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ELECTRONIC STRUCTURES OF VINYLAZIDE, VINYLNITRENE AND 2H-AZIRINE. MECHANISM OF THE REACTION FROM VINYLAZIDE TO 2H-AZIRINE

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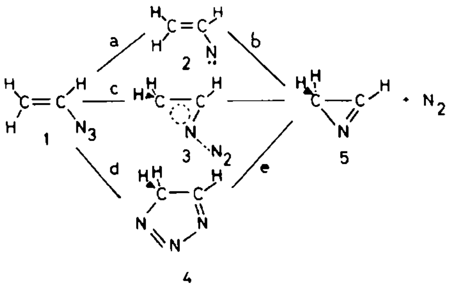
Abstract—The mechanism of the conversion of vinylazides into 2H-azirines is examined by use of *ab initio* MO calculations. It is ascertained that vinylazides have very weak bonds between the vinylnitrene and nitrogen molecule parts. It seems to decompose readily into the two fragments. This is one of the most characteristic features of vinylazides. The reaction is shown to proceed with N_2 at the tail of the vinylnitrene part. This mechanism accounts well for experimental results of the reaction.

Thermolysis or photolysis of vinylazide **1** gives 2H-azirine, **5**.[1] Three mechanisms have been proposed for the reaction. The first is the scheme that an intermediate vinylnitrene, **2**, is formed by release of a nitrogen molecule (N_2) (path a) from **1** and subsequently it isomerizes to 2H-azirine (path b).[1,2a] The second is a concerted mechanism (path c)[1,2b] in which elimination of N_2 is simultaneous with the ring closure through a transition state, **3**. In the last mechanism, vinyltriazole, **4**, is formed by an internal 1,3-dipolar addition (path d), and then it decomposes to **5** (path e).



Recently, Burke *et al.* studied the last mechanism by use of *ab initio* molecular orbital (MO) calculations[3] because diazopropene, an isolectronic molecule of vinylazide, is known to form 1H-pyrazole.[4] However, they did not discuss the elimination step of N_2. Bigot *et al.*[5] discussed the photochemical behaviour of 2H-azirine. However, they did not discuss the reaction forming **5** from a planar vinylnitrene. Taniguchi and his coworkers[6] have systematically investigated decomposition of vinylazides. They showed that E·**1** (which has an alkyl group at the transposition of the azide group) decomposes more rapidly to form 2H-azirine than the Z-isomer (cis-position). The reaction rate through the path e will not be influenced by such substitution. The results suggest that the reaction of vinylazide to 2H-azirine and N_2 proceeds through another path (path a–b or path c) rather than through the path d–e. It is, however, still unclear whether the reaction takes place via the intermediate.

In this paper, electronic structures of vinylazide, vinylnitrene, and 2H-azirine are investigated by use of *ab initio* MO calculations. The mechanism of the reaction from vinylazide to N_2 and 2H-azirine is also examined on the basis of the results obtained.

METHOD OF CALCULATION

All calculations are carried out by use of GAUSSIAN-76 program.[7] An STO-3G minimal basis sets internal to the program are used for all atoms. MP2 calculations[8] and frozen core double excitation CI calculations[9] are also carried out for some reac-

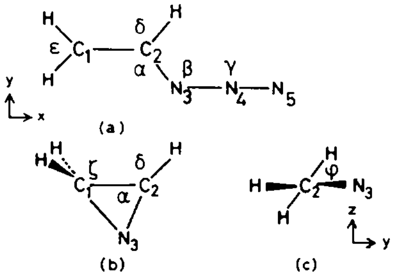


Fig. 1. Parameters for optimizing geometries of 2H-azirine and vinylazide.

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tions. Geometries of vinylazide, 2H-azirine, and vinylnitrene are determined by optimizing all parameters shown in Fig. 1. The path of the elimination of N_2 from vinylazide is obtained by optimizing parameters, r_{12}, r_{23}, r_{45}, α, β, γ, δ, ϵ, φ, ϵ, φ and ζ at a given r_{34}, and the path of isomerization of vinylnitrene to 2H-azirine is also calculated by optimizing r_{12}, r_{23}, δ, ϵ, φ and ζ at given α. The geometric parameters are sequentially and cyclically optimized through the parabola fitting of the energy. The optimized geometries of each point are listed in Tables 1 and 2 together with those of vinylazide, 2H-azirine and vinylnitrene. The C–H bonds lengths (1.09 A) are fixed in all calculations.

RESULTS AND DISCUSSION

Electronic structures of vinylazide and 2H-*azirine*

Figure 2 shows the optimized geometries of 1 and 5 together with their atomic orbital population (AOBP, values in parentheses are AOBP's with π [upper] and σ [lower] natures), atomic bond population (ABP), net charge of each atom in brackets.

ABP between N_3 and N_4 atoms is only 0.26. This is less than half of ABP between N_4 and N_5 ones

Table 1. Bond lengths (A), angles (°), and total energies (E_t, au) for several points along the ring closure paths of vinyazide

	I Vinylazide	II	III	IV	V	VI
r_{34}	1.35	1.54	1.64	1.74	1.84	2.04
r_{12}	1.32	1.32	1.32	1.45	1.45	1.46
r_{23}	1.50	1.47	1.46	1.23	1.26	1.27
r_{45}	1.15	1.16	1.15	1.16	1.15	1.15
α	120.0	119.9	121.1	71.1	69.9	70.8
β	255.3	255.6	257.6	245.2	245.3	249.4
γ	193.1	198.7	201.0	241.4	243.6	242.8
δ	121.7	121.2	120.7	144.3	144.3	148.3
ε	117.6	120.0	120.0	116.4	116.4	116.2
φ	0.0	0.0	0.0	90.0	90.0	90.0
ζ	180.0	180.0	180.0	169.3	169.3	162.7
E_t(+237)	-0.61040	-0.60164	-0.59897	-0.59408	-0.61343	-0.64658

Table 2. Bond lengths (A), angles (°), and total energies (E_t, au) for several points along the ring opening path of 2H-azirine

	I 2H-Azirine	II	III	IV	V	VI Vinylnitrene
α	75.4	85.4	95.4	100.0	110.0	118.2
r_{12}	1.448	1.403	1.454	1.430	1.346	1.336
r_{23}	2.263	1.248	1.246	1.244	1.421	1.435
δ	144.3	139.1	131.3	129.1	122.4	122.5
ε	116.4	119.2	119.6	117.0	120.0	120.0
φ	90.0	90.0	90.0	83.0	10.9	6.8
ζ	163.9	174.1	192.1	195.1	185.6	181.6
E_t(+130)	-0.16542	-0.13333	-0.09419	-0.07940	-0.09595	-0.10112

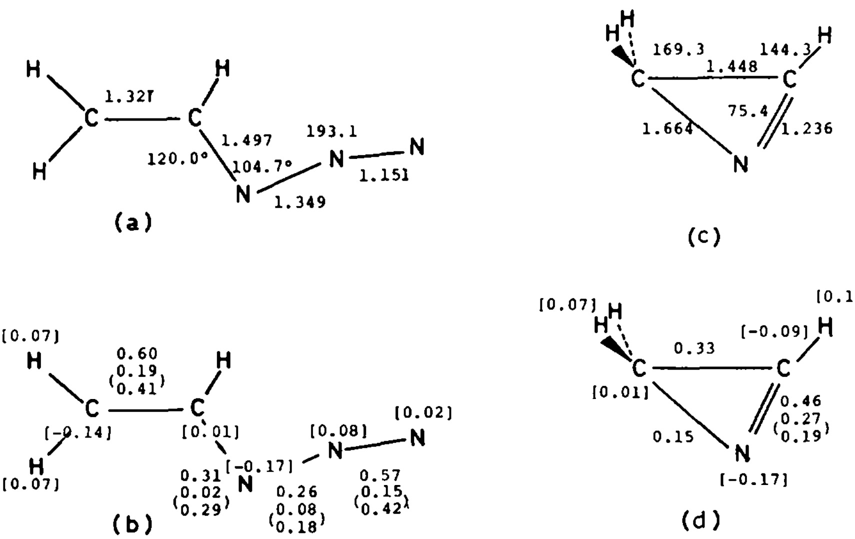
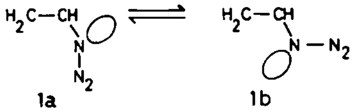


Fig. 2. Optimized geometries and population analysis of vinylazide and 2H-azirine. Values in (a) and (c) are optimized bond lengths and angles. Those in (b) and (d) are net charges (in brackets), ABP, and AOBP. Upper and lower values in parentheses are AOBP's with σ and π natures, respectively.

(0.57) which is close to that of N_2 (0.63). AOBP with π nature (0.02) in the C_2–N_3 bond is much smaller than those in C_1–C_2 (0.19) and N_4–N_5 (0.15) bonds. This result corresponds to the small rotational barrier along the C_2–N_3 axis mentioned below. Therefore, the C_2–N_3 bond has no π bond nature.

Total energy of **1a** optimized by Burke *et al.* is only 0.0006 is lower than that of **1b** we obtained. The rotational barrier along a C_2–N_3 axis is calculated to be negligibly small (5 kcal mol^{-1}).



1a 1b

Therefore, the rapid isomerization between these conformers is expected for vinylazide. This result is in line with the experimental fact that all IR and Raman bands concerned with azide group are split into two signals in low temperature.[6] In the reaction from vinylazide to 2H-azirine, **1b** is considered to be preferred to **1a** because the direction of the lone-pair orbital at N_3 is similar to that of the C_1N_3 bond in 2H-azirine. Therefore the former geometry is used for all discussions about vinylazide.

The optimized geometry of **5** is similar to that observed in 2,2-bis(p-methoxylphenyl)-3-methyl-2H-azirine.[10] The extraordinarily long C1–C3 bond is one of the most characteristic features of 2H-azirines (1.598 A in this 2H-azirine derivative) and it is well represented in the present calculations (1.664 A). The ABP calculated for the C_1N_3 bond (0.15) is very small. The negative charge on C_2 (−0.09) accounts for the upfield ^{13}C NMR chemical shift (136 ppm).[6]

Mechanism through vinylnitrene

The dissociation energy of the N_3N_4 bond is calculated by elongation of this bond without changing the other parameters of the optimized geometry and the potential energy profile is shown in Fig. 3. The potential curve has a maximum near r_{34} = 1.84 A and the energy difference between minimum of the curve (r_{34} = 1.34 A) and the maximum point is only 8.9 kcal mol^{-1}. Nitrogen molecule is predicted to be readily released from vinylazide. That is, it combines weakly with vinylnitrene. A weak N–N bond is common in other alkylazide.[11] This potential curve has a minimum at r_{34} = 2.25 A. The same minimum is also obtained in the decomposition of hydrazoic acid.[12]

The potential energy profile of the ring closure of singlet vinylnitrene is shown in Fig. 4, where all parameters are optimized at a given $C_1C_2N_3$ angle (α) or a dihedral angle (φ). The isomerization of the singlet vinylnitrene is calculated to have an activation energy of 19.2 kcal mol. However, no barrier is obtained when CI or MP2 calculations are performed for geometries optimized by SCF method.[13] The CI method or extended basis sets must be essential in order to estimate the activation energy more correctly. At any rate, 2H-azirine is predicted to be formed from planer vinylnitrene without any activation energy.

Table 2 shows that at the maximum point (α = 100.0°), the structure of reacting species is similar to 2H-azirine rather than the original vinylnitrene.

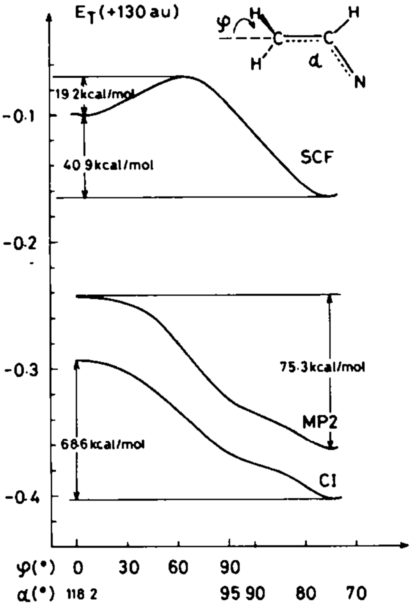


Fig. 4. Potential energy profiles for ring closure of vinylnitrene. SCF, MP2, and CID represent the methods in order to get these curves.

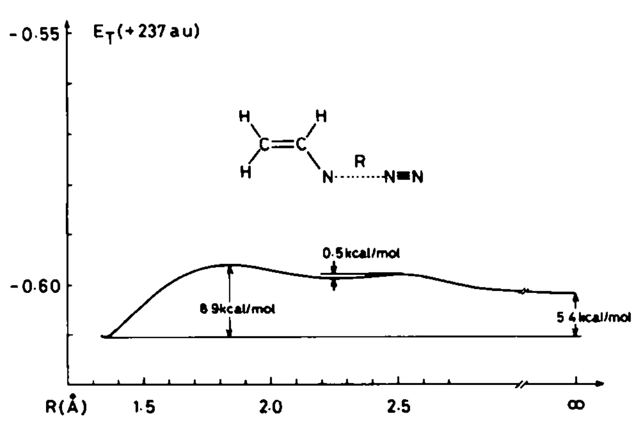


Fig. 3. Potential energy profile for the dissociation of N_2 from vinylazide.

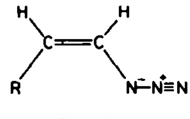
The dihedral angle of the CCN and CH_2 planes, φ, increases while the C_2N_3 bond length, r_{23}, is lengthened in the initial stage of the ring closure ($\varphi = 6.8°$ and $83.0°$, $r_{23} = 1.435$ and 1.224 A for $\alpha = 118.2°$ and $100.0°$, respectively). Therefore, the shift of the double bond from $C_1 = C_2$ to $C_2 = N_3$ is simultaneous with the formation of the three membered ring.

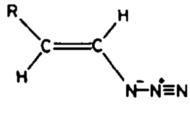
Concerted mechanism

The concerted mechanism through the transition state **3** is examined in this section. The minimum energy path of the decomposition of vinylazide by optimizing all parameters at a given N_3N_4 bond length which is changed within 1.35–2.04 A. Total energies and optimized parameters are listed in Table 1. The results listed in Table 1 show that in this molecule the geometry of the CH_2CHN moiety with r_{34} of less than 1.64 A is completely different from that with longer distances. That is, vinylazide with $r_{34} = 1.64$ A remains the initial geometry ($C_1C_2N_3$ angle is almost 120.0°, dihedralangle is 0.0°) while in longer distances vinylazide has already decomposed to form N_2 and 2H-azirine. On the other hand, Fig. 3 shows that lengthening of r_{34} does not cause destabilization for vinylazide, whereas the other parameters are unchanged. Therefore, it is considered that vinylazide with the bond distances of more than $r_{34} = 1.7$ A has two geometrical isomers, those of $\alpha = 70.0°$ and $120.0°$ (the CH_2CHN moiety is similar to 2H-azirine at $\alpha = 70°$ and to vinylazide at $\alpha = 120.0°$). In order to analyze this nature of vinylazide, geometries with the fixed r_{34} and α are optimized and results are shown in Fig. 5 together with the potential curve for 2H-azirine through singlet vinylnitrene. The figure shows that vinylazide with r_{34} of less than 1.7 A rapidly becomes unstable due to ring closure. On the other hand, that with $r_{34} = 2.04$ A has two different geometrical isomers as expected. This means that there are two potential curves for vinylazide and 2H-azirine + N_2, i.e. they are different paths from each other. In order to connect the two different paths, other geometrical parameters of vinylazide with $r_{34} = 2.03$ A are optimized at given φ. Figure 6 shows the potential energy profile of the reaction connecting these different paths. SCF calculation gives an activation energy, 22.6 kcal mol^{-1} but MP2 calculation gives only 3.5 kcal mol^{-1}. In this reaction, the correlation effect is essential as in the case of the ring closure of vinylnitrene.

Comparison of the two mechanisms

It is expected to have two barriers when the reaction proceeds through vinylnitrene. They are those for the elimination of N_2 and for the rotation of the CH_2 plane. However, results of MO calculations using CI or extended basis sets show that there is no barrier for the latter step. Therefore, this is not the stepwise mechanism that vinylazide decomposes to vinylnitrene and subsequently the intermediate closes its ring to form the final product. The rate determining step of the mechanism is decomposition of vinylazide to vinylnitrene and N_2. However, the rate difference between Z- and E-structures cannot be explained by this one step mechanism.


1b Z-Structure


1b E-Structure

On the other hand, there are two geometrical isomers for vinylazide with r_{34} of more than 1.7 A.

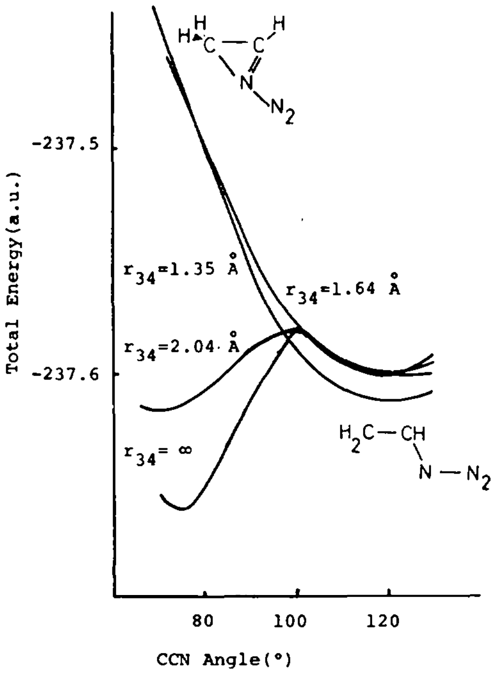


Fig. 5. Trial potential energy profile for ring closure of vinylazide.

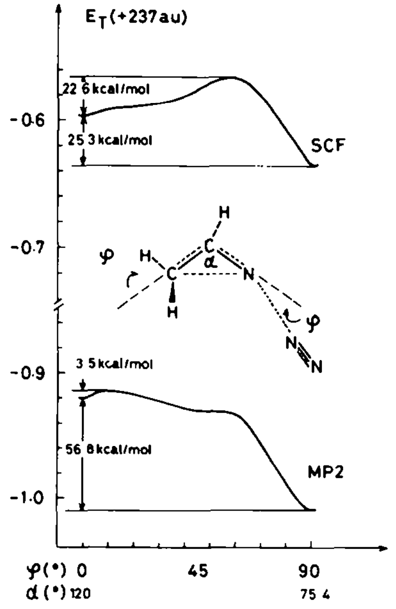


Fig. 6. Potential energy profiles for ring closure of vinylazide.

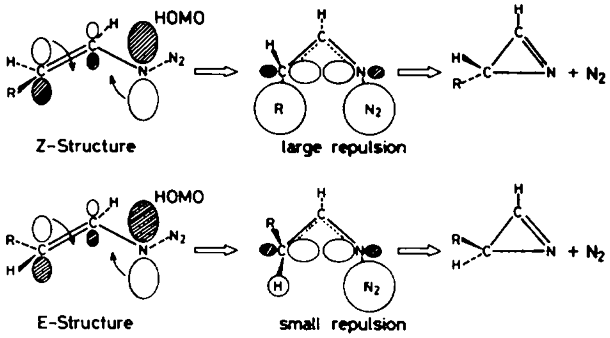


Fig. 7. Explanation of rate differences between E-structure and Z-structure of vinylazide derivatives.

One is the geometry similar to the reactant except for the position of the N_2 fragment and the other is that similar to 2H-azirine with N_2. Total energies of the isomers are nearly the same about the position of r_{34} more than 1.8 A. Around this region, the former may be converted into the latter without a high barrier as the previous section shows. The presence of N_2 near vinylnitrene explains well the substitution effect at C_1 reported by Taniguchi *et al.*[6] They found that E-vinylazides decompose more rapidly than Z-isomers. The substituent on the C_1-position makes vinylazides have **1b** conformation of its steric effect. The nodal property of HOMO of vinylazide causes conrotatory ring closure as Fig. 7 shows. In this closure, Z-structure is unfavorable because of the large steric repulsion between the substituent and the N_2 fragment. Thus, the concerted mechanism can explain the rate difference between Z- and E-structures.

The spin state of the system is unchanged throughout the reaction because vinylnitrene and N_2 interact each other though weak. This expectation is consistent with the experimental finding that the rate of the reaction is scarcely influenced by quenching reagents.[6] Therefore, the ring closure will proceed with N_2 loosely bound to vinylnitrene. It is, however, necessary to lengthen the N_3N_4 bond more than 1.8 A before 2H-azirine formation in order to have the barrier of the reaction small.

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