

## Enthalpy of isomerization of quadricyclane to norbornadiene

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### Abstract

Using a closed-bomb reaction calorimeter, the enthalpy of isomerization of quadricyclane (QC) to norbornadiene (NBD) in a benzene solution has been measured at room temperature in the presence of  $\text{HgBr}_2$ . In the pure liquid states, a value of  $-89.03 \pm 1.18 \text{ kJ mol}^{-1}$  was obtained. From the enthalpies of vaporization of QC and NBD measured using a vaporization calorimeter ( $37.85 \pm 0.04$  and  $34.83 \pm 0.10 \text{ kJ mol}^{-1}$ , respectively), the gaseous enthalpy of isomerization was also derived as  $-92.05 \pm 1.18 \text{ kJ mol}^{-1}$ .

### INTRODUCTION

The norbornadiene–quadricyclane (NBD–QC) reversible isomerization reaction has received considerable attention as an attractive model for solar energy storage [1]. The enthalpy of isomerization of this system, as a measure of its energy storage capability, has been determined by different methods [2–9], but published results are not in agreement. In this work, our aim is to obtain a more accurate enthalpy of isomerization of this reaction from direct calorimetric measurement. The catalysed isomerization method was used at room temperature. The catalyst chosen was  $\text{HgBr}_2$ ; its catalytic activity is satisfactory and this isomerization reaction is rapid and straightforward in benzene. The gaseous enthalpy of isomerization was derived from our results for the enthalpy of isomerization in liquid states and the enthalpies of vaporization of QC and NBD.

### EXPERIMENTAL

#### *Samples*

The NBD used (Tokyo Kasei) contained a small amount of inhibitor. Its purity was analysed by GLC (Varian 3700), with a 50 m FFAP quartz

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capillary column and flame ionization detector; the internal standard was toluene. In all, four impurities (except the inhibitor) were found (0.42%). The original sample was used in the mixing and vaporization experiments without further purification. QC was prepared from NBD by ultra-violet irradiation [10] and purified in a Perkin–Elmer spinning-band Auto Annular still (model 251) under reduced pressure. The product was identified by NMR, and its purity was analysed by GLC (Varian 3700) with a 25 m SE 30 quartz capillary column. The sole organic impurity (1.32%) was found to be NBD. The water content in the samples was determined by GLC with a thermal conductivity detector and a 3 m GDX-100 stainless steel column; benzene saturated with water at 20°C was used as the external standard. Both the QC and NBD samples contained about the same amounts of water (0.01%). Another sample of QC (containing 0.72% NBD and 0.01% water) was used for vaporization calorimetry.

### *Instrument*

An LKB-8721-4 closed-bomb reaction calorimeter was used to measure the heat of isomerization. Its structure and operation were described previously [11]. The thermostat was kept at  $24.98 \pm 0.001^\circ\text{C}$ . The thermistor thermometer in the bomb was calibrated against a quartz thermometer (HP 2804A) between 290 and 300 K, and a set of  $R-T$  values were fitted to an exponential equation,  $R = 0.0249150 \exp(3460.65/T)$ . In order to test the performance of the calorimeter, five electrical calibration experiments with the calorimeter containing 60 mL of pure water gave an energy equivalent of  $469.79 \pm 0.31 \text{ J K}^{-1}$  (mean  $\pm$  SDM). The standard reaction of tris(hydroxymethyl)aminomethane (Tris) with 0.1 N HCl was used to verify the results obtained by the calorimeter. Tris, provided by NIST (standard reference material 724a), was stored over a saturated solution of magnesium nitrate before use. In each experiment, 0.3 g of Tris was sealed in a glass ampoule, and then dissolved in 60 g of 0.1006 N HCl. The sample masses were obtained by weight and corrected for buoyancy. The energy equivalent of the calorimeter was calibrated in electrical energy just before each measurement of the heat of reaction with approximately the same temperature interval. The heat of breaking the ampoule was determined separately in blank experiments; the mean of eight experiments was  $3.21 \pm 0.07 \text{ J}$ . The enthalpy of reaction of Tris with 0.1 N HCl was measured as  $-29.721 \pm 0.043 \text{ kJ mol}^{-1}$  (mean and twice the SDM) which is in agreement with the NIST certified value,  $-29.770 \pm 0.032 \text{ kJ mol}^{-1}$ .

### *Catalyst*

Although many substances can catalyse this isomerization reaction [5, 8, 12–16], the catalyst used in isoperibol calorimetry should satisfy the

following requirements: (1) it is stable during the reaction process; (2) it has a high activity so that the reaction can proceed to completion over 20–30 min; (3) its activity is specific so that no side reactions occur; and (4) it is inert to the solvent or the products, i.e. it does not interact significantly with any one of them. Some catalysts reported in the literatures were tested. The reactants and products of these reaction were detected by NMR or GLC after different reaction periods. The experimental results showed that the activities of  $\text{CuSO}_4$  and  $\text{SnCl}_2$  were low, and that despite the high activity of  $\text{Ph}_3\text{P}=\text{SnCl}_2$  and  $(p\text{-BrC}_6\text{H}_4)\text{NSbCl}_6$ , they gave rise to obvious side reactions (indicated by the change of solutions colour). However, results for  $\text{HgBr}_2$  showed that it can meet the above requirements; a 0.1 mole fraction of  $\text{HgBr}_2$  is enough to catalyse the isomerization reaction to completion after 5 min at room temperature, and no other products except norboradiene were found.

### *Solvent*

Acetone, chloroform, benzene and dichloromethane were tested as solvents. The isomerization reaction was rapid and straightforward in each of these solvents. However, the Viton o-ring of the bomb swelled in the three polar solvents; therefore, benzene was used in the experiments.

### *Reaction calorimetry*

The experimental procedure for the isomerization reaction was similar to the reaction of Tris + HCl, except that about 0.1–0.2 g of QC (sealed in the glass ampoule) was used instead of Tris, and that about 30–50 mg  $\text{HgBr}_2$  (A.R. purity >99.5%) and 60 ml benzene (superpure, purity >99.7%), instead of 0.1 N HCl solution, were placed in the bomb.

The enthalpy of mixing of NBD with the same solution as was used in the isomerization reaction was also measured under the same conditions, except that NBD replaced QC in the glass ampoule.

### *Vaporization calorimetry*

The enthalpies of vaporization of NBD and QC were measured respectively using an LKB-8721-3 vaporization calorimeter. The procedures and corrections described in the Instrument Manual [17] were followed. In these experiments the heating power was 100 mW and the heating period was 600 s.

TABLE 1

The experimental results for the enthalpy of isomerization of QC to NBD in benzene solution with the catalyst  $\text{HgBr}_2$

$m(\text{QC})/\text{g}$	$m(\text{HgBr}_2)/\text{g}$	$\varepsilon/(\text{J K}^{-1})$	$\Delta T/\text{K}$	$Q/\text{J}$	$Q_b/\text{J}$	$Q_{\text{mix}}/\text{J}$	$\Delta_{\text{iso}}H_m^\ominus/(\text{kJ mol}^{-1})$
0.11529	0.03501	317.77	0.34324	-109.07	-3.21	0.94	-85.37
0.12799	0.04544	305.59	0.41270	-126.12	-3.21	1.05	-89.24
0.11342	0.04554	305.48	0.35856	-109.53	-3.21	0.93	-87.13
0.11505	0.03112	296.48	0.37344	-110.72	-3.21	0.94	-86.87
0.11849	0.04135	301.00	0.38546	-116.02	-3.21	0.97	-88.48
0.16524	0.04369	309.22	0.52407	-162.05	-3.21	1.36	-89.32
0.25796	0.04584	312.15	0.79739	-248.91	-3.21	2.12	-88.52
						Mean	-87.85
						$2 \times \text{SDM}$	$\pm 1.18$
						Corrected for purity	-89.03 $\pm 1.18$

Key:  $\varepsilon$ , energy equivalent of the system;  $Q$ , heat of the process;  $Q_b$ , heat of breaking the ampoule;  $Q_{\text{mix}}$ , heat of mixing of NBD with the solution in the process;  $\Delta_{\text{iso}}H_m^\ominus$ , enthalpy of isomerization of QC to NBD in pure liquids.

## RESULTS

The experimental results of the enthalpy of isomerization of QC to NBD and of the enthalpy of mixing of NBD with the  $\text{HgBr}_2$  solution in benzene are listed in Tables 1 and 2 respectively. The corresponding processes at 298.15 K are shown in the thermochemical equations

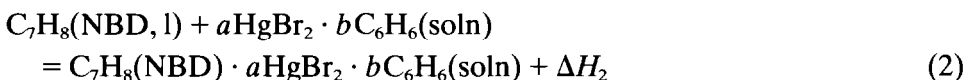
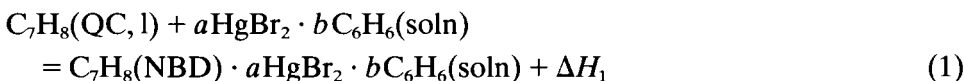


TABLE 2

The experimental results for the enthalpy of mixing of NBD and  $\text{HgBr}_2$  solution in benzene

$m(\text{NBD})/\text{g}$	$m(\text{HgBr}_2)/\text{g}$	$\varepsilon/(\text{J K}^{-1})$	$\Delta T/\text{K}$	$Q/\text{J}$	$Q_b/\text{J}$	$\Delta_{\text{mix}}H/(\text{J per g(NBD)})$	
0.11618	0.04210	303.61	0.00715	-2.17	-3.21	8.95	
0.11529	0.02740	327.37	0.00719	-2.35	-3.21	7.46	
0.11225	0.04231	306.59	0.00776	-2.38	-3.21	7.40	
0.11335	0.04288	307.28	0.00726	-2.23	-3.21	8.64	
0.12108	0.04028	303.53	0.00713	-2.16	-3.21	8.67	
						Mean	8.22
						$2 \times \text{SDM}$	$\pm 0.66$

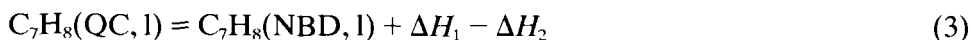
Key:  $Q$ , heat of the process;  $Q_b$ , heat of breaking the ampoule;  $\Delta_{\text{mix}}H$ , enthalpy of mixing of 1 g of NBD and the  $\text{HgBr}_2$  solution in benzene.

TABLE 3

Experimental results for the enthalpies of vaporization of QC and NBD at 298.15 K

$\Delta_v H_m^\ominus$ (QC)/(kJ mol <sup>-1</sup> )	$\Delta_v H_m^\ominus$ (NBD)/(kJ mol <sup>-1</sup> )
37.81	34.85
37.89	34.94
37.86	34.87
37.88	34.67
37.80	34.83
Mean 37.85	34.83
2 × SDM ± 0.04	± 0.10

where  $a$  and  $b$  are mole ratios of HgBr<sub>2</sub> and benzene to QC in the measurements,  $0.05 < a < 0.1$  and  $240 < b < 540$ ; and  $\Delta H_1$  and  $\Delta H_2$  are the enthalpies of processes (1) and (2) respectively. The standard enthalpy of isomerization of QC to NBD in liquids can be obtained from eqns. (1) and (2)



The results of the enthalpy of vaporization of QC and NBD at 298.15 K are listed in Table 3. The standard gaseous enthalpy of isomerization of QC to NBD is derived from these values.

## DISCUSSION

The experimental results for Tris + HCl indicate that the precision of the reaction calorimeter is satisfactory, and that no obvious systematic error has occurred. For isomerization calorimetry, experimental errors could come from: (1) an incomplete reaction; (2) the appearance of by-products; (3) the corrections for the heats of solution of reactant and product in benzene; and (4) the impurities in the sample. In the preliminary experiments, the isomerization reaction proceeded rapidly, so that after 5 min no reactant (QC) or product except NBD were detected by NMR and GLC. The calculated adiabatic temperature-rise of the calorimeter in the isomerization experiments remained constant when the reaction period was prolonged; this indicated that the isomerization reaction was over before the end of the reaction period of calorimetry.

The enthalpy of mixing of NBD with HgBr<sub>2</sub> solution in benzene was small: this implies that there was no strong interaction between the product (NBD) and the solvent (benzene) or the catalyst (HgBr<sub>2</sub>). The effect of any impurity in the QC sample on the enthalpy of isomerization was corrected and for the vaporization calorimetry, the errors from impurities were less than that of the experiments themselves, and so the uncertainties in the results of the enthalpies of isomerization and of vaporization were taken as twice the SDM of the experiments, respectively.

TABLE 4

Comparison with the literature results for the enthalpy of isomerization of QC to NBD

Reference	Method <sup>a</sup>	$\Delta_{\text{iso}}H_m^\ominus(\text{l})/(\text{kJ mol}^{-1})$	$\Delta_{\text{iso}}H_m^\ominus(\text{g})/(\text{kJ mol}^{-1})$
2	H		-95
3	B	$-37.6 \pm 1.5$	$-40.6 \pm 1.5$ <sup>c</sup>
4	T	$-88.7 \pm 0.8$ <sup>b</sup>	$-92 \pm 4$
5	C	$-109.5 \pm 1.0$	$-112.5 \pm 1.0$ <sup>c</sup>
6	B	$-88.3 \pm 3.7$	$-91.3 \pm 3.7$ <sup>c</sup>
7	H		$-92.80 \pm 4.80$
8	C	$-81 \pm 1$	$-84 \pm 1$ <sup>c</sup>
9	P	$-58.6 \pm 4.2$	$-61.6 \pm 4.2$ <sup>c</sup>
This work	C	$-89.03 \pm 1.10$	$-92.05 \pm 1.10$

<sup>a</sup> H, hydrogenation calorimetry; B, bomb calorimetry; T, thermal isomerization calorimetry; C, catalytical isomerization calorimetry; P, photocalorimetry. <sup>b</sup> In toluene solution at a mean temperature of 464 K. <sup>c</sup> Based on our enthalpies of vaporization.

For comparison, some literature results for the enthalpy of isomerization of QC to NBD and for the enthalpies of vaporization of both compounds are listed in Tables 4 and 5.

The vaporization enthalpies of both QC and NBD have been determined

TABLE 5

Summary of the thermochemical data of NBN, NBD and QC

Compound	Reference	$\Delta_{\text{v/s}}H_m^\ominus/(\text{kJ mol}^{-1})$	$\Delta_f H_m^\ominus(\text{g})/(\text{kJ mol}^{-1})$
NBN	18		$-52.05 \pm 2.72$ <sup>a</sup>
	6		$-62.0 \pm 3.3$ <sup>a</sup>
	1	$40.04 \pm 0.09$	$-54.92 \pm 1.06$
QC	3	$37.0 \pm 0.8$	
	2		$330.13 \pm 2.30$ <sup>b</sup>
	7		$329.80 \pm 3.99$ <sup>b</sup>
	6	$37.0 \pm 0.8$	$340.0 \pm 2.2$ <sup>a</sup>
	This work	$37.85 \pm 0.04$	
NBD	3	$32.9 \pm 0.8$	
	2		$235.0$ <sup>b</sup>
	7		$237.00 \pm 3.12$ <sup>b</sup>
	19		$235.7 \pm 2.1$ <sup>a</sup>
	6	$33.8 \pm 0.9$	$248.6 \pm 3.0$ <sup>a</sup>
	20		$243.0 \pm 2.5$
	This work	$34.83 \pm 0.10$	

<sup>a</sup> Based on our enthalpy of vaporization. <sup>b</sup> Based on our enthalpy of formation of NBN.

by Hall et al. [3] and Steele [6], respectively, from the vapor pressure measurements; these data were less accurate than ours determined by direct calorimetry.

The results for the enthalpy of isomerization of QC to NBD in liquid states reported in the literature are very scattered: from 37.6 to 109.4 kJ mol<sup>-1</sup>. These data were obtained by five different methods: (1) bomb calorimetry; (2) photocalorimetry; (3) hydrogenation calorimetry; (4) temperature-programmed calorimetry; and (5) catalyzed isomerization calorimetry. For bomb calorimetry (Hall et al. [3]), the main difficulty lies in the handling and containing of the unstable, volatile NBD without an inhibitor, so that the enthalpy of isomerization derived from their result is rather low. In the photocalorimetric work of Harel et al. [9], acetophenone was used as the sensitizer. As they pointed out, acetophenone is sensitive to oxygen in the solvent and a minor component of such an exoergic reaction could account for their lower  $\Delta H$  value. The calorimetric method of Maruyama et al. [8] is not precise; therefore their result is less accurate. In the metal-catalysed isomerization experiments of Wiberg and Connon [5], they found a very slow rate of temperature increase in addition to that expected from the heat transfer from the external bath, and this continued throughout the reaction period. This implies that the isomerization reaction is complex, and their result seems a little high.

Kabakoff et al. [4] studied the isomerization reaction in toluene using a temperature-programmed calorimeter. QC underwent a thermal isomerization to NBD between 408 and 493 K; the measured enthalpy of isomerization was  $-88.7 \pm 0.8$  kJ mol<sup>-1</sup> under the conditions of the actual process. In order to evaluate the enthalpy of isomerization in the gas phase at 25°C, they applied the following corrections: (1) neglecting the difference in the enthalpies of solution; (2) estimating the difference in the enthalpies of vaporization as  $-4 \pm 0.4$  kJ mol<sup>-1</sup> (our results estimate  $-3.0 \pm 0.1$  kJ mol<sup>-1</sup>); and (3) using the  $\Delta C_p$  in the liquid phase from the DSC determination, and the  $\Delta C_p$  in the gas phase from an estimation. Their final value was  $-92 \pm 4$  kJ mol<sup>-1</sup>.

Turner et al. [2] measured the heats of hydrogenation of QC and NBD in acetic acid; they were  $-284.9$  and  $-385.0$  kJ mol<sup>-1</sup> respectively. In order to deduce the gaseous data, Rogers et al. [7] pointed out that the estimated corrections for the enthalpies of solution, 5 kJ mol<sup>-1</sup> for NBD and 0 kJ mol<sup>-1</sup> for QC, should be added; and then the corrected gaseous enthalpy of isomerization became  $-95$  kJ mol<sup>-1</sup>. Rogers et al. [7] also measured the enthalpies of hydrogenation of QC and NBD in hexane,  $-384.72$  and  $-291.92$  kJ mol<sup>-1</sup> respectively, with an estimation of the overall confidence limits of this method to be about  $\pm 1\%$ . They suggested that the difference in the enthalpy of solution of QC and NBD in hexane was small; therefore they neglected this correction. The derived gaseous

enthalpy of isomerization from the results of Rogers et al. is  $-92.80 \pm 4.80 \text{ kJ mol}^{-1}$ .

Steele [6] determined the enthalpies of formation of QC and NBD in liquid states ( $302.1 \pm 2.1$  and  $213.8 \pm 3.0 \text{ kJ mol}^{-1}$  respectively) from bomb calorimetry. Using our accurate enthalpies of vaporization, the gaseous values become  $340.0 \pm 2.2$  and  $248.6 \pm 3.0 \text{ kJ mol}^{-1}$ . Although these results are about  $10 \text{ kJ mol}^{-1}$  different from those of Rogers et al. and others, their derived enthalpy of isomerization ( $-91.3 \pm 3.7 \text{ kJ mol}^{-1}$ ) is in agreement with those of Rogers et al. [7] Turner et al. [2] and Kabakoff et al. [4].

In our determinations, all results were obtained from direct calorimetry, and therefore no estimation was needed. The uncertainty of our data is the lowest in Table 4.

Some results for the gaseous enthalpies of formation of QC and NBD are listed in Table 5. For comparison, these data are re-calculated using our new enthalpies of vaporization for QC and NBD and our enthalpy of formation for norbornane (NBN) [1]. The latter is used to deduce those data from the enthalpies of hydrogenation and is more accurate. In addition, the literature results of NBN and the results for NBD of Skuratov et al. [19] from bomb calorimetry and of Walsh et al. [20] from equilibrium measurements, are also listed in Table 5.

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