October, 1975] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(10), 2667—2672 (1975) 2667

A Conformational Study of the NO_x(x=1 or 2)-catalyzed Isomerization of *cis*-2-Butene Using the INDO-UHF Method

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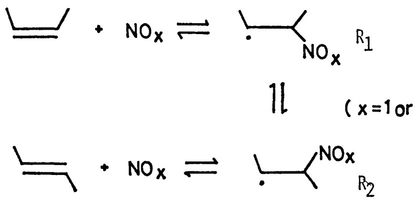
(Received March 12, 1975)

The NO_x(x=1 or 2)-catalyzed isomerization of *cis*-2-butene was investigated by means of the INDO-UHF theory, with a particular view to the energetic and conformational aspects of the reaction. The NO_2-addition process to form the intermediate radical (R_1) had no appreciable activation barrier, although the NO_2-fission process from the intermediate radical (R_2) had the C–NO_2 dissociation energy of 44.6 kcal/mol. Some characteristic features of the stretched C–C bond in the intermediate radical (R_1) were; (1) $r_{\mathrm{CC}}=1.45$ Å, which was roughly equal to the value (1.481 Å) in *cis*-2-butene at the transition state of its thermal isomerization; (2) a pseudo π-conjugation with a small π-character (about 13% of $E_{\mathrm{CC}}^{\mathrm{R}}$) in comparison with that (about 29% of $E_{\mathrm{CC}}^{\mathrm{R}}$) in *cis*-2-butene, and (3) approximately the same magnitude of the hfsc value (34.40—34.47 G) for the sp²-hydrid carbon as that (experimental value of 39.07 G) for the said atom in the ethyl radical. The calculated internal-rotation barrier of the intermediate radical (R_1) around the C–C bond (1.75—3.01 kcal/mol in the two rotating directions) was smaller than that (around 4 kcal/mol) obtained from the thermodynamic estimations. The energetically most stable or unstable rotamer was found in the staggered or the eclipsed configuration respectively; a hydrogen-bonding effect on the stabilization was observed in staggered configuration, although a remarkable effect of the homoconjugation or the repulsive interaction of unpaired and lone-paired electrons can be disregarded in the present internal-rotamer.

The isomerization about the C=C double bond of olefin with free-radical catalysts, especially with NO_x (x=1 or 2), has currently received considerable attention in connection with olefin consumption in photochemical smog. In regard to the gas-phase *cis*-2-butene isomerization catalyzed by NO_x(x=1 or 2), Cundall¹⁾ and Pitts *et al.*²⁾ have performed kinetic investigations of the gas-phase isomerization mechamism, and the mechanism may now be postulated qualitatively to be as follows:



In the above reaction paths, the NO_x catalyst actually diminishes the activation energy of the reaction fro 62.8 kcal/mol³⁾ in the thermal isomerization to 26.2 kcal/mol in the case of NO¹⁾ or 12.1±0.3 kcal/mol in the case of NO_2.²⁾ It has also been established with respect to the olefin isomerization that the reaction is catalyzed by such free radicals as I,⁴,⁵⁾ S,⁶⁾ HS,⁷⁾ and RS.⁸⁾ The isomerization mechanism, however, is still open to question on a molecular level in view of the fact that the energetics of the reaction paths have been studied only by means of thermodynamic estimations.

On the other hand, semi-empirical calculations have recently been carried out on the thermal *cis-trans* isomerization of such olefins as 2-butene and 2-pentene with a particular view to the activation barrier of the reaction.⁹⁾ For 2-butene, there was a considerable agreement of the calculated activation energy of 56.4 kcal/mol⁹⁾ with the experimental value, 62.8 kcal/mol.³⁾ However, there is no literature dealing with the free-radical catalyzed isomerization of olefins on the basis of the MO theory.

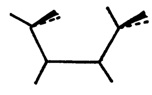
In this paper, we wish to report the application of the INDO-UHF method¹⁰⁾ to a conformational study of the energetics of the NO_x-catalyzed isomerization of *cis*-2-butene. The specific objectives of this study are: (1) to elucidate the mode of the interaction between the NO_x catalyst and *cis*-2-butene, (2) to provide information about the conformations of the intermediate radicals (R_1 and R_2), and (3) to discuss quantitatively the process of the internal rotation of the R_1 radical.

Method of Calculation

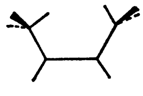
The following three systems were mainly investigated in this work: (a) the interacting system of NO_x (x=1 or 2) and *cis*-2-butene, involving the NO_x-addition process; (b) the intermediate radicals (R_1 and R_2), and (c) the internal rotation of the intermediate radical (R_1), augmented by the NO_x-fission process from the R_2 radical.

All the calculations on the above systems were performed by means of a semi-empirical INDO-UHF method¹⁰⁾ which is relatively reliable for bond angles, but less so for bond lengths.¹¹⁾ The integrations and parametrizations involved in the above method will not be repeated here, because they have been described in detail in Ref. 10.

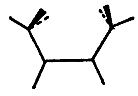
The geometries of *cis*-2-butene ($r_{\mathrm{CC}}=1.34$ Å in the double bond; $r_{\mathrm{CC}}=1.54$ Å in the single bond; $r_{\mathrm{CH}}=1.06$ Å; $\angle$C=C–C=$\angle$C=C–H=120°; $\angle$HCH=$\angle$CCH=109°28′) and NO_2 ($r_{\mathrm{NO}}=1.188$ Å; $\angle$ONO=134.1°) were obtained from a standard compendium,¹²⁾ while the bond length of NO ($r_{\mathrm{NO}}=1.159$ Å) in NO was obtained as an optimum one by the INDO-UHF calculation. With regard to the optimum rotation angle of the two methyl groups in *cis*-2-butene, the INDO calculations gave the best configuration as III, which has minimum electron and nuclear repulsions, among the following three possible configurations:



I



II



III

The bond index of E_{AB} for the A–B bond, which is defined as the energy contribution of the A–B bond to the total energy of a molecule, was evaluated by means of a method of energy partitioning:[13,14)]

$$E_{AB} = E^{R}_{AB} + E^{V}_{AB} + E^{J}_{AB} + E^{K}_{AB} + E^{N}_{AB}$$

where each energy term has the usual significance described in Refs. 13 and 14.

Results and Discussion

Interaction of the NO_x (x=1 or 2) Catalyst and cis-*2-Butene.* The ground state of $NO_x(x=1$ or 2) has a doublet-spin multiplicity and, hence, a free-radical character. Therefore, the SOMO (singly-occupied MO) of the NO_x, which expands predominantly around the nitrogen atom in the direction of the z-axis in Fig. 1, plays an important role in the interaction with the HOMO (highest-occupied MO) and LUMO (lowest-unoccupied MO) of *cis*-2-butene (π and π^* orbitals on the C=C double bond respectively). The interaction is favored under the maximum overlappings between the above frontier orbitals of the two reactants. In the modes of the interaction shown in Fig. 1, the bridge-type interaction was discarded because of the following reasons:

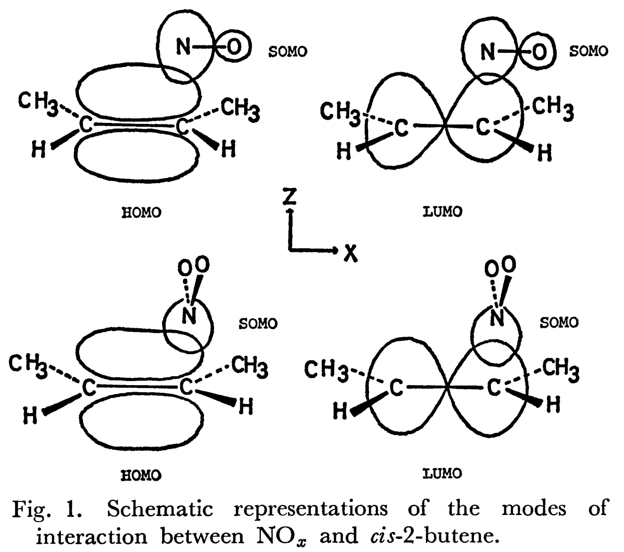


Fig. 1. Schematic representations of the modes of interaction between NO_x and *cis*-2-butene.

(a) the SOMO of the NO_x and the LUMO of *cis*-2-butene overlap unfavorably in the bridge structure; (b) the nearly equivalent rates of the exchange and isomerization reactions in such a system of di-iodoethylene and free-radical iodine atoms obviates the bridge structure,[15)] even though the EPR spectroscopy of the system of *cis*-2-butene and hydrogen bromide is positive for the bridge structure,[16)] and (c) the conformation of the intermediate radical formed in the isomerization of *cis*-2-butene by the sulfhydroyl radical does not favor the bridge structure.[7)] In this respect, the present INDO-UHF calculation indicates that the two possible interacting structures mentioned above cannot be distinguished from each other only by the total energy and the overlap population[17)] (0.002 at r_{CN}=3.0 Å) of the C–N bond.

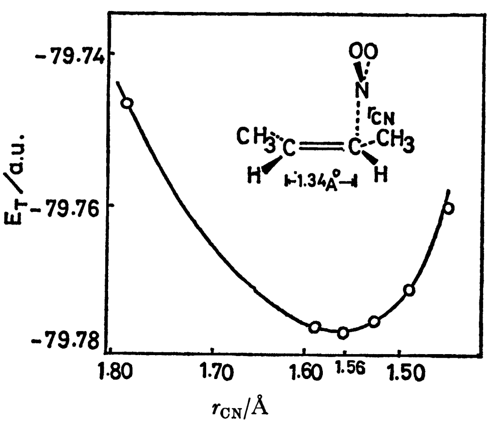


Fig. 2. Total energy of the system between NO_2 and *cis*-2-butene as a function of r_{CN}.

Next, let us discuss the energetic aspect of the interaction system of the NO_x and *cis*-2-butene, taking NO_2 as an example. So long as the C=C double bond of *cis*-2-butene is kept constant, the NO_2 catalyst approaches *cis*-2-butene, by the least motion, in the direction of the carbon p_z-orbital expansion. As can be seen from Fig. 2, the total energy (E_T) of the above interacting system as a function of r_{CN} indicates a monotoneous stabilization of the system until r_{CN}= 1.56 Å, which is longer than the usual C–N bond length (1.47 Å[12)]). With the approach of NO_2 to *cis*-2-butene, the electrons of the π-orbital of the latter flow into the former (predominantly into the two oxygen atoms) with an appreciable electron back-donation from NO_2 to the p_z-orbital of the remote carbon (not in CH_3 group) through the π-conjugation

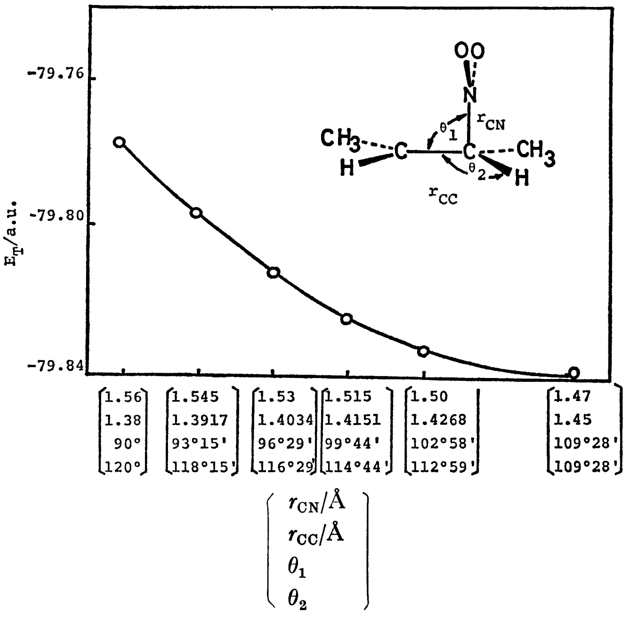
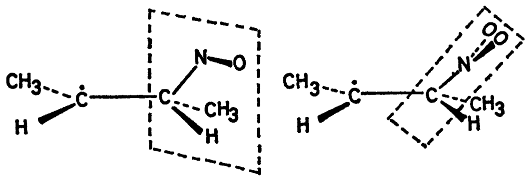


Fig. 3. Total energy for the NO_2-addition process.

of the C=C bond. Further interaction within r_{CN}=1.56 Å will require a stretching of the C=C bond and a change in the sp^2 hybridization of the carbon atom. We will, therefore, try to simulate the NO_2-addition process by changing the carbon hybridization=sp^2-sp^3, r_{CN}=1.56—1.47 Å, and r_{CC}=1.34—1.45 Å (see below), with the residual part retaining its equilibrium geometries. As Fig. 3 indicates, the process has no appreciable activation barrier, although the activation energy of 12.1±0.3 kcal/mol was given for the above NO_2-addition process by Pitts *et al.*[2)] The discrepancy between the INDO-UHF calculation and the experiment may be caused by the present incomplete MO-simulation; the exclusion of geometry optimizations (except for r_{CN}) in the process gave only the stabilization energy of 103.8 kcal/mol, a value which was obtained from the difference in the total energies between the intermediate radical (R_1) and the two reactants isolated.

Conformation of the Intermediate Radicals. It is necessary first to interpret the r_{CC} value of 1.45 Å for the intermediate radical (R_1) used for the MO-simulation mentioned above. Plots of the total energies (E_T) for the radical (R_1) *vs.* r_{CC} in Fig. 4 indicate that r_{CC}=1.45 Å gives the energetically most stable radical (R_1: x=1 or 2). This C–C bond length is slightly longer than that (1.430 Å[18)]) of the ethylene cation, but shorter than that (1.484 Å[18)]) of the ethyl cation or that (1.516 Å[18)]) of the ethyl radical. Interestingly, the r_{CC} value of 1.45 Å is roughly in harmony with that (1.481 Å[9)]) of 2-butene at the transition state in its thermal isomerization.

Next, we will discuss the rotation of NO_x(x=1 or 2) around the C–N bond in the intermediate radical (R_1). The rotation barrier of the C–NO ring was evaluated to be 4.08 kcal/mol, while that of the C–NO_2 ring was 1.82 kcal/mol. The former value is markedly larger than that in the methyl rotation of *cis*-2-butene (0.75 kcal/mol[19)]) or of ethane (2.88 kcal/mol[20)]), while the latter value of 1.82 kcal/mol is approximately of the same magnitude as the methyl rotation in *trans*-2-butene (1.95 kcal/mol[21)]). At any rate, the C–NO_x (x=1 or 2) ring has indeed a restriction in rotation because its rotation barrier is essentially large as compared with the free-rotation barrier (0.6 kcal/mol at room temperature). It should be stressed here that the NO_x rotation around the C–N bond does not appreciably change the C–C bond length (1.45 Å) over 0.02 Å in the intermediate radical (R_1), because r_{CC}=1.43 or 1.47 Å makes the radical (R_1) unstable at any rotation angle in comparison with the stability of the radical (R_1) at r_{CC}=1.45 Å. The energetically most stable intermediate radical (R_1) has the following conformation:



R_1 (x=1) R_1 (x=2)

The most stable intermediate radical (R_1)

In the R_1 (x=1), the bond axes of N–O and C–H are on the same plane, and the bond angle of C–N–O is 118°, smaller by 2° than that of nitrosomethane[22)]. In the R_1 (x=2), the O–O axis is perpendicular to the C–C bond axis. It is of interest here to discuss how the NO_x (x=1 or 2) rotation around the C–N bond changes the total energy and the energy-contribution terms of the radical (R_1). In Table 1, we list the total energy (E_T), and the attraction (E_I) and repulsion (E_{II} and E_N) terms as functions of some clockwise-rotation angles (θ). As can be seen form Table 1, the repulsions decrease monotonously until the R_1 takes its most stable conformation (θ=240° for NO and θ=90° for NO_2), with a normal augmentation of the attraction. It may be deduced, therefore, that the least repulsion, rather than the attraction, makes

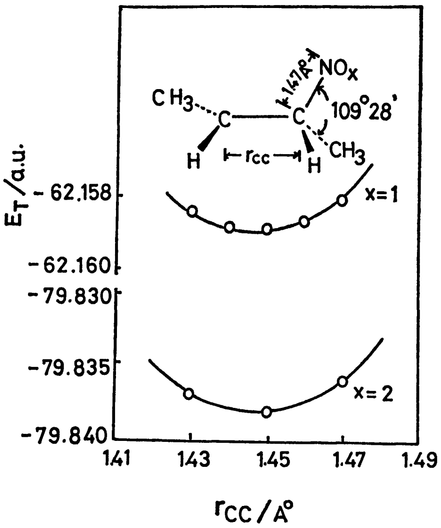


Fig. 4. Total energies of intermediate radical (R_1) as a fuction of r_{CC} (angle of C–N–O in R_1(x=1) =125°: taken from *p*-iodonitrosobenzene in M. S. Webster, *J. Chem. Phys.*, **24**, 555 (1956)).

TABLE 1. TOTAL ENERGIES AND THEIR ENERGY CONTRIBUTIONS IN THE NO_x(x=1 or 2)-ROTATION AROUND THE C-N BOND OF THE INTERMEDIATE RADICAL (R_1) (Values are in a.u. unit)

		R_1(x=1)		
θ	0° [a)]	120°	180°	240°
E_T	−62.150	−62.154	−62.151	−62.157
E_N	132.638	132.292	130.868	130.231
E_I	−357.653	−356.949	−354.075	−352.780
E_{II}	162.865	162.503	161.056	160.392
		R_1(x=2)		
θ	0° [a)]	45°	90°	120°
E_T	−79.836	−79.837	−79.838	−79.835
E_N	179.857	179.743	179.544	179.693
E_I	−480.906	−480.655	−480.245	−480.563
E_{II}	221.213	221.075	220.863	221.036

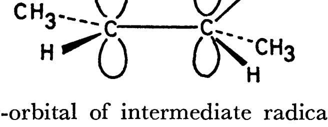
a) At this angle, the oxygen atom is on the C-C bond axis.

Table 2. Bond energies for the C–C bond of intermediate radical (R_1)
(Values are in a. u. unit)

	$R_1(x=1)$	$R_1(x=2)$	*cis*-2-Butene
E_{CC}	−1.161	−1.161	−2.062
E^R_{CC}	−1.249	−1.249	−1.696
s-s	−0.171	−0.173	−0.236
s-p_x	−0.583	−0.585	−0.682
p_x-p_x	−0.330	−0.327	−0.292
p_z-p_z	−0.107	−0.105	−0.398
p_y-p_y	−0.058	−0.059	−0.088
σ-total	−1.084	−1.085	−1.210
π-total	−0.165	−0.164	−0.486
E^V_{CC}	−11.081	−11.019	−12.213
E^J_{CC}	5.516	5.455	5.886
E^K_{CC}	−0.187	−0.186	−0.358
E^N_{CC}	5.840	5.839	6.318

the conformation of the R_1 shown above stable. This stabilization of a rotamer is sometimes caused by the aid of hydrogen bonding,[23] the *gauche* effect,[23–26] and the interaction effect of lone-paired electrons.[27] In this respect, the hydrogen bonding seems to be expected in the hydrogen and oxygen atoms on the same plane of the R_1 ($x=1$). However, the negative overlap population does not favor such a stabilization effect.

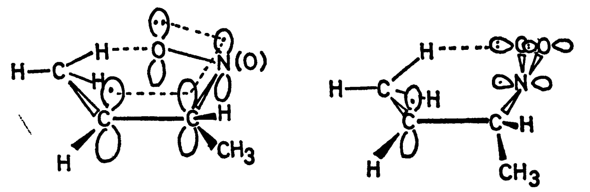
Now, let us extend the discussion to some characteristic features of the intermediate radical (R_1), paying particular attention to the C–C bond-nature and the hfsc (hyperfine splitting constant) of the sp^2-hybrid carbon. In Table 2 we list the E_{CC} and its contribution terms, together with those for *cis*-2-butene. The weakening of the C–C bond strength by the NO_x addition is well reflected in the relatively small E_{CC} and E^R_{CC} values in comparison with those in *cis*-2-butene. Interestingly, the electrostatic interaction ($E^V_{CC}+E^J_{CC}+E^N_{CC}$) becomes more repulsive in the intermediate radical (0.275 a.u.) than in *cis*-2-butene (−0.009 a.u.). This is attributable mainly to the fact that the exchange energy (E^K_{CC}) of the R_1 cannot overcompensate for the repulsion because of the diminution of the π-conjugation in the radical. It is noteworthy with respect to the π-conjugation that a weak π-conjugation (about 13% of E^R_{CC}) in the radical (R_1), as compared with that (about 29% of E^R_{CC}) in *cis*-2-butene, is possible by the aid of the following pseudo π-orbital:



Pseudo π-orbital of intermediate radical (R_1)

The pseudo π-orbital is also supported by the positive bond-order between the p_z-orbitals of the two carbon atoms (0.302 for R_1 ($x=1$) and 0.309 for R_1 ($x=2$)). In this case, the SOMO of R_1 ($x=1$ or 2) is strongly localized by the p_z-orbital of the sp^2-hybrid carbon (spin density=0.830 for R_1 ($x=1$) or 0.828 for R_1 ($x=2$)), and the interaction of this electron-unpaired p_z-orbital and the lone-pair orbitals on the oxygen atom seems to be favorably avoided in the optimum conformation of the intermediate radical (R_1). As to the hfsc values of the sp^2-hybrid carbon in the R_1, the calculated hfsc values, (+)34.47 G for R_1 ($x=1$) and (+)34.40 G for R_1 ($x=2$), are approximately of the same magnitude as that ((+)39.07 G[28]) obtained experimentally for the sp^2-hybrid carbon in ethyl radical.

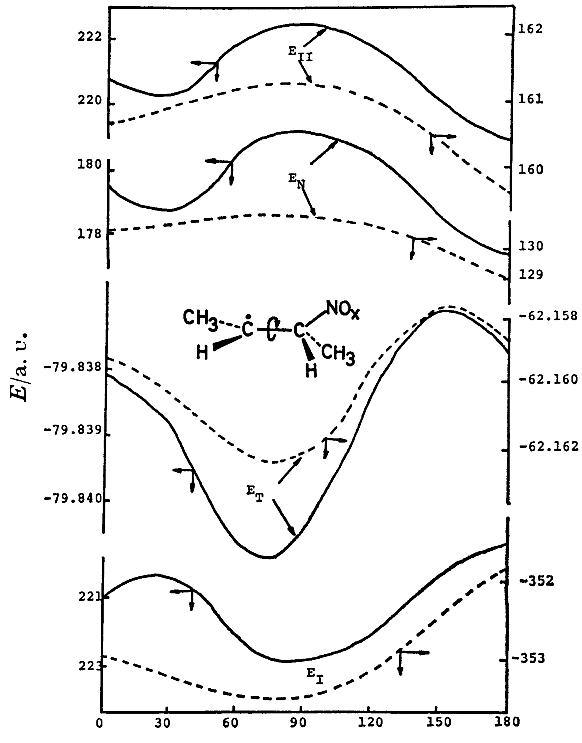
Internal Rotation of the Intermediate Radical. The intermediate radical (R_1) is transformed to the R_2 radical *via* its internal rotation around the C–C bond in two directions, *i.e.*, the clockwise and counterclockwise rotations shown in Fig. 5. As can be seen from Fig. 5, the clockwise rotation has the energetically most stable rotamer at $\theta\simeq60°$, with the most favorable attraction (E_I), while the other rotation has the energetically best conformation at $\phi\simeq120°$, with the least repulsions ($E_{II}+E_N$). These energetically stable conformers correspond to the staggered configurations, while the most unstable ones ($\theta=150°$ and $\theta=30°$) correspond to the eclipsed configurations (see Fig. 6). As may be seen from Fig. 6, the steric repulsion of the two methyl groups seems to destabilize the rotamer, even though the size of this repulsion, 0.4 kcal/mol,[2] is relatively small. We should also discuss the stabilization effects of homoconjugation and hydrogen bonding in the rotamer and the destabilization effect of the repulsive interaction between the unpaired and lone-paired electrons. In an eclipsed configuration ($\theta=90°$), the following coplanar conformation, obtained by the NO_x ($x=1$ or 2) rotation around the C–N bond, seems to be stabilized by the aid of the homoconjugation and the hydrogen bonding.



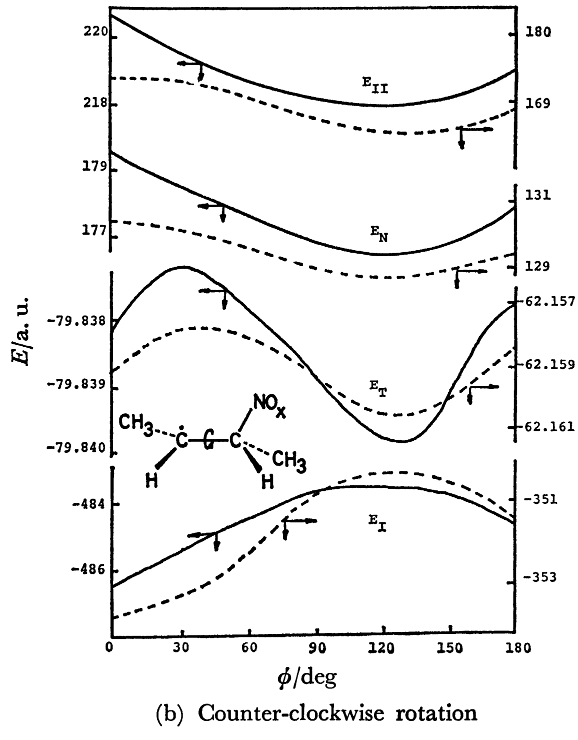
Homoconjugation and hydrogen bonding in the intermediate-radical rotamer

However, the NO_x rotation caused only electron and nuclear repulsions (augmented by the repulsion of the unpaired and lone-paired electrons), which overcome the above stabilization effects. On the other hand, the hydrogen bonding can be expected for the staggered configuration ($\theta=60°$) with a relative small interaction between the unpaired and lone-paired electrons.

Some remarks should be made with regard to the conformation of the rotamer. No change in the C–C bond length (1.45 Å) over ±0.02 Å was observed during the internal rotation of the intermediate radical (R_1), because the E_T values at $r_{CC}=1.43$ or 1.47 Å for the staggered and eclipsed conformers indicated the energetically destabilization of the rotamer. In addition, the fission of the NO_x from the intermediate radical (R_1) during the internal rotation cannot be expected in view of the fact that, at any rotation angle, the rotamer (R_1) was always more stable than the



(a) Clockwise rotation



(b) Counter-clockwise rotation

Fig. 5. Energies for the internal rotation of radical (R_1) as a function of the rotation angle (solid and dotted curves: R_1 ($x=2$) and R_1 ($x=1$) respectively).

system of the isolated NO_x and the isolated rotamer of *cis*-2-butene ($r_{CC}=1.45$ Å was used).

Now, let us discuss the activation barrier of the internal rotation of the radical (R_1). The clockwise-rotation barriers were calculated to be 3.01 kcal/mol for the R_1 ($x=1$) and 2.70 kcal/mol for the R_1 ($x=2$), while the counter-clockwise rotation-barriers were smaller, 1.82 kcal/mol for the former and 1.75 kcal/mol for the latter. The rotation barriers obtained from the present INDO-UHF calculations are relatively small as compared with those obtained from the thermodynamic estimations, 4.2 kcal/mol[29] for the R_1 ($x=1$) and 4±0.5 kcal/mol[2] for the R_1 ($x=2$). At any rate, it can be said that the NO_x ($x=1$ or 2) catalyst seems to depress extremely the activation barrier of the thermal internal-rotation of *cis*-2-butene, 62.8 kcal/mol.[3]

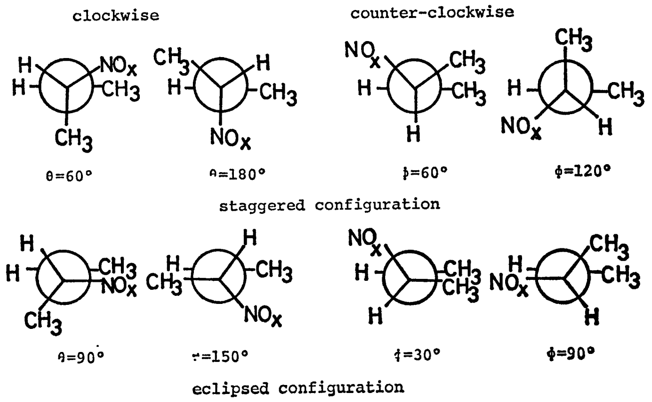


Fig. 6. Staggered and eclipsed configurations of the radical (R_1).

With regard to the intermediate radical (R_2) formed by the internal rotation of the R_1 radical, the R_2 radical is less stable by 0.36 kcal/mol ($x=1$) or 0.50 kcal/mol ($x=2$) than the R_1 radical. However, the electronic properties of the R_2 radical are not so very different from the R_1 radical in terms of the C–C and C–N bond energies ($E_{CC}=-1.158$ a.u. and $E_{CN}=-0.943$ a.u.), the spin density of the unpaired-electron orbital, and the hfsc value of the sp^2-hybrid carbon.

Finally, let us mention briefly the NO_x-fission process in the intermediate radical (R_2), taking the NO_2-fission as an example. The process was simulated much as in the case of the NO_2-addition process by changing $r_{CN}=1.47$—1.56 Å, $r_{CC}=1.45$—1.34 Å, and the hybridization of the carbon binding to NO_2= sp^3-sp^2. The monotoneous destabilization of the E_T values for the above simulated NO_2-fission process brought about a dissociation energy of 44.6 kcal/mol, a value of approximately the same magnitude as the experimental dissociation energy of the C–NO_2 bond, 60 kcal/mol.[2]

The calculations were carried out on a FACOM 230-75 at the Data Processing Center of Kyushu University.

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