Equilibria in the Hydrogenation of Polycylic Aromatics

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AVAILABILITY of inexpensive hydrogen from naphtha reforming has markedly increased the interest in hydrogenation equilibria. An important group of these equilibria are the hydrogenations of the polycyclic hydrocarbons. Published data on these equilibria are limited to the experimental determinations of Wilson (*6*) on the reaction of naphthalene to tetralin and calculations from spectroscopic data of Pitzer (*5*) on the reaction of naphthalene to decalin. Equilibria for the more complicated polycyclic systems can be estimated only by such procedures as those suggested by Bondi (*3*). These calculated and estimated values have not been verified experimentally.

One of the principal reasons for the absence of equilibrium data on polycyclic systems has been the lack of suitable analytical techniques. This situation has changed with the development of both the high mass spectrometer and gas chromatography. With these analytical techniques, investigations have been performed in a batch system to determine equilibrium constants for the hydrogenations of naphthalene, diphenyl, and phenanthrene. In the study of the naphthalene system, the results for the naphthalene-to-tetralin reaction, when compared with those of Wilson, check on the techniques used. The results for the naphthalene-to-decalin reaction directly test the equilibria calculated by Pitzer from spectroscopic data. The results for the diphenyl and phenanthrene systems measure the validity of Bondi's empirical procedures.

EXPERIMENTAL

All experiments were performed in a cylindrical stainless steel reactor 10 inches long and 1½ inches in diameter (300 cc. total volume). A longitudinal thermowell was located along the inside wall of the reactor. Temperatures determined at one-inch intervals along the length of the reactor with a calibrated iron constantan thermocouple varied about 3.5° C. from the average. The position of the catalyst was not accurately known in the naphthalene and diphenyl experiments. In the phenanthrene experiments, the catalyst position was known within ½ inch so that reaction temperature was determined within 2.0° C.

Pressure was measured with a conventional bourdon-tube gage. The gage was used in an inverted position and filled with mercury to reduce gas volume outside the reactor. It was connected to the reactor with a 10-inch section of ⅛-inch I.D. pressure tubing which was heated to near reactor temperature except close to the gage itself. The accuracy of the gage was determined while in position by comparison with a standardized gage before and after each experiment.

For the naphthalene system, the feeds were commercially available naphthalene, tetralin, and *trans*-decalin purified by distillation or liquid percolation over activated alumina, or both. For the diphenyl system the diphenyl feed (Eastman) was used without purication; the cyclohexylcyclohexane was prepared by hydrogenation of the diphenyl followed by percolation over activated alumina and distillation. For the phenanthrene system, a mixed perhydrophenanthrene feed was prepared by hydrogenation of phenanthrene followed by distillation; the phenanthrene was purified with sodium at 200° C. and distilled. In all experiments the catalyst charge was 1 gram of 0.5 or 10% platinum on gamma-alumina ground to pass a 100-mesh screen.

After loading with feed and catalyst, the reactor was evacuated and pressured with hydrogen to a selected initial pressure. Then it was heated to and held at the desired temperature until pressure reached a constant value. The time at constant temperature varied from about 30 minutes to about 70 hours depending upon temperature. Finally, the entire equilibrium product was rapidly withdrawn through heated pressure tubing and 10 inches of 12-mm. glass tubing, packed with 3-mm. glass beads wet with benzene, into a 600-ml. flask. The material held up in the pressure tubing; glass beads were washed into the flask with ether, most of which was later distilled off. No effort was made to determine the actual moles of hydrogen discharged from the reactor, nor was it found necessary to provide agitation inside the reactor to eliminate diffusional effects.

The product was analyzed by gas chromatography in an Aerograph instrument with helium as the carrier gas. A 20-foot Apiezon column was used for the naphthalene and phenanthrene systems; a 10-foot Carbowax column was used for the diphenyl system.

Peaks were identified by comparison with chromatographs of either nearly pure purchased compounds or compounds prepared by hydrogenation and separated by liquid chromatography or distillation or both. The prepared compounds were identified in all cases by low-voltage mass spectrometry, and the mass spectrometer results were confirmed by boiling temperature and refractive index when these data were available in the literature. The perhydrophenanthrenes were recovered only as a mixture from low-temperature hydrogenation. Similarly, what were assumed to have been the two asymetric octahydrophenanthrenes were also recovered as a mixture.

Compared with values for naphthalene, calibration factors of area per unit weight of tetralin, *trans*-decalin, and *cis*-decalin were all 1.00 ± 0.04. Compared to values for phenanthrene, a calibration factor of 1.00 ± 0.04 was determined for the mixture of perhydrophenanthrenes; calibration factors of 1.00 were assumed to apply to all other components in the phenanthrene system. A calibration factor of 1.00 compared to diphenyl was assumed for all components of that system. Duplicate analyses of the major products were, in general, within the 4% variation observed in the calibration factors. Duplicate analyses for minor products showed variations of up to 10% at about 5% concentration and 25 to occassionally 50% in the 1% concentration range.

Equilibria were calculated by the procedure of Gilliland (*4*) for all three systems. In all cases, hydrocarbon pressure was calculated with the perfect gas equation and was small compared to either total pressure or the vapor pressure of the equilibrium mixture. Hydrogen pressure was calculated by difference from the total pressure. Correction for the nonideality of hydrogen was made by assumption of an activity coefficient of $1.000 + 3.30 \times 10^{-4} P_{H_2}$ at all temperatures for all three systems. Thus, for example, calculated equilibrium constants for the naphthalene to tetralin reaction were:

$$Kp = \frac{(\text{moles tetralin})}{(\text{moles naphthalene})(P_{H_2} + 3.30 \times 10^{-4}\, P_{H_2}^{2})^{2}}$$

where P_{H_2} was in atmospheres.

Experimental and calculated data for the naphthalene system (No generally accepted technique for taking account of nonideality has been adopted. A technique such as that used by Wilson (*6*) introduces a larger correction.) are presented in Table I. In these experiments the temperature given is the average of the highest and lowest measured temperature and may be inaccurate by about 3.5° C. Similarly, data for the diphenyl system (Table II) are subject to the same error in temperature.

Data for the phenanthrene system are presented in Table III. The temperature uncertainty in these experiments is estimated to be 2.0° C. For the perhydro- and the octahydro-phenanthrenes; the analyses are given in order of decreasing retention time in the chromatographic column; with an Apiezon column this is also the order of decreasing boiling point. For the six possible perhydrophenanthrenes, only five gas-chromatography peaks appear that are large enough to be measured, but slight broadening of the third suggests the presence of two isomers of almost identical retention time. The highest boiling perhydrophenanthrene was found only at nonequilibrium under strongly hydrogenating conditions. The concentration of this isomer has been omitted from Table III because at equilibrium its concentration was always zero. Lighter hydrocarbons were produced in significant amounts only in the run at 459° C.; the feed hydrocarbon pressure would have been 1.8 atm. had no cracking taken place, but the production of mainly methane through butane increased hydrocarbon pressure to 8.2 atm.

DISCUSSION

Data from the naphthalene hydrogenations are compared with data from the literature in Figure 1. Results for the naphthalene-to-tetralin reaction agree with those of Wilson (*6*) and show that the batch technique is reliable as a means of determining equilibrium distributions. Results for naphthalene to *trans*-decalin verify the equilibrium calculated from spectroscopic data by Pitzer (*5*). The observed ratio of *trans*-to-*cis* decalin was slightly lower than that calculated by Pitzer but higher than that reported by Allinger (*1*) for the liquid system.

Data from the diphenyl hydrogenation are plotted in Figure 2. From these lines, the heats of hydrogenation and the relationships between absolute temperature and equilibrium constant were calculated to be:

System	$-\Delta H$, Kcal./G. Mole H_2	Log K_p
$C_{12}H_{10} \rightarrow C_{12}H_{16}$	18	$-21.71 + 11{,}750/T$
$C_{12}H_{16} \rightarrow C_{12}H_{22}$	18	$-22.37 + 11{,}750/T$
$C_{12}H_{10} \rightarrow C_{12}H_{22}$	18	$-44.08 + 23{,}500/T$

Assuming the correction for nonideality is accurate, the largest uncertainty in both the ΔH and log K_p values results from the 3.5° C. uncertainty in temperature. The ΔH value of 18 (calculated value 17.9) kcal./gram mole H_2 is probably uncertain by about 1 kcal./gram mole H_2. This value is in agreement with that for the tetralin to *trans*-decalin reaction but is about 1 kcal./gram mole H_2 larger than the value for alkyl substituted benzenes.

At a given temperature, the log K_p terms for the first two equilibria differ by 0.66, which differs slightly from the 0.60 dictated by the symmetry factors (*2*) for this system. At all temperatures

Table I. Experimental Determinations of Naphthalene-Hydrogenation Equilibria

Temp., ° C.	343	363	374	383	396	402	429
Feed	A	B	B	A	C	A	B
Total Pressure, Atm.	14.5	22.3	23.9	24.9	39.8	41.8	75.6
Hydrocarbon Pres., Atm.	2.0	2.7	2.7	2.9	3.7	3.6	3.6
Hydrocarbon; Mole %							
trans-Decalin	43.9	51.7	36.1	41.0	51.3	40.2	44.9
cis-Decalin	6.2	7.7	5.8	6.2	7.9	6.0	8.0
Tetralin	35.5	31.7	42.0	37.9	31.3	38.2	35.5
Naphthalene	14.4	8.9	16.1	14.9	9.5	15.6	11.6
–Log Equilibrium Constant							
$C_{10}H_8 + 2H_2 \rightarrow C_{10}H_{12}$	1.80	2.07	2.24	2.39	2.61	2.79	3.26
$C_{10}H_8 + 5H_2 \rightarrow C_{10}H_{18}$(trans)	5.00	5.79	6.29	6.55	7.08	7.53	8.77
Equilibrium c onstant							
$C_{10}H_{18}$(cis)$\rightarrow C_{10}H_{18}$(trans)	7.0	6.7	6.2	6.6	6.5	6.7	5.6

A = naphthalene B = tetralin C = *trans*-decalin

Table II. Experimental Determination of diphenyl-Hydrogenation Equilibria

Temp., ° C.	328	346	331	330	353	389	425	426
Feed	A	B	B	A	B	A	B	A
Total Pressure, Atm.	8.0	6.9	7.0	14.2	15.7	24.6	33.3	71.5
Hydrocarbon Pres,m Atm.	0.5	0.6	0.6	1.8	1.5	1.8	2.6	3.4
Hydrocarbon; Mole %								
Diphenyl	18.3	33.5	28.0	15.9	18.3	34.6	62.0	14.0
Cyclohexylbenzene	51.5	50.8	50.1	49.0	50.2	49.9	33.6	48.8
Cyclohexylcyclohexane	30.2	15.7	21.9	35.1	31.5	15.5	4.4	37.2
–Log Equilibrium Constant								
$C_{12}H_{10} + 3H_2 \rightarrow C_{12}H_{16}$	2.17	2.22	2.17	2.79	3.04	3.93	4.74	4.99
$C_{12}H_{10} + 6H_2 \rightarrow C_{12}H_{22}$	5.03	5.13	4.95	6.22	6.72	8.52	10.09	10.64

A = diphenyl B = cyclohexylcyclohexane

Table III. Experimental Determination of Phenanthrene-Hydrogenation Equilibria

Temp., ° C.	337	346	369	373	373	406	429	459
Feed	A	B	A	A	B	A	B	B
Total Pressure, Atm.	15.5	15.9	21.0	31.1	137.3	50.6	78.9	157.3
Hydrocarbon Pres., Atm.	0.5	0.9	0.9	0.9	1.1	0.9	1.1	8.2
	Hydrocarbon; Mole %							
Phenanthrene	33.1	44.2	53.0	23.7	0.0	30.7	27.6	11.5
Dihydro-	7.3	8.3	8.7	6.2	0.0	8.0	7.9	5.2
Tetrahydro-	22.3	22.7	19.0	20.8	0.0	22.2	23.4	14.9
Sym. Octahydro-	13.9	12.1	6.5	14.5	0.0	13.8	16.3	14.9
Asym. Octahydro-	3.2	2.9	1.6	3.3	0.0	3.6	3.7	5.0
Asym. Octahydro-	1.9	2.0	0.9	2.2	0.0	2.4	2.3	2.8
Perhydro-	0.3	0.3	0.3	0.8	1.5	0.5	1.0	1.8
Perhydro-	3.3	1.1	1.8	3.7	11.6	2.8	2.9	8.7
Perhydro-	3.3	1.1	1.1	3.6	12.0	2.8	2.9	8.3
Perhydro-	12.4	5.3	7.1	21.2	74.9	13.2	12.0	26.9
	–Log Equilibrium Constant							
$C_{14}H_{10} + H_2 \rightarrow C_{14}H_{12}$	1.83	1.91	2.09	2.07	. . .	2.28	2.45	2.53
$C_{14}H_{10} + 2H_2 \rightarrow C_{14}H_{14}$	2.52	2.64	3.06	3.03	. . .	3.54	3.88	4.34
$C_{14}H_{10} + 4H_2 \rightarrow C_{14}H_{18}$(sym.)	5.08	5.27	6.13	6.15	. . .	7.15	7.84	8.60
$C_{14}H_{10} + 7H_2 \rightarrow C_{14}H_{24}$(c)	8.65	9.16	10.01	10.44	. . .	12.28	13.67	14.86

A = mixture of perhydrophenanthrenes B = phenanthrene c = calculated for most abundant isomer only

$$\frac{(\text{diphenyl})(\text{cyclohexylcyclohexane})}{(\text{cyclohexylbenzene})^2} = 0.22$$

Experimentally, this ratio varied from 0.21 to the 0.25 that corresponds to the symmetry factor requirement. The first two of these reactions involve hydrogenation of isolated aromatic rings, but compared with the hydrogenation of toluene, substitution of phenyl or cyclohexyl in place of a methyl group makes both equilibria significantly "more aromatic."

Data for the more important reactions in the hydrogenation of phenanthrene are plotted in Figure 3. From these lines, the heats of hydrogenation and the relation between absolute temperature and equilibrium constant were calculated to be:

System	$-\Delta H$, Kcal./G. Mole H_2	Log K_p
$C_{14}H_{10} \rightarrow C_{14}H_{12}$	12	$-6.11 + 2{,}600/T$
$C_{14}H_{10} \rightarrow C_{14}H_{14}$	15	$-13.25 + 6{,}565/T$
$C_{14}H_{10} \rightarrow C_{14}H_{18}$(sym)	15	$-26.38 + 13{,}030/T$
$C_{14}H_{10} \rightarrow C_{14}H_{24}$	15	$-46.49 + 23{,}190/T$

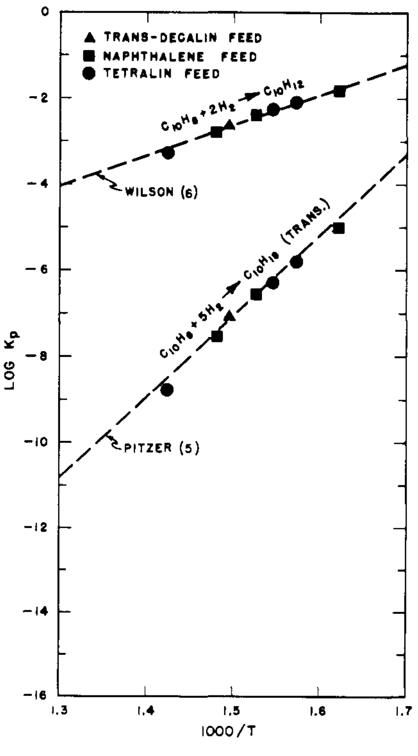

Figure 1. Naphthalene-hydrogen equilibrium constants as a function of temperature

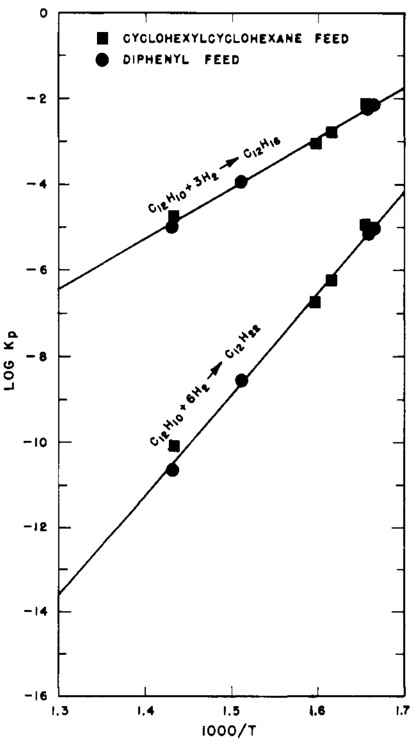

Figure 2. Diphenyl-hydrogen equilibrium constants as a function of temperature

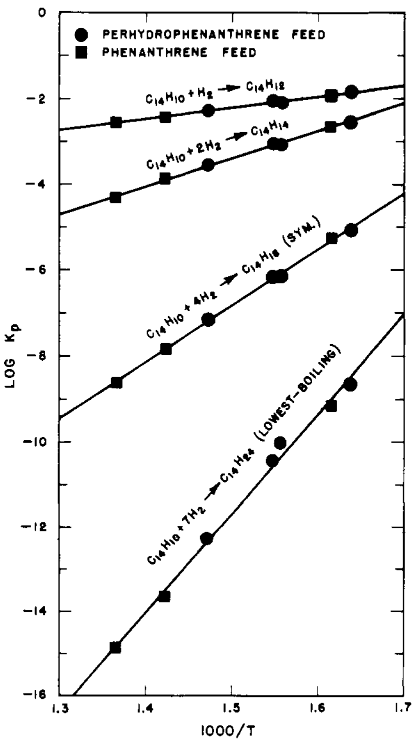

Figure 3. Phenanthrene-hydrogen equilibrium constants as a function of temperature

Since temperature was more accurately known the uncertainties in the ΔH and log K_p values resulting from uncertainties in temperature are smaller than with the diphenyl-hydrogen system. The ΔH values cannot be directly compared with other data because accurate heat of combustion data are not available for the major components of the phenanthrene-hydrogen system. In general, the ΔH values are in satisfactory agreement with those calculated using the empirical procedure of Bondi (*3*). Because the heats of hydrogenation are equal for the reactions of phenanthrene and tetrahydrophenanthrene and of tetrahydro- to octahydrophenanthrene and both involve two moles of hydrogen, the ratio of their equilibrium constants is independent of hydrogen pressure and temperature. Experimentally, this ratio

$$\frac{\text{(phenanthrene) (sym. octahydrophenanthrene)}}{\text{tetrahydrophenanthrene)}^2}$$

varied from 0.78 to 1.03 and averaged 0.87.

Data on the minor components included in Table III show that the symmetrical compound accounts for about 70% of the total octahydrophenanthrenes, and the lowest boiling one accounts for 60 to 75% of the total perhydrophenanthrenes. In neither case are the data sufficiently accurate to determine heats of isomerization.

The experimental data show that Bondi's empirically calculated equilibrium constants (*3*) are significantly too low. For phenanthrene to sym. octahydrophenanthrene, for example, the calculated constant is less than a tenth of the actual equilibrium constant.

CONCLUSION

The experimentally determined equilibrium data for selected polycyclic aromatic provide a firmer base for interpreting hydrogenation data. They emphasize that empirical correlations can be seriously in error and show the need for similar experimental data for other polycyclic systems. The techniques used in the present work should serve in studying such systems.

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Specific Heat of Some High Temperature Materials

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DEMAND FOR materials capable of withstanding extreme temperatures has increased sharply in the past few years. This has resulted from an increased emphasis on space and reactor programs, which require high temperature materials with specific properties. Selection, application, and evaluation of new materials require a through knowledge of their physical and mechanical properties.

This laboratory has performed precise specific heat determinations from room temperature to 1000° C. on various materials such as synthetic sapphire and $MoSi_2$ (*15*), TiB_2 (*14*), and several organic liquids (*13*).

The present investigation involves similar specific heat determinations of 45 materials, which have potential high temperature applications. Heat capacities were derived from heat content measurements, performed over the temperature range 30° to 800° C., for BeO, Be, BeO-Be and BeO-Be-Mo cermet mixtures; beryllides of Ta, Zr, Mo, Ti, and Cb; BeO-beryllide mixtures; SiC, SiC-graphite mixtures; and BN, BN-graphite mixtures. Smoothed specific heat results are presented for all samples, and the effectiveness of the additive law in predicting specific heats is demonstrated.

EQUIPMENT

The apparatus has been previously described in some detail (*15*). Briefly, the calorimeter is a modified version of Southard's apparatus (*12*), and the drop method is employed. Samples are heated to a known temperature and then dropped into the calorimeter, which measures the heat evolved in cooling the sample from the furance temperature to the calorimeter operating temperature (30° C.). Heat capacities are then derived from the heat content measurements by the usual methods.

Type 304 stainless steel buckets, previously calibrated for heat content in the calorimeter system from 30° to 800° C., were used to contain the samples. Samples were obtained from several companies as hot-pressed solids, machined to fit the sample containers. Data on the composition of several samples are given in Table I. Those not listed are not known beyond the nominal compositions indicated in Table II.

EXPERIMENTAL RESULTS

Heat content measurements were obtained over the temperature range from 30° to 800° C. at 100° to 150° C. intervals for approximately 25 samples, and at 200° C. intervals for the remainder of the samples, which were duplicates or near-duplicates of eariler ones. Specific heats were then derived from the enthalpy data.

Smoothed experimental results were obtained graphically from precise plots of specific heat—temperature and are shown in Table II. The probable absolute error in this calorimetric system has been calculated to be less than ±0.3% for heat content measurements and less than ±3% for specific heat. Measurements on synthetic sapphire, a calorimetric standard, indicate that this calculated error