Kinetics and Thermodynamics of the Thermal Gas-phase Interconversion of Hexakis(pentafluoroethyl)benzene and its *para*-Bonded (Dewar) Isomer

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Summary Equilibrium and kinetic studies on the title reaction show that the two isomers (**1**) and (**2**) are interconverted by a reversible unimolecular reaction, and lead to values for the enthalpy and entropy differences of the two isomers and activation parameters for their interconversion.

HEXAKIS(PENTAFLUOROETHYL)BENZENE (**1**)[1] and its *para*-bonded ('Dewar') isomer [hexakis(pentafluoroethyl)bicyclo[2,2,0]hexa-2,5-diene] (**2**)[2] form an unusual system in which the *para*-bonded isomer can be obtained by purely thermal reaction of the benzene, thus permitting accurate study of thermodynamic data *via* equilibrium measurements, and allowing direct measurement of activation parameters for the aromatic → *para*-bonded reaction as well as the more generally accessible reverse isomerisation.

Measurements were made in a conventional kinetic apparatus in which the gas-handling system was heated to

440 K to prevent condensation of the high-boiling reactants. Analysis was by direct gas-valve injection into a flame-ionisation gas-chromatograph (10·2 m SE 30 at 420 K with nitrogen carrier). At 453—602 K no compounds other than (**1**) and (**2**) were ever detected, and there was no pressure change during the reaction, thus confirming the stoicheiometry of equation (1).

Table 1. Energy parameters from kinetic and equilibrium studies.[a]

Reaction	Activation energy /kJ mol^{-1}	ΔH° ($=E_1 - E_{-1}$) /kJ mol^{-1}	ΔH°/kJ mol^{-1} from K_{eq}
(**1**) → (**2**) (k_1)	186·6 ± 1·1	34·9 ± 1·9	37·6 ± 0·3
(**2**) → (**1**) (k_{-1})	151·7 ± 1·5		

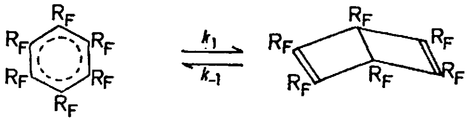
[a] Error limits here and in Table 2 are standard deviations.

Equilibrium measurements at 453—602 K, with total pressures of 10—40 mmHg,† gave equilibrium constants $K_{eq} = (p_D/p_B)_{eq}$ where p_D and p_B are the partial pressures of (**2**) and (**1**) respectively which were constant at a given temperature and independent of the direction of approach to equilibrium. The plot of ln K_{eq} *vs.* $1/T$ was a good straight line and provided the enthalpy and entropy changes shown in the Tables. It is of interest to note that thermal equilibrium favours the *para*-bonded isomer at temperatures above 551 K.

Table 2. Entropy parameters from kinetic and equilibrium studies.

Reaction	$\log_{10}(A/s^{-1})$	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	ΔS° ($=\Delta S^\ddagger_1 - \Delta S^\ddagger_{-1}$) / J K^{-1} mol^{-1}	ΔS°/J K^{-1} mol^{-1} from K_{eq}
(**1**) → (**2**) (k_1)	16·25 ± 0·12	53·8 ± 2·4	62·6 ± 3·8	68·2 ± 0·5
(**2**) → (**1**) (k_{-1})	12·99 ± 0·16	−8·7 ± 3·0		

Kinetic data were treated by plots of $\ln\{[(K_{eq}+1)\theta_0 - 1]/[(K_{eq}+1)\theta_t - 1]\}$ *vs.* time, where $\theta = p_B/(p_B + p_D)$, for runs starting with the benzene or benzene-rich mixtures, or the corresponding variation for runs starting with (**2**); the slopes of these graphs gave $(k_1 + k_{-1})$. Good straight-line plots were obtained for kinetic experiments at 456—525 K, and at a given temperature the slopes were independent of total pressure in the range 7—62 mmHg, and were the same whether the initial reactant was (**1**) or (**2**) or a mixture of the two. The same slopes were also obtained in a packed vessel and in the presence of but-2-ene, confirming the homogeneous unimolecular nature of the processes involved. The individual rate-constants k_1 and k_{-1}, obtained from $(k_1 + k_{-1})$ and K_{eq}, gave good Arrhenius plots corresponding to the parameters shown in the Tables (the entropies of activation are at 490 K, taking statistical factors as unity).



(1)

(1) $R_F = C_2F_5$ (2)

The kinetic and equilibrium data are in very satisfactory agreement. The enthalpy of reaction (aromatic → *para*-bonded) may be compared with the values of 117 kJ mol^{-1} and *ca.* 240 kJ mol^{-1} reported for the hexakis(trifluoromethyl)[3] and hexamethyl[4] derivatives respectively (entropy changes are not known for any system of this type other than the present one). The activation energies for the *para*-bonded → aromatic conversion are very similar for these three systems, suggesting that the differences arise mainly from increasing destabilisation of the benzene itself in the series methyl, trifluoromethyl, pentafluoroethyl. Indeed, a model of (**1**) cannot be constructed with conventional bond angles and atomic radii, and it may be that (**1**) has a puckered ring with consequent loss of resonance stabilisation energy. In the *para*-bonded isomers, steric strain between the substituent groups is reduced by the folding of the ring system across the central (bridge) bond; the positive entropy change for the conversion of (**1**) into (**2**) is consistent with increased rotational freedom in (**2**). The entropies of activation indicate that the transition state is similar to (**2**) rather than (**1**), *i.e.* probably folded to a similar extent. Concerted conversion of (**1**) and (**2**) is orbital-symmetry forbidden,[5] which may account for the kinetic stability of the *para*-bonded isomers, and the reaction may thus involve a biradical intermediate or biradical-type transition state.

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† mmHg = 133·322 Pa.

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