

## Ring Strain in Diiodocyclobutane

STIG SUNNER and CLAUS A. WULFF\*

*Thermochemistry Laboratory, Chemical Center, University of Lund,  
S-220 07 Lund 7, Sweden*

Bicyclobutane, free of cyclobutene, reacts quantitatively with iodine in a sealed vessel at temperatures between 78 and 100°C. The thermochemistry of this reaction has been studied to provide enthalpies of formation of diiodocyclobutane;  $\Delta H_f^\circ = 32.2 \pm 1.5$  and  $46.2 \pm 2$  kcal/mol for diiodocyclobutane liquid and gas, respectively. The "strain energy" in the four-carbon ring has been estimated as 32 kcal/mol.

The preparation of small polycyclic molecules in recent years presents an interesting opportunity to obtain thermochemical data for substituted cycloalkanes. In particular, the highly reactive bridgehead bond in bicyclobutane (hereafter BCB) allows the facile addition of  $I_2$  to form 1,3-diiodocyclobutane (hereafter CBI<sub>2</sub>). Wiberg *et al.*<sup>1,2</sup> have shown that the reaction gives a single product, albeit a mixture of *cis*- and *trans*-isomers. The thermochemical literature<sup>3,4</sup> indicates that data for CBI<sub>2</sub> would be the first data for an alicyclic diiodide. The addition, the question of iodine-iodine interaction induced excess strain in cyclobutane, seemed to be an interesting problem to attack. The development of a reliable closed-bomb reaction calorimeter<sup>5</sup> permits the handling of a normally volatile material at elevated temperatures. Reported below are enthalpies of reaction for the process  $BCB + I_2 = CBI_2$  in  $CCl_4$  solutions.

### EXPERIMENTAL

BCB was prepared<sup>1,6</sup> from 3-chlorocyclobutanecarboxylic acid, which, in turn, had been prepared<sup>7</sup> from 1,1-cyclobutanedicarboxylic acid (Aldrich). The initial BCB, admixed with cyclobutane and cyclobutene, was collected in hexane cooled in a dry-ice acetone bath. The BCB was separated from its impurities and the solvent by GLC on a dinonyl phthalate column in a Perkin Elmer F21 preparative scale GLC. The volatile BCB was collected in a Teflon valved glass cylinder maintained in a dry-ice acetone bath. The cylinder was connected to the GLC outlet by a condenser which had chilled acetone circulating through its jacket. Although the purification process provided clean BCB

\* Present address: Department of Chemistry, University of Vermont, Burlington, Vt. 05401, U.S.A.

Table 1. The enthalpy of reaction of BCB with I<sub>2</sub>.

Temperature, °C	Sample	g I <sub>2</sub> <sup>a</sup>	ΔH(kcal/mol)
78	I	0.021301	-14.07
78	I	0.024410	-14.36
99	I	0.021743	-13.91
99	II	0.004943	-13.85
99	II	0.011083	-14.09

<sup>a</sup> Corrected to vacuum.

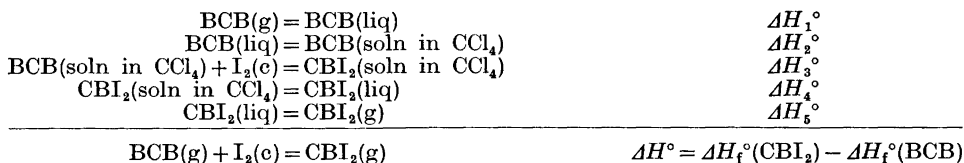
(as judged by GLC), the total yield was extremely small, *ca.* 0.3 % based on the original diacid. A comparison of results obtained with this material with those obtained for a sample containing some 5 % impurities indicates that for many thermochemical processes the impure material would be satisfactory. (This is particularly true for "strain energy" evaluations, which are themselves an ambiguous quantity.)

The calorimetry was performed in a sealed rotating-bomb reaction calorimeter<sup>5</sup> thermostated in a Hallikainen bath containing silicon oil. Preliminary experiments at 25° and 50°C were unsatisfactory because the reaction proceeded too slowly. At 78°C the reaction went to completion in 30–40 min, and at 99°C the reaction was complete in less than 30 min. Completeness of reaction was judged by the absence of the pink color of I<sub>2</sub> (the limiting reagent) in the CCl<sub>4</sub> solution.

Experiments were performed by breaking an ampoule of I<sub>2</sub> crystals (Mallinckrodt, resublimed) into an excess of BCB dissolved in freshly distilled CCl<sub>4</sub>. The raw data were corrected for heat effects engendered by the vaporization of the solvent mixture and for the condensation of I<sub>2</sub> vapor in the partially filled ampoules. The corrections were based on results obtained with empty ampoules and literature values for the vapor pressure and enthalpy of sublimation of I<sub>2</sub>.<sup>8</sup> Corrected results, based on the thermochemical calorie defined as 1 cal = 4.1840 joules, appear in Table 1 where the samples designations refer to BCB that does (I) or does not (II) contain the cyclobutane and cyclobutene impurities.

## DISCUSSION

To obtain a value for the enthalpy of formation of CBI<sub>2</sub> the following scheme was considered

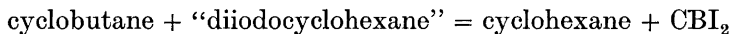


Wiberg *et al.*<sup>1</sup> have determined the vapor pressure of BCB between -21° and +8°C. From the temperature dependence of the vapor pressure they report  $\Delta H_1^\circ = -6041$  cal/mol over the temperature range of their experiments. Selecting  $\Delta C_p^\circ = 12$  cal/(mol K) for the condensation process, by comparison for data with other simple hydrocarbons,<sup>4</sup> we estimate  $\Delta H_1^\circ = -5.6$  kcal/mol at 298 K. Enthalpies of solution (or mixing) for non-polar systems tend to

be small and we have estimated  $\Delta H_2^\circ + \Delta H_4^\circ = 0 \pm 0.5$  kcal at 298 K. Our data for  $\Delta H_3^\circ$  do not permit a reliable estimate for  $\Delta C_p$ . The quantity is likely to be small, since the reaction does not involve vapors or polar substances, and, accordingly, we choose  $\Delta H_3^\circ = -14.1 \pm 1.0$  kcal at 298 K. Enthalpy of vaporization differences between bromo and iodo compounds and an estimate of the enthalpy of vaporization of dibromocyclobutane based on its boiling point<sup>9</sup> and Wadsö's correlations<sup>10</sup> lead to an estimated  $\Delta H_5^\circ = 14.0 \pm 1.0$  kcal at 298 K. The same estimate can be obtained by adding the enthalpy of vaporization difference for diiodobenzene-benzene to the enthalpy of vaporization of cyclobutane.<sup>3</sup> Summing  $\Delta H_1^\circ$  to  $\Delta H_5^\circ$  we obtain  $\Delta H^\circ = -5.7 \pm 2$  kcal/mol for  $\text{BCB}(\text{g}) + \text{I}_2(\text{c}) = \text{CBI}_2(\text{g})$ .

The enthalpy of formation of BCB has been determined as  $\Delta H_f^\circ = 51.9$  kcal/mol<sup>11</sup> leading to  $\Delta H_f^\circ = 46.2 \pm 2$  and  $32.2 \pm 1.5$  kcal/mol for  $\text{CBI}_2$  in the vapor and liquid phases, respectively.

The evaluation of "strain energy" is, at best, an ambiguous process.<sup>12</sup> Application of a group contribution scheme<sup>3</sup> leads to a predicted enthalpy of formation of 11.8 kcal/mol  $\text{CBI}_2(\text{g})$ . Comparison of this value with our experimental quantity indicates a difference, or "strain energy", of 32 kcal/mol, some 6 kcal/mol greater than that of the parent cyclobutane as derived by the same set of group parameters. The application of group parameters to an alicyclic diiodide has the disadvantage that the group parameter values are derived almost exclusively from data for non-cyclic compounds. A second, probably better, estimate can be derived from the  $\Delta H$  for the reaction



where "diiodocyclohexane" represents a moiety free of iodine-iodine interactions. The enthalpy of formation of this species can be estimated as  $\{2\Delta H_f^\circ(\text{iodocyclohexane}) - \Delta H_f^\circ(\text{cyclohexane})\} = 5.1$  kcal/mol from tabulated data.<sup>3</sup> This hypothetical reaction leads to a "strain energy" estimate of 5 kcal/mol more for  $\text{CBI}_2$  than for cyclobutane.

It appears that the four carbon ring in  $\text{CBI}_2$  is somewhat more "strained" than it is in cyclobutane. While it is tempting to ascribe the increased strain to an opening of the dihedral angle as a response to iodine-iodine repulsion, there is no supporting evidence. The inter-planar angles in 1,3-dibromo- and 1,3-chlorobromo-cyclobutanes have been reported as  $147 \pm 2^\circ$ .<sup>13</sup> While this represents a slight opening from the  $143 - 146^\circ$  reported for cyclobutane,<sup>14,15</sup> the uncertainties are too large to provide definitive conclusions regarding angle-substitution relationships. Structural information on  $\text{CBI}_2$  would be desirable.

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