# Thermodynamics of Vinyl Ethers. IV. Rotational Isomerism and the Relative Stabilities of the Geometric Isomers of Alkyl 1-Propenyl Ethers

ESKO TASKINEN and PIRJO LIUKAS

Department of Chemistry, University of Turku, SF-20500 Turku 50, Finland

Equilibrium concentrations of the E and Z forms of some alkyl 1-propenyl ethers have been determined in the neat liquid at various temperatures. The values of ΔH° and ΔS° of these reactions suggest the presence of planar s-cis and s-trans (but not the nonplanar gauche) rotamers in the E forms of the compounds studied. An exception is t-butyl 1-propenyl ether which probably adopts only the s-trans configuration in each of the geometric isomers. The enthalpy of the s-trans rotamer of the E isomer of methyl 1-propenyl ether is about 4.0 kJ mol^{-1} higher than that of the s-cis rotamer. The relatively high enthalpy and entropy values of compounds of the type (Z)-MeOC(R$_1$)= CHR$_2$, where R$_1$ and R$_2$ are alkyl groups, are explained to be due to steric interactions between the methoxy group and R$_1$ in the planar s-trans rotamer.

In previous papers,[1-3] the relative stabilities of various α,β-unsaturated (vinyl) ethers differing in either the degree of double bond substitution by alkyl groups or geometric isomerism about the double bond have been studied. A considerable increase of enthalpy (as well as entropy) has been observed to result from the introduction of an alkyl group at the β carbon of the vinyl group in a cis position with respect to the methoxy group as in the reaction

$$\text{(1)}$$

E form $\qquad$ Z form
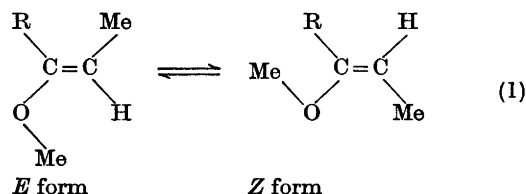
for which, in case R = Me, ΔH° (g, 298.15 K) = 9.85 ± 0.41 kJ mol^{-1} and ΔS° (g, 298.15 K) = 13.4 ± 0.9 J K^{-1} mol^{-1}.[3] In the compounds studied previously in this series, the group R has always been larger than hydrogen and therefore it was felt necessary to obtain thermodynamic data for reaction (1) in the case R = H. Compounds of this kind have been the subject of several investigations [4-7] among which the most extensive work is that of Okuyama et al.[6] These authors reported the values of the thermodynamic functions of isomerization for reaction (1) (R = H) but, unfortunately, the values of ΔH°, ΔS°, T, and the equilibrium constant K given are in mutual disagreement. In order to check the results of the above authors, the relative stabilities of a number of alkyl 1-propenyl ethers were determined over a relatively wide range of temperature (more than 100 K). In the experimental performance of the measurements, the procedure proposed by Okuyama et al.[6] was used with slight modifications.

EXPERIMENTAL

Materials. Methyl 1-propenyl ether (I). 1-Chloropropyl methyl ether was prepared from methanol, propionaldehyde, and hydrogen chloride by the procedure described by Swallen and Boord.[8] The crude chloro ether was dropped in boiling pyridine after which I could be isolated from the reaction mixture by fractional distillation. After redistillation from metallic sodium, the yield of I boiling at 318.9 − 320.6 K/101.0 kPa was about 60 % (lit.,[5] IZ b.p. 316.7 − 317.2 K/101.9 kPa, IE 321.2 − 321.7

K/102.8 kPa). The product consisted of *ca.* equimolar amounts of the geometric isomers, and it was fractionated further to give the isomer mixtures used in the equilibrations.

Ethyl 1-propenyl ether (II). A 50 % yield of propionaldehyde diethyl acetal (b.p. 396.2 − 397.2 K/101.3 kPa) was obtained from propionaldehyde (0.5 mol), ethanol (1.75 mol) and concentrated hydrochloric acid (1 cm³).[9] The acetal was heated with a small amount of sodium hydrogen sulfate in a distillation apparatus and the mixture of ethanol and II which was collected at 338 − 348 K was washed four times with water and the organic layer was dried over calcium chloride. The yield of II (b.p. 339 − 347 K/101.6 kPa, lit.,[10] II*Z* 342.2 K/100.6 kPa, II*E* 348.2 K/101.0 kPa) was about 23 %.

Isopropyl 1-propenyl ether (III). Propionaldehyde di-isopropyl acetal (b.p. 316.2 K/1.6 kPa) was prepared as described by Kulesza *et al.*[11] The yield was 34 %. The product was cleaved to a mixture of isopropyl alcohol and III by means of a catalytic amount of sulfanilic acid in the manner described above for II. The yield of III (b.p. 356.0 − 358.0 K/100.9 kPa, lit.,[10] III*Z* 356.2 K/100.0 kPa, III*E* 363.7 K/100.0 kPa) was 55 %.

s-Butyl 1-propenyl ether (IV). This product was prepared as described above for III. The di-*s*-butyl acetal of propionaldehyde (b.p. 340.2 K/1.3 kPa), which was obtained in 22 % yield, was cleaved to *s*-butyl alcohol and IV by distillation from sulfanilic acid. The yield of IV (b.p. 378.0 − 383.0 K/101.6 kPa) was about 20 %.

t-Butyl 1-propenyl ether (V). *t*-Butyl allyl ether was prepared from *t*-butyl alcohol, allyl

alcohol and sulfuric acid.[12] The product (b.p. 373.2 K/101.3 kPa) was obtained in *ca.* 6 % yield. It was isomerized to *t*-butyl 1-propenyl ether by means of potassium *t*-butoxide in 1,2-dimethoxyethane.[4] After redistillation from sodium, the yield of V (pure *Z* isomer) was 25 %. The product boiled at 370.2 − 371.2 K/98.7 kPa.

Phenyl 1-propenyl ether (VI). Allyl phenyl ether was obtained from allyl bromide, phenol and potassium carbonate in acetone.[13] The product (b.p. 349.2 − 350.2 K/1.6 kPa) was isolated in 80 % yield. It was isomerized to VI (pure *Z* isomer) as described above for V. The yield of the product (b.p. 336.2 K/1.2 kPa, lit.,[14] 344 K/2.0 kPa) was 50 %.

Mercuric acetate (E. Merck AG, *pro analysi*) was used as received.

NMR spectra. The NMR spectra of the vinyl ethers studied were recorded on a 60 MHz Perkin Elmer Model R 10 spectrometer at 307 K. Carbon tetrachloride was used as solvent and tetramethylsilane as internal standard. The concentrations of the vinyl ethers were *ca.* 20 % (v/v). In general, mixtures of isomers were used for recording the spectra and because of the relatively low concentrations of the *E* isomers in the mixtures, accurate peak positions and coupling constants for the *E* forms could not be measured. An exception is I. The NMR spectra are shown in Table 1.

Procedure. The purities of the vinyl ethers used as substrates in the equilibrations were higher than 98 %. This was found by gas chromatography and NMR spectra. The impurity was mainly the corresponding acetal, the peak of which was easily separated from those of the vinyl ethers in the gas chromatographic analysis.

Table 1. NMR spectra of some alkyl 1-propenyl ethers in carbon tetrachloride at 307 K. Peak positions are given in τ values.

$$R-O-CH=CH-CH_3$$
$$a \quad b \quad c$$

R	Isomer	a	b	c	d	e	f	Coupling constants/Hz
CH₃ d	*E* *Z*	3.74 4.20	5.34 5.71	8.45 8.45	6.56 6.46	− −	− −	J_{ab} 12.9, J_{bc} 6.9 J_{ab} 6.0, J_{bc} 6.9
CH₃CH₂ d e	*Z*	4.14	5.74	8.47	8.78	6.27	−	J_{ab} 6.0, J_{bc} 6.9, J_{de} 7.1
(CH₃)₂CH d e	*Z*	4.11	5.71	8.48	8.80	6.14	−	J_{ab} 6.3, J_{bc} 6.9, J_{ac} 1.6, J_{de} 6.4
CH₃CH₂(CH₃)CH [a] d e f g	*Z*	4.09	5.71	8.46	9.09	6.37	8.84	J_{ab} 6.0, J_{bc} 6.0, J_{de} 7.1 J_{fg} 5.1
(CH₃)₃C d	*Z*	3.93	5.71	8.49	8.75	−	−	J_{ab} 6.7, J_{bc} 6.0, J_{ac} 1.5
C₆H₅ d	*Z*	3.75	5.29	8.31	2.7 −3.3	−	−	J_{ab} 6.0, J_{bc} 6.9, J_{ac} 1.7

[a] The signal of the g proton was not detected.

During the equilibrations, the only detectable side reaction was a slight increase of the amount of the acetal. The isomerization experiments were conducted in the neat liquid with mercuric acetate as catalyst. The amount of the catalyst in the substrate varied from 5 to 10 mass %. The substrate-catalyst combinations were enclosed in small ampoules which were then kept at the appropriate temperatures. For the tracking of the progress of isomerization, ampoules were quickly transferred to an ice-water bath to "stop" the isomerization (this procedure was necessary only for equilibrations carried out considerably above room temperature; at lower temperatures, the slowness of the isomerization reaction made this step superfluous) after which the ampoules were broken and a small volume (ca. 20 % of the original sample size) of a suitable organic base (diethyl amine, triethyl amine) was added into the substrate-catalyst mixture to prevent isomerization during the analysis. Okuyama et al.[6] did not use any base in their experiments but it is our experience that the reproducibility of the subsequent gas chromatographic analysis was essentially better if the samples of the equilibrium mixture injected into the gas chromatograph contained sufficient amounts of some organic base. After the isomer ratios in successive samples were found to be unchanged, the state of equilibrium was considered having been attained and the following samples were analyzed over sufficiently extended periods of time (usually about three to five times the time necessary for the isomer ratio to become constant) to ascertain that the isomer ratio really remained unchanged. Moreover, in many cases the position of equilibrium was approached from both sides and the results of such experiments were in nice agreement. Peak areas, which were considered to be proportional to the molar concentrations of the isomers,[1] were determined by the cut-and-weigh method. The column used in the analyses contained 10 % Carbowax 1500 on Chromosorb G. The order of elution through this column was Z, E in each case.

Determination of normal boiling points. The normal boiling points of the compounds studied were determined by the gas chromatographic method described previously.[2] The following compounds were used for the preparation of the reference curve (compound, relative retention time, normal boiling point): ethyl vinyl ether, 0.166, 309.7 K; isobutyl vinyl ether, 0.299, 356.2 K; isobutylidene ethyl ether, 0.366, 366.7 K; 1-methoxycyclopentene, 0.622, 387.0 K; 1-ethoxycyclopentene, 1.000, 409.0 K. The following boiling points were obtained for the compounds I−V (compound, relative retention time, boiling point at 101.3 kPa): IZ, 0.181, 316.2 K; IE, 0.195, 321.4 K; IIZ, 0.238, 337.2 K; IIE, 0.263, 345.4 K; IIIZ, 0.299, 356.2 K; IIIE, 0.329, 363.0 K; IVZ, 0.487, 377.9 K; IVE, 0.564, 383.2 K; VZ, 0.409, 371.5 K; VE,

0.473, 376.8 K. For the determination of the boiling points of VIZ and VIE, the reference curve was made by means of the following data: 1-ethoxycyclopentene, 0.460, 409.0 K; 1-methoxycyclohexene, 0.540, 417.0 K; 1-ethoxycyclohexene, 0.697, 435.0 K; 1-propoxycyclohexene, 1.000, 455.9 K. The relative retention times of VIZ and VIE were 0.904 and 1.000 corresponding to normal boiling points of 450.9 and 455.9 K, respectively.

RESULTS

The primary results of the equilibration experiments are shown in Table 2. From the values of the equilibrium constant at various temperatures, the values of $\Delta G°$, $\Delta H°$, and $\Delta S°$ at 298.15 K for each $E \rightleftharpoons Z$ isomerization were calculated as described earlier[1] and the results are collected in Table 3. In each case, a strictly linear relation between $\Delta G°$ and temperature was observed. By means of eqns (2) and (10) given in Ref. 2 the values of $\Delta H°$ and $\Delta S°$ in the liquid state were converted to those in the ideal gas state at 298.15 K (Table 4).

DISCUSSION

In general, our results (Table 3) are in qualitative agreement with those of Okuyama et al.[6] in the sense that the entropy change in each $E \rightleftharpoons Z$ isomerization is positive and that the enthalpy of isomerization decreases as the size of the alkyl group R increases. Quantitatively, the agreement between our results and those of Okuyama et al. is, however, poor. For example, in the reaction V$E \rightleftharpoons$ VZ (R $=$ t-Bu) the entropy change is about 0.4 J K^{-1} mol^{-1} according to Okuyama et al. but 6.3 J K^{-1} mol^{-1} according to our results. Similarly, in II$E \rightleftharpoons$ IIZ (R $=$ Et), the values of $\Delta H°$ and $\Delta S°$ are ca. 1.6 kJ mol^{-1} and 7.9 J K^{-1} mol^{-1}, respectively, in the paper of Okuyama et al. but about -0.65 kJ mol^{-1} and 1.1 J K^{-1} mol^{-1} according to our results.

It seems that the simplest case in the $E \rightleftharpoons Z$ reactions studied is the reaction V$E \rightleftharpoons$ VZ (R $=$ t-Bu). This can be inferred from the bulky size of the t-Bu group, which makes the s-*cis* configuration (see below) highly unfavored even in the E isomer. In the Z isomer the s-*cis* configuration is completely out of question. Therefore, as the orientation of the t-BuO group apparently remains unchanged in the reaction, the values of $\Delta H°$ and $\Delta S°$ may be considered

Table 2. Values of the mean equilibrium constant K and its standard error for the $E = Z$ isomerization reactions of some alkyl 1-propenyl ethers in the neat liquid. Mercuric acetate was used as catalyst. c denotes catalyst concentration, t the time from the start of the equilibration when the first accepted sample was analyzed and n the number of independent determinations. Initial contents of the Z isomers in the equilibration mixtures (mol %): a 77.0; b 40.0; c 76.5; d 81.4; e 49.0; f 83.5; g 100.0.

R	T/K	c/mass %	Start from	t/d	n	$K(E \rightleftharpoons Z)$	R	T/K	c/mass %	Start from	t/d	n	$K(E \rightleftharpoons Z)$
Me	263.2	5—10	a	7	5	0.918 ± 0.013	i-Pr	373.2	5	e	0.3	4	2.59 ± 0.07
	283.2		a	4	4	0.964 ± 0.012		373.2		d	0.3	4	2.61 ± 0.05
	294.2		a	3	4	0.984 ± 0.013		387.2		d	0.3	4	2.52 ± 0.01
	313.2		a	1	2	0.989 ± 0.001		399.2		e	0.3	4	2.51 ± 0.03
	313.2		b	1	2	1.007 ± 0.007		399.2		g	0.3	5	2.50 ± 0.01
	328.2		a	0.7	4	1.023 ± 0.006		423.2		d	0.2	4	2.42 ± 0.03
	336.2		b	0.8	2	1.049 ± 0.004							
	336.2		a	0.8	2	1.047 ± 0.003	s-Bu	272.7	5	f	5	4	2.67 ± 0.05
	343.2		b	0.3	5	1.042 ± 0.017		284.2		f	3	5	2.65 ± 0.07
	356.2		b	0.1	2	1.057 ± 0.007		293.7		f	0.8	8	2.58 ± 0.09
	357.2		a	0.2	2	1.066 ± 0.003		303.7		f	0.8	4	2.53 ± 0.07
	373.2		a	0.2	2	1.084 ± 0.021		323.2		f	0.3	6	2.42 ± 0.02
	373.2		b	0.2	3	1.085 ± 0.010		347.2		f	0.8	6	2.37 ± 0.02
	388.2		a	0.2	4	1.105 ± 0.012		360.2		f	0.3	4	2.32 ± 0.03
	403.2		a	0.1	3	1.138 ± 0.005		370.2		f	0.8	4	2.27 ± 0.03
Et	283.2	5	c	7	6	1.495 ± 0.036		397.2		f	0.3	4	2.22 ± 0.05
	295.2		c	9	6	1.476 ± 0.026		413.2		f	0.7	3	2.17 ± 0.02
	303.7		c	3	6	1.488 ± 0.027							
	333.2		c	0.3	6	1.438 ± 0.020	t-Bu	270.2	10	g	14	6	5.32 ± 0.04
	353.2		c	0.7	6	1.411 ± 0.016		293.2		g	6	6	5.00 ± 0.17
	373.2		c	0.3	5	1.403 ± 0.016		303.2		g	3	4	4.93 ± 0.08
	395.2		c	0.3	5	1.395 ± 0.010		323.2		g	1.9	6	4.65 ± 0.08
	410.2		c	0.2	9	1.371 ± 0.031		343.2		g	0.3	7	4.45 ± 0.08
i-Pr	270.2	5	d	6	5	3.16 ± 0.04		355.2		g	1.7	7	4.29 ± 0.06
	283.2		d	5	8	3.10 ± 0.09		369.2		g	0.8	7	4.21 ± 0.07
	293.7		d	1.8	7	3.07 ± 0.03		384.2		g	0.8	8	4.08 ± 0.03
	308.2		e	1.7	4	2.92 ± 0.06		406.2		g	0.8	8	3.95 ± 0.09
	308.2		g	1.6	6	2.93 ± 0.07	Ph	299.2	5	g	35	6	2.75 ± 0.01
	323.2		d	1.8	4	2.77 ± 0.05		308.2		g	22	5	2.74 ± 0.01
	323.2		e	1.8	3	2.80 ± 0.01		329.2		g	13	7	2.64 ± 0.04
	323.2		g	1.8	4	2.83 ± 0.07		347.2		g	27	5	2.58 ± 0.02
	345.2		e	0.9	4	2.71 ± 0.01		359.2		g	8	6	2.54 ± 0.03
	345.2		g	0.9	4	2.72 ± 0.04		373.2		g	8	6	2.49 ± 0.01
	360.2		e	0.8	4	2.63 ± 0.02		383.2		g	6	4	2.42 ± 0.04
	360.2		g	0.7	4	2.62 ± 0.02		397.2		g	2	5	2.39 ± 0.02
								415.2		g	4	8	2.34 ± 0.03

Table 3. Values of the thermodynamic functions $\Delta G°$, $\Delta H°$ and $\Delta S°$ for the $E \rightleftharpoons Z$ isomerization reactions of some alkyl 1-propenyl ethers in the neat liquid at 298.15 K. The errors are twice the standard errors.

R	$\Delta G°$/kJ mol⁻¹	$\Delta H°$/kJ mol⁻¹	$\Delta S°$/J K⁻¹ mol⁻¹
Me	0.044 ± 0.019	1.26 ± 0.12	4.09 ± 0.35
Et	−0.969 ± 0.018	−0.65 ± 0.10	1.07 ± 0.28
i-Pr	−2.702 ± 0.023	−1.75 ± 0.13	3.20 ± 0.37
s-Bu	−2.324 ± 0.013	−1.43 ± 0.08	2.99 ± 0.22
Ph	−2.541 ± 0.026	−1.50 ± 0.14	3.50 ± 0.38
t-Bu	−3.959 ± 0.018	−2.08 ± 0.11	6.29 ± 0.31

Table 4. Values of the thermodynamic functions $\Delta H°$ and $\Delta S°$ for the $E \rightleftharpoons Z$ isomerization reactions of some alkyl 1-propenyl ethers in the gas phase at 298.15 K.

R	$\Delta H°/kJ\ mol^{-1}$	$\Delta S°/J\ K^{-1}\ mol^{-1}$
Me	0.43 ± 0.32	2.85 ± 0.61
Et	-1.97 ± 0.31	-0.72 ± 0.57
i-Pr	-2.84 ± 0.33	1.81 ± 0.62
s-Bu	-2.28 ± 0.31	1.98 ± 0.55
Ph	-2.30 ± 0.33	2.73 ± 0.63
t-Bu	-2.94 ± 0.32	5.26 ± 0.59

reflecting only the enthalpy and entropy changes due to the altered position of the methyl group attached to the double bond. In the gas phase at 298.15 K, $\Delta H° = -2.94$ kJ mol⁻¹, which shows that there is a kind of attraction between the oxygen atom and the methyl group of the Z isomer. A similar situation prevails in 1-chloropropenes in which the enthalpy of the Z isomer is reported to be *ca.* 3.8 kJ mol⁻¹ lower than that of the E isomer.[15] For a compilation of other similar examples, see Ref. 16.

Next let us consider the isomerization of IE to IZ (R=Me). It is generally accepted that methyl vinyl ether (MVE) exists as a mixture of at least two rotamers the most stable of which is the planar s-*cis* rotamer (see, for example, Ref. 17 and the references cited therein). Thus it seems justified to assume that IE also exists mainly in the s-*cis* configuration:

s-*cis*   s-*trans*
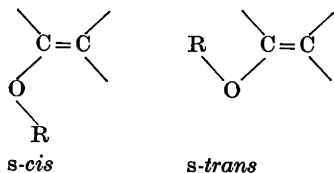
On the other hand, this configuration is impossible for IZ because of steric hindrance. Hence a change in the spatial orientation of the methoxy group is a necessity in the reaction IE⇌IZ. Apparently, the orientation of the methoxy group in IZ is the same as in the less stable rotamer of MVE. Owen and Seip[18] and Aroney *et al.*[19] have suggested that the second rotamer of MVE has a nonplanar heavy atom skeleton which results from the rotation of the methoxy group about the $O-C=$ bond. This view has been criticized by Katritzky *et al.*[20] and Cadioli and Pincelli.[17] The latter authors

studied the electronic structure of MVE through SCF calculations. The second rotamer of MVE was predicted to be s-*trans* with an enthalpy about 8.4 kJ mol⁻¹ higher than that of s-*cis*. The enthalpy of the nonplanar *gauche* rotamer (suggested by Owen and Seip[18] and Aroney *et al.*[19]) was calculated to be about 24 to 28 kJ mol⁻¹ higher than that of the s-*cis* rotamer. The experimental difference in the enthalpies of the two most stable rotamers of MVE, 4.8 ± 1.0 kJ mol⁻¹ in the gas phase at 298.15 K,[21] does not essentially differ from the value calculated by Cadioli and Pincelli.

The enthalpy change in IE⇌IZ is about 3.37 kJ mol⁻¹ more positive than in VE⇌VZ (Table 4), which apparently is to be ascribed to the rotation of the methoxy group from the s-*cis* configuration (in IE) to the other configuration, *gauche* or s-*trans* (in IZ). It seems, however, that IE exists as a mixture of two rotamers (*cf.* MVE) and hence the enthalpy of the mixture of rotamers is higher than that of the pure s-*cis* rotamer, which has the lower enthalpy. The difference between the enthalpies of the rotamers may be estimated as follows. Assuming that the entropy difference between the rotamers is negligible, the mol fraction of the less stable rotamer may be estimated to be about 0.15 (at 298.15 K) if it is further assumed (as a first approximation) that the enthalpy difference does not essentially differ from that between the rotamers of MVE (4.8 kJ mol⁻¹). If the enthalpies of the rotamers of IE are denoted by H_t and H_c where H_t is the enthalpy of the less stable rotamer and equal to $(H_c+4.8)$ kJ mol⁻¹ (as a first approximation), the following equation can be written:

$$H_t - [0.85H_c + 0.15(H_c + 4.8)] = 3.37 \qquad (2)$$

Hence $H_t - H_c$ is *ca.* 4.1 kJ mol⁻¹. If this enthalpy difference is used to estimate the mol fractions of the rotamers of IE (assuming $\Delta S = 0$), the mol fractions are obtained as 0.84 (s-*cis*) and 0.16 (s-*trans* or *gauche*). Eqn. (2) may now be replaced by

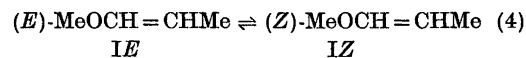$$H_t - [0.84H_c + 0.16(H_c + 4.1)] = 3.37 \qquad (3)$$

from which $H_t - H_c$ about 4.0 kJ mol⁻¹. The result achieved seems very reasonable.

The entropy change in the IE⇌IZ isomerization reaction, 2.85 J K⁻¹ mol⁻¹ in the gas phase at 298.15 K, is considerably less positive than
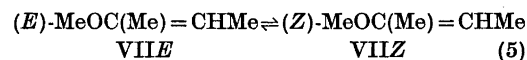
the entropy change in $VE \rightleftharpoons VZ$, 5.26 J K⁻¹ mol⁻¹. This is probably due to the presence of two rotamers in IE, which, through the entropy of mixing, increases the entropy of IE by as much as 3.66 J K⁻¹ mol⁻¹, if the mol fractions of the rotamers are taken as 0.84 and 0.16 (see above). Therefore, the entropy of isomerization of the pure s-*cis* rotamer of IE to IZ (which apparently exists as the pure s-*trans* rotamer, see later) should be about $3.66 + 2.85 \simeq 6.5$ J K⁻¹ mol⁻¹. The contribution of the entropy of mixing on the total entropy is, however, very sensitive to the values of the mol fractions of the rotamers and if the mol fractions are taken as 0.90 and 0.10, the "corrected" entropy change in I$E \rightleftharpoons$ IZ is obtained as 5.5 J K⁻¹ mol⁻¹. Hence the entropy change in this reaction is practically equal to that in $VE \rightleftharpoons VZ$, if the presence of rotational isomers in IE is taken into account.

It seems that the value of $\Delta S°$ in the reaction I$E \rightleftharpoons$ IZ is reasonable only if it is accepted that the configuration of the methoxy group of IZ is s-*trans*, which may be deduced as follows. If IZ existed in the nonplanar *gauche* configuration, this would imply the presence of two enantiomeric isomers in which the C atom of the methoxy group lies either below or above the plane formed by the group of the other heavy atoms $(O - C = C - C)$. In this case the value of the entropy change in the above reaction should be about 5.8 J K⁻¹ mol⁻¹ $(= R \ln 2)$ more positive than can be explained by the reasoning given above. However, as shown above, the "corrected" entropy change is very close to the entropy change in $VE \rightleftharpoons VZ$ in which no change in the configuration of the t-BuO group is expected. Hence only one rotamer is present in IZ and this rotamer must be s-*trans*. Thus it seems justified to assume that the configuration of the less stable rotamer of MVE is also s-*trans*, not *gauche*, in accordance with the predictions of Cadioli and Pincelli [17] and Katritzky et al. [20]

It is of interest to compare the values of $\Delta H°$ and $\Delta S°$ of the following reactions (gas phase, 298.15 K):

(E)-MeOCH = CHMe $\rightleftharpoons$ (Z)-MeOCH = CHMe (4)

     IE IZ

$\Delta H° = 0.43$ kJ mol⁻¹, $\Delta S° = 2.85$ J K⁻¹ mol⁻¹

(E)-MeOC(Me) = CHMe $\rightleftharpoons$ (Z)-MeOC(Me) = CHMe

    VIIE VIIZ (5)

$\Delta H° = 9.85$ kJ mol⁻¹, $\Delta S° = 13.4$ J K⁻¹ mol⁻¹ (Ref. 3)

A similar change of structure is seen to lead to very different values of $\Delta H°$ and $\Delta S°$ and, curiously enough, the enthalpy change is more positive in the latter reaction despite the *cis* methyl-methyl interaction in VIIE. As a possible explanation, it might be thought that the planar s-*trans* configuration is strongly unfavoured in VIIZ because of the close approach of the hydrogen atoms of the methoxy group and those of the α methyl group in this rotamer. As also the planar s-*cis* configuration is impossible in VIIZ, the methoxy group is forced to adopt a nonplanar configuration in which conjugation between the lone pair electrons of the oxygen atom and the π electrons of the double bond is essentially decreased, which leads to decreased stability. Thus it appears that VIIZ might exist as a mixture of several rotamers. On the contrary, VIIE probably exists only in the s-*cis* configuration because of the high enthalpy of the s-*trans* rotamer. The entropy of VIIZ is increased by the presence of several rotamers and therefore the entropy change in VII$E \rightleftharpoons$ VIIZ is exceptionally positive.

As to the values of $\Delta H°$ in the other isomerization reactions studied, a continuous decrease in $\Delta H°$ is observed as the size of the alkyl group increases. This probably reflects an increase of s-*trans* rotamers in the E isomers, due to the increase of strain in the s-*cis* configuration as the alkyl group becomes bulkier. It seems, however, that also the entropy term might favor s-*trans* rotamers because of restricted rotation of the alkyl group in the s-*cis* configuration. This should be apparent from the high entropy change, 37.5 ± 8.3 J K⁻¹ mol⁻¹, in the s-*cis* to s-*trans* reorientation of the t-BuO group in t-butyl formate.[22] The values of $\Delta S°$ in the above reactions are also qualitatively interpretable in terms of increased concentrations of the s-*trans* rotamers in the E isomers. A quantitative explanation of the enthalpy and entropy changes in these reactions is hardly possible.

REFERENCES

1. Taskinen, E. *J. Chem. Thermodyn.* 5 (1973) 783.
2. Taskinen, E. *J. Chem. Thermodyn.* 6 (1974) 271.
3. Taskinen, E. *J. Chem. Thermodyn.* 6 (1974). *In press.*
4. Price, C. C. and Snyder, W. H. *J. Amer. Chem. Soc.* 83 (1961) 1773.
5. Salomaa, P. and Nissi, P. *Acta Chem. Scand.* 21 (1967) 1386.
6. Okuyama, T., Fueno, T. and Furukawa, J. *Tetrahedron* 25 (1969) 5409.
7. Rhoads, S. J., Chattopadhyay, J. K. and Waali, E. E. *J. Org. Chem.* 35 (1970) 3352.
8. Swallen, L. C. and Boord, C. E. *J. Amer. Chem. Soc.* 52 (1930) 654.
9. Fischer, E. and Giebe, G. *Ber. Deut. Chem. Ges.* 30 (1897) 3053.
10. Farina, M., Peraldo, M. and Bressan, G. *Chim. Ind. (Milan)* 42 (1960) 967; *Chem. Abstr.* 55 (1961) 11284b.
11. Kulesza, J., Podlejski, J. and Druri, M. *Riechst. Aromen, Koerperflegem.* 16 (1966) 207; *Chem. Abstr.* 65 (1966) 10486h.
12. Lawesson, S.-O., Berglund, C. and Grönwall, S. *Acta Chem. Scand.* 15 (1961) 249.
13. Tarbell, D. S. *Org. React.* 9 (1944) 26.
14. Bieber, P. *Ann. Chim. (Paris)* 9 (1954) 674; *Chem. Abstr.* 50 (1956) 171c.
15. Alfassi, Z. B., Golden, D. M. and Benson, S. W. *J. Chem. Thermodyn.* 5 (1973) 411.
16. Waldron, J. T. and Snyder, W. H. *J. Amer. Chem. Soc.* 95 (1973) 5491.
17. Cadioli, B. and Pincelli, U. *J. Chem. Soc. Faraday Trans.* 2 (1972) 991.
18. Owen, N. L. and Seip, H. M. *Chem. Phys. Lett.* 5 (1970) 162.
19. Aroney, M. J., Le Fèvre, R. J. W., Ritchie, G. L. D. and Saxby, J. D. *Aust. J. Chem.* 22 (1969) 1539.
20. Katritzky, A. R., Pinzelli, R. F. and Topsom, R. D. *Tetrahedron* 28 (1972) 3441.
21. Owen, N. L. and Sheppard, N. *Trans. Faraday Soc.* 60 (1964) 634.
22. Oki, M. and Nakanishi, H. *Bull. Chem. Soc. Jap.* 43 (1970) 2558.