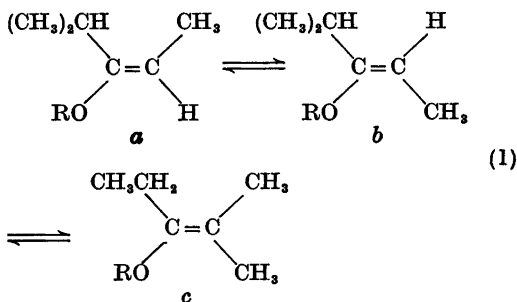# Thermodynamics of Vinyl Ethers. XIII.* Effect of the Alkoxy Group on the Relative Stabilities of Isomeric Alkoxyolefins
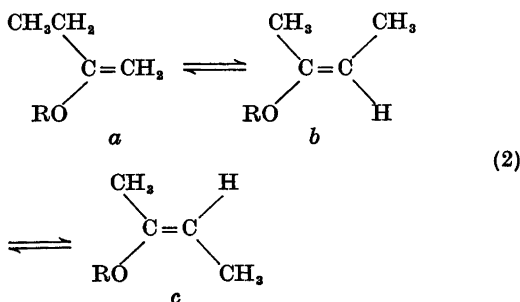
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The effect of the size of the alkoxy group on the relative stabilities of various isomeric alkyl-substituted vinyl alkyl ethers has been studied by chemical equilibration. Bulky alkoxy groups favor the relative stability of molecular struc-tures with an alkyl group in a *cis* position with respect to the alkoxy group. The results are explained in terms of rotational isomerism about the $C(sp^2) - O$ bond. The enthalpy of the *gauche* rotamer of methyl vinyl ether is probably about 12 kJ mol⁻¹ higher than that of the s-*cis* rotamer.

The present paper reports the results of a study of the effect of the size of the alkoxy group on the following equilibria:
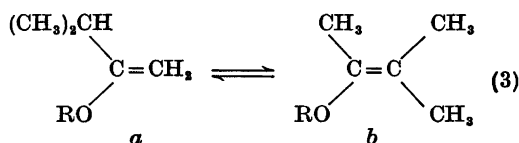
$$
\underset{a}{
\begin{array}{c}
(CH_3)_2CH \\
RO
\end{array}
C=C
\begin{array}{c}
CH_3 \\
H
\end{array}
}
\rightleftharpoons
\underset{b}{
\begin{array}{c}
(CH_3)_2CH \\
RO
\end{array}
C=C
\begin{array}{c}
H \\
CH_3
\end{array}
}
$$

$$
\rightleftharpoons
\underset{c}{
\begin{array}{c}
CH_3CH_2 \\
RO
\end{array}
C=C
\begin{array}{c}
CH_3 \\
CH_3
\end{array}
}
\tag{1}
$$

I: R = Me (Ref. 1); II: R = Et; III: R = Et₂CH

$$
\underset{a}{
\begin{array}{c}
CH_3CH_2 \\
RO
\end{array}
C=CH_2
}
\rightleftharpoons
\underset{b}{
\begin{array}{c}
CH_3 \\
RO
\end{array}
C=C
\begin{array}{c}
CH_3 \\
H
\end{array}
}
$$

$$
\rightleftharpoons
\underset{c}{
\begin{array}{c}
CH_3 \\
RO
\end{array}
C=C
\begin{array}{c}
H \\
CH_3
\end{array}
}
\tag{2}
$$

IV: R = Me (Ref. 2); V: R = Et; VI: R = (Me)₃CCH₂; VII: R = Bz; VIII: R = Et₂CH

Except for the interconversion of geometric isomers, the reaction studied involve changes in the number of methyl groups attached to the β carbon of the vinyl group: for instance, in IVa→IVb a methyl group is formally trans-ferred to the β *trans* position (*trans* to RO) and in IVa→IVc to the β *cis* position. The variation with RO of the enthalpy of reaction reflects the dependence on RO of the apparent stabiliz-ing effect of the β *cis* or β *trans* methyl group. The results achieved are used to estimate the variation with RO of the enthalpy change for reaction (3) involving a formal transfer of two methyl groups to the β carbon.

$$
\underset{a}{
\begin{array}{c}
(CH_3)_2CH \\
RO
\end{array}
C=CH_2
}
\rightleftharpoons
\underset{b}{
\begin{array}{c}
CH_3 \\
RO
\end{array}
C=C
\begin{array}{c}
CH_3 \\
CH_3
\end{array}
}
\tag{3}
$$

IX: R = Me (Refs. 3,4); X: R = Et (Ref. 4); XI: R = Et₂CH (Ref. 4); XII: R = (Me)₃CCH₂

EXPERIMENTAL

Materials. The isomeric vinyl ethers studied were prepared by the standard methods illus-trated in the previous parts of this series. II: boiling temperature (b.t.) 397 to 415 K at 100.0 kPa; III: b.t. 447 to 461 K at 100.0 kPa; V: b.t. 355 to 363 K at 100.2 kPa; VI: b.t. 409 to 411 K at 101.1 kPa; VIIa: b.t. 368 to 371 K at 1.6 kPa; VIIIa: b.t. 319 K at 1.7 kPa; XII: b.t. 424 to 426 K at 100.7 kPa. The *normal*

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* Part XII: Taskinen, E. *Acta Chem. Scand. B 29* (1975) 245.

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8

boiling temperatures were determined as described previously.[1] IIa, 395.0 K; IIb, 398.9 K; IIc, 404.7 K; IIIa, 445.2 K; IIIb, 450.9 K; IIIc, 455.9 K; Va, 361.1 K; Vb, 373.3 K; Vc, 368.9 K; VIa, 400.0 K; VIb, 411.0 K; VIc, 411.0 K; VIIa, 484.0 K; VIIb, 492.2 K; VIIc, 488.4 K; VIIIa, 412.2 K; VIIIb, 422.4 K; VIIIc, 422.4 K; XIIa, 414.4 K; XIIb, 435.0 K. The *NMR spectra* are available on request.

Equilibration procedure. The equilibrations were carried out in cyclohexane solution with iodine as catalyst.[3] The range of temperature covered by the experiments and the number of temperatures at which the experiments were carried out were: II, 284 to 405 K, 13; III, 284 to 415 K, 14; V, 273 to 404 K, 9; VI, 273 to 421 K, 8; VII, 282 to 426 K, 8; VIII, 258 to 402 K, 15; XII, 273 to 415 K, 9.

RESULTS

To save space, the values of the mean equilibrium constant K at various temperatures are not given here but are available on request. The value of ΔG° was calculated for each K value, and then ΔG° was plotted as a function of temperature T. If ΔG° proved to be a linear function of temperature ($\Delta C_p^\circ = 0$), the values of ΔG°, ΔH°, and ΔS° at 298.15 K were obtained by a linear least-squares treatment of ΔG° against T.[3] If however ΔG° was a nonlinear function of T, the values of K were fitted to the equation [5]

$$\ln K = A + B/T + C \ln T \qquad (4)$$

Table 1. Values of ΔG°, ΔH°, ΔS° and ΔC°_p in the liquid phase at 298.15 K for the isomerization reactions studied in this work together with some literature data. The errors are twice the standard errors.

Reaction	Compound	ΔG°/kJ mol^{-1}	ΔH°/kJ mol^{-1}	ΔS°/J K^{-1} mol^{-1}	ΔC_p°/J K^{-1} mol^{-1}
$a \rightarrow b$	I (Ref. 1)	5.55 ± 0.04	11.2 ± 0.2	19.0 ± 0.7	—
	II	4.72 ± 0.08	10.0 ± 0.5	17.7 ± 1.3	—
	II[a]	4.74 ± 0.07	10.6 ± 1.1	19.6 ± 3.4	-12 ± 23
	III	2.80 ± 0.02	3.9 ± 0.1	3.6 ± 0.3	—
	III[a]	2.80 ± 0.02	3.7 ± 0.3	3.1 ± 1.0	3 ± 6
	IV (Ref. 2)	-0.38 ± 0.07	-1.8 ± 0.2	-4.7 ± 0.7	—
	V	-0.45 ± 0.05	-1.4 ± 0.3	-3.1 ± 1.0	—
	VI	-0.10 ± 0.02	-0.8 ± 0.2	-2.3 ± 0.4	—
	VI[a]	-0.10 ± 0.03	-0.9 ± 0.3	-2.6 ± 0.5	2 ± 4
	VII	-0.37 ± 0.04	-0.6 ± 0.2	-0.8 ± 0.6	—
	VIII	0.36 ± 0.03	0.1 ± 0.2	-0.9 ± 0.6	—
	VIII[a]	0.37 ± 0.03	-0.1 ± 0.3	-1.5 ± 1.2	6 ± 10
	XII	1.40 ± 0.02	6.2 ± 0.2	16.1 ± 0.7	-24 ± 5
$a \rightarrow c$	I (Ref. 1)	1.66 ± 0.03	7.8 ± 0.2	20.7 ± 0.4	—
	II[a]	0.35 ± 0.04	7.0 ± 0.6	22.2 ± 2.0	-26 ± 13
	III	-1.13 ± 0.02	0.8 ± 0.1	6.5 ± 0.3	—
	III[a]	-1.13 ± 0.02	1.0 ± 0.3	7.1 ± 1.0	-4 ± 6
	IV (Ref. 2)	5.70 ± 0.11	8.5 ± 0.5	9.3 ± 1.4	—
	V	4.54 ± 0.04	7.8 ± 0.3	11.1 ± 0.9	—
	VI[a]	4.28 ± 0.02	7.4 ± 0.2	10.5 ± 0.7	-17 ± 5
	VII	4.24 ± 0.04	7.0 ± 0.2	9.1 ± 0.6	—
	VIII	2.19 ± 0.03	2.0 ± 0.2	-0.6 ± 0.6	—
	VIII[a]	2.20 ± 0.04	1.9 ± 0.3	-1.0 ± 1.2	5 ± 11
$b \rightarrow c$	I (Ref. 1)	-3.89 ± 0.05	-3.4 ± 0.3[b]	1.7 ± 0.8	—
	II	-4.40 ± 0.07	-4.2 ± 0.4	0.6 ± 1.0	—
	II[a]	-4.38 ± 0.06	-3.6 ± 0.8	2.7 ± 2.8	-14 ± 18
	III[a]	-3.93 ± 0.02	-2.7 ± 0.3	4.3 ± 1.2	-8 ± 7
	IV (Ref. 2)	6.10 ± 0.06	10.3 ± 0.3	13.9 ± 0.8	—
	V	4.99 ± 0.05	9.2 ± 0.3	14.2 ± 1.0	—
	VI[a]	4.38 ± 0.03	8.3 ± 0.3	13.0 ± 1.0	-19 ± 7
	VII	4.63 ± 0.03	7.7 ± 0.2	10.3 ± 0.5	—
	VIII	1.82 ± 0.03	1.9 ± 0.2	0.3 ± 0.5	—
	VIII[a]	1.82 ± 0.03	2.0 ± 0.3	0.5 ± 1.0	-2 ± 10

[a] Calculated from eqn. (4).   [b] The sign of ΔH° given in Ref. 1 is in error.

Table 2. Values of $\Delta H°$ and $\Delta S°$ in the gas phase at 298.15 K for the isomerization reactions studied in this work together with some literature data.

Reaction	Compound	$\Delta H°/\text{kJ mol}^{-1}$	$\Delta S°/\text{J K}^{-1}\text{ mol}^{-1}$
$a \rightarrow b$	I (Ref. 1)	11.6 ± 0.4	19.5 ± 0.9
	II[a]	10.9 ± 0.9	19.4 ± 2.5
	III[b]	4.6 ± 0.4	4.0 ± 1.2
	IV (Ref. 2)	0.5 ± 0.4	-1.6 ± 0.8
	V	0.6 ± 0.4	-0.6 ± 1.1
	VI[b]	1.0 ± 0.4	-0.3 ± 0.6
	VII	0.7 ± 0.4	0.3 ± 0.8
	VIII[c]	1.8 ± 0.4	0.9 ± 0.8
	XII	9.5 ± 0.4	19.6 ± 0.9
$a \rightarrow c$	I (Ref. 1)	9.0 ± 0.3	22.1 ± 0.7
	II[b]	8.5 ± 0.7	24.0 ± 2.1
	III[b]	2.6 ± 0.4	8.7 ± 1.2
	IV (Ref. 2)	10.3 ± 0.6	11.8 ± 1.5
	V	9.1 ± 0.4	12.7 ± 1.0
	VI[b]	9.2 ± 0.4	12.5 ± 0.9
	VII	7.7 ± 0.4	9.7 ± 0.8
	VIII[c]	3.6 ± 0.4	1.2 ± 0.8
$b \rightarrow c$	I (Ref. 1)	-2.6 ± 0.4	2.7 ± 1.0
	II[b]	-2.7 ± 0.9	3.7 ± 2.9
	III[b]	-1.9 ± 0.5	5.0 ± 1.3
	IV (Ref. 2)	9.9 ± 0.4	13.4 ± 0.9
	V	8.5 ± 0.4	13.3 ± 1.1
	VI[b]	8.3 ± 0.4	13.0 ± 1.1
	VII	7.1 ± 0.4	9.7 ± 0.7
	VIII[b]	1.9 ± 0.4	0.3 ± 0.7

[a] The values of $\Delta H°$(g) and $\Delta S°$(g) are based on the mean of the corresponding liquid-phase values given in Table 1. [b] Based on the corresponding liquid-phase values obtained from eqn. (4). [c] Based on the corresponding liquid-phase values obtained for a linear least-squares treatment of $\Delta G°$ vs. T.
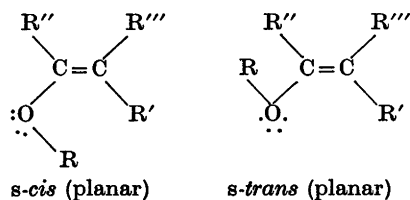
The use of this equation requires that $\Delta H°$ is a linear function of T ($\Delta C_p° = \text{constant}$). The values of the thermodynamic parameters of isomerization in the liquid phase at 298.15 K are shown in Table 1. The values of $\Delta H°$(g) and $\Delta S°$(g) at 298.15 K (Table 2) were evaluated from the liquid-phase data and the normal boiling temperatures.[1]

DISCUSSION

Rotation of the alkoxy group of alkoxyolefins about the $C(sp^2) - O$ bond leads to the following rotamers:

R''   R'''
  \   /
   C = C
  /   \
:O   R'
 ··
   \
    R
s-*cis* (planar)

R''   R'''
  \   /
R C = C
 \ /   \
 .O.   R'
 ··
s-*trans* (planar)

R''   R'''
R\   /
 \ C = C
  | \
:O: R'
gauche (nonplanar)
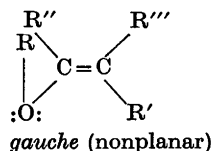
If R' = H and R is not too bulky, the s-*cis* rotamer is known to be the most stable rotameric form, but if R is bulky or R' is larger than hydrogen, the relative stability of the other rotamers increases (see, for example, Ref. 6 and the references cited therein). In the present compounds, R'' is always an alkyl group and it seems likely that the s-*trans* rotamer is unfavored owing to considerable crowding between R and R'' in this spatial arrangement. Thus it is evident that if both R' and R'' are alkyl groups or if R'' is an alkyl group and the alkoxy group is sufficiently bulky, the latter is forced to adopt the *gauche* configuration. The bulkiest alkoxy group in the present compounds is the Et_2CHO group the steric requirements of which

should be approximately equal to those of a t-BuO group (the Taft's E_s values [7] are 0.00, −1.54, and −1.98 for Me, t-Bu, and Et_2CH, respectively), and it might be expected that the Et_2CHO group should exist mainly in the *gauche* configuration irrespective of the bulkiness of the R′ and R″ groups. If a reaction involves a change in the spatial arrangement of the alkoxy group, the change is reflected in the values of the thermodynamic functions of isomerization. Thus it is convenient to divide the reactions studied into the following groups:

Group A. Reactions involving a formal transfer of a methyl group to the β *trans* position (R‴) with no (significant) change in the spatial orientation of the alkoxy group. Reactions Ib→Ic to IIIb→IIIc and IVa→IVb to VIIIa→VIIIb belong to this group.

Group B. Reactions involving a formal transfer of a methyl group to the β *cis* position (R′). The reactions may or may not involve a change in the arrangement of the alkoxy group: if R is bulky, such as Et_2CH, the *gauche* structure should be predominant in both the reactant and the reaction product, but if R is a small group, such as Me, the orientation of the alkoxy group changes from s-*cis* to *gauche*. This group involves the reactions Ia→Ic to VIIIa→VIIIc.

Group C. Reactions in which two methyl groups are formally transferred to the β carbon. The reactions may or may not involve a change in the orientation of the alkoxy group; see Group B. Reactions IXa→IXb to XIIa→XIIb belong to this group.

Reactions of Group A. In the following examples the values of $\Delta H°(g)$ and $\Delta S°(g)$ for formally similar isomerization reactions are given for R = Me, Et and Et_2CH. The Δ term is used to show the increments in $\Delta H°$ and $\Delta S°$ on going from R = Me to R = Et_2CH.

Thus, (i) in each series, the values of $\Delta H°$ increase by about 1 kJ mol⁻¹ and those of $\Delta S°$ by about 2.4 J K⁻¹ mol⁻¹ on going from R = Me to R = Et_2CH; (ii) the values of $\Delta H°$ are, on average, about 3.4 kJ mol⁻¹ more *negative* and those of $\Delta S°$ about 4.2 J K⁻¹ mol⁻¹ more *positive* in Series A1 than those in Series A2.

The greater exothermicity of the reactions of Series A1 may in part be due to the fact that the reactions involve replacement of an i-Pr group by an Et group whereby the destabilization between R and R″ decreases by about 0.8 kJ mol⁻¹.[3] However, since the difference in total strain between the c and b structures of Series A1 is likely to be at least equal to that between the b and a structures of Series A2,[3] it is evident that the *trans* methyl group (R‴) in the c isomers of Series A1 stabilizes the double bond more effectively than does the corresponding group in the b isomers of Series A2. Accordingly, the double-bond character of the ethylenic linkage in the c isomers of Series A1 is higher than that in the b isomers of Series A2; this is reasonable if the alkoxy group in the c isomer of Series A1 exists in the *gauche* configuration where conjugation of the lone-pair electrons of the oxygen atom with the π-electrons of the double bond should be at a minimum.

The positive change in $\Delta H°$ with increasing size of the R group in Series A2 is surprising: from ¹H and ¹³C NMR spectra of alkyl vinyl ethers it has been concluded that conjugation in the vinyloxy group decreases with increasing bulkiness of the alkyl group,[8-10] and hence the double-bond character of the ethylenic linkage and the stabilizing effect of the β methyl group should increase (*i.e.* $\Delta H°$ should become more negative) in the same sequence. Thus one might be tempted to draw the conclusion that the Et_2CH group does not adopt the *gauche* configuration if R′ = H, but this is not supported by the data shown below.

Reaction	$\Delta H°(g)$/kJ mol⁻¹	$\Delta S°$/J K⁻¹ mol⁻¹
(Series A1)		
Ib→Ic	−2.6	2.7
IIb→IIc	−2.7	3.7
IIIb→IIIc	−1.9	5.0
	$\Delta = +0.7$	$\Delta = +2.3$
(Series A2)		
IVa→IVb	0.5	−1.6
Va→Vb	0.6	−0.6
VIIIa→VIIIb	1.8	0.9
	$\Delta = +1.3$	$\Delta = +2.5$

Reactions of Group B

Reaction	$\Delta H°(g)$/kJ mol⁻¹	$\Delta S°(g)$/J K⁻¹ mol⁻¹
(Series B1)		
Ia→Ic	9.0	22.1
IIa→IIc	8.5	24.0
IIIa→IIIc	2.6	8.7
	$\Delta = -6.4$	$\Delta \simeq -13$

(Series B2)

IVa→IVc	10.3	11.8
Va→Vc	9.1	12.7
VIIIa→VIIIc	3.6	1.2
	$\Delta = -6.7$	$\Delta \cong -11$

Thus, (i) the apparent stabilizing effect of the β methyl group in position R' increases by about 6.5 kJ mol⁻¹ in each series on going from R = Me to R = Et₂CH; (ii) the entropy of the c isomer (relative to that of the a isomer) decreases by about 12 J K⁻¹ mol⁻¹ in the same sequence; (iii) on average, the values of $\Delta H°$ are about 1 kJ mol⁻¹ *less* positive and those of $\Delta S°$ about 10 J K⁻¹ mol⁻¹ *more* positive in Series B1 than the corresponding values in Series B2.

The changes of $\Delta H°$ and $\Delta S°$ with the bulkiness of the alkoxy group are satisfactorily explained if the configurations of the alkoxy groups are taken as proposed above, *i.e. gauche* for c (independent of the size of R), and s-*cis* for a in case R = Me, but *gauche* if R = Et₂CH. If we consider the reaction IVa→IVc, the *gauche* structure in IVc gives rise to two enantiomeric isomers with the R group either below or above the plane formed by the group C = C − O, thus increasing the values of $\Delta S°$ by the entropy of mixing, R ln 2≅5.8 J K⁻¹ mol⁻¹. Thus the "chemical" entropy change in IVa→IVc is 11.8−5.8 = 6.0 J K⁻¹ mol⁻¹. The positive entropy change might be ascribed to increased rotational freedom of the methyl group (in MeO) in the *gauche* structure of IVc. On the other hand, the spatial orientation of the Et₂CHO group in VIIIa→VIIIc remains essentially unchanged and hence the entropy change is small. The enthalpy change in IVa→IVc includes the energy required for the s-*cis* → *gauche* reorientation of the methoxy group while this energy is not included in the enthalpy change for VIIIa→VIIIc, since the configuration of the Et₂CHO remains unchanged in the reaction.

As stated above, the values of $\Delta S°$(g) for the reactions of Series A1 are about 4 J K⁻¹ mol⁻¹ more positive than those for Series A2, and correspondingly, those for Series B1 about 10 J K⁻¹ mol⁻¹ more positive than those for Series B2. Obviously, the high values of $\Delta S°$ in Series B1 are due to the fact that in the a isomer the rotational freedom of the i-Pr group is restricted by the *cis* methyl group; restricted

rotation decreases the entropy of the a isomer thus leading to the exceptionally high entropy change in $a→c$.[11]

Reactions of Group C

Reaction	$\Delta H°$(g)/kJ mol⁻¹	$\Delta S°$(g)/J K⁻¹ mol⁻¹
IXa→IXb	9.5	17.9
Xa→Xb	8.8	18.8
XIa→XIb	5.4	12.5
	$\Delta = -4.1$	$\Delta = -5.4$

The Δ terms are somewhat smaller than might be expected on the basis of the values of the corresponding Δ terms presented above.

It is of interest to consider the effect of R on the values of $\Delta H°$ and $\Delta S°$ for the interconversion of geometric isomers:

Reaction	$\Delta H°$(g)/kJ mol⁻¹	$\Delta S°$(g)/J K⁻¹ mol⁻¹
IVb→IVc	9.9	13.4
Vb→Vc	8.5	13.3
VIIIb→VIIIc	1.9	0.3
	$\Delta = -8.0$	$\Delta = -13$

As mentioned above, it is likely that in IVb→IVc the methoxy group is transferred from the s-*cis* to the *gauche* configuration, but in VIIIb→VIIIc the spatial arrangement of the Et₂CHO group remains unchanged. Does this mean that the difference (8 kJ mol⁻¹) in the values of $\Delta H°$(g) for these reactions should represent the energy required for the s-*cis*→*gauche* reorientation of the methoxy group? Obviously not exactly, since from what has been stated above it appears that the double bond of IVc is more effectively (by several kJ) stabilized by the β methyl group than that of IVb, while the double bonds of VIIIb and VIIIc should be equally stabilized by the β methyl group. Hence the enthalpy change in IVb→IVc is several kJ less positive than it would be if there were in the reaction no change in the stabilizing effect of the β methyl group. Accordingly, the difference in the values of $\Delta H°$ for the two reactions in question is several kJ less than the energy required for the s-*cis*→*gauche* reorientation of the methoxy group. Hence a more reasonable value for this process might be around 12 kJ mol⁻¹. In a previous study,[6] the enthalpy change for the s-*cis*→s-

trans reorientation of the methoxy group in methyl 1-propenyl ether was deduced to be about 4 kJ mol⁻¹. For comparison, the SCF calculations of Cadioli and Pincelli [12] suggest that the enthalpies of the s-*trans* and *gauche* rotamers of methyl vinyl ether should be about 8 and 26 kJ mol⁻¹, respectively, higher than the enthalpy of the s-*cis* rotamer.

In many of the reactions studied in this work (especially in VIa→VIc and XIIa→XIIb), considerable changes in the standard heat capacity were observed. An attempt to explain the differences in heat capacity between isomeric vinyl ethers has been published previously.[4]

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