# The Heat of Oxidation of 1,2-Di-n-butylhydrazine to Azo-n-butane

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1,2-Di-*n*-butylhydrazine in hexane solution has been oxidized to azo-n-butane with oxygen and Pd/C catalyst and with red mercuric oxide. Both methods led to the same calculated heat of hydrogenation ( $\Delta H_{\rm H}$ ) of the azo group in hexane,  $-16.4 \pm 0.3$  kcal/mol. This value is 10.6 kcal/mol less exothermic than the  $\Delta H_{\rm H}$  of carbon-carbon double bonds.

The reduction of unsaturated groups is a fundamental reaction in organic chemistry. Thermochemical studies of olefin hydrogenation<sup>1,2</sup> and the heat of reduction of carbonyl compounds<sup>3</sup> provide useful data for parameterization of molecular mechanics calculations. Although no quantitative studies of azoalkane hydrogenation could be found in the literature, one can calculate the heat of hydrogenation  $(\Delta H_{\rm H})$  from the heats of formation  $(\Delta H_f)$  of azoalkanes and their reduction products, 1,2-dialkylhydrazines.  $\Delta H_{\rm f}$  values of azoalkanes are well-known,<sup>4</sup> and force fields have been developed for these compounds.<sup>5</sup> However, the few  $\Delta H_f$  values known<sup>6</sup> for hydrazines (Table I) lead to discrepant values of  $\Delta H_{\rm H}$  of azoalkanes. No heat of sublimation has been reported for azoisobutyronitrile (AIBN) or its corresponding hydrazine.<sup>7</sup> Because this hydrazine probably has a greater vaporization heat than does AIBN, the solid-phase  $\Delta H_{\rm H}$  in Table I can be taken as a maximum for the gaseous compound. The  $\Delta H_{\rm f}$  of gaseous azobenzene has been determined,<sup>8-10</sup> but again the heat of sublimation of hydrazobenzene is lacking. Even if the gas-phase  $\Delta H_{\rm H}$  were known, it might not apply to aliphatic azo compounds because the effect of phenyl conjugation on  $\Delta H_{\rm H}$  is uncertain. sym-Dimethylhydrazine is the only simple aliphatic hydrazine that has been subjected to bomb calorimetry, but only 1 run out of 15 tried gave satisfactory combustion.<sup>14b</sup> Finally,  $\Delta H_{\rm H}$  of diimide depends on a mass spectrometric determination of  $\Delta H_{\rm f}$ , which shows wide variations among different laboratories. No direct determination of the  $\Delta H_{\rm H}$  of azoalkanes or the heat of oxidation  $(\Delta H_{ox})$  of hydrazines has been published. We report here the  $\Delta H_{ox}$  of 1,2-di-*n*-butylhydrazine, a value that leads directly to the  $\Delta H_{\rm H}$  of azo-*n*-butane in hexane and to the  $\Delta H_{\rm f}$ of di-n-butylhydrazine.

# Results

Because aliphatic hydrazines are subject to oxidation on standing in air, samples awaiting combustion under an oxygen atmosphere are likely to be unstable. We therefore chose solution calorimetry to determine the  $\Delta H_{\rm H}$  of azo-*n*-butane (ANB) using Turner's hydrogenation calorimeter.<sup>1</sup> Ethanol solutions of ANB were hydrogenated with a large excess of 10% Pd/C catalyst, but the heats obtained varied from -14.9 to -26.8 kcal/mol. It was found that fresh catalyst and ANB led to unexpectedly exothermic reactions and that the hydrogen uptake exceeded the theoretical value by as much as 30%. A second injection of ANB into the used catalyst gave lower  $\Delta H_{\rm H}$  values and usually more correct H<sub>2</sub> uptakes, but the reaction was slower. Although GC analysis of the mixture after reduction showed only di-n-butylhydrazine (DNBH), a control experiment revealed that *n*-butylamine would not have been detected. Thus, injection of 2.44 mmol of n-butylamine into the calorimeter charged with catalyst in ethanol led to the uptake of 1.64 mmol of  $H_2$ ; however, no *n*-butylamine

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TABLE I:	Heats of	Formation a	nd Hydrogenation	(kcal/
mol) of Azo	alkanes a	nd Hydrazine	es	•

compound	$\Delta H_{\rm f}({\rm s~or~l})^a$	$\Delta H_{\rm f}({\rm g})$	ΔH <sub>H</sub> <sup>b</sup>
NCMe <sub>2</sub> C-N=N-CMe <sub>2</sub> CN <sup>7</sup>	54.6°		-26.2°
NCMe <sub>2</sub> C-NHNH-CMe <sub>2</sub> CN <sup>7</sup>	28.5		_ ,
Ph-N=N-Ph <sup>8-10</sup>	74.1cd	96.1 <sup>10</sup>	-21.7°
Ph-NHNH-Ph	52.4c.e		
CH <sub>3</sub> -N=N-CH <sub>3</sub>		32.14,12, 35.613	-14.1/8
CH <sub>3</sub> -NHNH-CH <sub>3</sub> <sup>14</sup>	12.1 <sup>15,h</sup>	21.5	
H-N=N-H		50.7 <sup>16</sup> , 32 <sup>17</sup> , 36 <sup>18</sup> , >42.1 <sup>19</sup>	-17.2
H <sub>2</sub> NNH <sub>2</sub> <sup>20</sup>	12.1*	22.8	

<sup>a</sup> From the heat of combustion of liquid or solid compounds. <sup>b</sup> Heat of hydrogenation of the azo group. <sup>c</sup> Solid. <sup>d</sup> Average of values from refs 9 and 10. • Average of values from refs 8 and 11.  $\int$  Gas. \* Based on  $\Delta H_f$ of azomethane = 35.6 kcalmol. <sup>h</sup> Liquid. <sup>l</sup> Based on  $\Delta H_f(HNNH) = 40$ kcal/mol.

TABLE II: Oxidation of DNBH with O<sub>2</sub> and 10% Pd/C

DNBHª	catalyst <sup>b</sup>	run time <sup>c</sup>	O <sub>2</sub> uptake, mmol	$\Delta H_{e}^{d}$	Δ <i>T</i> , °C <sup>e</sup>	$\Delta H_{\mathrm{ox}}$	$\Delta H_{\mathrm{H}}^{g}$
0.98	none	160	0.56	116.89	0.4205	-50.15	-18.21
1.05	none	160	0.60	116.83	0.4467	-49.70	-18.67
1.28	180	30	0.64	138.69	0.4607	-49.92	-18.45
1.25	180	30	0.63	138.69	0.4514	-50.08	-18.28
1.35	180	30	0.67	138.69	0.4849	-49.82	-18.55
0.77	32	160	0.36	137.59	0.2801	-50.05	-18.32
1.35	32	160	0.69	137.59	0.4885	-49.79	-18.58

<sup>a</sup> mmol of DNBH injected. <sup>b</sup> Weight of catalyst used (mg). <sup>c</sup> Data acquisition time (min). <sup>d</sup> Heat equivalent of the calorimeter (cal/°C). <sup>e</sup> Temperature rise during oxidation. <sup>f</sup> Heat of oxidation of DNBH (kcal/ mol). <sup>g</sup> Calculated heat of hydrogenation of ANB (kcal/mol).

could be found by GC, presumably because it was adsorbed onto the catalyst. A variety of other catalysts were tried with ANB, but they gave slower reactions than Pd/C. Oxidizing DNBH with mercuric oxide or with oxygen and Pd/C catalyst<sup>21</sup> proved to be a more successful approach.

Oxidation of DNBH by  $O_2$  and Pd/C. The heats of oxidation for these reactions and the derived heats of hydrogenation of ANB are given in Table II.  $\Delta H_{\rm H}$  is simply equal to  $\Delta H_{\rm f}({\rm H_2O})$  $-\Delta H_{ox} = -68.32 \text{ kcal/mol}^{20} - \Delta H_{ox}$ . The time required for complete oxidation, as determined by GC analysis, was approximately 150 min in the absence of catalyst. This long reaction time allowed excessive heat loss from the calorimeter to its surroundings, thereby increasing the experimental error. Since small amounts of catalyst caused no significant rate enhancement, several runs were carried out with as much catalyst (by weight) as DNBH. Oxygen uptake was monitored with a gas buret and was found to be close to the stoichiometric amount when catalyst was present. Without Pd/C, the  $O_2$  uptake was 14% too high, suggesting that  $H_2O_2$  and/or azoxy-*n*-butane might have formed. However,  $H_2O_2$  would not be expected to survive in the presence

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TABLE III: Oxidation of DNBH with Red HgO

DNBH <sup>a</sup>	HgO <sup>b</sup>	run time <sup>c</sup>	$\Delta H_{e}^{d}$	Δ <i>T</i> , °C <sup>e</sup>	$\Delta H_{\mathrm{ox}}$	$\Delta H_{\mathrm{H}}^{g}$
1.28	11.05	160	113.49	0.3136	-27.81	-18.86
1.31	35.73	160	112.65	0.3259	-28.02	-18.64
3.05	50.9 <sup>h</sup>	120	132.86	0.6285	-28.18	-18.49

<sup>a</sup> mmol of DNBH injected. <sup>b</sup> Amount of HgO used (mmol). <sup>c</sup> Data acquisition time (min). <sup>d</sup> Heat equivalent of the calorimeter (cal/°C). <sup>e</sup> Temperature rise during oxidation. <sup>f</sup> Heat of oxidation of DNBH (kcal/ mol). <sup>s</sup> Calculated heat of hydrogenation of ANB (kcal/mol). <sup>h</sup> Propeller stirrer without magnetic stirring bar.

TABLE IV: Heat of Solution of DNBH in Hexane

DNBH <sup>a</sup>	$\Delta H_{e}^{b}$	$\Delta T$ , °C <sup>c</sup>	$\Delta H_{s}^{d}$
0.889	149.94	-0.0113	1.91
1.43	151.12	-0.0205	2.17
1.82	139.13	-0.0273	2.09
1.65	136.96	-0.0255	2.12

<sup>a</sup> mmol of DNBH injected. <sup>b</sup> Heat equivalent of calorimeter (cal/ °C). <sup>c</sup> Temperature change. <sup>d</sup> Calculated heat of solution (kcal/mol).

of Pd/C<sup>22</sup> and no azoxy-*n*-butane was detected by GC. Although formation of 14% H<sub>2</sub>O<sub>2</sub> would make  $\Delta H_{ox}$  less negative by 0.9 kcal/mol, oxidation with and without catalyst gave similar values of  $\Delta H_{ox}$  for DNBH.

**Oxidation of DNBH by HgO.** To verify the values reported in Table II, another series of experiments with red mercuric oxide as the oxidizing agent was undertaken (cf. Table III). The calorimeter was maintained under argon to ensure the absence of oxygen.  $\Delta H_{\rm H}$  was calculated as  $\Delta H_{\rm f}({\rm H_2O}) - \Delta H_{\rm f}({\rm HgO}) \Delta H_{\rm ox}$  where  $\Delta H_{\rm f}({\rm HgO}) = -21.7$  kcal/mol.<sup>20</sup> It is apparent that the values of  $\Delta H_{\rm H}$  are similar to those in Table II. The average  $\Delta H_{\rm H}$  of ANB from Tables II and III, weighting all runs equally, is -18.51 ± 0.20 kcal/mol.

In order to check our calorimetric procedures for systematic errors,  $\Delta H_{\rm H}$  of cyclohexene was redetermined. The value obtained, 26.7 kcal/mol, is close to the one in the literature<sup>1</sup>, 27.1  $\pm$  0.08 kcal/mol.

# The Heat of Solution of DNBH in Hexane

The heat of solution  $(\Delta H_s)$  was determined by adding DNBH to hexane under argon and allowing the solution to equilibrate overnight. Any residual O<sub>2</sub> was consumed by reaction with DNBH. Samples of DNBH were then injected into the calorimeter, and the temperature drop was recorded (Table IV). The average  $\Delta H_s$  is 2.07 ± 0.11 kcal/mol. The positive sign of this value indicates that heat was required from the surroundings to break up the hydrogen bonds of neat DNBH.

#### Discussion

The value of  $\Delta H_{\rm H}$  determined here (-18.51 ± 0.20 kcal/mol) corresponds to ANB in hexane going to neat liquid DNBH. In order to convert this value to  $\Delta H_{\rm H}$  for both compounds in hexane, it is necessary to add  $\Delta H_{\rm s}$  of DNBH in hexane, which was found to be 2.07 kcal/mol. The result is  $\Delta H_{\rm H}$  (ANB, hexane  $\rightarrow$  DNBH, hexane) = -16.4 ± 0.2 kcal/mol. Assuming that this value also applies to the gas phase, we calculate from the known  $\Delta H_{\rm f}$  of ANB(g) = 2.19 ± 0.90 kcal/mol<sup>4b</sup> that the  $\Delta H_{\rm f}$  of DNBH(g) is -14.2 kcal/mol.

In view of the present results, the  $\Delta H_{\rm H}$  of sym-dimethylhydrazine in Table I is not far from the correct value, especially when one considers that the  $\Delta H_{\rm f}$  of azomethane is derived indirectly.<sup>13</sup> If we assume that azomethane has the same  $\Delta H_{\rm H}$ as ANB and that the gas-phase  $\Delta H_{\rm H}$  equals the solution phase value, the most recent  $\Delta H_{\rm f}$  value of azomethane (35.6 kcal/ mol)<sup>13</sup> allows us to calculate that  $\Delta H_{\rm f}$  (Me–NH–NH–Me(g)) is 19.2 kcal/mol, which is 2.3 kcal/mol below the previous value.<sup>14</sup> The  $\Delta H_{\rm f}$  = 44.0 kcal/mol<sup>23</sup> of Me–NH<sup>•</sup> then means that the N–N bond dissociation energy of sym-dimethylhydrazine is 68.8 kcal/mol, which is just below the 70 kcal/mol N–N bond strength of hydrazine.<sup>24</sup>

As seen in Table I, determinations of the  $\Delta H_f$  of diimide vary from 32 to 50.7 kcal/mol. Although it has been suggested<sup>17</sup> that the highest of these values<sup>16</sup> arises from isodiazene, not diimide, a recent sophisticated theoretical calculation places the  $\Delta H_f$  of diimide at 49.6 kcal/mol.<sup>25</sup> If diimide and ANB are assumed to have the same  $\Delta H_H$ , one can subtract our  $\Delta H_H$  of ANB from the  $\Delta H_f$  of hydrazine(g), giving  $\Delta H_f$  (HNNH(g)) = 39.2 kcal/mol. This value is close to the average of the four  $\Delta H_f$  values in Table I.

Finally, it is noteworthy that the  $\Delta H_{\rm H}$  of the azo group is 10.6 kcal/mol less exothermic than that of olefins (~27 kcal/mol).<sup>1</sup> This difference is attributed to the higher C-H bond strength of the alkane than the N-H bond strength of the hydrazine, based on the following treatment. The  $\pi$  bond strength of ethylene<sup>6</sup> and diimide are given by eqs 1 and 2.

$$E_{\pi}(C_{2}H_{4}) = D(C_{2}H_{5}-H) - \Delta H_{f}(H^{\bullet}) - \Delta H_{f}(C_{2}H_{4}) + \Delta H_{f}(C_{2}H_{5}^{\bullet})$$
(1)

$$E_{\pi}(N_{2}H_{2}) = D(N_{2}H_{3}-H) - \Delta H_{f}(H^{\bullet}) - \Delta H_{f}(N_{2}H_{2}) + \Delta H_{f}(N_{2}H_{3}^{\bullet})$$
(2)

Combining eq. 1 with the definition of  $\Delta H_{\rm H}(C_2H_4)$  and  $D(C_2H_5-H)$  gives eq 3 and the same treatment for diimide gives eq 4.

$$\Delta H_{\rm H}({\rm C}_{2}{\rm H}_{4}) = {\rm E}_{\pi}({\rm C}_{2}{\rm H}_{4}) + 2\Delta H_{\rm f}({\rm H}^{\bullet}) - 2{\rm D}({\rm C}_{2}{\rm H}_{5}{\rm -H}) \quad (3)$$

$$\Delta H_{\rm H}({\rm N}_{2}{\rm H}_{2}) = {\rm E}_{\pi}({\rm N}_{2}{\rm H}_{2}) + 2\Delta H_{\rm f}({\rm H}^{\bullet}) - 2{\rm D}({\rm N}_{2}{\rm H}_{3}-{\rm H})$$
(4)

Since  $\Delta H_{\rm H}({\rm C}_2{\rm H}_4)$  is more negative than  $\Delta H_{\rm H}({\rm N}_2{\rm H}_2)$ , then  $E_{\pi}({\rm C}_2{\rm H}_4)$  must be smaller than  $E_{\pi}({\rm N}_2{\rm H}_2)$  or else  $D({\rm C}_2{\rm H}_5-{\rm H})$  must exceed  $D({\rm N}_2{\rm H}_3-{\rm H})$ . Even if conservative estimates are used to calculate  $E_{\pi}({\rm N}_2{\rm H}_2)$ , its value is likely to fall below  $E_{\pi}({\rm C}_2{\rm H}_4)$  (59.4 kcal/mol).<sup>6</sup> On the other hand,  $D({\rm N}_2{\rm H}_3-{\rm H})$  (<87.5 kcal/mol)<sup>26</sup> is surely below  $D({\rm C}_2{\rm H}_5-{\rm H})$  (98 kcal/mol), presumably due to the three-electron stabilization of the hydrazyl radical.

# **Experimental Section**

Preparation of DNBH. Di-*n*-butylhydrazine (DNBH) was prepared by LiAlH<sub>4</sub> reduction of *n*-butyraldehyde azine according to the procedure of Renaud and Leitch.<sup>27</sup> DNBH was purified by distillation at reduced pressure through a packed column: bp  $50-54 \circ C/3.5 \text{ mm Hg}$ , yield 90%. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 0.91 (6H, t, J = 6.7 Hz), 1.27–1.51 (8H, m), 2.78 (4H, t, J = 6.8 Hz), 3.05 (2H, br s). <sup>13</sup>C NMR (65 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 13.9, 20.4, 30.3, 51.0.

Solution Calorimetry—General. The calorimeter employed for these experiments was an updated version of the one used by Turner<sup>1</sup> for measuring the  $\Delta H_{\rm H}$  of C–C double bonds. Temperature was monitored by a thermistor connected to a 6-1/2digit voltmeter. The 350 data points were transferred to an IBM compatible computer by means of a metrabyte MBC-488 HPIB interface card. The resistance readings were converted to temperature (°C) versus time via software and were analyzed using Microsoft Excel and Cricket Graph. The calorimeter was calibrated electrically by passing an accurately determined current and voltage through a small heating coil, which was immersed in the calorimeter solution, for a carefully measured time interval. To ensure adequate stirring, especially with the dense HgO, the glass propeller was augmented by an electromagnetically driven stirring bar. Nicholas Adams of Rice University improved this water-submersible device considerably over the original design.<sup>28</sup>

Oxidation of DNBH by Oxygen Alone. A typical experiment involved charging the calorimeter with 280 mL of hexane. The apparatus was alternately filled with  $O_2$  and evacuated through several cycles, filled to a slightly positive pressure of oxygen, and allowed to equilibrate overnight. Four determinations of the heat equivalent ( $\Delta H_e$ ) of the calorimeter plus solvent and oxygen gave a value of 116.89 ± 0.35 cal/°C. Following equilibration, a known weight of DNBH was injected and the oxygen uptake was monitored by a gas buret. The calorimeter was allowed to equilibrate, and several more calibration/oxidation measurements were made. A correction for the error caused by ANB unavoidably present in the DNBH was made based on GC analysis. After oxidation, the reaction mixture was analyzed by GC to ensure that only ANB was present.

Oxidation of DNBH by Oxygen with Pd/C. The calorimeter was charged with hexane (280 mL), 10% Pd on carbon, and a positive pressure of oxygen. The apparatus was allowed to equilibrate, and its  $\Delta H_e$  was determined as above. Injection of DNBH led to temperature rises in the range 0.45–0.49 °C. Oxygen uptake was monitored in the same fashion as in the experiments containing no catalyst.

Oxidation of DNBH with Red HgO. The calorimeter was charged with 2–11 g of red HgO and 280 mL of hexane. The solution was thoroughly degassed via six cycles of sparging with argon followed by evacuation. The apparatus was placed under a positive pressure of argon and allowed to equilibrate in the usual fashion. The  $\Delta H_e$  of the calorimeter was determined, and after reequilibration, DNBH was injected. The excess of mercuric oxide shortened the time needed for complete oxidation.

Heat of Solution. After equilibration of the calorimeter under Ar, a 0.5-g sample of DNBH was injected. A small but rapid initial temperature drop was followed by a slow rise and leveling off of the temperature, due presumably to reaction of DNBH with residual  $O_2$ . The temperature rise was only one-tenth that expected for quantitative oxidation, suggesting that all  $O_2$  had been consumed. Additional injections of DNBH caused a temperature drop without the subsequent rise caused by oxidation. Four experiments gave the data in Table IV.

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