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A NEW HYDROGEN CALORIMETER

HEATS OF HYDROGENATION OF ALLYL AND VINYL UNSATURATION ADJACENT TO A RING

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Abstract—We have constructed a new calorimeter for the measurement of heats of hydrogenation of liquid olefins on palladium black catalyst in acetic acid or cyclohexane solution. The principal advantages of the calorimeter described here are that it requires samples of only 10 — 40μl, it permits repetitive sample injection and it operates under conditions for which reactions times are very short; all those reported here were complete in less than one minute. We have determined the heats of hydrogenation of sixteen allylic. vinylic, ethylidene and other olefins some of which are known from previous work and some of which are new. Comparison is made with known heats of hydrogenation and new results are interpreted in terms of strain energies. The strain energies of hexamethyldewarbenzene and its hydrogenation product are discussed. Both have remarkably low strain energies and both are probably rather flexible molecules which distort easily to relieve strain and crowding of their pendant Me groups.

THE enthalpy changes accompanying hydrogenation of olefins are fundamental to much current structural and conformational theory in organic chemistry.[1,2] Whatever may be one's persuasion regarding the controversy over resonance and hyperconjugation,[3] the heat of hydrogenation of any compound is an experimental fact which present or future theory must explain. Considering the importance of hydrogen calorimetry, it is surprising how few research groups have entered the field. The definitive work of Kisitiakowsky[4] was followed by a paper by Williams,[5] three by Skinner *et al.*[6–8] and a series by Turner *et al.*[9] In all, the heats of hydrogenation of fewer than 200 compounds have been determined in the past 35 years.

We have constructed a calorimeter which is so simple in design as to make the determination of heats of hydrogenation a rapid and routine operation rather than a specialized research field. The device has the added advantage of using only microliter samples, permitting purification by means of an ordinary gas chromatography column.

EXPERIMENTAL

Apparatus. The calorimeter was a cylindrical plastic screw-cap container as shown in Fig 1. The cap was drilled off center to receive a No. 1 one-hole rubber stopper into which was inserted an NMR tube which served as a thermistor well. The stopper was inserted upside down so that it would not be blown out by H_2 pressure inside the chamber. A horizontal pin flush with the cap prevented the stopper from being pushed into the chamber. A hypodermic needle protruded through the stopper to admit H_2. A second needle could be inserted through the stopper adjacent to the first for injecting the sample, a liquid olefin. Both needles are shown in place in Fig 1. A 25 µl fixed needle syringe of the kind used in gas chromatography was used to inject replicate samples of 20 µl. The syringe had a mechanical stop of the Chaney type[10] to ensure exact replication of samples. The thermistor[11] protruded to the bottom of the thermistor well which was partly filled with n-butyl phthalate to facilitate heat transfer. The thermistor leads were con-

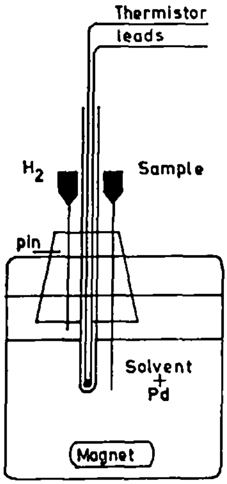

FIG 1. Reaction chamber of the calorimeter

nected across a Wheatstone bridge[12] in the usual way[13] and potential across the arms of the bridge was registered on a recorder[14] which shows full scale deflection for a 1 mv potential difference.

Constant potential was maintained across the bridge by a 6 v lead storage battery which was recharged after each use. A variable series resistance, usually about 3000 ohms, between the battery and the bridge controlled the sensitivity of the temperature sensing apparatus. The calorimeter, containing a magnetic stirring bar, was placed in a well in a styrofoam insulating block just large enough to accommodate it. The removable top of the insulating block was cut with a hole to facilitate cooling the calorimeter and to allow sample injection as described below. The hydrogen inlet needle was connected to a hydrogen tank by a leak proof "twist type" luer joint.[15] A stirring magnet spinning just below the calorimeter to activate the magnetic stirring bar within was powered by an external motor, thermally well shielded from the calorimeter. The drive shaft connecting the magnet to the motor was of a fibrous plastic to prevent heat transfer from the motor to the calorimeter. A "Variac" resistance was used to control the stirring speed. Under the conditions described here, stirring speed did not effect experimental observations to any detectable extent. Extremely high and extremely low stirring speeds were avoided but no strict controls were used.

Reagents. All reagents were obtained from Aldrich Chemical Co., except for octane from Shell Oil, cyclooctene and cyclooctane from Columbian Chemical Co., 1-pentene and n-pentane from Phillips Petroleum Co., and cyclohexene, hydrogen and 5% palladium catalyst on charcoal from Matheson, Coleman and Bell. All but a few of the alkenes were contaminated by 1 to 5% of impurity as indicated by gas chromatography.

Procedure. The substance to be hydrogenated was purified by collecting the principal effluent fraction from a gas chromatography column[16] by standard techniques.[17] Each purified sample was shown to be more than 99% pure by gas chromatography.

Twenty or twenty-five ml of solvent (initially glacial acetic acid, later, several other solvents) were placed in the calorimeter along with the stirring bar and 0·6 g of 5% Pd catalyst on charcoal. The threads of the calorimeter were coated with quick-drying sealant[18] and its cap was firmly tightened down over the sealant. After 10 min drying time, the calorimeter and charge were placed in the insulating block and the insulating top was clamped in place. The calorimeter was now ready for use; it needed only to be connected with the external circuitry.

We were troubled in preliminary work by slight resistance changes during a run at the copper-to-copper connections between the thermistor leads and the leads to the Wheatstone bridge. These were eliminated by the use of silver-to-silver knife clamps.

Catalyst activation. H_2 was admitted to the reaction chamber at a pressure of 2 atm, the valve on the H_2 tank was closed and excess H_2 was bled off through a T joint and clamp between the tank and calorimeter. The T joint was closed, and the entire procedure was repeated 4 or 5 times to flush the system clear of any residual air. During hydrogenation, the tank valve remained open and the regulating diaphragm was adjusted to maintain 2 atm pressure in the calorimeter throughout the subsequent steps. The heat of adsorption of hydrogen on the catalyst was registered on the recorder which rapidly went off scale during the flushing procedure. The recorder was brought back on scale by reducing the resistance of the variable arm of the Wheatstone bridge by one ohm. If a one-ohm change of the bridge resistance caused the recorder to go off scale in the opposite direction, the sensitivity was reduced by increasing the resistance in series with the wet cell. At the proper series resistance, it should be possible to keep the recorder on scale by manipulating the Wheatstone bridge, i.e., a one-ohm change of the bridge should bring about a slightly less than full-scale deflection of the recorder.

Under the conditions we describe, adsorption of H_2 on 0·6 g of catalyst brought about a change in temp of about a degree and was compensated for by a change of about 5 ohms on the Wheatstone bridge. After adsorption was complete (in about 3 min) the recorder stopped its rapid advance to the high temp end of the scale and commenced a slow drift downward due to heat leak away from the calorimeter.

Ambient temp was restored by holding a small piece of dry ice over the hole cut in the top of the insulation shield for that purpose. Cold CO_2 flowing down over the calorimeter decreased its temp by the necessary degree or so in less than a min. 2 or 3 more min sufficed to establish temp equilibrium indicated by a relatively steady base line as shown at the bottom of Fig 2. The entire reduction procedure took about 10 min.

Hydrogenation. The hydrogenation procedure began by injecting 20μl of a known standard which has a well-established heat of hydrogenation and noting the recorder deflection. The rubber stopper functioned as a septum and resealed itself when the needle was withdrawn. The known standard, l-hexene in these studies ($\Delta H = -30{\cdot}3$ kcal/mole),[8] played the same role as benzoic acid in oxygen calorimetry.

The calorimeter was then cooled by the dry-ice procedure just described and temp equilibrium was reestablished. A sample of the unknown was injected under conditions identical to those for the known. The ratio of recorder deflections enabled us to compute the heat of hydrogenation of the unknown. Reaction time was 20 sec – 1 min. The process may be repeated indefinitely. We have hydrogenated 40 samples on one catalyst charge.

Calculation of ΔH involved a simple ratio of recorder scale deflections SD, per millimole of sample injected, mM, to the heat of hydrogenation, ΔH.

$$\frac{\mathrm{SD/mM}}{\Delta H} = \frac{\mathrm{SD'/mM'}}{\Delta H'}$$

Primed quantities pertain to the known compound and unprimed quantities pertain to the unknown. If, as in this work, 1-hexene is used as the standard, substitution of densities, ρ, mol wts, MW, and $-30{\cdot}3$ kcal/mole for the heat of hydrogenation of the standard gives

$$\Delta H = -0{\cdot}242\,(\mathrm{Mw}/\rho)\,r$$

where r is the ratio of scale deflections, (SD/SD′).

After a series of hydrogenation runs, it was necessary to determine whether hydrogenation had been complete and to identify the reaction product. Hydrogen pressure was released, the apparatus was dismantled and the catalyst quickly settled to the bottom of the reaction vessel allowing withdrawal of two or three ml of supernatant liquid. In each case reported here, gas chromatographic analysis at high sensitivity yielded a chromatogram identical to that of the solvent with an extra peak identifiable as hexane and only one other peak identifiable as the hydrogenation product of the unknown.

Qualitative identification of the reaction product was usually carried out by making up a synthetic mixture of the expected reaction products in the solvent. Comparison of the gas chromatograms of the synthetic reaction mixture and the real one showed them to be identical. We have also employed standard IR and NMR identification techniques to reaction products which are sufficiently nonvolatile to permit easy evaporation of the solvent.

RESULTS AND DISCUSSION

We wished to determine the potentialities of the calorimeter by testing its precision, determining ΔH of hydrogenation for some known compounds and pursuing a new investigation into allylic and vinylic unsaturation and the possible interaction of these groups with an adjacent ring.

In order to get an idea of the precision of the method, we hydrogenated 11 replicate samples of 1-hexene and computed the relative average deviation of the scale deflections, SD, from their mean. The result was 0·49%.

Since the heat output of mixtures of olefin in a saturated solvent should be a linear function of the amount of olefin present, another test of precision is to obtain SD as a function of millimoles of olefin, fit the data by a least squares treatment of the data and obtain the standard deviation of individual points from the first degree curve so obtained. Accordingly, a number of samples large enough to be statistically meaningful was hydrogenated. The results are shown in Table 1. The meaning of the symbols is as follows: SD_{100} is the scale deflection for the pure olefin obtained from the least squares treatment, n is the number of data taken. σ is the standard deviation of all points from the linear function and the last column, the ratio of σ to SD_{100} multiplied by 100 is a kind of percent standard deviation which is one way of estimating a probable percent error. These data show that the ratio is less than one percent for three of the four compounds studied. Nonlinear behavior would indicate an error which depends on the amount of olefin in a nonlinear way, say a side reaction or incomplete hydrogenation.

TABLE 1. STANDARD DEVIATIONS FOR SD AS LINEAR FUNCTION OF mM OF OLEFINS

Compound	n	SD_{100}, inches	σ	(σ/SD_{100}) 100
Cyclohexene	15	9·08	0·125	1·38
Methallylbenzene	23	8·01	0·064	0·80
Allylbenzene	20	9·15	0·071	0·78
Vinylcyclohexane	19	9·58	0·084	0·87

One of the advantages of our calorimeter is that we are able to obtain a number of data large enough to treat statistically provided that the sample is available in sufficient amount. This is not true using a conventional calorimeter without a prohibitive expenditure of time.

TABLE 2. HEATS OF HYDROGENATION OF SOME SIMPLE OLEFINS

Compound	Number of Determinations	$-\Delta H$ kcal/mole This investigation	Previous results
1-Pentene	6	28·5 ±0·3	30·1[a]
1-Octene	5	28·3 ±0·6	28·78 ±0·24[b]
Cyclopentene	7	26·2 ±0·2	25·7
Cyclohexene	14	26·9 ±0·6	27·1 ±0·08[d]
Cyclooctene	3	22·4 ±0·3	22·98 ±0·10[d]

[a] Calculated from heats of combustion

[b] Ref 21

[c] Unpublished datum referred to in 9[b]

[d] Ref 2

Table 2 shows the heats of hydrogenation as determined by our method compared with previously determined values. Uncertainties included in this table are relative average deviations from the mean of a series of replicate determinations. They express, therefore, minimum random errors and are not confidence limits. It is difficult to arrive at a quantitative estimate of error in Table 1 but we feel that the data are reliable to within about a kilocalorie per mole, which is the standard in this field.

In view of the small sample size, 13–20 mg, it is remarkable that the results should be as good as they are. Good accuracy is due to the rapidity of hydrogenation under these conditions. Reaction times of 20 sec to 1 min make instrumental drift negligible and minimize errors due to extrapolation of heat-leak curves before and after reaction occurs. Watt and Walling[19] have shown that hydrogenation of higher monoolefins proceeds by a zero order reaction, hence their reaction times are directly proportional to sample size. all other things being equal. Zero order reactions are frequently limited by the catalyst surface area available to the reactants hence it is not surprising that by using a large amount of catalyst adsorbed on activated charcoal, we achieved a significant reduction in reaction time.

As solvents, we used glacial acetic acid, n-hexane, n-pentane, cyclohexane and cyclooctane. We did not observe the usual variation of reaction rate with solvent.[20] Indeed, reaction times in cyclohexane were shorter than those in glacial acetic acid contrary to the usual observation. In our early work, we relied on the most commonly used solvent in liquid-phase hydrogenation, glacial acetic acid. All results in Table 2, except those for 1-pentene and 1-octene were obtained using acetic acid.

The heat of solution of the reaction product* should be subtracted from the measured heat of hydrogenation to obtain the true heat of hydrogenation corrected for interactions between the reaction product and the solvent. This correction may increase or decrease the magnitude of the true heat of hydrogenation according to the sign of the heat of solution. We have observed this correction to be as high as 2·12 ± 0·14 kcal/mole[21] and it may well be higher in some cases. This is larger than experimental error, but the correction is usually ignored when deductions from experimental data are based on fairly gross differences in heats of hydrogenation.

Heat of solution errors pose a real problem, however, because they cast doubt on one of the strong points of hydrogenation calorimetry over traditional combustion calorimetry, that of greater accuracy of comparative enthalpy measurements. We therefore set out to reduce this error to a minimum.

Our method tends to minimize heat of solution error by its very nature because at least part of the error cancels out between the unknown and standard, both of which are hydrogenated in the same solvent. Only if the reaction products of the unknown and standard differ widely in their heats of solution is an error introduced. The error can be further reduced by choosing a solvent as similar to the reaction products as possible, thus approximating an ideal solution between reaction products and solvent.

We tried cyclooctane as the solvent for hydrogenation of cyclooctene but found that our cyclooctane contained an impurity which poisoned even the proportionately large amount of catalyst we used.

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* The quantity of interest is the heat of solution of the reaction product in the solvent because in thermochemistry, one is interested only in the initial and final states of the system and not in the intermediate states. (See also Ref 5).

We then hydrogenated 1-pentene in n-pentane of very high purity. There could be no heat of solution at all for n-pentane in itself and the heat of solution for n-hexane in n-pentane should be negligibly small, thus eliminating solvent error entirely. The results were somewhat low (Table 2). This could be the result of the difference between gas phase and liquid phase hydrogenation. (Compare the results in Refs 4 and 9). The low result however, could also be due to the volatility of n-pentane. Even the small changes in temperature encountered here could vaporize enough solvent to absorb a significant amount of heat. Although corrections could have been made, we chose to investigate cyclohexane, a solvent which is less volatile, was available to us in high purity and is structurally similar to the hydrogenation products of the olefins in Table 3. Cyclohexane was also the solvent for cyclooctene in Table 2.

We obtained approximate heats of solution of ethylbenzene, n-propylbenzene, ethylcyclohexane and n-propylcyclohexane in glacial acetic acid and in cyclohexane by injecting 20 µl samples of these products into the calorimeter under the conditions used for hydrogenation. The calorimeter was not designed for accurate determination of heats of solution, however, and we feel these results can be relied on only in a qualitative way. The heats of solution of these substances in cyclohexane were $\frac{1}{4}$ to $\frac{1}{2}$ as large as in acetic acid which represents a considerable reduction in heat-of-solution error. Since we also observed the shortest reaction times in cyclohexane, it was the solvent of choice in the work represented in Table 3 below.

TABLE 3. HEATS OF HYDROGENATION OF SOME OLEFINIC COMPOUNDS CONTAINING RINGS
$-\Delta H$ kcal/mole

	Previous work	This work
1. Allylcyclopentane	—	30·9 ±0·4
2. Allylbenzene	—	30·2 ±0·2
Allylbenzene	—	30·3 ±0·2[a]
3. Methallylbenzene	—	28·5 ±0·2
4. Phenylacetylene	70·1 ±0·2[b]	64·7 ±0·9
5. Vinylcyclopentane	—	28·4 ±0·2
6. Ethylidenecyclopentane	24·88 ±0·12[c]	24·2 ±0·2
7. 1-Ethylcyclopentene	23·56 ±0·11[c]	23·5 ±0·2
8. Vinylcyclohexane	—	27·9 ±0·8
9. Ethylidenecyclohexane	26·32 ±0·04[c]	26·2 ±0·3
10. 1-Ethylcyclohexene	25·08 ±0·13[c]	—
11. Hexamethyldewarbenzene	—	31·4 ±0·7

[a] Acetic acid solvent
[b] Ref. 7
[c] Ref 9e
[d] Ref 19

We attribute the maximum in Fig 2 to rapid transfer of heat generated by the reaction to the stirred reaction mixture followed by slow dissipation of heat from the reaction mixture to the calorimeter and its fittings. The graphical method used to treat the curve in Fig 2 amounts to extrapolating out the heat capacity of the calorimeter and fittings and comparing temperature increments of the solution independent of the calorimeter. Heat rise is measured by the vertical in Fig 2 in accord with Sturtevant's recommendation for fast reactions.[22]

Table 3 shows a series of experimental results for eleven compounds, each containing a double or triple bond and a ring. The first three allylic compounds show essentially normal behavior. Allycyclopentane and allylbenzene have heats of hydrogenation which are almost the same as the terminal double bond of a linear olefin. Methallylbenzene is lower than allylbenzene, but this is to be expected; the deviation is in the direction and of the magnitude one would expect for a double bond interacting with a Me group in the α position. These results indicate that neither the saturated rings nor the phenyl group interacts with the double bond in the β position.

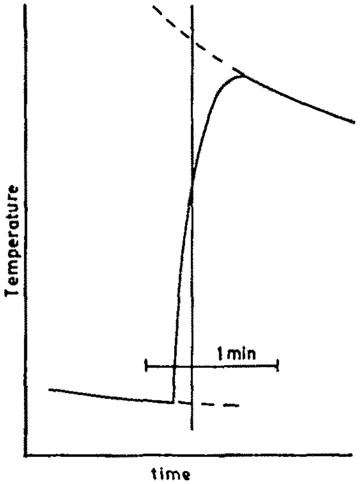


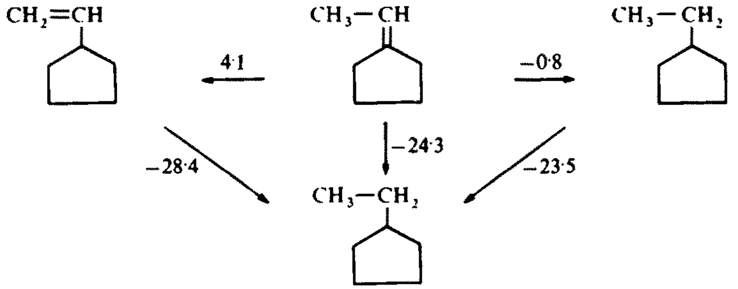
FIG 2. A typical temperature-time plot for hydrogenation

We observed a heat of hydrogenation for phenylacetylene of $-64·7 \pm 0·9$ kcal/mole in glacial acetic acid. This value does not agree with Flirtcroft and Skinner's value of $-70·1 \pm 0·2$ kcal/mole.[7] We hydrogenated more than two dozen samples, repeating the determination using cyclohexane or acetic acid as solvent without observing any significant variation in the heat of hydrogenation. As a further test for completeness of reaction we hydrogenated samples of phenylacetylene in its hydrogenation product, ethylbenzene, and plotted heat output as a function of concentration of phenylacetylene. The resulting function was linear, its slope gave a value ΔH in agreement with our entry in Table 2 and the intercept is a kcal/mole or less from the origin indicating a small heat of solution correction. Gas chromatographic examination of the reaction product mixture and comparison with a synthetic reaction mixture "doped" with the expected reaction product, ethylbenzene, revealed no abnormalities.

Kistiakowsky showed that the triple bond is very susceptible to interactions with adjacent groups. The methyl group in methylacetylene ($\Delta H = -69·70$ kcal/mole^{4a}) stabilizes the triple bond in acetylene ($\Delta H = -75·06$ kcal/mole^{4a}) by 5·36 kcal/mole while the methyl group in propene ($\Delta H = 30·12$ kcal/mole^{4b}) stabilizes the double bond in ethylene ($\Delta H = -32·82$ kcal/mole^{4a}) by about half as much, 2·70 kcal/mole. If we suppose that whatever stabilization takes place for a triple bond should be about twice that for a double bond, the heat of hydrogenation of styrene exclusive of the ring contribution (−27·68 kcal/mole[4e]) shows that the ring stabilizes the double bond in styrene by 5·12 kcal/mole and leads us to expect stabilization of acetylene of 10·24 kcal/mole. This gives a predicted value of −64·82 for the gas phase hydrogenation of the triple bond in phenylacetylene and a value slightly lower than that for the liquid phase hydrogenation. Compare our value of −64·7 ± 0·9 kcal/mole.

Further indication of significant interaction between the ring and the acetylenic linkage is provided by the yellow color of phenylacetylene indicative of a smaller π,π* energy-level separation in phenylacetylene than in either benzene or acetylene which are colorless.

Results 6–8 in Table 2 can be correlated with each other and with Turner's data[9] by the reaction scheme.



Our value for the heat of isomerization of ethylidenecyclopentane to ethylcyclopentene is −0·8 ± 0·4 kcal/mole as compared with Turner's value of −1·32 ± 0·23 kcal/mole.[9e] The comparison is valid within experimental error.

We have followed Turner's method[9h] of assessing strain energy for some of the molecules in Table 3. The heat of formation of ethylcyclopentane is −30·37 kcal/mole[23] at 25° which leads to heats of formation of −2·0, −6·1 and −6·9 kcal/mole for vinylcyclopentane, ethylidenecyclopentane and ethylcyclopentene respectively. The heats of formation of the hypothetical "strain free" molecules can be calculated by Franklin's method[24] and are −5·81, −9·65 and −9·65 kcal/mole. Comparison to the observed values lead to strain energies of 3·8, 3·6 and 2·8 kcal/mole as compared to cyclopentane which has a ring strain of 6·1 kcal/mole as compared with strain free C_5H_{10}. Evidently some stabilization takes place in all three molecules but it is not much and not very different from one molecule to another.

Similar calculations on vinylcyclohexane, ethylidenecyclohexane and ethylcyclohexene lead to strain energies of 2·4, 0·3 and 1·4 kcal/mole, based on a heat of formation of −41·05 for ethylcyclohexane at 25°.[24] The results are again similar and not very different from cyclohexane which has a strain energy of 0·15 kcal/mole as compared with strain free C_6H_{12}. The absolute values of these strain energies are suspect because they rest on the assumption that the heat of hydrogenation is the same in solution as it is in the vapor phase whereas those comparisons which have been made indicate a difference of a kcal/mole or more. Strain energies calculated by the same method do have meaning, however, when they are compared with each other.

Hexamethylbicyclo [2.2.0] hexa-2,5-diene, hexamethyldewarbenzene (HMDB) has a strain free heat of formation of −10·0 kcal/mole. Its heat of combustion in the liquid state has been given as $-1765 \pm 1{\cdot}1$ kcal/mole by Schafer[25] which leads to a heat of formation of 22 kcal/mole. One can obtain an approximate value for the heat of formation of HMDB vapor suitable for comparison with Franklin's data by adding the heat of vaporization of HMDB calculated from Trouton's rule to the heat of formation of liquid HMDB. Taking Trouton's constant to be 21 and the b.p. of HMDB to be about 152°,[25] the resultant heat of formation, 31 kcal/mole, leads to a strain energy of 41 kcal/mole, remarkably low for a molecule suffering the structural liabilities of fused four membered rings and seriously crowded Me groups.

Since doubt has already been cast on the absolute value of the strain energies computed here, it is useful to calculate the upper limit of the strain energy by an alternate method. The heat of isomerization of HMDB to hexamethylbenzene (HMB) is $-59{\cdot}5$ kcal/mole.[26] With the enthalpy of formation of HMB ($-38{\cdot}58$ kcal/mole[27]) and the enthalpy of vaporization (19·9 kcal/mole[28]), one may compute a heat of formation of HMB vapor which is $-18{\cdot}7$ kcal/mole. The heat of formation of HMDB has an upper limit of 40·8 kcal/mole, the algebraic sum of the heat of formation of HMB and the heat of isomerization of HMDB to HMB. The result is an upper limit to the heat of formation of HMDB because it contains the implicit assumption that isomerization of HMDB to HMB, both species being in the vapor state, proceeds with the same enthalpy change as the isomerization of HMDB liquid to HMB solid. We know, however, that the vapor-phase reaction brings about an enthalpy change which is smaller by the difference between the heat of vaporization of HMDB and the heat of sublimation of HMB. The calculated strain energy, 50·8 kcal/mole will also be high by the same amount.

Even the upper limit to the strain energy is lower than twice the strain energy of a cyclobutane or a substituted cyclobutene ring($\sim$26 kcal/mole) indicating that the HMDB molecule is more flexible than might be expected. Low strain energy suggests that some strain is lost through torsional relaxation. This thermochemical conclusion is in agreement with the structural studies of Cardillo and Bauer.[29]

Hydrogenation of HMDB under mild conditions, produces 1, 2, 3, 4, 5 endo, 6 endohexamethylbicyclo [2.20] hex-2-ene (HBH) in which only one of the double bonds present has been hydrogenated.[25] As a precaution against partial hydrogenation of both double bonds resulting in a mixture of products, we separated the reaction mixture from the catalyst and took a gas chromatogram at high sensitivity. The chromatogram was identical to that of pure cyclohexane except for one peak at long retention time corresponding to the reaction product. Evaporation of the cyclohexane produced a minute amount of clear oily liquid which by its absorption of IR radiation at 1680 cm^{-1}, its freezing point and NMR[30] spectrum proved to be HBH.

The heat of hydrogenation of HMDB is $-31{\cdot}4$ kcal/mole which leads to a strain energy of 35 kcal/mole and an upper limit of 45 kcal/mole for the reaction product by computing the heat for formation of HBH and comparing it with "strain free" HBH. While we have little confidence in the absolute strain energies for HMDB and HBH, we feel that the difference of 5·8 kcal/mole between them is significant as is the difference between the heat of hydrogenation of HMDB and 1,2-dimethylcyclobutene,[9h] $31{\cdot}4–25{\cdot}4 = 5{\cdot}0$ kcal/mole. We feel that hydrogenation, while it no doubt increases crowding about the carbon atoms involved, also increases the flexibility of the molecule as a whole by converting a rigid double bond into a single bond with free rotation. We propose that this added flexibility allows the molecule to assume a skewed conformation which confers stability by relaxing crowding and nonbonded repulsions among methyl groups with an over-all relaxation energy of about 5 kcal/mole.

Turner has proposed a similar conformational change during the hydrogenation of bicyclooctene to bicyclooctane but the magnitude of the relaxation energy is much smaller. One would expect any conformational relaxation in HMDB to be accompanied by a relatively large energy effect because of the severe crowding of the Me groups.

It may be that the skewed conformation is no longer able to align itself with the active sites on the Pd catalyst so as to receive adsorbed hydrogen. This would account for the extraordinary stability of the second double bond in HMDB under mild catalytic hydrogenation.

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