Short Communication

Structure–Stability Relationships in Unsaturated Sulfur Compounds. IV. A Thermodynamic Study of the Stabilization Caused by Alkyl Groups Attached to the α Carbon of Vinyl Sulfides

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The stabilization ability of different groups attached to an olefinic double bond has been widely studied over the last decades.[1–7] A methyl group, for example has been reported to stabilize olefinic double bonds from 11.0 to 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-pairs of electrons of the sulfur (oxygen) atom conjugate with the π orbital of the double bond.[8] Thus, the stabilization caused by different groups may differ from the corresponding stabilization in ordinary olefins. It has been reported that a methyl group attached to the β carbon of a vinyl sulfide may stabilize the double bond by 8.5 or 9.5 kJ mol^{-1}, depending on the conformation of the molecule.[9] The corresponding stabilization in vinyl ethers is reported to be from 4.3 to 8.3 kJ mol^{-1}.[10] The stabilization caused by an alkyl group attached to the α carbon of a vinyl ether has been calculated to be 6.9 kJ mol^{-1} based upon heats of hydrogenation.[11] Since the corresponding stabilization in vinyl sulfides has not yet been reported, it was of interest to study this effect.

In this communication the stabilization caused by an alkyl group attached to the α carbon of vinyl sulfides has been evaluated using $\Delta H^{\ominus}$ or $\Delta G^{\ominus}$ 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 $\Delta H^{\ominus}$ or $\Delta G^{\ominus}$ values for different reactions. The reliability of this method has been documented in earlier studies.[9] In cases where $\Delta H^{\ominus}$ value could not be acquired, the $\Delta G^{\ominus}$ value

$$\text{(1)}$$

1 R^1 = Me, R^2 = Me, R^3 = Me, R^4 = Et
2 R^1 = Me, R^2 = Me, R^3 = Pr, R^4 = H
3 R^1 = Me, R^2 = H, R^3 = Me, R^4 = Me
4 R^1 = Me, R^2 = H, R^3 = Et, R^4 = H
5 R^1 = Et, R^2 = H, R^3 = Et, R^4 = Me

was used instead. In this work the isomer equilibrium in eqn. (1) was studied. The thermodynamic data for reactions a→b in eqn. (1) are summarized in Table 1. The correction terms shown below were used in the evaluations.
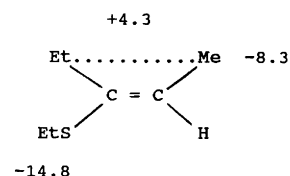
A methyl group attached to an olefinic double bond causes a stabilization of 11.8 kJ mol^{-1}.[4] An approximation was made based upon the assumption that the stabilization effect caused by an EtSCHR^1 group is equal to the effect caused by a methyl group. This assumption seems valid, since it has been shown that the stabilizing effects of different alkyl groups are equal.[12] A methyl group, as well as an ethyl group, attached to the β carbon of a vinyl sulfide stabilizes the molecule by 8.3 kJ mol^{-1}.[9]

Table 1. The values of the thermodynamic functions for reactions a→b, eqn. (1), in Me_2SO at 298 K and the stabilization energies caused by the α alkyl groups [*H*(R)]. The errors are twice the standard errors.

Reaction	$\Delta G^{\ominus}/kJ\ mol^{-1}$	$\Delta H^{\ominus}/kJ\ mol^{-1}$	$\Delta S/kJ\ K^{-1}\ mol^{-1}$	$H(R)$
1a→1b	−3.7(1)	−2.1(5)	+5(1)	−6.9
2a→2b	−1.0(1)	−0.7(3)	+1(1)	−9.5
3a→3b	−15.2(3)	−15.0(13)	+1(3)	−8.0
4a→4b		−11.1(14)[a]		−6.1
5a→5b	−13.1(2)[b]			

[a] $\Delta H^{\ominus}$ for this reaction has been obtained by combining $\Delta H^{\ominus}$ values for the reaction **3a→3b** and the reaction EtS(Me)=CHMe→EtSC(Et)=CH$_2$ (Ref. 9). [b] The temperature dependence of K could not be measured sufficiently accurately to lead to reliable values for $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$. T=348 K.

An ethylthio group attached to an olefinic double bond causes a stabilization of 14.8 kJ mol^{-1}.[6] Furthermore, a methyl and an ethyl group *cis* to each other destabilize the molecule by 4.3 kJ mol^{-1}.

As an example of this procedure the stabilization of the α alkyl group is calculated using reaction **1a→1b** [eqn. (2)] (the values are given in kJ mol^{-1}). To evaluate the

$$\text{(2)}$$
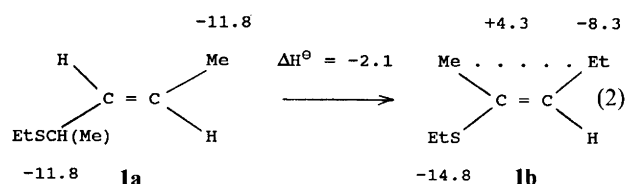
effect of the α alkyl group in **1b**, the stabilization due to the methyl and the EtSCH(Me) groups in the **1a** isomer in addition to the Me⋯Et *cis* interaction in **1b** must be subtracted and the stabilizations due to the ethyl and ethylthio groups in **1b** must be added to the $\Delta H^{\ominus}$ value of this reaction. The effect of the α alkyl group is thus $(-2.1-2\times11.8-4.3+8.3+14.8)$ kJ mol^{-1} = −6.9 kJ mol^{-1} and is stabilizing as compared with a hydrogen atom. The effect of the α alkyl groups in different reactions are summarized in Table 1. From a comparison of the five values it can be seen that they are in reasonably good agreement with each other, particularly when taking into account the many factors that comprise them. The mean value is −7.7 kJ mol^{-1} with a standard error of 0.6 kJ mol^{-1}. This means that an α alkyl group in a vinyl sulfide molecule causes a stabilization of 7.7(6) kJ mol^{-1}, i.e., about 4 kJ mol^{-1} less than in ordinary olefins, and presumably slightly more, ≈1 kJ mol^{-1}, than in vinyl ethers.[11]

Experimental

Materials. The preparation methods, boiling points and NMR data of 2-ethylthio-2-butenes and 3-ethylthio-2-pentenes are reported in Ref. 13. 3-Ethylthio-1-butene was prepared from 3-chloro-1-butene and sodium ethanethiolate as described by Tarbell and Lovett.[14] The product, collected at 128–132°C/100 kPa was obtained

in a yield of 50%. ^{1}H NMR data (ppm from Me$_4$Si, coupling constants in Hz): δ 1.21 (Me of EtS), 2.44 (CH$_2$ of EtS), J = 7.6 (Et), 1.31 (Me$_\alpha$), 3.31 (CHS), J = 6.4 (MeCH), 5.3–5.9 (CH =), 4.7–5.1 (= CH$_2$). ^{13}C NMR data (ppm from Me$_4$Si): δ 14.53 (Me of EtS), 24.37 (CH$_2$ of EtS), 20.12 (Me), 42.31 (−CH−), 140.61 (−CH =) and 113.56 (= CH$_2$). The mixture of 2-ethylthio-2-pentenes was prepared in 32% yield by the method described in Ref. 13, b.p. 158–160°C/100 kPa. The geometric isomers were identified by their ^{13}C NMR spectra using the arguments described in Ref. 13. ^{1}H NMR data: δ 1.20 (*trans*), 1.17 (*cis*) (Me of EtS), 2.64 (CH$_2$ of EtS), J = 7.3, 1.83 (*trans*), 1.94 (*cis*) (Me$_\alpha$), 5.2–5.7 (= CH), 2.13 (CH$_2$ of Et), 0.91 (*trans*), 0.93 (*cis*) (Me of Et), J = 6.8. ^{13}C NMR data (ppm from Me$_4$Si): δ 14.05 (13.93) (*trans*), 13.77 (13.38) (*cis*) (Me of EtS), 25.16 (22.12) (*trans*), 24.67 (23.40) (*cis*) (CH$_2$ of EtS), 14.05 (13.93) (*trans*), 15.17 (*cis*) (Me$_\alpha$), 128.31 (*trans*), 128.44 (*cis*) (C$_\alpha$), 128.77 (*trans*), 133.20 (*cis*) (C$_\beta$), 22.12 (25.16) (*trans*), 21.94 (22.70) (*cis*) (CH$_2$ of Et) and 13.93 (14.05) (*trans*), 13.77 (13.38) (*cis*) (Me of Et).

Equilibrations. The equilibration experiments were carried out in Me$_2$SO solution with potassium *tert*-butoxide as the catalyst.[13] The samples were analyzed by gas chromatography with NB-9C as the stationary phase. The values of the equilibrium constants K are given in Table 2. The values of the thermodynamic functions were calculated by the method described in Ref. 13.

Table 2. Equilibrium constants for rections a → b in eqn. (1).

T/K	$K(1b/1a)$	$K(2b/2a)$	$K(3b/3a)$	$K(5b/5a)^a$
298	4.47	1.48		
323	4.15	1.48	278	
348	4.06	1.43	205	93(7)[b]
373	3.81	1.39	136	
398	3.55	1.40	105	
423			81	
443			60	

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

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