Thermal Decomposition of *n*-Hexane at High Pressures

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THE BALLISTIC piston apparatus (*13*) affords a means for carrying out gas-phase reactions under conditions of high temperature and pressure and allows for the recovery of the sample for subsequent analysis. This investigation on *n*-hexane used reaction temperatures in the range of 1600° to 2800° R. with maximum pressures as high as 115,000 p.s.i. The little work reported on chemical reactions under such extreme conditions has been done by the Russians, and includes reactions involving nitrogen and hydrogen (*20*), nitrogen and oxygen (*18*), and methane and oxygen (*1*). No data on the thermal decomposition of hydrocarbons such as *n*-hexane under such conditions have come to the attention of the authors.

In some preliminary experiments on methane, when the conditions were sufficiently severe to cause a moderate fraction of the methane to react, the decomposition products were predominantly carbon and hydrogen. Higher hydrocarbons are less stable than methane at these elevated temperatures and study of the reactions of a paraffin hydrocarbon of moderate molecular weight promised to be more interesting. *n*-Hexane was selected as having a vapor pressure sufficiently high to allow addition of the desired quantities in the gas phase at room temperature.

It is necessary to dilute a material of high heat capacity such as *n*-hexane with a gas of low heat capacity to get temperatures sufficiently high for reaction. Hydrogen was selected as the diluent for one series of tests because it would be expected to react with unsaturated materials formed by the decomposition of *n*-hexane. Nitrogen was selected as an inert diluent for a second series of measurements because its heat capacity is similar to that of hydrogen. A small amount of helium was used in addition to nitrogen in one of the latter tests.

EXPERIMENTAL PROCEDURE

The ballistic piston apparatus (*13*) was used with the exception that the piezoelectric pressure gage and the thermal flux meter were not available until after the completion of the measurements described. A heavy piston having a stellite facing on the edge of the sample end was employed for all tests. The sample chamber is 3.0 inches in inside diameter and, for these tests, about 100 inches long initially. The gaseous samples involved approximately 1.4×10^{-4} pound-mole.

After the apparatus was assembled with the appropriate bottom contact wires and lead gage in the bottom closure, the lower chamber was evacuated to about 2-mm. pressure, then purged three times with one of the gases to be used in the sample, either nitrogen or hydrogen. This gas was passed through a trap immersed in a dry ice-trichloroethylene mixture to remove moisture. The apparatus was pumped down to a pressure of 10 mm. or less between purges, and to 1 to 2 mm. after the third purge when the pressure was recorded and chamber valves closed. The purging procedure was used because the lines connecting the vacuum system to the apparatus are of small bore; obtaining a reasonable vacuum through them was wasteful of time.

The *n*-hexane was placed in one of the absorption bulbs in the sample addition system and the bulb pumped for 10 to 15 seconds to remove air. After evacuation of lines, hexane vapor was admitted to the chamber, and addition was continued by vaporization of hexane until the desired quantity had been added, then the chamber pressure was measured, and the chamber valves were closed. After evacuation of lines, sufficient diluent gas was added to bring the chamber pressure to about 800 mm. and the pressure measured. The diluent gas was introduced into the bottom of the chamber to aid mixing. After standing at least 30 minutes, a control sample was drawn into an evacuated sample bulb, then the chamber pressure was reduced to that desired as an initial sample pressure. Meanwhile, the time-interval meters had been warmed up and checked out. Compressed air was admitted to the upper chamber, all valves were closed, and the piston was released.

After the shot, timing data were recorded, the air pressure remaining above the piston was vented, and the top closure was removed. Distance to the top of the piston from the top of the apparatus was measured to 1/64 inch with a weighted steel tape, and pressure of the sample was measured by the mercury manometer. These measurements allowed estimation of final sample quantity and thus led to leakage estimates. Two product samples were taken in evacuated sample bulbs.

The piston and bottom closure were then removed and the lead gage was recovered and measured.

MATERIALS

The *n*-hexane was Phillips Petroleum Co. research grade quoted as 99.85 mole % pure. Part of the tests were made with a sample which had been dried with sodium metal; however, a new sample was used to finish the tests and drying was not considered necessary. As the *n*-hexane was used for a calibration standard in the analysis of samples by mass spectrometer, no independent measure of purity is available.

The helium was obtained from Air Reduction Co. and was represented as 99.97% pure.

The hydrogen was electrolytic hydrogen obtained from the Matheson Co. No analysis was obtained of the cylinder; however, mass spectrometer analysis of a previous cylinder from this source showed as impurities (expressed in mole per cent) 0.4 nitrogen, 0.13 oxygen, 0.03 carbon dioxide, and 0.02 methane. The analysis data for sample mixtures before compression indicated about 0.11 mole % oxygen in the hydrogen used.

The nitrogen was obtained from Linde Air Products Co.

Table I. Data from *n*-Hexane Studies

Test No.	Initial Conditions[a]						Conditions at Minimum Volume		Leakage Fraction
	Driving air pressure, p.s.i.	Sample pressure, p.s.i.	Sample temp., ° R.	Sample composition, mole fraction			Piston approach, in.	Normalized vol.	
				n-Hexane	Nitrogen	Hydrogen			
111	618.6	1.9231	534.2	0.04973	...	0.95027	0.0188	2.503×10^{-4}	0.050
113[b]	618.4	1.9190	534.4	0.05005	0.83040[b]	...	0.0410	4.738	0.091
119	555.0	1.9263	528.9	0.10403	...	0.89597	0.0152	2.147	0.011
120	560.2	1.9225	528.1	0.03752	...	0.96248	0.0418	4.814	0.005
121	506.2	1.9183	526.5	0.08650	...	0.91350	0.0298	3.608	0.026
124	695.8	1.9249	529.3	0.04476	0.95524	...	0.0317	3.805	0.162
125	560.3	1.9216	529.9	0.09907	0.90093	...	0.0278	3.412	0.131
126	630.6	1.9241	529.4	0.03188	0.96812	...	0.0388	4.512	0.148
127	509.3	1.9221	523.3	0.08147	0.91853	...	0.0417	4.809	0.066
128	565.4	1.9250	530.2	0.05936	0.94064	...	0.0331	3.946	0.170
129	659.3	1.9262	527.0	0.06340	0.93660	...	0.0309	3.724	0.165
131	621.6	1.9233	528.7	0.07523	0.92477	...	0.0240	3.031	0.667
132	544.0	1.9039	529.5	0.04919	...	0.95081	0.0311	3.745	0.023
140	526.7	1.9202	531.5	0.06318	...	0.93682	0.0281	3.446	...
142	605.2	1.9233	537.6	0.06335	...	0.93665	0.0177	2.400	0.430
143	575.5	1.9063	530.5	0.08061	...	0.91939	0.0125	1.877	...

[a] Piston weight, 30.98 pounds for tests 111 through 132; 32.09 pounds for tests 140 through 143.
[b] For test 113, 0.11955 helium was present in addition to constituents shown.

and was reported as 99.95% pure. An analysis by mass spectrometer showed 0.04 mole % oxygen, 0.02 mole % argon, and 0.07 mole % water as impurities. The oxygen content is compatible with the analyses of control samples for tests.

All mass spectrometer analyses were preformed by the Montebello Laboratories of Texaco Inc.

EXPERIMENTAL RESULTS

Sixteen tests were made, eight with hydrogen and eight with nitrogen as the diluent for the *n*-hexane.

The initial conditions used are shown in Table I. The initial compositions shown were calculated from pressure measurements made during sample addition, and deviations from perfect gas behavior were taken into account. The distance of closest approach of the piston to the bottom is also shown. Normalized volume, V_2^*, the ratio of the minimum sample volume to initial sample volume, includes corrections for gage volume and the volume of timing contact holder and valve recesses. The values for leakage are based on measurements of sample volumes, temperatures, and pressures made after the tests but before samples for analysis were taken. Leakage was very large for tests 131 and 142, and moderately large for several other of these relatively high pressure tests. The piston weighed 30.98 pounds, but for the last three runs, numbers 140, 142, and 143, it weighed 32.09 pounds.

Table II shows the time data obtained by use of contact wires extending up from the bottom of the chamber. The heights of the wires above the bottom of the chamber recorded in Table II were measured with a depth micrometer to 0.0002 inch, and it is believed they are known to 0.001 inch at the time of piston contact in most cases. Times are accurate to ±1 microsecond. Piston velocities were calculated at point h_2 by use of Equation A64 (*14*), which uses the data for points 1, 2, and 3. [An A before an equation number signifies that this equation may be found in reference (*14*), which contains the derivation of equations.] Velocities are shown in Table II. Accelerations at point h_2, calculated from timing measurements, were not of sufficient accuracy to be useful.

Side contacts were installed near the end of this program. Partial data on three tests were obtained (*14*). Timing data from both side and bottom contacts are shown for test 143

Table II. Bottom Contact Timing Data

Test No.	Height of Bottom Contact[a], Inch				Time from First Contact[b], Microsec.			Velocity at h_2, Ft./Sec.
	h_1	h_2	h_3	h_4	θ_2	θ_3	θ_4	
111	0.2528	0.1877	0.1223	0.0790	99	203	284	-53.63
113	0.2504	0.1913	0.1365	0.0727	102	213	363	-45.00
119	0.2486	0.1926	0.1303	0.0556	90	198	347	-50.14
120	0.2675	0.1667	0.1188	0.0719	190	285	407	-42.75
121	0.4990	0.3463	0.1913	0.1010	258	536	725	-47.95
124	0.5057	0.3537	0.2014	0.0970	210	454	630	-56.48
125	0.4984	0.3513	0.2142	0.0986	224	452	674	-52.44
126	0.4868	0.3476	0.2135	0.1022	195	394	584	-57.84
127	0.4876	0.3450	0.2068	0.1041	261	517	747	-45.26
128	0.4960	0.3303	0.1908	0.0933	249	474	657	-53.47
129	0.5012	0.3519	0.2085	0.1020	210	423	601	-57.69
131	0.5027	0.3344	0.2023	0.1119	236	431	580	-57.80
132	0.5121	0.3506	0.2108	0.1046	254	491	698	-51.00
140	0.5305	0.3734[c]	0.1928[c]	0.0968[c]	225	521	692	...
142	0.5186	0.3609	0.2073	0.1072	232	459	625	-56.51
143	0.5160	0.3577	0.2104	0.1100	224	440	606	-57.84

[a] Measured from face of lower closure.
[b] First contact located at height h_1 from face of lower closure.
[c] Values believed in error by a constant amount but included for completeness.

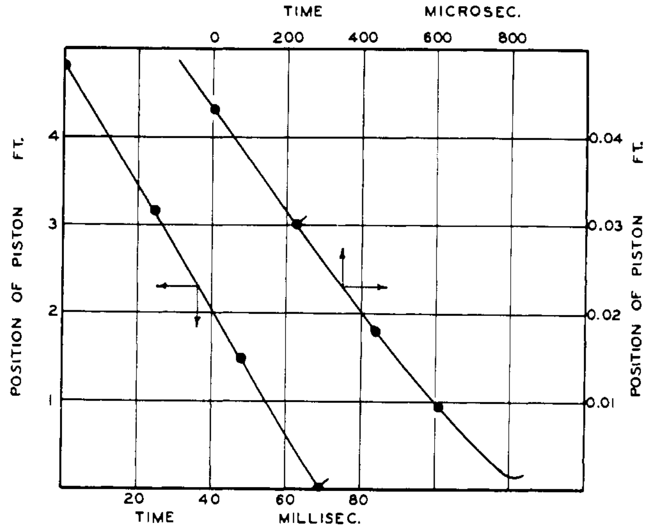

Figure 1. Position-time data, test 143

in Figure 1. The flagged point is common to the two curves shown; the curve on the right is a magnification by a factor of 100 of the lower end of the curve on the left.

Representative samples of the gas mixture being investigated were taken for each test before and after the firing of the ballistic piston apparatus. Mass spectrometer analyses are included in (*14*).

ANALYSIS OF DATA

Products. The analysis data (*14*) do not balance stoichiometrically, nor do the control analyses agree precisely with the compositions computed from measurements made during addition of the sample. The latter disagreements are generally within the error to be expected. As a set of compositions which did balance stoichiometrically was required, such adjusted analyses were computed (*14*) and are shown in Tables III and IV for the nitrogen-*n*-hexane and hydrogen-*n*-hexane studies, respectively. The origin of each value recorded is evident by footnotes to these tables. The adjustments made are within the accuracy of the mass spectrometer analyses. The free carbon shown for the nitrogen tests in Table III is in qualitative agreement with observation, with the exception of test 131, where no carbon was observed. A small amount of carbon may have been undetected by visual examination because graphite was present as a lubricant. However, it was easy to detect the physical difference between the graphite used as a lubricant and the carbon formed by decomposition of the *n*-hexane.

Compressional Process. The data were subjected to an analysis (*14*) to determine the conditions to which the samples were subjected. For this analysis the compressional process was divided into two parts: first, an isentropic compression from the initial conditions to a temperature T_1, and secondly, an isothermal compression at temperature T_1 to the maximum density. Volumetric data (*12*) based on the Lennard-Jones (6–12) potential and thermodynamic data in reference (*14*) were used. The analysis was based on the assumption of no leakage, ideal solutions (*11*), the covolume constant at value for the maximum pressure of the test, local equilibrium (*6*), no variation of gas properties throughout the gas volume, and no shock waves or friction in the gas. In addition, for the isentropic portion of the compression it was assumed that the composition was constant and that there was no heat transfer.

The results of the analysis are shown in Table V. The work done on the sample is actually small, being about 3 or 4 B.t.u. The temperatures for the isothermal path range from 1640° to 2764° R., and the maximum pressures for individual tests range from 26,200 to 115,160 p.s.i. The terms ($\Delta E_R - Q$) indicate a rather sizable absorption of energy in reaction or heat transfer, with the former much more probable. The time intervals during which the assumed isothermal compressions take place are also shown.

Table III. Analyses for Nitrogen–*n*-Hexane Studies

	Test No.							
Component	113	124	125	126	127	128	129	131
	Initial Composition, Mole Fraction[a]							
Helium	0.1196	...	...	...	...	...	...	...
Nitrogen	0.8304	0.9552	0.9009	0.9681	0.9185	0.9473[b]	0.9466[b]	0.9248
n-Hexane	0.0500	0.0448	0.0991	0.0319	0.0815	0.0527[b]	0.0534[b]	0.0752
	Final Composition, Mole Fraction							
Hydrogen[b]	0.0140	0.0586	0.0034	0.0760	0.0046	0.0302	0.0387	0.0118
Helium[c]	0.1077	...	...	...	...	...	...	...
Nitrogen[c]	0.7475	0.8479	0.8431	0.8679	0.8606	0.8499	0.8396	0.8312
n-Hexane	0.0052[b]	0.0046[b]	0.0510[c]	0.0020[b]	0.0379[c]	0.0076[b]	0.0059[b]	0.0130[b]
Hexene[b]	...	...	0.0004	...	0.0021	...	...	0.0022
Pentene[b]	...	...	0.0032	...	0.0030	0.0005	...	0.0022
Pentadiene[b]	...	...	0.0015	...	0.0016	...	...	0.0015
Butane[b]	...	0.0006	...	...	...	...	...	...
Butene[b]	0.0008	...	0.0110	...	0.0057	...	0.0011	0.0060
Butadiene[b]	...	...	0.0010	...	0.0014	0.0008	0.0006	0.0026
Butadiyne[b]	...	...	...	...	...	0.0002	0.0002	0.0006
Propane[b]	...	...	0.0054	...	0.0037	...	...	0.0032
Propene[b]	0.0030	0.0019	0.0202	0.0004	0.0158	0.0038	0.0041	0.0147
Ethane[b]	0.0040	0.0027	0.0152	0.0013	0.0140	0.0083	0.0056	0.0219
Ethene[b]	0.0103	0.0067	0.0250	0.0046	0.0301	0.0141	0.0099	0.0297
Methane	0.1035[c]	0.0741[c]	0.0195[b]	0.0474[c]	0.0195[b]	0.0778[c]	0.0881[c]	0.0545[c]
Benzene[b]	0.0032	0.0025	...	0.0004	...	0.0048	0.0047	0.0028
Toluene[b]	0.0008	0.0004	...	...	...	0.0020	0.0015	0.0021
Free Carbon[c, d]	0.0775	0.1039	0.0000	0.1080	0.0000	0.0611	0.0801	0.0180
γ[c, e]	1.111	1.127	1.069	1.115	1.067	1.115	1.127	1.113

[a] From sample synthesis measurements, except as noted.
[b] Mass spectrometer results reported on air-, carbon dioxide–, water-, and oxygen-free basis.
[c] Calculated from stoichiometric relations.
[d] Moles per mole of initial sample.
[e] Moles of final gas per mole of initial sample.

Table IV. Analyses for Hydrogen–n-Hexane Studies

Component	Test No. 111	119	120	121	132	140	142	143
	Initial Composition, Mole Fraction[a]							
Hydrogen	0.9503	0.8960	0.9625	0.9135	0.9508	0.9368	0.9367	0.9194
n-Hexane	0.0497	0.1040	0.0375	0.0865	0.0492	0.0632	0.0633	0.0806
	Final Composition, Mole Fraction							
Hydrogen[b]	0.7387	0.7819	0.8012	0.6800	0.7529	0.7054	0.7039	0.6618
n-Hexane	0.0049[c]	0.0450[b]	0.0022[c]	0.0233[c]	0.0066[c]	0.0104[c]	0.0115[c]	0.0200[c]
Hexene[c]	...	0.0012	...	...	...	...	...	...
Pentane[c]	...	...	0.0002	...	...	...	...	...
Pentene[c]	...	0.0018	...	0.0006	...	0.0004	0.0002	0.0004
Butane[c]	...	0.0044	...	0.0013	...	0.0004	0.0006	0.0008
Butene[c]	...	0.0048	0.0004	0.0023	...	0.0006	0.0010	0.0010
Butadiene[c]	...	...	...	...	...	...	0.0010	...
Propane[c]	0.0009	0.0228	0.0016	0.0070	0.0008	0.0026	...	0.0033
Propene[c]	0.0012	0.0101	0.0006	0.0038	0.0011	0.0017	0.0004	0.0025
Ethane[c]	0.0078	0.0512	0.0071	0.0361	0.0082	0.0138	0.0120	0.0222
Ethene[c]	...	0.0073	0.0012	0.0053	0.0021	0.0032	0.0025	0.0018
Methane	0.2465[b]	0.0695[c]	0.1855[b]	0.2403[b]	0.2283[b]	0.2615[b]	0.2669[b]	0.2862[b]
γ[b,d]	1.001	1.026	1.002	1.012	1.003	1.006	1.006	1.006

[a] From sample synthesis measurements.
[b] Calculated from stoichiometric relations.
[c] Mass spectrometer results reported on air-, carbon dioxide–, water-, and oxygen-free basis.
[d] Moles of final gas per mole of initial sample.

The compressibility factor at maximum compression, $(PV)/(RT)$, shows that the covolume equation of state (*12*) predicts significant departure from perfect gas behavior under the conditions of these tests.

The distributions of the products of decomposition of the n-hexane were computed, using the adjusted analyses of Tables III and IV, and are shown in (*14*). These conversions were computed on the basis of the fraction of the carbon from the decomposed n-hexane appearing in each product.

The fractions (*14*) of the total amount of n-hexane decomposed which appeared as various products are plotted on a cumulative basis as functions of the calculated reaction temperature in Figure 2 for the tests with nitrogen. There are marked shifts in the product distribution with temperature. At the lowest temperatures, unsaturates predominate. In the middle range, methane and free carbon predominate, but 0.15 of the n-hexane is converted to aromatics and 0.2 to 2-, 3-, and 4-carbon compounds. At the upper temperature range, free carbon and methane are the major products. Hydrogen, which is also produced, is not shown in Figure 2.

Similarly the conversion data (*14*) for the tests with

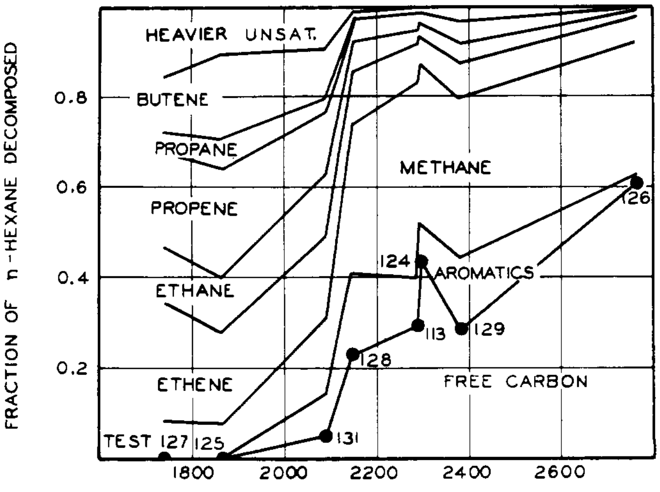

Figure 2. Cumulative product distribution in nitrogen–n-Hexane studies

Table V. Results for Isothermal Path Calculations

Test No.	Work Done on Sample, B.t.u.	Assumed Mole Ratio[a]	Results for Isothermal Reaction Assumption: Temp. of isothermal path, ° R.	Duration of isothermal path, microsec.	Max. pressure, p.s.i.	$\Delta E_R - Q$, B.t.u./lb. mole	Max. compressibility factor[b]
111	4.152	1.000	2524	423	67,050	13,905	1.844
113	3.605	1.060	2288	720	32,180	12,106	1.670
119	3.342	1.013	1640	664	81,590	12,681	2.859
120	3.760	1.000	2757	524	27,090	10,111	1.296
121	3.074	1.006	1890	567	30,630	8,885	1.585
124	3.905	1.065	2293	615	52,630	13,850	2.132
125	3.301	1.035	1861	374	55,550	9,710	2.629
126	4.198	1.060	2764	466	44,950	13,156	1.810
127	2.979	1.035	1738	966	26,200	9,701	1.850
128	3.651	1.060	2147	557	47,480	12,108	2.156
129	3.865	1.065	2381	274	62,510	10,438	2.372
131	3.837	1.060	2088	347	84,270	12,571	3.022
132	3.536	1.000	2283	705	31,550	11,725	1.435
140	3.594	1.000	2381	384	38,580	9,384	1.535
142	3.851	1.000	2234	216	66,610	13,376	1.988
143	3.820	1.000	1945	473	115,160	14,526	3.074

[a] Average number of moles per initial mole (N_{av}/N_0). [b] Maximum compressibility factor is that at maximum pressure.

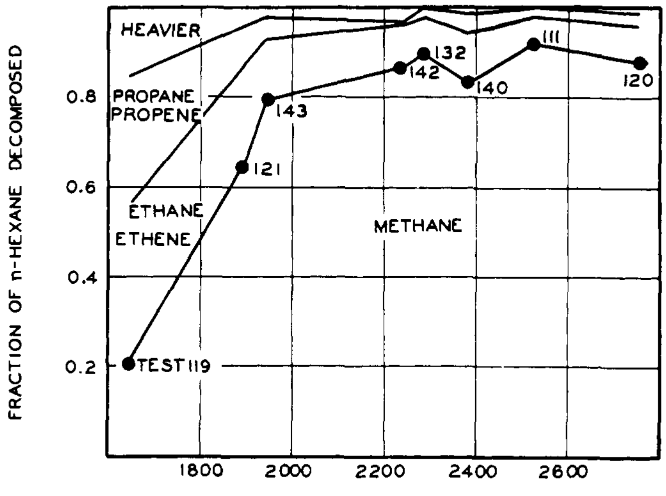

Figure 3. Cumulative product distribution in hydrogen–n-Hexane studies

hydrogen as a diluent are plotted in Figure 3. The trends in this case are very definite. At the lowest temperature there is a somewhat uniform distribution of saturated hydrocarbons through propane, with some high hydrocarbons. The amounts of unsaturates are small. In the middle and upper temperature ranges, 0.85 to 0.9 of the *n*-hexane is converted to methane, with ethane accounting for most of the remainder.

Some of the tests, particularly 124, would fit the trends of Figures 2 and 3 better if they were plotted at different temperatures. However, no account of the possible effects of pressure or duration on the distribution of reaction products was taken in plotting these data, and these factors may well account for some of the irregularities.

First-Order Reaction Rate Coefficients. It was possible to obtain some reaction rate coefficients for the decomposition of *n*-hexane from the results of these tests. It was assumed that the decomposition was irreversible and occurred only during the time represented by the isothermal path assumed for the calculations above. The mole fraction of *n*-hexane was then known at the beginning and at the end of this time because it was assumed to be equal to the initial and to the final mole fractions, respectively.

Calculations were first made on the basis of a first-order reaction, for which the equations are derived (*14*). The reaction rate was taken as represented by the equation

$$-\frac{dN_R}{d\theta} = k_R\underline{V}_B(f_R) = k_R\underline{V}_B n f_R^0 \tag{1}$$

This is essentially a defining relationship for the reaction rate coefficient, k_R. The reaction rate coefficient is obtained from the integral Equation A-55 using Equations A-46, A-52, and A-56, and tabulated fugacity data for *n*-hexane (*14*).

Equation A-55 was solved by numerical integration for all tests, and the calculated values of the reaction rate coefficient, k_R, for first order reaction are shown in Table VI. As a matter of interest, the maximum values of the activity coefficient for *n*-hexane, (f_R^0/P), obtained for each test are shown in Table VI. These ratios, which are of course unity for ideal gases, become very large under these rather extreme conditions.

The calculated first-order reaction rate coefficients are shown in Figure 4. As reaction rate coefficients are often represented by the conventional Arrhenius equation,

$$\frac{d(\ln k_R)}{d\left(\frac{1}{T}\right)} = -\frac{E'}{R} \tag{2}$$

a semilogarithmic plot of k_R against reciprocal temperature was used. Although there is a vague trend, the points do not make a good line even though data for two tests, numbers 131 and 143, were omitted on the basis of large apparent leakage. Inspection of the deviations of the points from a least squares line indicated considerable correlation with the value of maximum pressure. Accordingly, a regression analysis of k_R as a linear function of P_2 and $(1/T)$ was made giving as the result the equation

$$\ln k_R = 4.6665 - \frac{7639.4}{T_1} - 4.7801 \times 10^{-5} P_2 \tag{3}$$

with temperature in degrees Rankine and pressure in pounds per square inch. The coefficient of the reciprocal temperature corresponds to an activation energy of 15,179 B.t.u. per pound-mole (8.43 kcal. per gram mole).

Table VI. First-Order Reaction Rate Coefficients

Test No.	Diluent	Reciprocal Temp., ° R.$^{-1}$	Max. Pressure, P.S.I.	Max. Activity Coefficient[a]	Reaction Rate Coefficient[b] Calcd.	Corr.[c]
111	Hydrogen	3.962 × 10^{-4}	67,050	60.3	0.285	0.531
113	Nitrogen-Helium	4.371	32,180	7.05	0.723	0.255
119	Hydrogen	6.098	81,590	723.	0.023	0.098
120	Hydrogen	3.627	27,090	4.45	1.155	0.319
121	Hydrogen	5.291	30,630	7.00	0.658	0.215
124	Nitrogen	4.361	52,630	28.8	0.358	0.335
125	Nitrogen	5.373	55,550	51.9	0.092	0.099
126	Nitrogen	3.618	44,950	13.5	0.588	0.382
127	Nitrogen	5.754	26,200	4.89	0.342	0.091
128	Nitrogen	4.658	47,480	22.9	0.370	0.284
129	Nitrogen	4.200	62,510	52.0	0.239	0.359
131	Nitrogen	4.789	84,270	314.	0.054	0.230
132	Hydrogen	4.380	31,550	6.73	0.740	0.253
140	Hydrogen	4.200	38,580	10.7	0.646	0.310
142	Hydrogen	4.476	66,610	80.6	0.193	0.353
143	Hydrogen	5.141	115,160	4300.	0.0063	0.118

[a] Activity coefficient is defined as the quotient of fugacity of *n*-hexane in the pure state and pressure (f_R^0/P).
[b] (Lb. mole)/(cu. ft.)(atm.)(sec.). The units for the reaction rate coefficients are not consistent but follow precedent.
[c] Corrected to pressure at maximum compression of 54,000 p.s.i.

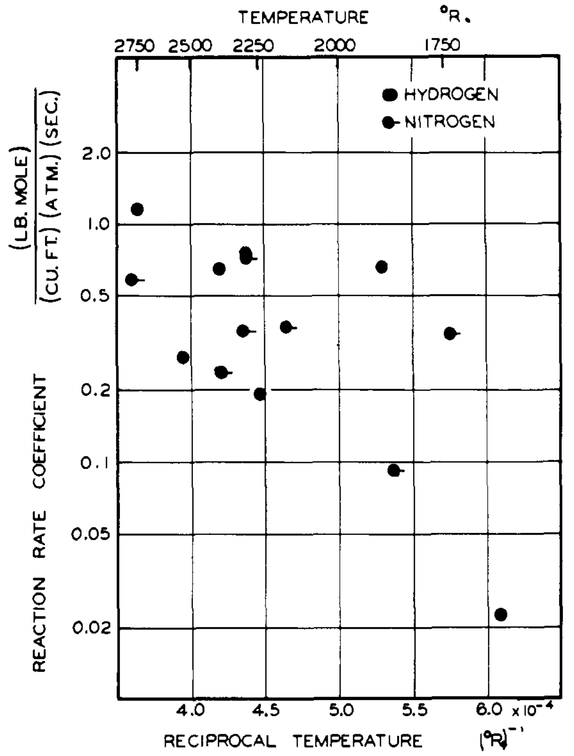

Figure 4. First-order reaction rate coefficients

Variances were not calculated, but rather the calculated values of reaction rate coefficients were corrected to those which would presumably haye been found if the maximum pressure had been equal to the mean for the tests, 54,000 p.s.i. This correction was made by use of the coefficient of the pressure found in Equation 3. The coefficients obtained in this manner are tabulated in Table VI and are plotted in Figure 5. The nature of this correction is such that all the variations of the actual calculated reaction rate coefficients from the relationship of Equation 3 are shown as variations of the corrected coefficient from the line in Figure 5. These variations are reasonably small, the maximum being a logarithm corresponding to a ratio of 1.57.

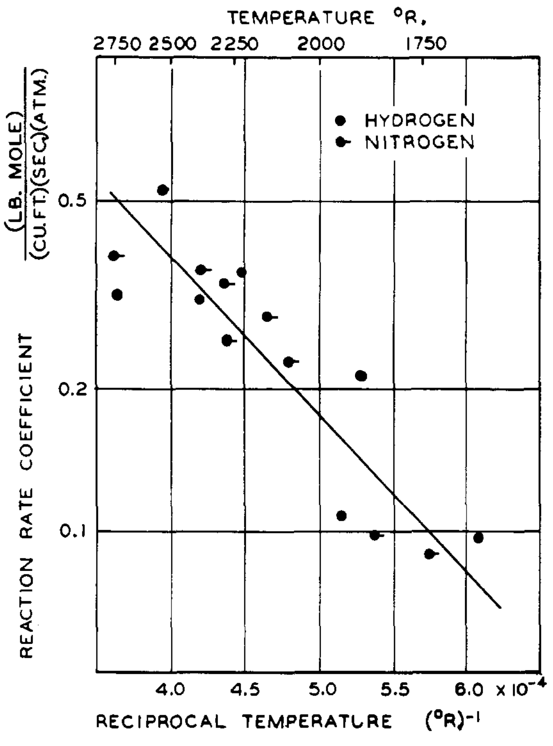

Figure 5. First-order reation rate coefficients corrected to 54,000 p.s.i. maximum pressure

In Figures 4 and 5 the points for the hydrogen and for the nitrogen tests have been distinguished, but no influence of the diluent on the reaction rate coefficient is detectable. This is in agreement with the assumption of a decomposition reaction with the reaction rate not being a function of the fugacity of components other than the n-hexane.

Although the regression Equation 3 gives a good fit of the data, it is incompatible with the basic premise that the reaction rate coefficient be a function only of the temperature. Therefore, Equation 1 does not describe the actual reaction rate, and the reaction is not first order.

One-Half–Order Reaction Rate Coefficients. Calculations were next made for one-half-order reaction. The defining equation (*14*) is

$$-\frac{dN_R}{d\theta} = k_R\underline{V}_B(f_R)^{1/2} = k_R\underline{V}_B(nf_R^0)^{1/2} \tag{4}$$

and the solution is given by Equation A-61, using Equations A-46, A-52, and A-62, and fugacity data (*14*). Numerical intregrations of Equation A-61 were performed for all tests, and the reaction rate coefficients calculated on the basis of this one-half-order reaction are shown in Table VII as calculated and are plotted in Figure 6. A least squares line is shown on Figure 6, corresponding to the equation:

$$\ln k_R = 2.6657 - \frac{2607.8}{T_1} \tag{5}$$

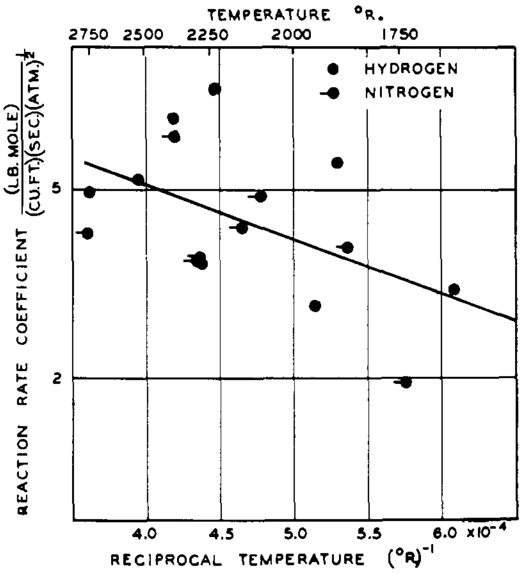

Figure 6. One-half–order reaction rate coefficients

The reciprocal temperature was taken as the independent variable for this regression.

The variations of the reaction rate coefficients from the regression line Equation 5 were compared with test data in a search for further correlation. No evidence of even weak correlation was found except with two variables, the time interval and the amount of n-hexane decomposed. The two tests showing the largest deviations from the line, numbers 127 and 142, had also the extremes in time interval $\Delta\theta$; however, the other tests showed no trend and regression with $\Delta\theta$ appeared to be unprofitable. The deviations of the reaction rate coefficients from the least squares line did show a somewhat weak correlation with the amount of *n*-hexane decomposed. A regression was therefore made with reciprocal temperature and amount of *n*-hexane decomposed as independent variables which yielded the equation

$$\ln k_R = 2.3227 - \frac{4648.4}{T_1} + 27.207\, s \qquad (6)$$

The amount of *n*-hexane decomposed is shown in Table VII.

Values of the reaction rate coefficients corrected to those which would presumably have been found if the amount of *n*-hexane decomposed had been constant at the mean of 0.04744 mole per mole of initial sample were calculated using the coefficient of s from Equation 6. These corrected values are shown in Table VII and are plotted in Figure 7. All the variation of the data from the regression Equation 6 is retained in Figure 7; hence comparison with Figure 6 shows that the fit has been improved. Two tests, numbers 142 and 143, show noticeably large deviations, while the rest of the data are much closer to the regression line.

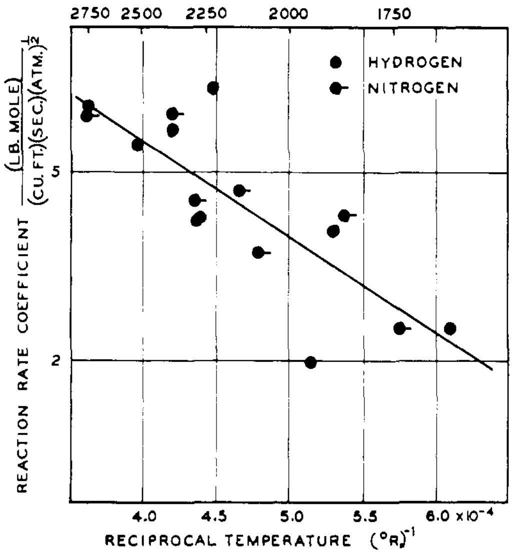

Figure 7. One-half–order reaction rate coefficients corrected to average amount of reaction

Another significant fact is that the slopes of the regression lines in the two figures are different. Activation energies E' as defined in Equation 2 were calculated for the data of Figures 6 and 7. The slope of Figure 6 yields an activation energy of 5180 B.t.u. per pound mole (2.88 kcal. per gram mole) for the half-order reaction (uncorrected) while from Figure 7 an activation energy of 9240 B.t.u. per pound mole (5.13 kcal. per gram mole) is obtained for the one-half order reaction corrected for regression with s.

SOURCES OF ERROR

The results shown are subject to errors as the result of the assumptions necessarily made in deriving the relationships used (*14*), and as a result of uncertainties in the data. The more important considerations are summarized here, and others are discussed elsewhere (*14*).

The equation of state employed (*12*) is believed to be much better than an assumption of perfect gases. It is, however, based on a statistical mechanical model (*2*) which is not well matched by the *n*-hexane. As the fugacity is sensitive to the equation of state, the reaction rate coefficients are less dependable than the pressures and temperatures. The assumption of constant covolumes for calculations other than that of fugacity is considered logical, particularly as the covolumes (*12*) are surprisingly constant for hydrogen, helium, nitrogen, and methane. The possible error introduced by the assumption of ideal solutions (*11*) is believed insignificant.

The assumption of local equilibrium (*6*), requiring that the internal energy be distributed among the various degrees of freedom of the molecules in the equilibrium manner, is inherent in these calculations. The relaxation times (*3, 5, 9, 10*) of the various molecular species present were considered (*14*), and it appears that only nitrogen may show a slight departure from local equilbrium under extreme ballistic piston conditions. At 2000° R. and a pressure of 20,000 p.s.i., a relaxation time of 3 microseconds is estimated for nitrogen, and 0.6 microsecond at 2000° R. and a pressure of 100,000 p.s.i.

In the determination of reaction rate coefficients the decomposition of the *n*-hexane was assumed irreversible and to take place only in the isothermal portion of the compressional process. Free energy considerations uphold the irreversibility; however, some evidence that there was a quantity of free radicals remaining at the end of the compressional process is discussed below. As these free radicals would be expected to attack the *n*-hexane, probably some additional *n*-hexane was decomposed subsequently.

Although some estimated leakages are shown in Table I, all calculations were made assuming no leakage. No correlations of the observed over-all leakages with calculated conditions, reaction rates, etc., were found, and it is not at all clear when the leakages did occur. It is believed that most of the observed leakage occurred after the piston had come to rest.

DISCUSSION OF RESULTS

The reaction rate coefficients for the apparent one-half-order reaction, in Table VII and Figures 6 and 7, represent the situation as well as can be expected in the absence of measurements of pressure and temperature. It is concluded that the diluent gas does not enter chemically into the rate-controlling steps of the decomposition of the *n*-hexane, as the calculated reaction rate coefficients for both first-

Table VII. One-Half–Order Reaction Rate Coefficients

Test No.	Diluent	Reciprocal Temp., ° R.$^{-1}$	*n*-Hexane Decompd.[a]	Reaction Rate Coefficient[b] Calcd.	Reaction Rate Coefficient[b] Corr.[c]
111	H	3.962×10^{-4}	0.0448	5.26	5.65
113	N-He	4.371	0.0442	3.60	3.93
119	H	6.098	0.0578	3.08	2.32
120	H	3.627	0.0353	4.93	6.86
121	H	5.291	0.0629	5.70	3.74
124	N	4.361	0.0396	3.52	4.35
125	N	5.373	0.0446	3.77	4.08
126	N	3.618	0.0297	4.02	6.52
127	N	5.754	0.0410	1.95	2.33
128	N	4.658	0.0442	4.17	4.55
129	N	4.200	0.0467	6.44	6.57
131	N	4.789	0.0607	4.84	3.37
132	H	4.380	0.0426	3.48	3.97
140	H	4.200	0.0527	7.05	6.11
142	H	4.476	0.0517	8.39	7.47
143	H	5.141	0.0605	2.82	1.97

[a] (Lb. mole) / (lb. mole initial sample).

[b] (Lb. mole) / (cu. ft.) (atm.)$^{1/2}$ (sec.). Units for reaction rate coefficient are not consistent but follow precedent.

[c] Corrected to amount of *n*-hexane decomposed = 0.04744 (lb. mole) / (lb. mole initial sample).

order and one-half-order kinetics show no differences between nitrogen and hydrogen as the diluent. As the reaction rate coefficients for one-half-order kinetics show no correlation with maximum pressure or the maximum ratio (f^0_R/P), an apparent order of one half is believed correct for the decomposition reaction. Unfortunately, the calculated reaction rate coefficients are particularly sensitive to the equation of state of the *n*-hexane because the ratio (f^0_R/P), which assumed large values under the conditions encountered, is an exponential function of the covolume of the *n*-hexane. As the accuracy of the equation of state (*12*) used for *n*-hexane is not known, there is some uncertainty in the determination of the apparent order of the reaction. Reaction mechanisms involving free radicals which yield an apparent one-half order have been postulated (*8, 17, 19*). Slightly different chain-ending steps yield apparent first-order and apparent 3/2-order reactions. Thus a one-half-order reaction is acceptable but not unique on these grounds.

Although the values of $(\Delta\mathbf{E}_R - \mathbf{Q})$ calculated for these tests and shown in Table V do not correlate with other parameters, there is at least one significant observation to be made: they are large positive numbers. If $\mathbf{Q}$ is assumed small, this large positive $\Delta\mathbf{E}_R$ indicates an appreciably endothermic reaction taking place. If the entire reaction of the initial sample to give the observed products took place at the calculated reaction temperature T_1, $\Delta\mathbf{E}_R$ for the nitrogen tests would be close to zero and that for the hydrogen tests would be negative, or exothermic. As examples, test 128, with nitrogen as a diluent, gives +65 (B.t.u. per pound-mole) and test 111, with hydrogen, gives −6075 (B.t.u. per pound-mole) for $\Delta\mathbf{E}_R$, to be compared with the experimental values of +12,108 and +13,905 (B.t.u. per pound-mole), respectively. These indications of endothermic reaction are interpreted as showing that the final products are not all formed at the reaction temperature. Rather, at the instant of maximum compression, which is the end of the assumed isothermal process, a considerable quantity of free radicals remains.

The qualitative behavior of the apparatus during a test gives information on the rate of reaction of free radicals subsequent to maximum compression to give the final observed products. This is a highly exothermic reaction; if it occurred rapidly enough—for instance, to extend the assumed isothermal path beyond maximum compression until the reaction was complete—this energy would be converted into kinetic energy of the piston, and the piston would return with a velocity comparable to its descending velocity. This would cause very noticeable oscillation of the apparatus such as has been observed on firings on pure components like nitrogen, and on firings on nitrogen-oxygen mixtures. As a matter of fact, practically no oscillations were observed; the apparatus behaved as though a sledge hammer had hit it and then exhibited essentially no further movement. It is concluded from these observations that the approximately isothermal portion of the path ended at maximum compression and that the temperature dropped very rapidly thereafter as the piston was accelerated upward. The free radicals finished the reactions sufficiently slowly so that little of the energy from the exothermic reaction was available to be converted to kinetic energy of the piston.

It is possible that the observed weak correlation of the one-half-order reaction rate coefficients with the amount of *n*-hexane decomposed is caused by the reactions of the free radicals remaining after maximum compression with some additional *n*-hexane. However, the observed correlation is too weak to make it profitable to introduce additional assumptions to explain it quantitatively.

The observed activation energies, as defined by Equation 2, are very low, being approximately 5200 and 9200 B.t.u. per pound-mole for the uncorrected and corrected half-order reactions, respectively. The apparent activation energy for the first-order reaction as corrected for maximum pressure was 15,200 B.t.u. per pound-mole (8.4 kcal. per gram mole) which is also low. Jost (*4*) quotes a value of 64.5 kcal. per gram mole for the activation energy of the first order decomposition of *n*-hexane at lower temperatures, about 500° C., and much lower pressures. Hinshelwood and others (*16*) found that the apparent activation energy for the first order decomposition of *n*-hexane shifted markedly with pressure in the subatmospheric range, and they quote apparent activation energies of 75 and 54 kcal. per gram mole for "low" and "high" pressures, respectively. Hinshelwood also found that added gases of certain kinds, such as propane, propylene, and ethane behaved like *n*-hexane in lowering the activation energy, while other gases such as methane, nitrogen, hydrogen, helium, and carbon dioxide had no effect.

Activation energies and frequency factors for the first-order decompositions of *n*-hexane from Jost (*4*) and Hinshelwood (*16*) are shown in Table VIII along with reaction rate coefficients calculated for a temperature of 2200° R. using their data. These are compared with the reaction rate coefficient for that temperature taken from the line of Figure 5, which represents the ballistic piston data corrected to a maximum pressure of 54,000 p.s.i. The agreement of the reaction rate coefficients is surprisingly good, particularly when it is realized that the values from Jost and from Hinshelwood are based on work at considerably lower temperature and much lower pressure, and that the reactions are not well represented by first-order kinetics over the range of pressures involved.

Table VIII. Comparison of Available Reaction Rate Data

Source	Activation Energy[a], Kcal. per G. Mole	Log A'	First-Order Reaction Rate Coefficients[b, c, d] k_c, Sec.$^{-1}$	First-Order Reaction Rate Coefficients[b, c, d] k_R
Jost (*4*)	64.5	14.58	1110	0.69
Hinshelwood: (*16*)				
Low pressure	75	17.0	3800	2.38
High pressure	54	12.2	368	0.23
Figure 5[e]	8.4	. . .	. . .	0.25

[a] The metric units are not consistent with the English units used elsewhere but have been retained because of convention.
[b] At temperature of 2200° R.
[c] $k_c = A' \exp. -E'/RT$.
[d] k_R in (lb. mole)/(cu. ft.)(atm.)(sec.).
[e] For a maximum pressure of 54,000 p.s.i.

The fact that extrapolation of literature data gives reaction rate coefficients similar to those estimated from ballistic piston data, whereas the activation energies determined from the latter data are markedly lower than those found by other investigators, tends to cast doubt on the apparent activation energies determined from ballistic piston data. However, as Hinshelwood (*16*) found a marked influence of pressure on apparent activation energy in the low-pressure region, it appears that these complicated decomposition reactions are not well understood even when occurring under moderate conditions, and that the computed apparent activation energies for both first-order and one-half-order may be of the right magitude.

The literature contains little information on the products of decomposition of *n*-hexane. Pearce and Newsome (*15*) studied the decomposition of *n*-hexane at moderate pressures and low temperatures. Kossiakoff and Rice (*7*) predicted decomposition products for low pressure and short contact time on the basis of free radical mechanisms. The product distribution from the tests with nitrogen as a diluent does not agree with either reference. This is not unexpected, however, as their reaction conditions are grossly different. No data on the decomposition of *n*-hexane in the presence of hydrogen were found in the literature.

CONCLUSIONS

The thermal decomposition of *n*-hexane under conditions of high pressures and temperatures is of apparent order of approximately one half, and has a low apparent activation energy, of the order of 5000 to 9000 B.t.u. per pound-mole (2.8 to 5.0 kcal. per gram mole). The mechanism undoubtedly involves free radicals to a considerable extent; however, some molecular reaction is not excluded. Hydrogen and nitrogen do not enter into any rate-controlling steps of the decomposition reaction. Many fragments remain at the instant of maximum compression in the ballistic piston apparatus. These fragments react sufficiently slowly during the decompression so that the heat of reaction involved does not contribute appreciably to the kinetic energy of the piston.

NOMENCLATURE

A' = Arrhenius frequency factor, sec.$^{-1}$
d = differential operator
E' = activation energy, B.t.u./lb. mole
$\Delta \mathbf{E}_R$ = change in molal internal energy due to reaction at constant temperature, B.t.u./lb. mole
e = base of natural logarithms 2.71828---
f_R = fugacity of reactant, atm.
f_R^0 = fugacity of reactant in pure state, atm.
h_i = height of contact i, in.
k_c = reaction rate coefficient in terms of concentrations, sec.$^{-1}$
k_R = reaction rate coefficient, lb. mole/(cu. ft.)(sec.)(atm.) or lb. mole/(cu. ft.)(sec.)(atm.)$^{1/2}$
ln = natural logarithm
N = number of moles, lb. mole
n = mole fraction
P = pressure, p.s.i.; atm.
$\mathbf{Q}$ = heat absorbed by one mole of system, B.t.u./lb. mole
R = molal gas constant, B.t.u./(lb. mole)(° R.)
° R. = degrees Rankine
s = $\mathsf{n}_0 - \gamma \mathsf{n}_f$, amount of reactant decomposed, lb. mole/lb.-mole of original sample
T = temperature, ° R.
$\mathbf{V}$ = molal volume, cu. ft./lb. mole
$\underline{V}$ = total volume, cu. ft.
$\underline{V}^*$ = normalized volume, $\underline{V}_B/\underline{V}_{B_0} = \mathrm{V}_B/\mathrm{V}_{B_0}$
$\mathbf{W}$ = work done by one mole of system, B.t.u./lb. mole
γ = stoichiometer ratio, (final moles gas)/(initial moles)
Δ = difference in
θ = time, sec.; millisec.; microsec.

Subscripts

av = average
B = pertaining to sample gas
f = final value of
R = pertaining to reactant or reaction
o = initial value of
1 = value at state 1, start of isothermal path
2 = value at state 2, maximum compression

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