

(E—Z) ISOMERISM OF VINYL SULFIDES AND ETHERS

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Enthalpic data for the (*E—Z*) isomerisation of 1-methoxy-1-propene, 1-methylthio-1-propene, 1-methoxy-2-methylthioethene and 1,2-bis(methylthio)ethene were analyzed on the basis of calculated (CNDO/2) energy differences between the isomers.

In the present communication we report the thermodynamic data for (*E—Z*) isomerisation of 1-methoxy-1-propene and 1,2-bis(methylthio)ethene. We tried to interpret the results by comparison of the energy difference between optimum conformations of the isomers, calculated by the MO CNDO/2 method, with the ΔH value, determined from the temperature dependence of $K(Z/E)$. This comparison was done also for some other vinyl sulfides whose equilibria had been measured already previously.

For the (*E—Z*) isomerisation of 1-methoxy-1-propene contradictory data can be found in the literature. Thus, for $K(Z/E)$, T , ΔH and ΔS the following respective values have been published: 0.968, 298, 3.8 and 5.85 (ref.¹); 2.45, 298, —, — (ref.²); 0.984, 294, 1.26 and 4.09 (ref.³), and 0.834, 298, —, — (ref.⁴). We determined therefore repeatedly the dependence of the equilibrium on temperature and verified the extent of side reactions. Our mean values $K(Z/E) = 1.106$ (at 384 K), $\Delta H = 1.1$ kJ \cdot mol⁻¹ and $\Delta S = 3.7$ kJ mol⁻¹, are close to the results of Taskinen and Liukas³; the significant entropy factor can be ascribed mainly to conformational effects.

According to refs⁵⁻⁷, methoxyethene exists in two low-energy conformations, *sp* and *ac*, the first being more stable. It is assumed¹⁻³ that with increasing bulk of alkyl in the RO-group the *sp* conformation energy of the (*Z*)-isomer rapidly increases which, naturally, affects the equilibrium position. Epiotis with collaborators^{8,9} assume that the higher stability of (*Z*)-isomers of substituted propenes is due to the attractive interaction between the CH₃ orbitals and the hetero atom *p_z* orbitals resulting in a charge transfer. We calculated the dependence of the bond energy on the CH₃ group conformation, using the CNDO/2 method (Santry — Segal parameterisation¹⁰): the lowest energy of the *sp*-conformation of H—C—C=C is in accord with the generally higher stability of this conformation in compounds H₃C—C=X (propene, acetaldehyde, acetone)¹¹. The lower calculated energy difference between the *sp* and *ap* conformations of the (*Z*)-isomer (3.9 kJ mol⁻¹

as compared with 4.6 kJ mol^{-1} for the (*E*)-isomer) agrees with the lower barriers to rotation in 1-propene derivatives¹²⁻¹⁴. Because of the rigid rotor approximation, used in the calculations, the barrier heights do not represent the actual situation. For both conformations of the CH_3 group the optimum conformation about the $\text{H}_3\text{CO}-\text{C}=\text{C}$ bond was calculated (Fig. 1). The *ac*-conformations with torsion angle $130 \pm 5^\circ$ are energetically advantageous for both isomers; in the (*E*)-isomer the *sp*-conformation (angle $0 \pm 5^\circ$) is of comparable energy. Rotation of the CH_3 group in the (*E*)-isomer is practically free (calculated energy difference 5 kJ mol^{-1}), in the (*Z*)-isomer torsional vibrations $\pm 120^\circ$ about the *ap*-position are possible. Therefore substituent at $\text{C}_{(2)}$ has no substantial effect on the alkoxy conformation. Assuming the *ac*-conformations with 130° angle (or the energetically equivalent *sp*-conformation of the (*E*)-isomer), we calculated $\Delta E(\text{Z}-\text{E})$ to be -3.1 kJ mol^{-1} in favour of the (*Z*)-isomer; equation (A) shows the main interactions (positive numbers denote repulsive interactions).

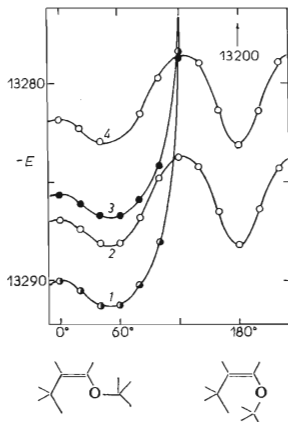
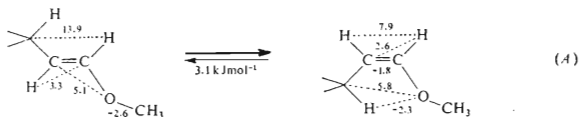
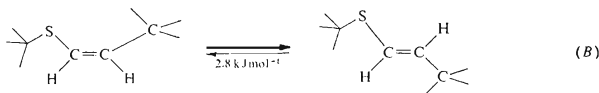


FIG. 1

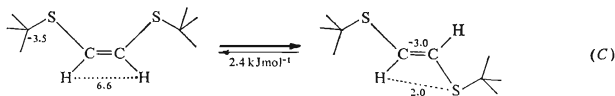
Dependence of the calculated energies of 1-methoxy-1-propene on the rotation angle about the $=\text{C}-\text{OCH}_3$ bond. Curves 1 (*Z*)-isomer, 2 (*E*)-isomer with *sp*-conformation of the $\text{H}-\text{C}-\text{C}=\text{C}$ segment; curves 3 (*Z*)-isomer, 4 (*E*)-isomer with *ap* conformation

For the analogous 1-methylthio-1-propene the equilibrium constant $K(Z/E)$ was found¹⁵ to be 0.94 at 323 K. For both isomers the ap -conformation of the $C=C-SCH_3$ bond was calculated (sp -basis set) to be energetically advantageous; in the (E)-isomer another minimum (sc -conformation, 30°) of somewhat higher energy (2.8 kJ mol^{-1}) was found. The calculated energy barriers for the (E)-isomer (2.5 and 5.5 kJ mol^{-1}) correspond to free rotation at 270 K whereas in the (Z)-isomer the rotation is again restricted to oscillation ($\pm 120^\circ$) about the ap -position. For the optimum conformations (equation (B)) the calculated energy difference $\Delta E(Z-E)$ was 2.80 kJ mol^{-1} . Since calculations, using the spd -basis set, were generally at variance with the experimental values, the calculations for sulfur compounds were performed only with the sp -basis set (Table I).



The equilibrium data found for thermal isomerisation of 1,2-bis(methylthio)-ethene at 439–490 K in cyclohexane, benzene and 1,4-dioxane are listed in Table II. At equilibrium, the (E)-isomer predominates and the enthalpy values (which are decisive) do not depend significantly on the solvent. However, substantial differences were found in the isomerisation rates which in cyclohexane and benzene are 40 times higher than in 1,4-dioxane. Probably, in dioxane the delocalization is influenced by solvation.

It follows from calculation using the sp -basis set that for the (E)- as well as (Z)-isomer the energy minimum is achieved in the ap -conformations of both the $H_3CS-C=C$ groups. Since methyl vinyl sulfide exists¹¹ at higher temperatures as a mixture of about 30% of s - cis and 70% of $gauche$ form, we performed also calculation with a fixed position of one $-SCH_3$ group (-106° relative to the sp -conformation of the $C-S-C=C$ segment) and found that the energy decreased systematically until the ap -position of the second $-SCH_3$ group was achieved. Rotation of the $-SCH_3$ group is free in the (E)-isomer but restricted in the (Z)-isomer. Equation (C) shows



the main interaction differences between the isomers calculated for the ap -conformations of both the $-SCH_3$ groups (the total energy difference is 2.4 kJ mol^{-1} in favour of the (E)-isomer). Due to compensation of bonding and antibonding interactions

in the (Z)-isomer and the great distance in the (E)-isomer the —S...S-interactions in both the isomers do not affect the result significantly. Using the *spd*-basis set, Epiotis and coworkers⁹ calculated $\Delta E(Z-E) = -20.3 \text{ kJ mol}^{-1}$ without describing the conformation; this calculation is at variance with the experimentally found equilibrium.

In our previous paper¹⁶ we published for 1-ethoxy-2-methylthioethene the following data: $K(Z/E) = 0.70$ at 433 K, $\Delta H = 9.9 \text{ kJ mol}^{-1}$ and $\Delta S = 20 \text{ J mol}^{-1} \cdot \text{K}^{-1}$. According to calculation, the energy minimum corresponds to the conformation with 150° torsion angle at the $\text{H}_3\text{CS}-\text{C}=\text{C}$ bond. In addition, for the (E)-isomer we found another, 10 kJ mol^{-1} higher, minimum, corresponding to the *sp*-conformation (0° angle). The difference between the energy minima, $\Delta E(Z-E)$, amounts

TABLE I
Energies calculated by the MO CNDO/2 method

Isomer	Part		Total energy kJ mol^{-1}
	monocentric	bicentric	
1-Methyl-1-propene			
Z	3 375.8	- 15 320.0	- 11 944.2
E	3 372.4	- 15 319.4	- 11 947.0
Z-E	3.4	- 0.6	2.8
1-Methoxy-1-propene			
Z	3 847.5	- 17 138.8	- 13 291.3
E	3 842.5	- 17 130.7	- 13 288.2
Z-E	5.0	- 8.1	- 3.1
1,2-Bis(methylthio)ethene- <i>ap</i> -conformation of both S-CH ₃ groups)			
Z	3 533.2	- 15 068.2	- 11 535.0
E	3 532.8	- 15 070.2	- 11 537.4
Z-E	0.4	2.0	2.4
1-Methoxy-2-methylthioethene			
Z	3 905.8	- 16 751.3	- 12 845.5
E	3 908.9	- 16 750.8	- 12 841.9
Z-E	- 3.1	- 0.5	- 3.6

to -3.6 kJ mol^{-1} (Table III); this calculation does not agree with the experimental value of ΔH . The reason can be neglect of the configurational electron interaction or use of the same geometric parameters for calculation of both isomers.

EXPERIMENTAL

A mixture of (*E*)- and (*Z*)-1-methoxy-1-propene was prepared by boiling 1-methoxy-1-chloropropane¹⁷ with pyridine and distillation of the product ($E/Z = 4 : 5$) which was freed of small amounts of propanal and methanol by distillation from sodium. The isomers, b.p. $54-48^\circ\text{C}/101 \text{ kPa}$, were separated by distillation on a column (40 TP), followed by preparative gas-liquid

TABLE II

Equilibration data for (*E*-*Z*) isomerisations

Solvent	$K(E/Z)$	ΔG	ΔH	ΔS
		kJ mol^{-1}		$\text{J mol}^{-1} \text{K}^{-1}$
1,2-Bis(methylthio)ethene				
Cyclohexane	1.82 ^a	2.14	2.8	2.4
Benzene	1.77 ^a	2.16	2.6	2.3
1,4-Dioxane	1.76 ^a	2.13	2.8	2.8
1-Methoxy-1-propene				
Benzene	0.90 ^b	0.33	1.1	3.7

^a 453 K; ^b 384 K.

TABLE III

Comparison of the calculated ΔE values with ΔH values (kJ mol^{-1})

Compound	ΔH	ΔE	$\Delta H - \Delta E$
$\text{H}_3\text{CS}-\text{CH}=\text{CH}-\text{SCH}_3$	2.8	2.4	-0.4
$\text{H}_3\text{CO}-\text{CH}=\text{CH}-\text{SCH}_3$	9.9 ^a	-3.6	-13.5
$\text{H}_3\text{C}-\text{CH}=\text{CH}-\text{SCH}_3$	1.9	2.8	-0.9
$\text{H}_3\text{C}-\text{CH}=\text{CH}-\text{OCH}_3$	-1.1	-3.1	2.0

^a $\Delta G_{433} = 1.25 \text{ kJ mol}^{-1}$; $\Delta S = 20 \text{ J mol}^{-1} \text{K}^{-1}$ (ref.¹⁶).

chromatography (20% squalane on Chromosorb W 0.2 mm, 5 m column, 35°C). Purity of the E and Z isomers was 95% and 96%, respectively and their IR spectra agreed with the reported ones¹⁸.

(Z)-1,2-Bis(methylthio)ethene was prepared by reaction of (Z)-1,2-dichloroethene with sodium methanethiolate¹⁹; its isomerisation²⁰ at 240°C afforded a mixture of (E)- and (Z)-isomers which were separated by chromatography on silica gel in benzene-hexane (1:9). The isomers were crystallized from light petroleum at -40°C.

The isomerisations were carried out in sealed ampoules in 1M solutions (Table II) in various solvents. In the case of 1-methoxy-1-propene the reaction was catalyzed with mercury acetate (10% of the substrate weight). The isomer content was followed by gas-liquid chromatography (for 1,2-bis(methylthio)ethene 2.4 m column with 5% Apiezon on Chromaton AWS, 150°C); for 1-methoxypropene the conditions were identical with those for preparative gas-liquid chromatography. The peak areas were calibrated, means of 6 determinations were taken.

The MO CNDO/2 calculations were carried out according to ref.^{21,22} using the following parameters. For vinyl sulfides: bond lengths ($\cdot 10^{-10}$ m) =C-H 1.08, CH₃-C= 1.50, C=O 1.22, CH₃O 1.426, O-C= 1.33, H₃C-S 1.817, =C-SR 1.74; angles in degrees: CH₃-C=C 122, C-O-C= 107, C-S-C= 104.5, C=C-O 123, C=C-S 124. For 1-methoxy-1-propene: C-C= 1.51, C=C 1.34; =C-H 1.08 (ref.⁵), =C-O 1.36; O-CH₃ 1.43, C-H 1.105 ($\cdot 10^{-10}$ m); angles: C=C-O 127.7, =C-O-C 116, C=C-H 117.5 and 119; other angles C-H 109.5 (ref. 5), C=C=C 122 (ref.²³).

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