Structure–Stability Relationships in Vinyl Sulfides. IV. Evaluation of the p–π Conjugation Energies in Vinyl Sulfides and Vinyl Ethers

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On the basis of equilibration studies it has been calculated that the 3p–2pπ conjugation energy in methyl vinyl sulfide is about 8 kJ mol^{-1} and the 2p–2pπ conjugation energy in methyl vinyl ethyl ether is about 26 kJ mol^{-1}.

In vinyl sulfides, as in vinyl ethers, the lone-pair electrons of the heteroatom conjugate with the π orbital of the double bond in the planar s-*cis* and s-*trans* conformations (Fig. 1), which stabilizes the molecule (resonance structures **1** and **2**).[1-5] In the non-planar *gauche* conformation this conjugation is hindered because of the orientation of the orbitals of the lone-pair electrons of the sulfur atom (Fig. 1).

$CH_2=CH-\ddot{S}-CH_3$ $\quad$ $\bar{C}H_2-CH=\overset{+}{S}-CH_3$

1 $\qquad$ **2**

There is, however, a principal difference in the behavior of the sulfur and oxygen atoms; the sulfur atom behaves as a π,δ-acceptor and the oxygen atom as a π-donor-δ-acceptor.[6,7] The calculated value (*ab initio* method) for the energy of this conjugation (p–π conjugation energy) in vinyl sulfides is 9 or 16 kJ mol^{-1} depending on the method used (according to the report the smaller value is the more reliable one).[8] The corresponding energy in vinyl ethers is 20 or 24 kJ mol^{-1} depending on the method used.[9] According to Kalabin *et al.* the extent of the p–π conjugation in vinyl sulfides is about a third of that in vinyl ethers.[10]

The p–π conjugation energies in vinyl sulfides and vinyl ethers can be estimated by evaluating the energy required to rotate the alkylthio group in alkyl vinyl sulfides (and the alkoxy group in alkyl vinyl ethers) from the s-*cis* conformation to the *gauche* conformation. In the present paper the magnitude of these conjugation energies are evaluated from the $\Delta H^{\ominus}$ values of the isomer pairs of some vinyl sulfides and vinyl ethers.

Results and discussion

In reaction (1) (the values in this reaction are expressed in kJ mol^{-1}) the EtS group rotates from the s-*cis* conformation (**a** isomer) to the *gauche* conformation (**b** isomer). In order to evaluate the energy needed for this rotation the following effects must be taken into account. In the *a* isomer there is the Me···Me *cis* interaction [4.4 kJ mol^{-1}, which is the $\Delta H^{\ominus}$ of reaction (*E*)-2-

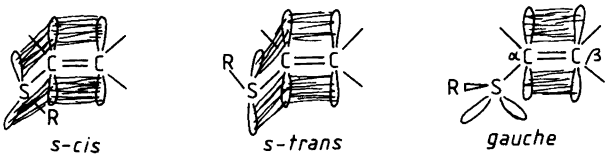
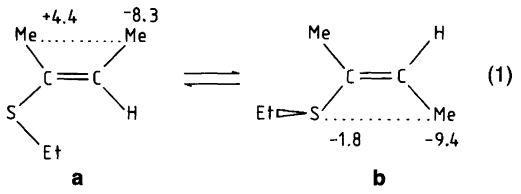


Fig. 1. Possible conformations of vinyl sulfides.



(1)

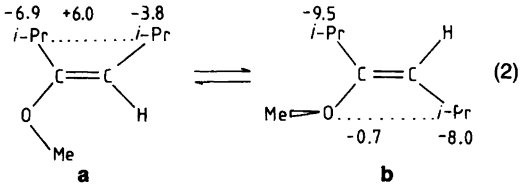
butene → (*Z*)-2-butene][11] and in the **b** isomer the stabilizing Me···S *cis* interaction (1.8 kJ mol^{-2}).[12] A methyl group attached to the β carbon (Fig. 1) of a vinyl sulfide stabilizes the double bond by 8.3 kJ mol^{-1} in cases where the lone pair electrons of the sulfur atom conjugate with the π orbital of the double bond (**a** isomer); and by 9.4 kJ mol^{-1} in cases, where this conjugation is hindered (**b** isomer).[13] Thus the conformation of the vinyl sulfide molecule does not have much effect on the stabilization caused by the alkyl group attached to the β carbon. On this basis it is probable that the conformation of the molecule does not greatly effect the stabilization caused by a methyl group attached to the α carbon either and the possible difference has been ignored (i.e. it is assumed that the stabilizations caused by the α methyl groups in the **a** and **b** isomers are equal). The calculated $\Delta H^{\ominus}$ for this reaction is thus (−9.4−1.8 + 8.3−4.4) = −7.3 kJ mol^{-1}, which is 5.8 kJ mol^{-1} more negative than the experimental value [$\Delta H^{\ominus}(1)$ = (−1.5±0.3) kJ mol^{-1}].[13] This means that the energy required to rotate the ethylthio group from the s-*cis* conformation to the *gauche* conformation, i.e. the 3p−2pπ conjugation energy in ethyl vinyl sulfides is 5.8 kJ mol^{-1}. The energy needed for the corresponding rotation of a methylthio group can be calculated from the value given above using the $\Delta H^{\ominus}$ values of the reaction

(*E*)-RSCH=CHMe → (*Z*)-RSCH=CHMe.

The $\Delta H^{\ominus}$ of this reaction is 2.0 kJ mol^{-1} larger when R=Me than when R=Et [$\Delta H^{\ominus}(1)$ = 2.0 kJ mol^{-1} for R=Me and 0.0 kJ mol^{-1} for R=Et].[12] In this reaction the alkylthio group turns out of the s-*cis* conformation and thus the methylthio group needs ca. 2 kJ mol^{-1} more energy for this rotation than the ethylthio group (evidently the reason for this is the fact that the ethyl group is larger than the methyl group and thus the steric strain in the s-*cis* conformation of (*E*)-ethyl 1-propenyl sulfide is larger than in the s-*cis* conformation of (*E*)-methyl 1-propenyl sulfide). Thus the energy needed to rotate the methylthio group from the s-*cis* conformation to the *gauche* conformation is (5.8+2.0) = 7.8 kJ mol^{-1} with an estimated error of 2 kJ mol^{-1}. This value is an estimation of the stabilization caused by the conjugation of the lone-pair electrons of the sulfur atom with the π orbital of the double bond (the 3p−2pπ conjugation) and it does not include the stabilization that the possible participation of the 3d orbitals of the sulfur atom may have, because it is independent of the conformation of the alkylthio group.[14] This value is a minimum value for the 3p−2pπ conjugation energy, because the methyl groups in the **b** isomer of reaction (1) evidently do not force the ethylthio group to rotate as much from the planar conformation as bulkier groups would. According to the *ab initio* calculations (44-31G method) the energy barrier for the rotation of the MeS group in methyl vinyl sulfide is ca. 9 kJ mol^{-1}, which is the calculated value for the 3p−2pπ conjugation energy in methyl vinyl sulfide.[8] This value is quite reasonable when compared with the experimental value evaluated above.

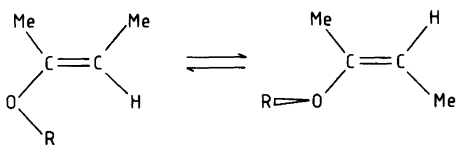
A methylthio group attached to an olefinic double bond stabilizes the double bond by almost 16 kJ mol^{-1}.[15] Thus the p−π conjugation is not the only effect that causes stabilization in alkyl vinyl sulfides. A possible explanation for the 'extra' stabilization is the participation of the 3d orbitals of the sulfur atom in the conjugation in the molecule as mentioned earlier in this paper.

The energy required for the corresponding rotation of a methoxy group can be determined from reaction (2) [$\Delta H^{\ominus}$(g) = (+13.0±0.6) kJ mol^{-1}].[16] In the evaluation the following effects must be taken into account. In the **a** isomer there is the *i*−Pr···*i*−Pr *cis* interaction, the magnitude of which is 6.0 kJ mol^{-1} (destabilizing) and in the **b** isomer the *i*−Pr···O *cis* interaction, −0.7 kJ mol^{-1} is stabilizing.[16] In the following discussion it has been supposed that the stabilization ener-



(2)

gies caused by methyl and isopropyl groups are equal.[17] A methyl group attached to the β carbon of a vinyl ether stabilizes the double bond of the molecule by 3.8 kJ mol^{-1} in cases where the lone-pair electrons of the oxygen atom conjugate with the π orbital of the double bond (**a** isomer) and by 8.0 kJ mol^{-1} in cases, where this conjugation is hindered (**b** isomer).[13] As a consequence of the conjugation in the molecule the *i*−Pr group attached to the α carbon of the **a** isomer stabilizes the double bond by 6.9 kJ mol^{-1} (calculated from the difference in the enthalpies of hydrogenation of ethyl vinyl ether and 2-ethoxypropene).[18] The corresponding data for the case where the resonance is diminished (isomer **b**) are not available, but it is evident that the *i*−Pr group stabilizes the double bond more than in the **a** isomer, but less than in ordinary olefins (11.8 kJ mol^{-1}),[11] i.e. the stabilization caused by the α substituent in the **b** isomer is (9.5±2.5) kJ mol^{-1}. The calculated $\Delta H^{\ominus}$ for reaction (2) is thus (−9.5−8.0−0.7 + 6.9−6.0 + 3.8) = −13.5 kJ mol^{-1}, which is 26.5 kJ mol^{-1} smaller than the experimental value mentioned earlier in this paper. This means that the energy required to rotate the methoxy group from the s-*cis* conformation to the *gauche* conformation is 26.5 kJ mol^{-1} with an estimated error of 3 kJ mol^{-1}. Thus the 2p−2pπ conjugation energy in methyl vinyl ethers is ca. 26.5 kJ mol^{-1}. The $\Delta H^{\ominus}$ of reaction (3) is 1.4 kJ mol^{-1} more positive when R=Me than when R=Et.[19] Thus an EtO



a **b** (3)

group requires 1.4 kJ mol^{-4} less energy for the s-*cis* → *gauche* rotation than does a MeO group and the estimation for the p−π conjugation energy in ethyl vinyl ether is (26.5−1.4) = 25.1 kJ mol^{-1}. This value is equal to the value for the stabilization caused by an ethoxy group attached to an olefinic double bond (25.4±0.5) kJ mol^{-1}, calculated from the difference in the enthalphies of hydrogenation of ethene and ethyl vinyl ether].[18,20] The stabilization caused by an alkoxy group attached to a double bond is therefore caused by the conjugation of the lone-pair electrons of the oxygen atom with the π orbital of the double bond.

Taskinen has also evaluated the 2p−2pπ conjugation energy in vinyl ethers using the same kind of method as above.[21] His result, 23 kJ mol^{-1}, is a little smaller than the one reported here, which is probably due to the fact that, in his evaluation, the α alkyl substituent was a Me group which is smaller than the *i*−Pr group used in the present study.

Gallinella *et al.* have performed *ab initio* calculations on 2-methoxypropene[9] which determined the energy needed for the rotation of the methoxy group. They used two bases for the calculations and found two stable conformations with both methods. The differences in energy of these two conformations was 24.4 or 19.8 kJ mol^{-1} depending on the method used. These are the calculated values for the 2p−2pπ conjugation energy in methyl vinyl ethers and are a little smaller than the value estimated above. This difference is probably because the size of the α alkyl group is smaller in the calculations than in the present study.

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