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Microwave Spectrum of *trans*-Nitrosoethylene-^{15}N and Pyrolysis Mechanism of Chloroacetaldehyde Oxime

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The microwave spectrum of *trans*-nitrosoethylene-^{15}N (nitrosoethene) generated by pyrolysis of chloroacetaldehyde oxime-^{15}N has been observed in the frequency range from 8.0 to 40.0 GHz. The rotational constants of the ^{15}N species are determined to be A = 50390(201), B = 5057.00(3), and C = 4605.29(3) MHz. The r_s-coordinates (a and b) of the nitrogen atom of *trans*-nitrosoethylene are determined to be 0.540(1) and 0.453 Å, respectively. The three r_0 structural parameters were fitted to four rotational constants (B and C) of the normal and ^{15}N species. The bond length of r(C—N) and two bond angles of ⟨C=C—N and ⟨C–N=O obtained are 1.439(10) Å, 117.1(10)°, and 112.7(10)°, respectively. The possible pyrolysis mechanism of chloroacetaldehyde oxime was discussed on the basis of detecting the three pyrolysates (CH_2=CH—^{15}NO, HC^{15}N, and CH_2=O) by microwave spectroscopy. © 1995 Academic Press, Inc.

1. INTRODUCTION

We have reported the microwave spectrum of the pyrolysate of chloroacetaldehyde oxime which is an unstable molecule (its lifetime is about 30 sec in the waveguide cell (*1*). We have also determined its rotational constants, nuclear quadrupole coupling constants due to the nitrogen atom, dipole moments, and its lowest vibrational frequency (*1*). The three planar molecules as candidates of the pyrolysate of chloroacetaldehyde oxime were predicted from two conditions of mass spectrum of m/z 57(C_2H_3NO) and the planarity of the molecule determined from microwave spectral analysis. They are *trans*-nitrosoehtylene (CH_2=CH-NO), *trans*-*N*-methyleneformamide (CH_2=N-CHO), and *trans*-glyoxalmonoimine (O=CH-CH=NH). The possible candidate of the pyrolysate seemed to be *trans*-nitrosoethylene by comparing the observed rotational constants with ones calculated for the three candidates, and by comparing the observed dipole moments, nuclear quadrupole coupling constants, and C–N torsional frequency with those of *trans*-nitrosocyclopropane (*2*) (see Table III).

In this work, we prepared the isotopic precursor-^{15}N to determine the pyrolysate of chloroacetaldehyde oxime. The pyrolysate of chloroacetaldehyde oxime was determined to be *trans*-nitrosoethylene by comparing the observed r_s-coordinates of the nitrogen atom and dipole moments with those calculated for the three candidates (see Table III). We obtained the three r_0 structural parameters of a bond length of r(C–N) and two bond angles of ⟨C=C–N and ⟨C–N=O. Furthermore, we proposed the possible pyrolysis mechanism of chloroacetaldehyde oxime by observing the microwave spectra of the pyrolysates of the normal and isotopic precursors.

2. EXPERIMENTAL DETAILS

Nitrosoethylene-^{15}N was generated by pyrolysis of chloroacetaldehyde oxime-^{15}N. The oxime was prepared using chloroacetaldehyde and the mixture of hydroxylamine

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TABLE I

Observed Rotational Transitions (MHz) of *trans*-Nitrosoethylene-^{15}N

Transition[a]	Obsd	O-C[b]	Transition[a]	Obsd	O-C[b]
1(0,1)<-0(0,0)	(9662.57	0.28)[c]	4(2,3)<- 3(2,2)	38646.65	-0.06
2(1,2)<-1(1,1)	18872.86	-0.08	4(3,2)<- 3(3,1)	38656.34	0.04
2(0,2)<-1(0,1)	19321.19	-0.04	4(3,1)<- 3(3,0)	38656.34	-0.05
2(1,1)<-1(1,0)	19776.29	0.02	4(2,2)<- 3(2,1)	38680.10	0.09
3(1,3)<-2(1,2)	28307.23	-0.06	4(1,3)<- 3(1,2)	39545.72	0.02
3(0,3)<-2(0,2)	———	[d]	7(1,6)<- 7(1,7)	12643.20	-0.02
3(2,2)<-2(2,1)	28987.07	0.04	8(1,7)<- 8(1,8)	(16253.20	0.30)[c]
3(2,1)<-2(2,0)	29000.29	-0.07	9(1,8)<- 9(1,9)	20310.80	-0.02
3(1,2)<-2(1,1)	29662.47	0.20	10(1,9)<-10(1,10)	24815.19	-0.16
4(1,4)<-3(1,3)	37739.12	0.00	11(1,10)<-11(1,11)	29764.12	0.14
4(0,4)<-3(0,3)	38615.63	-00.07			

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

[b] Observed − Calculated.

[c] Note used in the fitting.

[d] Overlapped with the spectral line ($4_{14} \leftarrow 3_{13}$) of formaldehyde.

hydrochloride (2 g) and its ^{15}N species (98 at.% ^{15}N: 2 g) according to the method used for producing normal species (*1*). The oxime was identified by boiling point and mass spectrum of the four ionic peaks of m/z 93($C_2H_4\,{}^{35}Cl\,{}^{14}NO$), 94($C_2H_4\,{}^{35}Cl\,{}^{15}NO$), 95($C_2H_4\,{}^{37}Cl\,{}^{14}NO$), and 96($C_2H_4\,{}^{37}Cl\,{}^{15}NO$) due to the normal and ^{15}N precursors (1:1) and the natural abundance of chlorine atoms (^{35}Cl:^{37}Cl = 3:1) at 12.8 eV. The mass spectrum of the pyrolysate obtained at 550°C showed two ionic peaks of m/z 57($C_2H_3\,{}^{14}NO$) and 58($C_2H_3\,{}^{15}NO$) which were found to be 1:1 from the relative intensity because of the mixture of the precursor.

A quadrupole mass spectrometer was employed with the ANELVA AQA-360. The conventional microwave spectrometer was employed with 100-kHz square-wave Stark modulation. The microwave spectrum was observed in the frequency range from 8 to 40 GHz. The three microwave sources used were a signal generator (HP-8672A) in the frequency range from 8 to 18 GHz and two phase-locked YIG-tuned GaAs oscillators (WJ 5600-301 F and WJ 5610-302 FD) for 18 to 26.5 GHz and 26.5 to 40 GHz.

3. RESULTS AND DISCUSSION

The observed microwave spectral lines of the pyrolysate were in very good agreement with the frequencies predicted from *trans*-nitrosoethylene-^{15}N. The spectral lines of the ^{15}N species were assigned by referring to Stark behaviors of the normal species. Furthermore, the observed microwave spectra showed some interesting pyrolysates, such as formaldehyde and hydrogen cyanide-^{15}N.

The *a*-type *R*- and *Q*-branch transitions were assigned in the ground vibrational state, as listed in Table I. The frequency data were fitted to the rotational and centrifugal distortion constants using Watson's *A*-reduced Hamiltonian (*3*). Table II gives the constants obtained from the least-squares fit of the spectral lines listed in Table I. The spectral line of the transition of 3(0, 3) ← 2(0, 2) listed in Table I could not be observed because this line was overlapped with that of the transition of 4(1, 4) ← 3(1, 3) of formaldehyde. The *b*-type *Q*-branch transitions of 1(1, 0) ← 1(0, 1) to 3(1, 2) ← 3(0, 3) predicted from the obtained rotational constants could not be observed because the power of the microwave tripler source used was very low.

The value of the obtained inertial defect (ΔI) was −0.15 uÅ^2. Therefore, the pyrolysate was concluded to be a planar molecule from the inertial defects of the normal and ^{15}N species. The substitution coordinates of the nitrogen atom were calculated from the four rotational constants of *B* and *C* of the normal and ^{15}N species, assuming the molecule to be planar, using the Kraitchman's equation (*4*)

$$a^2 = \frac{(I_b^* - I_b)(I_c^* - I_b^* - I_b)}{\mu(I_c - 2I_b)}$$

$$b^2 = \frac{(I_c^* - I_c - I_b^* + I_b)(I_b^* + I_b - I_c)}{\mu(2I_b - I_c)},$$

where $I^*_{g(g=b,c)}$ and I_g are the principal moments of inertia of the substituted and normal species, respectively, and μ is the reduced mass.

Table III gives the observed and calculated coordinates of the nitrogen atom. The obtained *a* and *b* coordinates are quite different from those calculated for *trans*-glyoxalmonoimine. Therefore we can rule it out from among the candidates. On the other hand, the observed coordinates are almost the same as those calculated for *trans*-nitrosoethylene and *trans*-*N*-methyleneformamide.

TABLE II

Observed Rotational Constants (MHz), Centrifugal Distortion Constants (kHz), and Inertial Defect (uÅ^2) of *trans*-Nitrosoethylene and Its Isotopic Species

	CH_2=CH-N=O[a]	CH_2=CH-^{15}N=O[b]
A	52635(173)[c]	50390(201)
B	5071.56(3)	5057.00(3)
C	4625.91(3)	4605.29(3)
Δ_J	1.67(60)	0.09(130)
Δ_{JK}	-5.8(33)	-9.6(36)
ΔI[d]	-0.002(33)	-0.15(2)

[a] Ref. (*1*).

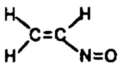
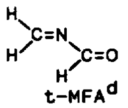
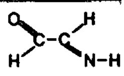
[b] This work.

[c] Error is 2.5 times the standard deviation.

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

TABLE III

Observed and Calculated Rotational Constants (MHz), Coordinates (Å) of Nitrogen Atom, Dipole Moments (D), C–N Torsional Frequency (ω) (cm^{-1}), and Nuclear Quadrupole Coupling Constants (MHz) due to Nitrogen Atoms in the Related Molecules

			Calcd		
	Obsd[a]	t-c-NSP[b]	 t-NSE[c]	 t-MFA[d]	 t-GMI[e]
A	52635(173)		53487	59627	55578
B	5071.56(3)		4905	5130	4609
C	4625.91(3)		4493	4723	4257
B+C	9697.47(6)		9398	9853	8866
|a|	0.540(1)[f]		0.601	0.585	1.778
|b|	0.453(2)[f]		0.501	0.509	0.177
μ_a	2.67(3)	2.846	2.15	3.57	2.47
μ_b	0.748(7)	0.852[g]	0.727	1.68	0.163
μ_t	2.77(3)	2.970	2.27	3.94	2.47
ω	150(20)	140			
				$CH_2=N-CH_3$[h]	$CH_3-CH=NH$[i]
χ_{aa}	0.34(43)	0.8(2)		1.9(3)	-3.51(21)
χ_{bb}	-6.28(33)	-6.05(13)[g]		-5.1(2)	1.01(61)
χ_{cc}	5.94(76)	5.25(13)[g]		3.2(2)	2.50(51)

a Ref.1.
b trans-cyclic-Nitrosopropane(t-c-NSP:Ref.2).
c trans-Nitrosoethylene(t-NSE).
d trans-N-Methyleneformamide(t-MFA).
e trans-Glyoxalmonoimine(t-GMI).
f This work.
g This molecule has the a-c symmetry plane(Ref.2).
h N-Methylmethanimine is the related molecule of t-MFA. [J.Demaison, J.Burie, J.M.Denis, and B.P.Van Eijck, J.Mol.Spectrosc., 107, 250-260 (1984)].
i trans-Ethylidenimine is the related molecule of t-GMI. [F.J.Lovas, R.D.Suenram, D.R.Johson, F.O.Clark, and E.Tiemann, J. Chem. Phys., 72, 4964-4972 (1980)].

Therefore, to distinguish between two candidates, the dipole moments were calculated from the bond moments for the candidates, as shown in Table III. This result shows that the calculated total dipole moment of *trans*-*N*-methyleneformamide is much larger than that of the observed pyrolysate, and that the observed μ_a, μ_b, and μ_{total} were quite close to those calculated from the bond moments for *trans*-nitrosoethylene.

Because it seems to be quite difficult to cleave at 550°C the C=C and N=O double bonds of the pyrolysate generated by dehydrochlorination reported for the deuterated precursor (*1*), it seems to be quite difficult to produce *N*-methyleneformamide ($CH_2=N-CHO$) by the pyrolysis of chloroacetaldehyde oxime. Therefore, we concluded that the observed pyrolysate is *trans*-nitrosoethylene, as stated above. This is also supported by comparing the observed nuclear quadrupole coupling constants due to the nitrogen atom and C-N torsional frequency with those of *trans*-cyclic-nitrosopropane (*2*) reported for normal species (*1*).

4. MOLECULAR STRUCTURE

The partial r_0 structure of *trans*-nitrosoethylene was obtained by fitting the three structural parameters to the four rotational constants of B and C of the normal and ^{15}N species. The fitted parameters were the bond length of r(C–N) and two bond angles of ⟨C=C–N and ⟨C–N=O, because these parameters were unknown in the nitroso compounds.

The assumed parameters of r(C–H) and ⟨H–C=C were referred to those of nitroethylene (*5*). The two bond lengths of r(C=C) and r(N=O) were assumed to be 1.335 and 1.220 Å as quoted for vinyl amine (*6*) and nitrosomethane (*7*), respectively.

The assumed and fitted parameters are shown in Table IV. The four rotational constants calculated from these parameters reproduce those observed within 0.6 MHz, as shown in Table IV.

The three structural parameters obtained were compared with those of the related molecules, as shown in Table V. The obtained r(C–N) bond length is almost the same as that calculated by ab initio MO calculation (*8*) and also those of nitrosomethane (*7*) and nitrosobenzene (*9*). This obtained bond length (C–N) is shorter than that of trifuoronitrosomethane (*10*) because CF_3 group seems to be an electron-attractive one, but is longer than those of *trans*-vinyl azide (*11*) and *trans*-vinyl isocyanate (*12*) because the accumulated double bonds of the above molecules seem to be much more conjugated to the adjacent carbon atoms than the N=O double bond of *trans*-nitrosoethylene (*1*).

TABLE IV

Structural Parameters^{a} and Calculated Rotational Constants (MHz) of *trans*-Nitrosoethylene

Assumed parameters	
r(C-H): 1.070^{b}	<H-C=C: 120.0^{b}
r(C=C): 1.335^{c}	r(N=O): 1.220^{d}
Fitted parameters	
r(C-N): 1.439(10)	
<C=C-C: 117.1(10)	<C-N=O: 112.65(100)

Rotational constants

	CH_2=CH-NO		CH_2=CH-^{15}NO	
	Obsd	Calcd^{e}	Obsd	Calcd^{e}
A	52635(173)	(52664)	50390(201)	(51546)
B	5071.56(3)	5071.59	5057.00(3)	5056.46
C	4625.91(3)	4626.10	4605.29(3)	4604.75

a Bond lengths in Å and angles in degrees.

b Ref. 5.

c Ref. 6.

d Ref. 7.

e Calculated by using the obtained structural parameters.

TABLE V

Comparison of Bond Length of $r(C-N)$ and Angles of $\langle C{=}C{-}N$ and $\langle C{-}N{=}O$ of *trans*-Nitrosoethylene with Those of Related Molecules[a]

Molecule	Fitted parameter			Assumed	
	r(C-N)	<C=C-N	<C-N=O	r(C=C)	r(N=O)
CF_3-NO[b]	1.512(16)		112.4(3)		1.198(4)
CH_3-NO[c]	1.49(3)		112.6(1)		1.220
C_6H_5-NO[d]	1.47(2)		116.0		1.170
CH_2=CH-NO_2[e]	1.470	123.8		1.337	
t-CH_2=CH-NO[f]	1.439(10)	117.1(10)	112.7(10)	1.335	1.220
(ab initio)[g]	1.441	125.7	112.3	1.316	1.184
CH_2=CH-NH_2[h]	1.397(40)	125.2(2)		1.335	
t-CH_2=CH-NNN[i]	1.397	122		1.332	
t-CH_2=CH-NCO[j]	1.380(5)	121.5(5)		1.335	

a Bond lengths in Å and angles in degrees.
b Trifluoronitrosomethane(Ref.10).
c Nitrosomethane(Ref.7).
d Nitrosobenzene(Ref.9).
e Nitroethylene(Ref.5).
f trans-Nitrosoethylene(This work).
g ab initio MO calculation(4-21G*)(Ref.8).
h Vinyl amine(Ref.6).
i trans-Vinyl azide(Ref.11).
j trans-Vinyl isocyanate(Ref.12).

The obtained bond angle of C=C–N is about 9° narrower than that calculated by ab initio MO calculation (*8*), and is also about 3° smaller than that of normal sp^2 hybridization (120°) of the carbon atom.

The obtained bond angle of C–N=O is almost the same as that calculated from ab initio MO calculation (*8*), and is also as that of nitrosomethane (*7*).

5. PYROLYSIS MECHANISM

We propose the possible pyrolysis mechanism of chloroacetaldehyde oxime, as shown in Fig. 1. The detection of $CH_2{=}CH{-}NO$ by pyrolysis of $ClCH_2{-}CH{=}NOD$ leads to the dehydrochlorination of the precursor (*1*), as shown in Fig. 1A. The fact that we observed the pyrolysates, formaldehyde and hydrogen cyanide-^{15}N, in this work indicates that the C=C and N=O double bonds of *cis*-nitrosoethylene (compound 2*), should be cleaved and rearranged to form $CH_2{=}O$ and $HC^{15}N$, as shown in Fig. 1B. Therefore, the generation of $CH_2{=}O$ and $HC^{15}N$ can be elucidated by proposing the formation of the four-membered ring molecule of 4H-1,2-oxazete (*13*) (compound 3*), as shown in Fig. 1. The C–C and O–N single bonds of the four-membered ring seem to be easily cleaved than the C=C and N=O double bonds, and formaldehyde and $HC^{15}N$ seem to be formed.

We conclude that *trans*-nitrosoethylene (compound 4), is produced by isomerization of compound 2 in Fig. 1, which seems to be generated by dehydrochlorination of chloroacetaldehyde oxime, and that formaldehyde and hydrogen cyanide are generated by cleavage of the four-membered ring molecule, which seems to be produced by cyclization of compound 2.

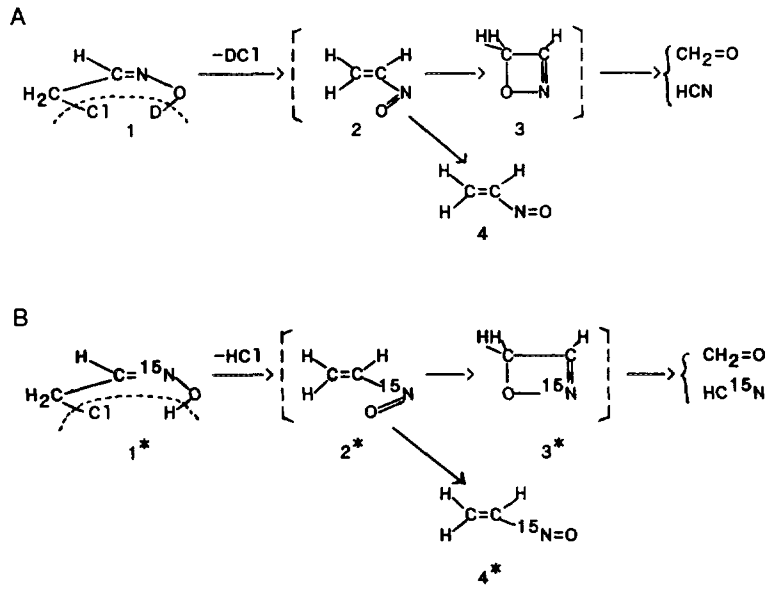


FIG. 1. Possible pyrolysis mechanism of chloroacetaldehyde oxime. (1) Deuterated precursor; (2) *cis*-nitrosoethylene; (3) 4H-1,2-xoazete; (4) *trans*-nitrosoethylene; (1*, 2*, 3*, and 4*) ^{15}N isotopic species.

This pyrolysis mechanism is supported by ab initio MO calculation reported by Sarasola *et al.* (*8*) and Ugalde (*13*). *cis*-Nitrosoethylene is less stable than *trans*-nitrosoethylene by about 1430 cm^{-1} (*8*). 4H-1,2-Oxazete (four-membered ring molecule) is more stable than *cis*-nitrosoethylene by about 940 cm^{-1}, but is less stable than *trans*-nitrosoethylene by about 490 cm^{-1} (*13*).

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