The Stabilization due to the Methyl Group in RSCH$_2$CH=CHCH$_3$

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Equilibrium constants for the isomerization reactions RSCH$_2$CH$_2$CH=CH$_2$ ⇌ (E)-RSCH$_2$CH=CHCH$_3$ ⇌ (Z)-RSCH$_2$CH=CHCH$_3$ have been measured and the energy differences of the isomers have been calculated. According to these results a methyl group stabilizes the double bond by 12.8(5) kJ mol^{-1} and the RSCH$_2$···CH$_3$ cis interaction is 3.7(4) kJ mol^{-1}.

There have been a few studies carried out concerning the stabilizing effects of alkyl groups attached to an olefinic double bond. Thus, for example, the stabilization caused by a methyl group lies between 11.0 and 12.5 kJ mol^{-1} in the gas phase [1-5] and at approximately 12.7 kJ mol^{-1} in the liquid phase.[5] The Me···Me cis interaction in (Z)-2-butene is reported to be between 4.0 and 4.7 kJ mol^{-1} in the gas phase[1-5] and about 3.7 kJ mol^{-1} in the liquid phase.[5] In alkylthio-substituted ethenes (alkyl vinyl sulfides) a methyl group attached to the β carbon stabilizes the double bond by only about 8 kJ mol^{-1} because of the resonance in the molecule,[6] and the cis interaction (Me···S) in vinyl sulfides is reported to be −1.8 kJ mol^{-1} (stabilizing).[7] It therefore seemed interesting to examine whether a heteroatom that is not attached directly to the C(sp^2) atom has any effect on the stabilization caused by the methyl group introduced to the other end of the double bond and whether the Me···Me cis interaction differed from the cis interaction between a methyl group and a chain with a heteroatom in it. In other words, does a heteroatom have any effect on the nature of the double bond? 1-(Alkylthio)butene proved to be a suitable compound for this experiment, because the presence of the sulfur atom helps the double bond to migrate in basic solution. By this method, the isomers in Scheme 1 were equilibrated at several temperatures and the energy differences of these isomers were calculated to obtain the magnitudes of the studied effects.

1 R = Me
2 R = Et
3 R = i–Pr
4 R = t–Bu
5 R = Ph
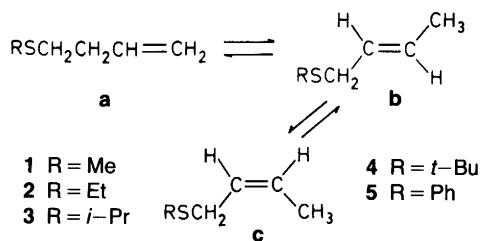
Scheme 1.

Results and discussion

In the a isomer of Scheme 1, the RSCH$_2$CH$_2$ group is attached to the double bond. In the b isomer, the RSCH$_2$ and CH$_3$ groups are attached to the double bond trans to each other, so that there is no steric strain between them. The effects of the RSCH$_2$CH$_2$ and RSCH$_2$ groups on the double bond can be assumed to be equal. Thus, the energy change for this reaction reflects only the effect of the methyl group attached to the double bond in the b isomer. The $\Delta G^{\ominus}$ of this reaction has to be used in the discussion, because the temperature dependence of the equilibrium constant K could not be measured accurately enough to obtain a reliable value for $\Delta H^{\ominus}$. The results are summarized in Table 1. It can be seen that the size of the alkyl group R has no effect on the energy change for the reaction. Thus, the methyl group stabilizes the double bond by 12.8(5) kJ mol^{-1}, which is a little more than the gas phase values in the literature for butene

Table 1. The $\Delta G^{\ominus}$ values at 333 K for reactions **a→b** in Scheme 1. The values refer to DMSO solution. The errors have been calculated from the errors in K.

R	$\Delta G^{\ominus}$/kJ mol^{-1}
Et	−12.7(5)
i−Pr	−12.8(4)
Ph	−13.1(5)

Table 2. The values of the thermodynamic functions for reactions **b→c** in Scheme 1 at 298 K. The values refer to DMSO solution. The errors are twice the standard errors.

R	$\Delta G^{\ominus}$/kJ mol^{-1}	$\Delta H^{\ominus}$/kJ mol^{-1}	$\Delta S^{\ominus}$/J K^{-1} mol^{-1}
Me	4.5(1)	3.7(4)	−2.9(10)
Et	4.2(1)	3.6(3)	−2.3(8)
i−Pr	3.7(1)	4.0(4)	1.0(12)
t−Bu	3.4(1)	3.7(4)	1.2(12)
Ph	3.6(1)	3.3(3)	−0.9(8)

(11.0–12.5 kJ mol^{-1})[1-5] and equal to the liquid phase value in Ref. 5 (12.7 kJ mol^{-1}). The obtained value is, however, about 5 kJ mol^{-1} larger than the corresponding stabilization in vinyl sulfides.[6] In the **b** isomer of Scheme 1 there is no steric strain, but in the **c** isomer there is the *cis* interaction between the RSCH$_2$ and CH$_3$ groups. The $\Delta H^{\ominus}$ of this reaction gives directly this *cis* interaction. The results are summarized in Table 2. It can be seen that the $\Delta H^{\ominus}$ values are equal within the limits of experimental error. Thus, the size of R has no effect on the studied *cis* interaction. The mean of these five $\Delta H^{\ominus}$ values in Table 2 is 3.7(4) kJ mol^{-1}, which is a little smaller than the gas phase values for the Me$\cdots$Me *cis* interaction given in the literature (4.0–4.7 kJ

mol^{-1})[1-5] and equal to the liquid phase value given in Ref. 5 (3.7 kJ mol^{-1}).

It can be seen from the results that the magnitudes of the studied effects are equal to the liquid phase values obtained for butene. Thus, the RSCH$_2$ group attached to the double bond behaves like a methyl group and the sulfur atom has no special effects on the double bond.

Experimental

Materials. The preparation of 1-(methylthio)-1-butenes and 1-(ethylthio)-1-butenes is described in Ref. 7.

Table 3. Chemical shifts (ppm from TMS) from the ^{1}H NMR spectra recorded (the coupling constants are expressed in Hz).

Compound	Isom.	δ(a)	δ(b)	δ(c)	δ(d)	δ(e)	δ(f)	J(ab)	J(cd)	J(ef)	J(de)
CH$_3$CH$_2$SCH$_2$CH=CHCH$_3$ a b c d e f	E	1.21	2.40	3.01	5.3–5.6		1.70	7.2	4.8	3.6	
CH$_3$CH$_2$SCH$_2$CH$_2$CH=CH$_2$ a b c d e f		1.23	2.40	2.4	2.4	5.4–6.2	4.7–5.2	7.5			
(CH$_3$)$_2$CHSCH$_2$CH=CHCH$_3$ a b c d e f	E	1.23	2.77	3.03	5.3–5.6		1.67	6.5	4.6	3.8	
(CH$_3$)$_2$CHSCH$_2$CH$_2$CH=CH$_2$ a b c d e f		1.25	2.87	2.3	2.3	5.5–6.2	4.8–5.1	7.0			
(CH$_3$)$_3$CSCH$_2$CH=CHCH$_3$ a b c d e	E	1.28	3.08	5.3–5.6		1.67					4.0
(CH$_3$)$_2$CSCH$_2$CHCH=CH$_2$ a b c d e		1.30	2.4	2.4	5.4–6.2	4.8–5.3					
C$_6$H$_5$SCH$_2$CH=CHCH$_3$ a b c d e	E	6.9–7.4	3.43	5.3–5.6		1.53					4.0
C$_6$H$_5$SCH$_2$CH$_2$CH=CH$_2$ a b c d e		6.7–7.3	2.8	2.3	5.4–6.3	4.7–5.2					

1-(Alkylthio)-2-butenes and 4-(alkylthio)-1-butenes were prepared either (when the alkyl group is small) from sodium, appropriate thiol and 1-chloro-2-butene or 4-bromo-1-butene in ethanolic solution[8] or (when the alkyl group is bulky) from the appropriate thiol, sodium hydroxide and 1-chloro-2-butene or 4-bromo-1-butene in ethanolic solution.[9] The products were: 1-(ethylthio)-2-butenes, yield 65 %, b.p. 415–417 K at 100 kPa; 1-(*i*-propylthio)-2-butenes, yield 70 %, b.p. 428–432 K at 100 kPa; 1-(*t*-butylthio)-2-butenes, yield 55 %, b.p. 437–440 K at 100 kPa; 1-(phenylthio)-2-butenes, yield 70 %, b.p. 381–383 K at 1.4 kPa; 4-(ethylthio)-1-butene, yield 58 %, b.p. 415 K at 100 kPa; 4-(*i*-propylthio)-1-butene, yield 75 %, b.p. 426 K at 100 kPa; 4-(*t*-butylthio)-1-butene, yield 45 %, b.p. 437 K at 100 kPa and 4-(phenylthio)-1-butene, yield 75 %, b.p. 391–392 K at 1.7 kPa.

NMR spectra. The ¹H NMR spectra were recorded with a 60 MHz spectrometer in 10–20 % CCl₄ solution with TMS as internal standard. The ¹³C NMR spectra were recorded with a 15 MHz spectrometer in 10–20 % CDCl₃ solution with TMS as internal standard. The spectra of 1-(methylthio)-1-butenes and 1-(ethylthio)-1-butenes are reported in Ref. 7, the ¹H spectra of other prepared compounds in Table 3 and the ¹³C spectra of other compounds in this study in Table 4.

Configurational assignments. The basis of the identification of the geometric isomers of 1-(alkylthio)-1-butenes is explained in Ref. 7. The geometric isomers of 1-(alkylthio)-2-butenes were identified by their thermodynamic stability. The less stable isomer is the *Z* isomer, because in this isomer there is the steric repulsion between the two groups *cis* to each other.

Equilibrations. The equilibration experiments were carried out in dimethyl sulfoxide solution with potassium *t*-butoxide as catalyst. The substrate concentration of the samples was 1–10 % (v/v) and the catalyst concentration approximately 0.5 mole %. Before the sample was analyzed, the catalyst was destroyed by addition of oxalic acid. The other details of the equilibrations are the same as in the experiments in Ref. 7. The values of the equilibrium constants K for the reactions studied are given in Table 5.

Table 4. Chemical shifts (ppm from TMS) from the ¹³C NMR spectra recorded.

Compound	Isom.	δ(a)	δ(b)	δ(c)	δ(d)	δ(e)	δ(f)
(CH₃)₂CHSCH₂CH=CHCH₃ a b c d e f	E	23.22	33.69 (32.89)	32.89 (33.69)	127.83 (127.31)	127.31 (127.83)	17.62
	Z	23.22	34.26 (33.69)	33.69 (34.26)	126.05	126.05	12.70
(CH₃)₂CHSCH₂CH₂CH=CH₂ a b c d e f		23.45	34.83 (34.26)	34.26 (34.83)	29.97	137.04	115.64
(CH₃)₃CSCH₂CH=CHCH₃ a b c d e f	E	31.00	42.21	31.00	127.83 (127.54)	127.54 (127.83)	17.73
	Z	31.00			126.22 (126.85)	126.85 (126.22)	12.64
(CH₃)₃CSCH₂CH₂CH=CH₂ a b c d e f		31.00	41.81	34.09	27.73	137.09	115.58
C₆H₅SCH₂CH=CHCH₃ a b c d e	E	125.5– 129.9	36.26	125.5– 129.9		17.62	
	Z	125.5– 129.9	36.3	125.5– 129.9		12.58	
C₆H₅SCH₂CH₂CH=CH₂ a b c d e		125.8– 136.6	33.34 (33.00)	33.00 (33.34)	136.35	116.10	

Table 5. Equilibrium constants for the reactions in Scheme 1.

T/K	K(1c/1b)	K(2c/2b)	K(3c/3b)	K(4c/4b)	K(5c/5b)
403	0.236				
393	0.228		0.326	0.368	
373	0.216	0.241	0.307	0.350	0.309
353		0.229	0.289	0.324	0.294
333[a]	0.183	0.210	0.266	0.305	0.274
313	0.174	0.193	0.236	0.283	0.252
299		0.183		0.252	

[a]The following equilibrium constants were determined only at 333 K (the errors have been estimated from the equilibration results): $K(2b/2a) = 98\pm15$, $K(3b/3a) = 102\pm15$ and $K(5b/5a) = 115\pm20$.

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