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Structure–Stability Relationships in Unsaturated Sulfur Compounds. I. On the Stable Conformations of Vinyl Sulfoxides

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The conformations of the stable rotamers of alkyl 1-propenyl sulfoxides have been studied in a thermodynamic and a ^{13}C NMR spectroscopic study. The most stable rotamer of the *E* isomer was found to have the anticlinal conformation. In the *Z* isomer the synclinal conformation is the most probable.

The configurations of the stable rotamers of vinyl sulfides have been widely studied.[1–6] All these studies agree in that the most stable configuration has the planar s-*cis* conformation. The less stable rotamer evidently has the planar (or nearly planar) s-*trans* conformation,[1,2] but the non-planar *gauche* conformation has also been proposed.[3–5] The conformations of alkyl vinyl sulfoxides have not received much attention and only one experimental study has been published.[7] In that paper it is briefly stated that the size of the alkyl group has no effect on the conformational preference of the molecule. According to *ab initio* MO calculations the most stable rotamer has the anticlinal conformation (Fig. 1).[8,9] In this conformation the two double bonds can conjugate with each other and this stabilizes the molecule. In the present paper the results from a thermodynamic and a ^{13}C NMR spectroscopic study are presented in an attempt to solve the problem of the configurations of the stable rotamers of alkyl vinyl sulfoxides.

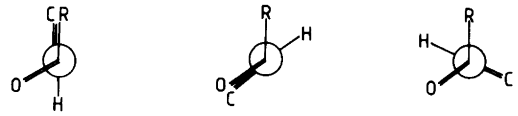
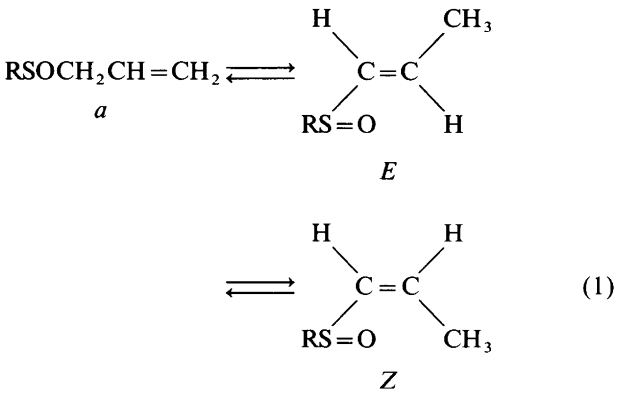


Fig. 1. Some conformations of vinyl sulfoxides.

Results and discussion



(1)

1 R = Me, **2** R = Et, **3** R = *i*-Pr, **4** R = *t*-Bu, **5** R = Ph

In this work the isomer equilibrium (1) was studied. The thermodynamic data for the $E \rightarrow Z$ reaction are summarized in Table 1. Sváta *et al.*[7] have also obtained these isomers in equilibrium and their results are in qualitative agreement with the present data. However, they have not measured the temperature dependence of the equilibrium constant *K*. It can be seen from Table 1 that $\Delta H^{\ominus}$ of this reaction and $\Delta G^{\ominus}$ in the case of R=Ph is within experimental error independent of the size of the alkyl group. In the corresponding vinyl sulfides $\Delta H^{\ominus}$ of the $E \rightarrow Z$ isomerization increases with decreasing size of the alkyl group.[1] This effect was explained as follows. When the alkyl group is large, the s-*cis* (synperiplanar) conformation is energetically highly disfavoured even in the *E* isomer and the $E \rightarrow Z$ isomerization will not involve any conformational changes. When the size of the alkyl group decreases, the s-*cis* conformation becomes energetically more favoured in the *E* isomer but not in the *Z* isomer because of the steric strain caused by the methyl group attached to the β carbon. Thus, when the alkyl group is small, the $E \rightarrow Z$ isomerization involves changes in the spatial orientation of the alkylthio group and $\Delta H^{\ominus}$ increases when the size of the alkyl group decreases.

In alkyl 1-propenyl sulfoxides the size of the alkyl group has no effect on $\Delta H^{\ominus}$ of the $E \rightarrow Z$ reaction. Thus it can be concluded that there is no change in the spatial orientation of the RS=O group in the $E \rightarrow Z$ reaction or that the change is the same for all alkyl groups R. One may therefore conclude that under these circumstances the synperiplanar conformation, Fig. 1, which is the most stable in methyl vinyl sulfide, is unlikely to be the most stable in vinyl sulfoxides, even for small alkyl groups. Steric strain makes this conformation energetically highly disfavoured in the *Z* isomer.

According to *ab initio* MO calculations the most stable

Table 1. The values of the thermodynamic functions for reactions $a \rightarrow E$ and $E \rightarrow Z$, eqn. (1), in DMSO at 298 K. The errors given are twice the standard errors.

Reaction	R	$\Delta G^{\ominus}$/kJ mol^{-1}	$\Delta H^{\ominus}$/kJ mol^{-1}	$\Delta S^{\ominus}$/J K^{-1} mol^{-1}
$a \rightarrow E$	Me	−3.8(1)	−5.3(8)	−5(2)
$a \rightarrow E$	Et	−4.7(1)	−4.7(3)	0(1)
$a \rightarrow E$	*i*-Pr	−8.8(1)	−7.7(2)	+4(1)
$a \rightarrow E$	*t*-Bu	−13.1(2)[a]		
$a \rightarrow E$	Ph	−5.0(4)[b]		
$E \rightarrow Z$	Me	+7.3(1)	+7.1(6)	−1(2)
$E \rightarrow Z$	Et	+7.4(1)	+7.5(6)	0(2)
$E \rightarrow Z$	*i*-Pr	+7.7(2)	+7.2(9)	−2(2)
$E \rightarrow Z$	*t*-Bu	+8.3(1)	+7.1(3)	−4(1)
$E \rightarrow Z$	Ph	+6.9(1)[b]		

[a,b]The temperature dependence of K could not be measured sufficiently accurately to obtain reliable values for $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$. [a]$T = 348$ K. [b]$T = 300$ K.

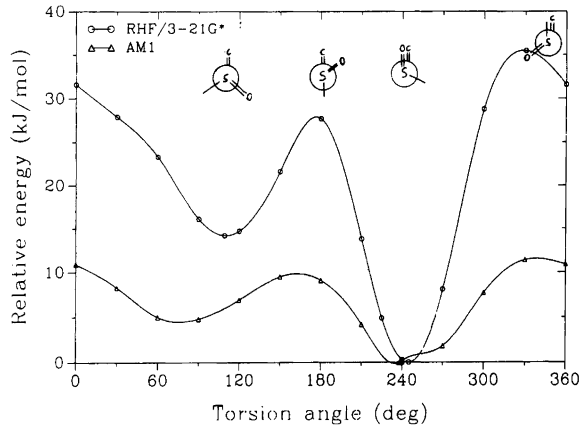


Fig. 2. The potential-energy curve for the C–S torsion of methyl vinyl sulfoxide acquired by *ab initio* MO calculations.[9]

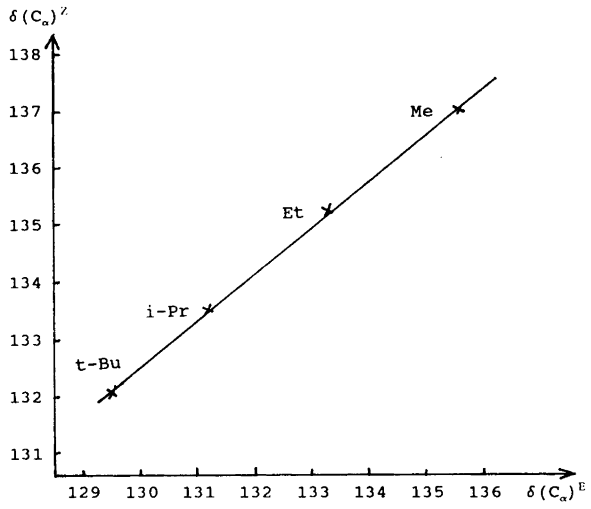


Fig. 4. $\delta(C_\alpha)^Z$ vs. $\delta(C_\alpha)^E$ for alkyl 1-propenyl sulfoxides.

rotamer of methyl vinyl sulfoxide has the anticlinal conformation as shown in Fig. 2.[9] In this conformation the S=O bond can conjugate with the C=C bond and thereby stabilize the molecule. This conformation, however, is energetically disfavoured in (*Z*)-alkyl 1-propenyl sulfoxide because of the steric strain between the S=O group and the Me group. The distance between the oxygen atom and the nearest hydrogen atom of the methyl group is only 190 pm, Fig. 3, as compared with the sum of the van der Waals' radii of oxygen and hydrogen atoms which is 260 pm.[10] Thus, this conformation is not possible in the *Z* isomer. According to the *ab initio* calculations the second stable rotamer has the syn-

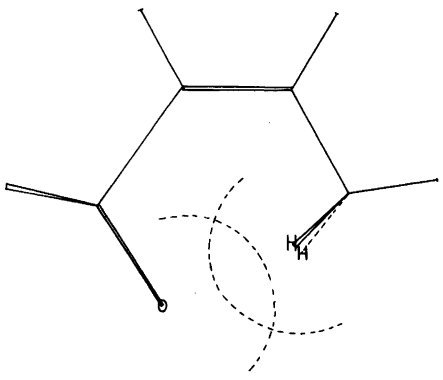


Fig. 3. The steric strain in the anticlinal conformation of (*Z*)-alkyl 1-propenyl sulfoxide.

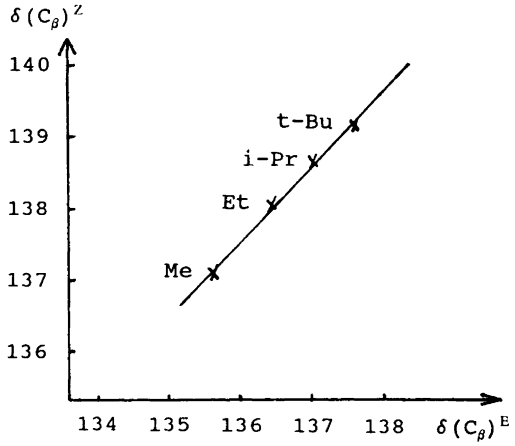


Fig. 5. $\delta(C_\beta)^Z$ vs. $\delta(C_\beta)^E$ for alkyl 1-propenyl sulfoxides.

Table 2. The boiling points and yields of the compounds synthesized.

Compound	Yield(%)	B.p./°C (Pa)	B.p. (lit.)[7]
Methyl 2-propenyl sulfoxide	18	55–62 (50)	64–65 (27)
(*Z*)-Methyl 1-propenyl sulfoxide	21	60–65 (55)	43–44 (5)
(*E*)-Methyl 1-propenyl sulfoxide	19	55–58 (50)	41–42 (6,5)
Ethyl 2-propenyl sulfoxide	21	80–82 (90)	49–50 (6,5)
(*Z*)-Ethyl 1-propenyl sulfoxide	18	78–84 (95)	47 (5)
(*E*)-Ethyl 1-propenyl sulfoxide	20	80–82 (95)	44–45 (5)
i-Propyl 2-propenyl sulfoxide	23	76–78 (50)	67–68 (71)
i-Propyl 1-propenyl sulfoxides	26	72–76 (45)	50–51 (13)
t-Butyl 2-propenyl sulfoxide	23	63–70 (14)	53–54 (6,5)
t-Butyl 1-propenyl sulfoxides	22	58–62 (4)	54–56 (4)
Phenyl 2-propenyl sulfoxide	18	70–75 (4)	104 (48)[12]

clinal conformation.[9] This conformation is the most probable one in the *Z* isomer, because there is no steric strain present. If this were the case, there would have to be a change in the spatial orientation of the RS=O group in the $E \rightarrow Z$ isomerization, but this change will apparently be the same for all alkyl groups R. This is consistent with the conclusion drawn earlier in this paper. $\Delta H^{\ominus}$ of the $E \rightarrow Z$ reaction is ca. $+7$ kJ mol^{-1} for all alkyl groups. This shows that the *Z* isomer is energetically less favoured than the *E* isomer. The present data do not reveal whether this is due to the steric strain presented in Fig. 3 or the higher energy level that the other stable conformation (*ab initio* calculations) possesses or maybe both of these conformations are present in the *Z* isomer.

Further evidence for this conclusion can be arrived at from the ^{13}C NMR shifts of the α and β carbons of the (*E*)- and (*Z*)-alkyl 1-propenyl sulfoxides presented in Table 4. These data show that the ^{13}C signals of the α carbons in both of the isomers shift upfield when the size of the alkyl group increases. This is caused by the

Table 3. Chemical shifts (ppm from Me_4Si) from the ^{1}H NMR spectra.

Compound	Isomer	δ(a)	δ(b)	δ(c)	δ(d)	δ(e)	*J*/Hz
$CH_3SOCH=CHCH_3$	*E*	2.48	6.0	−6.4	1.92		*J*(cd) = 4.8
a b c d	*Z*	2.53	5.9	−6.3	1.96		*J*(cd) = 4.8
$CH_3SOCH_2CH=CH_2$		2.44	3.38	5.0	−6.1		*J*(bc) = 6.6
a b c d							
$CH_3CH_2SOCH=CHCH_3$	*E*	1.24	2.74	6.0	−6.6	1.93	*J*(ab) = 7.2 *J*(de) = 4.8
a b c d e	*Z*	1.23	2.69	5.8	−6.5	1.96	*J*(ab) = 7.2 *J*(de) = 5.4
$CH_3CH_2SOCH_2CH=CH_2$		1.30	2.72	3.42	5.1	−6.2	*J*(ab) = 7.2
a b c d e							*J*(cd) = 6.6
$(CH_3)_2CHSOCH=CHCH_3$	*E*	1.22	2.76	5.8	−6.7	1.94	*J*(ab) = 6.8
a b c d e	*Z*	1.30	2.83	5.8	−6.7	1.97	*J*(de) = 5.4
$(CH_3)_2CHSOCH_2CH=CH_2$		1.22	2.80	3.49	5.0	−6.1	*J*(ab) = 6.8
a b c d e							*J*(cd) = 6.6
$(CH_3)_3CSOCH=CHCH_3$	*E*	1.20	5.9	−6.6	1.94		*J*(cd) = 5.4
a b c d	*Z*	1.26	5.9	−6.6	1.97		
$(CH_3)_3CSOCH_2CH=CH_2$		1.26	3.26	5.0	−6.2		*J*(bc) = 6.6
a b c d							
$C_6H_5SOCH_2CH=CH_2$		7.3–7.8	3.45	4.9	−6.0		*J*(bc) = 6.8
a b c d							

increased shielding effect due to the bulkier alkyl groups. Fig. 4 shows there is a reasonable linear relationship between the ^{13}C shifts of the α carbons of *E* and *Z* isomers with a slope of 0.80(2).

The effect of the size of the alkyl group on the ^{13}C signal of the β carbon in the (*E*)- and (*Z*)-alkyl 1-propenyl sulfoxides is smaller than on the signal of the α carbon and shifts downfield when the size of the alkyl group increases in both isomers. Once more a satisfactory linear relationship between the ^{13}C shifts of the β carbons of the *E* and *Z* isomers is observed, Fig. 5: slope = 0.98(1).

In alkyl 1-propenyl sulfides the ^{13}C signal of the β carbon of the *E* isomer shifts ca. 10 ppm downfield when R is changed from Me to *t*-Bu. This reflects the spatial orientation of the alkyl group since small alkyl groups will adopt the s-*cis* conformation and shield the β carbon whereas the *t*-BuS group in the s-*trans* conformation will have no shielding effect on the β carbon atom.[1] The ^{13}C signals of the β carbon of (*Z*)-alkyl 1-propenyl sulfides shift only ca. 3 ppm downfield when R is changed from Me to *t*-Bu. The reason for this is that there is no change in the spatial orientation of this isomer as the size of the alkyl group increases.[1] The change in the ^{13}C shift of the β carbon in both (*E*)- and (*Z*)-alkyl 1-propenyl sulfoxides when the size of the alkyl group increases is of the same magnitude as in the (*Z*)-alkyl 1-propenyl sulfides. This seems to indicate that the shielding effect of the alkyl group on the β carbon does not change in alkyl 1-propenyl sulfoxides when the size of the alkyl group increases. Therefore the synperiplanar conformation will not be possible in any one of the geometric isomers of alkyl 1-propenyl sulfoxides. One may therefore conclude that the conformation of alkyl 1-propenyl sulfoxide does not change during the $E \rightarrow Z$ isomerization or alternatively that the change is one in which the distance between the alkyl group and the β carbon does not alter. This is the case during the conformational change anticlinal → synclinal. Apparently the thermodynamic and the ^{13}C NMR data are consistent with the *ab initio* MO calculations. It therefore seems conceivable that the most stable rotamer of (*E*)-alkyl propenyl sulfoxides has the anticlinal conformation. Based on similar arguments one may conclude that the *Z* isomer is largely in the synclinal conformation.

Table 1 shows that $\Delta H^{\ominus}$-values, and particularly $\Delta G^{\ominus}$-values, of the isomerization reaction, in which the double bond migrates from the β,γ-position to the α,β-position, are negative and decrease when the size of the alkyl group

Table 4. Chemical shifts (ppm from Me_4Si) from the ^{13}C NMR spectra recorded.

Compound	Isomer	δ(a)	δ(b)	δ(c)	δ(d)	δ(e)
$CH_3SOCH=CHCH_3$	*E*	40.72	135.66	135.66	17.56	
a b c d	*Z*	40.15	136.98 (137.20)	137.20 (136.98)	14.98	
$CH_3SOCH_2CH=CH_2$		37.35	57.77	125.77	123.54	
a b c d						
$CH_3CH_2SOCH=CHCH_3$	*E*	5.95	47.01	133.20	136.46	17.67
a b c d e	*Z*	6.46	47.24	135.20	138.01	15.21
$CH_3CH_2SOCH_2CH=CH_2$		6.52	44.21	55.08	126.11	123.02
a b c d e						
$(CH_3)_2CHSOCH=CHCH_3$	*E*	15.27 (14.36)	51.53	131.20	137.09	17.79
a b c d e	*Z*	14.81 (14.13)	52.16	133.49	138.64	15.33 (15.10)
$(CH_3)_2CHSOCH_2CH=CH_2$		16.30	48.73	52.79	126.63	122.62
a b c d e		(14.18)				
$(CH_3)_3CSOCH=CHCH_3$	*E*	22.76	54.10	129.49	137.61	17.84
a b c d e	*Z*	22.59	54.73	132.06	139.09	15.73
$(CH_3)_3CSOCH_2CH=CH_2$		22.93	53.48	50.73	128.17	122.22
a b c d e						
$C_6H_5SOCH_2CH=CH_2$		122.6–130.0	59.58	122.6	–130.0	
a b c d						

increases. This shows that large alkylsulfinyl groups stabilize the double bond more than do small alkylsulfinyl groups or that large alkyl groups destabilize the allylic isomer more than do small alkyl groups. It is notable that the effect of the PhSO group attached to the double bond is as large as that of the MeSO or EtSO group. This is astonishing, because a Ph group is much larger than an Me or Et group. One cannot, however, explain the effect of the size of the alkyl group on $\Delta H^{\ominus}$-values in the reaction studied solely on the basis of these results; further experimental work needs to be done to solve this problem.

The results for the corresponding propenyl sulfides are much the same.[11] The size of the alkyl group, however, does not exert as large an effect on $\Delta H^{\ominus}$ of this reaction in sulfides as in sulfoxides.

Table 5. Equilibrium constants for reactions $a \rightarrow E$ in eqn. (1).

T/K	K(1*E*/1*a*)	K(2*E*/2*a*)	K(3*E*/3*a*)	K(4*E*/4*a*)[a]	K(5*E*/5*a*)[a]
300	4.45	6.60	33.9		7.5(10)[b]
323	4.09	5.86	27.2		
348	3.36	5.20	21.8	92(5)[b]	
373	2.95	4.60	18.5		
398	2.72	4.16	15.8		

[a] Temperature dependence of K could not be determined with reasonable accuracy. [b] Estimated error, based upon the results in the equilibrium experiments.

Table 6. Equilibrium constants for reactions $E \rightarrow Z$ in eqn. (1).

T/K	K(1*Z*/1*E*)	K(2*Z*/2*E*)	K(3*Z*/3*E*)	K(4*Z*/4*E*)	K(5*Z*/5*E*)[a]
300	0.055	0.052	0.047	0.037	0.064(2)[b]
323	0.064	0.063	0.054	0.044	
348	0.078	0.076	0.066	0.054	
373	0.094	0.095	0.082	0.064	
398	0.108	0.107	0.092	0.074	

[a] Temperature dependence of K could not be determined with reasonable accuracy. [b] Estimated error, based upon the results in the equilibrium experiments.

Experimental

Materials. 1-Propenyl and 2-propenyl sulfoxides were prepared by the method described by Sváta *et al.*[7] The products, their boiling points and yields are summarized in Table 2.

NMR spectra. ^{1}H NMR spectra, 60 MHz and ^{13}C NMR spectra, 15 MHz, were recorded for 10–20% solutions in CCl_4 and $CDCl_3$, respectively. The recorded ^{1}H NMR spectra are summarized in Table 3 and the ^{13}C NMR spectra in Table 4. All results are relative to Me_4Si.

Equilibrations. The equilibration experiments were carried out in Me_2SO solution with potassium *tert*-butoxide as the catalyst.[13] The samples were analysed by gas chromatography using XE-60 (compounds **1** and **2**), SP-3220 (compounds **3** and **4**) and SE-30 (compound **5**) as the stationary phase. The values of the equilibrium constants K are given in Tables 5 and 6.

References

1. Virtanen, R. *Acta Chem. Scand., Ser. B 40* (1986) 313.
2. Katritzky, A. R., Pinzelli, R. F. and Topsom, R. D. *Tetrahedron 28* (1972) 3441.
3. Muller, C., Schäfer, W., Schweig, A., Thon, N. and Vermeer, H. *J. Am. Chem. Soc. 98* (1976) 5440.
4. Samdal, S., Seip, H. M. and Torgrimsen, T. *J. Mol. Struct. 57* (1979) 105.
5. Kao, J. *J. Am. Chem. Soc. 100* (1978) 4685.
6. Lister, D. G. and Palmieri, P. *J. Mol. Struct. 32* (1976) 355.
7. Sváta, V., Procházka, M. and Bakos, V. *Collect. Czech. Chem. Commun. 43* (1978) 2619.
8. Kahn, S. D. and Hehre, W. J. *J. Am. Chem. Soc. 108* (1986) 7399.
9. Hotokka, M. and Kimmelma, R. *J. Mol. Struct. Theochem. 276* (1992) 167.
10. Gordon, A. J. and Ford, R. A. *The Chemist's Companion*, Wiley, New York 1972, p. 109.
11. Kimmelma, R. *Acta Chem. Scand., Ser. B 42* (1988) 550.
12. Ferry, C. W., Buck, J. S. and Baltzly, R. *Org. Synth. 22* (1942) 30.
13. Kimmelma, R. *Acta Chem. Scand., Ser. B 41* (1987) 344.

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