

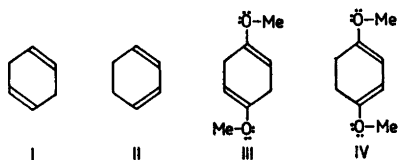
Thermodynamics of Vinyl Ethers. VII.* The Relative Stabilities of 1,4-Dimethoxy-1,4-cyclohexadiene and 1,4-Dimethoxy-1,3-cyclohexadiene

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The relative stabilities of 1,4-dimethoxy-1,4-cyclohexadiene and 1,4-dimethoxy-1,3-cyclohexadiene have been determined at various temperatures between 273.2 and 422.2 K by means of chemical equilibration. In cyclohexane solution at 298.15 K, the following values were obtained for the changes of the thermodynamic functions on going from the former to the latter: $\Delta G^\circ = -2.061 \pm 0.014$ kJ mol⁻¹, $\Delta H^\circ = -0.17 \pm 0.18$ kJ mol⁻¹, $\Delta S^\circ = 6.4 \pm 0.6$ J K⁻¹ mol⁻¹ and $\Delta C_p^\circ = -9.2 \pm 4.2$ J K⁻¹ mol⁻¹. In the ideal gas state at 298.15 K, the values of ΔH° and ΔS° were calculated to be -1.14 ± 0.35 kJ mol⁻¹ and 5.5 ± 0.8 J K⁻¹ mol⁻¹, respectively.

From the thermodynamic point of view, the relative stabilities of the isomeric carbocyclic dienes, 1,4-cyclohexadiene (I) and 1,3-cyclohexadiene (II), form an interesting subject of



investigation. The latter is a conjugated diene and thus it might be expected *a priori* that it should exhibit at least some of the enhanced thermodynamic stability characteristic of open-chain conjugated dienes, such as 1,3-butadiene. Against this background it seems surprising

that in the liquid phase at 368 K, the equilibrium mixture of I and II contains only 68.9 % of the conjugated diene (II).¹ Thus, at equilibrium, II is favored over I by a factor of only 2.22, and moreover, if the effect of statistical factors on the equilibrium in question is considered, it is observed that the preponderance of II is mainly due to the fact that II is statistically favored over I by a factor of 2. Hence the equilibrium constant for the reaction $I \rightleftharpoons II$ should be written as 1.11 if the effect of statistical factors on the position of equilibrium is eliminated. Accordingly, the Gibbs free energy difference between the isomers I and II is practically zero. As to the enthalpy difference, the enthalpy of hydrogenation (acetic acid, 298.15 K) of I to cyclohexane is reported^{2,3} to be *ca.* 1.3 kJ mol⁻¹ more negative than that of II, which shows that the enthalpy of the conjugated diene is only 1.3 kJ mol⁻¹ lower than that of the unconjugated diene (assuming, of course, that I and II are solvated to the same extent in acetic acid). Thus it appears that either conjugation is weak in 1,3-cyclohexadiene or it is much more strained than I. As a continuation of this author's investigations on the effect of structural factors on the stability of vinyl ethers it was of interest to find out the effect of substitution of methoxy groups for the 1,4-hydrogen atoms of I and II on the relative stabilities of the conjugated and nonconjugated diene. Hence the isomeric vinyl ethers 1,4-dimethoxy-1,4-cyclohexadiene (III) and 1,4-dimethoxy-1,3-cyclohexadiene (IV) were prepared and thermodynamics of their interconversion were studied.

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EXPERIMENTAL

Materials. A 76 % yield of a mixture of III and IV was obtained when 0.089 mol of 1,4-cyclohexanedione was treated with 0.196 mol of trimethyl orthoformate in methanol.⁴ The cleavage of the tetramethyl acetal of 1,4-cyclohexanedione to methanol and the isomeric vinyl ethers was effected by fractionation from a small amount of *p*-toluenesulfonic acid. The boiling temperature of the product containing 79 mol % of IV was 474–475 K/101.8 kPa.

NMR spectra (ca. 20 % solutions in CCl₄ at 306 K). III: τ 5.49 (C=C–H), 6.50 (O–CH₂), 7.25 (–CH₂–); IV: τ 5.26 (C=C–H), 6.50 (O–CH₂), 7.70 (–CH₂–).

Determination of normal boiling points.⁵ Reference curve (compound, normal boiling point, relative retention time): 1-methoxycyclopentene, 387.0 K, 0.245; 1-ethoxycyclopentene, 409.0 K, 0.298; 1-methoxycyclohexene, 417.1 K, 0.347; 1-ethoxycyclohexene, 435.0 K, 0.433; 1-propoxycyclohexene, 455.9 K, 0.608; 1-cyclopentoxycyclopentene, 479.7 K, 1.000. The relative retention times of III and IV were 0.878 and 0.773 leading to normal boiling points of 475.2 and 469.2 K, respectively.

Procedure. The performance of the equilibrations has been described previously.⁵ Cyclohexane was used as solvent and iodine as catalyst. At each temperature, the position of equilibrium was approached from both directions. One of the initial mixtures of III and IV consisted of 79 mol % of IV (the crude synthetic product) and the other 55 mol % of IV (obtained by fractionation of the crude synthetic product). As the equilibrium mixtures contained ca. 67 to 70 mol % of IV, the position of equilibrium could thus be approached from both directions. The column used in the GLC analyses was a 4 m column containing 10 % Carbowax 1500 on Chromosorb G. The compounds were eluted in the order IV, III. The areas of the peaks were integrated by means of a Hewlett-Packard 3370 B integrator.

RESULTS

The values of the mean equilibrium constant *K* and its standard error at various temperatures are shown in Table 1. As it turned out that the values of ΔH° and ΔS° of the reaction in question do not remain constant over the range of temperature covered by the measurements, the following equation⁶ was fitted to the values of *K*:

$$\ln K = A + B/T + C \ln T \quad (1)$$

This equation requires that ΔH° varies linearly as *T* ($\Delta C_p^\circ = \text{constant}$). The fitting was per-

Table 1. Values of the mean equilibrium constant *K* and its standard error for the iodine-catalyzed reaction 1,4-dimethoxy-1,4-cyclohexadiene \rightleftharpoons 1,4-dimethoxy-1,3-cyclohexadiene in cyclohexane solution at various temperatures. Substrate concentration 0.2 mol dm⁻³, catalyst concentration 0.008 mol dm⁻³.

<i>T</i> /K	<i>K</i>
273.2	2.281 ± 0.012
283.2	2.317 ± 0.017
294.5	2.317 ± 0.011
308.2	2.295 ± 0.002
323.7	2.267 ± 0.008
345.2	2.252 ± 0.004
355.2	2.215 ± 0.007
373.2	2.218 ± 0.011
400.2	2.161 ± 0.009
422.2	2.123 ± 0.013

formed on an IBM 1130 computer. The following results were obtained for the isomerization of III to IV in cyclohexane at 298.15 K:

$$\Delta G^\circ = -2.061 \pm 0.014 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = -0.17 \pm 0.18 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ = 6.4 \pm 0.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta C_p^\circ = -9.2 \pm 4.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

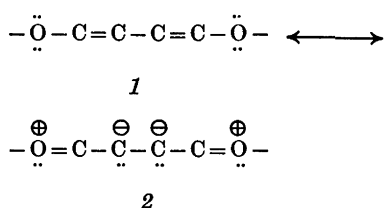
(the errors are twice the standard errors).

The values of ΔH° and ΔS° in the ideal gas state at 298.15 K were calculated to be -1.14 ± 0.35 kJ mol⁻¹ and 5.5 ± 0.8 J K⁻¹ mol⁻¹, respectively, by means of the equations for the standard enthalpy and standard entropy of vaporization at 298.15 K derived in Ref. 5.

DISCUSSION

The enthalpy of 1,3-cyclohexadiene (II) is reported to be ca. 1.3 kJ mol⁻¹ lower than that of 1,4-cyclohexadiene (I) in acetic acid at 298.15 K, and if the boiling points of I and II are taken as 358.8 and 353.7 K, respectively,⁷ the enthalpy of isomerization of I to II is calculated⁵ to be about -2.1 kJ mol⁻¹ in the ideal gas state at 298.15 K. As the enthalpy change for III→IV is about -1.14 kJ mol⁻¹ under the same external conditions, the values of ΔH° for I→II and III→IV are equal within experimental error. Thus the substitution of methoxy groups for the 1,4-hydrogen atoms of I and II has no observable effect on the enthalpy difference

between the conjugated and nonconjugated diene. This shows that although there is, in principle, a long conjugated system in IV ($-\text{O}-\text{C}=\text{C}-\text{C}=\text{C}-\text{O}-$), the stabilization brought about by this system is no greater than the stabilization due to the two ordinary vinyl ether functions ($\text{O}-\text{C}=\text{C}$) in III together. This is understandable, since the resonance structure 2 of the conjugated system in IV shows that an enhanced resonance would lead to a transfer of negative charge at adjacent carbon atoms, which causes structure 2 to be of relatively high energy.



On the other hand, it was shown in a previous part of this series⁸ that electropositive (electron-donating) alkyl groups when attached to the β -carbon of the ethylenic linkage of a vinyl ether tend to oppose the resonance between the lone-pair electrons of the oxygen atom and the π -electrons of the double bond, owing to their inductive effect. In III, there is an alkyl group formed by the ring carbon atoms attached to the β -carbon of each double bond, and thus the extent of resonance stabilization in III is not so pronounced as in vinyl ethers with no β -alkyl substituents. Hence, as the experimental results show, the methoxy groups of III and IV cause a similar stabilization in each compound.

The entropy difference between I and II may be estimated as follows. Assuming that the enthalpy of isomerization of I to II is -1.3 kJ mol⁻¹ in the liquid phase at 368 K at which temperature the equilibrium constant for I \rightarrow II is reported to be 2.22 (see introduction), the entropy change is *ca.* 3.1 J K⁻¹ mol⁻¹ in the liquid phase. If the value of ΔS° is assumed to be independent of temperature and if it is corrected to correspond to the ideal gas state,⁵ the entropy change in I \rightarrow II is obtained as about 2.0 J K⁻¹ mol⁻¹ at 298.15 K. However, II is statistically favored over

I by a factor of 2 and thus a term $R \ln 2 = 5.8$ J K⁻¹ mol⁻¹ should be subtracted from the observed entropy change to eliminate the effect of statistical factors on ΔS° . After this correction, the value of ΔS° (g, 298.15 K) for I \rightarrow II is obtained to be about -3.8 J K⁻¹ mol⁻¹. This is not far from the value -5.9 J K⁻¹ mol⁻¹, calculated from the intrinsic entropies of the above compounds, which have been reported by O'Neal and Benson.⁹ Hence there is a difference of *ca.* 9.3 J K⁻¹ mol⁻¹ in the experimental values of ΔS° (g, 298.15 K) for the reactions I \rightarrow II and III \rightarrow IV, although the entropy changes might be expected to be similar on account of apparently similar changes of structure in both reactions (the statistical factors of III and IV are equal). The reason for this difference is not clear, but it might be imagined that the methoxy groups are free to rotate about the O-C(*sp*²) bond in the conjugated diene (IV) because of only a weak conjugation between the methoxy groups and the double bonds. This assumption seems, however, to be in disagreement with the previous discussion concerning the stabilizing effect of methoxy groups on III and IV, which was deduced to be equal in both cases.

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REFERENCES

- Bates, R. B., Carnighan, R. H. and Staples, C. E. *J. Amer. Chem. Soc.* 85 (1963) 3030.
- Oberhammer, H. and Bauer, S. H. *J. Amer. Chem. Soc.* 91 (1969) 10, and Ref. 23 therein.
- Benson, S. W., Cruickshank, F. R., Golden, D. M., Haugen, G. R., O'Neal, H. E., Rodgers, A. S., Shaw, R. and Walsh, R. *Chem. Rev.* 69 (1969) 279, and Ref. 33 therein.
- House, H. O. and Kramar, V. *J. Org. Chem.* 28 (1963) 3362.
- Taskinen, E. *J. Chem. Thermodyn.* 6 (1974) 271.
- Clarke, E. C. W. and Glew, D. N. *Trans. Faraday Soc.* 62 (1966) 539.
- Handbook of Chemistry and Physics*, 50th Ed., The Chemical Rubber Co., Ohio, Cleveland 1969-1970, p. C-254.
- Taskinen, E. *J. Chem. Thermodyn.* 6 (1974). *In press.*
- O'Neal, H. E. and Benson, S. W. *J. Chem. Eng. Data* 15 (1970) 266.

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