

FORMALDEHYDE-HYDROXYCARBENE REARRANGEMENT*

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In the previous paper a procedure has been proposed which permits a search for stationary points on energy hypersurfaces by means of the calculations of reaction coordinates. The method is applied in this paper to semiempirical quantum chemical methods. The reaction coordinate calculations satisfy the boundary conditions required by the theory of absolute reaction rates and are free of any chemical hysteresis. On the basis of calculations a mechanism of the $\text{H}_2\text{CO} \rightleftharpoons \text{HCOH}$ rearrangement is suggested and the stability of hydroxycarbene is discussed.

Once all-valence electron methods were introduced, attempts were made to construct model energy hypersurfaces and to suggest or to verify reaction mechanisms. Ordinarily, the energy of a molecule has been expressed as a function of only one or two molecular coordinates and the stationary points were searched for as extrema of these simplified functions. The deficiencies of such a procedure are the rather arbitrary choice of coordinates relevant to the process and the assumption about the conservation of the other molecular coordinates in the course of the reaction. Considerable progress was achieved by the introduction of numerical procedures of McIver and Komornicki¹ and of Dewar^{2,3} in which a search for stationary points was made by the determination of extrema on curves which were assumed to be reaction coordinates. Though all coordinates of the molecule were taken into account, there still remained some arbitrariness in the choice of the coordinate representing the least energy path. Another shortcoming of the procedure is the so called "chemical hysteresis" which means that generally the reaction coordinates calculated for the forward and reverse reactions are different¹. Therefore in the latest calculations this approach has been abandoned and the stationary points (activated complexes) were searched for by direct geometry optimization^{4,5} beginning with a trial geometry based on symmetry considerations and chemical intuition.

The procedure reported in ref.⁶ defines the reaction coordinate as a direction of motion in the limiting case of zero velocity^{7,8}. The direction of the reaction coordinate was forced to be parallel to the energy gradient and to a particular eigenvector of the matrix of force constants⁶. The procedure is free of any chemical hysteresis and satisfies the boundary conditions required by the theory of absolute reaction rates. The program created in our laboratory permits the calculation of reaction coordinates defined in this way or according to McIver and Komornicki. The methods manageable are CNDO/2, INDO and MINDO/2. Both closed shell and open shell systems can be accommodated. The program was written in FORTRAN-IV and was tested on computers of the IBM 370 series.

* Part II in the series Calculation on Reaction Mechanisms by the Semiempirical Methods; Part I: This Journal 40, 1112 (1975).

In this paper the INDO treatment of the formaldehyde-hydroxycarbene rearrangement is presented and both the reaction mechanism and the stability of hydroxycarbene are discussed.

THEORETICAL

A remark on the concept "reaction coordinate". The concept of reaction coordinate is not inherent in treatments utilizing the theory of absolute reaction rates. For such a treatment it is only of relevance to examine stationary points on the energy hypersurface and their nearest surroundings. However, the calculation of reaction coordinates may facilitate finding structures that correspond to stationary points because they reduce examination of extrema on the multidimensional energy surfaces to examination of extrema on the two-dimensional curves of energy *vs* the reaction coordinate. Moreover the reaction coordinate gives us information about the sequence of stationary points through which the process may proceed. Hence the calculation of the reaction coordinate permits one to write down directly the equations for successive reaction steps.

The reaction coordinate can be defined from static and dynamic viewpoints. In the former case it is taken as the least energy path on the valley bottom of the energy hypersurface. In the latter⁷⁻⁹ it is defined as a direction of reaction for a velocity of reactants approaching zero. In our case the independent variable is length, which is in contrast to that of time in dynamic methods of chemical reactivity. This circumstance brings about some restrictions on the choice of a coordinate system since it is possible in some coordinate systems to compare only lengths of different vectors and consequently lengths of reaction coordinates. A coordinate system must satisfy the following requirements: *a*) all independent coordinates must be of uniform dimension-length; *b*) translation and rotation of the whole system must be avoided in a given coordinate system; *c*) the length of the straight line, *i.e.* the distance between two points in a given coordinate system must represent the length in the sense of the classical Euclidean geometry. Define the distance r between the points \mathbf{x}_A and \mathbf{x}_B as the norm of a difference vector $\Delta\mathbf{x} = \mathbf{x}_A - \mathbf{x}_B$, *i.e.* $r = (\Delta\mathbf{x}^T \cdot \Delta\mathbf{x})^{1/2}$. On applying the transformation matrix $\mathbf{A}(\mathbf{x}'_A = \mathbf{A}\mathbf{x}_A, \mathbf{x}'_B = \mathbf{A}\mathbf{x}_B, \text{ and } \Delta\mathbf{x}' = \mathbf{A}\Delta\mathbf{x})$ the distance r is changed to $r' = (\Delta\mathbf{x}'^T \mathbf{A}^T \mathbf{A} \Delta\mathbf{x})^{1/2}$. Then $r' = r$ only if \mathbf{A} is an unitary matrix. The length of the reaction coordinate is therefore not invariant with respect to a nonunitary transformation of the coordinate system. According to the classical Euclidean geometry it does not hold that in all coordinate systems a distance between two points in the space is a norm of the difference vector. Actually this holds only for cartesian coordinate systems. For this reason the length of the reaction coordinate may be identified with the norm of the difference vector only in cartesian coordinate systems or systems that can be derived from cartesian

systems by a unitary transformation. This is noted to overcome the invariance difficulties mentioned in ref.⁹.

The conditions a)–c) restrict considerably the choice of the coordinate system for calculations. The cartesian coordinate system cannot be used because it violates the condition b). A system of bond lengths, bond and dihedral angles does not satisfy the conditions a) and c). In this paper use has been made of a coordinate system which was derived from the cartesian coordinate system by a linear transformation $\mathbf{x}' = \mathbf{B}^T \mathbf{x}$, where columns of \mathbf{B} are eigenvectors of the matrix of force constants of the reactant. The origin of this system was identified with the geometrical center of a molecule. On transforming the gradient by means of the \mathbf{B} matrix, six components vanish with nonlinear molecules (with linear molecules five components vanish). The other $3N-6$ ($3N-5$) coordinates (where N stands for the number of atoms) of the vector \mathbf{x}' define the coordinate system used in this study. The system so defined satisfies the conditions a) through c).

Though the length of the reaction coordinate is tractable only with a coordinate system defined in this way, the equations presented in the next section hold in any coordinate system. Compared to the case of coordinates suggested, the norms of difference vectors between the individual points and curves representing reaction coordinates would be different but the stationary points found and their order would be the same. The resulting reaction coordinate would again be free of chemical hysteresis.

Calculations of positions of points on the reaction coordinate. Let E be energy, \mathbf{g} gradient at the point \mathbf{x} , \mathbf{c}_k the k -th eigenvector of the matrix of force constants in the n -dimensional space defined in the preceding section. We next define s_k as a scalar product $\mathbf{g}^T \mathbf{c}_k$. For a point \mathbf{x} to lie on the reaction coordinate, where the gradient is parallel to the eigenvector \mathbf{c}_m , it must hold

$$s = \left(\sum_{k \neq m} s_k^2 \right)^{1/2} = 0. \quad (1)$$

Consider a point \mathbf{x}' with the gradient \mathbf{g}' as an approximation of the point \mathbf{x} . In the case of a quadratic surface the point \mathbf{x} can be found by means of the following expression⁶

$$r_i = - \sum_{j \neq m} E_j^{-1} c_{ij} s'_j, \quad (2)$$

where $r_i = x_i - x'_i$, $s'_j = \sum_k c_{kj} g'_k$ and E_j is the j -th eigenvalue of the matrix of force constants. Since the real surface is not quadratic, Eq. (2) must be applied several times. Convergence was tested by means of Eq. (1). In our calculations, the iterative

procedure was terminated if $\sum_{k \neq m} s_k'^2 / (\mathbf{g}'^T \mathbf{g}')^{1/2} < 0.05$. If some E_j were small, the convergence was poor. For this reason a modified equation was used which is analogous to the Levenberg-Marquardt formula¹⁰ for the optimization of functions

$$\mathbf{r} = \mathbf{B}^T \mathbf{b} \quad (3)$$

Here $B_{ij} = \sum_{k \neq m} (E_k^2 + a)^{-1} c_{ik} c_{jk}$ and $b_i = \sum_{k \neq m} |E_k| c_{ik} s_k$. The constant a was assumed to be proportional to s (Eq. (1)). The absolute value of E_k in the expression for b_i ensures that the calculation converges only to points where all eigenvalues E_k for $k \neq m$ are positive. The calculated reaction coordinates conform therefore to the Murrell-Laidler rule¹¹, according to which it must hold for each point on the reaction coordinate (particularly in the vicinity of the activated complex) that the matrix of force constants has not more than one negative eigenvalue which may be E_m . Eq. (3) implies that the Murrell-Laidler's requirements¹¹ are satisfied as the only eigenvalue which may be negative is E_m and the corresponding eigenvector \mathbf{c}_m is a tangent to the reaction coordinate.

The actual calculations proceeded as follows: 1) the geometry of reactant was optimized; 2) the coordinate system was shifted to identify its origin with the geometrical center; 3) force constants were computed and the eigenvectors \mathbf{c}_k^0 were obtained; 4) Schmidt orthogonalization was performed to annihilate from eigenvectors \mathbf{c}_k^0 pure translation and rotation terms which were introduced into calculations by insufficient computer precision in numerical differentiation; 5) the first step of the length d was performed (0.015 nm in our calculations) along the \mathbf{c}_1^0 vector and Eq. (3) was several times applied to obtain the point \mathbf{x}^1 . The next step in the determination of the length d was carried out along the gradient direction (Eq. (1) in ref.⁶) and the procedure was iterated until the vicinity of the stationary point was achieved. Geometry of this point was obtained by a multiple application of Eq. (3) in which the summations in \mathbf{B} and \mathbf{b} extended over all indices k (standard Levenberg-Marquardt method¹⁰) until the square of the norm of the gradient was less than $2.57 \cdot 10^{-22}$ (J/m)². The next step was performed along the direction of \mathbf{c}_1^1 and the procedure was repeated until the stationary point was reached. It should be noted that the curves given by successive application of Eq. (3) indeed pass through the stationary points without chemical hysteresis.

RESULTS AND DISCUSSION

First an approximation reaction coordinate was calculated for the process studied according to the approach of Dewar^{2,3} and of McIver and Komornicki⁴. The procedure started from the optimized geometry of formaldehyde and then the H—C—O

angle was successively lowered by 10° while the other coordinates were optimized so that gradient components with respect to these coordinates vanished. The reaction course obtained is presented* in Fig. 1. Energies and structural parameters of compounds *I* and *III* and of the stationary point *II* are given in Table I, Wiberg bond indices, charges and dipole moments are given in Table II. Labelling of atoms is consistent with Fig. 1. The nature of the stationary point *II* was examined by means of the force constants matrix. It was found that this matrix possesses two negative eigenvalues. The structure can therefore be neither a minimum nor a saddle point and the reaction path calculated does not conform to the Murrell-Laidler rule about the reaction coordinate¹¹.

Next the method described in the preceding section was applied. The first step was performed along the eigenvector \mathbf{c}_1 of the force constants matrix with the lowest eigenvalue. It was found that the reaction course is more complex. Perspective views on the relevant structures lying on the reaction coordinate are presented in Fig. 2. Relevant energies and structural data are given in Tables I and II.

In the initial stage of motion the C_{2v} symmetry is preserved. The two hydrogen atoms reach over to the oxygen atom and the motion corresponds to the vibrational mode of the "scissors" type. Energy and the gradient increase strongly. Charges on hydrogen atoms grow to the detriment of the carbon charge. The dipole moment decreases (see structure *IV*). Once the HCO angle passes 90° the reaction coordinate is split and the break down of molecular symmetry occurs. The hydrogen atoms are not equivalent any longer, the molecule is nonplanar without any axis of rotation. Energy still increases, the gradient decreases, and the eigenvalue E_1 is negative. This abrupt geometry change is reversible in the sense that on passing along the reaction path in the opposite direction the molecule is again symmetrized by a jump. This segment of the reaction path was recalculated by inclusion of doubly excited states. It was shown that the jump is not due to the crossing of potential surfaces and that there is no extremum on the reaction path between *IV* and *V*. A more detailed analysis of this portion of the energy hypersurface will be reported later. Next calculation of the reaction coordinate leads to the structure *V* which corresponds to a stationary point. Negative E_1 implies that it is an activated complex. Wiberg bond indices and bond lengths show that the migrating hydrogen is about midway between oxygen and carbon. Its bonding towards carbon is stronger and its positive charge grows strongly so that negative charge originates on the other three atoms. Charge redistribution brings about an increase in the dipole moment. On proceeding further along the reaction coordinate, energy decreases and one arrives at the minimum *VI*

* Drawings of molecules represent real perspective pictures of models of molecules enlarged in the ratio $2 \cdot 10^{11} : 1$ as they would be taken by a camera with an objective of focal length f : 50 mm. Use was made of a program written by the author of this paper for plotter Calcomp on line with an IBM 370/135 computer.

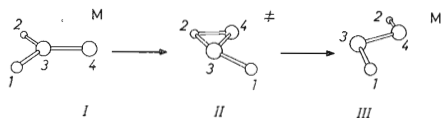


FIG. 1

Reaction Mechanism Calculated by the Method of Dewar, McIver, and Komornicki
 Numbering of structures is the same as in Tables I and II.

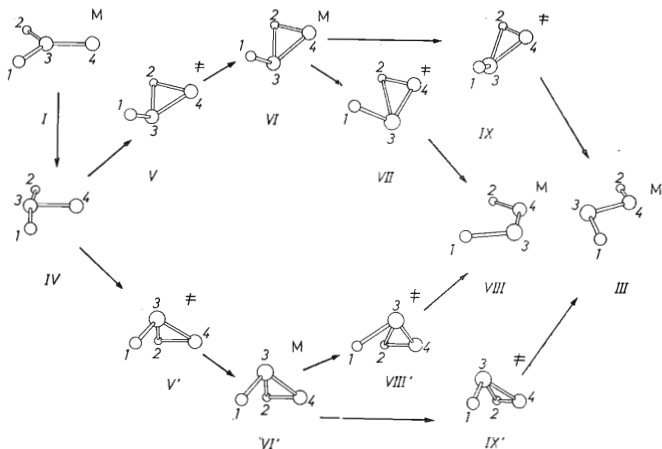


FIG. 2

Reaction Mechanism Suggested in This Work
 For additional details see Fig. 1.

FIG. 3

Structures of Hydroxycarbene in the First
 Excited Triplet State.

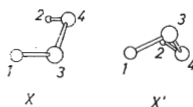


TABLE I

Energy E , Two Lowest Eigenvalues of the Matrix of Force Constants E_1 , E_2 , and Geometry Parameters of Crucial Points on the Formaldehyde-Hydroxycarbene Energy Hypersurface^a
For labelling of atoms see Figs 1—3.

Structure	$10^{16} E$, J	E_1 , J/m ²	E_2 , J/m ²	r_{13}	r_{23}	r_{24}	r_{34}	ϑ_{134}	ϑ_{143}	ϑ_{243}	ϑ_{1342}^b
I (minimum) ^c	-1.12235	232	283	0.1117	0.1117	0.2075	0.1249	122.51	122.51	26.99	180.0
II (apex)	-1.11277	-915	—	0.1132	0.1272	0.1152	0.1308	53.01	110.85	31.72	180.0
III (minimum) ^d	-1.11504	104	131	0.1131	0.1944	0.1040	0.1301	104.27	29.81	111.75	180.0
IV ^e	-1.11592	155	273	0.1126	0.1126	0.1624	0.1266	86.77	85.30	43.72	179.5
V (saddle point)	-1.11475	-523	160	0.1130	0.1213	0.1249	0.1307	109.60	59.29	56.63	108.0
VI (minimum) ^f	-1.11489	112	245	0.1133	0.1314	0.1141	0.1321	107.97	51.29	64.03	96.6
VII (saddle point)	-1.11424	-98	99	0.1134	0.1628	0.1060	0.1316	109.01	40.49	85.77	56.4
VIII (minimum) ^g	-1.11538	83	155	0.1128	0.2011	0.1044	0.1291	111.33	27.14	118.51	0.0
IX (saddle point)	-1.11420	-104	141	0.1134	0.1607	0.1059	0.1319	107.12	40.95	84.29	130.5
X (triplet state minimum)	-1.11305	—	—	0.1114	0.1968	0.1066	0.1283	128.48	—	113.51	91.5

^a Bond lengths r are in nm, angles ϑ in degrees; ^b The angle between the planes containing atoms 134 and 234; ^c Formaldehyde; ^d *trans*-Hydroxycarbene; ^e Gradient $1.700 \cdot 10^{-7}$ J/m; ^f π -complex; ^g *cis*-Hydroxycarbene.

TABLE II

Charges q , Wiberg Bond Indices p , and Dipole Moments D of Crucial Points on the Formaldehyde-Hydroxycarbene Energy Hypersurface
For labelling of atoms see Figs 1-3.

Structure	p_{13}	p_{23}	p_{24}	p_{34}	q_1	q_2	q_3	q_4	$10^{30} D, \text{Cm}$
<i>I</i>	0.938	0.938	0.041	2.034	-0.043	-0.043	0.322	-0.237	6.80
<i>II</i>	0.920	0.371	0.518	1.748	-0.053	-0.330	-0.027	-0.251	3.74
<i>III</i>	0.959	0.002	0.937	1.533	-0.036	0.167	-0.022	-0.109	5.87
<i>IV</i>	0.935	0.936	0.013	1.977	0.074	0.079	0.119	-0.271	6.20
<i>V</i>	0.955	0.533	0.407	1.531	-0.049	0.235	-0.057	-0.130	6.80
<i>VI</i>	0.965	0.345	0.590	1.334	-0.056	0.256	-0.053	-0.146	8.44
<i>VII</i>	0.960	0.136	0.807	1.361	-0.077	0.229	0.026	-0.178	10.54
<i>VIII</i>	0.960	0.048	0.910	1.582	-0.051	0.144	0.006	-0.099	11.47
<i>IX</i>	0.964	0.116	0.821	1.369	-0.057	0.233	-0.001	-0.175	6.24
<i>X</i>	0.846	0.007	0.757	1.423	0.013	0.109	-0.037	-0.085	5.50

which is very close to the activated complex V (the respective length of the reaction coordinate between V and VI is only 0.013 nm). Positive charge on the migrating hydrogen reaches its maximum and a typical structure of a π -complex is formed. OH bonding is stronger than CH bonding. The above noted split of the reaction coordinate brings about the formation of one of the two mirror-image forms of VI . In this case the existence of two enantiomers is due a trivalent asymmetric carbon. Another interesting feature of the two enantiomers is the circumstance that they cannot be interconverted in a single reaction step. The respective activated complex would be structure II but it was established that no reaction coordinate can pass over this structure. The only possible passage from one form of VI to the other is a two-step process *via* formaldehyde or one of hydroxycarbene isomers (*vide infra*).

With the structure VI the direction of the eigenvector c_1 corresponds to the shift of the migrating hydrogen which is perpendicular to the $H_{\text{migr}} \text{ CO}$ plane. There again a split of the reaction coordinate occurs since it is possible to proceed in the sense of a positive and negative directions on the vector c_1 . If we follow the reaction coordinate in the positive direction of c_1 , the CH bond weakens very rapidly, the OH bond becomes stronger and the dihedral angle HCOH diminishes. Energy increases and the eigenvalue E_1 decreases. After an initial growth the norm of gradient decreases and becomes zero at the structure VII which corresponds to a next saddle point. On following the reaction coordinate one arrives at *cis*-hydroxycarbene $VIII$ (for data on the latter see Tables I and II). The positive charge on the migrating hydrogen is about half of that in structure VI . Nevertheless, the dipole moment is still high ($1.15 \cdot 10^{-29}$ Cm) presumably because of a favourable structure. There is a considerable charge alternation along the HCOH skeleton. By its nature the CO bond in *cis*-hydroxycarbene lies somewhere between the ketone-like double and enolic single bonds. It is not as weak as in structure VI , where π bond weakening is maximum due to the $\sigma - \pi$ interaction, and not purely enolic as it might be assumed on the basis of its formula.

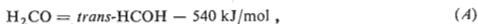
If a negative direction of the vector c_1 is followed from VI , then one arrives at *trans*-hydroxycarbene III over the activated complex IX . In contrast to $VIII$ with *trans*-hydroxycarbene there is no charge alternation and all positive charge is accumulated on the migrating hydrogen. Also the dipole moment is considerably lower; it is even lower than the dipole moment of formaldehyde. *Trans*-hydroxycarbene is $3.4 \cdot 10^{-20}$ J higher in energy than *cis*-hydroxycarbene. The two isomers are genuine minima on the energy hypersurface and the passage between them occurs over an activated complex (this process is also not simple and will be treated in more detail in a next paper). The higher stability of *cis*-hydroxycarbene with respect to the *trans* isomer may be assigned to a coulomb interaction between the hydrogen atoms that bear opposite charges.

It is interesting that the reaction mechanism can also be described roughly in terms of the empirical theory of maximal overlap. The essential feature of the reaction

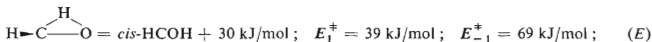
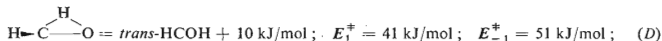
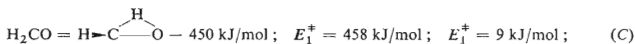
at the beginning is a decrease in overlap between the hydrogen $1s$ atomic orbitals and the carbon sp^2 hybrid orbitals. Apparently, a simultaneous shift of the two hydrogens is more favourable than a shift of a single hydrogen along a twofold distance. If the HCO angle is lower than 90° , the overlap noted rapidly approaches zero. At this stage the dominating role can be assigned to the overlap between the hydrogen $1s$ orbital and the bonding π orbital of the C—O bond. This overlap just reaches its maximum in the π -complex VI. In the next stage the effect of the π orbital steadily decreases and it is the interaction between hydrogen cation and lone pairs on oxygen which is getting important. This interaction brings about stabilization of *cis*- and *trans*-hydroxycarbenes. It is noteworthy that the process studied may probably be taken as a rather common case of a reaction with a symmetrical reactant and product which does not proceed over an activated complex of the same symmetry. This may serve as a warning against noncritical applications of the Woodward-Hoffmann orbital symmetry rules to chemical processes where the symmetry conservation is assumed.

All calculations performed refer to the energy hypersurface for the lowest singlet state of the molecule. Since the ground states of some known carbenes are triplet states, a question may be asked whether III and VIII indeed correspond to ground states. Excited states of I and III–IX will be examined in a later paper: Here we note only the results of CNDO/S calculations (involving configuration interaction) and of direct geometry optimizations of *cis*- and *trans*-carbenes. In both cases singlet ground states were favoured. Experimental data are lacking as there is only some evidence on methoxycarbene that its ground state is the singlet state^{12,13}. For both *cis*- and *trans*-hydroxycarbene the geometry optimization in the lowest triplet state gives a single pair of enantiomers X and X' whose energy and geometry parameters are listed in Tables I and II.

It is known that the angular dependence of the total energy is better accounted for by INDO than the dependence on bond lengths. This can be documented by reasonable bending force constants and barriers to internal rotation given by INDO and CNDO/2 (ref.¹⁴). It may thus be assumed that the error in energy involved in unimolecular rearrangements is lower than it is with dissociation and addition reactions. A further argument for this is a circumstance that the theoretical overestimation of bond energies is systematic. For reactions where the same number of bonds is being broken and the same number of bonds arises, a partial cancellation of errors in bond energies may be anticipated. The energy differences presented in this paper are believed to be at least in semiquantitative agreement with experiment. The total heat of reaction can be expressed by the following equations



For partial reaction steps, it was found



where E_1^\ddagger and E_{-1}^\ddagger are, respectively, energies of activation for forward and reverse reactions.

From equations (A) and (B) it follows that the formaldehyde-hydroxycarbene equilibrium is practically entirely shifted in favour of formaldehyde. A very low energy barrier of the reverse reaction of (C) implies that structure VI is converted almost quantitatively to the structure I immediately after its formation. The structures III and VI are predicted to be stable. The energies of activation for the reverse reactions of (D) and (E) are rather high. At low temperatures, unimolecular decomposition of hydroxycarbenes is therefore unlikely. It may be assumed that the extremely low pressure at which bimolecular processes will hardly occur and sufficiently low temperature are conditions under which hydroxycarbene might be stable. Such conditions are met for example in outer layers of some stars where hydroxycarbene was detected spectroscopically¹⁵. Possible existence of hydroxycarbenes with rather high barriers of inversion might indicate an important role of hydroxycarbenes in the synthesis of saccharides in the prebiotic state of the earth evolution.

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