

Short Communications

Relative Thermodynamic Stabilities of the Isomeric Cyclooctadienes

ESKO TASKINEN and KARI NUMMELIN

Department of Chemistry and Biochemistry, University of Turku, SF-20500 Turku, Finland

About a decade and a half ago, Turner *et al.*¹ measured the enthalpies of hydrogenation of a number of unsaturated cyclic hydrocarbons such as the three isomeric cyclooctadienes 1–3. As might be expected, the conjugated diene 3 proved to be the most stable species, the enthalpy of isomerization of the 1,5 diene (1) to the 1,3 form (3) being $-19.7 \pm 0.4 \text{ kJ mol}^{-1}$ in acetic acid at 298 K. Interestingly, the enthalpy of the 1,4 isomer (2) was found to be $6.7 \pm 1.3 \text{ kJ mol}^{-1}$ lower than that of 1. Owing to our interest in the thermodynamic stabilities of the alkoxy derivatives of some cyclic dienes (vinyl ethers),² we considered it worth the effort to determine also the relative stabilities of 1–3 by an independent route, *viz.* chemical equilibration (Allinger *et al.*³ have employed the same method but in a less quantitative sense and at a single temperature only).

Experimental. The equilibration experiments were conducted in DMSO solution (*ca.* 20 %) with KOBu-*t* (*ca.* 10 %) as catalyst. Commercial 1 and 3 were used for the equilibrations, after purification by fractional distillation with a Perkin-Elmer M 251 Auto Annular Still. The 1,4 form (2) was identified in the gas-chromatographic analyses of the equilibrium mixtures by means of its retention time as follows. The normal boiling points of 1, 2 and 3 are 148.5, 143.0 and 141.0 °C, respectively,¹ and since the retention times of 1 and

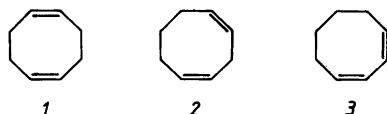


Table 1. Values of the mean equilibrium constant K for the equilibria between isomeric cyclooctadienes at various temperatures (n =the number of samples analyzed).^a

T/K	n	$K(3/1)$	$K(3/2)$	$K(2/1)$
333	6	1904(18)		
343	6	1712(14)		
353	6	1495(24)		
363	9	1165(13)		
373	5	939(13)	185(6)	5.10(0.22)
388	4	726(21)	142(1)	5.12(0.13)
403	5	637(7)	128(1)	4.97(0.06)
413	4	535(6)	113(1)	4.73(0.05)
423	6	464(6)	98.1(1.5)	4.73(0.07)
433	8	393(11)	87.0(0.9)	4.52(0.09)
443	4	359(18)	79.0(0.3)	4.54(0.22)

^a The uncertainties are the standard errors of the mean.

Table 2. Thermodynamic data (DMSO solution, 298.15 K) for the isomeric cyclooctadienes. The errors are twice the standard errors of a least-squares treatment of $\ln K$ vs. T^{-1} .

Reaction	$\Delta G^\ominus/\text{kJ mol}^{-1}$	$\Delta H^\ominus/\text{kJ mol}^{-1}$	$\Delta S^\ominus/\text{J K}^{-1} \text{ mol}^{-1}$
$1 \rightarrow 2$	-4.65(0.11)	-2.8(0.8)	6.3(2.0)
$2 \rightarrow 3$	-16.20(0.20)	-16.4(1.4)	-1(3)
$1 \rightarrow 3$	-20.94(0.22)	-19.4(0.9)	5.0(2.4)

3 were 4.88 and 3.07 min, respectively, a peak with a retention time of 3.35 min appeared to be well ascribable to the 1,4 form, especially, since no other significant peak between those of 1 and 3 could be detected. The position of the thermodynamic equilibrium was approached from two initial mixtures of isomers: (a) a mixture of 98 % of 3 and 2 % of 1, and (b) a mixture of 90 % of 3 and 10 % of 1. The equilibrations were carried out at 7 temperatures between 100 and 170 °C; the equilibrium $1 \rightleftharpoons 3$, however, was monitored at 4 additional temperatures down to 60 °C (since the peaks of 2 and 3 were not completely resolved, the peak area of 2 could not be determined with sufficient accuracy in samples equilibrated below 100 °C due to the low concentration of 2 at these temperatures). The equilibrated samples were quickly cooled by immersion into ice-water, followed by immediate analysis by GLC using a 25 m XE-60 capillary column (inner diameter 0.32 mm) with H_2 as the carrier gas. The apparatus consisted of a Perkin-Elmer Sigma 2B gas chromatograph and a Hewlett-Packard 3380 S integrator.

Results and discussion. The results of the equilibration experiments are shown in Tables 1 and 2. The enthalpy of isomerization of 1 to 3 ($-19.4 \pm 0.9 \text{ kJ mol}^{-1}$) is in excellent agreement with the data of Turner *et al.*, $-19.7 \pm 0.4 \text{ kJ mol}^{-1}$. The entropy of 3 is $5.0 \pm 2.4 \text{ J K}^{-1} \text{ mol}^{-1}$ higher than that of 1 but it appears that this difference arises from mere statistical factors: the 1,3 form is statistically favored over 1 by a factor of 2, which has an effect of $5.8 \text{ J K}^{-1} \text{ mol}^{-1}$ on the ΔS^\ominus value of the $1 \rightarrow 3$ reaction. Similarly, 2 is favored over 1 by the same statistical factor, and the observed entropy change for the $1 \rightarrow 2$ reaction, $6.3 \pm 2.0 \text{ J K}^{-1} \text{ mol}^{-1}$, is seen to correspond to this effect only. On the other hand, our enthalpy value for the $1 \rightarrow 2$ reaction, $-2.8 \pm 0.8 \text{ kJ mol}^{-1}$, is clearly different from the value, $-6.7 \pm 1.3 \text{ kJ mol}^{-1}$, suggested by the data of Turner *et al.* It is not easy to see the origin of this difference.

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