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Generation, Microwave Spectrum, and *Ab Initio* MO Calculation of *trans*-1-Nitrosopropene, $CH_3CH{=}CH{-}NO$ (*syn* form)

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trans-1-Nitrosopropene (*syn* form) was generated in the gas phase by pyrolysis of 1-chloro-1-methyl-2-(hydroxyimino)ethane and identified by microwave spectroscopy. The microwave spectrum of the pyrolysate was observed in the frequency range from 8.0 to 40.0 GHz. The rotational constants (MHz) were determined as $A = 34\,025(390)$, $B = 2315.62(2)$, and $C = 2198.54(2)$ for $CH_3CH{=}CH{-}NO$ (normal species) and $A = 34\,012(530)$, $B = 2300.04(3)$, and $C = 2182.70(2)$ for $CH_3CH{=}CH{-}^{15}NO$ (^{15}N isotopic species) in the ground vibrational state. The values of planar moment ($P_{cc} = (I_a + I_b - I_c)/2$) obtained for the normal and ^{15}N isotopic species were found to be 1.62(10) and 1.52(13) uÅ^2, respectively. These values are almost the same within the limit of errors. This suggests that the nitrogen atom lies in or is close to the *ab* inertial plane of the molecule and shows also that only two hydrogen atoms are located symmetrically out of the symmetry plane. The pyrolysate was determined to be *trans*-1-nitrosopropene by comparing the observed and calculated rotational constants, κ (Ray's asymmetric parameter), and r_s coordinates of the nitrogen atom. One vibrationally excited state was observed and assigned to the C–N torsional mode (158(50) cm^{-1}). Interesting pyrolysates such as hydrogen cyanide and acetaldehyde were also detected during the pyrolysis of the precursor. The lifetime of *trans*-1-nitrosopropene is found to be ca. 5 s in the waveguide cell.

1. INTRODUCTION

Nitrosoalkenes possess a large synthetic potential since they are comprised of both an alkene activated by an electron withdrawing group of nitroso one and 1,3-diene system having two double bonds of the C=C and N=O groups (*1*). Furthermore, the nitroso group itself reacts with a wide number of reagents (*2*) and allows an easy and simultaneous incorporation of the nitrogen and oxygen by the addition reactions (Diels–Alder (*3*), ene-reaction (*4*), and (2 + 2)-cycloaddition (*5*)). However, in spite of the interesting nitrosoalkenes, isolated nitrosocyclohexene was first reported only in 1976 (*6*).

Francotte *et al.* have prepared and characterized a series of halonitrosoalkenes by treating the α-polyhalooximes with $NaHCO_3$ or K_2CO_3 in dichloromethane (*1*). Only the nitrosoolefin of $Cl_2C{=}C(CH_3){-}NO$ could be isolated purely at room temperature, whereas the others were stable in solution for a few weeks and could be kept for months at −20°C.

Most of the transient nitrosoalkenes have been characterized by *in situ* cycloadditions (vide infrared spectrum) (*1*). Their instability can be explained by the ready decomposition of an intermediate oxazete (four-membered ring molecule) produced by intramolecular cyclization (*1*). This mechanism is supported by the fact that 4,4′-di-*tert*-butyl-4H-1,2-oxazete is isolated by thermolysis of the 2-*tert*-butyl-3,3-dimethyl-1-nitrosobutene (*7*).

Recently, we have succeeded in detecting by mass spectrometry and microwave spectroscopy the unstable nitrosoalkenes of *trans*-$XCH{=}CH{-}NO$ (*syn* form) **3** generated by pyrolysis of $XCHClCH{=}NOH$ **1** and its isotopic species, as shown in Fig. 1 (X = H (*8*, *9*) and Cl (*10*)). The lifetime of $CH_2{=}CH{-}NO$ and $ClCH{=}CH{-}NO$ are found to be ca. 30 and 60 s in the waveguide cell, respectively. The interesting pyrolysates, such as $XCH{=}O$ **5** and HCN **6** were detected during its pyrolysis. The fact suggests that the *trans–syn* form **3** of $XCH{=}CH{-}NO$ is first generated by isomerization of *anti* form **2,** while the by-products of $XCH{=}O$ and HCN are produced by cleavage of oxazete **4** generated by cyclization of **2** (*8–10*).

In this work, we attempted to generate and detect the unstable nitrosoalkenes by pyrolysis of 1-chloro-1-methyl-2-(hydroxyimino)ethane ($X = CH_3$). The observed pyrolysate was determined to be *trans*-1-nitrosopropene (*syn* form) by comparing the observed and calculated rotational constants and r_s coordinates of the nitrogen atom. For the structural parameters, we discuss the C–N torsional mode of the pyrolysate and the possible pyrolysis mechanism of the precursor by referring to the results of *ab initio* MO calculation (MP2/6–31G**).

2. EXPERIMENTAL DETAILS

trans-1-Nitrosopropene was produced by pyrolysis of 1-chloro-1-methyl-2-(hydroxyimino)ethane and also generated by the chemical reaction of the precursor with potassium hydroxide at room temperature using the vacuum solid–gas reaction (VSGR) method (*10*).

Although the microwave spectral lines of the chemical reaction product with KOH were stronger than those of the

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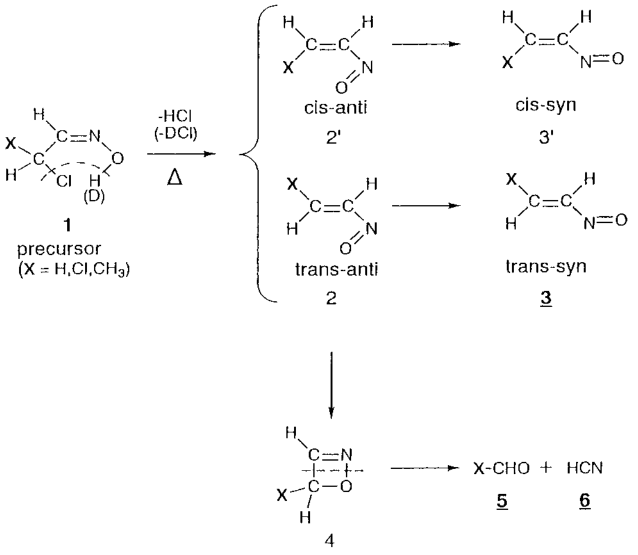


FIG. 1. Possible pyrolysis mechanism of $XCHClCH{=}NOH$ (X = H, Cl, and CH_3). The molecules of *3, 5,* and *6* were identified by microwave spectroscopy.

pyrolysate, their lines disappeared after ca. 10 min from the start of the reaction because the activation of KOH was lost. Therefore, we used the pyrolysis method for observing the microwave spectrum of this unstable molecule.

The precursor was prepared using hydroxylamine hydrochloride and 2-chloropropionaldehyde according to the method used for the preparation of 1,1-dichloro-2-(hydroxyimino)ethane (*10*). The aldehyde employed was generated by thermolysis of its trimer, which was donated by Wakasugi (Kureha Chemical Industrial Co.). The precursor was purified under vacuum distillation at 78°C/11 mmHg. Methanol used in preparation was furthermore separated by repeating a trap-to-trap distillation *in vacuo.* The normal precursor was identified by observing bp (78–79°C/11 mmHg) (*11*) and ^{1}H-NMR and mass spectra.

The ^{15}N isotopic precursor was also synthesized using the mixture of hydroxyl-amine hydrochloride (2 g) and its ^{15}N isotopic compound (99 atom% ^{15}N: 2 g, Matheson USA Co.), according to the method used for producing normal precursor. The mass spectrum of the ^{15}N isotopic precursor showed the new ionic peaks of 108 and 110 m/z, in addition to those of 107 (^{35}Cl) and 109 (^{37}Cl) m/z observed for normal precursor.

The mass spectrum of the pyrolysates of the normal precursor showed 27 (HCN), 36 ($H^{35}Cl$), 38 ($H^{37}Cl$), 44 (C_2H_4O), and 71 (C_3H_5NO) m/z. The ionic peak of 71 m/z showed a maximum intensity at 485°C, while those of 27 and 44 m/z increased as the pyrolysis temperature increases.

The mass spectrum of the pyrolysates (485°C) of the mixture of the normal and ^{15}N isotopic precursor showed the new ionic peaks of 28 ($HC^{15}N$) and 72 ($C_3H_5{}^{15}NO$) m/z.

The pyrolysis apparatus consisted of an unpacked horizontal quartz tube (300-mm length; 5-mm i.d.) heated in a handmade electric furnace (max. 1500°C). The pyrolysis temperature was monitored with a thermocouple fitted to the external wall of the quartz tube and controlled by Digital Temperature Controller (Asashi Rika Co.). The quartz tube was connected to an inlet port of the ionic chamber of the mass filter or to an inlet port on the side of Stark waveguide cell (3-m X-band waveguide). To observe the microwave spectrum of 1-nitrosopropene, it was necessary to use the high-speed rotary pump (350 l/min) because its lifetime was very short.

The quadrupole mass spectrometer employed was Anelva AQA-360 type and the sample pressure (5×10^{-6} Torr; 1 Torr = 133.32 Pa) of the ionic chamber was adjusted with the needle valve. A conventional microwave spectrometer was employed with 100-kHz square-wave Stark modulation. The microwave spectrum was observed in the frequency range from 8.0 to 40.0 GHz. The three microwave sources employed were a signal generator (HP-8672A) and two phase-locked YIG-tuned GaAs oscillators (WJ 5600-301DF and 5610-302DF).

3. *AB INITIO* MO CALCULATION

The GAUSSIAN 94 program (*12*) was employed in the *ab initio* SCF calculations of the molecules. Molecular geometry optimizations were performed by using second-order Møller–Plesset (MP2) perturbation theory (*13*) and 6-31G** basis set (*14*), and the vibrational frequencies were calculated at the MP2/6-31G** level of the theory.

The transition states produced in the pyrolysis mechanism were confirmed by the identification of only one negative eigenvalue obtained at the MP2/6-31G** level of theory. It was performed to verify that two stable points connect to the transition state in the intrinsic reaction coordinate (IRC) calculations (*15*).

4. RESULTS AND DISCUSSION

The microwave spectrum with the characteristic vibrational satellite of the pyrolysate observed at 485°C showed three equidistantly spaced groups ($B + C \simeq 4480$ MHz) between 26.5 and 40.0 GHz at 40 V/cm. They were readily assigned to a-type R-branch transitions (K structure) with $J = 6 \leftarrow 5$ to $J = 8 \leftarrow 7$. Furthermore, the observed microwave spectrum showed some interesting pyrolysates, such as acetaldehyde (*16*) and hydrogen cyanide (*17*). The microwave spectrum of the chemical reaction product of the precursor with KOH at room temperature was just the same as that of the pyrolysate. The microwave spectrum of the pyrolysate of the ^{15}N isotopic precursor was observed lower at the frequency side than that of K structure of the normal species by ca. 250 MHz.

The spectral lines of $K_{-1} = 0$ and 1 were assigned by observing their Stark behavior, while the $K_{-1} = 2$ lines showed broadening. The higher K_{-1} lines ($K_{-1} > 2$) were buried in K structure and could not be observed. The a-type R-branch transitions of the normal and ^{15}N isotopic species in

TABLE 1

Observed Rotational Transition Frequencies (MHz) of *trans*-$CH_3CH{=}CH{-}NO$ (*syn* form) and Its ^{15}N Isotopic Species in the Ground and Excited Vibrational States

Transition[a]	*trans*-$CH_3CH{=}CHNO$				*trans*-$CH_3CH{=}CH^{15}NO$	
	v = 0		v = 1		v = 0	
	ν_{obsd}	O-C[b]	ν_{obsd}	O-C[b]	ν_{obsd}	O-C[b]
3(1,3)←2(1,2)	13366.56	−0.09				
3(0,3)←2(0,2)	13541.39	+0.22				
3(1,2)←2(1,1)	13717.80	−0.08				
4(1,4)←3(1,3)	17821.79	−0.01				
4(0,4)←3(0,3)	18053.36	+0.01				
4(1,3)←3(1,2)	18289.97	−0.13				
5(1,5)←4(1,4)	22276.76	+0.15				
5(0,5)←4(0,4)	22564.26	+0.02				
5(1,4)←4(1,3)	22861.91	−0.07				
6(1,6)←5(1,5)	———[c]		26787.73	−0.18	26541.91	+0.26
6(0,6)←5(0,5)	27073.55	+0.07	27124.01	+0.18	26884.85	−0.03
6(1,5)←5(1,4)	27433.37	−0.06	27476.75[d]	−0.51	27245.46	−0.21
7(1,7)←6(1,6)	31184.79	−0.10	31250.64[d]	−0.64	30963.96	−0.01
7(0,7)←6(0,6)	31580.68	−0.07	31639.56	+0.08	31360.80	+0.10
7(1,6)←6(1,5)	32004.47	+0.12	32054.65[d]	−0.84	31785.35	+0.06
8(1,8)←7(1,7)	35638.17	−0.02	35714.18	+0.11	35385.56	−0.15
8(0,8)←7(0,7)	36085.73	−0.01	36152.75	−0.09	35834.19	−0.03
8(1,7)←7(1,6)	36574.70	+0.04	36633.18	−0.02	36324.39	+0.09
9(1,9)←8(1,8)					39806.73	−0.05

[a] $J'(K'_{-1}, K'_{+1}) \leftarrow J''(K''_{-1}, K''_{+1})$.

[b] $\nu_{obsd} - \nu_{calcd}$.

[c] Overlapped with the absorption line of acetaldehyde.

[d] Not used in the fitting.

the ground and excited vibrational states were assigned as shown in Table 1. The observed spectral lines were fitted using Watson's *A*-reduced Hamiltonian (*18*). Table 2 gives the molecular constants obtained from the least-squares fit of the lines shown in Table 1.

The *b*-type *Q*-branch transitions of $J_{1,J-1} \leftarrow J_{0,J}$ series were predicted in the frequency range of 31–40 GHz from the obtained rotational constants, but these transitions could not be assigned because of the disturbance of the dense spectral lines of the *A*–*E* splitting due to methyl group and/or excited vibrational states of acetaldehyde (*16*).

TABLE 2

Observed Rotational (MHz), Centrifugal Distortion (kHz) Constants, Planar Moments (u Å^2), and C–N Torsional Frequency (ω/cm^{-1}) of *trans*-$CH_3CH{=}CHNO$ (*syn* form) and *trans*-$CH_3CH{=}CH^{15}NO$ (*syn* form) in the Ground and Excited Vibrational States

	trans-$CH_3CH{=}CH{-}NO$		*trans*-$CH_3CH{=}CH{-}^{15}NO$
	v = 0	v = 1	v = 0
A	34025(390)[a]	32782(628)	34012(530)
B	2315.62(2)	2318.73(4)	2300.04(3)
C	2198.54(2)	2203.83(4)	2182.70(2)
Δ_J	0.19(18)		0.19(18)
P_{cc}[b]	1.62(10)		1.52(13)
ΔI[c]	−3.23(18)	−4.05(30)	−3.05(30)
ω		158(50)	

[a] Figures in parentheses are 2.5 times the standard deviation.

[b] $P_{cc} = (I_a + I_b - I_c)/2$.

[c] $\Delta I = I_c - I_a - I_b$.

The values of the planar moment (P_{cc}) were found to be 1.62(10) and 1.52(13) uÅ^2 for the normal and ^{15}N isotopic species in the ground vibrational state, respectively. These values are almost the same within the limit of errors. This fact suggests that the nitrogen atom lies in or is close to the *ab* inertial plane of the molecule. The value of ΔI ($=I_c - I_a - I_b = -3.23(18)$ uÅ^2) of the normal species shows also that only two hydrogen atoms of the methyl group are located symmetrically out of the molecular symmetry plane. It was found that this molecule has C_s symmetry and is a near-prolate symmetric top one ($\kappa = -0.993$).

To identify the pyrolysate observed, we assumed four possible pyrolysates (**2, 3, 2′,** and **3′** shown in Fig. 1), supported by mass peak of 71 *m*/*z* (C_3H_5NO), having the methyl group and discussion under Pyrolysis Mechanism. The candidates of **2, 3,** and **3′,** as shown in Table 3, were found to be the near-prolate symmetric top molecules, but **2′** was not because of $\kappa = -0.247$. Therefore, **2′** was omitted from their candidates. Table 3 gives the observed and calculated rotational constants (A, B, C), $B + C$, κ, the coordinates of the nitrogen atom, and the relative energy differences. Assuming this molecule to have C_s symmetry, the substituted coordinates of the nitrogen atom were calculated from Kraitchman's equation

TABLE 3

Observed and Calculated Rotational Constants (MHz), r_s Coordinates (Å) of Nitrogen Atom, and Relative Energies (kcal/mol) of *trans*-$CH_3CH{=}CHNO$ (*syn* form) and Its Isomers

	Obsd.	Calcd			
		trans–anti	*trans–syn*		*cis–syn*
		2[a]	*3*[a]	*3*[b]	*3′*[a]
A	34025(390)[c]	19361.54	33840.91	33820.21	16979.14
B	2315.62(2)	2777.26	2311.34	2316.54	2951.59
C	2198.54(2)	2465.58	2192.67	2197.43	2553.86
B+C	4514.16(4)	5242.84	4504.01	4513.97	5505.45
κ[c]	−0.993	−0.963	−0.993	−0.993	−0.945
$\lvert a \rvert$[d]	1.226(3)	1.421	1.221	1.236	0.884
$\lvert b \rvert$	0.442(5)	0.53	0.461	0.451	0.433
ΔE		3.9	0	0	0.91

[a] ab initio MO calculation at the MP2/6-31G** level.

[b] Calculated by using the structural parameters of $CH_3CH{=}CH$ and $CH_2{=}CH{-}NO$.

[c] Figures in parentheses are 2.5 times the standard deviation.

[c] $\kappa = (2B-A-C)/(A-C)$.

[d] Calculated from Kraitchman's equation by using I_b and I_c ($\Delta I = -3.12$ u Å^2).

(*19*) by using the four rotational constants of *B* and *C* of the normal and ^{15}N isotopic species and by assuming the value of ΔI ($=I_c - I_a - I_b$) to be -3.12 uÅ^2. The observed values were in good agreement with those of **3**(*trans*-1-nitrosopropene (*syn* form)) predicted by *ab initio* MO calculation and were in excellent agreement with those of **3** calculated by referring the structural parameters of $CH_3CH{=}CH_2$ (*20*) and $CH_2{=}CH{-}NO$ (*9*). The pyrolysate was determined to be *trans*-1-nitrosopropene **3.** This is consistent with the results of *ab initio* MO calculation (MP2/6-31G**) that **3** is the most stable among three candidates, as shown in Table 3. All of the conformation for $XCH{=}CH{-}NO$ generated by pyrolysis of XCHClCH=NOH (X = H, Cl and CH_3) were found to be only *trans–syn* form.

The barrier height (V_3) due to internal rotation of the methyl group of *trans*-1-nitrosopropene was obtained to be 1730 cal/mol by *ab initio* MO calculation (MP2/6-31G**). The *A–E* splitting was predicted to be −7.4 MHz for $2_{12} \leftarrow 1_{11}$ transition, 7.4 MHz for $2_{11} \leftarrow 1_{10}$, −2.1 MHz for $3_{13} \leftarrow 2_{12}$, and 2.1 MHz for $3_{12} \leftarrow 2_{11}$. The two transitions of $J = 2 \leftarrow 1$ were not observed because of the weak spectral lines. The spectral lines of $J = 3 \leftarrow 2$ were observable; however, the splittings of *A*- and *E*-levels were not observed because of very small *A–E* splittings. The fact indicates that the V_3 of *trans*-1-nitrosopropene may be higher than 1730 cal/mol.

The microwave spectrum of **3′,** the isomer of **3,** could not be assigned because of the dense spectral lines due to the *A–E* splitting caused by internal rotation of the methyl group and/or excited vibrational states of acetaldehyde (*16*).

5. EXCITED VIBRATIONAL STATE

Some of the observed spectral lines were assigned to two excited vibrational states (V_a and V_b). The vibrational satellites of V_a were observed at the higher frequency side than the line in the ground vibrational state by an interval of about 60–70 MHz for the $J = 7 \leftarrow 6$ to $8 \leftarrow 7$ transitions, while the V_b were observed in the neighborhood of the line in the ground vibrational state. Table 1 gives the spectral lines assigned for V_a, while those of V_b could not be completely assigned. The vibrational frequencies of the V_a and V_b states were estimated to be 158(30) and 170(30) cm^{-1}, respectively, from the relative intensity measurements. The ΔI value obtained for V_a was found to be $-4.05(30)$ uÅ^2. This value suggests that the vibration of the V_a state is of an out-of-plane mode because the absolute value of ΔI is larger than one of $-3.23(18)$ uÅ^2 obtained for the ground vibrational state (*21*). The V_a state corresponding to the vibrational frequency of 158 cm^{-1} can be ascribed to the excited state due to the C–N

TABLE 4

Assumed and Fitted Structural Parameters[a] of *trans*-$CH_3CH{=}CHNO$ (*syn* form) and Reproduced Rotational Constants (MHz)

Assumed parameters

$r(N{=}O)$: 1.220[c] $r(C_2{-}C_3)$: 1.501[b] $r(C_1{-}H_1)$: 1.081[b]

$r(C_3{-}H_5)$: 1.085[b] $r(C_3{-}H_{3,4})$: 1.089[b] $r(C_2{-}H_2)$: 1.091[b]

$\angle C_2{=}C_1{-}N$: 116.1[d] $\angle C{-}N{=}O$: 112.9[d] $\angle C_1{=}C_2{-}C_3$: 124.3[d]

$\angle C_2{-}C_3{-}H_5$: 111.2[b] $\angle C_2{-}C_3{-}H_{3,4}$: 111.2[b] $\angle C_2{=}C_1{-}H_1$: 120.5[b]

$\angle C_1{=}C_2{-}H_2$: 119.0[d]

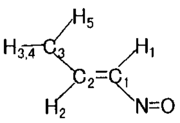
Fitted parameters

	$r(C{=}C)$	$r(C{-}N)$	$\angle C_1C_2C_3$	$\angle C{-}N{=}O$
Set I	1.359(9)	1.409(9)	124.86(3)	[112.9][e]
Set II	1.352(8)	1.415(8)	[124.3]	113.49(5)
ab initio	1.344	1.419	124.91	112.49

Rotational constants

	Normal	Set I		Set II	
	Obsd	Calcd	O–C	Calcd	O–C
A	34025(156)	[34173][f]		[34169]	
B	2315.619(8)	2315.61	0.01	2315.62	0.01
C	2198.542(9)	2198.55	−0.01	2198.54	0.01

	^{15}N species	Set I		Set II	
	Obsd	Calcd	O–C	Calcd	O–C
A	34012(212)	[33731]		[33735]	
B	2300.041(9)	2300.05	−0.01	2300.04	0.01
C	2182.698(9)	2182.69	0.01	2182.7	0.01



[a] Bond lengths in Å and angles in degrees.

[b] Ref. 20.

[c] Ref. 23.

[d] Ref .9.

[e] Assumed parameters.

[f] Not used for the fit of the structural parameters.

TABLE 5

Comparison of the Structural Parameters[a] of *trans*-XCH═CHNO (*syn* form) and Those of *X*CH═CH$_2$ (*X* = CH$_3$, H, and Cl) in the Heavy Atoms Skeleton Studied by *Ab Initio* MO Calculation and Microwave Spectroscopy

	trans-CH$_3$CH=CH-NO[b]			*trans*-CH$_2$=CH-NO[c]		*trans*-ClCH=CH-NO[d]		CH$_3$CH=CH$_2$[e]	CH$_2$=CH$_2$[f]	ClCH=CH$_2$[g]
	Set I	Set II	ab initio[h]		ab initio[h]		ab initio[h]			
r(X-C)	[1.501][i]	[1.501]	1.491	[1.089]	1.079	1.716(5)	1.709	1.501(4)	1.087(1)	1.726(1)
r(C=C)	1.359(9)	1.352(8)	1.344	[1.335]	1.341	1.320(5)	1.344	1.336(4)	1.339(1)	1.333(1)
r(C-N)	1.409(9)	1.415(8)	1.419	1.439(10)	1.426	[1.434]	1.419			
r(N=O)	[1.221]	[1.221]	1.249	[1.220]	1.248	[1.220]	1.251			
∠X-C-C	124.86(3)	[124.3]	124.927	[121.0]	121.87	123.0(5)	123.64	124.3(3)	121.3(1)	122.7(1)
∠C-C-N	[116.1]	[116.1]	116.83	117.0(10)	116.66	[116.1]	114.75	121.5(3)		119.6(2)
∠C-N-O	[112.9]	113.49(5)	112.49	112.9(10)	112.22	[112.9]	112.22			

[a] Bond lengths in Å and angles in degrees.
[b] This work.
[c] Used the structural parameters, improved those shown in Ref. (*9*).
[d] Ref. (*10*).
[e] Ref. (*20*).
[f] Ref. (*25*).
[g] Ref. (*24*).
[h] Used MP2/6-31G** level.
[i] The square brackets indicate the assumed parameters.

torsional mode because the variation of the rotational constants corresponding to the C–N torsional mode with the vibrational quantum number is much larger than that corresponding to the C–C torsional mode. The result of *ab initio* MO calculation (RHF/6-31G**) showed the C–N and C–C torsional frequencies to be 143 and 216 cm^{-1}, respectively. The vibrational frequency of 158(30) cm^{-1} obtained from *trans*-1-nitrosopropene (*syn* form) is very close to the C–N torsional frequencies of *trans*-nitrosoethene (150(20) cm^{-1}) (*8*), *trans*-1-chloro-2-nitrosoethene (120(30) cm^{-1}) (*10*), and *trans*-nitrosocyclopropane (140 cm^{-1}) (*22*) within the errors. Therefore, we assigned the V_a state to the C–N torsional mode. On the other hand, the V_b state might be assigned tentatively to the C–C torsional mode.

6. MOLECULAR STRUCTURE

The partial r_0 structural parameters of *trans*-1-nitrosopropene (*syn* form) were obtained by fitting three parameters (Set I and Set II) to four rotational constants of *B* and *C* of the normal and ^{15}N isotopic species. Set I was made up of two bond lengths of *r*(C═C) and *r*(C—N) and an angle of ∠C—C—C, while Set II consisted of their two bond lengths and an angle of ∠C—N—O. On the replacement of the hydrogen atom of *trans*-nitrosoethene by the methyl group, their two bond lengths and the angle of ∠C—C—C may be expected to change by the effect of the substituted group, while the angle of ∠C—N—O may be slightly changed.

Table 4 gives the assumed and fitted structural parameters and the observed and reproduced rotational constants, respectively. The assumed structural parameters were quoted from those of propylene (*20*), nitrosomethane (*23*), and *trans*-nitrosoethene (*9*). The four rotational constants calculated from these parameters listed in Table 4 were in good agreement with those observed within 0.01 MHz. The structural parameters of both Set I and Set II were consistent with the optimized structural parameters obtained by the *ab initio* MO calculation (MP2/6-31G**) as shown in Table 5, while the assumed bond lengths of *r*(C—C) and *r*(N═O) were different from the theoretical values by ca. 0.01 and 0.03 Å, respectively.

The fitted structural parameters of Set I and Set II were compared with those of the similar molecules, as shown in Table 5. The obtained *r*(C═C) is longer than that of propylene (*20*) because the nitroso group behaves as the electron withdrawing one. The obtained *r*(C—N) is slightly shorter than that of *trans*-nitrosoethene (*9*) because the methyl and nitroso groups take *trans* position, so-called *trans* effect.

The obtained ∠C–N–O is almost the same as that of *trans*-nitrosoethene (*9*) and is consistent with the result calculated by *ab initio* MO calculation. The obtained ∠C–C–C is almost the same as that of propylene (*20*). The order of ∠*X*—C—C of *trans*-*X*CH═CH—NO (*syn* form) is found as follows: X = CH$_3$ > Cl > H. Since the van der Waals radius of the methyl group (2.0 Å) is larger than those of the chlorine atom (1.8 Å) and hydrogen atom (1.2 Å), and the bond length of *r*(C–CH$_3$) is shorter than that of *r*(C–Cl), the repulsion between the methyl group and the hydrogen atom in *cis* position is, therefore, found to be the largest among the *X* groups. This trend is almost the same as that of *X*CH═CH$_2$ (X = CH$_3$ > Cl (*24*) > H (*25*)).

7. PYROLYSIS MECHANISM

The pyrolysates of 1-chloro-1-methyl-2-(hydroxyimino)ethane and its ^{15}N precursor were determined to be *trans*-1-

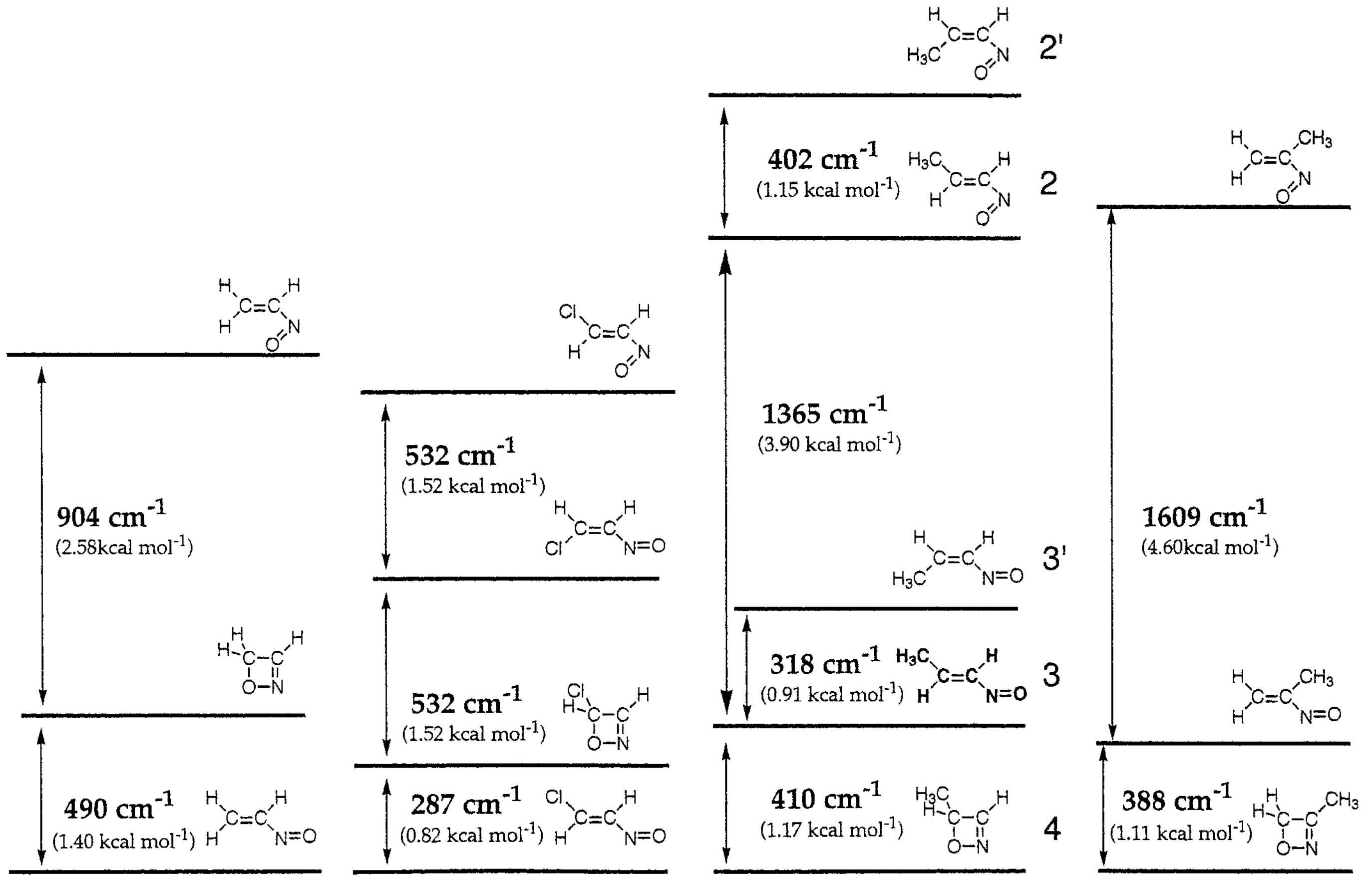


FIG. 2. Relative energy differences between the two isomers of the pyrolysates of *X*CHClCH═NOH. Calculated for $X = \mathrm{H}$ and $\mathrm{CH_3}$ by MP2/6-31G** level without consideration of the zero-point vibrational effect and for $X = \mathrm{Cl}$ by MP2/6-311G** level (*26*). (1 cm^{-1} = 11.96 J/mol, 1 kcal/mol = 4.184 kJ/mol).

nitrosopropene **3,** *trans*-1-nitrosopropene^{15}N, acetaldehyde **5,** hydrogen cyanide **6,** and hydrogen cyanide^{15}N. The spectral lines of **3** appeared at even lower pyrolysis temperature (350°C), while those of **5** and **6** appeared at higher pyrolysis temperature.

Although the two possible *syn* forms, **3** and **3′,** were, respectively, predicted by isomerization of **2** and **2′** generated by the pyrolysis of $\mathrm{CH_3CHClCH{=}NOH}$, as shown in Fig. 1, only **3** was detected by microwave spectroscopy.

Figure 2 shows the result of their relative energy differences (**4:** 0, **3:** 1.17, **3′:** 2.08, **2:** 5.07, **2′:** 6.22 kcal/mol [1 cal/mol = 4.184 J/mol = 0.3498 cm^{-1}]) obtained from *ab initio* MO calculation (MP2/6-31G**) without consideration of the zero-point vibrational effect. The reason why **3** was generated by the pyrolysis of the precursor is that **3** may be the most stable among possible pyrolysates **2, 2′,** and **3′,** except for **4.** The **3** may be generated by the isomerization of the unstable molecule **2,** while **3′** could not be detected because it was less stable than **3** by 0.91 kcal/mol and **2′** is also less stable than **2** by 1.15 kcal/mol.

On the other hand, **5** and **6** may be produced by another passway *via* intermediate, **4,** from **2,** as shown in Fig. 1. The microwave spectra of isotopic species (HC^{15}N) and $\mathrm{CH_2{=}O}$ generated by pyrolysis of $\mathrm{CH_3CHClCH{=}^{15}NOH}$ were observed. These facts suggest that they are generated by cleavage of the four-membered ring produced by intramolecular cyclization of $\mathrm{CH_3CH{=}CH{-}^{15}N{=}O}$, **2.** The pyrolysis mechanism of $X = \mathrm{CH_3}$ of *X*CHClCH═NOH was consistent with those of $X = \mathrm{H}$ (*8, 9*) and Cl (*10*), as shown in Fig. 1.

As shown in Fig. 2, the four-membered ring molecules of $X = \mathrm{H}$ and Cl are slightly less stable than the corresponding *X*CH═CH—NO (*trans–syn* form), while the two four-membered ring isomers of $X = \mathrm{CH_3}$ are slightly more stable than *X*CH═CH—NO (*trans–syn* form) and $\mathrm{CH_2{=}C}X\mathrm{{-}NO}$ (*syn* form), respectively. Figure 2 shows the relative energy differences between two isomers of the possible pyrolysates of *X*CHClCH═NOH ($X = \mathrm{H}$, Cl, and $\mathrm{CH_3}$) calculated by MP2/6-31G** level for $X = \mathrm{H}$ and $\mathrm{CH_3}$ and by MP2/6-311G** level for $X = \mathrm{Cl}$ (*26*). These indicate that the two four-membered ring molecules substituted by the methyl group become slightly more stable than the nitroso molecule.

This result of *ab initio* MO calculation suggests that it is possible to detect **4** ($X = \mathrm{CH_3}$) by microwave spectroscopy.

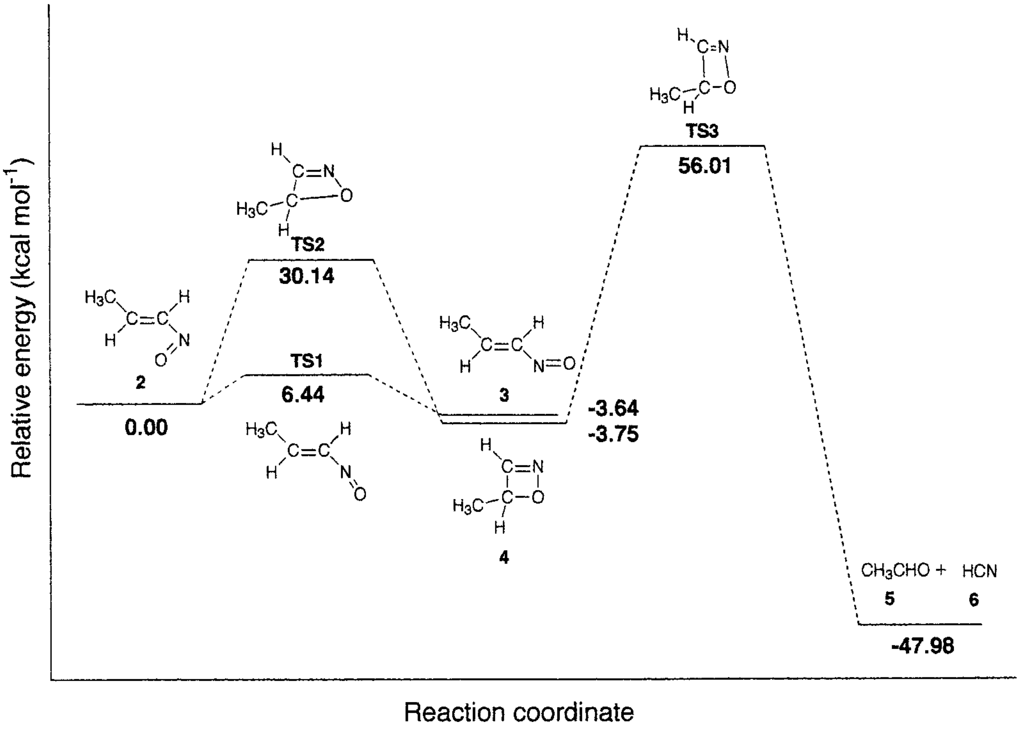


FIG. 3. Potential energy surfaces for the pyrolysis of $CH_3CHClCH{=}NOH$ from **2** to *trans*-$CH_3CH{=}CHNO$ (*syn* form), $CH_3{=}O$, and HCN. Calculated by MP2/6-31G** level of theory, taking account of the zero-point vibrational effect.

8. REACTION ENERGY PROFILE

Figure 3 shows the potential energy surfaces for the pyrolysates of 1-chloro-1-methyl-2-(hydroxyimino)ethane such as *trans*-1-nitrosopropene (*anti* form) **2,** *trans*-1-nitrosopropene (*syn* form) **3,** 4-methyl-4H-1,2-oxazete **4,** acetaldehyde **5,** hydrogen cyanide **6,** and the transition states (TS1, TS2, and TS3), referring to the values for the total and zero-point energies for the products and reactants calculated at the MP2/6-31G** level of theory (*27*). The TS1 corresponds to the isomerization of **2** to form **3,** the TS2 to the ring closure of **2** to form **4,** and the TS3 to the cleavage of **4** to form **5** and **6.**

The TS1 is found to lie 6.44 kcal/mol above **2,** as shown in Fig. 3. On the other hand, the TS2 is found to lie 30.14 kcal/mol above **2,** and TS3 to lie 59.76 kcal/mol above **4.** The calculated energy difference of $X = CH_3$ (29.62 kcal/mol) between the activation energy of the first reaction (from **2** to **4**) and that of the second reaction (from **4** to **5** and **6**) is larger than that of $X = H$ (23.91 kcal/mol) (*28*). The larger activation energy is similar to the experimental results of Weiser and Berndt (*7*). They reported that 4,4-di-*tert*-butyl-4H-1,2-oxazete (four-membered ring molecule) was generated by vacuum pyrolysis of 2-*tert*-butyl-3,3-dimethyl-1-nitrosobutene at 220°C, while it was necessary to increase the pyrolysis temperature to above 240°C to obtain di-*tert*-butylketone and hydrogen cyanide.

The activation energy of 30.14 kcal/mol calculated for the cyclization of **2** of $X = CH_3$ is smaller than that of **2** of $X = H$ (49.96 kcal/mol (*28*)), but this is definitely large in comparison with the usual thermal activation energies of ~12–24 kcal/mol of symmetry-allowed reactions, such as conrotatory ring closure (*29*).

It is interesting to know how to cleave the four-membered ring **4** of $X = CH_3$ in the comparison of the optimized structures (*27*) of **4** and TS3. The four-membered ring ($>C_2$—O—N═C_1—H) of **4** is almost planar because the two dihedral angles of $\angle C_2C_1NO$ and $\angle OC_2C_1N$ are 0.3° and −0.3°, respectively, and the two bond lengths of $r(C_2{-}C_1)$ and $r(O{-}N)$ are 1.485 and 1.452 Å, respectively. On the other hand, the ring structure of TS3 is distorted and twisted ($\angle C_2C_1NO$: 19.9° and $\angle OC_2C_1N$: −30.4°, $r(C_2{-}C_1)$: 1.719 and $r(O{-}N)$: 2.084 Å). The two dihedral angle and bond lengths calculated for TS3 become much larger and longer than those of **4.** These results suggest that the four-membered ring twists and the two bonds of C_2–C_1 and O–N of TS3 lengthen and are cleaved to form acetaldehyde and hydrogen cyanide.

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