of the chemical reactions follow such reaction paths along which the reacting molecules undergo minimal structural changes. Similarity index is then a simple quantity in terms of which the extent of structural (electronic) reorganization can be characterized. Thus, e.g., we have been able to demonstrate that if the allowed and forbidden reactions are compared by the value of similarity index (comparing the electronic structure of the reactant with the product), then the values for allowed reactions are systematically higher than for the forbidden ones.^{15,17} The method, originally developed only for the comparison of concerted mechanisms of allowed and forbidden reactions, was recently generalized so as to be applicable also to nonconcerted reaction paths which, especially for forbidden reactions, may provide a reasonable alternative to concerted reaction paths. The detailed formalism of this generalization is sufficiently described in the original study¹⁰ and so we report again only the basic ideas to the extent necessary for the purpose of this study.

In contrast to one-step concerted mechanism which is characterized by a simple kinetic scheme



Scheme 5



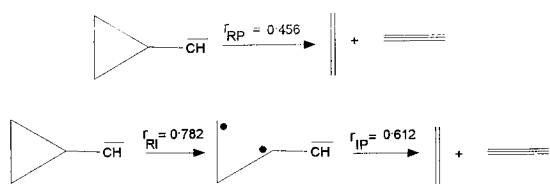
the nonconcerted mechanism of a pericyclic process is described by a scheme involving a biradical or zwitterionic intermediate



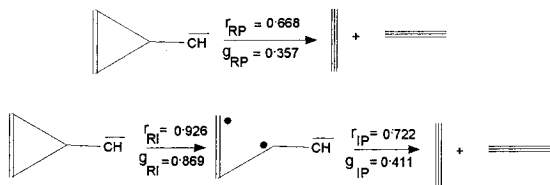
If now the extent of the electron reorganization in the concerted process is characterized by the value of the similarity index r_{RP} , it is natural to ask whether it would be possible to characterize by the values of similarity indices also the stepwise process. The answer to this question is affirmative and as demonstrated in ref 10, the quantity characterizing the extent of electron reorganization in this case is the product of r_{RI} and r_{IP} which separately characterizes each individual reaction step. The relative ease of concerted and stepwise reaction mechanism can thus be estimated by comparing the values of r_{RP} with the product $r_{RI}r_{IP}$. Reactions for which $r_{RP} > r_{RI}r_{IP}$ can be expected to be concerted, while the preference of nonconcerted mechanism is characterized by the inequality $r_{RP} < r_{RI}r_{IP}$. This simple criterion was applied to a number of pericyclic reactions, both forbidden and allowed, and as demonstrated of ref 10 this simple criterion is indeed able to determine the preferred reaction path in many cases. However, for some more complicated reactions we also met the situation where the difference between the r_{RP} and the product $r_{RI}r_{IP}$ was too small to be of any importance so that the above simple criterion is insufficient. In order to remedy this insufficiency we proposed in ref 10 to use the second order similarity indices g_{RP} , g_{RI} , and g_{IP} instead of first order ones, and, as demonstrated therein, this second order criterion is indeed able to discriminate between the alternative reaction paths properly. For that reason it would be interesting to apply this simple similarity criterion also to "complex" carbene reactions. As an example of closely related parent system let us analyze first the addition of carbene to ethene where two alternative reaction mechanisms can be characterized by the Scheme 5.

Calculated values of first and second order similarity indices for both alternative reaction mechanisms are given in the scheme. As it is possible to see, the product $r_{RI}r_{IP}$ is equal to r_{RP} in this case so that the first order similarity criterion is again unable to decide. The same criterion based on second order similarity indices is, however, able to remedy the insufficiency, and the condition $g_{RI}g_{IP} > g_{RP}$ is satisfied in this case. This suggests that the two-step or at least the very asynchronous one-step mechanism is apparently more favorable for this reaction. This result is quite interesting since the preference of nonsynchronous reaction mechanism was in this case predicted not only by direct MO calculations⁷ but also by much more sophisticated spin-coupled calculations.⁸ In a similar way it would be possible to analyze also the other "complex" reactions, and in Schemes 6 and 7 are summarized the results for reactions (a) and (b). As it is possible to see, the stepwise or very asynchronous mecha-

Scheme 6



Scheme 7



nism is predicted by these simple calculations to be more favorable than the concerted one for reaction (a), while for the reaction (b) neither the first order nor second order similarity criterion allows one to decide which of the alternative reaction mechanisms should be more favorable. Such a prediction, at least for reaction (a), seems to be quite consistent with the stepwise nature of closely related carbene to ethene addition, but unfortunately the direct quantum chemical analysis seems to prefer the concerted mechanism. On the other hand, the reaction (b) is predicted by direct calculations to be stepwise. We are thus in a situation where the predictions of simple similarity model and of quantum chemical calculations contradict or are not conclusive enough. Even if we are aware of the simplicity of similarity approach where eventual exceptions cannot be excluded, there are, in our opinion, some specific points for “complex” reactions which deserve a special comment. These points are especially important for the stepwise reaction (b), where neither the first nor second order similarity indices are able to discriminate between the alternative reaction mechanisms. According to our experience such a situation is typical for reactions, the description of which is extremely sensitive to electron correlation so that only the highest quality ab initio calculations can be expected to give reliable results. However, in calculations reported in study,¹⁸ the electron correlation was included via perturbation theory which is known to be nonvariational. As a consequence there is no guarantee that perturbational corrections do indeed converge to true solutions so that it is not possible to exclude a situation that the correlation contributions are either underestimated or overestimated. For that reason it is very difficult to estimate whether the precision of the calculations for the reactions (a) and (b) is indeed comparable. As a consequence it is not at all clear whether the predicted preference for the concerted mechanism of the reaction (a) is not only the consequence of the insufficient inclusion of correlation into the calculations in this case and that the reaction is not in fact, like the closely related process (b), stepwise. To answer this crucial problem, true variational methods like MCSCF or spin-coupled theory would be required. Such calculations were not so far reported for “complex” reactions so that any conclusion concerning the mechanism of these reactions

cannot be regarded as definitive. For that reason we consider it better to postpone the final discussion of the mechanism of reactions (a) and (b) until such calculations are reported for them.

Despite the above uncertainty in the predictions of similarity model, the successful applications of similarity approach are still numerous enough¹⁰ to encourage us to express our belief that the similarity approach represents a simple alternative to obtaining an interesting insight into the detailed mechanism of chemical reactions and that it can be found useful in situations where the rapid but still reliable estimates of the preferred reaction mechanism are required as, e.g., in programs for the computer designed synthesis.

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