

Thermal Rearrangement of Methane, *n*-Butane, *n*-Hexane, and *n*-Octane in the Presence of Hydrogen

J. B. OLIN, H. C. WIESE, and B. H. SAGE

Chemical Engineering Laboratory, California Institute of Technology, Pasadena, Calif.

AS PART of a reconnaissance study of the behavior of hydrogen-paraffin hydrocarbon systems, an investigation was made in a ballistic piston apparatus (2) to determine the influence of hydrogen upon the thermal rearrangement of methane, *n*-butane, *n*-hexane, and *n*-octane. Preliminary investigations (1, 3) had indicated that the presence of hydrogen materially decreases the formation of free carbon, and for this reason it appeared that use of mixtures of hydrogen and paraffin hydrocarbons might yield conditions under which substantial quantities of low-entropy compounds would be formed. In the interest of brevity, review of the extensive literature upon the thermal rearrangement of hydrocarbons is omitted.

EQUIPMENT AND METHODS

The ballistic piston apparatus employed in the present study has been described in detail (2). The equipment consisted of a heavy-walled steel cylinder 3 inches in diameter within which a piston was located. The piston was restrained at the upper end of the cylinder, and samples of hydrogen and the paraffin hydrocarbon of interest were introduced to the space below the piston at a pressure somewhat below atmospheric pressure. Air was added to the space above the piston until the desired driving force was established. A shear pin was used to release the piston, which compressed the sample rapidly to high temperatures and pressures by a travel of about 8 feet. Oscillation of the piston was avoided by venting the driving gas from the upper side of the piston during the first upstroke, so that the piston came to rest near the top of the cylinder. The position of the piston as a function of time and the thermal losses from the apparatus were measured. However, the results did not justify detailed analytical treatment of the temperature-time history of the samples.

The compositions of the samples were determined either from measurements of the temperature and pressure in the

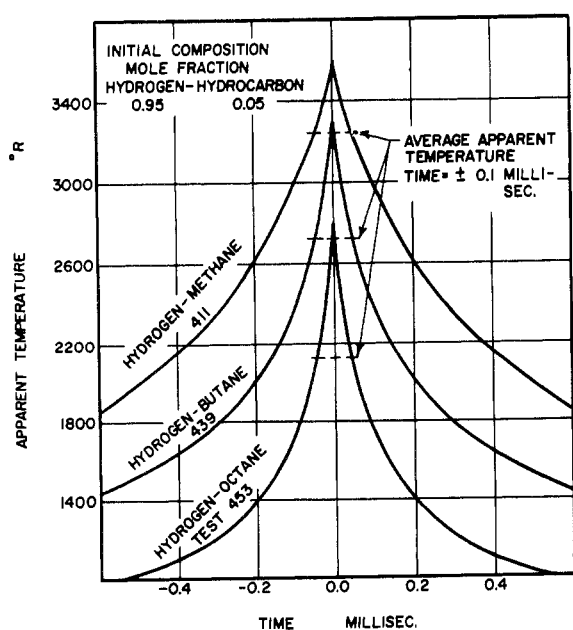


Figure 1. Apparent temperature-time relations

Table I. Purity of Materials Employed

Component	Purity, Mole Fraction		Source
	Reported	Analysis ^a	
Hydrogen	0.9980	0.9944	Matheson Co.
Helium	0.9997	0.9984	Air Reduction Co.
Oxygen	...	0.9924	Linde Air Products Co.
Nitrogen	0.9995	0.9987	Linde Air Products Co.
Methane	...	0.9997	Texaco, Inc.
<i>n</i> -Butane	0.995	...	Phillips Petroleum Co.
<i>n</i> -Hexane	0.9985	...	Phillips Petroleum Co.
<i>n</i> -Octane	≥ 0.996	...	National Bureau of Standards

^aBy mass spectrographic techniques.

sample chamber as a function of the quantity of each component introduced, or by mass spectrographic analysis upon a subsample withdrawn from the sample chamber. The compositions of the samples after compression were established by mass spectrographic analysis. Minor corrections were made in the final compositions in order to permit stoichiometric agreement with the initial values. However, the distribution among the several hydrocarbons was kept the same as the distribution indicated by the mass spectrographic analysis.

The experimental data obtained from the ballistic piston were treated by a modification and simplification of a method developed by Longwell (1, 3). The compression process was treated as following an isentropic path at constant composition to the point of minimum volume of the system and then a path of isentropic expansion. This simplification is not descriptive of the actual process but permits a comparative evaluation of the behavior as a function of maximum apparent temperature. The maximum apparent temperature was calculated from the measured change in volume, upon the assumption of isentropic compression at the initial composition (4).

The apparent temperature as a function of time during compression and expansion of mixtures of hydrogen with methane, *n*-butane, and *n*-octane is shown in Figure 1. The time-position history of the piston on the downstroke was established by direct experimental measurements (3). The high apparent temperatures associated with these processes do not exist for more than a few milliseconds. The time-average value for 0.2 millisecond is indicated on Figure 1. It was obtained as follows:

$$T_a = \frac{1}{0.0002} \int_{T_{MA} = -0.0001}^{T_{MA} = 0.0001} T_a d\theta \quad (1)$$

where T_a represents time-average temperature in °R., T_a space-average temperature in °R., T_{MA} maximum apparent temperature in °R., and θ time in seconds. The factors entering into the integral shown in Equation 1 were evaluated using the data of Figure 1. Maximum apparent temperature as evaluated by Longwell (1) was not employed in this investigation.

MATERIALS

The hydrogen was prepared by electrolytic methods. Mass spectrographic analysis showed it to contain 0.0056

Table II. Experimental Conditions

Test No.	Initial Conditions ^a		Conditions at Minimum Volume ^b				
	Air pressure, p.s.i.	Sample pressure, p.s.i.	Piston approach, in.	Max. apparent temp., ° R.	Max. apparent pressure, p.s.i.	Max. apparent pressure ratio	Volumetric compression ratio ^c
METHANE-HYDROGEN							
Approximate Initial Composition, Mole Fraction							
Hydrogen 0.95, Methane 0.05							
411	316.1	2.8803	0.4598	3600	4,300	1,500	218
413	635.8	2.8801	0.0611	6000	46,900	16,300	1507
414	759.3	2.8765	0.0362	6800	88,900	30,900	2398
420	579.8	2.8739	0.7240	3100	2,200	770	136
Hydrogen 0.80, Methane 0.20							
423	239.2	2.8662	0.8313	2400	1,600	550	119
424	399.8	2.8760	0.1505	3500	11,200	3,900	629
425	204.3	2.8797	1.225	2200	1,000	350	85
426	299.7	2.8827	0.3338	3000	4,900	1,700	293
427	500.0	2.8740	0.0702	4100	27,000	9,400	1204
Hydrogen 0.37, Methane 0.63							
429	299.7	2.8808	0.2386	2100	4,300	1,500	405
430	448.9	2.8851	0.0484	2600	21,900	7,600	1635
435	187.0	2.8789	1.1765	1600	690	240	87
436	226.9	2.8803	0.6161	1800	1,500	510	160
<i>n</i> -BUTANE-HYDROGEN							
Hydrogen 0.95, <i>n</i> -Butane 0.05							
438	300.7	2.8799	0.3053	2800	4,900	1,700	320
439	391.7	2.8814	0.1511	3300	12,100	4,200	647
440	596.0	2.8789	0.0443	4000	36,300	12,600	1754
441	187.1	2.8823	1.2241	2000	890	310	85
442	156.3	2.8762	1.9995	1800	520	180	52
Hydrogen 0.80, <i>n</i> -Butane 0.20							
444	228.0	2.9769	0.5183	1400	1,300	430	195
445	371.3	2.8910	0.0488	1900	14,300	4,950	1637
446	330.4	2.8756	0.0860	1800	9,100	3,150	1120
447	419.3	2.8779	0.280	1600	3,500	1,200	340
448	189.0	2.8812	0.892	1300	720	250	116
449	159.2	2.8812	1.7035	1200	400	140	61
<i>n</i> -HEXANE-HYDROGEN							
Hydrogen 0.96, <i>n</i> -Hexane 0.04							
120	560.2	1.9225	0.0418	4000	33,100	17,200	2077
Hydrogen 0.95, <i>n</i> -Hexane 0.05							
111	618.6	1.9231	0.0188	3800	52,900	27,500	3995
132	544.0	1.9039	0.0311	3600	34,300	18,000	2670
504	207.4	2.8784	1.2612	1700	720	250	80
505	268.9	2.8866	0.4320	2200	2,700	940	231
506	166.5	2.8892	2.3177	1600	410	140	50
Hydrogen 0.94, <i>n</i> -Hexane 0.06							
140	526.7	1.9202	0.0281	3100	30,700	16,000	2902
142	605.2	1.9233	0.0177	3400	53,300	27,700	4167
Hydrogen 0.92, <i>n</i> -Hexane 0.08							
143	575.5	1.9063	0.0125	3000	53,400	28,000	5328
Hydrogen 0.91, <i>n</i> -Hexane 0.09							
121	506.2	1.9183	0.0298	2700	28,800	15,000	2772
Hydrogen 0.90, <i>n</i> -Hexane 0.10							
119	555.0	1.9263	0.0152	2600	52,000	27,000	4658
<i>n</i> -OCTANE-HYDROGEN							
Hydrogen 0.99, <i>n</i> -Octane 0.01							
452	207.4	2.8750	0.8465	1700	1,100	370	121
454	185.0	2.8630	1.3229	1600	740	260	77
455	156.3	2.8592	2.1242	1400	340	120	50
Hydrogen 0.98, <i>n</i> -Octane 0.02							
450	268.9	2.7503	0.3573	2000	2,800	1,000	282
Hydrogen 0.96, <i>n</i> -Octane 0.04							
451	393.7	2.8814	0.0835	2600	16,000	5,550	1042
453	524.6	2.8815	0.0456	2800	25,900	9,000	1715

^a Piston weight 32.04 pounds for all tests except 111, 119, 120, 121, and 132: 30.98 pounds; tests 140, 142, 143: 32.09 pounds. Initial sample volume, 0.407 cu. foot. ^b Closest piston approach measured

with lead crusher gage. Maximum temperatures and pressures calculated from these data, assuming isentropic compression and no chemical reaction. ^c Ratio of maximum to minimum volume of sample.

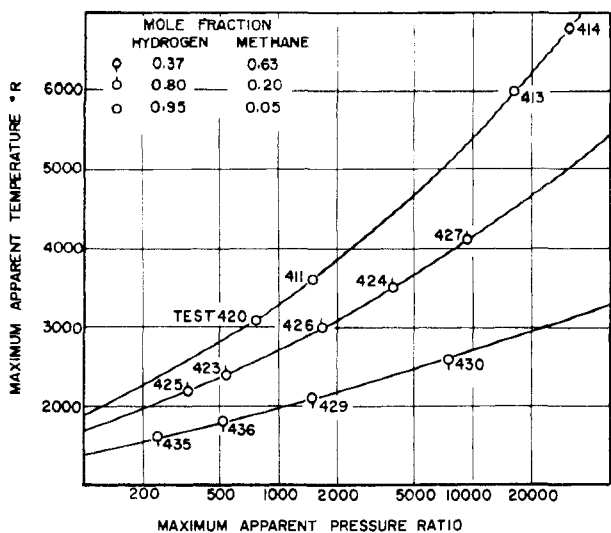


Figure 2. Effect of apparent pressure ratio upon apparent temperature in the hydrogen-methane system

mole fraction impurities. Methane was obtained from a well in the San Joaquin Valley of California. After passage over calcium chloride, activated charcoal, and Ascarite at pressures in excess of 500 p.s.i., it was shown by mass spectrographic analysis to contain less than 0.0003 mole fraction impurities. The *n*-butane and *n*-hexane were obtained as instrument grade and research grade hydrocarbon, respectively.

Table I sets forth analytical information for samples of the component gases employed. Purities that were found by mass spectrographic analysis to be lower than reported purities may have resulted in part from contamination during handling, although several different samples were analyzed during the program. The purity of the samples was sufficient for reconnaissance measurements of the type carried out in this study. In treating the data obtained, the minor quantities of impurities present in the original components were not considered.

EXPERIMENTAL RESULTS

Methane-Hydrogen System. The experimental conditions for the methane-hydrogen system tests are recorded in Table II. Figure 2 illustrates the variation in apparent temperature with maximum pressure ratio. The initial and final compositions of the samples and the conversion of methane to other compounds are available in tabular form (4).

To permit comparison of the hydrogen-methane system with other systems involving methane, data on the thermal rearrangement of methane in the methane-nitrogen and the methane-helium systems (1) are given in Tables III and IV. A tabulation of initial and final compositions is available from the American Documentation Institute (4).

The fraction of methane in the hydrogen-methane and the inert gas-methane systems which is converted to other compounds is shown in Figure 3 as a function of maximum apparent temperature. No significant rearrangement of methane in the presence of hydrogen occurs until a temperature of approximately 4000° R. is reached. Above this temperature there is a rapid increase in the fraction conversion, which reaches as much as 0.04 mole fraction at 6000° R. Disparity between the experimental points at the higher maximum apparent temperatures for the initial mixtures involving 0.95 mole fraction hydrogen and 0.05 mole fraction methane is evident but not unexpected because of the limitations of determining the small mole fractions with precision.

The only compound produced from the thermal rearrangement of methane in the presence of hydrogen was ethane. There was a total of 0.0011 mole fraction ethane

at a maximum isothermal reaction temperature of 6000° R., corresponding to a maximum apparent pressure ratio of approximately 16,000. The marked thermal stability of methane in the presence of hydrogen is evident.

The data of Figure 3 show no significant trends resulting from an increase in the mole fraction of hydrogen in the original sample. The samples which contained the largest amount of hydrogen reached the highest maximum apparent temperatures because the isentropic rate of change of temperature with pressure for the samples rich in hydrogen was greatest.

Figure 3 shows that the fraction of methane converted to other compounds in the helium-methane and the nitrogen-methane systems is much greater than in the hydrogen-methane system under the same conditions. The data concerning the thermal rearrangement of methane in the absence of hydrogen indicate the formation of large amounts of free carbon. The decomposition products of the samples which underwent the most extreme conditions were predominantly carbon and hydrogen. There was little if any tendency for the formation of carbon in connection with the thermal rearrangement of methane in the presence of hydrogen.

***n*-Butane-Hydrogen System.** The experimental conditions associated with the thermal rearrangement of *n*-butane in the presence of hydrogen are given in Table II. The initial and final compositions are available (4). A substantial group of saturated and unsaturated compounds of lower molecular weight than *n*-butane were found in the product.

Figure 3 also shows the conversion of *n*-butane as a function of maximum apparent temperature. Again, the data associated with the higher mole fraction of hydrogen are associated with the higher apparent temperatures. A rapid increase in the mole fraction of *n*-butane subject to thermal rearrangement appears to exist at apparent temperatures above 2000° R., and the thermal rearrangement reaches substantial completeness at apparent temperatures

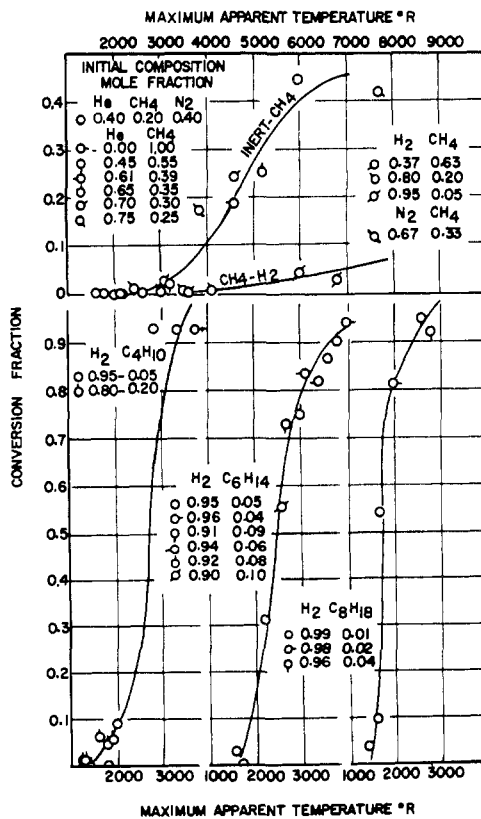


Figure 3. Thermal rearrangement of hydrocarbons in the presence of hydrogen

Table III. Experimental Conditions for Methane with Inert Gas

Test No.	Initial Conditions ^a		Conditions at Minimum Volume ^b				
	Air pressure, p.s.i.	Sample pressure, p.s.i.	Piston approach, in.	Max. apparent temp., ° R.	Max. apparent pressure, p.s.i.	Max. apparent pressure ratio	Volumetric compression ratio ^c
23	1001.4	4.463	0.0731	2000	18,970	4,250	1313
25	1004.5	2.270	Methane 1.00				
			0.0214	7700	131,700	58,000	4132
26	1004.5	2.706	Helium 0.75, Methane 0.25				
			0.0292	5200	78,700	29,100	3122
29	1004.6	3.707	Helium 0.65, Methane 0.35				
			0.0581	3200	38,200	10,300	1637
31	1006.5	2.952	Helium 0.45, Methane 0.55				
			0.0368	4600	64,100	21,700	2521
35	1004.7	3.464	Helium 0.70, Methane 0.30				
			0.1071	4600	27,700	8,000	913
86	697.8	1.920	Nitrogen 0.67, Methane 0.33				
			0.0262	3850	48,000	25,000	3441
87	807.2	1.975	Helium 0.40, Methane 0.20, Nitrogen 0.40				
			0.0319	6000	62,200	31,500	2874

^a Piston weight, 30.94 pounds for tests 23 through 35; 30.98 pounds for tests 86 and 87. Initial sample volume, 0.407 cu. foot. ^b Closest piston approach measured with lead crusher gage. Maximum

temperatures and pressures calculated from these data, assuming isentropic compression and no chemical reaction. ^c Ratio of maximum to minimum volume of sample.

Table IV. Fraction of Rearranged Methane Appearing in Product

Test No.	Ethyne	Ethene	Ethane	Propene	Propane	Benzene	Free Carbon	Max. Apparent Temp., ° R.	Max. Apparent Pressure Ratio
25	0.006	0.050	0.048	0.006	0.006	...	0.882	7700	58,000
26	0.007	0.080	0.112	0.026	0.015	0.022	0.738	5200	29,100
29	...	0.434	0.145	0.241	0.184	3200	10,300
31	...	0.136	0.168	0.048	0.035	0.087	0.505	4600	21,700
35	...	0.128	0.087	0.026	...	0.087	0.671	4600	8,000
86	...	0.166	0.191	0.054	...	0.140	0.434	3850	25,000
87	...	0.041	0.044	0.007	...	0.014	0.894	6000	31,500

between 3000° and 4000° R. Detailed information about the change in fraction of initial *n*-butane rearranged in the interval of maximum apparent temperatures from 2000° to 2700° R. was not obtained. Within this interval, however, the mole fraction of *n*-butane rearranged changed from 0.09 to 0.93. The experimental data were not extensive enough to establish any differences in behavior between samples containing 0.80 and 0.95 mole fraction hydrogen.

The products from the rearrangement of the two mixtures of hydrogen and *n*-butane are shown in Figure 4. At apparent temperatures below 1800° R., the quantities of ethane and ethene are greater with lower apparent temperature. At apparent temperatures above 2000° R. the quantity of methane increases rapidly, and it represents, for all practical purposes, the total product of rearrangement of *n*-butane in the presence of hydrogen at temperatures above 3400° R. Nearly 30% of the *n*-butane decomposed at 1800° R. is propane, whereas at 2800° R. propane represents only about 2% of the product of decomposition of *n*-butane. However, only 10% of *n*-butane was decomposed at 2000° R.; it was in excess of 90%, at 2800° R.

***n*-Hexane-Hydrogen System.** The experimental conditions for the *n*-hexane-hydrogen system tests are recorded in Table II and the initial and final compositions are also available in tabular form (4). Some of these data arose from an earlier investigation of thermal decomposition of *n*-hexane (3) and are included for the sake of completeness. A relatively large number of hydrocarbons were found in the products from the *n*-hexane-hydrogen mixtures.

The conversion of *n*-hexane as a function of maximum apparent temperature is shown in Figure 3. The complete

thermal rearrangement of *n*-hexane in the presence of hydrogen did not occur until a maximum apparent temperature of approximately 4000° R. was attained. This behavior is similar to that of *n*-butane. Under the conditions investigated, *n*-hexane appeared in the presence of hydrogen to have a stability comparable to that of *n*-butane.

Figure 4 shows the distribution of products resulting from the thermal rearrangement of *n*-hexane. Within the time available for reaction, the thermal rearrangement of *n*-hexane occurs at a higher apparent temperature than the rearrangement of *n*-butane. The primary product of the thermal rearrangement of *n*-hexane is methane. The slight decrease in the quantity of methane formed at apparent temperatures between 3800° and 4000° R. is not believed to be significant. Ethane is also a major product. At a maximum apparent temperature of 2600° R., it amounts to approximately 30% of the *n*-hexane subject to rearrangement.

At a maximum apparent temperature of 3400° R. the reaction products from the *n*-hexane-hydrogen system are comprised of approximately 0.86 mole fraction methane and the remainder compounds of higher molecular weight. With the *n*-butane-hydrogen system the reaction products at this temperature are 0.95 mole fraction methane and the remainder compounds of higher molecular weight. The thermal rearrangement of *n*-hexane at a maximum apparent temperature of 3400° R. appears to be somewhat slower than that of *n*-butane.

***n*-Octane-Hydrogen System.** Experimental conditions for tests on *n*-octane and hydrogen are presented in Table II, and the initial and final compositions have been tabulated

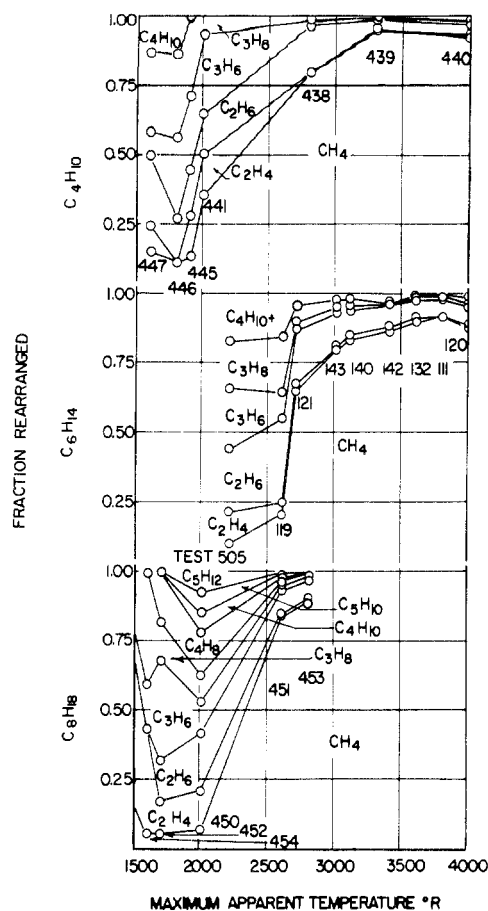


Figure 4. Products of thermal rearrangement of hydrocarbons in the presence of hydrogen

(4). Again, a large number of hydrocarbons of lower molecular weight than *n*-octane were encountered in the product.

The thermal rearrangement of *n*-octane as a function of maximum apparent temperature is illustrated in Figure 3. The thermal rearrangement of *n*-octane within the period available for reaction is slight until a maximum apparent temperature of 1600° R. is reached; at this temperature it increases rapidly, and becomes substantially complete at 2400° R.

The distribution of products resulting from the thermal rearrangement of *n*-octane in the presence of hydrogen is shown in Figure 4. When the maximum apparent temperatures are below 1600° R., no compounds of higher molecular weight than propane occur. At 1400° R. the principal product of the thermal rearrangement of *n*-octane is ethene. As maximum apparent temperatures of 2000° R. are approached, however, there is a marked increase in other compounds of higher molecular weight. Above 2000° R. the fraction of methane rises rapidly, and the quantity of ethene decreases from about 0.12 mole fraction to a negligible value at 2600° R.

In the formation of methane from the thermal rearrangement of *n*-butane, *n*-hexane, and *n*-octane, the fraction of the initial hydrocarbons converted to methane increased rapidly with increase in maximum apparent temperature. The maximum apparent temperature at which 50% of the initial hydrocarbon was converted to methane was highest for *n*-hexane and lowest for *n*-octane.

To illustrate in detail the behavior of hydrocarbons of high molecular weight, the formation of ethane from the four systems investigated is shown in Figure 5. The largest quantities of ethane were formed from *n*-hexane at about 2600° R., and *n*-octane at 2100° R. At a maximum apparent temperature of 2800° R., 0.155 of the *n*-butane was

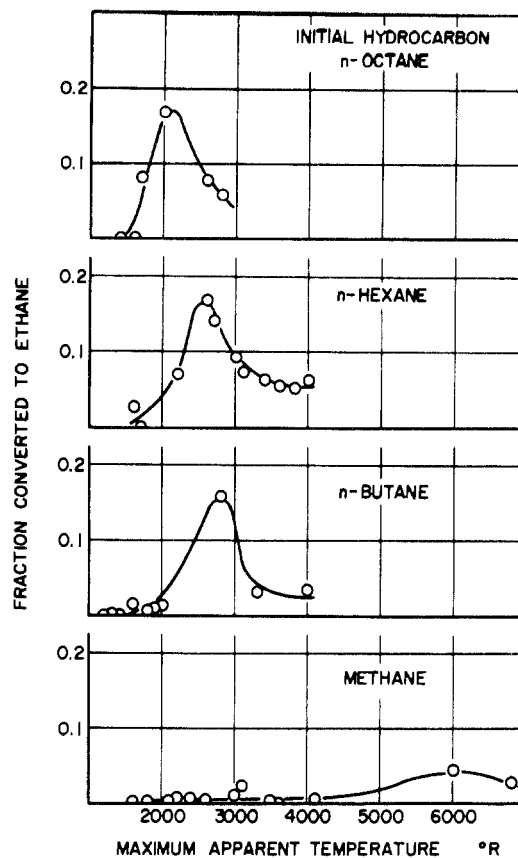


Figure 5. Fraction of initial hydrocarbon converted to ethane

converted. There is a trend toward maximum conversion at higher temperature as the molecular weight of the initial hydrocarbon decreases. In all cases, the formation of ethane reached a maximum and again decreased as the maximum apparent temperature increased.

The complete absence of detectable free carbon in connection with the thermal rearrangement of the hydrocarbons investigated was an interesting aspect of this study. The ballistic piston apparatus was a satisfactory reconnaissance tool, but the behavior of samples in the apparatus was difficult to interpret in detail.

ACKNOWLEDGMENT

This work was carried out with the financial support of Texaco, Inc. The Montebello Laboratory, Texaco, Inc., made the spectrographic analyses reported. The experimental work was accomplished under the general direction of H.H. Reamer. Virginia Berry prepared the data in a form suitable for publication.

LITERATURE CITED

- (1) Longwell, P.A., "Chemical Reactions of Methane and of *n*-Hexane in Ballistic Piston Apparatus," Ph.D. thesis, California Institute of Technology, Pasadena, 1957.
- (2) Longwell, P.A., Reamer, H.H., Wilburn, N.P., Sage, B.H., *Ind. Eng. Chem.* **50**, 603-10 (1958).
- (3) Longwell, P.A., Sage, B.H., *J. CHEM. ENG. DATA* **5**, 322-30 (1960).
- (4) Olin, J.B., Wiese, H.C., Sage, B.H., Am. Document Inst., Washington 25, D.C., Document 6662 (1961).

RECEIVED for review March 24, 1960. Accepted November 30, 1960. Material supplementary to this article has been deposited as Document 6662 with the ADI Auxillary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting \$1.25 for photoprints or \$1.25 for 35mm. microfilm. Advance payment is required. Make checks or money orders payable to Chief, Photoduplication Service, Library of Congress.