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Thermodynamics of vinyl ethers
V. The relative stabilities of 4-methylene-1,3-dioxolane and 4-methyl-1,3-dioxole

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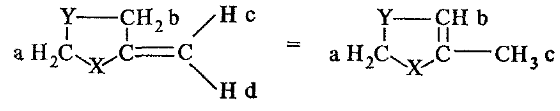
The relative stabilities of 4-methylene-1,3-dioxolane (I) and 4-methyl-1,3-dioxole (II) have been determined at various temperatures by means of chemical equilibration. The following values of the standard thermodynamic functions were obtained for the isomerization I = II in dioxan solution at 298.15 K: $\Delta G^\circ = -(1.80 \pm 0.07)$ kJ mol^{-1}, $\Delta H^\circ = (1.1 \pm 0.5)$ kJ mol^{-1}, and $\Delta S^\circ = (9.6 \pm 1.3)$ J K^{-1} mol^{-1}. In the gas phase, the values of ΔH° and ΔS° were estimated to be $-(0.5 \pm 0.6)$ kJ mol^{-1} and (7.5 ± 1.4) J K^{-1} mol^{-1}, respectively.

1. Introduction

The problem of the effect of ring size on the relative stabilities of alkylidenecycloalkanes and their endocyclic isomers, 1-alkylcycloalkenes, seems to have been settled quite reliably.$^{(1-3)}$ However, in the case of their heterocyclic counterparts, very little is known about the effect of the position of the ethylenic linkage on stability, and quantitative studies in this field seem to be limited to five- and six-membered heterocycles with one O atom in the ring.$^{(4)}$ I have now determined the relative stabilities at several temperatures of the exo-endo isomeric compounds, 4-methylene-1,3-dioxolane (I) and 4-methyl-1,3-dioxole (II) (X = Y = O in each case). Attempts to determine the standard Gibbs free energy and standard enthalpy differences between isomeric compounds closely related to those studied in this work have been reported$^{(5-7)}$ with a result that the endocyclic isomer is much more stable than the exocyclic isomer, the enthalpy of the latter being about 40 kJ mol^{-1} higher than that of the former. However, it was later pointed out by Gelas *et al.*$^{(8)}$ that the endocyclic compound used in these studies, believed to be 2,4-dimethyl-1,3-dioxole, was actually the saturated compound 2-methyl-1,3-dioxolane, as subsequently confirmed by Pihlaja and Heikkilä.$^{(9)}$ Hints for the slightly greater thermodynamic stabilities of the endocyclic forms



(I) (II)

of some derivatives of 4-methylene-1,3-dioxolane come from the synthetic works of Gelas *et al.*(8) and Dietrich *et al.*(10) who have found that the exocyclic compounds studied are isomerized at about 420 K to mixtures of isomers containing 70 to 75 moles per cent of the 1,3-dioxole derivatives.

2. Experimental

MATERIALS

4-Methylene-1,3-dioxolane (I). 4-Chloromethyl-1,3-dioxolane was prepared from 3-chloro-1,2-propanediol and paraldehyde. Equal amounts of the reactants were refluxed with hexane and *p*-toluenesulfonic acid in an azeotropic water-removal assembly until the completion of the acetal formation, after which 4-chloromethyl-1,3-dioxolane could be isolated by fractional distillation. The yield of the product boiling at 422.2 to 423.2 K and 101.3 kPa was 87 per cent. The product was converted to 4-methylene-1,3-dioxolane by slow distillation from an excess of solid potassium hydroxide.(11) The purified product, boiling temperature 362.7 K at 100.4 kPa, was obtained in 37 per cent yield.

4-Methyl-1,3-dioxole (II). A mixture of approximately equal amounts of I and II, obtained by isomerization of I by *p*-toluenesulfonic acid in dihexyl ether, was subjected to fractional distillation, which gave practically pure II (the mole fraction of I in the mixture was less than 0.02). The product boiled at 352.7 K at a pressure of 101.1 kPa. Spectral properties: The n.m.r. spectra were recorded on a 60 MHz Perkin Elmer Model R 10 spectrometer at 307 K. Carbon tetrachloride was used as solvent and tetramethylsilane as internal standard. The i.r. spectra of thin layers of the pure substances between KBr windows were recorded on a Perkin Elmer Model 180 spectrophotometer.

The n.m.r. spectra had the following features:

4-Methylene-1,3-dioxolane:
$10^6\tau$: 6.12 (c), 5.67 (b, d), 4.82 (a).
4-Methyl-1,3-dioxole:
$10^6\tau$: 8.18 (c), 4.54 (a), 4.06 (b); $J_{bc} = 1.7$ Hz.

The i.r. spectra showed:

4-Methylene-1,3-dioxolane:
$\sigma/\mathrm{cm}^{-1} = 3118$ (=C—H stretch), 1687, 1712 (?) (C=C stretch).
4-Methyl-1,3-dioxole:
$\sigma/\mathrm{cm}^{-1} = 3151$ (=C—H stretch), 1690, 1737 (?) (C=C stretch).

PROCEDURE

The use of an inert saturated hydrocarbon, such as cyclohexane, as solvent and iodine as catalyst in the equilibrations proved unsatisfactory because of extensive polymerization of the substrate under these conditions. However, the equilibrations ran smoothly in dioxan with *p*-toluenesulfonic acid as catalyst (catalyst concentration 1.0×10^{-3} mol dm^{-3}). Initial substrate concentration was kept at about 1.0 mol dm^{-3}. Starting from the endocyclic isomer, 4-methyl-1,3-dioxole, some polymerization of the substrate could not be avoided, but in general material losses due to polymerization did not exceed 20 to 30 per cent of the original substrate concentration. Moreover, within the limits of experimental error, the same relative concentrations of the isomeric species at equilibrium could be achieved by starting from any of the isomers.

At elevated temperatures (around 380 K), the equilibrium mixture was attained within a few minutes while several days were necessary for the achievement of equilibrium at 296.2 K. Before injection into the gas chromatograph, the samples of the equilibrium mixtures were made alkaline by a tenfold amount, relative to the amount of catalyst in the sample, of triethylamine. The column used in the g.l.c. analyses was a 4 m column containing 10 per cent Carbowax 1500 on Chromosorb G. The order of elution through this column was II, I. The peaks were integrated by means of a Hewlett-Packard 3370 B integrator. The integrated areas were assumed to correspond to the amounts of the isomers.(12) For other experimental details, readers are referred to part I of this series.(12)

3. Results

The values of the mean equilibrium constant and its standard error are shown in table 1. The values of the equilibrium constant are based on at least four determinations, the position of equilibrium having been approached from both sides at every temperature studied. The values of the standard thermodynamic functions of isomerization of 298.15 K were calculated as described previously.(12) The following results were obtained for the isomerization of 4-methylene-1,3-dioxolane to 4-methyl-1,3-dioxole in dioxan at 298.15 K: $\Delta G^\circ = -(1.80 \pm 0.07)$ kJ mol^{-1}, $\Delta H^\circ = (1.1 \pm 0.5)$ kJ mol^{-1}, and $\Delta S^\circ = (9.6 \pm 1.3)$ J K^{-1} mol^{-1}, the errors being twice the standard errors.

TABLE 1. Values of the mean equilibrium constant and its standard error for the reaction 4-methylene-1,3-dioxolane (I) = 4-methyl-1,3-dioxole (II) in dioxan solution at various temperatures. Substrate concentration about 1.0 mol dm^{-3}; *n* denotes the number of determinations

T/K	n	K(I = II)	T/K	n	K(I = II)
296.2	4	2.13 ± 0.03	348.7	7	2.18 ± 0.03
313.2	5	2.10 ± 0.02	364.2	4	2.26 ± 0.04
324.2	6	2.11 ± 0.03	373.2	5	2.26 ± 0.03
333.2	4	2.10 ± 0.03	383.2	4	2.29 ± 0.03

4. Discussion

Let us consider the values of ΔH°(l, 298.15 K) of the reaction I = II:

	ΔH°(l, 298.15 K)/kJ mol^{-1}	Solvent	Reference
$X = Y = CH_2$	−16.2	Acetic acid	13
$X = O, Y = CH_2$	− 4.7	Diethyl ether	4
$X = Y = O$	+ 1.1	Dioxan	This work

The values of ΔH° approach zero as the number of O atoms in the ring increases. More representative values of the standard enthalpy changes in the above reactions are obtained, however, if the values of ΔH° are compared in the gaseous state. The conversion of the values of ΔH°(l, 298.15 K) to those of ΔH°(g, 298.15 K) may be done by means of equation (2) in reference 14, if the normal boiling temperatures of the compounds are known, and if it is assumed that the enthalpy differences in the liquid state are not affected by solvation. This seems to be true for the case $X = Y = CH_2$ as should be apparent from the enthalpy change -16.2 kJ mol^{-1} at 298.15 K, calculated from the enthalpies of formation of the liquid olefins.(15) As the boiling temperatures of methylenecyclopentane and 1-methylcyclopentene are equal within 1 K,(16, 17) the enthalpy difference between the gaseous olefins in question is practically equal to the value of ΔH° in the liquid state. In the case $X = O$, $Y = CH_2$, the exo isomer boils about 19 K higher than the endo isomer and therefore, the enthalpy change in the gaseous state is approximately -7.8 kJ mol^{-1}. In the case $X = Y = O$, the enthalpy of the exo isomer is calculated to be about 0.5 kJ mol^{-1} higher than that of the endo isomer in the gaseous state at 298.15 K. Hence the values of ΔH°(g, 298.15 K) for I = II are about -16.2, -7.8, and -0.5 kJ mol^{-1} in cases $X = Y = CH_2$, $X = O$, $Y = CH_2$, and $X = Y = O$, respectively.

In going from I to II, the number of substituents attached to the double bond increases from two to three. In a recent study,(4) it was shown that the stabilizing power of alkyl groups on the double bond of 2-methylenetetrahydrofuran is only about 30 to 50 per cent of the stabilizing power of alkyl groups on the double bond of the corresponding olefin, methylenecyclopentane. Therefore, the relatively low standard enthalpy change in the case $X = O$, $Y = CH_2$ (in comparison with the case $X = Y = CH_2$) may be explained to be mainly or totally due to the weak stabilizing power of the ring alkyl group on the double bond of the endocyclic isomer.

The value of ΔH° for I = II, when $X = Y = O$, seems surprising because none of the expected(5–7) high stabilization in II, due to the presence of the O—C=C—O grouping, is observed. On the contrary, if we compare the value of ΔH°(g, 298.15 K) in cases $X = O$, $Y = CH_2$, and $X = Y = O$, the more positive enthalpy change in the latter case shows that some destabilizing factor is present in 4-methyl-1,3-dioxole because no extra stabilization, relative to 2-methylenetetrahydrofuran, can be expected to exist in 4-methylene-1,3-dioxane. In the latter molecule, resonance stabilization is probably even less than in the former, due to the additional O atom in the dioxolane ring, which through its inductive effect disfavors electron delocalization between the X oxygen atom and the double bond.

The standard entropy of isomerization of 4-methylene-1,3-dioxolane to 4-methyl-1,3-dioxole can be calculated(14) to be (7.5 ± 1.4) J K^{-1} mol^{-1} in the gas phase. For comparison, the entropy change in the liquid state for 2-methylenetetrahydrofuran = 5-methyl-2,3-dihydrofuran has been obtained as (8.0 ± 2.0) J K^{-1} mol^{-1},(4) which leads to a ΔS°(g, 298.15 K) of about 4.2 J K^{-1} mol^{-1},(14) if the normal boiling temperatures of the above compounds are taken (4) as 373 and 354 K, respectively. From equilibrium(1) and enthalpy of hydrogenation(13) studies in acetic acid at 298.15 K the values of ΔG° and ΔH° for methylenecyclopentane = 1-methylcyclopentene are -17.45 and -16.2 kJ mol^{-1}, respectively, and thus the value of ΔS°(l, 298.15 K) is about 4.2 J K^{-1} mol^{-1}. Since the normal boiling temperatures of the compounds concerned are equal within 1 K,(16, 17) they are expected(14) to have practically equal standard entropies of vaporization at 298.15 K, and thus the standard entropy change should be about 4.2 J K^{-1} mol^{-1} in the gaseous state, too. However, according to Herling *et al.*(2) the value of ΔS°(g, 298.15 K) for the reaction in question is about 12 J K^{-1} mol^{-1}. In any case the entropy change for methylenecyclopentane = 1-methylcyclopentene is roughly in line with the values of ΔS°(g, 298.15 K) for the preceding two reactions involving the heterocyclic ethers.

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