The Gas-phase Thermal Isomerization of Some Tri- and Tetra-fluoro-Dewar Benzenes

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The kinetics of the gas-phase thermal isomerization of 1,2,3,5- and 1,2,4,5-tetrafluorobicyclo[2.2.0]hexa-2,5-diene into the corresponding tetrafluorobenzenes have been studied over a temperature range of 320—390 K and a pressure range of 100—2 000 N m^{-2}. The reactions are homogeneous, obey a first-order law, and are unimolecular. The temperature dependence of the rate constants is given by the Arrhenius equations (1) for 1,2,3,5-tetrafluorobicyclo[2.2.0]hexa-2,5-diene, and (2) for 1,2,4,5-tetrafluorobicyclo[2.2.0]hexa-2,5-diene. The rate constants

$$\log (k/\mathrm{s}^{-1}) = 13.73 \pm 0.30 - \frac{116.9 \pm 2\ (\mathrm{kJ\ mol^{-1}})}{2.303\,RT} \quad (1)$$

$$\log (k/\mathrm{s}^{-1}) = 10.42 \pm 0.99 - \frac{96.4 \pm 7\ (\mathrm{kJ\ mol^{-1}})}{2.303\,RT} \quad (2)$$

of the thermal isomerization of 1,3,5-, 1,2,5-, and 2,3,5-trifluorobicyclo[2.2.0]hexa-2,5-diene into corresponding trifluorobenzenes have been measured at 353 K, and the following values of $-\log (k/\mathrm{s}^{-1})$ were obtained: 2.3 ± 0.2, 2.4 ± 0.2 and 2.6 ± 0.2, respectively. The influence of fluorine substitution on the thermal stability of the Dewar structure is discussed.

The thermal isomerization of valence bond isomers of benzene [1—3] has received a great deal of attention in recent years. In particular the isomerization of Dewar benzenes to corresponding benzenes has been studied both theoretically [2,4—7] and experimentally.[4,8—16]

Recently the kinetics of thermal isomerization of pentafluoro-,[9,10] hexafluoro-,[8,17] and perfluoro-alkyl [14] Dewar benzenes have been investigated. The thermal rearrangements of Dewar benzenes have activation energies greater than 160 kJ mol^{-1}.[18] The unusual exothermicity of Dewar benzene itself, 295 kJ mol^{-1},[2,4] is worth noting. Among Dewar benzenes, derivatives containing perfluoroalkyl substituents [19,20] are the most stable. A mechanism involving a biradical-type intermediate has been proposed for the thermal isomerization of such systems.[2,4,5,8—12,18,21] The effect of substituents on the rate constants of thermal isomerization of fluorinated Dewar benzenes has been noted.[22]

We report here an investigation of the gas-phase kinetics of the thermal isomerization of some tri- and tetrafluoro-Dewar benzenes which, combined with previously published data,[8—12] enables us to analyse the effect of fluorine substitution on the stability of the Dewar structure.

EXPERIMENTAL

1,3,5-Tri-, 1,2,4-tri-, 1,2,3,5-tetra-, and 1,2,4,5-tetrafluorobenzene were obtained from Fluorochem Ltd. 1,3,5-Tri-, 1,2,5-tri-, 2,3,5-tri-, 1,2,4,5-tetra-, and 1,2,3,5-tetrafluorobicyclo[2.2.0]hexa-2,5-diene were prepared by photolysis of the corresponding fluorinated benzenes. The methods for preparation and purification of these Dewar isomers were described earlier.[23] The compounds were stored at the temperature of liquid nitrogen.

Gas-phase kinetics studies were performed using a conventional high-vacuum system.[9] Thermal reactions were carried out in a 160 cm^3 cylindrical quartz vessel housed in a electric furnace which was maintained at ±0.2 K. The products of the thermolysis were analysed by g.l.c. using a 4 m column packed with 60—80 mesh Chromosorb impregnated with 15% (w/w) dinonyl phthalate.

RESULTS AND DISCUSSION

The thermal isomerization of fluorinated Dewar benzenes leads to the corresponding aromatic compounds which were identified by their retention time and ^1H n.m.r. spectrum. No other products, apart from fluorinated benzene, were found in any of the vapour-phase experiments. The experimental conditions and the results of the isomerization of 1,2,3,5- and 1,2,4,5-tetrafluoro-Dewar benzene are listed in Tables 1 and 2. The rearomatization rate of these Dewar benzenes fitted a first-order kinetic equation. Arrhenius plots of rate constants for isomerization of tetrafluoro-Dewar benzenes are shown in Figures 1 and 2. Arrhenius parameters have been calculated from experimental data by the least-squares method. Equations (1) and (2) have been obtained for the rearomatization of 1,2,3,5-tetra-

TABLE 1

Thermal isomerization of 1,2,3,5-tetrafluorobicyclo-[2.2.0]hexa-2,5-diene

T/K	Reactant pressure (p/N m^{-2})	t/s	Conversion (%)	$10^4k/s^{-1}$
319.6	54.1	2.88×10^4	13.4	0.0501
331.2 *	207.2	1.62×10^4	30.4	0.224
338.7	279.2	7.20×10^3	35.1	0.600
342.2	540.5	6.60×10^3	40.7	0.791
350.2 *	198.2	1.80×10^3	34.4	2.34
362.2	81.1	9.00×10^2	53.0	8.40
369.7	360.3	2.40×10^2	27.5	13.41
370.9	225.2	7.20×10^2	60.6	12.86
375.6	99.1	6.00×10^2	81.9	28.53
375.9	135.1	2.40×10^2	49.7	28.61
384.6	180.1	1.80×10^2	77.1	67.33
389.2	153.1	1.20×10^2	88.3	179.1
389.9	324.3	4.5×10^1	71.6	279.9

* Packed vessel.

TABLE 2

Thermal isomerization of 1,2,4,5-tetrafluorobicyclo-[2.2.0]hexa-2,5-diene

T/K	Reactant pressure (p/N m^{-2})	t/s	Conversion (%)	10^4k/s^{-1}
326.2 *	468.4	2.52×10^4	28.1	0.131
333.2	1 199.9	2.16×10^4	55.8	0.379
334.7 *	738.6	1.62×10^4	45.2	0.371
343.9 *	585.3	7.20×10^3	30.1	0.496
344.4	2 266.4	12.63×10^3	57.1	0.671
350.2 *	522.4	5.40×10^3	21.1	0.440
352.7	266.6	2.70×10^3	35.1	1.60
355.7 *	774.7	2.70×10^3	29.1	1.28
365.2 *	324.3	1.08×10^3	39.4	4.65
365.4	450.4	1.50×10^3	32.9	2.66
368.7	133.3	0.96×10^3	33.6	4.26
368.7	133.3	0.60×10^3	33.6	6.82
368.7 *	288.2	0.18×10^3	20.0	12.40
374.7 *	400.0	0.50×10^3	16.6	5.00
375.2	648.6	0.48×10^3	22.2	5.23
381.2	1 729.6	0.42×10^3	28.5	8.00
385.4	1 199.8	0.18×10^3	50.4	39.03
386.2	1 199.8	0.30×10^3	65.2	35.20
387.7 *	702.6	0.15×10^3	71.9	84.33
393.7	576.5	0.12×10^3	76.0	119.0

* Packed vessel.

fluoro-Dewar benzene and for the rearomatization of

$$\log (k/\mathrm{s}^{-1}) = 13.73 \pm 0.30 - \frac{116.9 \pm 2\ (\mathrm{kJ\ mol}^{-1})}{2.303\,RT} \quad (1)$$

$$\log (k/\mathrm{s}^{-1}) = 10.42 \pm 0.99 - \frac{96.4 \pm 7\ (\mathrm{kJ\ mol}^{-1})}{2.303\,RT} \quad (2)$$

1,2,4,5-tetrafluoro-Dewar benzene. The error limits are standard deviations calculated by ordinary statistical methods and do not include any provision for systematic error.

The data in Tables 1 and 2 as well as Figures 1 and 2 show that the value of the rate constant was independent within experimental error of the degree of conversion.

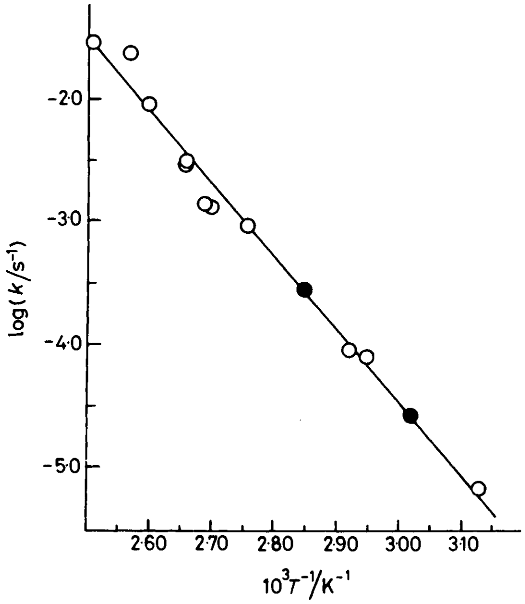


FIGURE 1 Arrhenius plot of first-order rate constants for isomerization of 1,2,3,5-tetrafluoro-Dewar benzene: ●, packed vessel

The values of the rate constants for thermal isomerization of 1,2,4,5-tetrafluoro-Dewar benzene were unchanged when the reactions were carried out in a reaction vessel packed with glass tubes which increased the surface-to-volume ratio by a factor of 6.5. Hence surface reactions in the packed vessel may be neglected and the reaction under study may be considered to be homogeneous in nature. In a series of experiments the initial pressure of the substrate was changed 2—4 fold and it has been found that the rate constants were independent of the initial pressure. Thus at pressures greater than 54 N m^{-2} thermal isomerization was studied in a region in which a unimolecular reaction takes place. In the light of these considerations the thermal isomerization of 1,2,3,5- and 1,2,4,5-tetrafluoro-Dewar benzene is both first-order and homogeneous.

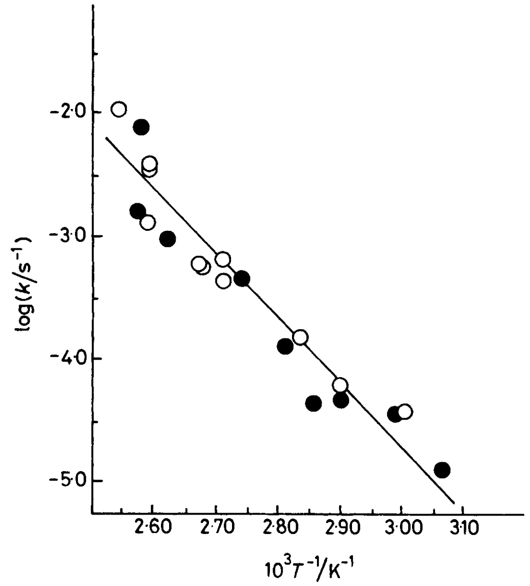


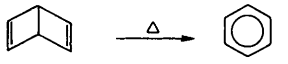
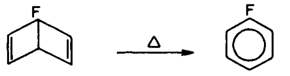
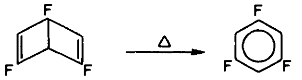
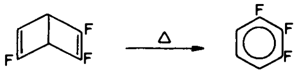
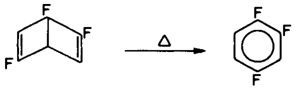
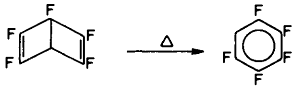
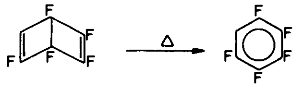
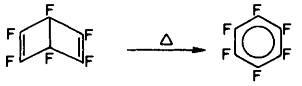
FIGURE 2 Arrhenius plot of first-order rate constants for isomerization of 1,2,4,5-tetrafluoro-Dewar benzene: ●, packed vessel

The thermal instability of 1,2,5-, 1,3,5-, and 2,3,5-trifluoro-Dewar benzenes coupled with the long tedious preparation required to obtain a pure sample makes an exhaustive kinetic investigation of their rearomatization impractical. Thus the values of their rate constants at 353 K have been obtained by assuming first-order kinetics. Taking into account the instability of the valence isomers of trifluorobenzenes, calculations were biased by significant errors estimated to be 40%. The kinetic data for the thermal isomerization of Dewar benzene and its fluorinated derivatives are summarized in Table 3.

The kinetic results obtained in this study are consistent with those reported in the literature[10,18] for other fluorinated Dewar benzenes. It is therefore to be expected that thermal isomerization of other lower fluorinated Dewar benzenes may also be regarded as a first-order homogeneous, unimolecular reaction. Arrhenius parameters observed for the thermal isomeriz-

TABLE 3

Kinetic data for thermal isomerization of Dewar benzene and its fluorinated derivatives

Reaction	E/kJ mol^{-1}	log (A/ s^{-1})	$-$log (k_{353K}/ s^{-1})	Ref.
	103 *		5.3 †	11
			2.7 †	13
			2.3	This study
			2.6	
			2.4	
	96	10.4	3.8	
	117	13.7	3.6	
	107	12.5	3.3	9, 10
	107	12.4	3.4	9, 10
	115	13.2	3.8	8

* Estimated value based on van Tamelen *et al.*[24,25]. Breslow *et al.*[13] have recommended a value of 96 kJ mol^{-1}. † log k at 297 K.

ation of tetrafluoro-Dewar benzenes are comparable to those for other derivatives of Dewar benzene.[18] The activation energy of these reactions varies within the range 96—128 kJ mol^{-1}, whilst the pre-exponential coefficient does not differ much from the 'normal' one. The similarity of the values of Arrhenius parameters studied so far indicates a biradical mechanism, similar to that proposed earlier.[2,4,5,8-12,18,21]

The rate constants for thermal rearomatization seem to indicate a general trend towards increased thermal stability of the Dewar structure with an increase in the number of fluorine substituents. The values of the rate constants for isomerisation of the tetrafluoro-Dewar benzenes are about ten-fold higher than those for trifluoro-Dewar benzenes. Fluorine substitution at the bridge bond of the Dewar structure decreases its thermal stability whilst substitution at the olefinic bonds increases it significantly. For higher fluorinated Dewar benzenes these factors seem to be more complex.

The activation energy for thermal isomerization of fluorinated Dewar benzenes is comparable to that observed for Dewar benzenes with other substituents, *i.e.* CF_3, C_2F_5.[18] Furthermore the heats of formation of Dewar benzenes are also comparable.[14,18] However, the enthalpy changes for photoisomerization to fluorinated Dewar benzenes differ considerably. ΔH° Values of 214,[11] 117,[14] and 35[26] kJ mol^{-1} for valence photoisomerization of hexafluorobenzene, hexakis(trifluoromethyl)-benzene, and hexakis(pentafluoroethyl)benzene, respectively. Presumably these differences in enthalpy are caused by destabilisation of the benzene ring due to a decrease in resonance energy conferred by the substituents (in descending order) F, CF_3, and C_2F_5. This destabilization effect is weaker in the case of lower fluorinated benzenes, *i.e.* the trifluorobenzenes and tetrafluorobenzenes studied here.

We acknowledge financial support from the Polish Academy of Science (Project MR I-9).

[1/1024 *Received, 26th June,* 1981]

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