Irradiation Experiments. Irradiations were carried out by exposing the 3-mm tubular cell described above to light from a medium-pressure 450-W mercury lamp (Hanovia) with 0.1 M $FeCl_3$ solution as a filter. The tube was transferred to the cavity of an ESR spectrometer and the $PhNO_2^{-}\cdot$ peak described above was scanned at short intervals. A plot of $1/H \times w^2$ vs. time was linear. Its slope was proportional to $3k_b$ with the proportionality factor being determined by the above-described measurements on standard nitroxide solutions.

Acknowledgment. The authors express their gratitude to the National Science Foundation for a Grant, GP-42837-X, supporting this work.

References and Notes

(1) R. D. Guthrie, G. W. Pendygraft, and A. T. Young, *J. Am. Chem. Soc.*, **98**, 5877 (1976).

(2) R. D. Guthrie and N. S. Cho, *J. Am. Chem. Soc.*, **97**, 2280 (1975).

(3) J. Smid, *Angew. Chem., Int. Ed. Engl.*, **11**, 112 (1972).

(4) A. Streitwieser, Jr., D. G. Chang, and A. T. Young, *J. Am. Chem. Soc.*, **94**, 4888 (1972).

(5) R. D. Guthrie, D. P. Wesley, G. W. Pendygraft, and A. T. Young, *J. Am. Chem. Soc.*, **98**, 5870 (1976).

(6) A referee has pointed out that the observed rate reduction might be explained by a hydrogen-atom extraction from 9-aminofluorene by FD·. This seems to us an energetically unlikely reaction but we cannot rule out this alternative. The other indications of reversibility suggest that our interpretation of the 9-aminofluorene experiment is correct.

(7) P. B. Ayscough and P. P. Sayent, *Proc. Chem. Soc., London*, 94 (1963).

(8) (a) K. U. Ingold in "Free Radicals", J. K. Kochi, Ed., Wiley-Interscience, New York, 1973, p 52; (b) B. G. Gowenlock, P. P. Jones, and D. R. Snelling, *Can. J. Chem.*, **41**, 1911 (1963).

(9) T. E. Hogen-Esch, *J. Am. Chem. Soc.*, **95**, 639 (1973).

(10) (a) G. Baum in "Studies of Synthesis of Benzocyclopropenes. I. Thermolysis and Photolysis of Indazoles. II. Aryne Cyclization Processes", Ph.D. Dissertation, Ohio State University, 1965; (b) G. Baum, R. Bernard, and H. Shechter, *J. Am. Chem. Soc.*, **89**, 5307 (1967); (c) G. Baum and H. Shechter, *J. Org. Chem.*, **41**, 2120 (1976).

Generation of Butatrienone (Vinylideneketene) by Flash Vacuum Pyrolysis and Measurement of Its Microwave Spectrum

Ronald D. Brown,* Roger F. C. Brown, Frank W. Eastwood, Peter D. Godfrey, and Donald McNaughton

Contribution from the Department of Chemistry, Monash University, Clayton, Victoria, 3168, Australia.

Received January 2, 1979

Abstract: Butatrienone (vinylideneketene) has been generated by flash vacuum pyrolysis of buta-2,3-dienoic trifluoroacetic anhydride. The microwave spectrum has been observed and assigned in the region 8–83 GHz. Rotational and centrifugal distortion constants have been determined for $CH_2{=}C{=}C{=}C{=}O$, $CHD{=}C{=}C{=}C{=}O$, and $CD_2{=}C{=}C{=}C{=}O$. The dipole moment was found to be $\mu_a = 1.967 \pm 0.019$ D ($6.47 \pm 0.06 \times 10^{-30}$ C·m). There is evidence that butatrienone is a planar molecule of C_{2v} symmetry, and that the heavy atoms lie along a straight line.

The generation of propadienone (methyleneketene) and the assignment of its microwave spectrum have recently been reported.[1-3] This provided a strong stimulus to attempting the synthesis and the study of the microwave spectrum of the next member, butatrienone (vinylideneketene), of the series formaldehyde, ketene, propadienone. Moreover, the rotational spectrum of propadienone implied some rather unsuspected properties of the molecule—either the chain of heavy atoms is nonlinear or there are unusually large vibrational effects upon the spectrum. It was of interest to determine whether these effects are further enhanced in the next member of the series. We report here the generation for the first time of butatrienone, and the assignment of the microwave spectra of butatrienone, monodeuterated butatrienone, and dideuterated butatrienone. The method of generation of butatrienone, a transient species, by pyrolysis of butadienoic trifluoroacetic anhydride is unsuitable for most experiments on chemical trapping or low-temperature collection, and further spectroscopic and chemical characterization will require an alternative method for its formation.

Experimental Section

Materials. Butadienoic acid, mp 65–66 °C (^1H NMR ($CDCl_3$) δ 5.29 ($CH_2{=}$), 5.68 ($=CH-$) (AB_2 system, $J = 4.36$ Hz), 10.2 (CO_2H)) was prepared from but-3-ynoic acid[4] by the method of Eglinton et al.[5]

[4,4-D_2]Butadienoic Acid. Treatment of but-3-ynoic acid (4.25 g) under the conditions described,[5] but using D_2O (100 mL, 99% isotopic purity), gave [4,4-D_2]butadienoic acid (1.8 g, 42% (^1H NMR ($CDCl_3$) δ 5.68 (s, $=CH-$), 10.5 (s, CO_2H)) probably partially deuterated in the 2 position. Mass spectral analysis of the pyrolysate of the resulting butadienoic trifluoroacetic anhydride (see below) showed a peak at *m/e* 68 attributed to $C_4D_2O^{+}\cdot$, while the monodeuterated species was undetectable. Repetition of the procedure using D_2O of 75 and 50% isotopic purity gave samples of butadienoic acid which on conversion to the mixed anhydride and pyrolysis showed peaks at *m/e* 68, 67, and 66 for the same ion corresponding to isotopic ratios D_2:DH:H_2 of 58:32:10 and 13:47:40, respectively, in the mass spectrometer.

Butadienoic Trifluoroacetic Anhydride (1). The mixed anhydride was prepared by a procedure similar to that of Emmons et al.[6] A solution of butadienoic acid (840 mg) in methylene chloride (1 mL) was cooled to 0 °C and trifluoroacetic anhydride (3 mL) was added. After 10 min the more volatile material was evaporated under partial vacuum and the residue was distilled from bulb to bulb (50 °C air bath, 20 mmHg) to yield the anhydride (1.4 g, 77%) as a colorless liquid: IR (neat) 1971, 1848, 1786 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.49 (CH_2), 5.81 (CH) (AB_2 system, $J = 4.02$ Hz); mass spectrum *m/e* 181 ($M^{+} + 1$, 10%), 180.0037 ($M^{+}\cdot$, 22%, $C_6H_3O_3F_3$ requires 180.0034), 152 (22%), 97 (24%), 84 (14%), 69 (100%), 67 (76%), 66 (30%).

1,2,3-Butatrien-1-one (2). This was generated by flash vacuum pyrolysis of butadienoic trifluoroacetic anhydride (**1**).

$$CH_2{=}C{=}CHCO_2COCF_3\ (\mathbf{1}) \xrightarrow[\text{pyrolysis}]{\text{flash vacuum}} CH_2{=}C{=}C{=}C{=}O\ (\mathbf{2}) + CF_3CO_2H$$

The pyrolysis furnace was a 400 × 25 mm i.d. silica tube, heated to 520 °C. Spectra were obtained by pumping the pyrolysate directly through the spectrometer from the furnace. Spectra of the following compounds and mixtures were run separately at a pyrolysis temper-

0002-7863/79/1501-4705$01.00/0

Table I

A. Rotational Transition Frequencies (MHz) of Butatrienone ($\mathrm{CH_2{=}C{=}C{=}C{=}O}$)

rotational transition	obsd frequency	obsd − calcd frequency	rotational transition	obsd transition	obsd − calcd frequency
$4_{14} \leftarrow 3_{13}$	17 205.76	0.01	$7_{44} \leftarrow 6_{43}$	30 343.23	0.01
$4_{13} \leftarrow 3_{12}$	17 261.23	−0.06	$7_{43} \leftarrow 6_{42}$		
$5_{15} \leftarrow 4_{14}$	21 507.07	−0.08	$8_{18} \leftarrow 7_{17}$	34 411.81	0.02
$5_{14} \leftarrow 4_{13}$	21 576.53	−0.04	$8_{17} \leftarrow 7_{16}$	34 522.24	0.01
$5_{33} \leftarrow 4_{32}$	21 603.42	0.01	$8_{36} \leftarrow 7_{35}$	34 565.08	0.01
$5_{32} \leftarrow 4_{31}$			$8_{35} \leftarrow 7_{34}$		
$5_{42} \leftarrow 4_{41}$	21 738.78	−0.05	$9_{19} \leftarrow 8_{18}$	38 712.41	−0.03
$5_{41} \leftarrow 4_{40}$			$9_{18} \leftarrow 8_{17}$	38 837.37	−0.02
$6_{16} \leftarrow 5_{15}$	25 808.60	0.08	$9_{37} \leftarrow 8_{36}$	38 885.44	−0.01
$6_{15} \leftarrow 5_{14}$	25 891.87	0.05	$9_{36} \leftarrow 8_{35}$		
$6_{34} \leftarrow 5_{33}$	25 924.01	−0.01	$9_{46} \leftarrow 8_{45}$	39 129.24	−0.01
$6_{33} \leftarrow 5_{32}$			$9_{45} \leftarrow 8_{44}$		
$6_{43} \leftarrow 5_{42}$	26 086.59	0.04	$17_{2,16} \leftarrow 16_{2,15}$	73 291.59	0.02
$6_{42} \leftarrow 5_{41}$			$17_{2,15} \leftarrow 16_{2,14}$	73 291.89	−0.05
$7_{17} \leftarrow 6_{16}$	30 109.85	−0.01	$18_{2,17} \leftarrow 17_{2,16}$	77 602.24	0.01
$7_{16} \leftarrow 6_{15}$	30 207.08	0.04	$18_{2,16} \leftarrow 17_{2,15}$	77 602.71	0.03
$7_{35} \leftarrow 6_{34}$	30 244.58	0.00	$19_{2,18} \leftarrow 18_{2,17}$	81 912.87	−0.03
$7_{34} \leftarrow 6_{33}$			$19_{2,17} \leftarrow 18_{2,16}$	81 912.43	0.01

B. Rotational Transition Frequencies (MHz) of Mono- and Dideuteriobutatrienone

$\mathrm{CHD{=}C{=}C{=}C{=}O}$			$\mathrm{CD_2{=}C{=}C{=}C{=}O}$		
rotational transition	obsd frequency	obsd − calcd	rotational transition	obsd frequency	obsd − calcd
$4_{14} \leftarrow 3_{13}$	16 472.33	−0.01	$4_{14} \leftarrow 3_{13}$	15 817.87	0.01
$4_{04} \leftarrow 3_{03}$	16 509.86	−0.01	$4_{04} \leftarrow 3_{03}$	15 867.44	−0.02
$4_{13} \leftarrow 3_{12}$	16 551.43	0.02	$4_{32} \leftarrow 3_{31}$	15 880.39	−0.04
$7_{17} \leftarrow 6_{16}$	28 826.58	−0.02	$4_{31} \leftarrow 3_{30}$		
$7_{07} \leftarrow 6_{06}$	28 892.26	0.02	$4_{13} \leftarrow 3_{12}$	15 919.36	0.01
$7_{16} \leftarrow 6_{15}$	28 965.00	0.03	$7_{17} \leftarrow 6_{16}$	27 681.14	0.00
$7_{35} \leftarrow 6_{34}$	28 935.21	0.00	$7_{07} \leftarrow 6_{06}$	27 767.82	−0.01
$7_{34} \leftarrow 6_{33}$			$7_{35} \leftarrow 6_{34}$	27 790.78	0.05
$8_{18} \leftarrow 7_{17}$	32 944.62	0.00	$7_{34} \leftarrow 6_{33}$		
$8_{08} \leftarrow 7_{07}$	33 019.64	0.04	$7_{44} \leftarrow 6_{43}$	27 819.30	0.04
$8_{17} \leftarrow 7_{16}$	33 102.72	−0.03	$7_{43} \leftarrow 6_{42}$		
$8_{36} \leftarrow 7_{35}$	33 068.81	0.08	$7_{16} \leftarrow 6_{15}$	27 858.77	0.02
$8_{35} \leftarrow 7_{34}$			$8_{18} \leftarrow 7_{17}$	31 635.52	0.01
$8_{45} \leftarrow 7_{44}$	33 141.08	−0.02	$8_{08} \leftarrow 7_{07}$	31 734.47	−0.04
$8_{44} \leftarrow 7_{43}$			$8_{36} \leftarrow 7_{35}$	31 760.80	−0.03
$9_{19} \leftarrow 8_{18}$	37 062.58	0.00	$8_{35} \leftarrow 7_{34}$		
$9_{18} \leftarrow 8_{17}$	37 240.42	−0.03	$8_{45} \leftarrow 7_{44}$	31 793.35	−0.06
$9_{37} \leftarrow 8_{36}$	37 202.18	−0.08	$8_{44} \leftarrow 7_{43}$		
$9_{36} \leftarrow 8_{35}$			$8_{17} \leftarrow 7_{16}$	31 838.48	−0.01
$9_{46} \leftarrow 8_{45}$	37 283.55	0.02	$9_{19} \leftarrow 8_{18}$	35 589.80	−0.02
$9_{45} \leftarrow 8_{44}$			$9_{09} \leftarrow 8_{08}$	35 701.15	−0.05
$16_{2,15} \leftarrow 15_{2,14}$	66 072.53	0.02	$9_{37} \leftarrow 8_{36}$	35 730.95	0.01
$16_{2,14} \leftarrow 15_{2,13}$	66 073.40	−0.11	$9_{36} \leftarrow 8_{35}$		
$17_{2,16} \leftarrow 16_{2,15}$	70 201.47	0.10	$9_{46} \leftarrow 8_{45}$	35 767.62	0.02
$17_{2,15} \leftarrow 16_{2,14}$	70 202.62	−0.17	$9_{45} \leftarrow 8_{44}$		
$20_{2,19} \leftarrow 19_{2,18}$	82 588.06	−0.16	$17_{2,16} \leftarrow 16_{2,15}$	67 454.40	0.00
$20_{2,18} \leftarrow 19_{2,17}$	82 590.72	0.17	$17_{2,15} \leftarrow 16_{2,14}$	67 457.36	0.00
			$21_{2,20} \leftarrow 20_{2,19}$	83 323.26	0.01
			$21_{2,19} \leftarrow 20_{2,18}$	83 328.82	0.00

Table II. Rotational and Distortion Constants for Butatrienone

parameter[a]	$\mathrm{CH_2{=}C{=}C{=}C{=}O}$	$\mathrm{CHD{=}C{=}C{=}C{=}O}$	$\mathrm{CD_2{=}C{=}C{=}C{=}O}$
b_p	$-(2.22 \pm 0.36) \times 10^{-5}$	$-(5.91 \pm 0.70) \times 10^{-5}$	$-(9.53 \pm 0.20) \times 10^{-5}$
B_0	2160.70 ± 0.04	2073.61 ± 0.04	1996.12 ± 0.02
C_0	2146.82 ± 0.04	2053.85 ± 0.04	1970.75 ± 0.02
D_J	$(2.41 \pm 0.10) \times 10^{-4}$	$-(2.77 \pm 0.72) \times 10^{-4}$	$-(2.68 \pm 0.26) \times 10^{-6}$
D_{JK}	-0.427 ± 0.040	-0.243 ± 0.020	-0.135 ± 0.005
H_{JKK}	0.0109 ± 0.006	$(6.79 \pm 2.2) \times 10^{-3}$	$(3.73 \pm 0.76) \times 10^{-3}$
I_{JKKK}	$(2.56 \pm 0.22) \times 10^{-3}$	$(5.11 \pm 0.78) \times 10^{-4}$	$(1.33 \pm 0.28) \times 10^{-4}$
H_{JJK}	$-(3.32 \pm 20) \times 10^{-6}$	$-(6.35 \pm 20) \times 10^{-5}$	$(5.9 \pm 20) \times 10^{-6}$
I_{JJKK}	$(1.31 \pm 1.64) \times 10^{-6}$	$-(3.29 \pm 6) \times 10^{-6}$	$-(1.2 \pm 2) \times 10^{-6}$
I_{JJJK}	$-(1.7 \pm 2.6) \times 10^{-7}$	$(5.1 \pm 10) \times 10^{-7}$	$(1.2 \pm 3) \times 10^{-7}$

[a] Errors are two standard deviations obtained from a least-squares fit.

Table III. Quadrupole Mass Spectrometer Results

m/e	rel intensity	assignment
114	7	$CF_3COOH^{+\cdot}$
97	14	$CF_3CO^{+\cdot}$
95	14	CF_2COOH^+
69	100	CF_3^+
67	7	$H_2C{=}C{=}CHCO^+$ and $H_2C{=}C{=}C{=}C{=}O^{+\cdot}$ (^{13}C)
66	65	$H_2C{=}C{=}C{=}C{=}O^{+\cdot}$
51	12	$CF_2^{+\cdot}$
45	19	CO_2H^+
38	7	$C_3H_2^{+\cdot}$
37	5	C_3H^+

ature of 520 °C and at room temperature, to distinguish the lines of butatrienone from any other possible reaction products: butadienoic acid,[5] but-3-ynoic acid,[4] but-2-ynoic acid,[5] trifluoroacetic acid, trifluoroacetic anhydride, and the products formed by treatment of but-3-ynoic acid and of but-2-ynoic acids with trifluoroacetic anhydride.

We were unable to make any quantitative estimate of the yield of butatrienone in the vapor issuing from the furnace, although the anhydride precursor was reduced to less than 1/10 of its initial pressure after passage through the hot furnace. The yield of trifluoroacetic acid was at least 90 molar % of the anhydride entering the furnace. However, the appearance of solid deposits on the walls of the short tube between the furnace and the spectrometer and inside the spectrometer cell indicated substantial polymerization or decomposition of the butatrienone during its passage into and through the spectrometer.

The microwave spectrometer was a standard 5-kHz Stark modulated instrument having a 3-m long G-band waveguide (47.55 × 22.15 mm) cell, with a sample inlet from the pyrolysis furnace at one end, and a liquid nitrogen trap backed by a 100 L s^{-1} mechanical vacuum pump at the other. A gas stream inlet pressure of around 2.5 Pa was used in the initial investigation of the microwave signals, and an inlet pressure of around 0.25 Pa was used for measurement of lines. The microwave source used for investigations from 8 to 40 GHz was a Hewlett-Packard KO3-8690A phase-locked backward wave oscillator system. For investigations above 40 GHz, the microwave sources used were an OKI-70V10A klystron and an OKI-80V10A klystron, phase-locked to the backward wave oscillator in P band. Frequencies were measured with a Hewlett-Packard 5246 L counter, calibrated against a Sulzer Model 2.5 C laboratory frequency standard.

The microwave spectrometer was interfaced with a Varian V75 computer, and lines were recorded by computer averaging at minimal pressure, minimal detector current, and maximum gain. In this way pressure broadening and power broadening were minimized to give greater accuracy of measurement. Line center frequencies were obtained by computer fitting a theoretical Lorentzian curve to the computer-averaged spectral lines.

For Stark effect measurements the electric field calibration was based on measurements on OCS, for which the electric dipole moment was taken to be 0.715 21 D.[7]

The mass spectra of the precursors and pyrolysis products were monitored using a conventional quadrupole mass spectrometer. A continuous flow at 2 Pa was maintained through the pyrolysis chamber to a liquid nitrogen trap backed by a 30 L s^{-1} mechanical vacuum pump. The pyrolysis mixture was sampled through a Teflon needle valve which permitted approximately 1 × 10^{-4} Pa through the mass spectrometer.

Results

The lines attributable to butatrienone formed a series of transitions characteristic of a prolate rotor with centrifugal distortion near the symmetric top limit. The spectrum was assigned by observation of a number of R-branch lines between 8 and 83 GHz. The frequencies of measured lines are recorded in Tables IA and IB. They are found to be well represented by applying the rotational Hamiltonian for rotors of this class.[8]

$$
\begin{aligned}
H = {}& \tfrac{1}{2}(B + C)J(J + 1) + [A - \tfrac{1}{2}(B + C)]W_{J_\tau}(b_p) \\
& - D_J J^2(J + 1)^2 - D_{JK}J(J + 1)\langle P_z{}^2\rangle \\
& + H_{JJK}J^2(J + 1)^2\langle P_z{}^2\rangle + H_{JKK}J(J + 1)\langle P_z{}^4\rangle \\
& + I_{JJKK}J^2(J + 1)^2\langle P_z{}^4\rangle + I_{JKKK}J(J + 1)\langle P_z{}^6\rangle + \\
& I_{JJJK}J^3(J + 1)^3\langle P_z{}^2\rangle
\end{aligned}
$$

where

$$
\begin{aligned}
W_{J_\tau}(b_p) = {}& K_{-1}{}^2 + C_1 b_p + C_2 b_p{}^2 + C_3 b_p{}^3 \\
& + C_4 b_p{}^4 + C_5 b_p{}^5
\end{aligned}
$$

B and C are rotational constants, b_p is Wang's asymmetry parameter, the D's, H's, and I's are centrifugal distortion constants,[9b] and C_1, C_2, etc., are expansion coefficients for the near symmetric top.[9a] The results of least-squares fits of these parameters to the observations are presented in Table II.

Stark measurements were made on the 2_{02}–1_{01} transitions of butatrienone, monodeuterated butatrienone, and dideuterated butatrienone. The dipole moments were found to be $\mu_a = 1.967 \pm 0.019$, 1.953 ± 0.026, and 1.966 ± 0.017 D, respectively.

Passage of the pyrolysate through the quadrupole mass spectrometer gave spectra indicating the presence of butatrienone. Mass spectral data recorded at 70 eV are presented in Table III.

Discussion

The spectral data that relate to the molecular structure of butatrienone, namely, moments of inertia and the inertial defect, are presented in Table IV. The information is inadequate for establishing the complete geometry of the molecule but nevertheless some geometrical insight is derivable. The line intensities in the recorded spectra alternate depending on whether K_{-1} is odd or even, the ratio being consistent with the theoretically expected values of 3:1 for equivalent protons in the case of $CH_2{=}C{=}C{=}C{=}O$ and 1:2 for equivalent deuterons in $CD_2{=}C{=}C{=}C{=}O$. This is clear evidence that the molecule has C_{2v} symmetry and thus that the heavy atoms are collinear. In this situation there are five independent bond lengths and an unknown bond angle.

The most direct information that we can derive from the moments of inertia is firstly the very small inertial defect, which is consistent with the molecules being planar (as is required if the structure has C_{2v} symmetry). Secondly, we can derive the distance of a hydrogen nucleus from the a and b inertial axes. For the present kind of molecule the distance of a hydrogen from the a axis is $d = [I_a/2m_H]^{1/2}$. The distance may also be calculated by using Kraitchman's isotopic substitution equations.[10] The estimates of d obtained by these methods are similar to those calculated in the same manner for the related molecules formaldehyde and ketene (see Table V) and, for an assumed C-H bond length of 108 pm, correspond to an HCH angle of 119 ± 9° when we use I_a, and 130 ± 12° when we use Kraitchman's equations.

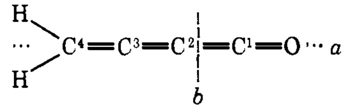
Table IV. Moments of Inertia and Inertial Defects (amu Å^2)

molecule	$C_2H{=}C{=}C{=}C{=}O$	$CHD{=}C{=}C{=}C{=}O$	$C_2D{=}C{=}C{=}C{=}O$
I_a	1.605 ± 0.110	2.980 ± 0.120	3.736 ± 0.100
I_b	233.895 ± 0.002	243.716 ± 0.002	253.179 ± 0.002
I_c	235.407 ± 0.002	246.061 ± 0.002	256.438 ± 0.002
Δ	−0.093 ± 0.120	−0.635 ± 0.120	−0.477 ± 0.100

Table V. Calculated Perpendicular Distance (d) of the Hydrogen Atoms from the a Axis

molecule	d from Kraitchman's equations/pm	d from I_a/pm
formaldehyde	96	94
ketene	94	94
butatrienone	100 ± 8	93 ± 6

We can also use Kraitchman's equations to compute the distance of the hydrogen atoms from the b axis, the value obtained being 314 ± 2 pm. Once again, we can derive from this the value of the HCH angle if we make the following assumptions, based on data[11] for ketene, allene, and butatriene, about bond lengths: C-O = 116 pm, C_1-C_2 = 130 pm, C_2-C_3



= 129 pm, C_3-C_4 = 129 pm, C-H = 108 pm. The result is 121 ± 2.5°. (The error limits were estimated by assuming that the adopted bond lengths may be uncertain by ±1 pm.)

We conclude that, whereas the rotational spectrum of propadienone indicates nonlinearity of the heavy-atom chain, or unusually large vibrational effects, the spectrum of butatrienone implies that the molecule is planar with C_{2v} symmetry, and, as far as we can tell, similar to formaldehyde and ketene in its general structural features.

Acknowledgment. This work was supported by a grant from the Australian Research Grants Committee.

References and Notes

(1) R. F. C. Brown, F. W. Eastwood, and G. L. McMullen, *J. Am. Chem. Soc.*, **98**, 7421 (1976).
(2) R. F. C. Brown, F. W. Eastwood, and G. L. McMullen, *Aust. J. Chem.*, **30**, 179 (1977).
(3) G. L. Blackman, R. D. Brown, R. F. C. Brown, F. W. Eastwood, and G. L. McMullen, *J. Mol. Spectrosc.*, **68**, 488 (1977).
(4) I. Heilbron, E. R. H. Jones, and F. Sondheimer, *J. Chem. Soc.*, 604 (1949).
(5) G. Eglinton, E. R. H. Jones, G. H. Mansfield, and M. C. Whiting, *J. Chem. Soc.*, 3197 (1954).
(6) W. D. Emmons, K. S. McCallum, and A. F. Ferris, *J. Am. Chem. Soc.*, **75**, 6047 (1953).
(7) J. S. Meunter, *J. Chem. Phys.*, **48**, 4544 (1968).
(8) G. W. King, R. M. Hainer, and P. C. Cross, *J. Chem. Phys.*, **11**, 27 (1943).
(9) W. Gordy and R. L. Cook, "Microwave Molecular Spectra", Interscience, New York, 1970: (a) pp 184-187; (b) pp 220-231.
(10) J. Kraitchman, *Am. J. Phys.*, **21**, 17 (1953).
(11) "Tables of Interatomic Distances and Configuration in Molecules and Ions. Supplement 1956-1959", *Chem. Soc., Spec. Publ.*, **No. 18** (1965).

Kinetic Studies on the Nucleophilic Addition to Double Bonds. 1. Addition of Amines to Electrophilic Carbon-Carbon Double Bonds[†]

B. Schreiber, H. Martinek, P. Wolschann, and P. Schuster*

Contribution from the Institut für Theoretische Chemie und Strahlenchemie der Universität Wien, A-1090 Wien, Austria.
Received January 8, 1979

Abstract: Kinetic and thermodynamic data are reported for the primary elementary step of nucleophilic addition to polar carbon-carbon double bonds in aprotic solvents (acetonitrile and chloroform). As nucleophiles primary, secondary, and tertiary amines were applied. The rapid reaction techniques used are stopped-flow (SF) and temperature-jump (TJ) relaxation.

I. Introduction

The nucleophilic attack on carbon-carbon double bonds has been the subject of numerous investigations which were summarized in review articles.[1,2] It represents the primary step of nucleophilic addition and various other consecutive reactions. The former process, in general, follows a mechanism of type 1 which consists of two distinct elementary steps at least:

$$\mathrm{L} + \mathrm{B} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{LB} \qquad (1a)$$

$$\mathrm{LB} + \mathrm{E} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \mathrm{P} \qquad (1b)$$

L stands here for the molecule containing the electrophilic carbon-carbon double bond. B is a base, e.g., an amine (B = RR′R″N). The primary addition step (1a) leads to an association complex (LB) which for electrically neutral B is a zwitterion. When B is a primary or secondary amine intramolecular proton transfer may immediately follow reaction 1a or even occur simultaneously. The second reaction step (1b) involves an electrophile E and its nature will largely depend on the particular structure of L and B. There are various examples in which reaction 1a appears to be rate determining. In protic solvents usually the reaction with the proton (E = H^+) dominates. Commonly one works under conditions which make the step 1b irreversible for practical purposes ($k_{32} \sim 0$). The primary nucleophilic attack is often too fast for conventional kinetic studies and hence only equilibrium constants $K = k_{12}/k_{21}$ or overall rates $k' = k_{12}k_{23}/(k_{21} + k_{23})$ have been measured. Chemical relaxation and flow techniques offer a possibility to obtain direct information.

Stopped-flow (SF) measurements in most cases were found to be too slow to achieve the time resolution required. Temperature-jump (TJ) relaxation appears to be particularly suited as far as the time range is concerned but, on the other hand, has to face certain obstacles: in protic solvents the reaction mechanism is more involved than eq 1 indicates since both the solvent and its autodissociation product may act as nucleophiles as well and consequently several parallel reactions have to be included explicitly in a detailed kinetic analysis. Aprotic sol-

---

[†] Dedicated to Professor O. E. Polansky.

0002-7863/79/1501-4708$01.00/0