RELATIVE THERMODYNAMIC STABILITIES OF THE ISOMERIC PROPENYLBENZENES

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The relative thermodynamic stabilities of 2-propenylbenzene (allylbenzene), and the E and Z forms of 1-propenylbenzene were determined over the temperature range 50–170 °C by chemical equilibration in DMSO solution with t-BuOK as catalyst. The values of the thermodynamic parameters $\Delta G^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ at 298·15 K for each isomerization reaction between the title compounds were evaluated.
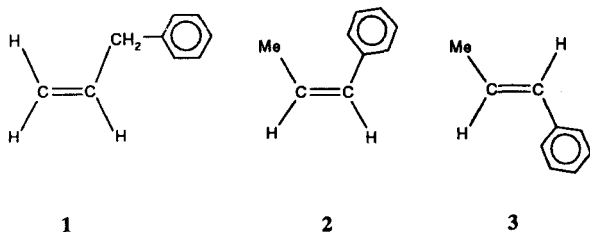
INTRODUCTION

During the last six decades, a large number of thermo-chemical data have become available for a variety of both simple and less simple organic compounds,[1] but adequate experimental thermochemical data are still lacking for many relatively simple molecules, such as the three isomeric propenylbenzenes 1, 2 and 3. Apparently, the only usable experimental thermochemical data for these compounds are the enthalpy hydrogenation of 1, which has been determined in both cyclohexane and acetic acid solutions,[2] and the derived enthalpy of formation.[1] Owing to the many interesting aspects (π–π conjugation, steric strain, twist angle of the Ph group about the Ph–vinyl bond) in the structures and energies of these molecules, determination of the relative thermodynamic stabilities of 1–3 was considered desirable. Hence the relative equilibrium concentrations of the title compounds were determined at several temperatures in DMSO solution with t-BuOK as catalyst, and the values of the thermodynamic parameters $\Delta G^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ at 298·15 K for each of

1   2   3

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the three isomerization reactions involved were evaluated from the equilibration data, using the van't Hoff equation.

RESULTS AND DISCUSSION

The relative equilibrium concentrations of 1–3 at various temperatures, together with the values of the thermodynamic parameters of isomerization at 298·15 K, are given in Table 1. Expectedly, the *trans* form (3) of the 1-propenylbenzenes is the dominating species, and the non-conjugating allylbenzene (1) the minor component in the equilibrium mixtures. In the following, the thermodynamics of reactions $1 \rightarrow 3$ and $2 \rightarrow 3$ are considered in detail.

The value of $\Delta H^{\ominus}$ for $1 \rightarrow 3$, $-23·3 \pm 0·5$ kJ mol^{-1} in DMSO solution, is (in absolute value) higher than might be expected on the basis of available thermochemical data. Considering the nature and number of substituents attached to the C=C systems of these compounds, it is seen that each C=C moiety carries an alkyl group (or, in 1, a Ph-substituted alkyl group). Since the double bond stabilizing ability of an alkyl group is essentially independent of the nature of the group in question,[3] the value of $\Delta H^{\ominus}$ for $1 \rightarrow 3$ might be expected to be determined by the double bond stabilizing effect of the Ph group in 3. This effect, *ca* -18 kJ mol^{-1} from the difference between the gas-phase enthalpies of hydrogenation of the C=C bonds of ethene[4] and the Ph-substituted ethene, styrene,[5] is *ca* 5 kJ mol^{-1} less negative than the experimental reaction enthalpy for $1 \rightarrow 3$ in DMSO solution. Clearly, at least part of this difference may be ascribed to the different phases involved. An approximate correction of the

Table 1. Values of the mean percentage composition of the equilibrium mixtures of **1–3** at various temperatures in DMSO solution, together with the values of the thermodynamic parameters of isomerization at 298·15 K

$t/°C$	$c(1)/\%$	$c(2)/\%$	$c(3)/\%$	Reaction	$\Delta G^\ominus/\text{kJ mol}^{-1}$[a]	$\Delta H^\ominus/\text{kJ mol}^{-1}$[a]	$\Delta S^\ominus/\text{J K}^{-1}\text{ mol}^{-1}$[a]
50	0·085	2·82	97·10	$\mathbf{1 \rightarrow 2}$	$-9\cdot66 \pm 0\cdot13$	$-12\cdot3 \pm 0\cdot6$	$-8\cdot9 \pm 1\cdot5$
75	0·157	3·81	96·03	$\mathbf{1 \rightarrow 3}$	$-19\cdot25 \pm 0\cdot11$	$-23\cdot3 \pm 0\cdot5$	$-13\cdot6 \pm 1\cdot2$
100	0·261	4·88	94·87	$\mathbf{2 \rightarrow 3}$	$-9\cdot60 \pm 0\cdot07$	$-11\cdot0 \pm 0\cdot3$	$-4\cdot7 \pm 0\cdot8$
125	0·434	5·97	93·60				
150	0·627	7·02	92·35				
170	0·825	8·11	91·06				

[a] The errors are twice the standard errors.

experimental $\Delta H^\ominus$ value for $\mathbf{1 \rightarrow 3}$ to the gas phase may be made by estimation of the enthalpies of vaporization (at 298·15 K) of the two compounds from their normal boiling temperatures.[6] A survey of the boiling-point data given in the *Beilstein Handbook* (Hauptwerk and the first three Supplements) shows that the normal boiling points of **1**, **2** and **3** are *ca* 156, 167 and 176 °C, respectively. The difference, 20 °C, in the boiling points of **3** and **1** suggests[6] that the enthalpy of vaporization of **3** at 298·15 K is *ca* 3·2 kJ mol⁻¹ higher than that of **1**. Hence the gas-phase enthalpy of isomerization of **1** to **3** is calculated to be about $-20\cdot1$ kJ mol⁻¹, not far from the stabilizing effect of the Ph group in styrene. On the other hand, the marked decrease in entropy for $\mathbf{1 \rightarrow 3}$, $-13\cdot6 \pm 1\cdot2$ J K⁻¹ mol⁻¹ in DMSO solution, is in excellent agreement with the gas-phase value, $-13\cdot8$ J K⁻¹ mol⁻¹, calculable by means of the group parameters of Benson *et al.*[7]

In DMSO solution, the *trans* form of 1-propenylbenzene is (on an enthalpy basis) $11\cdot0 \pm 0\cdot3$ kJ mol⁻¹ more stable than the *cis* form (**2**). Proceeding as shown above, the corresponding gas-phase value may be estimated to be *ca* 9·4 kJ mol⁻¹ by means of the difference, 10 °C, in the normal boiling points of **3** and **2**. This value, 9·4 kJ mol⁻¹, is in considerable disagreement with the API value, 4·2 kJ mol⁻¹,[8] but in good agreement with theoretical calculations which suggest an enthalpy difference of 11 kJ mol⁻¹.[9] The higher enthalpy of the *cis* form is, of course, a result of the proximity of the Me and Ph groups in this compound, which forces the Ph group to rotate out of the plane of the olefinic system, thus disturbing the stabilizing conjugative interaction between the two unsaturated moieties. According to recent molecular mechanics calculations on **2**,[10] the twist angle in question is either 38·5° (MMP2) or 45·7° (MM2'), both of which are considerably larger than the angle (16–28°) suggested by photoelectron spectroscopy.[11] For comparison, calculations by the COSMIC force field[12] lead to a twist angle of 41·4° for **2**, and to an enthalpy difference of 9·7 kJ mol⁻¹ between **2** and **3**, in good agreement with the estimated gas-phase value given above. The COSMIC force field, in addition to

the other force fields mentioned above, suggests a planar structure for the *trans* isomer **3**, in agreement with photoelectron spectroscopic studies.[11,13]

Previously, we have determined the relative stabilities of the isomeric vinyl ethers **4–6**,[14] which are structurally related to the compounds in the present study. For $\mathbf{4 \rightarrow 5}$, the value of $\Delta H^\ominus$, $-9\cdot0 \pm 0\cdot5$ kJ mol⁻¹ in cyclohexane solution, is *ca* 3 kJ mol⁻¹ less than that for the corresponding olefins, $\mathbf{1 \rightarrow 2}$. This shows that the double bond stabilizing ability of a Ph group is smaller in vinyl ethers than in olefins, a finding which agrees with previous results for similar effects of alkyl groups.[15] The structural change in $\mathbf{4 \rightarrow 5}$ corresponds to that in $\mathbf{1 \rightarrow 2}$, suggesting similar values of $\Delta S^\ominus$ for these reactions; this indeed is the case, cf. the respective $\Delta S^\ominus$ values of $-8\cdot4 \pm 1\cdot2$ and $-8\cdot9 \pm 1\cdot5$ J K⁻¹ mol⁻¹. On the other hand, for the other reactions, $\mathbf{4 \rightarrow 6}$ and $\mathbf{5 \rightarrow 6}$, the values of the thermodynamic parameters are essentially different from those for the related reactions $\mathbf{1 \rightarrow 3}$ and $\mathbf{2 \rightarrow 3}$. For example, the values of $\Delta H^\ominus$ and $\Delta S^\ominus$ are 6·5 kJ mol⁻¹ and 6·6 J K⁻¹ mol⁻¹ for $\mathbf{5 \rightarrow 6}$ but $-11\cdot0$ kJ mol⁻¹ and $-4\cdot7$ J K⁻¹ mol⁻¹ for $\mathbf{2 \rightarrow 3}$. The differences, about 17·5 kJ mol⁻¹ in the enthalpy values and 11·3 J K⁻¹ mol⁻¹ in the entropy values for the seemingly identical structural changes, arise mainly from changes (*s-cis* to *gauche*) in the steric orientation of the MeO group in the reaction $\mathbf{5 \rightarrow 6}$.[14,15]

4   **5**   **6**
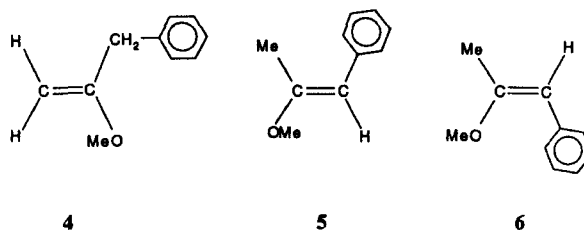
EXPERIMENTAL

The equilibration experiments were carried out in DMSO solution (25 vol.-% in substrate), with *t*-BuOK

(*ca* 10%, m/v) as catalyst.[16] To facilitate attainment of the thermodynamic equilibrium, the substrate for the equilibrations was a mixture of isomers with composition not far from those of the final equilibrated samples. The mixture was obtained by treatment of commercial 1 with *t*-BuOK in DMSO followed by distillation. Prior to GLC analysis of the equilibrated samples using a 50 m capillary column of type Silar 9 C, the catalyst was destroyed by addition of boric acid in dioxane. At each temperature, the values of the mean isomer composition given in Table 1 are based on 5–7 samples.

REFERENCES

1. J. B. Pedley, R. D. Naylor and S. P. Kirby, *Thermochemical Data of Organic Compounds*, Chapman and Hall, London and New York (1986).
2. D. W. Rogers and F. J. McLafferty, *Tetrahedron* **27**, 3765–3775 (1971).
3. C. T. Mortimer, *Reaction Heats and Bond Strengths*, p. 52. Pergamon Press, Frankfurt am Main (1962).
4. G. B. Kistiakowsky, H. Romeyn, Jr, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *J. Am. Chem. Soc.* **57**, 65–75 (1935).
5. M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky and W. E. Vaughan, *J. Am. Chem. Soc.* **59**, 831–841 (1937).
6. E. Taskinen, *J. Chem. Thermodyn.* **6**, 271–280 (1974).
7. S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw and R. Walsh, *Chem. Rev.* **69**, 279–324 (1969).
8. F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun and G. C. Pimentel, *Selected Values of Physical and Thermochemical Properties of Hydrocarbons and Related Compounds*, Carnegie Press, Pittsburg, PA (1953).
9. G. Favini and M. Simonetta, *Theor. Chim. Acta* **1**, 294–301 (1963).
10. S. Tsuzuki, K. Tanabe, Y. Nagawa and H. Nakanishi, *J. Mol. Struct.* **212**, 45–52 (1989).
11. T. Kobayashi, T. Arai, H. Sakuragi, K. Tokumaru and C. Utsunomiya, *Bull. Chem. Soc. Jpn.* **54**, 1658–1661 (1981).
12. *Nemesis Software Package, Version 1.1.* Oxford Molecular, Oxford (1992).
13. J. P. Maier and D. W. Turner, *J. Chem. Soc., Faraday Trans. 2* **69**, 196–206 (1973).
14. E. Taskinen and P. Ylivainio, *Acta Chem. Scand., Ser. B* **29**, 1–6 (1975).
15. E. Taskinen, *J. Chem. Thermodyn.* **6**, 345–353 (1974).
16. E. Taskinen and K. Nummelin, *Acta Chem. Scand., Ser. B* **39**, 791–798 (1985).