Short Communication

Structure–Stability Relationships in Unsaturated Sulfur Compounds. VIII. Thermodynamics of the Geometric Isomers of Vinyl Sulfides, Sulfoxides and Sulfones

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The relative stability of the geometric isomers of 1,2-disubstituted ethenes has been widely studied.[1,2] Usually two substituents *cis* to each other cause steric strain, which makes the Z isomer the less stable one. Thus the strain between two *cis* methyl groups is ca. 4 kJ mol^{-1}.[2] In some cases, however, e.g., in *tert*-butyl 1-propenyl ether[3] and 1-chloro-1-propene[1] the Z isomer is the more stable one. For 1-chloro-1-propene the reason for this is the attraction between the positive charge in the methyl group and the negative charge in the chlorine atom in the Z isomer (Scheme 1).[1] Two *cis* methoxy groups also cause stabilization, which can, at least partly, be explained by the resonance structures in Scheme 2.[4] A similar explanation has been given for the relatively high stability of the Z isomer of 1,2-dichloroethene.[5]

In alkyl 1-propenyl sulfides there also seems to be electrostatic attraction between the sulfur atom and the methyl group when they are *cis* to each other, because $\Delta H^{\ominus}$ of the $E{\rightarrow}Z$ isomerization of *tert*-butyl 1-propenyl sulfide, which involves no changes in the spatial orientation of the *t*-BuS group, is -1.8 kJ mol^{-1}.[6] $\Delta H^{\ominus}$ of the $E{\rightarrow}Z$ reaction for 1,2-bis(ethylthio)ethene is
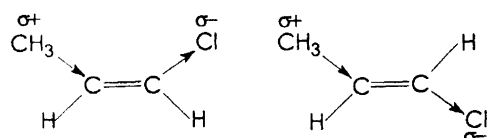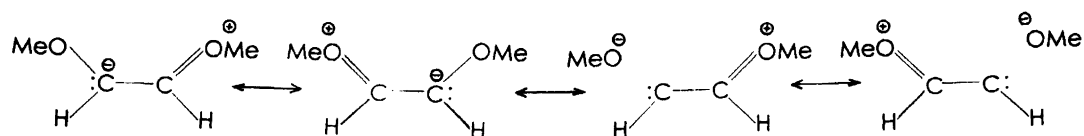
-2.9 kJ mol^{-1} and for 1-ethoxy-2-ethylthioethene is $+1.5$ kJ mol^{-1}; however this reaction involves rotations of the EtO– and EtS– groups. In the absence of these rotations, $\Delta H^{\ominus}$ of this reaction would also be negative.[6] Thus there is attraction between two sulfur atoms and a sulfur atom and an oxygen atom *cis* to each other.

$\Delta H^{\ominus}$ of the $E{\rightarrow}Z$ reaction of alkyl 1-propenyl sulfoxides and sulfones are highly positive, which evidently is caused by steric strain in the Z isomers.[7,8] *Ab initio* calculations, however, point to the existence of a hydrogen bond in the Z isomers between the oxygen atom and the hydrogen atom of the methyl group, which suggests that there is also attraction in the Z isomers of these compounds.[9]

Thus there are some interesting aspects in the $E{\rightarrow}Z$ isomerizations of vinyl sulfides, sulfoxides and sulfones and the aim of this study is to explore these aspects.

Results and discussion

$$(1)$$
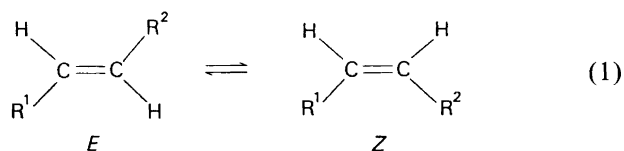
In this work the $E{\rightarrow}Z$ isomerization in eqn. (1) was studied. The $\Delta H^{\ominus}$ (or $\Delta G^{\ominus}$) values for the studied reactions are summarized in Table 1. It can be seen that

Scheme 1.

Scheme 2.

Table 1. The values of the thermodynamic functions for the studied reactions at 298 K. The errors are twice the standard errors.

Reaction	R^1	R^2	$\Delta H^{\ominus}$/kJ mol⁻¹	$\Delta G^{\ominus}$/kJ mol⁻¹	Ref.
(1)	Me	Me	+4.3		2
(2)	Me	Et	+4.3		2
(3)	Me	*i*-Pr	+4.0		2
(4)	Me	*t*-Bu	+16.2		2
(5)	Et	Et	+6.8		2
(6)	EtS	Me	+0.0(3)	+1.2(6)	6
(7)	EtS	Et	−0.7(6)	−0.8(1)	
(8)	EtS	*i*-Pr	+0.1(1)	+1.6(1)	
(9)	EtS	*t*-Bu	+10.1(4)	+10.4(1)	
(10)	EtS	Ph		+5.3(4)[a]	
(11)	EtSO	Me	+7.5(6)	+7.4(1)	7
(12)	EtSO₂	Me	+9.8(7)	+10.8(2)	8
(13)	(*E*)-MeCH=CHSO	Me		+6.3(2)[a,b]	
(14)	(*Z*)-MeCH=CHSO	Me		+4.9(4)[a,b]	
(15)	(*E*)-MeCH=CHSO₂	Me		+9.2(5)[a,b]	8
(16)	(*Z*)-MeCH=CHSO₂	Me		+4.0(6)[a,b]	8
(17)	*t*-BuS	Et		−0.1(1)[a]	
(18)	*t*-BuS	Me	−1.8(1)	−0.9(1)	6
(19)	PhS	Et	+1.1(4)	+0.5(1)	
(20)	PhS	Me	−0.3(1)	−0.1(1)	6
(21)	*i*-PrS	Et	−1.2(4)	−0.4(1)	
(22)	*i*-PrS	Me	+0.2(1)	−0.7(1)	6

[a] The temperature dependence of K could not be measured sufficiently accurately to obtain reliable values for $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$.
[b] $\Delta G^{\ominus}$ values are statistically corrected.

the Me⋯Me, Me⋯Et and Me⋯*i*-Pr *cis* interactions are all ca. +4 kJ mol⁻¹. Only the Me⋯*t*-Bu *cis* interaction is larger, i.e., +16 kJ mol⁻¹. The Et⋯Et *cis* interaction is ca. +7 kJ mol⁻¹.

In ethyl 1-propenyl sulfide the $E \rightarrow Z$ isomerization involves a change in the spatial orientation of the EtS group,[6] which increases the enthalpy of the Z isomer by 1.8 kJ mol⁻¹.[6] The EtS⋯Me, EtS⋯Et and EtS⋯*i*-Pr *cis* interactions are thus all ca. −2 kJ mol⁻¹, i.e., there is some attraction in all these cases. The EtS⋯*t*-Bu *cis* interaction is considerably larger, i.e., about +8 kJ mol⁻¹, which shows that there is considerable steric strain in this case. Because the EtS⋯*i*-Pr interaction is ca. −2 kJ mol⁻¹, it can be concluded that an *i*-Pr group can rotate into a position in which it does not cause more steric strain than a methyl group.

The difference between the Me⋯Me and the Me⋯*t*-Bu *cis* interactions is 12 kJ mol⁻¹, which is almost as large as the corresponding difference in ethyl vinyl sulfides (10 kJ mol⁻¹). The $\Delta G^{\ominus}$ value for the $E \rightarrow Z$ isomerization of 1-ethylthio-2-phenylethene is +5.3 kJ mol⁻¹. This isomerization also involves the rotation of the EtS group, which increases the $\Delta G^{\ominus}$ value of this reaction by ca. 1.8 kJ mol⁻¹. In the absence of this rotation the $\Delta G^{\ominus}$ value would be +3.5 kJ mol⁻¹, i.e., there is evidently some steric strain in the Z isomer. This strain does not, however, force the phenyl ring out of the C=C plane, because if this were the case, it would increase the electron density at the β carbon (because the resonance caused by the phenyl group would decrease). The ¹³C shifts of the β carbons of the geometric isomers are about the same, so there is no increase in the electron density.

$\Delta H^{\ominus}$ of the $E \rightarrow Z$ isomerization of alkyl 1-propenyl sulfoxides are ca. +7 kJ mol⁻¹ [7] and $\Delta H^{\ominus}$ for the corresponding reaction of alkyl 1-propenyl sulfones are ca. +11 kJ mol⁻¹.[8] Thus there is considerable steric strain in the Z isomers of all of these compounds. According to *ab initio* MO calculations the most stable rotamer of both (*Z*)-methyl 1-propenyl sulfoxide and sulfone has the S=O bond eclipsing the double bond.[9] In (*Z*)-alkyl 1-propenyl sulfoxides the conformation with the lone-pair of electrons of the sulfur atom *cis* to the double bond is also a stable one and it is sterically considerably less strained. It has been suggested that a hydrogen bond is formed between the oxygen atom and the hydrogen atom of the β methyl group, which would explain the high stability of the most stable conformation. This problem can also be studied with the aid of the ¹³C NMR shifts. The ¹³C signals of the β carbons of the Z isomers of alkyl 1-propenyl sulfoxides are ca. 1.5 ppm downfield from the corresponding signals of the E isomers. The corresponding difference in alkyl 1-propenyl sulfones and di(1-propenyl) sulfones are 0.5–1 ppm upfield,[7] i.e., the conjugation in the Z isomers of alkyl 1-propenyl sulfoxides is weaker than in the E isomers, while the situation is quite the reverse in alkyl 1-propenyl sulfones.[8] A possible reason for this is that in the Z isomers of 1-propenyl sulfoxides, the conformation where the lone-pair electrons of the sulfur atom eclipse the methyl group is also present and this diminishes the steric strain, but probably also diminishes the conjugation in the molecule.

In *tert*-butyl 1-propenyl sulfide, $E \rightarrow Z$ isomerization does not involve rotation of the *t*-BuS group.[6] The ¹³C signal of the β carbon of the Z isomer is almost 7 ppm

upfield from the corresponding signal of the E isomer,[6] i.e., the electron density in the β carbon of the Z isomer is higher than in the E isomer. The reason for this is probably the attraction between the sulfur atom and the β methyl group. This attraction may increase the conjugation in the molecule and the electron density in the β carbon.

In di(1-propenyl) sulfide, $E,E{\rightarrow}E,Z$ and $E,Z{\rightarrow}Z,Z$ isomerizations do not involve conformational changes.[6] The ^{13}C signal of the β carbon in the Z configuration is 2–3 ppm upfield from the corresponding signal of the E configuration.[6] Thus the tendency is the same as in tert-butyl 1-propenyl sulfide and the explanation is evidently the same.

When $\Delta G^{\ominus}$ values of the $E{\rightarrow}Z$ reactions of di(1-propenyl) sulfoxides and sulfones are considered, the fact that the E,Z isomer is statistically favoured by a factor of two must be taken into account. To eliminate the effect of this statistical factor, the term $RT\ln 2$ (1.7 kJ mol^{-1} at 298 K) must be added to $\Delta G^{\ominus}$ of reaction (E,E)-di(1-propenyl) sulfoxide$\rightarrow(E,Z)$-di(1-propenyl) sulfoxide, and the same factor must be subtracted from $\Delta G^{\ominus}$ of reaction (E,Z)-di(1-propenyl) sulfoxide$\rightarrow(Z,Z)$-di(1-propenyl) sulfoxide. The same goes for the corresponding reactions of di(1-propenyl) sulfones. The $\Delta G^{\ominus}$ values given in Table 1 for these reactions are statistically corrected. It can be seen that the $\Delta G^{\ominus}$ value for the $E,E{\rightarrow}E,Z$ reaction of di(1-propenyl) sulfoxide (sulfone) is about the same as for the $E{\rightarrow}Z$ reaction of alkyl 1-propenyl sulfoxide (sulfone). $\Delta G^{\ominus}$ of the $E,Z{\rightarrow}Z,Z$ reaction is 2 kJ mol^{-1} less for sulfoxide and 5 kJ mol^{-1} less for sulfone than for the $E{\rightarrow}Z$ reaction of the alkyl 1-propenyl sulfoxide (sulfone). A possible explanation for this is that when the first methyl group is transferred to the Z position, the spatial orientation of the 1-propenyl group changes in a way that diminishes the conjugation in the molecule. Thus the transfer of the second methyl group from the E to the Z position does not exert as large an effect on the conjugation and $\Delta G^{\ominus}$ of this reaction is smaller than in the reaction in which the first methyl group is transferred to the Z position. The difference is smaller in di-propenyl sulfoxides as in sulfones. The reason for this is probably the lone-pair electrons of the sulfur atom in di-1-propenyl sulfoxide, which allows the (E,Z)-di(1-propenyl) sulfoxide to adopt a conformation that does not diminish the conjugation much and thus the transfer of the second methyl group has a larger effect on the conjugation as in the corresponding sulfone.

$\Delta G^{\ominus}$ of the $E{\rightarrow}Z$ isomerization of tert-butyl 1-butenyl sulfide is -0.1 kJ mol^{-1}, which is almost 2 kJ mol^{-1} larger than that of the corresponding reaction of tert-butyl 1-propenyl sulfide. The same tendency can be seen in the corresponding phenyl compounds phenyl 1-butenyl sulfide ($\Delta H^{\ominus} = +1.1$ kJ mol^{-1}) and phenyl 1-propenyl sulfide ($\Delta H^{\ominus} = -0.1$ kJ mol^{-1}). There is probably some steric strain between the t-BuS and Et groups (PhS and Et groups) in the Z isomer even though earlier in this

paper it was stated that there is no steric strain between an EtS and an i-Pr group cis to each other. $\Delta G^{\ominus}$ of the corresponding reaction of isopropyl 1-butenyl sulfide is -0.4 kJ mol^{-1}, i.e., about the same as in isopropyl 1-propenyl sulfide. Thus it can be concluded that there is no steric strain between the i-PrS and Et groups cis to each other.

$\Delta G^{\ominus}$ of reaction (23) is $+6.8(1)$ kJ mol^{-1}. In this
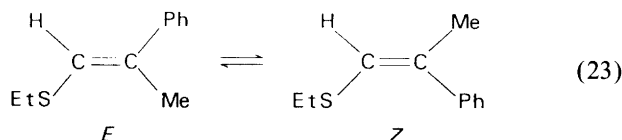
reaction there is no change in the spatial orientation of the EtS group, because the Me group cis to the EtS group forces the EtS group out of the s-cis conformation even in the E isomer. $\Delta G^{\ominus}$ for the corresponding reaction with no Me group in the β carbon was mentioned earlier in this paper to be 5.3 kJ mol^{-1}, i.e., less than in reaction (23). This is astonishing, because this reaction involves energy-demanding change in the spatial orientation of the EtS group. The reason for this is probably the behaviour of the phenyl group. When there is only the Ph group attached to the β carbon the C=C=Ph angle widens in the Z isomer and this diminishes the steric strain. When there is a Ph and an Me group attached to the β carbon, the C=C–Ph angle cannot widen, because the Me group opposes it. To diminish the steric strain the plane of the Ph group rotates out of the C=C–S plane, which diminishes the conjugation caused by the phenyl group and weakens the stability of the Z isomer. The ^{13}C NMR shifts offer some evidence for the above conclusions. From Table 2 it can be seen that the signal of the β carbon of the Z isomer is 1.4 ppm upfield from the corresponding signal of the E isomer. This shows that the electron density in the β carbon of the Z isomer is higher than in the E isomer, which is caused by the weakening of the conjugation caused by the Ph group. The ^{13}C shifts of the β carbon of the E and Z isomers of ethyl vinyl sulfide with only the Ph group in the β carbon are about the same (Table 2). In corresponding vinyl ethers the same tendency can be seen and the reason is evidently the same.[10,11]

Experimental

Materials. The preparation of isopropyl, tert-butyl and phenyl 2-butenyl sulfides are described in Ref. 12. The corresponding 1-butenyl sulfides were obtained by isomerization and were not isolated. The E and Z isomers of 1-butenyl sulfides were the two largest components in the equilibrium mixture. The characterization of the 2-butenyl sulfides is reported in Ref. 12. Other alkyl and vinyl sulfides is prepared by the method described in Ref. 6.

Table 2. Chemical shifts (ppm from TMS) from the ^{13}C NMR spectra recorded.

Compound	Isomer	δ(a)	δ(b)	δ(c)	δ(d)	δ(e)	δ(f)
CH₃CH₂SCH=CHCH₂CH₃	E	14.58	26.71	121.65	132.57	26.31	13.67
a b c d e f	Z	15.44	27.80	124.00	131.37	22.53	13.44
CH₃CH₂SCH=CHCH(CH₃)₂	E	14.54	26.64	120.04	137.66	31.92	22.42
a b c d e f	Z	15.50	27.92	122.31	137.00	28.81	22.32
CH₃CH₂SCH=CHC(CH₃)₃	E	14.33	26.39	118.07	141.10	33.91	29.40
a b c d e f	Z	15.08					30.66
CH₃CH₂SCH=CHC₆H₅	E	14.45	26.39		137.00	124–129	
a b c d e	Z	15.25	29.53		136.90	124–129	
O=S(CH=CHCH₃)₂	E,E	133.44	134.90	16.32			
a b c	Z,Z	132.52	134.42	13.45			
	E,Z	133.28	134.74	16.00 (E)			
		132.53	134.47	13.39 (Z)			
CH₃CH₂SCH=C(CH₃)C₆H₅	E	15.70	28.11		142.06	17.57	123–130
a b c d e f	Z	15.26	28.82		140.65	17.57	123–130

Table 3. Chemical shifts (ppm from TMS) and coupling constants from the ^{1}H NMR spectra.

Compound	Isomer	δ(a)	δ(b)	δ(c)	δ(d)	δ(e)	δ(f)	J/Hz
CH₃CH₂SCH=CHCH₂CH₃	E	1.25	2.61	5.87	5.57	2.08	0.99	J(ab)=7.3
a b c d e f			J(cd)=15.1		J(de)=6.7			J(ef)=7.4
	Z	1.26	2.63	5.85	5.49	2.08	0.98	J(ab)=7.2
			J(cd)=9.4		J(de)=6.8			J(ef)=7.5
CH₃CH₂SCH=CHCH(CH₃)₂	E	1.27	2.59	5.5–5.8		2.3	1.01	J(ab)=7.3
a b c d e f								J(ef)=7.4
	Z	1.28	2.61	5.3–5.7		2.6	0.98	J(ef)=6.6
CH₃CH₂SCH=CHC(CH₃)₃	E	1.21	2.58	5.5–5.9		0.96		J(ab)=7.3
a b c d e	Z	1.20	2.58	5.3–5.7		0.95		J(ab)=7.3
CH₃CH₂SCH=CHC₆H₅	E	1.39	2.84	6.4–6.8		7.2–7.4		J(ab)=7.4
a b c d e	Z	1.38	2.81	6.2–7.4		7.2–7.4		J(ab)=7.3
CH₃CH₂SCH=C(CH₃)C₆H₅	E	1.32	2.75	6.31	2.10	7.1–7.4		J(ab)=7.4
a b c d e	Z	1.25	2.62	5.99	2.12	7.1–7.4		J(ab)=7.6

Table 4. Equilibrium constants for the studied reactions.

T/K	K(7Z/7E)	K(8Z/8E)	K(9Z/9E)	K(19Z/19E)	K(21Z/21E)	K(23Z/23E)
443			0.0540			0.1458
423		0.523	0.0499			0.1376
403		0.519				
398			0.0416			0.1242
373	1.280	0.520	0.0335	0.875		0.1078
353	1.320			0.870	1.100	
348			0.0266			0.0935
333	1.320	0.518		0.845	1.120	
323						0.0794
313	1.310			0.818	1.160	
298	1.390					0.0640

NMR spectra. ^{1}H NMR spectra, 80 MHz and ^{13}C NMR spectra, 15 MHz, were recorded for 10–20% solutions in CDCl₃. The recorded ^{1}H NMR spectra are summarized in Table 3 and the ^{13}C NMR spectra in Table 2. All results are relative to TMS.

Equilibrations. The equilibration experiments were carried out in dimethyl sulfoxide solution with potassium *tert*-butoxide as catalyst.[7,12] The samples were sealed in glass ampoules and the ampoules kept in thermostatted ovens at appropriate temperatures to establish equilib-

rium. The samples were analyzed by gas chromatography using NB-9C as the stationary phase. The values of the thermodynamic parameters were evaluated by linear least-squares treatment of the ln K versus T^{-1}.[5] The values of the equilibrium constant K are given in Table 4. The following equilibrium constants were determined at one temperature only, because the temperature dependence of K could not be determined with reasonable accuracy. The maximum errors are estimated errors, based upon the results in the equilibrium experiments: $K(10Z/10E)=0.18(2)$, $(T=373\ K)$; $K(13Z/13E)=0.16(2)$, $(T=300\ K)$; $K(14Z/14E)=0.07(1)$, $(T=300\ K)$; $K(17Z/17E)=1.02(5)$, $(T=300\ K)$.

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