Structure–Stability Relationships in Vinyl Sulfides. III. Stabilization Caused by Different Alkylthio and Phenylthio Groups Attached to an Olefinic Double Bond

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The stabilization energies of different alkylthio and phenylthio groups attached to an olefinic double bond have been evaluated with respect to the energy differences of the isomerization reactions of some unsaturated sulfides, in which the double bond migrates from the β,γ- to the α,β-position. According to these results the stabilization energies (in kJ mol^{-1}) are: MeS 15.6, EtS 14.8, i-PrS 15.7, t-BuS 17.5 and PhS 14.4.

The structure–stability relationships of alkenes have been widely studied,[1] e.g. the stabilization caused by an alkyl group attached to an olefinic double bond is reported to be 11.0-12.8 kJ mol^{-1}.[2-7] In alkyl vinyl sulfides the lone-pair electrons of the sulfur atom conjugate with the π orbital of the double bond. Hence the stabilization caused by an alkylthio group attached to an olefinic double bond is not very predictable and offers an interesting item of study.

In this paper, the stabilization energies of different alkylthio and phenylthio groups (MeS, EtS, i-PrS, i-BuS and PhS) attached to an olefinic bond have been evaluated using the $\Delta G^{\ominus}$ and $\Delta H^{\ominus}$ values for the isomerization reactions of some unsaturated sulfides.

Results and discussion

The stabilization energies caused by various structural factors can be evaluated by combining the $\Delta H^{\ominus}$ or $\Delta G^{\ominus}$ values for different reactions. The reliability of this method has been proved.[8] In this work the isomer equilibrium in eqn (1)

$$\text{(1)}$$
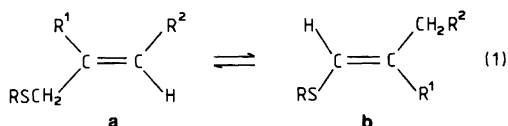
$$\begin{array}{c} \text{1} \quad R = Me, R^1 = R^2 = H \\ \text{2} \quad R = Me, R^1 = H, \overset{\circ}{R} = Me \\ \text{3} \quad R = Me, R^1 = Me, R^2 = H \\ \text{4} \quad R = Et, R^1 = R^2 = H \\ \text{5} \quad R = Et, R^1 = H, R^2 = Me \\ \text{6} \quad R = Et, R^1 = Me, R^2 = H \\ \text{7} \quad R = Et, R^1 = Et, R^2 = Me \\ \text{8} \quad R = i\text{-Pr}, R^1 = H, R^2 = Me \\ \text{9} \quad R = t\text{-Bu}, R^1 = R^2 = H \\ \text{10} \quad R = t\text{-Bu}, R^1 = H, R^2 = Me \\ \text{11} \quad R = Ph, R^1 = R^2 = H \\ \text{12} \quad R = Ph, R^1 = H, R^2 = Me \end{array}$$

was studied. The thermodynamic data for these reactions are summarized in Table 1. The following correction terms are used in the evaluations: a methyl group attached to an olefinic bond stabilizes the molecule by 11.8 kJ mol^{-1}.[4] An approximation is made according to which the stabilizing effect caused by an RSCH$_2$ group is equal to the effect caused by a methyl group (it has been shown that the stabilizing effects of different alkyl groups are equal).[9] The steric strain, when three methyl groups are attached to the double bond, is assumed to be as large as the steric strain in 2-methyl-2-butene, i.e. 7.7 kJ mol^{-1}, which is the difference between the experimental and calculated (the steric factors are neglected) values for the standard enthalpy of formation of 2-methyl-2-butene.[5] A methyl group attached to

Table 1. Values of the thermodynamic functions for the reactions given in eqn. (1) and the stabilization energies caused by the alkylthio and phenylthio groups [*H*(RS)]. The values of the thermodynamic functions refer to solution in Me$_2$SO. The errors are twice the standard errors.

Reaction	$\Delta G^{\ominus}$/kJ mol^{-1}	$\Delta H^{\ominus}$/kJ mol^{-1}	$\Delta S^{\ominus}$/kJ mol^{-1}	H(RS)/kJ mol^{-1}
(1a)→(1b)	−11.53(11)	−13.9(5)	−7.9(13)	17.4
(2a)→(2b)	−0.17(6)	−0.2(3)	−0.1(9)	15.5
(3a)→(3b)	−10.19(2)	−11.4(1)	−4.1(3)	13.9
(4a)→(4b)	−11.98(7)	−11.8(10)	+0.6(33)	15.3
(5a)→(5b)	−0.39(4)	+0.3(3)	+2.3(10)	15.0
(6a)→(6b)	−11.17(49)	−11.8(15)	−2.0(33)	14.3
(7a)→(7b)	−4.62(11)	−5.3(9)	−2.4(26)	14.6
(8a)→(8b)	−1.26(5)	−0.4(3)	+2.8(7)	15.7
(9a)→(9b)	−13.59(2)	−13.7(13)	−0.5(38)	17.2
(10a)→(10b)	−3.04(4)	−2.5(2)	+1.9(7)	17.8
(11a)→(11b)	−11.82(10)	−10.8(6)	+3.3	14.3
(12a)→(12b)	+0.60(1)	+0.8(1)	+0.7(2)	14.5

the β-carbon of a vinyl sulfide stabilizes the molecule by 8.3 kJ mol^{-1} in the cases where the lone-pair electrons of the sulfur atom conjugate with the π orbital of the double bond.[8] Furthermore, there is the Me⋯S *cis* interaction, the magnitude of which is −1.8 kJ mol^{-1} (stabilizing)[10] and the geminal interaction between two ethyl groups attached to the same C (sp^2) atom (3.0 kJ mol^{-1}), which is the difference between the experimental and the calculated (neglecting steric interactions) values for the standard enthalpy of formation of 2-ethyl-1-butene).[5] The geminal interaction between two methyl groups is negligible on the same basis.[5] The correction terms mentioned above are summarized in Fig. 1. When a methyl group and an RSCH$_2$ group are attached to the same end of a double bond, the steric strain is assumed to be as large as the strain in 2-methyl-1-butene (2.7 kJ mol^{-1}, as mentioned above). When an ethyl group and an RSCH$_2$ are attached to one end of a double bond and a methyl group to the other, the steric strain is estimated to be as
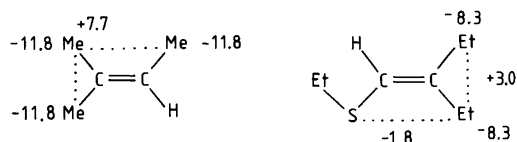

Fig. 1. The correction terms (in kJ mol^{-1}) used in the evaluation of the stabilization energies caused by alkylthio and phenylthio groups attached to an olefinic bond.

large as the strain in 2-methyl-2-butene plus the strain in 2-ethyl-1-butene (7.7 and 3.0 kJ mol^{-1}, respectively, as mentioned above).

As an example of the evaluation method the stabilization caused by an ethylthio group is evaluated using reaction **6a** → **6b** (the values are given in kJ mol^{-1}).
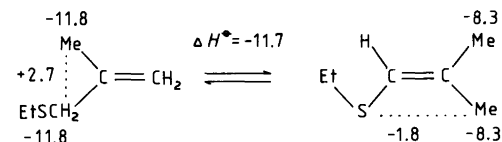
In order to determine the effect of the ethylthio group in **6b**, the stabilizations of the Me and EtSCH$_2$ groups in **6a** must be subtracted and the stabilizations of the methyl groups, the EtS⋯Me *cis* interaction in **6b** and the *geminal* Me⋯EtSCH$_2$ interaction in **6a** must be added to the $\Delta H^{\ominus}$ of this reaction. The effect of the EtS group is thus (−11−7 − 2×11.8 + 2.7 + 2×8.3 + 1.8) = −14.2 kJ mol^{-1} compared with the stabilization caused by a hydrogen atom. The effects of different alkylthio groups in different reactions are summarized in Table 1. It can be seen that the different estimates for each alkylthio group are in reasonably good agreement. The mean values of the effects of each alkylthio group are *H*(MeS) = −15.6 kJ mol^{-1}; *H*(EtS) = −14.8 kJ mol^{-1}; *H*(*i*-PrS) = 15.7 kJ mol^{-1}; *H*(*t*-BuS) = −17.5 kJ mol^{-1}; and *H*(PhS) = −14.4 kJ mol^{-1}.

In **1b** and **2b** the methylthio group can adopt the energetically favorable s-*cis* conformation,[10] whereas in **3b** the Me group, which is *cis* to the methylthio group forces the molecule to adopt the s-*trans* conformation.[10] This increases the energy of this isomer and diminishes the stabilization caused by the MeS group in **3b**, as can be seen from the data in Table 1. The stabilization caused by the MeS group in **3b** is somewhat smaller than the corresponding stabilization in **1b** and **2b**.

According to the values in Table 1 the conformations that the EtS group can adopt have no distinct effect on the stabilization caused by the EtS group, which is reasonable, since in ethyl vinyl sulfide both of the planar conformations are equally favored.[10]

The mean stabilizations caused by the MeS groups in the first two reactions is -14.6 kJ mol^{-1}, i.e. a little larger than the stabilization caused by the ethylthio group. The reason for this is evidently the fact that the MeS group is predominantly in the energetically favorable s-*cis* conformation and that this conformation is energetically more favorable for R = MeS than for R = EtS.

The stabilization caused by the *t*-BuS group is ca. 3 kJ mol^{-1} larger than the stabilization caused by the EtS group. The reason for this cannot be the conformation of the *t*-BuS group, because a group as large as this cannot adopt the planar s-*cis* conformation.[11] A possible reason for the observed stabilizations is the inductive effect exerted by the alkyl groups. The electron-releasing effect of the *t*-Bu group is larger than that of the Et group[12] and this may cause an increase in the resonance and in the stability of a *t*-butyl vinyl sulfide molecule (compared with an ethyl vinyl sulfide molecule).

The PhS group stabilizes the molecule to the same extent as the EtS group, which shows that the phenyl group exerts no special influence on the resonance in (**12b**).
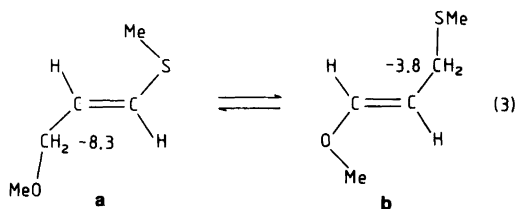
The stabilization caused by an ethoxy group attached to an olefinic bond is reported to be 25.4(5) kJ mol^{-1},[13,14] which is much larger than the corresponding stabilization caused by an alkylthio group. The reason for this is evidently the fact that the p–π conjugation is much stronger in vinyl ethers than in vinyl sulfides.[15] The difference in the stabilizations caused by an ethoxy and ethylthio group attached to an olefinic bond is
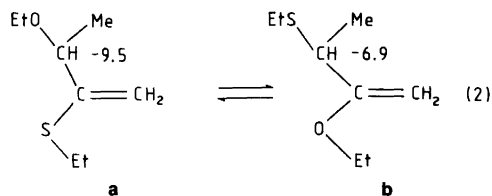
thus $(25.4 -14.8) = 10.6$ kJ mol^{-1}. This difference can also be estimated using eqn. (2) $[\Delta H^{\ominus}$ (**1**) $= -12.2$ kJ $mol^{-1}]$. A methyl group attached to the α-carbon of a vinyl ether is reported to stabilize the molecule by 6.9 kJ mol^{-1}.[13] The stabilization caused by the α-group in the **b** isomer is estimated to be the same. In the corresponding vinyl sulfide (**a** isomer) the stabilization caused by the α-alkyl substituent is larger than in vinyl ethers (because the resonance is weaker in vinyl sulfides than in vinyl ethers, the double bond behaves more like an olefinic double bond), but smaller than in ordinary olefins (-11.8 kJ mol^{-1}). When the mean value of these two values (9.5 kJ mol^{-1}) is used in the evaluation, the difference in the stabilizations caused by the ethoxy and ethylthio groups is $(11.6 + 9.5 - 6.9) = 14.2$ kJ mol^{-1}.

An estimate of the difference in the stabilizations caused by methoxy and methylthio groups can be obtained using eqn. (3). The $\Delta H^{\ominus}$ of this reaction is not known, but the $\Delta G^{\ominus}$(1323 K) $= -9.3$ kJ mol^{-1}.[16] The β-alkyl substituent stabilizes the vinyl sulfide (**a** isomer) by 8.3 kJ mol^{-1} (s-*cis* conformation) and the vinyl ether (**b** isomer) by 3.8 kJ mol^{-1} (s-*cis* conformation).[8] Thus the difference in the stabilizations caused by the methoxy and methylthio groups is $(9.3 - 3.8 + 8.3) = 13.8$ kJ mol^{-1}.

These two values for the difference in the stabilizations caused by alkoxy and alkylthio groups are more than 3 kJ mol^{-1} larger than the value calculated earlier in this paper (10.6 kJ mol^{-1}). This is, however, quite reasonable because of the many approximations made. The values calcu-

lated for the stabilizations caused by alkylthio groups are quite reliable, having been evaluated by several methods using different reactions and different correction terms.

Experimental

Materials. The preparations of alkyl and phenyl 1-propenyl sulfides, 1-(methylthio)-1-butenes, 1-(ethylthio)-1-butenes, 2-methyl-1-(methylthio) propene, 1-(ethylthio)-2-methylpropene and 2-ethyl-1-(ethylthio)-1-butene are described in a previous paper,[10] as are the preparations of 1-(alkylthio)-2-butenes and 1-(phenylthio)-2-butenes.[6] Alkyl allyl sulfides (except allyl methyl sulfide, which was commercially available) and allyl phenyl sulfide were prepared by the method of Tarbell and Lovett.[17] The products were: allyl

ethyl sulfide, yield 53 %, b.p. 391–394 K at 100 kPa (lit.,[18] b.p. 386–387 K at 99.5 kPa), allyl *tert*-butyl sulfide, yield 40 %, b.p. 417–418 K at 100 kPa (lit.,[18] b.p. 352–354 K at 12 kPa) and allyl phenyl sulfide, yield 80 %, b.p. 380–382 K at 28 kPa (lit.,[19] b.p. 332–333 K at 0.20 kPa).

NMR spectra. ^{1}H NMR spectra were recorded with a 60 MHz spectrometer in 10–20 % CCl_4 solution with $SiMe_4$ as an internal standard. ^{13}C NMR spectra were recorded with a 15 MHz spectrometer in 10–20 % $CDCl_3$ solution with $SiMe_4$ as an internal standard. The spectra of some of the compounds have been reported previously.[6,10] The ^{1}H NMR spectra of the alkyl and phenyl allyl sulfides and 3-(ethylthio)-2-methyl-1-propene are summarized in Table 2 and the ^{13}C NMR spectra of these compounds in Table 3.

Table 2. ^{1}H NMR chemical shifts (ppm from $SiMe_4$) and coupling constants (in Hz).

Compound	δ(a)	δ(b)	δ(c)	δ(d)	δ(e)	J
$CH_3SCH_2CH=CH_2$ a b c d	1.95	3.01	5.3–6.1	4.8–5.2		J(bc) 6.6
$CH_3CH_2SCH_2CH=CH_2$ a b c d e	1.19	2.39	3.05	5.4–6.1	4.8–5.2	J(ab) 7.2 J(cd) 6.8
$CH_3CH_2SCH_2CCH_3=CH_2$ a b c d e	1.20	2.35	3.01	1.77	4.73	J(ab) 7.2
$(CH_3)_3SCH_2CH=CH_2$ a b c d	1.28	3.13	5.4–6.2	4.8–5.3		J(bc) 7.0
$C_6H_5SCH_2CH=CH_2$ a b c d	7.0–7.3	3.41	5.3–6.2	4.8–5.2		J(bc) 6.4

Table 3. ^{13}C NMR chemical shifts (ppm from $SiMe_4$).

Compound	δ(a)	δ(b)	δ(c)	δ(d)	δ(e)	δ(f)
$CH_3SCH_2CH=CH_2$ a b c d	14.18	36.89	134.23	116.67		
$CH_3CH_2SCH_2CH=CH_2$ a b c d e	14.47	24.59	34.37	134.63	116.61	
$CH_3CH_2SCH_2CCH_3=CH_2$ a b c de f	14.32	24.79	38.98	141.46	20.68	113.13
$(CH_3)_3CSCH_2CH=CH_2$ a b c d e	31.00	42.49	32.03	135.49	116.50	
$C_6H_5SCH_2CH=CH_2$ a b c d	126.18–136.06	37.13	133.66	117.52		

Table 4. Equilibrium constants for reactions (1a)→(1b)–(7a)→(7b).

T/K	K(1b/1a)	K(2b/2a)	K(3b/3a)	K(4b/4a)	K(5b/5a)	K(6b/6a)	K(7b/7a)
474						15.57	
453						17.7	
433						21.15	
423	20.0						
415						23.5	
403	24.6	1.05					
393		1.06	20.0				
373	33.7	1.04	24.3		1.20		4.30
353	44.8		30.0		1.20		4.50
333	57.7	1.08	37.7	78	1.17		5.06
323				85			
313		1.05	48.8	99	1.19		5.81
299		1.08	60.4	125	1.17		6.55
291				142			

Table 5. Equilibrium constants for reactions (8a)→(8b)–(12a)→(12b) and the reaction given in eqn. (2).

T/K	K(8b/8a)	K(9b/9a)	K(10b/10a)	K(11b/11a)	K(12b/12a)	K[(2)]
440						50.0
424						54.4
403						63.3
393	1.60	61	2.68	40.5	0.849	
373	1.61	82	2.81	49.3	0.837	88.5
353	1.60	102	2.91	61.8	0.827	
333	1.63	139	3.05	72.3	0.810	
313	1.66	178	3.28	95.5	0.797	
299				117		

Configurational assignments. The basis of the identification of the geometric isomers of 1-(alkylthio)-1-butenes has been discussed previously[10] and the geometric isomers of 1-(alkylthio)-2-butenes were identified by their thermodynamic stability.[6]

Equilibrations. The equilibration experiments were carried out in Me_2SO solution with potassium *tert*-butoxide as the catalyst.[6] The values of the equilibrium constants K are given in Tables 4 and 5.

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