charged with 0.00111 mole of silver each. The other two legs were charged with 0.00111 mole of gold. About 0.218 mole of mercury was vaporized into the tube under vacuum and the tube was sealed off. Different amounts of mercury were contained in the four legs at the time the tube was placed in the furnace. A week later the tube was removed. Within a 5% uncertainty, each of the four legs contained the same volume of metal—i.e., the final composition of each leg was $N_{\mathrm{Hg}} = 0.980 \pm 0.001$. Evidently the mercury vapor pressure over 2 mole % silver in mercury is nearly the same as that over 2 mole % gold in mercury, in agreement with the isopiestic balance results.

DISCUSSION

Alloy vapor pressure measurements made at this laboratory have been on alloys more concentrated than 0.001 solute mole fraction. Determining the slope of the solvent activity with concentration at infinite dilution by any presently known method of measurement appears impossible; thus, Raoult's limiting law for infinite dilution is not directly subject to test. One can only look for trends in activity behavior at such concentrations for which adequate measurements can be made, searching for indications of approach to the limiting law with increasing dilution.

All systems for which vapor pressures have been measured at this laboratory have shown no tendency to approach Raoult's law as dilution is increased. A few of these systems (*2, 4, 5, 9*) have been discussed in publications. The systems appearing in the present paper are illustrative of the preceding discussion.

For the silver-cadmium system, the data lie on a line that, within the uncertainty of the data, seems to be straight, with a nonunit slope.

The gold-mercury and silver-mercury systems apparently have nearly the same activity at the same concentration between 97 and 98%, and at 99.2% mercury. Clearly, the behavior of the silver-mercury system must undergo a marked change at some solute concentration greater than 0.7%. Whether the silver-mercury system behaves similarly to the gold-mercury system in the concentration range from 98 to 99.2% is not clear, because data are lacking. For the gold-mercury system, either of two rather different types of behavior could easily be followed for solutions more dilute than 0.8 mole % of gold; these cannot be distinguished from the present data. The gold-mercury curve might continue smoothly out toward infinite dilution, as does that for the tin-mercury system (*1*), or it might undergo a marked change in behavior at or below 0.8% gold, yielding a line similar to that for silver-mercury. Similar behavior of the lead-cadmium system has been published (*5*).

The similarity in the data for both mercury systems does not seem unreasonable, considering the atomic size and chemical similarity of the two solutes.

ACKNOWLEDGMENT

The authors thank Guy R.B. Elliott for his discussion and helpful suggestions.

LITERATURE CITED

(1) Conant, D.R., J. Chem. Eng. Data **14**, 9 (1969).
(2) Conant, D.R., Elliott, G.R.B., *Ibid.*, **13**, 354 (1968).
(3) Elliott, G.R.B., Lemons, J.F., *Advan. Chem. Ser.* No. **39**, 153 (1963).
(4) Elliott, G.R.B., Lemons, J.F., Swofford, H.S., Jr., Los Alamos Scientific Laboratory Report, **LA-2997**, 1963.
(5) Elliott, G.R.B., Lemons, J.F., Swofford, H.S., Jr., *J. Phys. Chem.* **69**, 933 (1965).
(6) Hultgren, R., Orr, R.L., Anderson, P.D., Kelley, K.K., "Selected Values of Thermodynamic Properties of Metals and Alloys," p. 62-65, 123-128, Wiley, New York, 1963.
(7) Roeser, W.F., Wenzel, H.T., *Bur. Stds. J. Res.* **10**, 275 (1933).
(8) Schenker, H., Lauritzen, J.I., Jr., Corruccini, R.J., Lonberger, S.T., "Reference Tables for Thermocouples," Nat. Bur. Stds., Circ. **561**, 1955.
(9) Swofford, Harold, S., Jr., Elliott, Guy, R.B., Los Alamos Scientific Laboratory Report, **LA-3657**, 1967.

Received for review November 15, 1968. Accepted March 28, 1969. Work done under the auspices of the U. S. Atomic Energy Commission.

Equilibrium Hydrogenations of Multi-Ring Aromatics

C. G. FRYE and A. W. WEITKAMP[1]
Research and Development Department, American Oil Co., Whiting, Ind. 46394

Chemical equilibria were determined for the naphthalene-hydrogen, indene-hydrogen, acenaphthene-hydrogen, and fluorene-hydrogen systems. Measurements were made over ranges of temperature and pressure appropriate to a totally vaporized system. Equilibrium constants and heats of hydrogenation are given.

PUBLISHED equilibria for hydrogenation of multi-ring aromatic hydrocarbons are limited to the naphthalene-hydrogen (*3, 5, 7, 11*), diphenyl-hydrogen (*5*), and phenanthrene-hydrogen (*5*) systems. A previously reported technique (*5*), modified to assure more accurate temperature measurements, has been used to determine the equilibria in the indene-hydrogen, acenaphthene-hydrogen, and fluorene-hydrogen systems, as well as to redetermine and extend the temperature range for the naphthalene-hydrogen system.

EXPERIMENTAL

Fluorene, indene, acenaphthene, and naphthalene were desulfurized with Raney nickel in methanol and were either redistilled or recrystallized. Purity, as determined by gas chromatography, was 99.0 mole % or better. Electrolytic hydrogen (Liquid Carbonic Division of General Dynamic Corp.), certified to be 99.9% pure, was used without further purification.

The apparatus and techniques to establish equilibrium and to withdraw material for analysis have been described (*5*), except that a Pd-on-charcoal catalyst (Matheson, Coleman, and Bell) was used in the present experiments. The

---

[1] Present address: Research and Development Department, Amoco Chemicals Corp., Whiting, Ind. 46394

selection of paladium as the catalyst was based upon experimental observations showing a significantly lower hydrocracking relative to hydrogenation activity, compared to the platinum-on-alumina catalyst used in the earlier work. Also, the uncertainty of the temperature measurement was reduced to about 1° C. because the catalyst was placed on a flat stainless-steel tray that contained a calibrated thermocouple. To assure accuracy in the pressure measurement, the pressure gage was standardized, before and after each experiment, against a Seegers Instrument Co. precision pressure gage whose accuracy was ±1 p.s.i. by dead weight calibration over the range used. The uncertainty in the experimental pressure measurements was estimated to be 3 p.s.i. at pressures below 250 p.s.i. and 4 p.s.i. above 250 p.s.i. Products were analyzed by mass spectrometry and gas chromatography. Structures were assigned to isomers on the basis of conformational analysis and kinetic yields, where other identifying characteristics were unavailable (*5*, *10*).

The determination of equilibria in batch equipment requires that there is no shift in composition during sampling and that the recovered sample be representative of the product leaving the reactor. To meet these requirements, samples were withdrawn rapidly, compared to the time required to establish equilibrium; the catalyst was located at the opposite end of the reactor from the outlet, so that any altered product would tend to remain in the reactor as part of the 1 atm. of product that was not recovered; glass beads in the recovery system were wet with benzene to prevent product fog from passing through the system and being lost; the sample line was washed with ether, and the washings were combined with the main product.

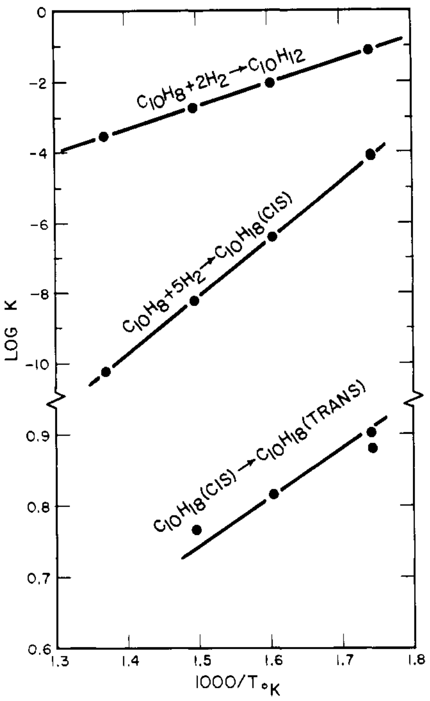


Figure 1. Naphthalene-hydrogen equilibrium

RESULTS AND DISCUSSION

Complete experimental data for the naphthalene-hydrogen, indene-hydrogen, acenaphthalene-hydrogen, and fluorene-hydrogen systems are given in Tables I through IV. Corresponding plots of the logarithms of the equilibrium constants against reciprocal temperature are shown in Figures 1 through 4.

Naphthalene-hydrogen. For the naphthalene-to-tetralin reaction, the correlating line is

$$\log K = 6460/T - 12.40$$

This relationship gives about the same calculated equilibrium constant as was previously reported (*3*, *5*, *11*) at 400° C. At lower temperatures, the older correlations give values for the equilibrium constants which are slightly too high. For the naphthalene-to-*cis*-decalin reaction, the correlating equation

$$\log K = 16500/T - 32.88$$

gives results in agreement with the results of Miyazawa and Pitzer (*7*) and Frye (*5*) at high temperature. Again, the older correlations give values that are slightly higher at lower temperatures.

Table I. Naphthalene-Hydrogen Equilibrium

	Operating Conditions					
Temperature, ° C.	301.5	301.0	351.0	396.0	396.5	457.0
H_2 pressure, atm.	5.20	6.07	19.4	9.66	37.1	58.7
H_2 fugacity, atm.	5.23	6.10	19.5	9.70	37.7	60.1
Hydrocarbon press., atm.	0.90	0.90	0.95	1.00	1.00	1.10
1000/T° K.	1.740	1.742	1.601	1.495	1.494	1.370
	Products, Mole %					
Naphthalene	19.12	12.60	8.13	82.66	15.56	44.37
Tetralin	35.09	29.73	27.38	14.66	39.21	42.50
cis-Decalin	5.35	6.39	8.56	0.17	6.65	2.10
trans-Decalin	40.44	51.28	55.93	2.51	38.59	11.03
	Log Equilibrium Constant[a]					
Naphthalene to tetralin	−1.17	−1.18	−2.05	−2.73	−2.75	−3.58[b]
Naphthalene to *cis*-decalin	−4.14	−4.19	−6.43	. . .	−8.25	−10.22
cis-Decalin to *trans*-decalin	0.877	0.902	0.814	. . .	0.765	0.719

[a] The correction for the imperfect behavior of hydrogen gas at elevated pressure was made according to the procedures of Gilliland (*6*). For all temperatures, the hydrogen fugacity (activity) was calculated as $F_{H_2} = P_{H_2}$ (1 + 0.00033 P_{H_2}) where P_{H_2} was in atmospheres. Thus, for example, the equilibrium constant for the naphthalene to tetralin reaction was calculated as K = tetralin/(naphthalene) $(P_{H_2} + 0.00033\ P_{H_2}^{\ 2})^2$ where the amounts of hydrocarbons are in moles. [b] The 457° C. value for the naphthalene to *cis*-decalin equilibrium constant was not used in the calculation of the best line by the least squares technique for the reason given in the discussion of the *cis*- to *trans*-decalin equilibrium.

The heats of hydrogenation likewise differ slightly from those obtained previously.

	$-\Delta H$, Kcal./Mole	
	This work	Literature
Naphthalene to tetralin	29.8	32.0 (*9*)
Naphthalene to *cis*-decalin	76.0	76.7 (*7*)

The older heats of hydrogenation, particularly for tetralin, are slightly higher and probably less accurate.

Because of the high-pressure operation and the low concentration of *cis*-decalin, the *trans*-decalin–*cis*-decalin ratio may have increased above the equilibrium value during sampling in the run at 457° C. (The logarithn of the equilibrium constant for the naphthalene to *cis*-decalin reaction will also be slightly affected.) The equilibrium constant *vs.* temperature relationship for the *cis*- to *trans*-decalin reaction, excluding the run at 457° C., is

$$\log K = 695/T - 0.301$$

This equation is in satisfactory agreement with all other results and has the proper entropy term ($\log 2 = 0.301$) for a *d,l* pair difference between the two isomers. The equilibrium ratios of *trans*-decalin-*cis*-decalin observed in the present vapor phase experiments are slightly lower than those determined by Allinger and Coke (*1*) in the liquid phase. For example, at 600° K., the ratio calculated from the equation is 7.2, compared to 7.9 observed in the liquid system. The value of 3170 cal. per mole for the heat of isomerization is in agreement with the 3040 ± 770 cal. per mole calculated from heat of combustion data (*9*) and with the gas phase value of 3120 ± 400 cal. per mole calculated from liquid phase data (*1*).

Indene-Hydrogen. Results for the reactions

indene + $H_2 \rightarrow$ indane

indane + $3H_2 \rightarrow$ *cis*-hydrindane

trans-hydrindane $\rightarrow$ *cis*-hydrindane

yield, respectively, the following relationships between equilibrium constant and temperature.

$$\log K = 4990/T - 6.21$$

$$\log K = 10052/T - 20.01$$

$$\log K = -310/T + 0.602$$

The concentrations of indene in the runs at 400° and 460° C. were substantially higher than in the other experiments. Consequently, an arbitrary weighting factor of three was used on these high-temperature data to obtain the least squares equation for the indene to indane equilibrium. The heat of hydrogenation of indene to indane was 23 kcal. per mole. This value is only an approximation because of uncertainties in the indene analysis. It appears to be significantly less than the value of 27.5 kcal. per mole reported (*8*) for the cyclopentene to cyclopentane reaction, and suggests a substantial ring strain in the indene compared to the cyclopentene molecule. At 700° K., the logarithm of the equilibrium constant for the indene to indane reaction is 0.91. This value is 0.43 less than the corresponding value for the cyclopentene to cyclopentane reaction (*8*). Because symmetry effects should give a difference in the other direction, the data again suggest a marked influence of the aromatic ring on the olefinic five-membered ring.

Compared to the tetralin to *cis*-decalin reaction, the equilibrium curve for the indane-to-*cis*-hydrindane reaction is displaced by 0.49 in log *K* over the whole range of experimental data. Thus, the heat of hydrogenation is the same as for the tetralin to *cis*-decalin reaction—i.e., 45.8 kcal. per mole. The equilibrium constant is about 3.1 times that for the tetralin to *cis*-decalin reaction.

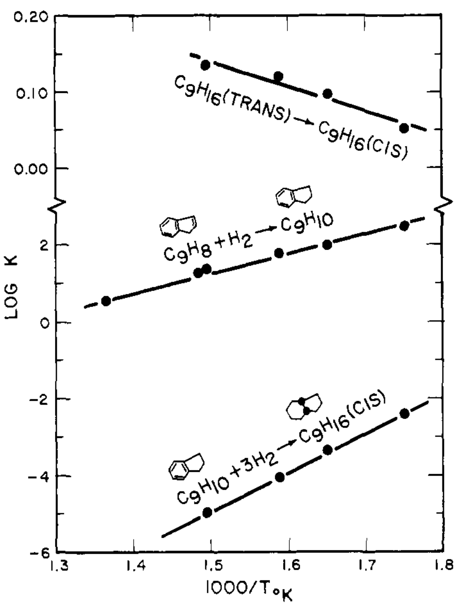


Figure 2. Indene-hydrogen equilibrium

Table II. Indene-Hydrogen Equilibrium

			Operating Conditions			
Temperature, ° C.	298.5	332.5	356.5	396.0	400.5	460.0
Hydrogen press., atm.	4.6	10.9	16.5	30.4	8.1	9.0
Hydrogen fugacity, atm.	4.6	11.0	16.6	30.7	8.1	9.0
Hydrocarbon press., atm.	1.4	0.7	1.5	1.6	0.8	0.9
1000/*T*° K.	1.750	1.651	1.588	1.494	1.484	1.364
			Hydrocarbon, Mole %			
Indene	0.047	0.048	0.058	0.10	0.68	3.13
Indane	58.54	51.24	58.29	65.85	97.65	95.78
cis-Hydrindane	21.93	27.07	23.68	19.63	0.95	0.53
trans-Hydrindane	19.47	21.63	17.95	14.42	0.72	0.56
			Log Equilibrium Constant			
$C_9H_8 + H_2 \rightarrow C_9H_{10}$	2.43	1.98	1.78	1.33	1.24	0.53
$C_9H_{10} + 3H_2 \rightarrow C_9H_{16}$ (cis)	-2.42	-3.40	-4.05	-4.99	...	...
C_9H_{16} (trans) $\rightarrow C_9H_{16}$ (cis)	0.051	0.097	0.120	0.134	...	...

The equilibrium results for the reaction of *trans*-hydrindane-to-*cis*-hydrindane agree with those of Allinger and Coke (*2*) at high temperature and those of Blanchard and Schleyer (*4*) at low temperature. The calculated heat of isomerization is −1420 cal. per mole. An "entropy" term of 0.63 obtained by least-squares analysis of the experimental results was adjusted to 0.602 (= log 4.0) in the final equation given above to correspond to a symmetry number difference of 2 and a *d,l* pair difference of 2 between the isomers.

Acenaphthene-Hydrogen. Results for the reactions

$$\text{acenaphthene} + 2H_2 \rightarrow \text{tetrahydroacenaphthene}$$

$$\text{acenaphthene} + 5H_2 \rightarrow \text{perhydroacenaphthene}$$

yield, respectively, the following relationships between equilibrium constant and temperature.

$$\log K = 5850/T - 11.76$$

$$\log K = 12874/T - 27.87$$

The presence of the five-membered ring in acenaphthene introduces additional strain in the naphthalene part of the structure. This is reflected by a 27 kcal. per mole heat of reaction for acenaphthene to tetrahydroacenaphthene, compared to about 30 kcal. per mole for the naphthalene-to-tetralin reaction. The corresponding value for tetrahydro- to the all-trans perhydroacenaphthene (see Table III for structure) is 32 kcal. per mole, compared to 46 kcal. per mole for tetralin to *cis*-decalin.

Of the six possible stereoisomeric perhydroacenaphthenes, three (a, c, e in Table III) were present in roughly equal amounts. Other isomers constitute only minor constituents in the equilibrium product.

With regard to the hydrogenation of acenaphthylene to form acenaphthene, attempts were made to determine the amount of acenaphthylene, both by gas chromatography and mass spectrometry. No measurable amount was found by either method of analysis. From known mass spectrometer calibration factors, it can be concluded that the acenaphthylene-to-acenaphthene ratio was in all cases less than 1 to 500. Thus, at equilibrium, the acenaphthylene-to-acenaphthene ratio will be smaller than the indene-to-indane ratio at the same temperature and hydrogen pressure.

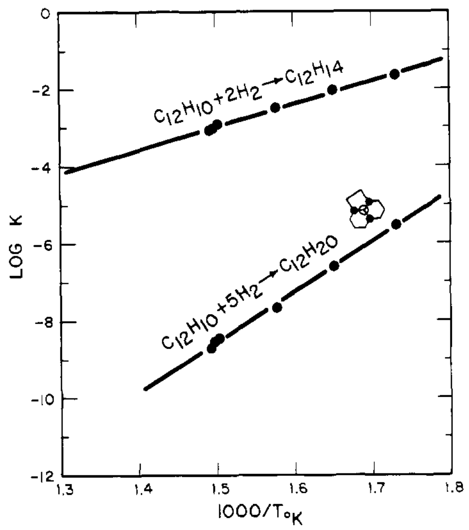


Figure 3. Acenaphthene-hydrogen equilibrium

Fluorene-Hydrogen. Results for the reactions

$$\text{fluorene} + 3H_2 \rightarrow cis\text{-hexahydrofluorene}$$

$$\text{fluorene} + 6H_2 \rightarrow \text{perhydrofluorene (total)}$$

$$\text{fluorene} + 6H_2 \rightarrow \text{perhydrofluorene (all-cis derivative only)}$$

yield, respectively, the following relationships between equilibrium constant and temperature.

$$\log K = 9242/T - 19.00$$

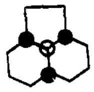
$$\log K = 17830/T - 38.66$$

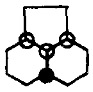
$$\log K = 18339/T - 37.76$$

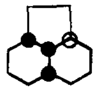
The heats of reaction for the hydrogenation of fluorene to the *cis*-hexahydrofluorene and to the all-cis perhydrofluorene are both about 14 kcal. per mole of hydrogen.

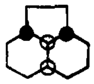
Table III. Acenaphthene-Hydrogen Equilibrium

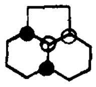
	Operating Conditions							
Temperature, ° C.	296.5	305.0	333.0	361.0	393.0	397.0	396.5	395.0
Hydrogen press., atm.	75.8	8.7	14.2	23.5	32.0	88.1	33.3	33.0
Hydrogen fugacity, atm.	77.7	8.7	14.3	23.7	32.3	90.7	33.7	33.4
Hydrocarbon press., atm.	0.5	1.0	1.1	1.1	1.2	0.7	0.9	0.9
1000/T° K.	1.755	1.730	1.650	1.577	1.501	1.492	1.493	1.497
	Hydrocarbon, Mole %							
Acenaphthene	...	33.74	31.30	32.42	41.69	...	45.84	41.83
Tetrahydro	...	53.01	55.73	54.42	47.59	...	44.33	44.85
Decahydro[a]	35.8	4.45	4.72	5.05	4.63	31.0	3.93	5.09
Decahydro[b]	2.1	0.26	0.31	0.36	0.32	3.4	0.35	0.40
Decahydro[c]	34.6	5.15	4.14	4.32	3.30	35.7	3.10	4.23
Decahydro[d]	T	0.03	0.05	0.01	0.01	0.1	0.07	0.23
Decahydro[e]	26.3	3.19	3.67	3.21	2.32	27.6	2.19	3.10
Decahydro[f]	1.2	0.16	0.19	0.21	0.14	2.2	0.19	0.27
	Log Equilibrium Constant							
$C_{12}H_{10} + 2H_2 \rightarrow C_{12}H_{14}$	...	−1.68	−2.06	−2.53	−2.96	...	−3.06	−3.02
$C_{12}H_{10} + 5H_2 \rightarrow C_{12}H_{20}$[a]	...	−5.58	−6.60	−7.68	−8.50	...	−8.70	−8.53

(a)


(b)


(c)


(d)


(e)


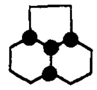
(f)


Table IV. Fluorene-Hydrogen Equilibrium

	Operating Conditions				
Temperature, ° C.	295.0	303.0	332.5	363.5	389.5
Hydrogen press., atm.	72.5	8.06	15.7	24.2	38.6
Hydrogen fugacity, atm.	74.3	8.08	15.8	24.4	39.1
Hydrocarbon press., atm.	0.7	0.5	1.0	1.1	1.1
1000/T° K.	1.750	1.736	1.651	1.571	1.509
	Hydrocarbon, Mole %				
Fluorene	...	49.16	38.56	57.89	51.16
trans-Hexahydro-	...	6.78	7.10	5.91	6.54
cis-Hexahydro-	...	28.25	30.15	25.11	27.01
Perhydro (a)[a]	0.33	0.05	0.08	0.08	0.25
Perhydro (b)	13.76	2.25	3.70	1.58	2.23
Perhydro (c)	48.86	8.26	11.43	5.11	6.91
Perhydro (d)	11.28	1.60	2.62	1.25	1.74
Perhydro (e)	23.83	3.39	5.93	2.82	3.81
Perhydro (f)	1.94	0.26	0.43	0.23	0.32
	Log Equilibrium Constant				
$C_{13}H_{10} + 3H_2 \rightarrow C_{13}H_{16}$ (cis)	...	-2.96	-3.70	-4.53	-5.05
$C_{13}H_{10} + 6H_2 \rightarrow C_{13}H_{22}$ (f)	...	-7.71	-9.15	-10.73	-11.75
$C_{13}H_{10} + 6H_2 \rightarrow C_{13}H_{22}$ (Total)	...	-5.93	-7.40	-9.04	-10.08
$C_{13}H_{10}$ (trans) $\rightarrow C_{13}H_{16}$ (cis)	...	0.620	0.627	0.627	0.616

[a] Perhydrofluorene compounds a, b, c, d, and e are of unknown structure. Compound f is the cis-syn-cis derivative.

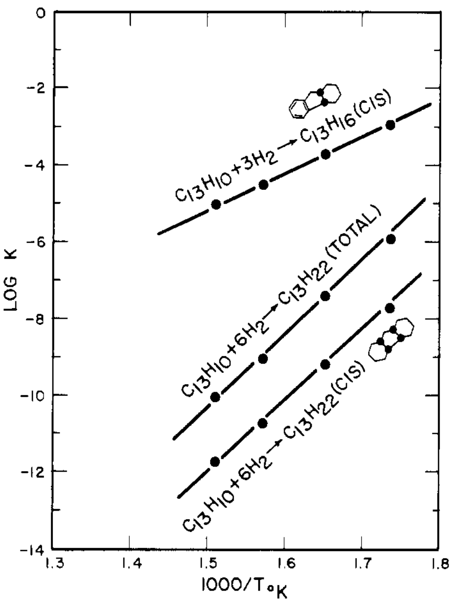


Figure 4. Fluorene-hydrogen equilibrium

This is about 1.3 kcal. lower than was observed for the tetralin to *cis*-decalin and indane to *cis*-hydrindane reactions, and indicates a substantial strain in these aromatic ring structures.

Two hexahydrofluorene derivatives—a cis and trans derivative—are possible. The observed cis-to-trans ratio of these two compounds is 4.2 ± 0.2. Within the accuracy of the data, this ratio is independent of temperature, which implies zero heat of isomerization. This is an unusual result and suggests that there is an approximate cancellation of two or more strain effects with change in temperature.

The ratio, $(cis\text{-hexahydro})^2$-to-(fluorene) (perhydrofluorene), is independent of hydrogen pressure. Experimentally, over the range from about 300° to 400° C., this ratio for the all-cis perhydrofluorene decreases from 62 to 46. The ratio for the total perhydrofluorene decreases from 1.03 to 0.93 over the same interval.

Only the "all-cis" (i.e., cis-syn-cis) of the perhydro compounds was reliably identified. Data for the other perhydro compounds whose structures are unknown are given in Table IV. The most abundant compound constitutes almost 50% of the equilibrium mixture, the next most abundant almost 25% and the next two about 12.5% each.

LITERATURE CITED

(1) Allinger, N.I., Coke, J.L., *J. Am. Chem. Soc.* **81**, 4080 (1959).
(2) *Ibid.*, **82**, 2553 (1962).
(3) Allam, M.I., Vlugter, J.C., *J. Inst. Petrol.* **52**, 385 (1966).
(4) Blanchard, K.R., Schleyer, P.R., *J. Org. Chem.* **28**, 247 (1963).
(5) Frye, C.G., J. CHEM. ENG. DATA **7**, 592 (1962).
(6) Gilliland, E.R., "High Pressure Processes," p. 69, Massachusetts Institute of Technology, Cambridge, Mass., 1949.
(7) Miyazawa, T., Pitzer, K.S., *J. Am. Chem. Soc.* **80**, 60 (1958).
(8) Rossini, F.D., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds"(API Res. Proj. **44**), Carnegie Press, Pittsburgh, Pa., 1953.
(9) Speros, D.M., Rossini, F.D., *J. Phys. Chem.* **64**, 1723 (1960).
(10) Weitkamp, A.W., *Advan. Catalysis* **18**, 1 (1968).
(11) Wilson, T.P., Caflish, E.G., Hurley, G.F., *J. Phys. Chem.* **62**, 1059 (1958).

RECEIVED for review November 29, 1968. Accepted February 19, 1969.