trated to dryness under reduced pressure at room temperature. The residue was treated with 80 ml. of ice-cold water, and the insoluble material was filtered and washed with 20 ml. of cold acetone. The dry product (0.9 g.) melted at 181–183° dec. After two recrystallizations from glacial acetic acid, it melted at 183–185° dec. Calcd. for $C_8H_8O_3$ (152.1): C, 63.1; H, 5.3. Found: C, 62.5; H, 5.4. A test for nitrogen was negative. The substance is soluble in hot acetone and glacial acetic acid, and is sparingly soluble in hot ethanol and in water. It reduces Fehling solution. Its absorption spectra at *p*H 2 and 10 are given in Fig. 1.

A 2,4-dinitrophenylhydrazone was prepared by the addition of 5 ml. of the 2,4-dinitrophenylhydrazine reagent[13] to a solution of 0.1 g. of the product in 20 ml. of ethanol. The red crystalline powder (0.12 g.) melted at 277–280°; after two recrystallizations from ethanol–ethyl acetate. it melted at 280° dec. Calcd. for $C_{14}H_{12}N_4O_6$ (332.3): C, 50.6; H, 3.6; N, 16.9. Found: C, 50.7; H, 3.8; N, 17.1.

A semicarbazone was prepared by the addition of 0.25 g. of semicarbazide hydrochloride to a hot solution of 0.2 g. of the product in 10 ml. of water containing 0.6 g. of sodium acetate. The mixture was heated for 5 minutes on the steam-bath and chilled; the resulting crystalline product (0.2 g.) melted at 165° dec. After 3 recrystallizations from water it melted at 168° dec. Calcd. for a semicarbazone of a dimer, $C_{17}H_{19}N_3O_6$ (361.35): C, 56.5; H, 5.2; N, 11.6. Found: C, 56.4; H, 5.4; N, 11.6.

An osazone was prepared by the addition of 0.6 g. of phenylhydrazine hydrochloride and of 0.5 ml. of saturated sodium bisulfite solution (to prevent the formation of tarry products) to a hot solution of 0.2 g. of the product in 10 ml. of water containing 1.1 g. of sodium acetate. The mixture was heated for about 20 minutes on the steam-bath and chilled; the resulting yellow product (0.25 g.) melted at 190°. After 5 recrystallizations from ethanol–water it melted at 198–199°. Calcd. for $C_{20}H_{18}N_4O$ (330.3): C, 72.7; H, 5.45; N, 16.9. Found: C, 72.3; H, 5.6; N, 16.7.

For the oxidation of the product with periodate, 600 mg. (2.6 millimoles) of $NaIO_4$ was added to a solution of 200 mg. (1.3 millimoles) of *p*-hydroxymandelaldehyde in 300 ml. of water. The mixture was allowed to stand overnight at room temperature, extracted 10 times with 50-ml. portions of ether, and the combined ether extracts were concentrated to dryness. The residue was dissolved in 5 ml. of ethanol; 2 ml. of glacial acetic acid and 0.5 ml. of phenylhydrazine were added. The resulting phenylhydrazone melted at 176°. A mixed melting point with an authentic sample of the phenylhydrazone of *p*-hydroxybenzaldehyde showed no depression.

The quantitative determination of the formic acid produced on oxidation with periodate was performed in the manner described by Potter and Hassid.[14] When 100 mg. (0.65 millimole) of *p*-hydroxymandelaldehyde in 150 ml. of water was treated with 140 mg. (0.65 millimole) of $NaIO_4$, only 14.3 mg. (0.31 millimole) of formic acid was released. However. upon treatment of same amount of the aldehyde with 350 mg. of $NaIO_4$, the expected amount (30.3 mg., 0.66 millimole) of formic acid was released.

Reaction of *p*-Hydroxycinnamic Acid Methyl Ester with HNO_2.—To a solution of the ester (1 g., 0.0056 mole) in 15 ml. of dioxane was added a solution of $NaNO_2$ (0.4 g., 0.0056 mole) in 15 ml. of water; the mixture was acidified with 5 *N* hydrochloric acid to *p*H 2. Upon standing at room temperature for 4 hours, a yellow precipitate (0.65 g., yield 58%) separated. After recrystallization from ethanol. the product melted at 148°. Calcd. for $C_{10}H_9O_5N$ (223.2): C, 53.8: H, 4.1; N, 6.3. Found: C, 53.6; H, 3.8; N, 6.4. The same product was obtained when 0.2 g. of the ester was treated with 0.1 g. of $NaNO_2$ in 300 ml. of dilute aqueous hydrochloric acid (*p*H 2). Saponification of the product with 2 *N* alcoholic KOH gave an acid which melted at 223–225° after recrystallization from ethanol. Calcd. for $C_9H_7O_5N$ (209.1): N, 6.7. Found: N, 6.7. Johnson and Kohmann[15] prepared 3-nitro-4-hydroxycinnamic acid and reported a melting point of 223° for the compound; they also reported a melting point of 142–144° for the methyl ester.

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[13] G. D. Johnson. THIS JOURNAL. **73**, 5888 (1951).

[14] A. L. Potter and W. Z. Hassid. *ibid.*. **70**, 3488 (1948).

[15] T. B. Johnson and E. F. Kohmann. *ibid.*. **37**, 166. 1876 (1915).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE RICE INSTITUTE]

Heats of Hydrogenation. I. Apparatus and the Heats of Hydrogenation of Bicyclo[2,2,1]heptene, Bicyclo[2,2,1]heptadiene, Bicyclo[2,2,2]octene and Bicyclo[2,2,2]octadiene

BY RICHARD B. TURNER, W. R. MEADOR AND R. E. WINKLER

RECEIVED FEBRUARY 25. 1957

A calorimeter for the measurement of heats of catalytic hydrogenation in solution is described together with the results obtained for hydrogenations of bicyclo[2,2,1]heptene (−33.1 kcal./mole). bicyclo[2.2.1]heptadiene (−68.1 kcal./mole). bicyclo[2,2,2]octene (−28.3 kcal./mole) and bicyclo[2,2,2]octadiene (−56.2 kcal./mole) in acetic acid at 25°.

Some years ago Kistiakowsky[1] and his associates measured the heats of catalytic hydrogenation of a variety of unsaturated organic substances in the gas phase at 82°. The results obtained for the fifty-one compounds that were included in this investigation, have had important theoretical consequences of continuing interest. Since the gas phase technique is applicable only to substances possessing appreciable volatility, extension of the method to the liquid phase (29°) was undertaken in the Harvard laboratories by Williams,[2] and the heats of hydrogenation of nine additional compounds were determined by the latter procedure in 1942. Since that time no further experiments involving direct measurements of heats of hydrogenation have been reported, and in view of the considerable potential of the method, a continuation of this study appeared to be most desirable. The present paper constitutes the first report of work carried out in this Laboratory with the object of examining heat changes involved in reactions of the type

$$\text{X(dissolved)} + \text{H}_2\text{(gas)} \longrightarrow \text{Y(dissolved)}$$

conducted in acetic acid solution at 25°.

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[1] (a) G. B. Kistiakowsky. H. Romeyn. J. R. Ruhoff. H. A. Smith and W. E. Vaughan. THIS JOURNAL. **57**, 65 (1935): (b) G. B. Kistiakowsky. J. R. Ruhoff. H. A. Smith and W. E. Vaughan. *ibid.*. **57**, 876 (1935): (c) **58**. 137 (1936): (d) **58**. 146 (1936): (e) M. A. Dolliver. T. L. Gresham. G. B. Kistiakowsky and W. E. Vaughan. *ibid.*. **59**. 831 (1937): (f) M. A. Dolliver. T. L. Gresham. G. B. Kistiakowsky. E. A. Smith and W. E. Vaughan. *ibid.*. **60**. 440 (1938): (g) J. B. Conn. G. B. Kistiakowsky and E. A. Smith. *ibid.*. **61**, 1868 (1939). See also J. B. Conant and G. B. Kistiakowsky. *Chem. Revs.*. **20**. 181 (1937).

[2] R. B. Williams. THIS JOURNAL. **64**. 1395 (1942).

Method.—Determination of the heats of hydrogenation of compounds included in the present series was carried out by measuring the change in temperature of the calorimeter and its contents due to simultaneous hydrogenation of the compound in question and of the platinum oxide catalyst. At the end of each hydrogenation run the calorimeter was cooled and was calibrated electrically over the temperature range and time interval recorded in the hydrogenation experiment. Correction of observed temperature changes, expressed in ohms, for the heating effects of stirring and for heat exchange between the calorimeter and its surroundings was made by application of an improved form of the Regnault–Pfaundler equation.[3] The results were further corrected for heat dissipation in the heater leads during electric calibration and for small heat changes within the calorimeter accompanying condensation of acetic acid from the vapor phase during hydrogenation. The heat of hydrogenation was calculated finally as the difference between the total heat evolved and that associated with reduction of the catalyst, the latter quantity being determined separately.

Apparatus.—The calorimeter (Fig. 1), which is based on the Williams design,[2] consists of a silvered Dewar flask of approximately 450 ml. capacity with a recessed 34/45 ground glass joint at the top, through which the calorimeter head is introduced. Two 19/38 recessed joints also pass through the top of the calorimeter and carry vacuum-jacketed glass tubes—of which one (A) is shown—for the support of ampoules (B) of catalyst and of the test substance. One of these tubes extends a few millimeters below the solvent surface and terminates at its upper end in a 14/20 ground glass joint equipped with a stopcock (C) through which hydrogen can be admitted in order to displace air from the calorimeter and solvent prior to a run (see Procedure).[4] The second tube (not shown) is cut off just below the recessed joint and is closed at the upper end by a ground glass stopper.

The calorimeter head is constructed of a 34/45 ground glass joint, closed at each end and evacuated, through which pass the stirrer shaft housing and connecting tubes to the thermometer and heater wells (D and E, respectively). The stirrer shaft housing is joined to the hydrogen inlet tube (F) which makes connection through a 10/30 ground glass joint and manifold to an open end manometer, a jacketed, mercury-filled measuring buret that serves as the hydrogen reservoir and a pump for evacuating the system.

Stirring is accomplished by means of a glass propeller and shaft (G) which passes through loose-fitting Teflon guides (H) to one member of a magnetic coupling[5] enclosed in a vacuum tight glass housing, of which the cover (J) provides the bearing surface for the stirrer. The stirring assembly is driven by a variable speed, thyratron-controlled, d.c. motor[6] coupled to the driving magnet through a right angle gear box and universal joints to permit flexibility of alignment. Tests of the motor and control system established that the variation in speed at any given setting is less than 1%.

The thermometer is a Western Electric 14-B thermistor, temperature coefficient of resistance at 25°, −3.9% per degree C., nominal resistance at 25°, 2000 ohms. This unit was stabilized by heating to 105° for two months prior to use[7] and has proved to be entirely reliable. The thermistor has been compared periodically against a Beckmann thermometer and no significant variations in the temperature response of the element have been observed.

Resistance changes are measured with a conventional Wheatstone bridge circuit employing a Shallcross No. 817-B decade box (total resistance 1111.1 ohms) and a Leeds and Northrup No. 2430 d.c. galvanometer. Variation of the voltage across the bridge provides a sensitivity adjustment, which is normally set so that a temperature change of 0.001°, corresponding to a resistance change of about 0.1 ohm, produces a galvanometer deflection of 2–3 mm.

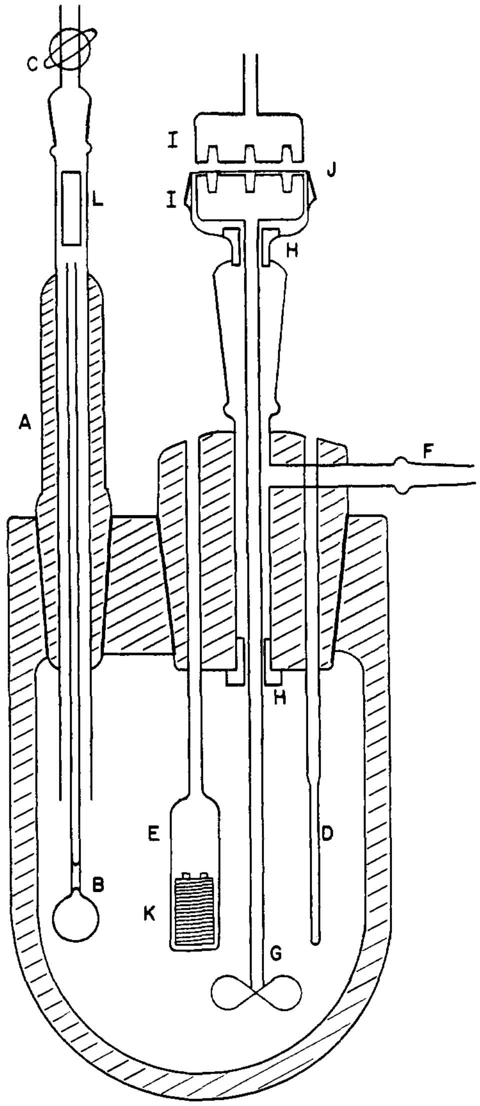

Fig. 1.—A, vacuum-jacketed ampoule support tube; B, evacuated ampoule; C, stopcock to hydrogen cylinder; D, thermometer well; E, heater well; F, connection to buret system and manometer; G, stirrer; H, Teflon guides; I, magnetic coupling; J, stirrer bearing surface; K, heater; L. magnet. Shaded portions are evacuated.

The electric heater (K) consists of 8.4 ft. of enameled manganin wire (B. and S. 36, total resistance 96 ohms) wound on a Teflon form and immersed in mineral oil in the well E. Leads from the heater and from the resistance thermometer pass out through the connecting tubes to terminals mounted on the calorimeter head. Power dissipation in the heating element is determined in the usual way[8] by means of a potential divider, a standard resistance (10 ohms) and a potentiometer.

During operation the calorimeter is immersed to a point just above the hydrogen inlet tube F in a thermostat bath held constant at 24.6 ± 0.004°. The parts of the assembly that project above the surface of the bath are surrounded by a copper can, to which a coil of copper tubing is soldered. Thermostat water is circulated through the coil and through the jacket of the gas-measuring buret.

Procedure.—**Hydrogenation Run.**—The calorimeter containing 225 ml. of acetic acid is assembled with evacuated

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[3] W. P. White, "The Modern Calorimeter," Chemical Catalog Co. (Reinhold Publ. Corp.), New York, N. Y., 1928, p. 41.

[4] This arrangement permits thorough clearance of dissolved air from the solvent and was found to be essential for obtaining reproducible results.

[5] "Lew" Magnetic Stirrer, Scientific Glass Apparatus Co., Bloomfield, N. J.

[6] Model 6701, Servospeed, Paterson, N. J.

[7] *Cf.* M. J. Rand and L. P. Hammett, THIS JOURNAL, **72**, 287 (1950).

[8] J. M. Sturtevant, Chapter X in A. Weissberger, "Physical Methods of Organic Chemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1945.

ampoules of catalyst and of the test substance,[9] wired to small magnets (L of Fig. 1), suspended in the supporting tubes by means of externally mounted Alnico magnets. Stopcocks and joints are sealed with apiezon grease, and, after the apparatus has been tested for leaks, the entire system is evacuated and filled with hydrogen through stopcock C. Hydrogen is then allowed to bubble slowly through the solvent for 10 minutes with stirring to remove dissolved air. At the end of this period the evacuation and filling process is repeated several times, and the system is finally closed at C under 3 mm. positive pressure. After heating the contents of the calorimeter to a point slightly above the bath temperature by means of the electric heater (K), the stirring rate is adjusted to the desired speed, and the system is allowed to come to equilibrium as indicated by linearity of the time–temperature curve. The ampoule of the test substance is then broken by allowing it to drop to the bottom of the calorimeter, and the time–temperature curve is followed until a constant slope is again obtained. At this point the volume of hydrogen in the buret (measured under 3 mm. positive pressure) and atmospheric pressure are noted, and the catalyst ampoule is broken. Temperature measurements are made at intervals until the time–temperature curve is once again linear. The pressure of hydrogen in the calorimeter is maintained slightly above atmospheric pressure throughout the reaction.

Calibration Run.[10]—At the end of the hydrogenation run, the calorimeter and its contents are cooled by allowing the temperature of the bath (refrigerated) to fall to about 18°. The bath temperature is then returned to 24.6°, and the calorimeter is brought to thermal equilibrium. The rating period is followed as before, and when the temperature at which the hydrogenation reaction was initiated is reached, the volume of hydrogen in the buret (3 mm. positive pressure) and atmospheric pressure are again recorded. The calorimeter heater is turned on, and the voltage drop across the heater and across the standard resistance, as well as the temperature of the calorimeter, are noted at intervals. The voltage applied to the heater is chosen so that the rate of heating in the hydrogenation run is duplicated as nearly as possible. When the temperature reaches a point approximating the maximum achieved during the hydrogenation run, the heater is switched off, the time being noted, and the time–temperature curve is followed until it is finally linear. The calorimeter is then dismantled and thoroughly cleaned with aqua regia in preparation for the next run.

The volume of hydrogen absorbed by the sample is calculated from the pressure–volume data and is corrected to standard conditions, allowance being made for the hydrogen absorbed by the catalyst, for the free space in the evacuated catalyst ampoule and for the partial pressure of acetic acid. In cases where discrepancies have been noted in the calculated and theoretical values for hydrogen absorption, the heats of hydrogenation reported are based upon hydrogen uptake. This procedure avoids possible complications resulting from losses of trace amounts of sample through retention in the ampoule stem or through evaporation and provides partial compensation for the presence of small amounts of impurities. In the few runs where discrepancies in hydrogen uptake of more than 1% have been observed (for example, see Paper IV), a special effort has been made to ascertain the nature of the impurities.

Tests of the Calorimeter.—Several preliminary tests were carried out for the purpose of assessing the precision and accuracy of results given by the calorimeter. It was first determined that the energy equivalent of the calorimeter, expressed in cal./ohm.[11] is independent of the rate of heat input over a given temperature interval. The results of a typical test run, in which the rate of stirring was the same as that employed in the hydrogenation experiments, are recorded in Table I. Since the resistance–temperature response of the thermistor may not be treated as linear over resistance intervals greater than 10 ohms (approximately 0.112°), the energy equivalent as a function of resistance is dependent to some degree upon the total resistance change. The difference in this value for successive hydrogenation and calibration runs can, however, easily be held to less than 2 ohms, and hence no significant error is introduced by extrapolation of the calibration data to the resistance interval of the hydrogenation run.

TABLE I

ELECTRIC CALIBRATION OF THE CALORIMETER CONTAINING 225 ML. OF ACETIC ACID

(Total resistance change, 50 ohms)

	Energy input, cal./min.	Energy equivalent, cal./ohm
1	2.624	1.708
2	5.823	1.716
3	9.813	1.707
	Average	1.710 ± 0.004[a]

[a] Standard deviation.

No attempt has been made in the present investigation to obtain resistance readings with a precision exceeding 0.05) ohm (~0.0005°). The major part of the deviation (0.23%) recorded in Table I can thus be attributed to this source. Somewhat less precise results are expected for the hydrogenation runs (Tables II, III and IV), but in only a few cases has the experimental variation been appreciably greater than ±0.5%, and in many instances it has been significantly less.

Of the compounds that have been examined in this Laboratory thus far, five were included in the earlier investigations. An estimate of the accuracy of the present data can therefore be made by comparison of our results with those obtained previously (Table II). The experimental value reported by Williams[2] for the heat of the reaction

TABLE II

HEATS OF HYDROGENATION OF FIVE REFERENCE COMPOUNDS

	ΔH, kcal./mole This investigation	Previous results
Diethyl fumarate	−28.94 ± 0.05	−29.08 ± 0.15[a]
Cyclohexene	−27.10 ± .08	−28.59 ± .01[b]
Cycloheptene	−25.85 ± .09	−26.52 ± .02[c]
cis-Cycloöctene	−22.98 ± .10[d]	−23.53 ± .04[e]
Cycloheptatriene	−70.49 ± .39	−72.85 ± .01[e]

[a] Data of R. B. Williams (ref. 2) corrected for the heat of solution of diethyl fumarate. [b] Gas phase data (82°) of Kistiakowsky (ref. 2c). [c] Gas phase data (82°) of Kistiakowsky (ref. 2g). [d] R. B. Turner and W. R. Meador, THIS JOURNAL, 79, 4133 (1957).

$$\text{diethyl fumarate(liq.)} + H_2\text{(gas)} \longrightarrow \text{diethyl succinate (dissolved)}$$

is −28.98 ± 0.15 kcal./mole. When this figure is corrected for the heat of solution of diethyl fumarate in acetic acid (~100 cal./mole) a value of −29.08 ± 0.15 kcal./mole is obtained, which agrees with our result within experimental error. Since Williams' instrument was compared with the Kistiakowsky gas phase calorimeter by measurement of the heat of hydrogenation of heptene-1 and appropriate correction of the liquid phase results to the gas phase at 82°, it may be concluded that all three calorimeters give concordant values, although the actual measurements apply to different conditions of state. A direct comparison of our results for the heats of hydrogenation of cyclohexene, cycloheptene and *cis*-cycloöctene with the Kistiakowsky values is unfortunately not possible in the absence of the requisite thermodynamic data. It will be observed, however, that the solution measurements on these monoölefins run about 0.5 to 1.5 kcal./mole lower than the corresponding gas phase values, as compared with a difference of about 0.5 kcal. between liquid phase and gas phase results for heptene-1 noted by Williams.[2] A somewhat larger correction term would be expected for cycloheptatriene with three double bonds,[12] and in this case a rough comparison of the solution and gas phase data can be made in the following manner. Calculation of the "resonance energy" of cycloheptatriene from the heat of hydrogenation of this substance and three

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[9] Approximately 100 mg. of platinum oxide is used in each run. Organic samples of a size sufficient to absorb 1 to 5 mmoles of hydrogen are employed.

[10] Each hydrogenation run is calibrated individually.

[11] The calorie employed throughout this investigation is defined as 4.1833 International Joules.

[12] See the discussion commencing on p. 1399 of reference 2.

times the heat of hydrogenation of cycloheptene gives, for the gas phase, a value of 6.7 kcal./mole. A corresponding calculation employing the solution data furnishes a value of 7.1 kcal./mole. The agreement is closer than might have been expected in view of complications that may arise in solution work from solvent–solute interactions. It would appear, however, that such effects are small in the case of relatively non-polar molecules, and it seems unlikely that the over-all error in our results is greater than about 1%. With regard to precision and accuracy, the present calorimeter is therefore comparable to that described by Williams, who used somewhat larger quantities of material than were employed in this work.

Materials.—The **platinum** oxide catalyst was obtained in a single batch from Baker and Co., Newark, N. J., and was thoroughly mixed and equilibrated with air at constant humidity prior to weighing. X-Ray examination of this material, carried out through the courtesy of Dr. J. Waser, revealed the presence of small amounts of free platinum mixed with the platinum oxide.

Acetic acid employed as the solvent was J. T. Baker Chemical Co. reagent grade, which was stirred with platinum in a hydrogen atmosphere and distilled before use. The solvent was prepared in large batches to ensure uniformity in any given series of experiments. Periodic calibration of the catalyst in various solvent samples, however, showed no significant variation in heat evolved.

Electrolytic **hydrogen** was supplied from a cylinder through a Deoxo purifier (Baker and Co., Newark, N. J.).

Diethyl fumarate, Eastman Kodak Co. product, was twice distilled at atmospheric pressure, b.p. 213–214°, n^{20}_D 1.4412. The **cyclohexene** employed in this investigation was obtained from the American Petroleum Institute, sample No. 522-5S, impurity, 0.023 ± 0.02%. **Cycloheptene**, b.p. 113°, n^{25}_D 1.4562, was made available through the courtesy of Dr. W. von E. Doering. The sample was prepared by acid-catalyzed dehydration of cycloheptanol and was purified by distillation through a 4-ft., 50-plate column packed with glass helices. **Cycloheptatriene** (tropilidene), n^{20}_D 1.5239, was prepared by F. L. Detert, Hickrill Chemical Research Foundation, from benzene and diazomethane according to the procedure of Doering and Knox.[13a] The material used for hydrogenation was part of the same sample employed in the thermodynamic studies of Waddington and his associates,[13b] who report a m.p. of −75.24° and a purity of 99.986 mole % for this substance. This specimen is therefore purer than the sample, m.p. −79.5°, used by Kistiakowsky.[2g] **Bicyclo[2,2,1]heptene**, purified by passage through a Perkin–Elmer vapor fractometer, was also provided by Dr. Doering. We are further indebted to Drs. S. J. Cristol and J. Hine for samples of **bicyclo[2,2,1]heptadiene**, b.p. 82.1–82.3°, n^{20}_D 1.4700, and of **bicyclo[2,2,2]octene**, m.p. 114–115°. **Bicyclo[2,2,2]octadiene**, m.p. 57°, was prepared especially for the hydrogenation work through the courtesy of Dr. C. A. Grob.[14] At Dr. Grob's suggestion the material was subjected to vapor phase chromatography and was found to be entirely homogeneous.

Results and Discussion

The values obtained for the heats of hydrogenation of the platinum oxide catalyst and of the various olefins are given in Tables III and IV, respectively. The heat evolved in reduction of the catalyst is expressed as cal./100.0 mg. and that for the olefins as kcal./mole. The averages of individual determinations on the various compounds are listed together with the corresponding standard deviations. Since the heats of hydrogenation of the olefins were uniformly determined as the difference between the total heat evolved and that associated with reduction of the catalyst, the uncertainty in the latter value is included as an appropriate term in the deviations reported for the unsaturated compounds.

The progress of hydrogenation was followed volumetrically as well as calorimetrically. The reactions are initially fast owing to rapid reduction of the platinum oxide, which is complete in less than two minutes. The subsequent rates of reduction exhibit considerable variation from compound to compound and are generally higher for those substances showing a high heat of hydrogenation per double bond than for those for which the heat of hydrogenation per double bond is low.

TABLE III

HEAT OF HYDROGENATION OF THE CATALYST (ACETIC ACID)

PtO_2, mg.	$-\Delta H$, 25°, cal./100.0 mg.
99.67	30.86
100.08	30.90
101.00	31.13
100.80	30.99
100.61	31.75
99.85	30.75
Average	30.95 ± 0.13

TABLE IV

HEATS OF HYDROGENATION OF VARIOUS OLEFINS (ACETIC ACID SOLUTION)

Compound	Mmoles	PtO_2, mg.	$-\Delta H$, 25°, kcal./mole
Diethyl fumarate	2.592	99.71	28.99
	2.980	101.60	28.88
	Average		28.94 ± 0.05
Cyclohexene	3.695	100.31	27.03
	3.796	99.98	27.16
	Average		27.10 ± 0.08
Cycloheptene	2.717	100.40	25.92
	2.837	99.70	25.78
	Average		25.85 ± 0.09
Cycloheptatriene	1.144	99.50	70.86
	1.061	99.80	70.12
	Average		70.49 ± 0.39
Bicyclo[2.2,1]heptene	2.974	99.95	33.34
	2.491	99.90	32.93
	Average		33.13 ± 0.21
Bicyclo[2,2,1]heptadiene	1.855	99.23	68.14
	1.754	99.52	68.62
	1.637	99.20	67.58
	Average		68.11 ± 0.41
Bicyclo[2,2,2]octene	3.115	100.10	27.90
	3.086	99.62	28.45
	3.079	99.43	28.40
	Average		28.25 ± 0.20
Bicyclo[2.2.2]octadiene	1.741	100.48	56.30
	2.006	100.26	56.20
	1.455	100.04	56.13
	Average		56.21 ± 0.10

With reference to recent discussions of the phenomenon of "homoallylic resonance,"[15] the question of the existence or absence of homoallylic stabilization (*cf.* structure IV) in bicyclo[2,2,1]-heptadiene (I) is one of considerable interest. This substance has been shown by Winstein[16] to

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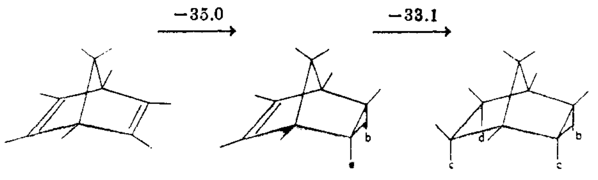
[13] (a) W. von E. Doering and L. H. Knox, THIS JOURNAL, **72**, 2305 (1950); (b) H. L. Finke, D. W. Scott, M. E. Gross, J. F. Messerly and G. Waddington, *ibid.*, **78**, 5469 (1956).

[14] *Cf.* C. A. Grob, H. Kny and A. Gagneux, *Helv. Chim. Acta*, **40**, 130 (1957).

[15] (a) M. Simonetta and S. Winstein, THIS JOURNAL, **76**, 18 (1954); (b) E. E. van Tamelen, *ibid.*, **77**, 1704 (1955); (c) J. Hine, J. A. Brown, L. H. Zalkow, W. E. Gardner and M. Hine, *ibid.*, **77**, 594 (1955).

[16] S. Winstein and M. Shatavsky, *Chemistry & Industry*, 59 (1956); THIS JOURNAL, **78**, 592 (1956).



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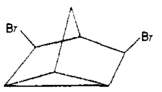
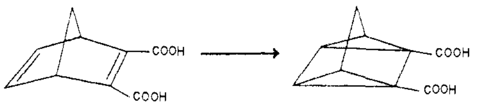
IV



V

undergo bromination with double bond participation to give, among other products, *cis*-3,5-dibromonortricyclene (V).[17] Bridging in the bicycloheptadiene system also has been observed by Cristol and Snell,[18] who showed that bicyclo[2,2,1]-heptadiene-2,3-dicarboxylic acid (VI) is readily converted into tetracyclo$[2,2,1,0^{2,6}0^{3,5}]$heptane-2,3-dicarboxylic acid (VII) on irradiation with ultraviolet light. The formation of bridged products in these reactions, however, does not demonstrate the existence of homoallylic resonance in the resting bicycloheptadiene and bicycloheptadienedicarboxylic acid molecules, since bridging in these cases may be conditioned by attack of an electrophilic reagent or by radiation induced excitation. In this connection it should be noted that the shifts observed in the spectra of 2,5-dihydroacetophenone[19] and of various bicycloheptadiene and bicyclooctadiene derivatives[20] are subject to similar restrictions of interpretation. In any event it is clear that homoallylic resonance, if present in these systems, must be small since the orientation of the π-orbitals involved is not favorable for efficient overlap.[21]



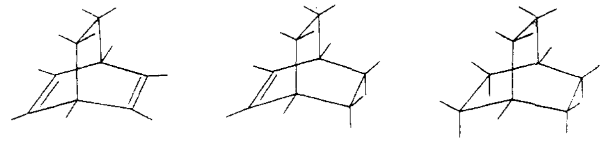
VI VII

A quantitative investigation of this problem by the hydrogenation method has now been undertaken. Although interpretation of the data is unfortunately complicated by uncertainties in the magnitudes of certain steric interactions and strain effects, the results indicate that structures of type IV make no important contribution to the energy of the bicycloheptadiene molecule.

The heats of hydrogenation of bicyclo[2,2,1]-heptene (II) and of bicyclo[2,2,1]heptadiene (I) are −33.13 ± 0.21 and −68.11 ± 0.41 kcal./mole, respectively. As a basis for estimating "homoallylic resonance energy" in the diene system, twice the bicycloheptene value, or −66.26 ±0.42 kcal./mole, has been taken as a point of reference. If, in accordance with the procedure adopted by Kistiakowsky,[16] "resonance energy" in the diene is defined as the difference between the heat of hydrogenation observed for this substance and that calculated for the "non-resonating" reference model, the "resonance energy" estimated for bicycloheptadiene is ***negative*** and equal to −1.9 kcal./mole. An alternate, but entirely equivalent, approach involves comparison of the heat change calculated for hydrogenation of the diene to olefin (−35.0 kcal./mole) with that observed for reduction of the olefin to the corresponding paraffin (−33.1 kcal./mole). Now hydrogenation of the first double bond of bicycloheptadiene results in the introduction of two hydrogen atoms (a and b of II) that do not encounter the steric repulsions a → c and b → d (*cf.* III) introduced on hydrogenation of bicycloheptene. Since an increase in steric compression in the reduction product will be reflected in a relative decrease in the heat of hydrogenation, the heat change calculated for reduction of "non-resonating" bicycloheptadiene from twice the figure for bicycloheptene will be too low. The apparent value for "resonance energy" must therefore be revised upwards to correct for this effect. The magnitude of the correction term is difficult to assess, but in view of the value assigned to the rotational barrier in ethane (2.8 kcal./mole),[22] it seems unlikely that the interactions in question can involve more than about one kcal. To the extent that this approximation is valid, and within the limits of experimental error, it would appear that bicycloheptadiene is devoid of homoallylic stabilization.

A further obvious complication in the treatment of the bicycloheptene–bicycloheptadiene system arises from the high degree of strain associated with these molecules. The heat of hydrogenation of bicycloheptene is one of the highest yet recorded, being 6 kcal. higher than that of cyclohexene, and the heat developed in the conversion of bicycloheptadiene into bicycloheptene is surpassed only by the heat of hydrogenation of *cis*-di-*t*-butylethylene.[23] Clearly, if the strain energy in bicycloheptadiene is more than twice that of the corresponding monoölefin, calculations of the type indicated above can lead to an apparent negative resonance energy.

In an effort to limit the uncertainties attending the strain problem, we have investigated the heats of hydrogenation of the relatively unstrained bicyclo[2,2,2]octene (IX) and bicyclo[2,2,2]octadiene (VIII) molecules. The results obtained for



VIII IX X

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[17] Similar attempts on the part of van Tamelen (reference 15b) to demonstrate participation in reactions of 1,4-cyclohexadiene were unsuccessful.

[18] S. J. Cristol and R. L. Snell, THIS JOURNAL, **76**, 5000 (1954).

[19] K. Bowden and E. R. H. Jones, *J. Chem. Soc.*, 52 (1946); see also E. A. Braude, E. R. H. Jones, F. Sondheimer and J. B. Toogood, *ibid.*, 607 (1949), and D. J. Cram and H. Steinberg, THIS JOURNAL, **73**, 5691 (1951).

[20] E. R. H. Jones, G. H. Mansfield and M. C. Whiting, *J. Chem. Soc.*, 4073 (1956).

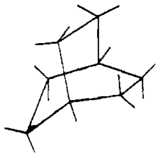
[21] C. A. Coulson, "Valence," Oxford University Press, London, 1952, p. 71.

[22] K. S. Pitzer, *Chem. Revs.*, **27**, 39 (1940).

[23] Paper VI of this series (forthcoming).

these substances are −28.25 ± 0.02 and −56.21 ± 0.10 kcal./mole, respectively. Since the heat change calculated for the process VIII → IX (−28.0 kcal./mole) is, within experimental error, essentially identical with that observed for the transformation IX → X, the "resonance energy" of bicyclooctadiene must be equated to the correction terms that are applied. As in the case of bicycloheptadiene, account must be taken of the discrepancy introduced by the appearance of two additional 1:3 hydrogen-hydrogen repulsions in the second step of the hydrogenation sequence VIII → XI → X. Assuming for these interactions the arbitrary figure taken in the bicycloheptadiene treatment, the stabilization energy in bicyclooctadiene is estimated to have a maximum value of the order of one kcal. However, in the light of arguments presented in the following paragraphs, there is reason to believe that the steric repulsion correction for bicyclooctadiene should be less than that for bicycloheptadiene. Thus, although a definitive statement regarding homoallylic resonance in bicyclooctadiene cannot be made, the present results suggest that stabilization of this sort is minimal.

The heat of hydrogenation of bicyclooctene to bicyclooctane (−28.3 kcal./mole) is surprisingly high in view of the number of 1:2- and 1:3-eclipsed interactions that appear in the latter product. Cyclohexene, which affords a reduction product possessing a staggered conformation, has a heat of hydrogenation of −27.1 kcal./mole. One would therefore anticipate that the heat of hydrogenation of bicyclooctene would lie somewhat below this value. A consistent argument based upon conformational properties can be advanced in explanation of this apparent anomaly. The conformation of bicyclooctane shown in structure X is totally eclipsed and possesses six 1:2- and six 1:3- opposed hydrogen-hydrogen interactions, as well as three pairs of opposed carbon-carbon bond repulsions. This arrangement represents an energy maximum for non-bonded interactions, which can be relieved considerably by twisting about the central axis to give a partially eclipsed conformation XI. Examination of molecular models indicates that twisting amounting to about 10° can be accommodated without distortion of bond angles. Similar twisting in bicycloheptane is restricted by the presence of one-carbon bridging. Since a small reduction in each of the interactions noted above can account for a relatively large total energy change, the high heat of hydrogenation of bicyclooctene can be attributed to heat evolution accompanying the conformational transition X → XI. As an alternative to this suggestion it will be noted that if twisting in bicyclooctene is also permitted, the accompanying increase in torsional strain of the double bond will be reflected in a corresponding increase in the heat of hydrogenation of this substance.



XI

Although a final decision between these alternatives cannot be made at the present time, we prefer the second explanation for the following reasons. The heat change accompanying hydrogenation of bicyclooctadiene to bicyclooctene, a process that results in the introduction of two 1:2- and two 1:3- opposed hydrogen-hydrogen interactions,[24] is also abnormally high (−28.0 kcal./mole) when compared with the cyclohexene value. This result is difficult to explain in terms of a totally eclipsed conformation for bicyclooctene but can be rationalized if bicyclooctene possesses a twisted structure.

Comparison of the heats of hydrogenation of cyclopentene and cyclohexene with those of bicycloheptene and bicyclooctene provides an interesting illustration of the relative importance of angle strain and non-bonded repulsions in these systems. The heat evolved in the hydrogenation of cyclopentene[2a] is 1.7 kcal. *less* than that produced in the hydrogenation of cyclohexene, despite the fact that bond angles in the former substance must deviate from the normal values. Since in five-membered carbocycles departures from planarity are relatively small,[25] the hydrogen atoms of cyclopentane are all eclipsed, or nearly so, whereas the hydrogen atoms of cyclohexane ("chair" form) adopt a staggered arrangement. In this case it is clear that steric repulsion effects predominate.

The situation with respect to bicycloheptene and bicyclooctene differs from that found in the monocyclic compounds and can best be deduced from inspection of models. It is observed that, apart from certain minor differences, the same numbers of interactions—*e.g.*, two 1,2- and four 1,3-hydrogen-hydrogen repulsions—are introduced in the hydrogenation of both olefins. Whereas bicyclooctane, and probably also bicyclooctene, can twist off from the position of maximum eclipsing, a similar adjustment in the bicycloheptane-bicycloheptene system is not possible, and steric factors would hence be expected to raise the heat of hydrogenation of bicyclooctene relative to that of bicycloheptene. The fact that the heat of hydrogenation of bicyclooctene is almost 5 kcal. lower than that of bicycloheptene must therefore be attributed to angle strain in bicycloheptene, which is more severe than in the case of cyclopentene owing to geometric requirements of the bridged system.

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HOUSTON, TEXAS

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(24) In this connection it should be pointed out that eclipsing of the bridge-head hydrogen atoms by two ethylenic hydrogens is relieved on hydrogenation.

(25) J. E. Kilpatrick, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2483 (1947); C. G. Le Fèvre and R. S. W. Le Fèvre, *J. Chem. Soc.*, 3549 (1956).