Acta Chemica Scandinavica, 1996: 50: 783–787
Printed in UK – all rights reserved

ACTA
CHEMICA SCANDINAVICA
ISSN 0904-213X

Structure–Stability Relationships in Unsaturated Sulfur Compounds VII. Stabilization Energies due to Alkyl Groups Attached to the α and β Carbons of Vinyl Sulfones

Reijo Kimmelma* and Timo Peltola

Department of Chemistry, University of Turku, FIN-20500 Turku, Finland

Kimmelma, R. and Peltola, T., 1996. Structure–Stability Relationships in Unsaturated Sulfur Compounds VII. Stabilization Energies due to Alkyl Groups Attached to the α and β Carbons of Vinyl Sulfones. – Acta Chem. Scand. 50: 783–787. © Acta Chemica Scandinavica 1996.

According to thermodynamic results a methyl or ethyl group attached to the β carbon of a vinyl sulfone causes a stabilization of ca. 13 kJ mol^{-1}. The corresponding stabilization caused by an α alkyl group is ca. 10 kJ mol^{-1}.

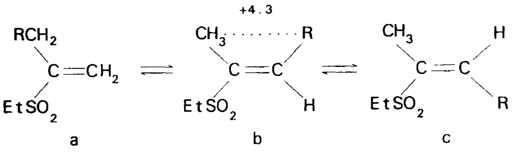
The stabilizing ability of different groups attached to an olefinic double bond has been widely studied over recent decades.[1–7] For example, a methyl group has been reported to stabilize the olefinic double bond by 11.0–12.8 kJ mol^{-1}.[1–5] In vinyl sulfides, as well as in vinyl ethers, the double bond is not an 'ordinary' double bond since the lone-pair electrons of the sulfur (oxygen) atom may conjugate with the π orbital of the double bond.[8] Thus, the stabilization caused by different groups differs from the corresponding stabilization in ordinary olefins, e.g., a methyl group attached to the β carbon of a vinyl sulfide stabilizes the double bond by ca. 8 or 9 kJ mol^{-1}, depending on the conformation of the molecule.[9] The corresponding stabilization in vinyl ethers is reported to be 4–8 kJ mol^{-1}.[10] The stabilization caused by an alkyl group attached to the α carbon of a vinyl sulfide is ca. 8 kJ mol^{-1} according to a thermodynamic study,[11] whereas the corresponding stabilization in vinyl ether is ca. 7 kJ mol^{-1} based upon heats of hydrogenation.[12] In vinyl sulfones the S=O bonds conjugate with the C=C bond when they are in the same plane and this conjugation may have some effect on the stabilization caused by the alkyl groups attached to the double bond of a vinyl sulfone. These kinds of stabilization have never been studied. The only experimental structure–stability study carried out on substituted vinyl sulfones is of the effect of the size of the alkyl group on the *E*→*Z* isomerization of alkyl 1-propenyl sulfones.[13] However, the conformations of the stable rotamers of vinyl sulfones have been studied both experimentally[13–18] and theoretically.[19–21] According to most of these studies the most stable rotamer adopts the conformation in which one of the S=O bonds is *cis* to the double bond.

In this paper the stabilization caused by alkyl groups attached to the α and β carbons of vinyl sulfones has been evaluated using $\Delta H^{\ominus}$ or $\Delta G^{\ominus}$ values for the isomerization reactions of some substituted vinyl sulfones. Some aspects of the conformations of these compounds are also presented.

Results and discussion

The stabilization energies caused by various structural factors can be evaluated by combining the $\Delta H^{\ominus}$ values for different reactions. The reliability of this method has been shown.[9] In some cases the temperature dependence of equilibrium constant K could not be measured accurately enough to obtain a reliable $\Delta H^{\ominus}$ value. In these cases the $\Delta G^{\ominus}$ value was used instead.

With the aid of $\Delta G^{\ominus}$ of reaction (I) the stabilization due to the β alkyl group in the **b** isomer can be evaluated. $\Delta G^{\ominus}$ of reaction **1a**→**1b** is -9.0 kJ mol^{-1} (Table 1). In the **b** isomer there is steric strain between the two methyl groups (Me···Me *cis* interaction, which is $+4.3$ kJ mol^{-1})[4] and this must be subtracted from the $\Delta G^{\ominus}$ of this reaction to determine the effect of the β methyl group. Thus $H(\beta\text{-Me}) = (-9.0 - 4.3)$ kJ $\mathrm{mol}^{-1} = -13.3$ kJ mol^{-1}. The Me···Et *cis* interaction is as large as the Me···Me *cis* interaction[4] and $\Delta G^{\ominus}$ of reaction (I), when R=Et, is -8.0 kJ mol^{-1}.



(I)

---

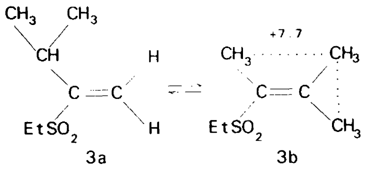
* To whom correspondence should be addressed.

Table 1. The values of the thermodynamic functions for the studied reactions in *tert*-butyl alcohol at 298 K. The errors are twice the standard errors.

Reaction	$\Delta G^\ominus$/kJ mol^{-1}	$\Delta H^\ominus$/kJ mol^{-1}	$\Delta S^\ominus$/J K^{-1} mol^{-1}
1a→**1b**	−9.0(4)^a		
1b→**1c**	+13.8(2)	+14.1(5)	1(1)
2a→**2b**	−8.0(3)^a		
2b→**2c**	+13.3(2)	+13.1(8)	−1(2)
3a→**3b**	−1.5(7)^a		
4a→**4b**	−3.6(1)[13]	−4.3(4)[13]	−2(1)[13]
5a→**5b**	−11.5(2)	−12.5(6)	−4(2)
6a→**6b**	+2.6(5)^a		
7a→**7b**	−9.5(4)^a		
8a→**8b**	+11.3(4)^a		

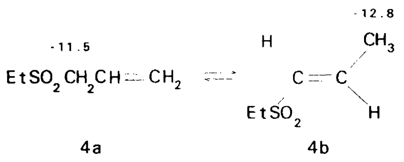
^{a}The temperature dependence of K could not be measured sufficiently accurately to obtain reliable values for $\Delta H^\ominus$ and $\Delta S^\ominus$.

By the method described above H(β-Et) = −12.3 kJ mol^{-1}, i.e., the first alkyl group attached to the β carbon of a vinyl sulfone stabilizes the double bond by 12.8 kJ mol^{-1} (≈13 kJ mol^{-1}), which is as much as in 'ordinary' olefins.



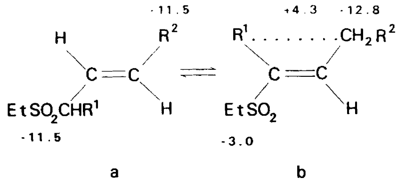
(II)

With the aid of $\Delta G^\ominus$ values of reactions **1a**→**1c** and **3a**→**3b** the stabilization caused by the second methyl group attached to the β carbon of a vinyl sulfone can be evaluated. In both of these reactions a methyl group migrates to the *cis* position of the β carbon, which causes steric strain in these isomers. Thus, if there are changes in the spatial orientation of the ethylsulfonyl group, these changes are obviously similar in these two reactions, and the effects of these rotations cancel each other when one $\Delta G^\ominus$ value is subtracted from the other. Moreover, in **3a**→**3b** a second methyl group migrates to the β carbon. The three methyl groups in **3b** cause steric strain. This is assumed to be as large as the strain in 2-methyl-2-butene, *viz.* 7.7 kJ mol^{-1}, which is the difference between the experimental and calculated (neglecting the effects of steric factors) values for the standard enthalpy of formation of 2-methyl-2-butene.[22] The energy change in reaction **1a**→**1c** is the sum of the $\Delta G^\ominus$ value of reaction **1a**→**1b** and the $\Delta H^\ominus$ value of reaction **1b**→**1c**. The effect of the second methyl group in the β carbon is thus [−1.5−(−9.0+14.1)−7.7] kJ mol^{-1} = −14.3 kJ mol^{-1}. Another estimation for this stabilization can be acquired using reactions **2a**→**2c** and **3a**→**3b**. The second estimation is [−1.5−(−8.0+13.1)−7.7] kJ mol^{-1} = −14.3 kJ mol^{-1}. Thus it can be concluded that both of the methyl groups attached to the β carbon of a vinyl sulfone stabilize the double bond as much as in ordinary olefins. The first methyl group attached to the β carbon of a vinyl sulfide is reported to stabilize the double bond by ca. 8 kJ mol^{-1} and the second by ca. 9 kJ mol^{-1}.[9]



(III)

With the aid of reaction (III) the stabilization caused by an $EtSO_2$ group attached to a double bond can be evaluated. $\Delta H^\ominus$ of this reaction is −4.3 kJ mol^{-1}.[13] The $EtSO_2CH_2$ group should stabilize the double bond as much as an alkyl group, i.e., 11.5 kJ mol^{-1}.[4] The methyl group in the β carbon of **4b** stabilizes the double bond by 12.8 kJ mol^{-1} as evaluated above. Thus the effect of the $EtSO_2$ group is [−4.3−(−12.8)−11.5] kJ mol^{-1} = −3.0 kJ mol^{-1}, i.e., an $EtSO_2$ group attached to a double bond stabilizes it by only 3 kJ mol^{-1}, which is considerably smaller than the corresponding stabilization of an EtS group (ca. 15 kJ mol^{-1}).[13]



(IV)

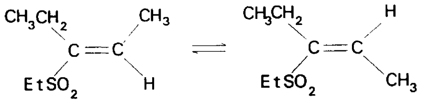
With the aid of $\Delta H^\ominus$ (or $\Delta G^\ominus$) of reaction (IV) the stabilization of an α alkyl group of a vinyl sulfone can be evaluated. $\Delta H^\ominus$ of reaction **5a**→**5b** is −12.5 kJ mol^{-1}. Taking into account the effects in the isomers of reaction (IV), H(α−Me) = (−12.5−4.3+12.8+3.0−11.5) kJ mol^{-1} = −12.5 kJ mol^{-1}. Reaction **6a**→**6b**: H(α−Me) = (+2.6−4.3+12.8+3.0−11.5−11.5) kJ mol^{-1} = −8.9 kJ mol^{-1}. Reaction **7a**→**7b**: H(α−Et) = (−9.6−4.3+12.8+3.0−11.5) kJ mol^{-1} = −9.6 kJ mol^{-1}. The mean value is thus −10.3 kJ mol^{-1} with a standard error of 1.1 kJ mol^{-1}, i.e., an alkyl group attached to the α carbon of a vinyl sulfone causes a stabilization of 10(1) kJ mol^{-1}. The corresponding stabilization in vinyl sulfides is reported to be 7.7(6) kJ mol^{-1}.[11]

According to *ab initio* MO calculations the most stable rotamers of (E)- and (Z)-methyl-1-propenyl sulfone have an *anticlinal* conformation, i.e., one of the S=O bonds is *cis* to the double bond.[21] A thermodynamic study of (E)- and (Z)-alkyl 1-propenyl sulfones points to the same conclusion.[13] According to these studies the E→Z reaction of these compounds does not involve any changes in the spatial orientation of the alkylsulfonyl group. The conformation of ethyl vinyl sulfides with no α substituent changes from s-*cis* to s-*trans* in the E→Z isomerization and the conformation of ethyl vinyl sulfides with an α substituent changes from s-*cis* to *gauche*.[23] These conformational changes reflect in the ^{13}C NMR shifts of the β carbons of these compounds,[23] e.g., the ^{13}C signals of the Z isomers of α substituted vinyl sulfides are 4–5 ppm downfield from the signals of the E isomers, which shows that the conjugation in the Z isomers is weaker than in the E isomers. The difference in the ^{13}C shifts of the β carbons of the E and Z isomers of the compounds in the present study is only ca. 1 ppm, which is consistent with the thermodynamic results, i.e., that there is no change in the orientation of the $EtSO_2$ group in the $E \rightarrow Z$ isomerization of α-substituted vinyl sulfones.

In E isomers of alkenes $HC_\alpha R{=}C_\beta HCH_3$ the ^{13}C signal of the β carbon moves 8.2 ppm and 1.8 ppm upfield, when R is changed from H to Me and from Me to Et, respectively.[24] In the Z isomers the corresponding changes are 9.4 and 1.4 ppm upfield. This means that the electron density increases in the β carbon, when the size of the alkyl group increases. Bulky alkyl groups have larger electron-releasing effects than small ones, which obviously explains the above tendency.[7] In the corresponding sulfones $EtSO_2CR{=}CHCH_3$ the ^{13}C signal of the β carbon changes analogously (5.4 and 1.7 ppm upfield) in the Z isomer (which corresponds to the E isomer of the alkene mentioned above), but in the E isomer the changes are 7.2 ppm upfield (from H to Me) and 0.4 ppm downfield (from Me to Et), i.e., the change from Me to Et decreases the electron density in the β carbon even though the inductive effects of these groups should increase it. This suggests that the conjugation in the molecule diminishes, when R is changed from Me to Et, but only in the E isomer. This argument is, in fact, supported by the thermodynamic data.

Table 2. The boiling points (°C/Pa) and yields of the synthesized compounds.

Compound	Yield (%)	B.p./°C/Pa
2-Ethylsulfonyl-2-butene + isom.	19	74–78/200
3-Ethylsulfonyl-1-butene	21	72–76/200
2-Ethylsulfonyl-2-pentene + isom.	18	78–84/200
3-Ethylsulfonyl-2-pentene + isom.	18	78–84/200
2-Ethylsulfonyl-3-methyl-2-butene + isom.	52	86–88/200



8a 8b (V)

$\Delta G^\ominus$ of the $E \rightarrow Z$ isomerization of the studied compound decreases from 13.8 to 11.3 kJ mol^{-1} on going from R=Me to R=Et, i.e., in the case R=Et the energy of the E isomer is higher than 'expected'. Evidently an Et group in the α carbon causes steric strain in the E isomer more than does a Me group and this strain probably forces the $EtSO_2$ group to turn slightly to a position with diminished conjugation.

The ^{13}C shift of the β carbon of the E isomer of the corresponding vinyl sulfide $EtSHR{=}CHCH_3$ changes analogously with the alkenes mentioned above, but in the Z isomer the ^{13}C signal of the β carbon shifts 1.7 and 0.1 ppm downfield, when R is changed from H to Me and from Me to Et, respectively. Thus an α-alkyl substituent diminishes the conjugation in the molecule. The reason for this is obviously the fact that the alkyl groups in the α and β (*cis* to S) carbons force the EtS group out of the S–C=C plane, which diminishes the conjugation in the molecule.

Experimental

Materials. The α-alkyl substituted vinyl sulfides were prepared first by the method described in Ref. 23. The sulfides were oxidized to sulfones with H_2O_2 by the method described in Ref. 25. The yields and boiling

Table 3. Chemical shifts (ppm from Me_4Si) and coupling constants (Hz) from the ^1H NMR spectra.

Compound		δ(a)	δ(b)	δ(c)	δ(d)	δ(e)	δ(f)	J/Hz	
$CH_3CH_2SO_2C(CH_2CH_3){=}CHCH_3$ a b c d e f	E	1.35	2.93	3.22	1.13	6.75	1.88	J(ab) = 8.0 J(ef) = 7.1	J(cd) = 7.5
	Z	1.37	2.95	3.20	1.11	6.27	1.88	J(ab) = 8.0 J(ef) = 7.8	J(cd) = 6.8
$CH_3CH_2SO_2C(CH_3){=}CHCH_3$ a b c d e	E	1.30	2.91	1.96	6.75	2.0		J(ab) = 6.9 J(de) = 7.1	J(cd) = 2.1
	Z	1.22	2.97	1.96	6.27	2.0		J(ab) = 7.5 J(de) = 7.1	J(cd) = 2.1
$CH_3CH_2SO_2C(CH_3){=}CHCH_2CH_3$ a b c d e f	E				6.63				
	Z	1.32	2.96	2.02	6.15	2.51	1.05	J(ab) = 7.5 J(de) = 7.5	J(cd) = 2.1 J(ef) = 7.8
$CH_3CH_2SO_2C(CH_3){=}C(CH_3)_2$ a b c d		1.28	2.93	2.14	2.00 1.89			J(ab) = 7.5	J(cd) = 2.1
$CH_3CH_2SO_2CH(CH_3)CH{=}CH_2$ a b c d e f		1.43	2.93	3.67	1.35	5.2–6.2		J(ab) = 8.8 J(ce) = 8.0	J(cd) = 8.9

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

Compound		δ(a)	δ(b)	δ(c)	δ(d)	δ(e)	δ(f)	δ(g)
$CH_3CH_2SO_2C(CH_2CH_3)=CHCH_3$ a b c d e f g	*E*	6.63	46.77	141.03	19.39 (26.16)	13.16	138.36	13.16
	Z	6.18	48.72	141.22	26.16 (19.39)	13.53 (14.62)	137.24	13.53 (14.62)
$CH_3CH_2SO_2C(CH_3)=CHCH_3$ a b c d e f	*E*	6.91	46.01	135.24 (134.99)	20.39	138.03	13.96	
	Z	6.55	48.11	134.99 (135.24)	20.39	138.94	14.78	
$CH_3CH_2SO_2C(CH_3)=CHCH_2CH_3$ a b c d e f g	*E*	6.76	45.74 (46.34)	133.29	21.55	144.10	20.76	12.50
	Z	6.36	48.02	133.29	21.82	145.62	20.15	13.50
$CH_3CH_2SO_2C(CH_3)=C(CH_3)_2$ a b c d e f		6.15	47.96	128.89	23.52 (21.48)	147.17	15.26[a] 21.48[b] (23.52)	
$CH_3CH_2SO_2CH(CH_3)CH=CH_2$ a b c d e f		5.36	43.28	60.25	11.50	131.71	120.94	

[a] *cis* to the $EtSO_2$ group. [b] *trans* to the $EtSO_2$ group.

Table 5. Equilibrium constants for the studied reactions.[a]

T/K	*K*(**1c**/**1b**)	*K*(**2c**/**2b**)	*K*(**5b**/**5a**)
443	0.0244	0.0260	18.8
423	0.0206	0.0218	22.6
398	0.0162	0.0170	28.4
373	0.0117	0.0135	38.6
348	0.00901	0.0107	46.9
323		0.00668	70.2
298	0.00376	0.00460	101

[a] The following equilibrium constants were determined at one temperature only, because the temperature dependence of *K* could not be determined with reasonable accuracy. The errors are estimated, based upon the results in the equilibrium experiments: *K*(**1b**/**1a**) = 22.2(9), (*T* = 348 K), *K*(**2b**/**2a**) = 16.0(5), (*T* = 348 K), *K*(**3b**/**3a**) = 1.6(3), (*T* = 373 K), *K*(**6b**/**6a**) = 2.2(3), (*T* = 398 K), *K*(**7b**/**7a**) = 21.2(9), (*T* = 373 K).

points are summarized in Table 2. The products were mainly a mixture of the geometric isomers.

NMR spectra. ^{1}H NMR spectra (80 MHz) and ^{13}C NMR spectra (15 MHz) were recorded for 10–20% solutions in $CDCl_3$. 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 *tert*-butyl alcohol solution with potassium *tert*-butoxide as the catalyst.[7,21] The substrate concentration of the samples was 10–50% depending on the sulfone and temperature, and the catalyst concentration was 0.1–0.2 wt%. The samples were sealed in glass ampoules and the ampoules kept in thermostatted ovens at appropriate temperatures to establish equilibrium. The samples were analyzed by gas chromatography using NB-9C as the stationary phase. Before the analysis the sample was cooled in ice and the catalyst was destroyed with oxalic acid to prevent isomerization during the analysis. At each temperature, five to eight samples were analyzed at equilibrium and the mean value was calculated. In some cases the values of the parallel experiments differed too much to determine a reliable temperature dependence of *K*. In those cases only the $\Delta G^{\ominus}$ value is reported. 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 5.

References

1. Kistiakowsky, G. B., Ruhoff, J. R., Smith, H. A. and Vaughan, W. E. *J. Am. Chem. Soc. 57* (1935) 876.
2. Mayer, E. F. and Stroz, D. G. *J. Am. Chem. Soc. 94* (1972) 6344.
3. *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, American Petroleum Institute, Carnegie Press, Pittsburg, PA 1953.
4. Pedley, J. B., Naylor, R. D. and Kirby, S. P. *Thermochemical Data of Organic Compounds*, Chapman and Hall, London 1986.
5. Kimmelma, R. *Acta Chem. Scand., Ser. B 41* (1987) 344.
6. Kimmelma, R. *Acta Chem. Scand., Ser. B 42* (1988) 550.
7. Hine, J. *Structural Effects on Equilibria in Organic Chemistry*, Wiley, New York 1975.
8. Katritzky, A. R., Pinzelli, R. F. and Topsom, R. D. *Tetrahedron 28* (1972) 3441.
9. Kimmelma, R. and Taskinen, E. *Acta Chem. Scand., Ser. B 41* (1987) 271.
10. Taskinen, E. *J. Chem. Thermodyn. 6* (1974) 345.
11. Kimmelma, R. *Acta Chem. Scand. 48* (1994) 606.
12. Dolliver, M. A., Gresham, T. L., Kistiakowsky, G. B., Smith, E.A. and Vaughan, W. E. *J. Am. Chem. Soc. 60* (1938) 440.
13. Kimmelma, R. *Acta Chem. Scand. 47* (1993) 1201.
14. Vajda, E., Hnyk, D., Rozsondai, B., Podlaha, J., Podlahová, J. and Hašek, J. *J. Mol. Struct. 239* (1990) 265.
15. Vajda, E., Friedman, P., Hargittai, I., Hnyk, D., Schäfer, L. and Siam, K. *J. Mol. Struct. 213* (1989) 309.

16. Naumov, V. A., Ziatdinova, R. N. and Berdnikov, E. A. *J. Struct. Chem.* (1981) 382.
17. Nagel, B. and Remizov, A.B. *J. Gen. Chem.* (1978) 1089.
18. Bzhezovskii, V. M., Kalabin, G. A., Trofimov, B. A., Efremova, G. G. and Gusarova, N. K. *Bull. Akad. Sci. USSR, Div. Chem. Sci.* (1980) 715.
19. Hotokka, M. and Kimmelma, R. *J. Mol. Struct., Theochem* *276* (1992) 167.
20. Kimmelma, R. and Hotokka, M. *J. Mol. Struct., Theochem* *285* (1993) 71.
21. Hotokka, M. and Kimmelma, R. *J. Mol. Struct., Theochem* *313* (1994) 313.
22. Cox, J. D. and Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London 1970, pp. 142–152.
23. Virtanen, R. *Acta Chem. Scand, Ser. B* *40* (1986) 313.
24. De Haan, J. W. and van de Ven, L. J. *J. Org. Magn. Reson.* *5* (1973) 147.
25. Sváta, V., Procházka, M. and Bakos, V. *Collect. Czech. Chem. Commun.* *43* (1978) 2619.