Preparation and the Microwave and Infrared Spectra of Vinyl Ketene

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Vinyl ketene (1,3-butadiene-1-one) has been synthesized by vacuum pyrolysis of 3-butenoic 2-butenoic anhydride. The microwave and infrared spectra of vinyl ketene in the gas phase at room temperature have been studied. The *trans*-rotamer has been identified, and the spectroscopic constants were found to be $\tilde{A} = 39571(48)$ MHz, $\tilde{B} = 2392.9252(28)$ MHz, $\tilde{C} = 2256.0089(28)$ MHz, $\Delta_J = 0.414(31)$ kHz, and $\Delta_{JK} = -34.694(92)$ kHz. The electrical dipole moment was found to be 0.987(23) D with $\mu_a = 0.865(14)$ D and $\mu_b = 0.475(41)$ D. A tentative assignment has been made for 17 of the 21 normal modes of vibration.

Introduction

Vinyl ketene (1,3-butadiene-1-one) has been proposed as an intermediate from the dehydrochlorination of *trans*-2-butenoyl chloride [1]. Rousseau et al. have proposed a red compound, stable up to − 160 °C, from the flash thermolysis of spiro[2,3]hexan-4-ones to be the free vinyl ketene, since the reaction with methanol gave methyl vinylacetate [2]. Very recently Terlouw et al. have reported that the major product from the gas phase thermal decomposition of ethyl but-3-ene-1-yne ether is vinyl ketene identified from its mass spectrum and photoelectron spectrum [3]. However, the present study appears to be the first where vinyl ketene has been isolated and unambiguously identified. The microwave and infrared spectra of vinyl ketene will be presented and a tentative vibrational assignment will be proposed.

Vinyl ketene can have two planar rotamers of which the *trans* configuration shown in Fig. 1 is expected to be the more abundant one at room temperature. At present only the *trans*-rotamer has been observed in the microwave spectrum and the major features in the infrared spectrum can be explained on the basis of just one rotamer. In the structurally related molecule vinyl allene (1,2,4-pentatriene) [4] only the *trans*-rotamer has been observed so far, while for vinyl isocyanate [5] and vinyl azide (6] both the *trans* and *cis* configurations have been reported.

Experimental Procedures

Vinyl ketene was first found in this laboratory in the products from the vacuum pyrolysis of *trans*-2-butenoic anhydride (crotonic anhydride from E. Merck, Darmstadt), but the use of the mixed 3-butenoic 2-butenoic anhydride as a precursor gave better yields. The mixed anhydride was prepared from 3-butenoic acid and *trans*-2-butenoyl chloride (both from E. Merck, Darmstadt) using standard methods. The pyrolysis proceeded as follows: after evacuation of the system the precursor was left at room temperature and its vapors passed

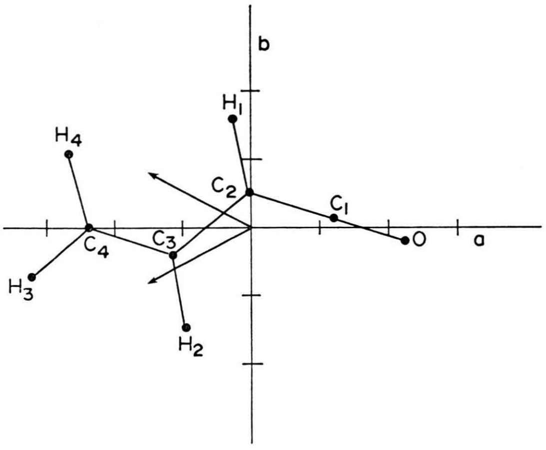

Fig. 1. Assumed structure of *trans*-vinyl ketene in the principal axis system. Distance are: $C_1{=}O$ 1.171 Å, $C_2{=}C_1$ 1.306 Å, $C_3{-}C_2$ 1.43 Å, $C_4{=}C_3$ 1.335 Å, and all C−H 1.088 Å. Angles are $C_1C_2H_1 = 117°$, $C_1C_2C_3 = C_2C_3C_4 = 122.5°$, $C_1C_3H_2 = C_3C_4H_3 = H_3C_4H_4 = 120°$. The arrows indicate the positive ends of the two possible directions of the electric dipole moment.

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through a quartz tube of 12 mm inner diameter, heated to 520 °C over 20 cm. Following the quartz tube was a cold trap at − 65 °C and one at − 196 °C. The product in the − 196 °C trap was purified by trap-to-trap distillation at − 85 °C until the infrared spectrum showed no further changes. The first fractions mainly consisted of carbon dioxide, propyne, and some propene.

Vinyl ketene has a greenish yellow color in the solid and the liquid phases. It melts at − 85 ± 10 °C. It polymerizes slowly in the cold melt and rapidly in the gas phase at room temperature at pressures above ca. 5 Torr. There are some indications that the gas phase polymerization is autocatalytic.

The microwave spectra in the region 8000 to 30,000 MHz were recorded at room temperature with a Hewlett Packard 8460 A MRR spectrometer. The electric field strength in the Stark cell was calibrated using the dipole moment of OCS [7], $\mu = 0.71521\,D$. Vinyl ketene decomposed slowly in the Stark cell.

Infrared spectra in the region 4000—450 cm^{-1} were recorded on a Digilab FTS 20 Fourier spectrometer using 10 cm and 3 m gas cells. Since vinyl ketene polymerizes at low (5 Torr) pressures, only relatively weak spectra have been obtained.

Microwave Spectrum

The microwave spectrum of vinyl ketene shows patterns typical for a slightly asymmetric prolate top rotor ($\varkappa = -0.99$) with low-lying vibrational states. Figure 2 shows the $J = 5 \leftarrow 4$ a-type R-branch transitions. The observed frequencies for the transitions of the ground vibrational state are given in Table 1. Table 2 gives the spectroscopic

Table 1. Observed and calculated frequencies in MHz of *trans*-Vinylketene in the vibrational ground state.

Transition	Observed frequency	Calculated frequency
$2_{0,2}-1_{0,1}$	9 297.474	9 297.478(6)[a]
$2_{1,2}-1_{1,1}$	9 161.069	9 161.078(7)
$2_{1,1}-1_{1,0}$	9 434.917	9 434.910(7)
$3_{0,3}-2_{0,2}$	13 945.250	13 945.248(7)
$3_{1,3}-2_{1,2}$	13 741.350	13 741.356(10)
$3_{1,2}-2_{1,1}$	14 152.105	14 152.104(10)
$3_{2,2}-2_{2,1}$	13 947.695	13 947.590(7)
$3_{2,1}-2_{2,0}$	13 949.040	13 949.100(7)
$4_{0,4}-3_{0,3}$	18 591.850	18 591.856(8)
$4_{1,4}-3_{1,3}$	18 321.315	18 321.323(11)
$4_{1,3}-3_{1,2}$	18 868.985	18 868.984(11)
$4_{2,3}-3_{2,2}$	18 596.455	18 596.447(7)
$4_{2,2}-3_{2,1}$	18 600.210	18 600.222(8)
$4_{3,2}-3_{3,1}$	18 598.880	18 598.885(8)
$4_{3,1}-3_{3,0}$	18 598.880	18 598.881(8)
$5_{0,5}-4_{0,4}$	23 236.910	23 236.915(11)
$5_{1,5}-4_{1,4}$	22 900.870	22 900.875(12)
$5_{1,4}-4_{1,3}$	23 585.440	23 585.443(14)
$5_{2,4}-4_{2,3}$	23 245.020	23 245.013(6)
$5_{2,3}-4_{2,2}$	23 252.555	23 252.561(11)
$5_{3,3}-4_{3,2}$	23 248.880	
$5_{3,2}-4_{3,1}$	23 248.880	23 248.891(6)
$5_{4\ 2}-4_{4,1}$	23 250.850	
$5_{4,1}-4_{4,0}$	23 250.850	23 250.854(11)
$6_{0,6}-5_{0,5}$	27 880.030	27 880.039(19)
$6_{1,6}-5_{1,5}$	27 479.930	27 479.913(16)
$6_{1,5}-5_{1,4}$		28 301.374(20)
$6_{2,5}-5_{2,4}$	27 893.225	27 893.214(10)
$6_{2,4}-5_{2,3}$	27 906.430	27 906.411(19)
$6_{3,4}-5_{3,3}$	27 899.065	27 899.052(9)
$6_{3,3}-5_{3,2}$	27 899.065	27 899.088(9)
$6_{4,3}-5_{4,2}$	27 901.180	27 901.192(12)
$6_{4,2}-5_{4,1}$	27 901.180	27 901.192(12)
$6_{5,2}-5_{5,1}$	27 904.610	27 904.599(20)
$6_{5,1}-5_{5,0}$	27 904.610	27 904.599(20)

[a] Numbers in parentheses are one standard error in units of the last digit.

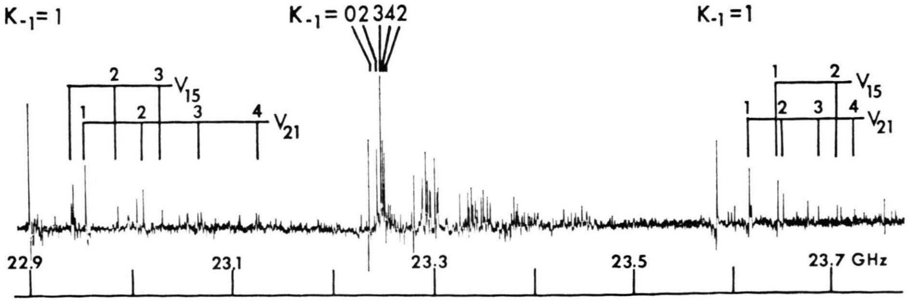

Fig. 2. The microwave spectrum of the $J = 5 \leftarrow 4$ transitions of *trans*-vinyl ketene at room temperature. The intensity difference between the two ground state $K_{-1} = 1$ lines illustrates the decay of vinyl ketene in the microwave cell in ca. 25 minutes.

Table 2. Spectroscopic constants and moments of inertia of *trans*-Vinylketene.

	Experimental	Predicted[a]	
$\tilde{A}$	39 571(48)[b]	40 181	MHz
$\tilde{B}$	2 392.9252(28)	2 439	MHz
$\tilde{C}$	2 256.0089(28)	2 300	MHz
Δ_J	0.414(31)		kHz
Δ_{JK}	− 34.694(92)		kHz
σ[c]	26.5		kHz
I_a[d]	12.771(16)	12.58	uÅ^2
I_b	211.197(16)	207.17	uÅ^2
I_c	224.015(16)	219.75	uÅ^2
$I_c - I_a - I_b$	0.047(23)	0.0	uÅ^2

[a] Calculated from the assumed structure, Figure 1. The expected rotational constants for the corresponding *cis*-rotamer are $A = 13905$ MHz, $B = 3582$ MHz and $C = 2848$ MHz.

[b] Numbers in parentheses represent one standard error in units of the last digit.

[c] Standard deviation of the fit.

[d] Calculated using the conversion factor $B^* I_b = 505379.0(38)$ MHz · uÅ^2.

constants obtained by fitting these transitions to Watson's reduced Hamiltonian [8]:

$$\begin{aligned}\mathscr{H} = {} & \tfrac{1}{2}(\tilde{B} + \tilde{C})\,P^2 + [\tilde{A} - \tfrac{1}{2}(\tilde{B} + \tilde{C})]\,P_a^2 \\ & + \tfrac{1}{2}(\tilde{B} - \tilde{C})(P_b^2 - P_c^2) \\ & - \Delta_J\,P^4 - \Delta_{JK}\,P^2\,P_a^2 - \Delta_K\,P_a^4 \\ & - 2\,\delta_J\,P^2(P_b^2 - P_c^2) \\ & - \delta_K[P_a^2(P_b^2 - P_c^2) + (P_b^2 - P_c^2)\,P_a^2]\,,\end{aligned}$$

where P, P_a, P_b and P_c are the operators for the total angular momentum and its components along the principal inertial axes. $\tilde{A}$, $\tilde{B}$ and $\tilde{C}$ are Watson's reduced rotational constants and the deltas are quartic centrifugal distortion constants. Due to the limited data Δ_K, δ_J and δ_K were fixed at zero. The small, positive inertial defect $I_c - I_a - I_b$ confirms that the molecule is planar. An approximate structure of *trans*-vinyl ketene is shown in Figure 1. The rotational constants calculated from this structure are also given in Table 2. The good agreement with the experimental rotational constants confirm that it is *trans*-vinyl ketene.

The observed and calculated Stark coefficients and the electric dipole moment of *trans*-vinyl ketene are shown in Table 3. The two possible orientations of the dipole moment are shown in Figure 1. It may be expected that the dipole moment is directed along the ketene group just as it is in methyl ketene [9].

Table 3. Stark coefficients and dipole moment of *trans*-vinyl ketene.

Transition	$\lvert M \rvert$	$\Delta\nu/E^2$ (obs.)[a]	$\Delta\nu/E^2$ (calc.)
$4_{0,4}-3_{0,3}$	1	−0.280	−0.283
	2	0.205	0.207
$4_{1,4}-3_{1,3}$	0	−0.114	−0.121
	1	1.264	1.274
	2	5.461	5.460
$5_{1,5}-4_{1,4}$	0	0.141	0.138
	1	0.427	0.425
	2	1.280	1.286

$\mu_a^2 = 0.749(24)\ D^2$ [b]

$\mu_b^2 = 0.226(39)\ D^2$

$\mu_{\text{total}} = 0.987(23)\ D$

$\mu_a = 0.865(14)\ D$

$\mu_b = 0.475(41)\ D$

[a] The units are MHz · V^{-2} · cm^2.

[b] Numbers in parentheses represent the estimated error in units of the last digit.

A few transitions of vinyl ketene in the assumed $v_{21} = 1$ and $v_{15} = 1$ vibrational states were measured in order to confirm the vibrational assignment. The transitions were chosen to get the maximum A-dependence and a minimum centrifugal distortion contribution. These transitions were used to calculate the rigid rotor rotational constants. For comparison the corresponding ground state transitions were treated in the same way. Table 4 lists for the three states the transitions used, the rigid rotor rotational constants, the moments of inertia and the inertial defects. Since ν_{21}, the vinyl torsional vibration, is an out-of-plane vibration it is expected that the inertial defect for the $v_{21} = 1$ state is

Table 4. Selected transitions of *trans*-vinyl ketene in the ground, the $v_{21} = 1$ and the $v_{15} = 1$ vibrational states. Rigid rotor rotational constants[a], moments of inertia and inertial defects for these states.

	Ground state	$v_{21} = 1$	$v_{15} = 1$	
$5_{1,4}-4_{1,3}$	23585.440	23618.330	23647.255	MHz
$5_{1,5}-4_{1,4}$	22900.870	22957.280	22944.240	MHz
$5_{2,3}-4_{2,2}$	23252.555	23297.250	23305.570	MHz
$5_{2,4}-4_{2,3}$	23245.020	23289.595	23298.220	MHz
A	39641	36580	42686	MHz
B	2392.9	2395.1	2400.0	MHz
C	2256.0	2262.8	2259.4	MHz
I_a	12.75	13.82	11.84	uÅ^2
I_b	211.20	211.01	210.57	uÅ^2
I_c	224.02	223.34	223.68	uÅ^2
$I_c - I_a - I_b$	0.07	−1.49	1.27	uÅ^2

[a] Calculated from the transitions listed using the rigid rotor tables in C. H. Townes and A. L. Schawlow, Microwave Spectroscopy, McGraw-Hill, New York 1955.

negative and the inertial defect for the $v_{21} = 1$ state is actually found to be -1.5 uÅ^2. Thus the inertial defects confirm the vibrational assignment that ν_{21} is the lowest vibration of vinyl ketene with an in-plane bending mode, ν_{15}, nearby.

There are still many unassigned lines in the microwave spectra. Some of these stem undoubtedly from decomposition products and many arise from molecules in excited vibrational states, but none of the lines could be confidently assigned either to *b*-type transitions of the *trans*-rotamer or to transitions of the *cis*-rotamer.

Infrared Spectra and Assignment

The gas phase infrared spectrum of vinyl ketene in the range 3600—400 cm^{-1} is shown in Figure 3. A proof of the identity of vinyl ketene is given by the intensity and wavenumber of a very strong band at 2137 cm^{-1}, just 14 cm^{-1} below that of ketene itself [10], strongly indicating the presence of a ketene group. The vinyl group is indicated by a strong band at 1626 cm^{-1} and two out of plane vibrations at 976 and 875 cm^{-1} [11]. Since vinyl ketene has only C_s symmetry the band contours of in-plane vibrations will be A/B hybrids with the degree of A or B-type depending on the direction of the oscillating dipole [12]. All out-of-plane vibrations will have C-type bands with strong Q branches and relatively weak P and R branches. The PR-branch separations of *trans*-vinyl ketene are calculated to be 13.5, 11.3, and 20.3 cm^{-1} for the pure A, B, and C-type bands, respectively, using the formulas of Seth-Paul [12]. For the *cis*-rotamer the PR-branch separations are calculated to be 15.9, 13.3, and 23.9 cm^{-1}, respectively, for A, B, and C-type bands. The observed band contours are all either A/B-hybrids with PR-branch separations in the range 11.5—12.5 cm^{-1} or C-type bands that are partially resolved. The spacing of the fine structure in these bands is ca. 2.4 cm^{-1}, which is close to 2A of *trans*-vinyl ketene, but about 5A for the *cis*-rotamer. Thus, all the strongest bands clearly belong to the *trans*-rotamer. The wavenumbers of the central minima or of the dominant Q-branches of the absorption bands in Fig. 3 are listed in Table 5.

Vinyl ketene has 21 normal vibrations of which 15 are in-plane vibrations (symmetry species a′) and 6 are out-of-plane vibrations (species a″). By analogy to vinyl allene [4] and ketene [10] four vibrations (the C=C=O in-plane bend, two skeletal in-plane bends, and the vinyl torsion) can be expected to have wavenumbers below the range covered. In fact, it is clearly seen in the microwave spectrum, Fig. 2, that two vibrations have wave-

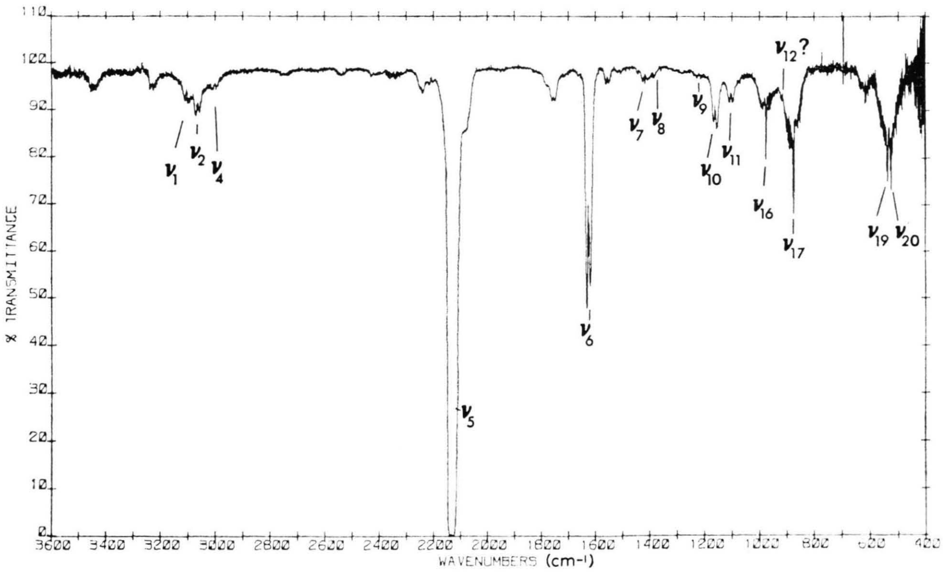

Fig. 3. The infrared gas spectrum of vinyl ketene at room temperature. Cell length 10 cm, pressure ca. 4 Torr, resolution 1 cm^{-1}.

numbers so low that the excited states have significant populations at room temperature. A rough estimate from the relative intensities gives the lowest vibration, the vinyl torsion ν_{21}, at ca. 105 cm^{-1} and the next lowest, an in-plane skeletal bend ν_{15}, at ca. 155 cm^{-1}. Since the C_2–H_1 and C_3–H_2 bonds are nearly antiparallel (Fig. 1), it may be expected that three of the six vibrations associated with them can be very weak in the infrared spectrum if they couple to form "in-phase" and "out-of-phase" vibrations. The assignment proposed in Table 5 is based on the band contours and on the assignments for vinyl allene [4], ketene [10] and 1,3-butadiene [13].

In the C–H stretching region there are clearly three bands and possibly a fourth, but this is so overlapped that a band center cannot be determined. In the C–H bending region all bands are weak or very weak and the assignments of ν_8 and ν_9 are rather questionable. The vinyl CH_2 in-plane rocking vibration must be expected in the 850 to 1000 cm^{-1} region, but there are two relatively strong C-type bands in this region and the presence of an A/B hybrid band is not clear. However, there is a slight extra dip between the two bands; this might be the central dip of an A/B-type band and is thus tentatively assigned to ν_{12}. The two C-type bands are two of the three vinyl C–H out-of-plane vibrations, but the third, which can be expected in the region 500—1100 cm^{-1}, could not be located. This is to be expected due to the antiparallel arrangement of the C_2–H_1 and C_3–H_2 bonds as explained above. The two C-type bands at 526 and 540 cm^{-1} may be assigned to two ketene group out-of-plane vibrations.

In the spectrum are several weak or very weak bands that have been left unassigned. Some of these bands are in typical combination/overtone regions, while others may be fundamentals of *cis*-vinyl ketene or impurities.

Table 5. Infrared transitions of vinyl ketene in the gas phase.

Wave-number (cm^{-1})	Band type	Relative intensity[a]	Assignment[b]	Approximate description
3448	A/B	w		
3230	A/B	w		
3106	A/B	w	ν_1	
3065	A/B	w	ν_2	olefinic C–H str.
3003	A/B	vw	ν_4	
2750	A/B	vw		
2535	A/B	vw		
2420	A/B	vw		
2245	A/B	vw		
2207	A/B	vw	$2\nu_{11}$	2*1102 = 2204
2137	A/B	vs	ν_5	ketene C=O str.
2090	sh, A/B	w		ν_5 *cis* ?
1785	sh	vw		
1755	A/B	w	$2\nu_{17}$	2*875 = 1750
1720	sh, A/B	vw		
1626	A/B	s	ν_6	vinyl C=C str.
1557	A/B	w		
1418	A/B	w	ν_7	vinyl CH_2 scissors
1392	A/B	vw	ν_8	=C−C= str.
1220	A/B	vw	ν_9 ?	C−H bend
1161	A/B	m	ν_{10}	C−H (ketene) bend ?
1102	A/B	w	ν_{11}	ketene C=C str.
976	C	m	ν_{16}	vinyl twist
915 ?[c]	A/B		ν_{12} ?	vinyl CH_2 rock
875	C	m	ν_{17}	vinyl CH_2 wag
633 ?[d]		vw		ν_9(e) propyne
615 ?[d]	A/B	vw		
540	C	m	ν_{19}	ketene C–H out-of-plane bend
526	C	m	ν_{20}	C=C=O out-of-plane bend
ca. 155[e]	—	—	ν_{15}	in plane skeletal bend
ca. 105[e]	—	—	ν_{21}	vinyl torsion

[a] vs = very strong; s = strong, m = medium, w = weak, vw = very weak.

[b] Question marks at uncertain assignments.

[c] The existence of this band is very uncertain.

[d] Possibly the strongest band in propyne, ν_9(e), overlapping an A/B hybrid band from vinyl ketene.

[e] Estimated from the microwave spectrum. The uncertainty is 30 cm^{-1}.

Conclusion and Discussion

The microwave spectrum of vinyl ketene shows clearly the *trans*-rotamer, while no lines could be assigned to the *cis*-configuration. This indicates that the *trans*-vinyl ketene is much more abundant than the *cis*-vinyl ketene. This is supported by the infrared spectrum, where all measurable PR-branch separations of A/B hybrid bands are in the range expected for the *trans*-rotamer and about 1 cm^{-1} less than the smallest separation expected for the *cis*-rotamer. Further, the spacings in the partially resolved C-type bands are of the magnitude expected for *trans*-vinyl ketene but much too large for *cis*-vinyl ketene. Thus, all the strongest infrared bands can be assigned to the *trans* conformation, while there are no positive assignments to the *cis* form. If it is assumed that the low frequency shoulder on ν_5, the very strong ketene band at 2137 cm^{-1}, is the ν_5 of the *cis*-rotamer, then from the infrared spectrum Fig. 3 a rough estimate for the trans:cis abundance is 10:1 at room temperature. This is an upper limit for the *cis*-conformation.

The dipole moment of *trans*-vinyl ketene was found to be 0.987(23) *D*. This is surprisingly smaller than in ketene (1.414(10) *D*) [14] and methyl ketene (1.790(15) *D*) [9].

Of the 21 normal vibrations of vinyl ketene four are not observed, two have been roughly estimated from the microwave spectrum and three are uncertain. A complete vibrational assignment will first be possible with the knowledge of the infrared spectrum of vinyl ketene in the condensed phase, of the far-infrared spectrum, and preferably of the Raman spectrum.

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Note added in proof: It has been brought to my attention that R. D. Godfrey and M. Woodruff at Monash University, Australia, in an independent study have observed the microwave spectra of vinyl ketene in the pyrolysis products of vinylacetic anhydride. A report onthis will appear shortly.

[1] R. W. Holder, H. S. Freiman, and M. S. Stefanchik, J. Org. Chem. **41**, 3303 (1976).

[2] G. Rousseau, R. Bloch, P. Le Perchec, and J. M. Conia, J. C. S., Chem. Comm. **1973**, 795.

[3] J. K. Terlouw, P. C. Burgers, and J. L. Holmes, J. Amer. Chem. Soc. **101**, 225 (1979).

[4] P. Klaboe, T. Torgrimsen, D. H. Christensen, H. Hopf, A. Eriksson, G. Hagen, and S. J. Cyvin, Spectrochim. Acta **30** A, 1527 (1974).

[5] A. Bouchy and G. Roussy, J. Mol. Spectrosc. **68**, 156 (1977).

[6] R. G. Ford, J. Mol. Spectrosc. **65**, 273 (1977).

[7] J. S. Muenter, J. Chem. Phys. **48**, 4544 (1968).

[8] J. K. G. Watson, J. Chem. Phys. **46**, 1935 (1967).

[9] B. Bak, J. J. Christiansen, K. Kunstmann, L. Nygaard, and J. Rastrup Andersen, J. Chem. Phys. **45**, 883 (1966).

[10] C. B. Moore and G. C. Pimentel, J. Chem. Phys. **38**, 2816 (1963).

[11] W. J. Potts and R. A. Nyquist, Spectrochim. Acta **15**, 679 (1959).

[12] W. A. Seth-Paul, J. Mol. Struct. **3**, 403 (1969).

[13] Yu. N. Panchenko, Spectrochim. Acta **31** A, 1201 (1975).

[14] H. R. Johnson and M. W. P. Strandberg, J. Chem. Phys. **20**, 687 (1952).