

Infrared Spectrum and General Valence Force Field of *syn*-Vinyl Alcohol

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Abstract: The infrared spectra of matrix-isolated vinyl alcohol and nine D and ¹⁸O isotopically substituted species have been recorded from 200 to 4000 cm⁻¹ at 4 K. Vinyl alcohol has been found to be a major product in very low pressure pyrolysis of cyclobutanol or 3-thietanol diluted with excess argon. In the matrix spectra all but the C-H stretching fundamentals of *syn*-vinyl alcohol have been assigned. The infrared transition frequencies of all isotopic species and the centrifugal distortion constants obtained in the analysis of the rotational spectrum have been used to determine a general valence force field of *syn*-vinyl alcohol. The experimental force field has been compared to force constants from an ab initio calculation.

Until very recently little was known of the vibrational spectrum of vinyl alcohol.¹ A knowledge of its infrared spectrum is important for the detection of vinyl alcohol or other simple enol compounds as reaction intermediates. Hawkins and Andrews² reported the detection of an unknown compound among the reaction products of atomic oxygen with ethylene in solid argon after UV irradiation. They attributed several weak lines in the infrared spectrum to vinyl alcohol on the basis of the isotopic shifts observed for the reaction products between isotopic species of oxygen and ethylene.

In the preceding paper³ an investigation of the rotational spectra of ten isotopic species of *syn*-vinyl alcohol is reported together with the determination of its substitution structure. Having found a convenient route for the production of *syn*-vinyl alcohol with good yield we have recorded a more complete infrared spectrum of *syn*-vinyl alcohol in an argon matrix at 4 K. Furthermore, the analysis of the infrared spectra of nine isotopically substituted species has enabled us to unambiguously assign all fundamentals except for the C-H stretching modes. The assignment was supported by a normal coordinate analysis.

Experimental Section

Apparatus. Infrared spectra were measured in the region 200–4000 cm⁻¹ with a Perkin-Elmer Model 325 spectrophotometer. The spectrometer was calibrated by measuring reference gases in the usual manner.⁴ A liquid-helium bath cryostat equipped with CsI windows was used.⁵ Matrices 300–500- μ m thick were deposited onto the cold window. Matrix deposition rates were measured by means of a small He-Ne laser⁶ and were held between 100 and 150 μ m/h. Both deposition of the matrices and measurements of the infrared spectra were made at liquid-helium temperature.

Production of Vinyl Alcohol and Identification of Its Infrared Spectrum. Cyclobutanol or 3-thietanol was pyrolyzed⁷ in a straight quartz tube (8-mm inner diameter, 1-m long) ending 5 cm in front of the cold window. A 16-cm long electric oven which could be heated up to 1050 °C was installed at the midpoint of the quartz tube. The oven temperature was measured with a chromel–alumel thermocouple. Mixtures of cyclobutanol and argon (1:700) were prepared in advance and stored in a 10-L Pyrex bulb (see Figure 1). The pressure of the mixture flowing through the pyrolysis tube was measured between the regulating valve and the quartz tube and was adjusted between 500 and 550 mtorr. The resulting flow rates correspond to 5–5.5 μ mol/s with an average flow velocity of about 7 m/s. The gas mixture passed the hot zone in ap-

proximately 20 ms. Decomposition started at about 800 °C. In order to get the best yields of vinyl alcohol and to avoid the presence of interfering transitions from cyclobutanol in the infrared spectra pyrolysis was run at 1000 °C. Figure 2 shows a typical spectrum for the pyrolysis products of the parent species of cyclobutanol.

By comparing the intensities of strong transitions of vinyl alcohol, acetaldehyde, and ethylene it was possible to determine the molar ratio of vinyl alcohol:acetaldehyde. Under the condition given above the fraction of vinyl alcohol equalled that of acetaldehyde. Decreasing the cyclobutanol fraction in the quartz tube down to 1:3500 with other conditions unchanged doubled the concentration of vinyl alcohol with respect to acetaldehyde. Increasing the cyclobutanol fraction in the gas mixture up to 1:10 and depositing additional argon through separate inlets in order to maintain a constant dilution in the matrix decreased the yield of vinyl alcohol by a third with respect to the first experiment. This observation indicated that collisions between vinyl alcohol and argon are less effective in tautomerizing the former to acetaldehyde than collisions between vinyl alcohol itself and other reaction products. However, at the highest dilution, the weakest transitions of vinyl alcohol could no longer be detected. As a compromise a cyclobutanol:argon ratio of 1:700 was used generally for preparing the matrices and for recording their spectra.

A second experiment was carried out for each species of cyclobutanol with a slightly modified setup in order to distinguish between infrared transitions originating from vinyl alcohol and those from other products of the thermal decomposition of cyclobutanol. The fully open quartz tube of the former setup at the cryostat end was closed up to a small orifice with a diameter of 0.2 mm. Undiluted gaseous cyclobutanol was flowed slowly through the tube at a pressure of 60 mtorr. Argon was added via four separate inlets and codeposited with the pyrolysis products on the matrix. Residence time of the reaction mixture in the hot zone was drastically increased. A major part of vinyl alcohol was thereby converted to acetaldehyde. At the beginning of this experiment before heating the oven pure cyclobutanol was deposited in the first 20–30- μ m-thick part of the matrix. Thereby traces of unreacted cyclobutanol might be recognized in the first experiment. A typical case is demonstrated in Figure 2. By comparison of the spectra in Figure 2 transitions from vinyl alcohol can be traced easily. This procedure was crucial for the assignments of the spectra for isotopic species of vinyl alcohol where not all spectra of isotopically substituted impurities were known.

Initially we tried to pyrolyze cyclobutanol by flowing it through a heated Knudsen cell made of boron nitride.⁸ At temperatures of 550–650 °C we detected cyclobutanone, ethylene, acetaldehyde, water, and *s-cis*- and *s-trans*-butadiene from their infrared spectra in an argon matrix. However, no vinyl alcohol was found.

Chemicals. The synthesis of ¹⁸O and deuterated species of cyclobutanol is described in the preceding paper.³ The isotopic purity of the samples was determined by comparison of the peak intensity of corresponding transitions for the different isotopic species of vinyl alcohol.

Vinyl alcohol-¹⁸O contained 20% of the parent species. Rapid back-exchange produced 30–40% parent species in vinyl alcohol-*O-d*. The D₂C=CDOH spectra showed transitions of (*E*)- and (*Z*)-HDC=CDOH⁹ each with about 10% abundance. Two samples of cyclobutanol were prepared with a different degree of deuteration in the α position

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Table I. Observed Infrared Transitions (cm⁻¹) of Isotopic Species of *syn*-Vinyl Alcohol in Argon Matrices at 4 K

H ₂ C=CHOH			H ₂ C=CH ¹⁸ OH			H ₂ C=CHOD			H ₂ C=CDOH		
assignment	obsd ^a	i ^b	assignment	obsd ^a	i ^b	assignment	obsd ^a	i ^b	assignment	obsd ^a	i ^b
$\nu_{15}(A'')$	405.8	s	$\nu_{15}(A'')$	404.4	s	$\nu_{15}(A'')$	<u>321.2</u>	s	$\nu_{15}(A'')$	404.4	s
	<u>413.3</u>	s		<u>411.9</u>	s		328.3	s		<u>411.7</u>	s
$\nu_{11}(A')$	<u>486.1</u>	w	$\nu_{11}(A')$	<u>480.6</u>	w	$\nu_{11}(A')$	<u>459.4</u>	w	$\nu_{11}(A')$	<u>481.2</u>	w
	488.8	w		483.3	w		<u>462.9</u>	w		484.1	w
$\nu_{14}(A'')$	<u>698.2</u>	vw	$\nu_{14}(A'')$	<u>695.2</u>	vw	$\nu_{14}(A'')$	<u>697.8</u>	w	$\nu_{14}(A'')$	685.8	w, sh
$\nu_{13}(A'')$	<u>813.7</u>	s	$\nu_{13}(A'')$	<u>813.6</u>	s	$\nu_{13}(A'')$	<u>813.8</u>	s		<u>687.5</u>	w
	813-818	m, sh		815-818	m, sh		816-818	s	$\nu_{13}(A'')$	<u>798.1</u>	w
$\nu_{10}(A')$	<u>942.6</u> ^c	w	$\nu_{10}(A')$	<u>931.0</u>	m	$\nu_{10}(A')$	<u>882.0</u>	m		794-797	w
	944.3 ^c	w		936.9	vw	$\nu_{12}(A'')$	<u>960.1</u>	m	$\nu_{12}(A'')$	<u>814.1</u>	vs
$\nu_{12}(A'')$	960.2	w	$\nu_{12}(A'')$	960.2	w		963.0	m		815.8	s
	963.1	w		963.5	w	$\nu_9(A')$	<u>973.4</u>	s		817.1	s
	<u>971.4</u>	m		<u>971.4</u>	m	?	1026.7	m	$\nu_{10}(A')$	<u>901.1</u>	vw
FR: ^d $\nu_9/$	1074.8	s	FR: ^d $\nu_9/$	1063.5	m, sh	?	1033.0	w	$\nu_9(A')$	<u>990.0</u>	s
$\nu_{14} + \nu_{15}$	1077.5	s	$\nu_{14} + \nu_{15}$	<u>1066.7</u>	vs	?	1054.2	w	$\nu_{14} + \nu_{15}(A')$?	1087.1	w
	<u>1079.0</u> ^e	vs		1106.3	w	?	1089.0	w	$\nu_8(A')$	1137.4	s
	1117.4	m		<u>1113.5</u>	m	?	1181-1183	w		<u>1138.4</u>	vs
	1118.4	m	?	1141.8	w	?	1184.2	w	$\nu_7(A')$	<u>1302.0</u>	m
	<u>1121.3</u> ^e	s	$\nu_8(A')$	<u>1298.4</u>	w	?	1188.7	vw	?	1371.0	vw
$\nu_8(A')$	<u>1300.2</u>	m	$\nu_7(A')$	<u>1320.5</u>	w	?	1196-1198	m	?	1379.0	w
$\nu_7(A')$	<u>1325.5</u>	w	?	1344	vw	$\nu_8(A')$	<u>1198.8</u>	s	?	1393.1	m
$\nu_6(A')$	1409.4	w	?	1393	vw		1200.2	s	?	1478.9	vw
$\nu_{13} + \nu_{14}(A')$	1512.3	w	?	1404.5	w	$\nu_7(A')$	<u>1313.9</u>	w	?	1483.5	w
	1513.8	w	?	1417	w	$\nu_6(A')$	<u>1404.7</u>	w	?	1504.9	w
FR: ^d $\nu_5/2\nu_{13}$	<u>1622.4</u> ^e	s	FR: ^d $\nu_5/2\nu_{13}$	<u>1621.5</u>	s	FR: ^d $\nu_5/2\nu_{13}$	1620.6	s	FR: ^d $\nu_5/2\nu_{13}$	<u>1607.2</u>	vs
	1625.0	s		<u>1660.5</u>	s		1622.7 ^f	s		1610.2	s
	<u>1661.9</u> ^e	vs		1661.7	s		1648.5	w		<u>1619.7</u>	m
	1663.0	s, sh	$\nu_1(A')$	<u>3608.9</u>	s		1661.7 ^f	s		1621.9	w
$\nu_1(A')$	<u>3619.9</u>	s		3614.2	w	$\nu_1(A')$	<u>2672.0</u>	s	$2\nu_{12}(A')$?	1651.2	m
	3625.4	m					2674.4	m	$\nu_1(A')$	<u>3621.0</u>	s
										3626.3	m

D ₂ C=CHOH			<i>(E)</i> -HDC=CHOH and <i>(Z)</i> -HDC=CHOH ^g			D ₂ C=CDOH, <i>(E)</i> -HDC=CDOH, and <i>(Z)</i> -HDC=CDOH ^h					
assignment	obsd ^a	i ^b	assignment	obsd ^a	i ^b	assignment	obsd ^a	i ^b	assignment	obsd ^a	i ^b
$\nu_{15}(A'')$	390.6	s	$\nu_{15}(A'')$ -Z	395.3	m	$\nu_{15}(A'')$	391.4	s	$\nu_8(A')$ -E	1135.7	m
	<u>397.4</u>	s		<u>402.6</u>	m		<u>398.2</u>	s		<u>1136.8</u>	m
$\nu_{11}(A')$	<u>422.5</u>	m	$\nu_{15}(A'')$ -E	<u>408.2</u>	m	$\nu_{15}(A'')$ -Z	395.2	w	FE: ^d $\nu_7/$	1140.6	s
	424.1	m	$\nu_{11}(A')$ -Z	<u>439.1</u>	w		<u>403.0</u>	m	$\nu_{12} + \nu_{15}$?	1152.2	m
$\nu_{14}(A'')$?	563.6	vw		441.1	vw	$\nu_{15}(A'')$ -E	<u>407.3</u>	m		1157.9	m
$\nu_{13}(A'')$	<u>658.7</u>	s	$\nu_{11}(A')$ -E	<u>460.8</u>	w	$\nu_{11}(A')$	<u>418.2</u>	w	?	1166.4	w
	659.9	s		462.4	w		419.8	w	$\nu_{13} + \nu_{14}$?	1212.8	w
$\nu_{12}(A'')$	926.8	w	$\nu_{14}(A'')$ -Z	<u>632.6</u>	m	$\nu_{14}(A'')$ -Z	626.1	w	?	1283.3	w
	929.6	w	$\nu_{13}(A'')$ -Z	<u>747.0</u>	m		<u>628.0</u>	m	?	1292.8	m
	<u>939.1</u>	m	$\nu_{13}(A'')$ -E	<u>781.8</u>	m	$\nu_{13}(A'')$	<u>649.6</u>	vs	?	1298.6	w
				783.1	w		658.7	w	?	1309.2	vw
$\nu_9(A')$	<u>990.8</u>	s	$\nu_{12}(A'')$ -E	<u>963.5</u>	w	$\nu_{13}(A'')$ -Z	707-710	w	?	1315.0	vw
FR: ^d $\nu_8/2\nu_{14}$	<u>1110.4</u> ^e	m	$\nu_9(A')$ -Z	1052.2	s		<u>711.1</u>	m	?	1319.9	w
	<u>1121.6</u> ^e	vs		<u>1054.2</u>	s	$\nu_{12}(A'')$	<u>757.6</u>	w	?	1497	vw
	1123.7	s	$\nu_8(A')$ -E	<u>1089.2</u>	s	$\nu_{10}(A')$	<u>792.1</u>	w	?	1508	vw
?	1317.2	w		1090.4	m, sh	$\nu_{10}(A')$ -Z	<u>858.2</u>	vw	?	1556.8	w
$\nu_6(A')$	<u>1343.9</u>	w	$\nu_8(A')$ -Z	<u>1221.7</u>	m	$\nu_9(A')$	962-965	m	?	1571.4	w
FR: ^d $\nu_5/$	<u>1601.2</u> ^e	s	?	1238.5	vw		<u>966.0</u>	s	FR: ^d $\nu_5/2\nu_{10}$	<u>1574.2</u>	s
$\nu_{12} + \nu_{13}$	<u>1619.7</u> ^c	s	?	1239.4	vw	?	974.9	m		1576.8	s
$\nu_1(A')$	<u>3622.0</u>	s	?	1297.9	w	$\nu_8(A')$	<u>989.1</u>	m		1590.7	s
	3626.2	m	?	1360.9	vw	?	1019	w		<u>1592.5</u>	vs
			$\nu_5(A')$ -Z,E (?)	<u>1637.0</u> ⁱ	m	$\nu_8(A')$ -Z	<u>1048.3</u>	s	?	1603.4	m
			$\nu_5(A')$ -Z,E (?)	<u>1638.9</u> ⁱ	m	?	1123.8	m	?	1615.7	m
									$\nu_1(A')$	<u>3621.6</u>	s

^a Underlined frequencies were used in the normal coordinate analysis. ^b Estimated relative intensity, sh = shoulder. ^c Average value was used for normal coordinate analysis. ^d FR = Fermi resonance. ^e Correction for Fermi resonance perturbations was made with use of the underlined frequencies. ^f No correction for Fermi resonance was possible due to near coincidence with transitions of the parent species. ^g Transitions with additional specifications *E* or *Z* for the assignment refer to (*E*)- or (*Z*)-HDC=CHOH, respectively. ^h Transitions with additional specifications *E* or *Z* for the assignment refer to (*E*)- or (*Z*)-HDC=CDOH, respectively; those with no additional specifications refer to D₂C=CDOH. ⁱ Average value of 1638.0 cm⁻¹ was used in the refinement for both species.

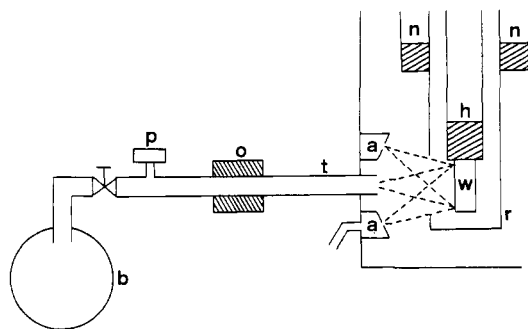


Figure 1. Schematic diagram of the pyrolysis system and the cryostat: (b) 10-L storage bulb, (p) pressure transducer, (o) electric oven, (t) quartz tube, (a) additional argon nozzles, (w) CsI window, (r) radiation shield, (h) liquid helium, and (n) liquid nitrogen.

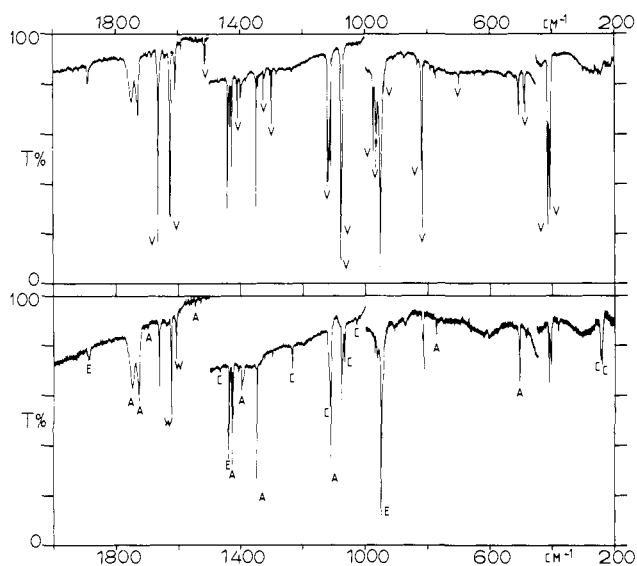


Figure 2. Infrared spectra of matrix-isolated vinyl alcohol. Upper spectrum: reaction products from pyrolysis of cyclobutanol:argon 1:700, oven temperature 1000 °C and flow rate 5 $\mu\text{mol/s}$; V = transitions assigned to vinyl alcohol. Lower spectrum: reaction products from pyrolysis of undiluted cyclobutanol with argon added afterwards, oven temperature 1050 °C and pressure 60 mtorr; A = acetaldehyde, C = cyclobutanol, E = ethylene, and W = water.

which yielded $\text{D}_2\text{C}=\text{CHOH}$, (*E*)- and (*Z*)- $\text{HDC}=\text{CHOH}$, and the parent species after pyrolysis in the ratios 4:1:1:0.25 and 1:1:1:1.

3-Thietanol was prepared from epichlorohydrin and H_2S .¹⁰

Results

Vibrational Assignment in Vinyl Alcohol. The maxima of the observed absorption lines of $\text{H}_2\text{C}=\text{CHOH}$ are listed in Table I. Many of the transitions consisted of two or more individual absorption lines. These lines which were also observed at the high M:A ratio of 1:3500 must result from different trapping sites of vinyl alcohol in the argon matrix. The interpretation is supported by an often similar structure of the corresponding transitions in isotopic species of vinyl alcohol.

The assignment of many vibrational transitions of vinyl alcohol was not clear at the beginning. Therefore, we calculated the complete *ab initio* force field using the 4-21G basis set¹¹ at the structure which was predicted by Bouma and Radom.¹² Subsequently the *ab initio* harmonic force constants were scaled by

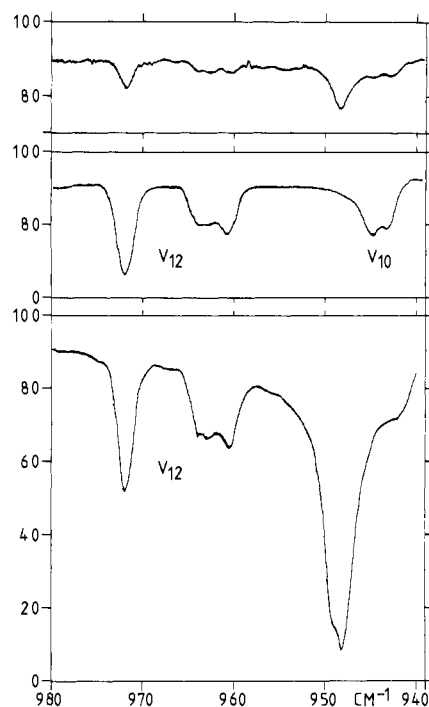


Figure 3. Expanded infrared spectra of the pyrolysis products of 3-thietanol and cyclobutanol. Upper trace: reaction products from undiluted 3-thietanol yielding little vinyl alcohol. Center trace: reaction products from 3-thietanol:argon 1:700 with an optimal yield of vinyl alcohol. Lower trace: reaction products from cyclobutanol:argon 1:700 as in Figure 2.

using scale factors transferred from ethylene, propylene, and methanol.¹³ Predicted transition frequencies from the scaled *ab initio* force field helped in the vibrational assignment of vinyl alcohol.

At this stage the assignment for the following transitions was settled: The strong doublet at $406\text{--}413\text{ cm}^{-1}$ corresponds to $\nu_{15}(\text{A}'')$, the weaker lines at $486\text{--}489\text{ cm}^{-1}$ to $\nu_{11}(\text{A}')$, the strong band at 814 cm^{-1} to $\nu_{13}(\text{A}'')$, the strongest line in the spectrum at 1079 cm^{-1} to $\nu_9(\text{A}')$, the two doublets at $1622\text{--}1625$ and $1662\text{--}1663\text{ cm}^{-1}$ to ν_5 and $2\nu_{13}$ in Fermi resonance with each other, and 3620 cm^{-1} to $\nu_1(\text{A}')$. In the region of $1300\text{--}1400\text{ cm}^{-1}$ three weak lines were observed and tentatively assigned to ν_6 , ν_7 , and $\nu_8(\text{A}')$. The assignment is not yet solved for a strong band at 1121 cm^{-1} where no fundamental was expected, the region between 900 and 1000 cm^{-1} which was overlapped by the strong transition ν_7 of ethylene, and ν_{14} predicted at 670 cm^{-1} . In order to avoid the interfering transition ν_7 of ethylene, vinyl alcohol was prepared by thermal decomposition of 3-thietanol, where thioformaldehyde appeared instead of ethylene.⁷ The resulting matrix spectrum is shown in Figure 3. At $943\text{--}944\text{ cm}^{-1}$ a new transition of vinyl alcohol appeared which was hidden before under the ethylene band. The final assignment of the absorption lines in the region of $940\text{--}980\text{ cm}^{-1}$ was based on ^{18}O isotopic shifts and the site structure of the bands which were similar for all isotopic species.

Furthermore, the infrared intensities were calculated from the dipole moment derivatives $\partial\mu_i/\partial R_j$ determined in the *ab initio* calculation. The results agreed reasonably with the experimental intensities in the matrix spectrum. The fundamental ν_{14} was predicted to be the weakest transition in the infrared spectrum near the detection limit. Indeed a very weak band was then identified at 698 cm^{-1} . The assignment of this transition to ν_{14}

(9) The prefix *Z* denotes isotopic species for which the heavier substituents at each carbon are located on the same side of the double bond. Otherwise the prefix *E* is used.

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Table II. Observed Frequencies (cm^{-1}) of *syn*-Vinyl Alcohol Used for the Calculation of the General Valence Force Field,^a Uncertainties (σ), Calculated Frequencies, and Differences (Δ)

$\text{H}_2\text{C}=\text{CHOH}$					$\text{H}_2\text{C}=\text{CH}^{18}\text{OH}$				
	obsd	σ	calcd	Δ		Δ_{obsd}	σ	Δ_{calcd}	$\Delta\Delta^b$
ν_1	3619.9	18.1	3629.4	-9.5	ν_1	-11.0	1.3	-12.4	1.4
ν_5	1647.8	16.5	1661.9	-14.1	ν_5	-2.1	1.0	-1.6	-0.5
ν_7	1325.5	6.6	1322.8	2.7	ν_7	-5.0	0.7	-5.0	0.0
ν_8	1300.2	6.5	1309.6	-9.4	ν_8	-1.8	0.4	-1.8	0.0
ν_9	1090.0	11.0	1091.1	-1.1	ν_9	-16.0	1.8	-16.3	0.3
ν_{10}	943.4	4.7	944.9	-1.5	ν_{10}	-12.4	2.0	-12.6	0.2
ν_{11}	486.1	2.4	486.5	-0.4	ν_{11}	-5.5	0.7	-5.8	0.3
ν_{12}	971.4	4.9	971.9	-0.5	ν_{12}	0.0	0.2	0.0	0.0
ν_{13}	813.7	4.1	814.0	-0.3	ν_{13}	-0.1	0.2	0.0	-0.1
ν_{14}	698.2	3.5	697.8	0.4	ν_{14}	-3.0	0.5	-2.9	-0.1
ν_{15}	413.3	2.1	414.3	-1.0	ν_{15}	-1.4	0.4	-1.8	0.4
$\text{H}_2\text{C}=\text{CDOH}$					$\text{H}_2\text{C}=\text{CHOD}$				
	obsd	σ	calcd	Δ		obsd	σ	calcd	Δ
ν_1	3621.0	18.1	3629.3	-8.3	ν_4	2672.0	13.4	2646.5	25.5
ν_5	1615.0	16.1	1620.3	-5.3	ν_7	1313.9	6.6	1309.1	4.8
ν_7	1302.0	6.5	1307.0	-5.0	ν_8	1198.8	6.0	1199.5	-0.7
ν_8	1138.4	5.7	1135.9	-1.1	ν_9	973.4	4.9	974.4	-1.0
ν_9	990.0	5.0	989.1	0.9	ν_{10}	882.0	4.4	879.7	2.3
ν_{10}	901.1	4.5	901.6	-0.5	ν_{11}	462.9	2.3	463.6	-0.7
ν_{11}	481.2	2.4	480.9	0.3	ν_{13}	813.8	4.1	814.0	-0.2
ν_{12}	814.1	4.1	814.8	-0.7	ν_{14}	697.8	3.5	697.4	0.4
ν_{13}	798.1	4.0	797.8	0.3	ν_{15}	321.2	1.6	320.3	0.9
ν_{14}	687.5	3.4	687.9	-0.4					
ν_{15}	411.7	2.1	412.1	-0.4					
$\text{D}_2\text{C}=\text{CHOH}$					$\text{D}_2\text{C}=\text{CDOH}$				
	obsd	σ	calcd	Δ		obsd	σ	calcd	Δ
ν_1	3622.0	18.1	3629.4	-7.4	ν_1	3621.6	18.1	3629.3	-7.7
ν_5	1611.0	16.0	1617.7	-6.7	ν_5	1583.0	15.8	1563.1	19.9
ν_6	1343.9	6.7	1338.7	5.2	ν_8	989.1	5.0	987.1	2.0
ν_8	1120.0	7.0	1122.0	-2.0	ν_9	966.0	4.8	965.7	0.3
ν_9	990.8	5.0	991.2	-0.4	ν_{10}	792.1	4.0	789.7	2.4
ν_{11}	422.5	2.1	422.5	0.0	ν_{11}	418.2	2.1	417.7	0.5
ν_{12}	939.1	4.7	938.7	0.4	ν_{12}	757.6	3.8	757.1	0.5
ν_{13}	658.7	3.3	658.4	0.3	ν_{13}	649.6	3.2	648.4	1.2
ν_{15}	397.4	2.0	397.4	0.0	ν_{15}	398.2	2.0	397.2	1.0
$(Z)\text{-HDC}=\text{CHOH}$					$(E)\text{-HDC}=\text{CHOH}$				
	obsd	σ	calcd	Δ		obsd	σ	calcd	Δ
ν_5	1638.0	11.0	1635.7	2.3	ν_5	1638.0	11.0	1637.8	0.2
ν_8	1221.7	6.6	1221.3	0.4	ν_9	1089.2	5.4	1090.0	-0.8
ν_9	1054.2	5.3	1051.4	2.8	ν_{11}	460.8	2.3	461.4	-0.6
ν_{11}	439.1	2.2	438.7	0.4	ν_{12}	963.5	4.8	964.4	-0.9
ν_{13}	747.0	3.7	747.1	-0.1	ν_{13}	781.8	3.9	781.9	-0.1
ν_{14}	632.6	3.2	633.1	-0.5	ν_{15}	408.2	2.0	408.9	-0.7
ν_{15}	402.6	2.0	403.1	-0.5					
$(E)\text{-HDC}=\text{CDOH}$ and $(Z)\text{-HDC}=\text{CDOH}$									
	obsd	σ	calcd	Δ		obsd	σ	calcd	Δ
$\nu_8\text{-}E$	1136.8	5.7	1135.2	1.6	$\nu_{14}\text{-}Z$	628.0	3.1	628.2	-0.2
$\nu_8\text{-}Z$	1048.3	5.3	1048.5	-0.2	$\nu_{15}\text{-}Z$	403.0	2.0	402.6	0.4
$\nu_{10}\text{-}Z$	858.2	4.3	859.7	-1.5	$\nu_{15}\text{-}E$	407.3	2.0	407.2	0.1
$\nu_{13}\text{-}Z$	711.1	3.6	711.0	0.1					

^a Derived from experimental data and ab initio calculations (see text). ^b Shifts between ^{18}O species and parent species are listed.

was strongly supported by the strong transition at 1121 cm^{-1} which appeared to be the combination $\nu_{14} + \nu_{15}$ in Fermi resonance with ν_9 at 1079 cm^{-1} .

Above 2000 cm^{-1} only the O-H stretching mode ν_1 at $3620\text{--}3625\text{ cm}^{-1}$ could be assigned. All C-H stretching modes were seriously overlapped by strong transitions from ethylene and acetaldehyde.

Practically all observed absorption lines of vinyl alcohol could be explained in terms of fundamental and combination bands originating from the *syn* conformer. In the matrix spectra no indication was found for the presence of a second conformer. Every absorption line in the infrared spectrum of the pyrolysis products of cyclobutanol could be attributed to *syn*-vinyl alcohol, ethylene, acetaldehyde, or water.

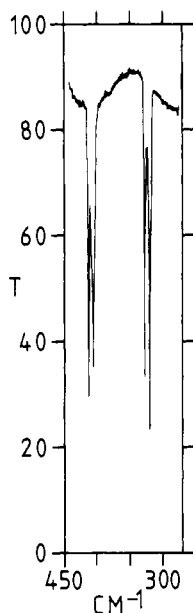
Assignment for Isotopic Species. Vibrational transitions of

$\text{H}_2\text{C}=\text{CH}^{18}\text{OH}$ and $\text{H}_2\text{C}=\text{CHOD}$ were readily assigned with the help of the ab initio force constants and the experience gained during the analysis of the parent species. Small amounts of (*E*)- and (*Z*)-HDC=CHOH and traces of $\text{H}_2\text{C}=\text{CHOH}$ were detected in the spectrum of the $\text{D}_2\text{C}=\text{CHOH}$ sample. The assignment of observed transitions to these species proved to be difficult. By comparing two samples with ratios of 1:1:1 and 4:1:1:0.25 for $\text{D}_2\text{C}=\text{CHOH}$, (*E*)- and (*Z*)-HDC=CHOH, and $\text{H}_2\text{C}=\text{CHOH}$, respectively, the transitions could be allocated to $\text{D}_2\text{C}=\text{CHOH}$ but not to (*E*)- or (*Z*)-HDC=CHOH individually. A distinction between the latter two species was not possible from the experiments alone, since their ratio was always the same. They were assigned with the help of preliminary adjustments of the force constants based on the previously assigned isotopic species. A similar problem existed for the spectrum of the $\text{D}_2\text{C}=\text{CDOH}$

Table III. Observed Centrifugal Distortion Constants (kHz) of *syn*-Vinyl Alcohol Used for the Calculation of the GVFF^a

	H ₂ C=CHOH			H ₂ C=CH ¹⁸ O		
	obsd	calcd	Δ	obsd	calcd	Δ
Δ _J	7.75	7.91	-0.16	7.02	7.20	-0.18
Δ _{JK}	-60.7	-61.3	0.6	-58.9	-58.9	0.0
Δ _K	914	930	-16	918	931	-13
δ _J	1.667	1.690	-0.023	1.458	1.482	-0.024
δ _K	29.06	27.89	1.17	27.05	26.01	1.04
	H ₂ C=CDOH			H ₂ C=CHOD		
	obsd	calcd	Δ	obsd	calcd	Δ
Δ _J	7.45	7.51	-0.06	7.79	7.89	-0.10
Δ _{JK}	-36.2	-37.2	1.0	-49.3	-48.8	-0.5
Δ _K	500.4	511.9	-11.5	608	619	-11
δ _J	1.86	1.87	-0.01	1.784	1.795	-0.011
δ _K	25.1	24.3	0.8	27.77	26.73	1.04
	(E)-HDC=CHOH			(Z)-HDC=CHOH		
	obsd	calcd	Δ	obsd	calcd	Δ
Δ _J	5.78	5.91	-0.13	7.87	8.07	-0.20
Δ _{JK}	-43.9	-44.1	0.2	-44.3	-43.4	-0.9
Δ _K	785	799	-14	558.1	566.1	-8.0
δ _J	1.142	1.161	-0.019	1.849	1.874	-0.025
δ _K	23.05	22.26	0.79	29.59	28.92	0.67
	D ₂ C=CHOH			D ₂ C=CDOH		
	obsd	calcd	Δ	obsd	calcd	Δ
Δ _J	5.83	5.98	-0.15	5.595	5.685	-0.090
Δ _{JK}	-28.0	-27.1	-0.9	-20.3	-20.2	-0.1
Δ _K	457.7	465.8	-8.1	282.8	289.8	-7.0
δ _J	1.268	1.288	-0.020	1.400	1.411	-0.011
δ _K	24.03	23.61	0.42	19.59	19.00	0.59

^aObserved values from the analyses of the rotational spectra in the gas phase³ and calculated values from the GVFF in the second column of Table V and their differences Δ.

**Figure 4.** Expanded infrared spectrum of OH/OD torsional transitions of vinyl alcohol and vinyl alcohol-*O-d*.

sample. The assignment of the simultaneously present (*E*)- and (*Z*)-HDC=CDOH was based on the line intensities and force constant calculations alone without recourse to samples with different concentrations.

In many cases the assignments profited from the band profiles originating from site effects in the argon matrix. A typical example is shown in Figure 3 for ν_{12} where three absorption lines were resolved. The same site effect is seen for this mode in the spectra of other isotopic species. Figure 4 demonstrates the site splittings for the strong OH torsion which are similar for all hydroxyl species. The intensity distribution of the deuterioxy species, however, reverses from the general pattern.

Table IV. Definition of the Internal Coordinates for *syn*-Vinyl Alcohol

$S_1 = r(\text{O}-\text{H}_1)$	O—H stretch
$S_2 = r(\text{C}_1-\text{H}_2)$	C—H stretch
$S_3 = r(\text{C}_2-\text{H}_3)$	C—H stretch
$S_4 = r(\text{C}_2-\text{H}_4)$	C—H stretch
$S_5 = R(\text{C}_1=\text{C}_2)$	C=C stretch
$S_6 = R(\text{C}_1-\text{O})$	C—O stretch
$S_7 = 6^{-1/2}[2\alpha(\text{H}_3\text{C}_2\text{H}_4) - \beta(\text{C}_1\text{C}_2\text{H}_3) - \beta(\text{C}_1\text{C}_2\text{H}_4)]$	CH ₂ s bend
$S_8 = 2^{-1/2}[\beta(\text{C}_1\text{C}_2\text{H}_3) - \beta(\text{C}_1\text{C}_2\text{H}_4)]$	CH ₂ rock
$S_9 = 6^{-1/2}[2\gamma(\text{C}_2\text{C}_1\text{O}) - \beta(\text{C}_2\text{C}_1\text{H}_2) - \beta(\text{OC}_1\text{H}_2)]$	CCO bend
$S_{10} = 2^{-1/2}[\beta(\text{C}_2\text{C}_1\text{H}_2) - \beta(\text{OC}_1\text{H}_2)]$	CCH in plane bend
$S_{11} = \beta(\text{C}_1\text{OH}_1)$	COH bend
$S_{12} = [\tau(\text{H}_3\text{C}_2\text{C}_1\text{O}) + \tau(\text{H}_4\text{C}_2\text{C}_1\text{O}) + \tau(\text{H}_3\text{C}_2\text{C}_1\text{H}_2) + \tau(\text{H}_4\text{C}_2\text{C}_1\text{H}_2)]/2$	C=C torsion
$S_{13} = \tau(\text{H}_3\text{C}_2\text{C}_1\text{H}_4)$	CH ₂ wag
$S_{14} = \tau(\text{OC}_1\text{C}_2\text{H}_2)$	CCH out of plane
$S_{15} = \tau(\text{H}_1\text{OC}_1\text{C}_2)$	OH torsion

The maxima of the observed absorption lines for the isotopically substituted species of vinyl alcohol are listed in Table I. Transition frequencies whose assignment was not certain were later omitted in the force field adjustments.

General Valence Force Field (GVFF) of *syn*-Vinyl Alcohol

Experimental Data and Weighting Scheme. A total of 80 vibrational frequencies from 10 isotopic species of *syn*-vinyl alcohol which could be assigned unambiguously were used for the GVFF refinement. They are collected in Table II. The strongest absorption line was considered in the refinement for those transitions where site structures were resolved. In addition 40 quartic centrifugal distortion constants from 8 isotopic species were taken into account. They were determined from the rotational transitions as reported in the preceding paper³ and are listed in Table III. Since different sorts of experimental data were considered in the

GVFF refinement, statistical weights were attached according to the following estimated uncertainties: 0.5% for the vibrational frequencies except for the ^{18}O species, 10% plus 0.2 cm^{-1} for the ^{18}O shifts, and 10% for all centrifugal distortion constants.

The C=C stretching modes $\nu_5(\text{A}')$ were strongly perturbed by Fermi resonance in nearly all isotopic species. Also the COH bending modes around 1100 cm^{-1} were similarly perturbed in several isotopic species. Corrections have been applied on the basis of relative intensities¹⁴ and on isotopic shifts¹⁵ for the following systems: $\nu_5/2\nu_{13}$ and $\nu_9/\nu_{14} + \nu_{15}$ for $\text{H}_2\text{C}=\text{CHOH}$ and $\text{H}_2\text{C}=\text{CH}^{18}\text{OH}$, $\nu_5/\nu_{12} + \nu_{13}$ for $\text{D}_2\text{C}=\text{CHOH}$, $\nu_5/2\nu_{10}$ for $\text{D}_2\text{C}=\text{CD-OH}$, and $\nu_8/2\nu_{14}$ for $\text{D}_2\text{C}=\text{CHOH}$. Deperturbed frequencies are given in Table II and larger uncertainties were allowed in these cases.

GVFF Refinement. The internal coordinate system used is defined in Table IV. The atomic numbering scheme refers to Figure 1 in the preceding paper³ where the molecular geometry for the normal coordinate analysis is given.

The normal modes of vinyl alcohol have to be classified according to $11\text{A}' + 4\text{A}''$. In the harmonic approximation the centrifugal distortion constants depend on the force constants of the A' block only.

For the A'' block 31 vibrational frequencies were available in order to determine 10 force constants. Their refinement shows a remarkable degree of compatibility. In the final fit all A'' frequencies were reproduced within 1.2 cm^{-1} as shown in Table II. The force constants were accurately determined from the experimental data. They are listed in Table V.

In the A' block the situation is quite different. The 49 infrared frequencies and 40 centrifugal distortion constants were not sufficient to determine 66 force constants. Moreover, important frequencies were missing since the C-H stretching modes could not be assigned. Therefore, the C-H stretching force constants were fixed at 80% of the values from the ab initio calculation. Furthermore, uncertainties in the data were larger for those transitions affected by Fermi resonance. In order to reduce the number of interaction constants to be determined criteria similar to those defined by Hollenstein and Günthard¹⁶ were introduced. All interaction constants between the C-H and O-H stretching modes and the remaining modes were neglected: $F_{ij} = 0$; $i = 1, 2, 3, 4$; $j = i + 1, \dots, 11$. Furthermore, interactions between coordinates which refer to widely separated nuclei in the molecule were omitted: $F_{5,11} = F_{6,7} = F_{6,8} = F_{7,11} = F_{8,11} = 0$. Finally, local symmetry was assumed for the CH_2 group which fixed $F_{5,8} = F_{7,8} = 0$. After several refinement steps it became obvious that further improvements depended on releasing the constraint $F_{6,8} = 0$. The ab initio value of this constant was also substantially different from zero. In the final refinement a total of 23 force constants were adjusted which were based on the experimental data only. The results are given in the first column of Table V.

All but one off-diagonal force constant agree in sign and order of magnitude with the ab initio values as can be seen from Table V. The larger among them are better determined and tend to be smaller than the ab initio values. In order to make use of the predictive power of ab initio calculations we transferred the small off-diagonal force constants which were zeroed first or which showed large standard deviations ($F_{5,9}$ and $F_{7,10}$) from the ab initio values scaled by a factor of 0.8^{13} except for the interaction constants with the O-H and C-H stretching modes which remained zero since their influence was hardly noticed on the other force constants. The resulting force field after refinement of the remaining force constants of the A' block is shown in Table V for comparison with the purely experimental force field and the ab initio values. The calculated transition frequencies of the A' block and the centrifugal distortion constants which are listed in Tables II and III, respectively, refer to this force field. It is regarded as the best approximation to the true force field of *syn*-vinyl alcohol.

Discussion and Conclusions

The thermal decomposition of cyclobutanol or 3-thietanol has been studied with the aim of observing the infrared spectrum of

Table V. General Valence Force Field^a of *syn*-Vinyl Alcohol

force constant	empirical-quantum chemical combination			
	empirical	empirical-quantum chemical	quantum chemical	quantum chemical ^b
A' Block				
O-H stretch	$F_{1,1}$	7.350 (16)	7.350 (16)	8.714
C=C stretch	$F_{5,5}$	8.806 (180)	8.614 (142)	9.988
	$F_{5,6}$	0.513 (92)	0.586 (84)	0.533
	$F_{5,7}$	-0.195 (23)	-0.161 (15)	-0.265
	$F_{5,8}$	0.0^d	0.0248 ^e	0.031
	$F_{5,9}$	0.199 (139)	0.1542 ^e	0.193
	$F_{5,10}$	0.110 (22)	0.099 (21)	0.197
	$F_{5,11}$	0.0^d	-0.0091 ^e	-0.011
C-O stretch	$F_{6,6}$	6.225 (134)	6.136 (93)	7.071
	$F_{6,7}$	0.0^d	-0.0079 ^e	-0.010
	$F_{6,8}$	0.092 (17)	0.076 (14)	0.070
	$F_{6,9}$	0.163 (80)	0.200 (32)	0.275
	$F_{6,10}$	-0.254 (24)	-0.268 (23)	-0.360
	$F_{6,11}$	0.434 (23)	0.432 (17)	0.580
CH_2 s bend	$F_{7,7}$	0.448 (5)	0.445 (5)	0.544
	$F_{7,8}$	0.0^d	-0.0016 ^e	-0.002
	$F_{7,9}$	-0.027 (10)	-0.012 (9)	-0.023
	$F_{7,10}$	0.0025 (48)	-0.0153 ^e	-0.019
	$F_{7,11}$	0.0^d	-0.0060 ^e	-0.008
CH_2 rock	$F_{8,8}$	0.476 (5)	0.484 (5)	0.624
	$F_{8,9}$	0.104 (10)	0.098 (8)	0.122
	$F_{8,10}$	-0.058 (9)	-0.061 (8)	-0.043
	$F_{8,11}$	0.0^d	-0.0075 ^e	-0.009
CCO bend	$F_{9,9}$	0.933 (10)	0.926 (10)	1.059
	$F_{9,10}$	0.101 (31)	0.121 (25)	0.064
	$F_{9,11}$	-0.053 (9)	-0.040 (9)	-0.084
CCH in plane bend	$F_{10,10}$	0.614 (6)	0.619 (7)	0.685
	$F_{10,11}$	-0.049 (5)	-0.056 (5)	-0.076
COH bend	$F_{11,11}$	0.752 (4)	0.761 (5)	0.977
A'' Block				
C=C torsion	$F_{12,12}$	0.1193 (6)		0.150
	$F_{12,13}$	0.0032 (5)		0.008
	$F_{12,14}$	0.0299 (6)		0.019
	$F_{12,15}$	-0.0052 (9)		-0.003
CH_2 wag	$F_{13,13}$	0.1299 (3)		0.197
	$F_{13,14}$	0.0303 (5)		0.037
	$F_{13,15}$	-0.0029 (9)		-0.002
CCH out of plane	$F_{14,14}$	0.2184 (20)		0.316
	$F_{14,15}$	0.0359 (30)		0.048
OH torsion	$F_{15,15}$	0.0727 (8)		0.085

^a The interaction force constants which are not listed were set to zero. Stretching force constants are in $\text{mdyn}/\text{\AA}$, and bending and torsional force constants are in $\text{mdyn}\cdot\text{\AA}$. ^b The ab initio force constants were calculated by using the 4-21G basis set¹¹ at the structure which was predicted by Bouma and Radom.¹² Ab initio force constants which are not listed in the table are the following: $F_{1,2} = -0.0095$, $F_{1,3} = 0.0002$, $F_{1,4} = -0.0426$, $F_{1,5} = 0.0017$, $F_{1,6} = 0.0135$, $F_{1,7} = -0.0014$, $F_{1,8} = -0.0254$, $F_{1,9} = -0.1049$, $F_{1,10} = -0.0229$, $F_{1,11} = 0.2334$, $F_{2,2} = 5.9317$, $F_{2,3} = 0.0275$, $F_{2,4} = 0.0194$, $F_{2,5} = 0.0428$, $F_{2,6} = -0.0365$, $F_{2,7} = 0.0502$, $F_{2,8} = 0.1372$, $F_{2,9} = 0.0400$, $F_{2,10} = -0.0049$, $F_{2,11} = -0.0133$, $F_{3,3} = 5.7680$, $F_{3,4} = -0.0040$, $F_{3,5} = 0.0797$, $F_{3,6} = 0.0466$, $F_{3,7} = 0.0491$, $F_{3,8} = -0.1631$, $F_{3,9} = -0.0344$, $F_{3,10} = 0.0296$, $F_{3,11} = 0.0337$, $F_{4,4} = 5.9397$, $F_{4,5} = 0.0621$, $F_{4,6} = 0.1444$, $F_{4,7} = -0.0113$, $F_{4,8} = -0.0256$, $F_{4,9} = -0.1235$, $F_{4,10} = 0.0096$, $F_{4,11} = 0.0235$. ^c Numbers in parentheses represent one standard deviation. ^d Not fitted. ^e Not fitted, but set at 80% of the ab initio value.

vinyl alcohol. Besides vinyl alcohol only ethylene or thioformaldehyde, respectively, and acetaldehyde were found among the decomposition products trapped in an argon matrix. Depending on the experimental conditions the ratio vinyl alcohol:acetaldehyde could be increased up to 2:1. In the region between 200 and 2000 cm^{-1} all fundamentals of *syn*-vinyl alcohol were identified. No

indication for the existence of a second conformer was obtained from the matrix spectra.

Recently, Hawkins and Andrews² reported the observation of vibrational transitions of vinyl alcohol produced in reactions of oxygen atoms with ethylene in an argon matrix after UV irradiation. The analysis of their spectra was less complete since more products were formed simultaneously and the transitions of vinyl alcohol were weaker than in our investigation. Our results confirm their observations and assignments of strong transitions. They observed additional absorption lines in regions of strong transitions which were not present in our spectra. They might be due to increased site splittings in the matrix after the photolytic reactions or indicate interactions between vinyl alcohol and other products.

The normal coordinate analysis produced the first rather complete GVFF of a simple enol compound. Comparison with force constants of molecules with analogous partial structures revealed some characteristic features of the GVFF of *syn*-vinyl alcohol. The partial double bond character of the C—O bond arising from the interaction of the lone pairs at the oxygen with the C=C double bond is reflected in the large C—O stretching force constant of 6.14 mdyn/Å. Formic acid which is isoelectronic with vinyl alcohol shows a similar increase of the C—O stretching force constant of 6.1–6.23 mdyn/Å¹⁷ compared to methanol with 5.27–5.28 mdyn/Å.^{13b,18} The increase of the C—O stretching

force is also reflected in the decrease of the C—O bond length going from methanol to vinyl alcohol.³ The partial double bond character of the C—O bond is further demonstrated by the increase of the frequency of OH torsion in vinyl alcohol with respect to methanol (413 vs. 271 cm⁻¹). The corresponding force constant of 0.073 mdyn Å in vinyl alcohol is almost tripled compared to 0.027 mdyn Å in methanol.^{13b,18}

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Registry No. H₂C=CHOH, 557-75-5; H₂C=CH¹⁸OH, 90134-15-9; H₂C=CHOD, 64066-40-6; H₂C=CDOH, 90134-16-0; D₂C=CHOH, 90134-17-1; (*E*)-HDC=CHOH, 90134-18-2; (*Z*)-HDC=CHOH, 90134-19-3; D₂C=CDOH, 90134-20-6; (*E*)-HDC=CDOH, 90134-21-7; (*Z*)-HDC=CDOH, 90134-22-8.

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Communications to the Editor

Reaction of Cyclic Ketene Acetal and Carbon Disulfide through Macrozwitterion

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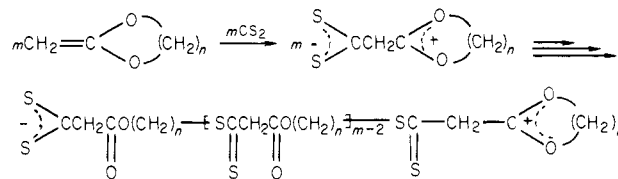
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It has been reported that ketene *N,N*- and *N,S*-acetals, which belong to a class of the most electron-rich olefins, react easily with heterocumulenes to give betaines.¹ It is also known that the unsaturated carbon-carbon double bond of ketene acetals is highly polarized and the β-carbon atom has a strong anionoid character because of the electron-donating property or the mesomeric effect of oxygen atom. Therefore, most of ketene acetals are susceptible to attack by the protic substrates and undergo cationic polymerization.²⁻³ From a different viewpoint, radical ring-opening polymerizations have been also reported.⁴

It is anticipated that cyclic ketene acetals may react with carbon disulfide to form betaines, which react successively with each other to afford macrozwitterions.



We now report a new reaction of 4-methyl-2-methylene-1,3-dioxolane (I) with carbon disulfide and a structure of the resulting product.

The reaction of I with CS₂ was carried out at 80 °C for 48 h in a glass ampule treated with 3-(triethoxysilyl)propylamine to prevent cationic homopolymerization of I on the glass surface.⁵ If the reaction of I with CS₂ proceeds via the zwitterion mechanism, the resulting copolymer should be the alternating structure. However, the elemental analyses indicated that the obtained copolymer consists of I and CS₂ with the ratio of 2:1, contrary to our expectation. Here, we must call attention to the copolymer (composition of I and CS₂; 2:1) containing dithioester structure of malonic acid. It has been reported that the dithioester of cyanomalonic acid exists exclusively as an enthiol form at equilibrium.⁶ Therefore, it can be assumed that dithiomalonate formed by the reaction of I with CS₂ tautomerizes to enthiol form, which may react easily with I to give monothio ortho acetate. The IR spectrum of the copolymer showed characteristic absorption bands at 1745 and 1700 cm⁻¹ attributable to ester C=O and 1530 cm⁻¹ assignable to unsaturated C=C. ¹H NMR spectrum indicated the peaks at 5.90 (s, 1 H), 5.21 (m, 2 H), 3.02–3.40 (br,

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(5) In a 100-mL sealed polymerization tube, 2 g (0.02 mol) of I and 5 g (0.06 mol) of CS₂ were heated at 80 °C for 48 h. After the tube was cooled and opened, the reaction mixture was poured into a large excess of *n*-hexane to precipitate the copolymer. Purification of the copolymer was carried out by the reprecipitation from chloroform to methanol. The precipitated gum-like material was dried under reduced pressure at room temperature for 2 days to give 2.45 g of an orange red copolymer: *M_n*, 11 000 (by GPC); softening point 65–75 °C. Anal. Calcd for (C₅H₈O₂)₂(CS₂)₁: C, 47.79; H, 5.85; S, 23.20. Found: C, 47.47; H, 5.91; S, 22.87.

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