

# Infrared Spectroscopy and Conformation of Alkyl Vinyl Ketone Monomer

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## Synopsis

The correlation between IR spectra and conformations was examined in alkyl vinyl ketone monomer. The stretching absorption bands of double bonds shift to lower wave number with the decrease in Taft's  $\sigma^*$  values of alkyl groups, and, conversely, the deformation band of the vinyl group shifts to the higher wave number. The inductive effect of the alkyl group is apparently three times larger in *s-cis* conformation than that in the *s-trans*. Absorption coefficients in the double-bond stretchings ( $A_{C=O}$  and  $A_{C=C}$ ) were measured in each conformation. Both conformations have a nearly equal value of  $A_{C=O}$ . The ratio ( $A_{s-cis}/A_{s-trans}$ )  $C=C$  is  $3.4 \pm 1.0$ . The ratios ( $A'_{C=O}/A'_{C=C}$ ) are  $4.5 \pm 0.6$  for the *s-cis* conformation and  $15 \pm 2$  for the *s-trans* conformation in all alkyl vinyl ketones studied.

## INTRODUCTION

The IR spectrum of methyl vinyl ketone (MVK) was measured at a temperature between  $-75^\circ\text{C}$  and  $80^\circ\text{C}$ , by Noack and Jones,<sup>1</sup> and it was suggested that the MVK was in an equilibrium condition between the two conformations, *s-trans* and *s-cis*. We also reported that the MVK was an equilibrium mixture of the two conformations.

In this paper we measured IR spectra of alkyl vinyl ketone [methyl vinyl ketone (MVK), ethyl vinyl ketone (EtVK), *n*-propyl vinyl ketone (*n*-PrVK), iso-propyl vinyl ketone (*i*-PrVK), cyclo-hexyl vinyl ketone (*c*-HexVK), tert-butyl vinyl ketone (*t*-BuVK), and phenyl vinyl ketone (PhVK)], and then analyzed their conformation for polymerization. From the two conformations, all the alkyl vinyl ketones (AVK's) seem to have two coupled spectra of *s-trans* and *s-cis* conformations, respectively. The ratio of populations (*s-cis*/*s-trans*) increased with the bulkiness of the alkyl group ( $E_s^0$ ).<sup>2</sup>

Kossanyi<sup>3</sup> reported that  $\nu_{C=O}$  bands in all the AVK's and  $\nu_{C=C}$  bands in a few AVK's were measured in pairs. Bowles et al.<sup>4</sup> reported that  $\nu_{C-C}$ ,  $\delta_{CH=CH}$  out of plane and  $\delta_{CH_2}$  out of plane in the MVK were assigned with the two conformations. Katritzky et al.<sup>5</sup> reported the relation between the population of the conformations and the absorption coefficients of the  $\nu_{C=C}$  bands ( $A_{C=C}$ ) by assuming the  $A_{C=C}$  value of the propenal and *t*-BuVK.

We found that seven kinds of the AVK's have absorption spectra of the *s-trans* and *s-cis*. The positions of their spectra were dependent on the alkyl groups, referring to propenal, the MVK, and so on that have already been published.<sup>3,5-8</sup>

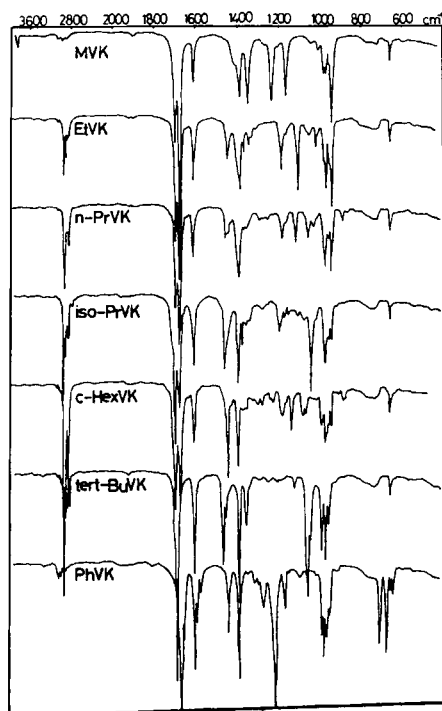


Fig. 1. IR spectra of alkyl vinyl ketone.

## EXPERIMENTAL

**Synthesis of AVK** was described in our previous paper.<sup>9</sup>

**IR measurement of AVK.** The IR spectra were measured in carbon tetrachloride at 25°C by use of the Shimadzu IR 27 G Type and Beckman IR 10 Type instrument with an NaCl cell and 0.1–0.5 mm spacers. As the calibration of the

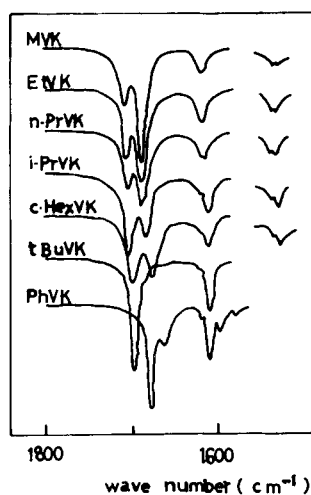


Fig. 2. IR spectra of alkyl vinyl ketone in the range of 1600–1800  $\text{cm}^{-1}$ . The bands due to the  $\nu \text{C}=\text{C}$  region are shown on the right-hand side of the figure.

frequencies were carried out by using H<sub>2</sub>O vapor and polystyrene,<sup>10</sup> errors in frequencies can be estimated to be 4 cm<sup>-1</sup> (in the region of 3100–2000 cm<sup>-1</sup>), 1 cm<sup>-1</sup> (2000–1600 cm<sup>-1</sup>), and 3 cm<sup>-1</sup> (1600–600 cm<sup>-1</sup>). The resolution was below 1 cm<sup>-1</sup>.

Measurements of the double-band stretching absorption coefficients ( $A'$ ) were carried out with a 0.5 cm<sup>-1</sup> slit width (in  $\nu$  C=C). All the AVK's were measured three times at different concentrations. The absorption coefficients were obtained by integrating the  $\epsilon^a$  values.

The separation of the two  $\nu$  C=C bands was carried out by assuming the absorption shapes to be similar. Although errors of the absorption coefficients obtained were about 10% for the A C=O bands and about 20% for the A C=C bands except for those for the *t*-BuVK *s*-trans, errors in the ratios of the absorption coefficients were smaller.

## RESULTS AND DISCUSSION

### Assignments of Absorption Bands

If the alkyl group of the AVK has a mass, the absorptions with a vinyl ketone skeletal structure (CH<sub>2</sub>=CH—CO—R) appear as 18 absorption bands similar to propenal. Figure 1 shows the IR spectra of the AVK and Table I indicates the skeletal bands for AVK.

**3000–3100 cm<sup>-1</sup>.** It was found that there were three absorption bands of vinyl group  $\nu$  C—H in this region for all AVK's. We identified  $\nu$  CH<sub>2</sub> asymmetric and  $\nu$  CH, and  $\nu$  CH<sub>2</sub> symmetric in order starting from high frequency.

**1600–1800 cm<sup>-1</sup>.** Kossanyi reported that the  $\nu$  C=O bands in all the AVK's and the  $\nu$  C=C bands in a few AVK's were observed as pair bands. In this study, each AVK could be measured having two  $\nu$  C=C bands (Fig. 2). From the change in the  $\epsilon^a$  C=C value in the bulkiness of the alkyl group, the high frequency bands were assigned to the *s*-trans conformer and the low to the *s*-cis conformer. It is contrary to the assignment of the  $\nu$  C=C bands in the case of the  $\nu$  C=O bands. In other words, the high frequency band of the  $\nu$  C=O bands was assigned to the *s*-cis conformer. Two  $\nu$  C=O overtone bands and only one  $\nu$  C=O overtone band in the *s*-cis were observed in the AVK.

**1000–1400 cm<sup>-1</sup>.** The  $\delta$  CH<sub>2</sub> in plane band of MVK was measured at 1400 cm<sup>-1</sup>.<sup>3</sup> The  $\delta$  CH<sub>2</sub> in plane band of the other AVK was also observed at the same frequency band at 1400 ( $\pm 1$ ) cm<sup>-1</sup>. Although Bowles et al.<sup>4</sup> assigned the  $\delta$  CH rock to 1281 cm<sup>-1</sup> in MVK, we observed two corresponding bands (1277 cm<sup>-1</sup> and 1292 cm<sup>-1</sup>) in each AVK except for *t*-BuVK. The result was confirmed from the fact that the two  $\delta$  CH in plane were assigned to methyl acrylates.<sup>11</sup> These bands in all the AVK's have assigned the *s*-cis conformation to a high frequency band and the *s*-trans conformation to a low frequency due to the variation of  $\epsilon^a$  by means of the alkyl group. The *s*-trans and *s*-cis conformations in  $\nu$  C—C of MVK were observed at 1245 cm<sup>-1</sup> and 1178 cm<sup>-1</sup>, respectively. In addition, the other AVK were also assigned to corresponding bands. Also, each AVK had two  $\nu$  C—R bands in the region of 1015–1050 cm<sup>-1</sup> except for *t*-BuVK.

**900–1000 cm<sup>-1</sup>.** It is well known that three kinds of C—H vinyl deformation modes, that is, the  $\delta$  CH=CH out of plane, the  $\delta$  CH<sub>2</sub> out of plane, and the CH<sub>2</sub> rock appear in this region. Each AVK had five bands, respectively. These bands

TABLE I  
 Skeletal Bands in Alkyl Vinyl Ketones<sup>a</sup>

Mode (cm <sup>-1</sup> )	MVK	Etvk	<i>n</i> -PrVK	<i>i</i> -PrVK	<i>c</i> -HexVK	<i>t</i> -BuVK	PhVK	$\rho^*$ (cm <sup>-1</sup> )
$\nu\text{CH}_2$ as	3103	3103	3104	3107	3105	3110	3092	ca. -25
$\nu\text{CH}$	3060	3063	3063	3064	3063	3066	3066	-20
$\nu\text{CH}_2$ s	3025	3027	3025	3027	3026	3030	3038	-18
$\nu\text{C}=\text{O}$ s-trans	1688	1689	1688	1683	1678	1684	1668	12
$\nu\text{C}=\text{O}$ s-cis	1707	1706	1704	1702	1698	1695	1678	38
$\nu\text{C}=\text{O}$ s-trans overtone	3360	3360	3360	3342	3320	—	3290	—
$\nu\text{C}=\text{O}$ s-cis overtone	3410	3400	3401	3404	3370	3380	3341	—
$\nu\text{C}=\text{C}$ s-trans	1619	1620	1620	1619	1619	1618	1619	4.3
$\nu\text{C}=\text{C}$ s-cis	1616	1617	1616	1615	1615	1613	1613	13
$\nu\text{C}=\text{C}$ s-cis overtone	3232	3230	3218	3230	3224	3222	3220	—
$\delta\text{CH}_2$ ip	1399	1399	1399	1400	1401	1399	1401	—
$\delta\text{CH}$ s-trans	1277	1274	1274	1268	1270	—	?	41
$\delta\text{CH}$ s-cis	1292	1285	1281	1274	1278	1265	1281	113
$\delta\text{C}-\text{C}$ s-trans	1245	1203	1193	1123	?	—	1232	—
$\delta\text{C}-\text{C}$ s-cis	1178	1121	1131	1051	1074	1074	?	—

$\delta\text{C}-\text{R}$ s-trans	1062	1048	1044	1035	1041	—	1027	—
$\delta\text{C}-\text{R}$ s-cis	1045	1035	?	1026	1029	1015	?	—
$\delta\text{CH}=\text{CH}$ op s-trans	981	983	982	982	982	—	993	-8.3
$\delta\text{CH}=\text{CH}$ op s-cis	991	994	994	997	999	1001	1002	-33
$\delta\text{CH}=\text{CH}$ op s-cis overtone	—	—	—	—	—	1993	2000	—
$\delta\text{CH}_2$ op s-trans	951	956	958	965	961	—	?	-63
$\delta\text{CH}_2$ op s-cis	963	968	969	975	974	983	978	-67
$\delta\text{CH}_2$ op s-trans overtone	1908	1916	1920	1932	1920	—	?	—
$\delta\text{CH}_2$ op s-cis overtone	1931	1938	1938	1953	1948	1968	1958	—
$\text{CH}_2$ rock	940	948	950	953	951	965	963	-80
$\delta\text{C}-\text{R}$ ip s-trans	836	835	834	836	830	—	838	—
$\delta\text{C}-\text{R}$ ip s-cis	823	816	815	810	813	801	?	—
$\delta\text{C}-\text{R}$ op s-trans	760	758	?	750	753	—	764	—
$\delta\text{C}-\text{R}$ op s-cis	776	770	766	762	760	749	753	—
$\delta\text{CH}_2=\text{CH}$ op s-trans	660	662	661	664	662	—	605	-24
$\delta\text{CH}_2=\text{CH}$ op s-cis	606	615	618	620	616	628	—	-71
$\delta\text{C}=\text{C}-\text{C}$	485	491	494	494	495	499	492	-42
$\sigma^*$	0.00	-0.10	-0.115	-0.19	-0.15	-0.30	0.60	—

<sup>a</sup> s: symmetric; as: asymmetric; ip: in plane; op: out of plane.

TABLE II  
 Absorption Bands Assigned to Alkyl Groups<sup>a</sup>

Mode	Wave number (cm <sup>-1</sup> )						
	MVK	EtVK	<i>n</i> -PrVK	<i>i</i> -PrVK	<i>c</i> -HexVK	<i>t</i> -BuVK	PhVK
$\nu$ CH <sub>3</sub> as	2965 w	2947 m		2963 st		2963 st	
$\nu$ CH <sub>3</sub> s	2860 w sh.	2912 m	2928 m sh.	2863 m		2869 m	
$\nu$ CH <sub>3</sub> as s-trans	1420 m sh.	1445 m		1456 m sh.		1476 st	
s-cis	1440 m sh.	1458 m	1454 m	1467 st		1476 st	
$\delta$ CH <sub>3</sub> s s-trans	1360 s	1354 m		1384 m			
s-cis	1380 m sh.	1379 m	1379 m sh.	1353 m		1400	
$\delta$ CH <sub>3</sub> rock s-trans	1020 w			1401 m sh.		1365 m	
s-cis	1014 sh.			1367 m			
$\nu$ CH <sub>2</sub> as		2983 st			2981 st		
$\nu$ CH <sub>2</sub> s		2878 m			2857 st		
$\delta$ CH <sub>2</sub> s-trans		1405 m sh.	1405 w sh.				
s-cis		1416 w sh.	1414 w sh.				
$\delta$ C—H s-trans				1331 w sh.			
s-cis				1338 w sh.			
$\nu$ C—H (benzene)					1329 w		3035 w sh.
$\delta$ C—H ip							1100 w 1076 w
$\delta$ C—H op							720 st 687 st
combination band							3392 w

<sup>a</sup> s: symmetric; as: asymmetric; ip: in plane; op: out of plane; st: strong; m: medium; w: weak.

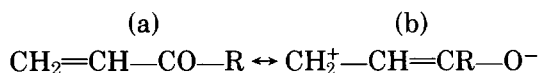
were distinguished in order of low absorption frequency to no. 5 from no. 1, except for *t*-BuVK. The band of  $\delta$  CH<sub>2</sub> out of plane and  $\delta$  CH=CH out of plane were observed for the two bands, respectively, in the case of the MVK and methyl acylate.<sup>4</sup> It is thought that nos. 2, 3 and nos. 4, 5 appear to have two bands, respectively, due to the conformation of the AVK. From this fact, it was concluded that the band of nos. 2 and 3 are  $\delta$  CH<sub>2</sub> out of plane in the *s*-trans and *s*-cis conformations, the bands of nos. 4 and 5 are  $\delta$  CH=CH out of plane of *s*-trans and *s*-cis conformations, and finally, the band of no. 1 is CH<sub>2</sub> rock.

**400–900 cm<sup>-1</sup>.** Four kinds of modes, that is,  $\delta$  C—R in plane, out of plane,  $\delta$  CH<sub>2</sub>=CH out of plane, and  $\delta$  C=C—C in plane were observed as pair for each AVK except for *t*-BuVK.

**The Band of the Alkyl Group.** Many kinds of modes in the alkyl group of AVK are assigned with a reference to the IR spectra of alkyl methyl ketone and carboxylates, as listed in Table II. These were observed as pair bands in the case of the methyl, ethyl, and isopropyl groups, but were not clear in *n*-propyl and *c*-hexyl groups.\* The bands of the many *s*-cis conformers were measured at higher frequency than that of *s*-trans conformation as a result of the calculation of  $\epsilon^a$ .

### Effect of the Alkyl Group on the Frequencies of the Skeletal Bands

The frequencies of the skeletal bands were plotted against Taft's  $\sigma^*$  values<sup>12</sup> for the alkyl group to estimate the effect of the alkyl group, as shown in Figures 3(a) and 3(b). There were good linear relations between the frequency of skeletal band and Taft's  $\sigma^*$  values. The tendencies ( $\rho^*$ ) of the relation that is, slopes, are shown in the parentheses in the figure. Although the frequencies of the  $\nu$  C=O and the  $\nu$  C=C bands in the *s*-trans conformation were about the same values compared with Taft's  $\sigma^*$  values, the frequencies of that in the *s*-cis conformation were shifted to a lower frequency according to the decrease in the  $\sigma^*$  value. AVK takes two stable resonance structures as shown in the following scheme:



As the carbonyl and vinyl groups arrange in the same direction and ionic structure (b) is stable in the case of the *s*-trans conformation, the effect of the alkyl group on the frequencies of the skeletal modes is small.

On the other hand, the vinyl group of the *s*-cis conformation is largely affected by the alkyl group due to opposing direction of the alkyl group to the vinyl group. The  $\rho^*$  values of the  $\nu$  C=O bands are 38 cm<sup>-1</sup> in the *s*-cis conformation and 12 cm<sup>-1</sup> in the *s*-trans conformation. O'Sullivan and Sadlar<sup>13</sup> reported that the value in the  $\nu$  C=O band of alkyl methyl ketone (AMK) was 52.56 cm<sup>-1</sup>. It seems that the  $\rho^*$  value in the *s*-trans conformation was small due to the stabilization of the resonance ion structure, and value in the *s*-cis conformation took an intermediate value between the value of the AMK and the value of the *s*-trans conformation due to the relaxation of the influence on the vinyl group. Although the frequencies of the  $\delta$  CH=CH out of plane and  $\delta$  CH<sub>2</sub>=CH out of plane bands in the *s*-trans conformation were almost constant in value as shown in nos. 4 and 8 of Figure 3(b), those in the *s*-cis conformation and the frequencies of  $\delta$  CH<sub>2</sub> out of plane and  $\delta$  CH<sub>2</sub> rock were shifted to a higher frequency with a decrease in the

\* These values were calculated from Ref. 4.

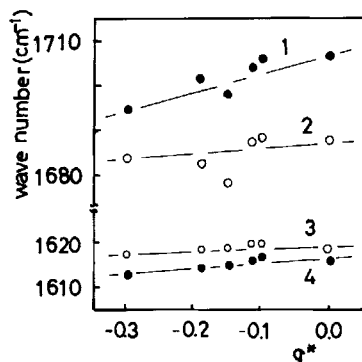


Fig. 3(a). Effect of the alkyl group on the skeletal absorption bands. The wave numbers of the double-bond stretchings are plotted against the  $\sigma^*$  value: (1)  $\nu\text{C}=\text{O}$  s-cis ( $\rho^* = 38\text{ cm}^{-1}$ ); (2)  $\nu\text{C}=\text{O}$  s-trans ( $\rho^* = 12\text{ cm}^{-1}$ ); (3)  $\nu\text{C}=\text{C}$  s-trans ( $\rho^* = 4.3\text{ cm}^{-1}$ ); (4)  $\nu\text{C}=\text{C}$  s-cis ( $\rho^* = 13\text{ cm}^{-1}$ ).

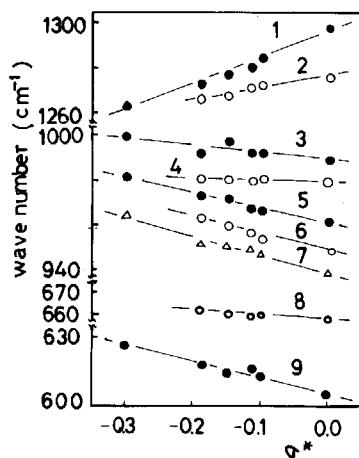


Fig. 3(b). Effect of the alkyl group on the skeletal absorption bands. The wave numbers of the deformation bands are plotted against the  $\sigma^*$  value: (1)  $\delta\text{CH}$  s-cis ( $\rho^* = 113\text{ cm}^{-1}$ ); (2)  $\delta\text{CH}$  s-trans ( $\rho^* = 41\text{ cm}^{-1}$ ); (3)  $\delta\text{CH}=\text{CH}$  op s-cis ( $\rho^* = -33\text{ cm}^{-1}$ ); (4)  $\delta\text{CH}=\text{CH}$  op s-trans ( $\rho^* = -8.3\text{ cm}^{-1}$ ); (5)  $\delta\text{CH}_2$  op s-cis ( $\rho^* = -67\text{ cm}^{-1}$ ); (6)  $\delta\text{CH}_2$  op s-trans ( $\rho^* = -63\text{ cm}^{-1}$ ); (7)  $\delta\text{CH}_2$  rock ( $\rho^* = -80\text{ cm}^{-1}$ ); (8)  $\delta\text{CH}_2=\text{CH}$  op s-trans ( $\rho^* = -24\text{ cm}^{-1}$ ); (9)  $\delta\text{CH}_2=\text{CH}$  op s-cis ( $\rho^* = -71\text{ cm}^{-1}$ ).

$\sigma^*$  value. These shifts can be explained clearly by assuming that the force constants in the CH vinyl vibration increase with decrease in  $\nu\text{C}=\text{C}$ .

Moreover, the ratios of the slope ( $\rho$  s-cis/ $\rho$  s-trans) were about the same value, namely, 3 (3.2 in the  $\nu\text{C}=\text{O}$ , 3.0 in the  $\nu\text{C}=\text{C}$ , 4.0 in the  $\delta\text{CH}=\text{CH}$  out of plane, 3.0 in the  $\delta\text{CH}_2=\text{CH}$  out of plane, and 2.5 in the CH rock).

It was reported that the frequencies of the  $\delta\text{CH}=\text{CH}$  and  $\delta\text{CH}_2$  out of plane bands were also shifted by the inductivity of the vinyl substituent.<sup>14</sup> We concluded from the above-mentioned results that the frequencies of the AVK are shifted according to the inductivity effect of the alkyl group. The frequencies of the s-cis conformation are affected by more than three times in the case of the s-trans conformation. The shifts in the double-bond stretchings were supported by means of the LCAO—MO—SCF—CNDO/2 approach.\* The band orders were smaller in the s-cis than in the s-trans conformation (Table III). The results

\* As PVK has a benzene ring and the  $\Delta\delta$  is affected by a shielding of benzene ring, the ratio of s-cis conformer has not been evaluated.

† We measured the NMR spectra of *i*-PVK at  $-130^\circ\text{C}$ , but could not detect the conformational signals. We observed only a tendency of the separation for two conformations.



TABLE III  
Formal Charge Differences of Double-Bond Atoms and  $\pi$ -Bond Order in Double Bonds

AVK	MVK	EtVK	<i>n</i> -PrVK	<i>i</i> -PrVK	<i>c</i> -HexVK	<i>t</i> -BuVK	PhVK <sup>a</sup>
Formal charge difference							
C=C <i>s</i> -trans	0.0359	0.0365	0.0359	0.0367		0.0371	0.0499
C=C <i>s</i> -cis	0.0523	0.0540	0.0538	0.0565	0.0574	0.0531	-0.0273
( <i>s</i> -cis/ <i>s</i> -trans)	1.457	1.479	1.499	1.540		1.431	
C=O <i>s</i> -trans	0.5072	0.5012	0.4988	0.5184		0.5086	0.4929
C=O <i>s</i> -cis	0.5178	0.5118	0.5094	0.5247	0.5424	0.5182	0.4778
( <i>s</i> -cis/ <i>s</i> -trans)	1.021	1.021	1.021	1.012		1.019	0.969
$\pi$ -Bond order							
C=C <i>s</i> -trans	0.9587	0.9585	0.9586	0.9579		0.9571	0.9571
C=C <i>s</i> -cis	0.9570	0.9567	0.9568	0.9564	0.9481	0.9553	0.9587
C=O <i>s</i> -trans	0.9170	0.9183	0.9181	0.9128		0.9158	0.9025
C=O <i>s</i> -cis	0.9126	0.9139	0.9137	0.9091	0.8948	0.9070	0.9073

<sup>a</sup> These values in PhVK were calculated for the planar conformations.

TABLE IV  
 Double-Bond Stretching Absorption Coefficients of AVK's

AVK	MVK	EtVK	<i>n</i> -PrVK	<i>i</i> -PrVK	<i>t</i> -BuVK	PhVK
A' C=O <i>s</i> -cis (1/mol-cm <sup>2</sup> )	2080	2230	2230	3290	4570	5350
A' C=O <i>s</i> -trans (1/mol-cm <sup>2</sup> )	4500	3490	3260	1670	250	1780
A' <i>s</i> -cis/A' <i>s</i> -trans) C=O	0.46	0.64	0.68	1.97	18.3	3.0
A' C=C <i>s</i> -cis (1/mol-cm <sup>2</sup> )	357	514	551	702	1090	1250
A' C=C <i>s</i> -trans (1/mol-cm <sup>2</sup> )	296	237	224	120	25.3 <sup>a</sup>	120
(A' <i>s</i> -cis/A' <i>s</i> -trans) C=C	1.21	2.17	2.46	6.00	43	10.4
(A' C=O/A' C=C) <i>s</i> -cis	4.69	4.34	4.05	4.32	4.19	4.28
(A' C=O/A' C=C) <i>s</i> -trans	15.21	14.73	14.55	13.92	9.88 <sup>a</sup>	14.83
A' C=O <i>s</i> -cis/(A' C=O <i>s</i> -cis + A' C=O <i>s</i> -trans)	0.284	0.390	0.406	0.663	0.948	0.750
A C=C <i>s</i> -cis	1313	1318	1357	1149	1150	1667
A C=C <i>s</i> -trans	405	389	377	356	327	480
(A <i>s</i> -cis/A <i>s</i> -trans) C=C	3.24	3.39	3.60	3.23	3.52	3.47
A C=O (1/mol-cm <sup>2</sup> )	6160	5720	5490	4960	4820	7130
$\Delta\delta$ (ppm) <sup>b</sup>	0.281	0.373	0.371	0.496	0.658	0.52

<sup>a</sup> The errors of these values are relatively large.

<sup>b</sup> Chemical shift difference of two geminal vinylic hydrogen atoms.

are contrary to the spectra. For this reason, the results calculated should be checked carefully.

### Double-bond Stretching Absorption Coefficients

Absorption coefficients ( $A$ ) of the double-bond stretching were changed by the ratio of the population of the two conformation (Fig. 2). As the two  $\nu$  C=C bands can be measured in the AVK,  $A'$  values were obtained directly by the separation of the bands, where the  $A'$  value is the absorption coefficient of each conformation in the equilibrium condition at 25°C in carbon tetrachloride (Table IV). The ratios of the  $A'$  values ( $A'$  s-cis/ $A'$  s-trans) were changed in the range of 0.46 (MVK) to 18.3 (*t*-BuVK) in the  $\nu$  C=O bands and 1.21 (MVK) to 43 (*t*-BuVK) in the  $\nu$  C=C bands according to the bulkiness of the alkyl group. On the other hand, the ratios ( $A'$  C=O/ $A'$  C=C) were about the same value, namely,  $4.5 \pm 0.6$  in the s-cis and  $15 \pm 2$  in the s-trans conformation except for *t*-BuVK s-trans.

Erskine and Waight<sup>15</sup> reported that ratio ( $A$  C=O/ $A$  C=C) was in the s-trans conformation in the cyclic enones. Our results approximately coincide with the reported values. The population of each conformation can be obtained by the comparison with the proportion of  $\epsilon^a$  C=O s-cis against the chemical shift difference ( $\Delta\delta$ ) of the two geminal vinylic protons.<sup>1</sup> As the  $\Delta\delta$  has a better linear relation with proportion of the  $A'$  C=O s-cis. The proportion of the s-cis conformation can be assumed in the expression of [ $A'$  s-cis/ $A'$  s-cis +  $A'$  s-trans]. The ratio of the two  $A$  C=C values is a constant value of about  $3.4 \pm 0.5$ . From the results, the population of the s-cis conformation in the phenyl vinyl ketone was 0.75.\*

### CONCLUSIONS

As the isomerization rate between the two conformations was too fast,<sup>†</sup> all kinds of IR absorption could not be clarified due to the overlap. However, the absorption seems to appear as pair bands. The frequencies of many kinds of the bands in the AVK were shifted according to the inductivity of the alkyl group. The stretching of the double bond was shifted to a lower frequency. The deformation of the vinyl group was generally shifted to a higher frequency because of the inductive effect of the alkyl group. The ratios of the slopes in the two conformational bands ( $\rho$  s-cis/ $\rho$  s-trans) were about the same value, i.e., 3. The shifts of the frequencies of the double-bond stretchings were supported by the change in the  $\pi$ -bond orders. The population of each conformation was determined by means of the chemical shift difference of the two geminal-vinylic protons. The population of the s-cis conformation was obtained by the difference in the population of  $A'$  C=O s-cis. The ratios of the absorption coefficients ( $A'$  C=O/ $A'$  C=C) were  $4.5 \pm 0.6$  in the s-cis and  $15 \pm 2$  in the s-trans conformations. The ratio ( $A$  s-trans/ $A$  s-cis) C=C was  $3.4 \pm 1.0$ . Measurements of the dependence on temperature were not performed with all of the AVK. In the future we hope to use more precise IR instruments with variable temperatures.

\* The  $\nu$ CH<sub>2</sub> asymmetry bands in EVK, *n*-PVK, *i*-PVK, *c*-HVK have one shoulder absorption at high frequency, respectively [ca. 3092 cm<sup>-1</sup> (EVK), ca. 3090 cm<sup>-1</sup> (*n*-PVK), ca. 3094 cm<sup>-1</sup> (*i*-PVK), ca. 3094 cm<sup>-1</sup> (*c*-HVK)].

### References

1. K. Noack and R. N. Jones, *Can. J. Chem.*, **39**, 2225 (1961).
2. (a) A. Kinoshita, I. Naito, Y. Namariyama, M. Nakazata, and K. Murase, *Bull. Tech. Assoc. Graphic Arts (Jpn.)*, **15**(4), 101 (1975); (b) I. Naito, A. Kinoshita, and T. Yonemitsu, *Bull. Chem. Soc. Jpn.*, **49**, 339 (1976).
3. J. Kossanyi, *Bull. Soc. Chim. Fr.*, 1704 (1965).
4. A. J. Bowles, W. O. George, and W. F. Maddams, *J. Chem. Soc.*, (**B**), 810 (1969).
5. A. R. Katritzky, R. F. Prizell, and R. D. Tomson, *Tetrahedron*, **28**, 3449 (1972).
6. R. K. Harris and R. E. Witkowski, *Spectrochim. Acta*, **20**, 1651 (1964).
7. R. K. Harris, *Spectrochim. Acta*, **20**, 1129 (1964).
8. R. R. Birge, W. C. Pringle, and P. A. Leermakers, *J. Am. Chem. Soc.*, **93**, 6715 (1971).
9. I. Naito, A. Kinoshita, and Y. Namariyama, *Nippon Kagaku Kaishi*, **1**, 166 (1976).
10. M. Kotake, Ed., *Jitsuken Kagaku Kohza Zoku 10*, Maruzen, Tokyo 1964, p. 159.
11. A. J. Bowles, W. O. George, and D. B. Cunliffe-Jones, *J. Chem. Soc.*, (**B**), 1070 (1970).
12. M. S. Newman, Ed., *Steric Effects in Organic Chemistry*, Wiley, New York, 1956, p. 598.
13. D. H. O'Sullivan and P. W. Sadler, *J. Chem. Soc.*, 4144 (1957).
14. W. J. Potts and R. A. Nyugst, *Spectrochim. Acta*, **15**, 679 (1959).
15. R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960).

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