Enthalpy and Kinetics of Isomerization of Quadricyclane to Norbornadiene. Strain Energy of Quadricyclane[1]

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Abstract: The enthalpy and kinetics of the thermal isomerization of quadricyclane (**1a**) and its 1,5-dicarbomethoxy derivative **1b** to the corresponding norbornadienes **2a** and **2b** have been determined by temperature-programmed calorimetry. The following isomerization enthalpies were observed: ΔH_{isom}(**1a** → **2a**, toluene solution) = -21.2 ± 0.2 kcal mol^{-1}; ΔH_{isom}(**1b** → **2b**, toluene solution) = -18.5 ± 0.3 kcal mol^{-1}. The heat of formation of **1a** is estimated to be 77.7 ± 1.0 kcal mol^{-1}. The estimated strain energy of **1a** is 96 kcal mol^{-1}. The kinetic parameters were found to be for **1a** → **2a** (in solution in toluene), $E_a = 38.3 \pm 0.1$ kcal mol^{-1}; $\log A = 15.0 \pm 0.1$; for **1b** → **2b** (in solution in toluene), $E_a = 34.9 \pm 0.3$ kcal mol^{-1}; $\log A = 14.3 \pm 0.2$. The isomerization **1a** → **2a** was also investigated in the gas phase.

The unusual reactivity of quadricyclane and its derivatives,[3] observed in many varied transformations,[4] has been attributed to the high strain energy of these systems. In this publication, we report data on the strain energy obtained from calorimetric studies of the thermal isomerization of quadricyclane (**1a**) and of its 1,5-dicarbomethoxy derivative **1b.**

1 2

a, R = H b, R = COOMe

The first thermochemical data on **1a** was reported by Turner and coworkers who measured the enthalpy of hydrogenolysis of **1a** to norbornane.[5] Turner, *et al.*, also determined the enthalpy of hydrogenation of norbornadiene (**2a**).[6] Combining these data, they deduced a value of -24 ± 0.9 kcal mol^{-1} for the enthalpy of isomerization of **1a** → **2a.** A second value for this enthalpy can also be deduced from the recent data of Hall, *et al.*,[7] who measured the heats of combustion of the two compounds. The enthalpy difference is found to be -10 ± 0.5 kcal mol^{-1}. Because of the large discrepancy between the sets of data, we have investigated the problem using a direct calorimetric method.

Calorimetric Measurements

We have measured the enthalpy of isomerization of **1** to **2** in a temperature-programmed calorimeter, in which the heat flow $\dot{Q}$ due to a reaction is evaluated from the recorded temperature difference between a sample and a reference cell. Integration of the heat-flow curve yields the heat of reaction; analysis of the shape of the curve can also provide the kinetic information (discussed later).[8] The compound to be studied, either neat or in solution, is contained in a small sealed Pyrex ampoule. The solution measurements can be considered to be performed at constant pressure since the vapor pressure above the solution does not change greatly in the temperature range in which the isomerization is observed. A typical thermogram for the isomerization **1a** → **2a** is shown in Figure 1, and the enthalpies of isomerization for both **1a** and **1b** are reported in Table I.

The enthalpy of isomerization of **1a** → **2a** in toluene solution has been determined to be -21.2 ± 0.2 kcal mol^{-1}.[9] The isomerization was also studied in the gas phase (base-washed ampoules were used). These experiments provide the internal energy change ΔE_{isom} since the reaction was studied at constant volume. The measured ΔE_{isom} is -19 ± 1 kcal mol^{-1}. Evaluation of ΔH_{isom} from ΔE_{isom} is not readily made since in our experiments both pressure and temperature were continuously varied. We therefore consider only the implications of the solution measurements in the remaining discussion.

Corrections to Apply to the Observed ΔH_{isom}

In order to evaluate the enthalpy of isomerization in the gas phase at 298°K, ΔH_{isom} (g, 298°K), we have to apply the following corrections to the results listed in Table I: (i) a correction for differences in the heats of solution, (ii) a correction for differences in the heats of vaporization, (iii) a correction to reduce the results to the standard temperature of 298°K; the thermograms indicate that the isomerizations **1a** → **2a** and **1b** → **2b** occur in the temperature range of ~408 to ~493°K and of ~387 to ~470°K, respectively. We shall, however, take 464 and 440°K, respectively, as the experimental temperatures; these are the temperatures at which the maximum heat flux due to the reaction is observed.

All the information needed to make the above corrections is not known. However, we have estimated these corrections as follows. The first correction can be considered negligible

Table I. Heat of Isomerization for 1a and 1b

Compd	Solvent	Run	w_1, mg	w_{solv}, mg	$-Q_{\text{exp}}$, cal	$-Q_0$,[a] kcal mol^{-1}
1a[b]	Toluene-d_8	17	59.32	112.15	13.68	21.24
		20	65.32	139.05	15.17	21.40
		23	61.47	131.07	14.08	21.09
					Av[c]	21.2 ± 0.2
1a[d]	Gas phase	54	26.02		5.19	18.39
		55	31.35		6.83	20.08
		71	28.95		5.99	19.07
					Av[c]	19.2 ± 1.0
1b[e]	Toluene-d_8	28	59.12	149.38	5.20	18.32
		31	62.06	127.86	5.57	18.69
		53	71.69	430.96	6.27	18.23
		61	73.00	543.78	6.61	18.87
					Av[c]	18.5 ± 0.3

[a] Solutions: $Q_0 = \Delta H_{\text{isom}} = \Delta H_2(T_f) - \Delta H_1(T_i)$, where T_i, T_f are the initial and final temperatures; gas phase: $Q_0 = \Delta E_{\text{isom}} = \Delta E_2(P_f, T_f) - \Delta E_1(P_i, T_i)$, where E is the internal energy, and P_i, P_f are the initial and final pressures. [b] $T_i = 135°$, $T_f = 220°$. [c] All errors are reported as $\pm 2\bar{s}$; see ref 9. [d] $P_i = 12$–14, $P_f = 14$–17 atm (calculated assuming ideal gas behavior). [e] $T_i = 115$, $T_f = 200°$.

Table II. Enthalpies of Formation of 1a and 2a and Strain Energy of 1a[a]

Ref	Method	$\Delta H_f°$ (1a)	$\Delta H_f°$(2a)	Strain energy (1a)[b]
7	Combustion	60.54 ± 0.26	50.59 ± 0.26	78.7
11	Combustion $+\Delta H_v°$ (2a)		55.9	
5[c]	Hydrogenation $+\Delta H_f°$ (norbornane)	79.6	55.7	97.8[d]
Present work	Scanning Calorimetry	77.7 ± 1.0[e]		96 ± 1

[a] All values are in kcal mol^{-1}. [b] Calculated using the strainless increments of ref 13 which lead to $\Delta H_f°$ (1a, strain free) = −18.2 kcal mol^{-1}. [c] Calculated using the revised value $\Delta H_f°$ (norbornane) = −12.4 kcal mol^{-1} (see ref 7) instead of the value used by Turner, *et al.*,[5] $\Delta H_f°$ (norbornane) = −8.4 kcal mol^{-1}. [d] The value quoted by Turner, *et al.*,[5] is 95 kcal mol^{-1}. [e] Based on $\Delta H_f°$ (2a) = 55.7 kcal mol^{-1}.

Table III. Kinetic Data for the Isomerization of 1a and 1b[a]

Compd	Solvent	Run	E_a[b], kcal mol^{-1}	Log A[b]	10^4k(150°), sec^{-1}	$\Delta H^{\ddagger}$(150°), kcal mol^{-1}	$\Delta S^{\ddagger}$(150°), cal deg^{-1} mol^{-1}
1a	Toluene-d_8	17	38.41	15.05	0.162	37.55	7.59
		20	38.20	14.98	0.178	37.36	7.32
		23	38.31	15.04	0.179	37.47	7.59
		Av[c]	38.3 ± 0.1	15.0 ± 0.1	0.17 ± 0.01	37.5 ± 0.1	7.5 ± 0.2
1a	Gas phase	54	38.49	15.09	0.161	37.96	6.25
		55	37.80	14.74	0.167	36.74	5.77
		71	38.70	15.22	0.172	37.86	8.42
		Av[c]	38.3 ± 0.5	15.0 ± 0.5	0.17 ± 0.01	37.5 ± 0.6	7.8 ± 2.2
1b	Toluene-d_8	28	34.96	14.32	1.83	34.12	4.29
		31	34.74	14.19	1.80	33.90	3.73
		53	35.17	14.41	1.80	34.33	4.74
		61	34.59	14.13	1.85	33.74	3.43
		Av[c]	34.9 ± 0.3	14.3 ± 0.2	1.82 ± 0.01	34.0 ± 0.3	4.1 ± 0.6

[a] For the exact experimental conditions, see Table I. [b] Calculated from the central portion of the thermogram (*ca.* 30–40° range). [c] All errors are reported as $\pm 2\bar{s}$; see ref 9.

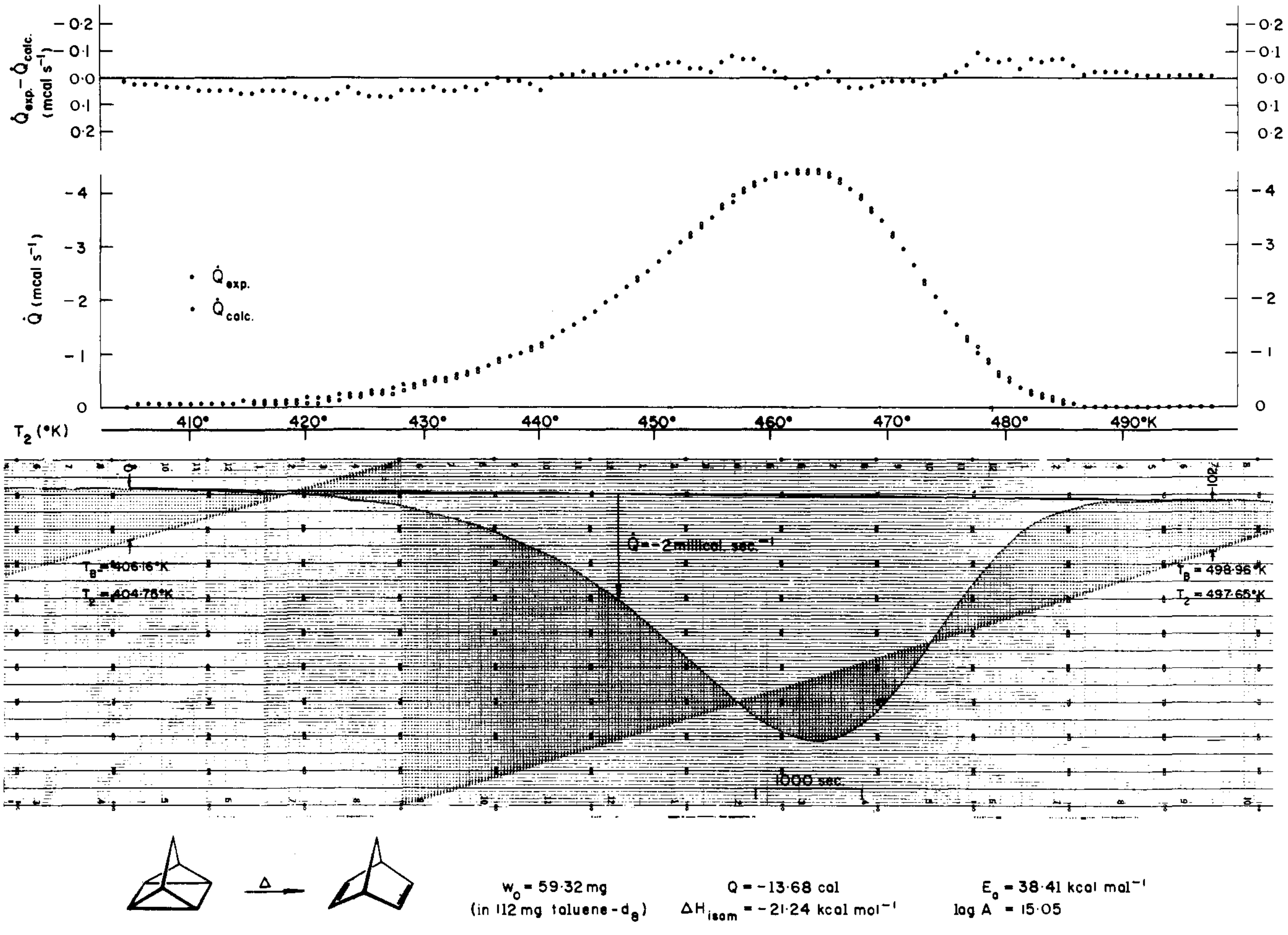

Figure 1. Experimental and calculated thermograms for the isomerization of quadricyclane to norbornadiene. The experimental recording displays both the linearly increasing block temperature (T_B) and the heat flux ($\dot{Q}$), calculated from the temperature difference ($T_1 - T_2$) between the reference and the sample cells, as a function of time.

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in comparison with the other heat effects: heat of mixing of hydrocarbons are very small. The second correction ii to be applied to the measured heat of isomerization **1a** → **2a** is immediately evaluated to −1 ± 0.1 kcal mol^{-1} since the heats of vaporization of both **1a** and **2a** are known [$\Delta H_v°$(**1a**) = 8.84 ± 0.04, $\Delta H_v°$(**2a**) = 7.87 ± 0.02 kcal mol^{-1}].[7] The third correction iii can be calculated using Kirchhoff's equation:

$$\Delta H_{\mathrm{isom}}(\mathrm{g},T_0) = \Delta H_{\mathrm{isom}}(\mathrm{g},T) - (T - T_0)\Delta C_{\mathrm{p}}$$

where $\Delta C_{\mathrm{p}} = \Sigma C_{\mathrm{p}}(\text{products}) - \Sigma C_{\mathrm{p}}(\text{reactants})$, the specific heats being taken at the mean temperature $(T - T_0)/2$. Taking the specific heat data of Hall, *et al.*[7] [C_{p} (**1a**) = 33.25 and C_{p}(**2a**) = 27.74 cal deg^{-1} mol^{-1}], we find a correction of +1.1 kcal mol^{-1}; using the tables of O'Neal and Benson,[10] we calculate a correction of −0.5 kcal mol^{-1} to bring the measured enthalpy of isomerization to 298°K.

In view of these uncertainties in the last correction, we estimate

$$\Delta H_{\mathrm{isom}}(1\mathrm{a} \longrightarrow 2\mathrm{a},\ \mathrm{g},\ 298°\mathrm{K}) = -22 \pm 1\ \mathrm{kcal\ mol^{-1}}$$

This value is in good agreement with the isomerization enthalpy derived by Turner, *et al.*[5]

The corrections to apply to the isomerization enthalpy observed for the reaction **1b** → **2b** cannot be estimated since no data are available for the heats of sublimation of **1b** and of vaporization of **2b.**

Enthalpy of Formation and Strain Energy of Quadricyclane

To calculate the enthalpy of formation of quadricyclane, we can combine our value for the enthalpy of isomerization with the value for the enthalpy of formation of **2a.** This value is also subject to controversy. The relevant data available in the literature are listed in Table II. Taking a value of 55.7 kcal mol^{-1} for $\Delta H_f°$(**2a**,g), we find $\Delta H_f°$(**1a**,g) = 77.7 ± 1 kcal mol^{-1}. Calculation of the enthalpy of formation of strain-free **1a** using the "strainless" increments of Schleyer, *et al.*,[13] gives −18.2 kcal mol^{-1}. The estimated strain energy of quadricyclane is thus 96 ± 1 kcal mol^{-1}. This strain energy value is substantially higher than that presented by Hall, *et al.*,[7] and agrees closely with the original estimate of Turner, *et al.*[5] It is instructive to compare the experimental strain energy of **1a** with the simple estimate obtained by summing the strain of its constituent rings. The sum of twice the cyclopropane strain (56 kcal mol^{-1})[13] and the cyclobutane strain (27 kcal mol^{-1})[13] is 83 kcal mol^{-1}. Therefore, the extra strain introduced by fusing the three small rings to form the *syn*-tricyclo[3.1.0.0^{2,4}]-hexane system and by the one carbon bridge amounts to 13 kcal mol^{-1}.

Kinetic Data

The kinetic data are collected in Table III; they were obtained by fitting the observed thermograms to theoretical first-order curves (see Figure 1). The kinetic parameters of the isomerization of **1a** in toluene solution are in excellent agreement with the data of Edman,[14] who reported E_{a} = 38.3 kcal mol^{-1} and $\Delta S^{\neq}$ = +7.5 cal mol^{-1} deg^{-1} (log A = 15.1)[15] in acetonitrile.[16] Our gas-phase kinetic data, determined in the pressure range 12–17 atm (the pressure change in a given run was 2–3 atm), agree well with the solution-phase data. The significantly different values reported by Frey[17] (E_{a} = 33.5 kcal mol^{-1}; log A = 12.8) were obtained from measurements in the gas phase at low pressure (1–18 mm).

The kinetic parameters for the isomerization of **1b** → **2b** have not been previously reported.[18] The data in Table III show that the activation energy for the process **1b** → **2b** is smaller by an amount of 3.4 ± 0.5 kcal mol^{-1} than that observed for **1a** → **2a.** It is remarkable that the substituent effect observed here is comparable in magnitude to those observed in simple cyclobutane pyrolysis.[19] This suggests that the quadricyclanes also isomerize *via* a diradical mechanism. If the isomerizations of quadricyclanes were concerted, the transition states should occur much earlier on the reaction coordinate[24] than those for either diradical or concerted decomposition of cyclobutanes; the isomerizations of quadricyclanes are exothermic, while the decompositions of cyclobutanes are endothermic [ΔH_{isom}(cyclobutane → 2 ethylenes) = +18.12 kcal mol^{-1}; see ref 9, pp 141 and 143]. The substituent effect would then be smaller than those observed. However, we should caution that the above application of Hammond's postulate[24] to reject the concerted pathway for the quadricyclanes rearrangement may be misleading since a comparison is made between two molecular reorganizations in which the total coordinate changes are drastically different.

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(18) Haselbach and Martin (see ref 4g) quote a private communication from H. Prinzbach and M. Joyeux stating that E_{a} = 27 kcal mol^{-1} for the rearrangement **1b** → **2b.** Experimental conditions are not given.
(19) Values for the α-carbomethoxy group effect are: 4.0 ± 1.7 kcal mol^{-1} from studies in the bicyclo[2.2.0]hexane series,[20] 5.2 ± 0.8 kcal mol^{-1} from the pyrolysis of methyl cyclobutanecarboxylate,[21] and 4.0 ± 1.0 kcal mol^{-1} from pyrolysis rate data for dimethyl cyclobutane-1,2-dicarboxylate.[22]
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