

THERMODYNAMICS OF VINYL ETHERS—XV†

HALOGEN-CONTAINING VINYL ETHERS

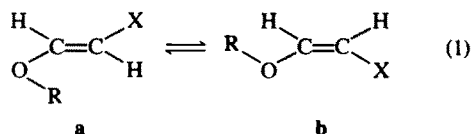
E. TASKINEN* and E. SAINIO

Department of Chemistry, University of Turku, 20500 Turku 50, Finland

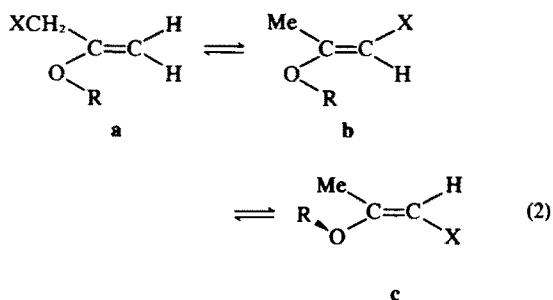
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Abstract—Thermodynamics of geometrical and prototropic isomerization reactions on some halogen-containing vinyl ethers of the types $\text{ROCH}=\text{CHX}$ ($\text{X} = \text{Cl}, \text{Br}$), $\text{ROC}(\text{CH}_2\text{X})=\text{CH}_2$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$), and $\text{ROC}(\text{CHMeCl})=\text{CH}_2$ ($\text{R} = \text{Me}, \text{Et}, \text{Et}_2\text{CH}$) have been studied. In $\text{ROCH}=\text{CHX}$ the *cis* (or *Z*) isomer is thermodynamically the more stable isomer, the higher stability of the *Z* isomer being due to its lower enthalpy. The relative stability of the *E* and *Z* forms is, however, reversed if the α H atom is replaced by a Me group. In systems like $\text{O}=\text{C}=\text{X}$ the double-bond stabilizing ability of the halogen atom decreases in the order $\text{Cl} > \text{Br} > \text{F}$, in contrast to the case in haloalkenes, where the corresponding order is $\text{F} > \text{Cl} > \text{Br}$.

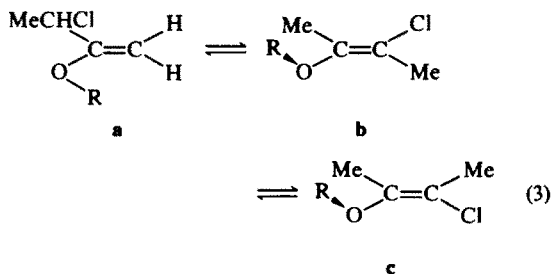
The present work is concerned with the thermodynamics of geometrical and prototropic isomerization reactions shown below:



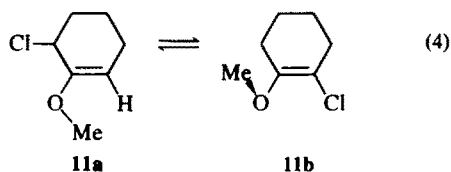
- 1, $\text{X} = \text{Cl}, \text{R} = \text{Et}$;
- 2, $\text{X} = \text{Cl}, \text{R} = \text{Et}_2\text{CH}$;
- 3, $\text{X} = \text{Br}, \text{R} = \text{Et}$



- 4, $\text{X} = \text{F}, \text{R} = \text{Et}$;
- 5, $\text{X} = \text{Cl}, \text{R} = \text{Me}$;
- 6, $\text{X} = \text{Cl}, \text{R} = \text{Et}$;
- 7, $\text{X} = \text{Cl}, \text{R} = \text{Et}_2\text{CH}$;
- 8, $\text{X} = \text{Br}, \text{R} = \text{Et}$



- 9, $\text{R} = \text{Me}$;
- 10, $\text{R} = \text{Et}_2\text{CH}$



RESULTS AND DISCUSSION

The values of ΔG^\ominus , ΔH^\ominus and ΔS^\ominus in the liquid phase at 298.15 K, obtained from the van't Hoff equation, are shown in Table 1. The data reveal many interesting facts. A few of them will be briefly discussed here.

Table 1. Thermodynamic data at 298.15 K for the isomerization reactions studied in this work. Unless otherwise noted, the solvent is cyclohexane and the errors are twice the standard errors

Compound	Reaction	$\Delta G^\ominus/\text{kJ mol}^{-1}$	$\Delta H^\ominus/\text{kJ mol}^{-1}$	$\Delta S^\ominus/\text{J K}^{-1} \text{mol}^{-1}$
1 ^a	a \rightarrow b	-4.04 ± 0.03	-5.3 ± 0.2	-4.3 ± 0.5
2 ^a	a \rightarrow b	-5.16 ± 0.03	-5.5 ± 0.2	-4.6 ± 0.5
3 ^b	a \rightarrow b	-3.9 ± 0.1	-5.1 ± 1.0	-7 ± 3
4	a \rightarrow b	6.69 ± 0.10	7.3 ± 0.4	1.4 ± 1.1
	b \rightarrow c	1.9 ± 0.4	2.7 ± 1.8	3 ± 5
	a \rightarrow c	9.6 ± 0.3	9.9 ± 1.1	4 ± 3
5	a \rightarrow b	-0.32 ± 0.04	-1.7 ± 0.2	-4.5 ± 0.5
	b \rightarrow c	5.15 ± 0.07	7.0 ± 0.3	2.8 ± 0.8
	a \rightarrow c	5.80 ± 0.14	5.2 ± 0.6	-2.1 ± 1.5
6	a \rightarrow b	-3.48 ± 0.04	-1.5 ± 0.1	-4.8 ± 0.4
	b \rightarrow c	5.71 ± 0.12	7.1 ± 0.6	4.7 ± 1.8
	a \rightarrow c	5.22 ± 0.10	5.2 ± 0.5	-0.3 ± 1.4
7	a \rightarrow b	0.40 ± 0.03	-0.7 ± 0.2	-5.8 ± 0.5
	b \rightarrow c	4.14 ± 0.14	5.6 ± 0.7	5.7 ± 2.0
	a \rightarrow c	4.56 ± 0.12	5.4 ± 0.6	2.7 ± 1.7
8 ^c	a \rightarrow b	3.8 ± 0.1	1.4 ± 1	-8 ± 4
9	a \rightarrow b	5.37 ± 0.19	5.0 ± 0.9	5.4 ± 2.5
	b \rightarrow c	4.11 ± 0.16	4.1 ± 0.8	0.0 ± 2.2
	a \rightarrow c	7.45 ± 0.04	8.9 ± 0.2	4.8 ± 0.6
10	a \rightarrow b	0.88 ± 0.11	0.4 ± 0.6	-1.7 ± 1.6
	b \rightarrow c	4.33 ± 0.22	6.1 ± 1.3	5.8 ± 3.6
	a \rightarrow c	5.17 ± 0.09	6.3 ± 0.5	3.9 ± 1.4
11	a \rightarrow b	7.93 ± 0.09	14.1 ± 0.7	20.8 ± 2.0

^aNeat. ^bIn dioxan, $K_{293} = 5.0$, $K_{323} = 4.0$, the errors are estimated errors.

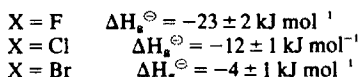
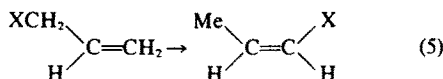
^c $K_{298} = 4.6$, $K_{323} = 4.4$, the errors are estimated errors; the concentration of the c isomer was too low to be detected.

†Part XIV: E. Taskinen and E. Mustonen, *Acta Chem. Scand. B* in press.

The Z forms of 1–3 are thermodynamically more stable than the corresponding E forms. This finding is in line with reported data on some 1,2-disubstituted ethylenes, such as 1,2-dimethoxyethylene, 1,2-dihaloethylenes and 1-halopropenes (for a compilation of these data see Ref. 1). Attempts to explain this so-called "cis effect" have been summarized.¹ Our data refer to the liquid phase and since the boiling temperatures of the Z forms of 1–3 appeared to be some 15–20 K higher than those of the E forms, it follows² that the standard enthalpies of vaporization at 298.15 K of the Z forms should be 2.5 to 3.2 kJ mol⁻¹ higher than those of the E forms. Hence the value of $\Delta H^\ominus(g)$ in, for example, 1a → 1b is about -2 to -3 kJ mol⁻¹. The negative entropy changes in the E → Z (a → b) reactions concerned may, at least partly, arise from the fact that the E isomers probably exist as mixtures of rotational isomers, the rotation occurring about the O–C_{sp} bond,³ i.e. the entropy of the E isomer is raised by the entropy of mixing.

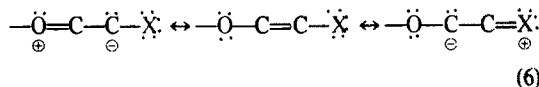
Replacement of the α H atoms in 1–3 by Me groups reverses the relative stability of the geometric isomers (the b and c forms of 4–8), in agreement with previous results on related (but not halogen-containing) compounds.^{4,5} If an additional Me group is introduced to the β carbon (compounds 9a and 9b, 10a and 10b), the E isomer maintains its higher thermodynamic stability.

The values of ΔH_1^\ominus for 4a → 4b, 6a → 6b and 8a → 8b are +7.3, -1.9 and +1.4 kJ mol⁻¹, respectively. On the other hand, for the formally similar reaction (5) the values of ΔH_2^\ominus are as follows:⁶



Thus in haloalkenes the double-bond stabilizing ability of the halogen atoms decreases in the order F > Cl > Br, while the corresponding order is Cl > Br > F in vinyl ethers. The values of the difference ΔH_1^\ominus (vinyl ether) – ΔH_2^\ominus (1-halopropene) are 30, 10 and 5 for the F-, Cl- and Br-derivatives, respectively. The weak stabilizing ability of the halogen atoms in vinyl ethers may be explained as follows.

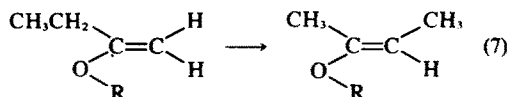
Considering the resonance structures (6) it is obvious that the



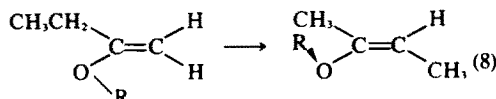
oxygen and halogen atoms on adjacent C atoms tend to "push" the π electrons of the double bond into opposite directions, thus decreasing the resonance that exists between the O atom and the double bond in alkoxyethylenes (vinyl ethers) or between the halogen atom and the double bond in haloethylenes (1-halopropenes). Fluorine, which causes the greatest stabilization in haloethylenes, thus most efficiently opposes the resonance in the vinyloxy group.

Let us now consider the effect of the size of the alkoxy group on the isomer equilibria. For the reaction a → b (compounds 5, 6, 7) the values of ΔG^\ominus , ΔH^\ominus and ΔS^\ominus are essentially independent of the alkoxy group, which agrees

with previous results for the formally similar reaction (7).⁷ Surprisingly, the values of ΔH^\ominus remain unchanged



and those of ΔS^\ominus increase by about 5 J K⁻¹ mol⁻¹ on going from 5a → 5c to 7a → 7c. For comparison, the values of $\Delta H^\ominus(g)$ and $\Delta H^\ominus(l)$ for reaction (8) decrease by about 6.7 kJ mol⁻¹ and 11 J K⁻¹ mol⁻¹ on going



from R = Me to R = Et;CH.⁷ In addition, the values of ΔH^\ominus and ΔS^\ominus of the reaction a → b (compounds 9 and 10) are more sensitive to the size of the alkoxy group than those for the reaction a → c (9, 10). Thus it appears that the values of ΔH^\ominus and ΔS^\ominus for reactions involving a formal transfer of a chlorine atom into a cis position with respect to the alkoxy group are less sensitive to the size of the alkoxy group than those for reactions involving a similar transfer of a Me group.

The values of $\Delta H^\ominus(l)$ and $\Delta S^\ominus(l)$ for 1-methoxy-6-methylcyclohexene → 1-methoxy-2-methylcyclohexene are 7.7 kJ mol⁻¹ and 14 J K⁻¹ mol⁻¹, respectively.² These values are considerably less positive than those for the analogous reaction 11a → 11b. This is surprising since the values of ΔH^\ominus and ΔS^\ominus for reaction (8) with R = Me are⁴ about 10.2 kJ mol⁻¹ and 14 J K⁻¹ mol⁻¹ more positive than those for the reaction 5a → 5c (the common feature of the four reactions in question is that they involve the transfer of a chlorine atom or a Me group from an allylic position to a cis position with respect to the OMe group).

EXPERIMENTAL

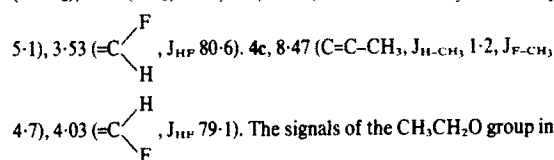
The NMR spectra were recorded in CCl₄ at 60 MHz with TMS as internal reference. The chemical shifts are shown in τ value (ppm) and the coupling constants in Hz. A mixture of isomers was usually employed for recording the spectra. The vinyl ethers were prepared by the conventional methods amply illustrated in the previous parts of this series (usually by the route ketone (or aldehyde) → acetal → vinyl ether).

Compound 1. A sample of 1 was donated by Prof. Alpo Kankaaperä.⁸

Compound 2. By transacetalization from chloroacetaldehyde diethyl acetal and 3-pentanol. Boiling temp. (b.t.) about 415 K. NMR: 2a, 3.53 (H_a), 4.54 (H_b, J 11.1), 6.51 (O–CHEt₂), 8.46 (CH₂), 9.10 (CH₃). 2b, 3.74 (H_a), 5.04 (H_b, J 4.2), 6.47 (O–CHEt₂), 8.41 (CH₂), 9.07 (CH₃).

Compound 3a. B.t. 339 K at 12 kPa. NMR: 3.33 (H_a), 4.71 (H_b, J 11.8), 6.25 (CH₂), 8.73 (CH₃, J 7.1). 3b. B.t. ab. 361 K at 12 kPa. NMR: 3.46 (H_a), 5.00 (H_b, J 4.3), 6.09 (CH₂), 8.71 (CH₃, J 7.1).

Compound 4. Fluoroacetone diethyl acetal (b.t. 408–410 K at 99 kPa) was dropped into boiling quinoline containing some *p*-toluenesulfonic acid. A mixture of EtOH and 4 (mostly 4a) was collected at 338–343 K at 101 kPa. The alcohol was removed by extraction with water and the organic layer was dried (CaCl₂). NMR: 4a, 5.43 (CH₂F, J_{H,F} 46.7), 5.98 and 5.82 (=CH₂), 6.27 (OCH₂), 8.70 (CH₃, J 7.0). 4b, 8.22 (C=C–CH₃, J_{H-CH₃} 1.2, J_{F-CH₃}



4b and **4c** were observed at 8.87 and 8.76 (CH₃) and at 6.54 and 6.47 (CH₂), but it remained unsettled which of these peaks should be ascribed to each isomer, since both isomers were present in almost equal amounts, and there was some disturbing peak overlapping.

Compound 5. B.t. 378 to 393 K at 103.4 kPa. NMR: **5a**, 6.12 (CH₂), 5.78 and 5.94 (=CH₂, *J*_{gem} 2.5), 6.42 (CH₃); **5b**, 4.84 (=C-H), 6.47 (CH₃O), 8.09 (C=C-CH₃); **5c**, 4.93 (=C-H), 8.10 (C=C-CH₃).

Compound 6. B.t. 387 to 394 K at 100.6 kPa. NMR: **6a**, 6.10 (CH₂Cl), 5.79 and 5.95 (=CH₂, *J*_{gem} 2.4), 6.3 (CH₂O), 8.70 (CH₃, *J* 6.9); **6b**, 4.84 (=C-H), 6.3 (CH₂O), 8.09 (C=C-CH₃), 8.73 (CH₃, *J* 6.9); **6c**, 4.93 (=C-H).

Compound 7. Prepared as **2**. B.t. 339 to 340 K at 2.0 kPa. NMR:

7a, 6.13 (CH₂Cl), 5.78 and 5.98 (=CH₂, *J*_{gem} 2.1), 6.1 (O-CH<), 8.5

(CH₂), 9.05 (CH₃). **7b**, 4.80 (=C-H), 6.1 (O-CH<), 8.10

(C=C-CH₃), 8.5 (CH₂), 9.05 (CH₃). **7c**, 4.95 (=C-H).

Compound 8. B.t. 314 to 315 K at 2.6 kPa. NMR: **8a**, 6.24 (CH₂Br), 5.79 and 6.01 (=CH₂, *J*_{gem} 2.2), 6.24 (OCH₂), 8.7 (CH₃); **8b**, 4.96 (=C-H), 8.06 (C=C-CH₃), 6.2 (OCH₂), 8.8 (CH₃).

Compound 9. B.t. 395 to 400 K at 101 kPa. NMR: **9a**, 8.41 (CH₃-CHCl-), 5.66 (-CHCl-, *J* 6.9), 5.81 and 6.05 (=CH₂, *J*_{gem} 2.6), 6.42 (OCH₃); **9b**, 8.05 (CH₃), 6.51 (OCH₃).

Compound 10. From **9** and 3-pentanol by transacetalization. B.t. 339 to 340 K at 1.3 kPa. NMR: **10a**, 8.41 (CH₃-CHCl-), 5.69

(-CHCl-), 5.84 and 6.15 (=CH₂), 6.3 (O-CH<), 9.1 (CH₃). **10b**,

8.01 and 8.11 (2CH₃-C=C), 6.3 (O-CH<), 9.1 (CH₃).

Compound 11. B.t. 342 to 343 K at 0.8 kPa. NMR: **11a**, 5.30 (-CHCl-), 5.70 (=C-H, *J* 3.3), 6.50 (CH₃), 7.5-8.6 (ring hydrogens).

Configurational assignment. The *Z* and *E* (*cis* and *trans*) configurations of **1-3** are easily assigned from the magnitude of the vicinal coupling constant *J*_{H_H} across the double bond.⁹ By comparing the chemical shift data for the geometric isomers of **1** and **6** (for an analogous example see Ref. 10) one is led to the conclusion that the more stable geometric isomer of **6** has the *E* configuration (i.e. **6b**). Moreover, since the boiling temperatures of

the *E* forms of **1** (Ref. 8) and **3** (this work) are 15-20 K lower than those of the *Z* forms, it seems unlikely that replacement of the α hydrogens of either **1** or **3** by methyl groups could reverse the relative volatility. This was verified by experiment, since the less stable geometric isomers of **5-7** were found to concentrate in the distillation pot during fractionation of the synthetic mixtures of isomers. The same arguments based on the relative volatility should also apply to the identification of the geometric isomers of **9** and **10**. Finally, the thermochemical data of isomerization for **4-10** are reasonable only if the more stable geometric isomer has the *E* configuration (**b**).

Equilibrations. The solvent-catalyst combinations used were: neat-Hg(OAc)₂ for **1** and **2**; dioxane-Hg(OAc)₂ for **3**; cyclohexane-I₂ for **4-11**. The equilibrated samples were analyzed by GLC; this method, however, was not applicable to the bromine-containing compounds (**3** and **8**), since they were found to decompose during the GLC analyses. Thus the equilibrium constants of the isomers of **3** and **8** were determined from their NMR spectra. The equilibration procedure has been illustrated in the previous papers of this series. The ranges of temperature covered by the equilibration experiments were the following: **1**, **6**, **7** and **11**, 282-423 K; **2**, 300-406 K; **3**, 293-323 K; **4**, 350-424 K; **5**, 325-423 K; **8**, 298-323 K; **9**, 323-405 K; **10**, 303-402 K. Most of the present halogen-containing compounds were prone to decompose in our preparative gas-chromatograph, and hence the mixtures of isomers of sufficiently different isomer composition, necessary for the equilibrations, were obtained by fractionation of the synthetic products.

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