THE THERMAL STABILITY OF PARAFFINIC AND OLEFINIC HYDROCARBONS

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The relative stability of hydrocarbons determines the course of the pyrolytic reactions, a complete knowledge of which would make possible the choice of optimum conditions for obtaining desired hydrocarbons and would simplify the formulation of the mechanism of the reaction. Unfortunately, strictly comparable data are not wholly available. However, by a comparison of the results obtained on paraffins and olefins under comparable conditions, their relative stabilities can be estimated with some order of accuracy. Furthermore, when the results are not obtained under comparable conditions, a comparison of conclusions gives the next best order of stability.

A small per cent conversion of hydrocarbons would offer a basis for a comparison of their stabilities, since under this condition secondary reactions would not be present or would be negligible. Some investigators have utilized this method, while others have produced maximum yields of liquids or gases, obtaining decomposition up to 100 per cent. These latter results often give conclusions which contradict the ones obtained at low per cent conversion.

STABILITY OF PARAFFINIC HYDROCARBONS

Different stabilities for the lower paraffins were recognized by the earliest investigators, yet it remained for experimenters in the last decade or so, using the better analytical methods available, to obtain the decomposition data from which results might be reasonably compared.

The stability of paraffins depends upon their ability to withstand decomposition and isomerization. Only the resistance to decomposition has been reported, and therefore can be used as a basis for comparison. From this viewpoint, the stability of the normal and isoparaffins through hexane decreases with an increase in molecular weight. However, the stability of the iso versus the normal paraffin is not so well defined, because isobutane is more stable than *n*-butane, except that they are the same at 600°C., while isopentane is less stable than *n*-pentane and 2-methylpentane is less stable than *n*-hexane.

The data for pyrolysis of normal paraffins are summarized in table 1 and show that for a given set of conditions the shorter the chain the greater the resistance to heat. Hence, it is concluded that through *n*-hexane the stability decreases with increasing chain length.

The initial decomposition temperatures of some paraffins were obtained by noting the pressure change (17, 19, 20) when the hydrocarbons were heated for one hour in a glass bulb. It was claimed that specific products were formed for a restricted range of temperatures. Thus, for *n*-butane the initial temperature of decomposition was found to be 400°C. In the first temperature range, from 400° to 450°C., the products were methane and propene; from 450° to 499°C. ethane and ethylene were additional products, the breaking of the 2–3 carbon-to-carbon bond being characteristic of this temperature range; above 499°C., hydrogen and butene were obtained in addition to the above hydrocarbons. These results were not confirmed (11) in a flow method at 365°C., owing to formation of ethane, ethylene, and hydrogen along with the predicted methane and propene. The results obtained with *n*-pentane (17, 19, 20) by the bulb method indi-

TABLE 1

Pyrolysis of normal paraffinic hydrocarbons

CONDITIONS			HYDROCARBON, PER CENT DECOMPOSITION						REFERENCE NO.
Temp.	Time	Pressure	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	
°C.		*atm.*							
430	8.9–9.0 hrs.	1.0				6.0			5
430	4.0 hrs.	1.0					5.0		
430	2.0 hrs.	1.0						8.0	
650	12 sec.	1.0		6.0					21
650	11 sec.	1.0			16.0				
650	10 sec.	1.0				32.7			
950	Constant	1.0		35.8	48.7	63.0			1
			HYDROCARBON, PER CENT EXPANSION						
725	Constant	1.0						Complete decomposition	6
750	Constant	1.0		63.0	88.8	103.6	Complete decomposition		6
950	Constant	1.0	3.7	87.5	144.0	215.0			6
1100	3.2 × 10^{-3} sec.	(50 mm.)			109.0				
1100	2.5 × 10^{-3} sec.	(50 mm.)		86.0		158.0			26
1400	3.0 × 10^{-3} sec.	(50 mm.)	28.0	186.0	246.0				26

cated that the initial decomposition temperature was 391°C.; between 391° and 426°C. two groups of hydrocarbons were found in the ratio of 4 of group a to 1 of group b:

$$\text{(a)}\ CH_3CH_3 + CH_3CH{=}CH_2$$
$$\text{(b)}\ CH_3CH_2CH_3 + CH_2{=}CH_2$$

The second range of temperature was 426° to 450°C., the products of which included those obtained in the first range plus methane and unidentified butenes. The third range was 450° to 499°C., and the products consisted of the above hydrocarbons plus hydrogen and possibly a pentene. Evidence against these claims was obtained (5) when *n*-pentane was pyrolyzed at 396°C., yielding C_1, C_2, C_3, C_4, and C_5 hydrocarbons and hydrogen.

TABLE 2

Pyrolysis of straight- and branched-chain paraffins

CONDITIONS			HYDROCARBON, PER CENT DECOMPOSITION					REFERENCE NO.
Temp.	Time	Pressure	n-C_4H_{10}	iso-C_4H_{10}	n-C_5H_{12}	iso-C_5H_{12}	neo-C_5H_{12}	
°C.	*seconds*	*atmospheres*						
555	82.3	48.39	56.0					28
555	86.5	48.39		26.0				
560	16.6	0.1				8.25		5
575	20.5	0.087					4.0	5
575	16.1	0.1			4.9			5
600	30.0	1.0	22.0					12
600	27.0	1.0		22.0				12
650	10.0	1.0	32.7					21
650	11.0	1.0		26.7				21
			HYDROCARBON, PER CENT EXPANSION					
1100	2.5×10^{-3}	(50 mm.)	158.0	142.0				28

In spite of the disagreement concerning the relative stabilities of different carbon-to-carbon bonds in normal butane and normal pentane, the data offer a comparison of the initial decomposition temperatures of those hydrocarbons studied, since the experiments were made under comparable conditions. Thus, the results show that the stabilities of butane (400°C.), pentane (391°C.), and hexane (343°C.) decrease in this order.

Data on the relative stability of straight- and branched-chain paraffins are presented in table 2, which shows that *n*- and iso-butane have the same stability at 600°C., a result which should be checked, because at 555°, 650°, and 1100°C. isobutane is the more stable. Furthermore, it is shown that when isobutane is the more stable, it is so by a small margin except at

555°C. and 48.39 atmospheres pressure. Hence, it is concluded that at low pressure isobutane is slightly more stable, while under high pressure it is more than twice as stable as *n*-butane. In table 2 there are also data which show that the stability of neo-, *n*-, and iso-pentane decreases in the order named.

TABLE 2a

Decomposition of paraffins

(20 per cent)

HYDROCARBON	TEMPERATURE	TIME	PRESSURE
	°C.	*seconds*	*atmospheres*
C_3H_6	600	35	1
C_3H_6	600	28	7
C_3H_6	650	10.0	1
C_3H_6	650	5.9	7
C_3H_6	700	1.3	1
C_3H_6	700	2.0	7
n-C_4H_{10}	600	17	1
n-C_4H_{10}	600	13	7
n-C_4H_{10}	650	3.5	1
n-C_4H_{10}	650	3.2	7
iso-C_4H_{10}	650	4.0	1
iso-C_4H_{10}	650	4.5	7

TABLE 3

Temperatures of initial decomposition of straight- and branched-chain paraffins

HYDROCARBON	TEMPERATURE
	°C.
Isobutane	428
n-Butane	400
n-Pentane	391
Isopentane	383
n-Hexane	343
2-Methylpentane	339

The effect of pressure upon the relative stability of propane, *n*-butane, and isobutane (3a) is shown in table 2a. At 600° and 650°C., pressure reduces the resistance of propane and *n*-butane to decomposition, while at 650° and 700°C. in the case of the butanes the pressure effect is not so great.

A comparison of the initial decomposition temperatures of straight- and branched-chain paraffins (17) shows that isobutane is more stable than *n*-butane, while *n*-pentane is more stable than isopentane and *n*-hexane more than 2-methylpentane. It is concluded that as the molecular weight increases the difference in initial temperatures of decomposition for the normal and iso compounds decreases. The data which are recorded in table 3 show also that isobutane is more stable than isopentane, which is more stable than 2-methylpentane. It is, therefore, further concluded for the hydrocarbons discussed that the stability decreases with an increase in the molecular weight.

The stability of the first three members of the paraffin series is established, while the evidence for the C_4, C_5, and C_6 compounds is not so clear cut. However, the paraffins studied are placed in order of decreasing stability as follows: methane, ethane, propane, isobutane, butane, neopentane, *n*-pentane, isopentane, *n*-hexane, and 2-methylpentane.

Concerning the paraffins above the hexanes, the experiments (3) on the thermal decomposition of mixtures of hydrocarbons obtained by fractionating Pennsylvania petroleum which was made up largely of paraffins is to be noted. It was shown that stability was not always a direct function of the size of the paraffin molecule. It was concluded that "if stability is graphed against the boiling point of the paraffins, there results a curve having the maximum stability at about 250° representing the compounds $C_{12}H_{26}$ to $C_{15}H_{32}$, minima at the lowest boiling points (C_5H_{12} to C_9H_{20}), and the highest boiling points ($C_{19}H_{40}$ to $C_{23}H_{48}$)."

STABILITY OF OLEFINIC HYDROCARBONS

The olefinic hydrocarbons undergo three type reactions: (1) formation of higher hydrocarbons by polymerization or other reactions, (2) decomposition, and (3) isomerization.

Polymerization and formation of higher hydrocarbons

Polymerization is a characteristic reaction of the olefins. The primary effect of heat upon an olefin is activation of the double bond, since the average value of 39,000 ± 4,000 calories in the polymerization process is much lower than the activation energies of the other bonds for cracking reactions: C=C, 125,000; C—C, 79,500; C—H, 93,000 calories. The data of table 4 show the different values of the energies of activation of the C=C bond in the polymerization process, and 39,000 ± 4,000 calories is taken as an average value. Thus, considering the energy of activation and assuming that the other energy requirements are satisfied, polymerization precedes decomposition, since the latter is so small that it can be neglected (27).

TABLE 4

Energies of activation

HYDROCARBON	ACTIVATED BOND	ENERGY OF ACTIVATION	REFERENCE NO.
		calories	
Ethylene	C=C	39,000 ± 4,000	22
Ethylene	C=C	37,700 ± 200	13
Propene	C=C	38,000 ± 500	13
2-Butene	C=C	38,000 ± 1,000	13
Isobutene	C=C	43,000 ± 1,000	13
"Amylene"	C=C	38,000 ± 2,000	13
Ethane	C—C	79,500	23
Methane	C—H	93,000	23

TABLE 5

Oil yield from olefinic hydrocarbons at constant feed rate

OLEFIN	TEMPERATURE	PRESENT CHANGE IN VOLUME	CRUDE OIL YIELD IN WEIGHT PER CENT OF GAS PASSED	PER CENT OF CHARGE DISAPPEARING
	°C.	*per cent*	*weight per cent*	*per cent*
Ethylene				
Propene				
1-Butene	600	−23.4	12.86	46.0
2-Butene	600	−25.40	5.20	35.0
Ethylene	650	−2.7	1.5	10.1
Propene	650	+4.0	5.25	13.1
1-Butene	650	−10.7	29.82	80.2
2-Butene	650	−7.46	27.00	80.0
Ethylene	700	−15.25	12.25	33.8
Propene	700	10.0	20.36	54.4
1-Butene	700	30.0	35.83	97.9
2-Butene	700	27.40	37.00	97.4
Ethylene	750	−16.40	28.24	52.4
Propene	750	20.0	35.60	89.6
1-Butene	750	43.90	39.62	98.7
2-Butene	750	38.90	39.62	97.9
Ethylene	800	−11.80	36.10	71.0
Propene	800	30.0	40.6	98.5
1-Butene	800	57.0	39.45	99.0
2-Butene	800	52.8	37.90	99.5

A similar conclusion, namely, that the formation of higher hydrocarbons is the predominant reaction, is reached from the data (2) of table 5, in which it is recorded that the volume decreases at 600° and 650°C. during the pyrolysis of 1- and 2-butene. Furthermore, the data at 600°, 650°, and 800°C. show that 2-butene is more resistant to oil formation than 1-butene, while at 700°C. the opposite is true, and at 750°C. they behave in the same way. The data show also that combination is the primary reaction for ethylene from 650° to 800°C. and that it undergoes this reaction to a smaller extent than propene, which in turn yields less oil than the butenes except at 800°C. Thus at 650°C. the order of decreasing stability toward the formation of higher hydrocarbons is: ethylene, propene, 2-butene, and 1-butene; at 800°C. propene and the butenes show about the same stability.

TABLE 6

Formation of higher hydrocarbons from olefinic hydrocarbons

HYDROCARBON	TEMPERATURE	TIME OF CONTACT	PRESSURE	CONVERSION
	°C.	*minutes*	*lbs. per sq. in.*	*weight per cent*
Ethylene	371	18.7	2000	21.6
Propene	371	18.2	2000	5.6
Ethylene	395	6.5	3000	46.4
Propene	399	6.4	3000	12.7
Ethylene	455	5.3	3000	59.3
Propene	457	5.3	3000	43.4
Ethylene	456	4.1	500	20.6
Propene	455	5.7	500	16.3

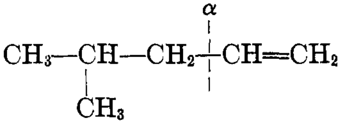
It should be pointed out that the maximum yields of liquids from ethylene, propene, 1-butene, and 2-butene require temperatures of 810°, 790°, 775°, and 755°C., respectively. This shows that 1-butene is more stable than 2-butene by 20°C., which contradicts the above conclusion. This difference is probably due to difference in experimental methods used.

A comparison of the stabilities of ethylene and propene at pressures from 500 to 3000 lbs. per square inch showed (25) that ethylene was converted to liquids to a greater extent than propene when treated under the same conditions. This conclusion is opposite to the ones above, and it is difficult to explain except by differences in experimental method or pressure. The data are summarized in table 6.

Decomposition

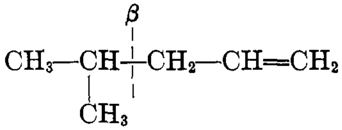
The second type reaction in pyrolyzing olefins is decomposition; in this connection the double-bond rule (24) should be mentioned. To illustrate this rule, the pyrolysis of 1- and 2-butene (9) may be explained. Since the C=C bond is the point of strength during olefinic decomposition, the adjacent C—C bond (α) will be stronger relatively than the C—C bond one removed (β) from the C=C linkage, and alternate strong and weak C—C bonds will continue along the chain, the effect diminishing as the distance from the double bond is increased. Thus, for example, 1-butene, $CH_2{=}CHCH_2CH_3$ is less stable than 2-butene, $CH_3CH{=}CHCH_3$, because the latter has no beta carbon-to-carbon bond.

On the basis of this assumption the products obtained during the pyrolysis of 4-methyl-1-pentene (preponderance of propene over ethylene) are explained: if the α-bond is broken ethylene would be the most important product,



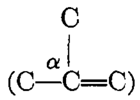
$$\mathrm{CH_3{-}\underset{\displaystyle CH_3}{CH}{-}CH_2\overset{\alpha}{\mid}CH{=}CH_2}$$

while if the β-bond broke then propene would be predominant.



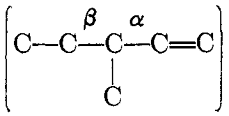
$$\mathrm{CH_3{-}\underset{\displaystyle CH_3}{CH}\overset{\beta}{\mid}CH_2{-}CH{=}CH_2}$$

The latter is the experimental fact and is in harmony with the rule. Furthermore, the greater stability of 2-butene $(\mathrm{C}\overset{\alpha}{—}\mathrm{C}{=}\mathrm{C}\overset{\alpha}{—}\mathrm{C})$ and isobutene



$$(\mathrm{C}\overset{\alpha}{—}\overset{\displaystyle\mathrm{C}}{\mathrm{C}}{=}\mathrm{C})$$

over 3-methyl-1-pentene (7)



$$\left[\mathrm{C{—}C\overset{\beta}{—}\underset{\displaystyle C}{C}\overset{\alpha}{—}C{=}C}\right]$$

is visualized when their skeletons are compared, since the latter has a $\overset{\beta}{\mathrm{C—C}}$ bond. On the other hand, 1-butene is more stable than isobutene (27) at 1100°C. and the opposite is true at 650°C. (10).

The results obtained in decomposing olefins are recorded and discussed according to the experimental method used. Any differences in conclusions may be partly explained on this basis.

The initial temperatures and the relative extent of decomposition as measured by means of a static (bulb) method show that ethylene is the most stable of the normal olefins studied, requiring the highest temperature of 380° to 400°C. The results (2) are summarized in tables 7 and 8, respectively, which show that the stability decreases in the order: ethylene, propene, 2-butene, and 1-butene.

Using a different experimental bulb method (20) the initial temperatures and extents of decomposition were measured for the pentenes (18). The results showed that trimethylethylene was more stable than 2-pentene, which was more stable than 1-pentene.

TABLE 7

Temperatures of initial decomposition of olefinic hydrocarbons

(Bulb method)

OLEFIN	TEMPERATURE RANGE	
	Lower	Upper
	°C.	*°C.*
Ethylene	380	400
Propene	357	375
2-Butene	350	375
1-Butene	325	350

TABLE 8

Per cent decomposition of olefinic hydrocarbons

(Bulb method)

TEMPERATURE	TIME	PER CENT DECOMPOSITION			
		C_2H_4	C_3H_6	1-C_4H_8	2-C_4H_8
°C.	*minutes*				
375–580	360	0.0	2.0	7.4	5.3
500	45	6.8	11.5		
500	39			11.5	12.1
600	12	28.3	52.8		
600	9			58.7	53.2
700	1	25.8	64.8		

The results (2) obtained in flow experiments are summarized in table 9, and show that from 650° to 900°C. the 1- and 2-butenes are of the same stability and that they are more susceptible to heat than propene and ethylene. At 600°C., however, 2-butene is more stable than 1-butene.

Other flow experiments (8, 9, 10), shown in table 10, include the work performed at 650° and 700°C. The results show that 2-pentene is less stable than isobutene at 700°C.; at 650°C. the order of decreasing stability is propene, isobutene, 2-butene, and 1-butene.

TABLE 9

Per cent decomposition of olefinic hydrocarbons

(Flow method: constant feed rate)

TEMPERATURE	PER CENT DECOMPOSITION			
	C_2H_4	C_3H_6	1-C_4H_8	2-C_4H_8
°C.				
600			45.9	35.0
650	10.1	13.0	80.2	80.0
700	33.8	54.4	97.9	97.4
750	52.4	89.6	98.7	97.9
800	71.0	98.5		
850	88.0		99.1	98.8
900	95.4		99.1	98.4

TABLE 10

Per cent decomposition of olefinic hydrocarbons

(Flow method)

TEMPERATURE	CONTACT TIME	PER CENT DECOMPOSITION				
		C_3H_6	1-C_4H_8	2-C_4H_8	iso-C_4H_8	2-C_5H_{10}
°C.	*seconds*					
650	11.0		57.0			
650	13.0			44.0	11.1	
650	30.0	16				
700	4.1				21.0	
700	12.0				30.2	
700	3.5					83.0
700	11.4					91.0

The study (27) of the lower olefins at a high temperature (1100°C.) and short contact times (0.002 to 0.014 second) showed that they fall into two groups, namely, ethylene–propene and the butenes, the latter being less stable. The data show that ethylene is much more resistant to an increased contact time than propene and the butenes. The order of decreasing stability is ethylene, propene, 2-butene, 1-butene, and isobutene. The lower stability of isobutene as compared with 1- and 2-butene is contradictory to the conclusion from table 10. Here, again, there may be some variable factor which thus far has eluded the various investigators and which is being recalled by "differences in the experimental method." However, it is to be noted, in this case, that there is a difference in the pressure. The results are summarized in table 11.

Isomerization

In connection with isomerization of the olefins, it has been shown that at 600° to 650°C. the isomerization of 1- and 2-butenes takes place with about the same ease (9). In the case of the pentenes, 1-pentene yields 2-pentene and vice versa (7) at 550° to 600°C., and under the same conditions isopropylethylene and trimethylethylene were formed from 2-pentene; above 450°C. isopropylethylene yielded trimethylethylene (18). Thus, it is observed that the branched pentenes are more resistant to heat than the normal pentenes, and that the normal butenes are more stable than the normal pentenes. These changes may be summarized as follows:

TABLE 11

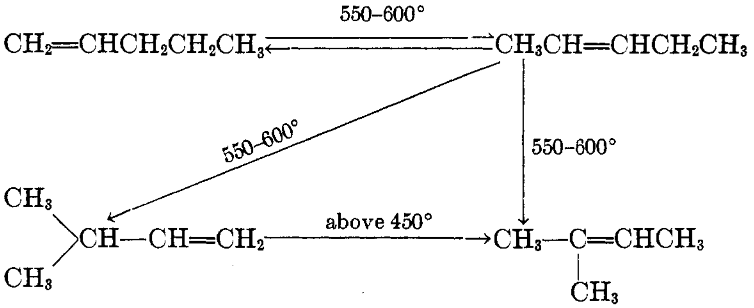
Per cent decomposition of olefinic hydrocarbons at 1100°C. and 50 mm. pressure

OLEFIN	CONTACT TIME $\times 10^3$	PER CENT DECOMPOSED	CONTACT TIME $\times 10^3$	PER CENT DECOMPOSED
	seconds	*per cent*	*seconds*	*per cent*
Ethylene	2.2	23.0	6.1	34.2
	4.1	24.0	14.0	46.2
Propene	2.2	27.4	5.8	65.6
	4.3	55.6	12.0	71.8
2-Butene	2.5	67.6	5.8	85.5
	3.0	77.2	11.0	91.0
1-Butene	1.9	69.6	7.9	89.9
	3.7	89.3	13.0	95.2
Isobutene	2.8	71.7	7.1	98.1
	4.0	92.2	11.0	100.0

Butenes

$$\mathrm{CH_2{=}CHCH_2CH_3 \xrightleftharpoons{600\text{–}650°C.} CH_3CH{=}CHCH_3}$$

Pentenes



The study of the relative stability of the olefinic hydrocarbons is complicated by their ability to form higher hydrocarbons by polymerization or other reactions, decomposition, and isomerization.

The relative stability toward liquid formation has been measured from 600° to 800°C. At 600°C. the stability decreased as follows: ethylene, propene, 2-butene, and 1-butene; at 800°C. propene formed liquid to the same extent as 1- and 2-butene. Thus it is seen that with increasing temperatures these olefins approach the same stability. On the other hand, at 371° to 457°C. and high pressures ethylene is less stable toward polymerization than propene. These contradictory conclusions may be explained by differences in experimental method as well as by differences in the conditions.

The primary decomposition of olefins is negligible compared with the polymerization and is, therefore, not a fair measure of their relative stability. However, when based upon the extent of and initial temperatures of decomposition the following order of decreasing stability is estimated at 600° to 700°C.: ethylene, propene, isobutene, 2-butene, 1-butene, trimethylethylene, 2-pentene, and 1-pentene, while at 1100°C. isobutene was found to be less stable than 1-butene.

The meager data reported for the relative stability toward isomerization lead to the conclusion that 1- and 2-pentene are less stable than 1- and 2-butene. The pentene stability decreases in the order trimethylethylene, isopropylethylene, 2-pentene, and 1-pentene, while 1- and 2-butene are about equally stable.

The relative stability of the butenes offers a test of the double-bond rule. Thus isobutene and 2-butene should be more stable than 1-butene because the latter has a beta carbon-to-carbon bond. Such was found to be the case at 650°C., while at 1100°C. and 50 mm. pressure isobutene was the least stable.

STABILITY OF DIOLEFINIC HYDROCARBONS

The lower diolefins of both the allene and the conjugated types are generally more susceptible to polymerization and decomposition than monoölefins. Most of the study has been devoted to polymerization, but under conditions which permit of few comparisons.

Allene was found (16) to decompose to the extent of 80.5 per cent at 500°C. and 86 seconds contact time, 90 per cent of it forming liquid products. Methylallene, on the other hand, which was completely decomposed at 500°C. and a contact time of 36 to 37 seconds was converted (10) into 73.0 per cent liquid, the balance being gas. Thus, allene is more susceptible to polymerization and more resistant to decomposition than methylallene. Di-, tri-, and tetra-methylallenes polymerize (14,15) at about 150° to 175°C. if the contact time is long enough.

Butadiene slowly polymerizes at room temperature (29). The influence of the position of methyl groups on the polymerization of butadienes has been demonstrated (31) with the result that the dimethylbutadienes were found to possess stabilities increasing in the following order: 2,3-, 1,2-, 1,1-, 1,3-, and 1,4-dimethylbutadiene. Thus, as the methyl groups are moved from the center of the molecule the stability increases. The data are summarized in table 12. The tetra- and hexa-methylbutadienes possess less tendency to polymerize than do the dimethylbutadienes (31).

STABILITY OF PARAFFINIC AND OLEFINIC HYDROCARBONS

A comparison of the relative stability of the paraffins and olefins is only qualitative even when the best conditions are obtained, owing to the fact that the former undergo decomposition as the primary reaction, while the olefins polymerize and with them decomposition is a secondary reaction. Thus, in the following discussion the conclusions from different experimental results are occasionally contradictory, and a comparison would not be justified. It seems best, therefore, to interpret each set of data independently and to await improvement in experimental results before generalizing too sharply.

A comparison of the relative stability of the paraffins and olefins when based upon initial temperatures of decomposition as measured by a change of pressure when heated for six hours in a silica bulb shows that the paraffins are more stable. A summary of the results (2) is presented in table 13.

Using a static method and a heating time of one hour the C_5 olefins, except 1-pentene, were more stable than the corresponding paraffins. The data (17) are recorded in table 14.

The results of a direct comparison based upon per cent decomposition of isobutene and isobutane (12) are shown in table 15; from these results it was concluded that isobutene is the more stable.

The results summarized in table 16 show that at 1100°C. and a given contact time the expansion is greater from the pyrolysis of a paraffin (26) than from the corresponding olefin (27). However, it should be pointed out that an olefin cannot be completely decomposed to yield as great an

TABLE 12

Polymerization of dimethylbutadienes

(At 100°C. for 30 days)

Position of methyl groups in dimethylbutadiene	2,3−	1,2−	1,1−	1,3−	1,4−
Per cent polymerized	100	91	57	51	33
Per cent converted to dimer	54	53	43	32	20
Per cent converted to higher polymer	46	38	14	19	12
Mean molecular weight of higher polymers	1377	919	432	1334	795

TABLE 13

Temperatures of initial decomposition (°C.) of paraffinic and olefinic hydrocarbons

HYDROCARBON	TEMPERATURE RANGE	
	Lower	Upper
	°C.	°C.
Methane	540	675
Ethane	450	485
Propane	425	460
n-Butane	400	435
Ethylene	380	400
Propene	357	375
2-Butene	350	375
1-Butene	325	350

TABLE 14

Initial temperatures of decomposition of paraffinic and olefinic hydrocarbons

HYDROCARBON	INITIAL TEMPERATURE OF DECOMPOSITION
	°C.
1-Pentene	389
2-Pentene	400
n-Pentane	391
2-Methyl-2-butene	433
2-Methylbutane	383

expansion as a paraffin, because each mole of olefin contains 1 less mole of hydrogen than the corresponding paraffin.

The data (2) of table 17 lead to the same conclusion as those of table 16.

TABLE 15

Decomposition of isobutene and isobutane

HYDROCARBON	TEMPERATURE	CONTACT TIME	DECOMPOSITION
	°C.	*seconds*	*per cent*
Isobutane	600	24–26	20–25
Isobutene	600	18	1.2
Isobutene	600	198	20.0

TABLE 16

Per cent expansion at 1100°C. of paraffinic and olefinic hydrocarbons

HYDROCARBON	EXPANSION	CONTACT TIME × 10^3
	per cent	*seconds*
Ethane	86	2.5
Propane	109	3.2
Isobutane	142	2.5
n-Butane	158	2.6
Ethylene	3	4.1
Propene	24	4.3
2-Butene	62	2.5
1-Butene	65	3.7
Isobutene	95	2.5

TABLE 17

Per cent expansion at constant feed rate of paraffinic and olefinic hydrocarbons

TEMPERATURE IN °C.	PER CENT EXPANSION FOR EACH HYDROCARBON						
	C_2H_6	C_2H_4	C_3H_8	C_3H_6	n-C_4H_{10}	1-C_4H_8	2-C_4H_8
700	32.7	−15.25	52.5	10.0	87.5	30.0	27.4
750	63.0	−16.40	88.8	20.1	103.6	43.9	38.9
800	63.9	−11.80	105.0	30.1	140.0	57.0	52.8
850		+1.3	106.0	46.2		73.9	68.3
900	71.0	+13.1	119.0	64.2		104.0	100.0

From table 18 it is concluded that under atmospheric pressure the olefins yield maximum quantities of liquids at a temperature from 65° to 85°C. lower than the corresponding paraffins, but it is to be noted that the paraffins must partly, at least, undergo decomposition before liquids can be formed.

Specific conclusions concerning the relative stability of paraffins and olefins can be made only from strictly comparable data which are not available as yet. Even a comparison of the conclusions based upon present information leads to some inconsistencies. In order, therefore, to obtain the valuable data that measurement of relative stability offers, further and more complete investigations are necessary.

TABLE 18

Temperature of maximum production (2) of liquid from paraffinic and olefinic hydrocarbons at atmospheric pressure

HYDROCARBON	TEMPERATURE FOR MAXIMUM LIQUID
	°C.
Ethane	890
Propane	865
n-Butane	840
Ethylene	810
Propene	790
1-Butene	775
2-Butene	755

CONCLUSIONS

1. The relative stability of the paraffins toward decomposition decreases in the following order: methane, ethane, propane, isobutane, butane, neopentane, *n*-pentane, isopentane, *n*-hexane, and 2-methylpentane.

2. At 600°C. the stability of the olefins toward the formation of higher hydrocarbons decreases in this order: ethylene, propene, 2-butene, and 1-butene; at higher temperatures the specific behavior is lost and they are of the same order of stability. At 371° to 457°C. under high pressure, ethylene is less stable than propene. These differences are probably due to different experimental methods or conditions.

3. Toward decomposition the following order of decreasing stability is estimated at 600° to 700°C.: ethylene, propene, isobutene, 2-butene, 1-butene, trimethylethylene, 2-pentene, and 1-pentene; isobutene was found to be less stable than 1-butene at 1100°C. and 50 mm. pressure.

4. Toward isomerization 1- and 2-pentene are less stable than 1- and 2-butene, which are about the same. The pentene stability decreases in the order: trimethylethylene, isopropylethylene, 2-pentene, and 1-pentene.

5. The diolefins are more susceptible to polymerization than the mono-

olefins. The dimethylbutadienes become more stable as the methyl groups are moved from the center of the molecule.

6. Specific conclusions as to the relative thermal stabilities of paraffins and olefins are not wholly warranted as yet, because strictly comparable data are unavailable.

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