Our results therefore confirm the conclusion of Richards and Staehler and Richards and Mueller that the atomic weight of potassium is very close to 39.096.

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Kinetics of Dissociation of Typical Hydrocarbon Vapors[1]

BY ROBERT N. PEASE AND JOHN M. MORTON

The reactions of pure hydrocarbons are of special interest from the theoretical standpoint since the breakage and formation of only three types of linkage (the C—C, C—H and H—H bonds) are involved in the whole series. In principle,[2] the activation energies of such reactions can be calculated to a first approximation, but in practice questions arise as to allowances to be made for the nature of substituent groups and of the molecule as a whole. In order to supply data on such points from experiment, rate measurements have been made on representatives of four principal series of hydrocarbons. The substances chosen were *n*-heptane from the paraffin series, ethylbenzene from the substituted benzene series, pentene-2 from the olefin series and cyclohexane from the naphthene series. In addition some comparative data have been obtained on related compounds, namely, benzene, toluene, xylene and ethylcyclohexane.

Method and Apparatus

Rate measurements were made by both flow and static methods, the former being supplemented by analysis. The flow experiments consisted in passing the vapor of the substance through a heated Pyrex reaction tube, and collecting and analyzing the products. The static experiments were run in parallel, the rates of pressure change being simultaneously determined in two reaction tubes, one of which had received an interior coating of potassium chloride.

The flow experiments were carried out as follows. The liquid hydrocarbon dropped from an inclined buret into a vaporizing chamber. The vapor then passed into the reaction tube. The rate of dropping was controlled by adjusting two stopcocks sealed into the line.[3] From the reaction tube, the vapors were led into an ice-cooled trap, and thence through a trap at −79° into a gas buret. The first trap was in reality a buret with water as the confining liquid. This permitted accommodating a quantity of condensed vapors without altering the dead space. The second trap was of small volume (about 3 cc.). The uncondensed gases were analyzed for unsaturated substances soluble in ordinary concentrated sulfuric acid, for ethylene by absorption in bromine water, for hydrogen by oxidation with copper oxide at 250° and for methane and ethane by oxidation with copper oxide at 550°. In some cases butadiene was deter-

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[1] A part of this investigation was financed from funds donated to the American Petroleum Institute by John D. Rockefeller.

[2] Eyring, *Chem. Rev.*, **10**, 103 (1932); Sherman and Eyring, THIS JOURNAL, **54**, 2661 (1932).

[3] The stopcocks were lubricated with a glycerine–glucose preparation.

mined by brominating the contents of the trap at −79°, separating the crystals of butadiene tetrabromide and weighing.

The static experiments were carried out as follows. The apparatus consisted essentially of two reaction tubes in parallel connected to two sides of a mercury manometer. These in turn constituted one side of another manometer, the other arm of which was open to the air. This permitted simultaneous pressure readings on the two bulbs. To this system was connected a bulb containing the liquid hydrocarbon, and a vacuum pump. The bulb and pump could be shut off from the rest of the apparatus by adjustable mercury seals. In making a run, the reaction bulbs were brought to temperature by means of an electrically heated furnace, the whole apparatus was thoroughly evacuated,[4] vapor was admitted to the reaction bulbs on the minute and pressure readings taken.

The hydrocarbons were for the most part the best obtainable commercial products. They were fractionated, and their purity checked by boiling point and density determinations. The cyclohexane contained a little benzene which was removed by refluxing with concentrated sulfuric acid and by fractional crystallization. The ethyl cyclohexane was prepared by hydrogenating ethylbenzene over a nickel catalyst at 150–180°.

Results

Some work was done on each of the nine compounds—*n*-heptane, pentene-2, cyclohexane, ethylbenzene, ethylcyclohexane, benzene, toluene and *o*- and *m*-xylene. For purposes of rough comparison of rates, values for the number of cc. of gas generated per 100 cc. of hydrocarbon vapor introduced per second of heating time are collected in Table I. The substances divided naturally into two classes. Benzene and the methylbenzenes (toluene and the xylenes) are very decidedly the more stable. Thus, at 630° the volumes of gas formed are 25 to 400 times less than those obtained from cyclohexane under like conditions. At 550°, the volume obtained from ethylbenzene is about one-half that from cyclohexane; and the volumes obtained from pentene-2, ethylcyclohexane and *n*-heptane are 3 to 6 times those obtained from cyclohexane. It was found that at 630° with up to 5% conversions, the gas from benzene was almost pure hydrogen and an equivalent amount of diphenyl could be obtained by evaporation of the residual benzene. Toluene and the xylenes gave mixtures of hydrogen and hydrocarbons even at low conversions, indicating

TABLE I

RELATIVE RATES OF GAS FORMATION

Substance	Cc. of gas per second of contact time, per 100 cc. vapor in. At 550°	At 630°	Substance	Cc. of gas per second of contact time, per 100 cc. vapor in. At 630°
n-Heptane	0.63	...	*m*-Xylene	0.067
Ethylcyclohexane	.52	...	Benzene	.056
Pentene-2	.35	...	Toluene	.018
Cyclohexane	.10	1.73	*o*-Xylene	.004
Ethylbenzene	.058	...		

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[4] It was especially important to free the supply of liquid hydrocarbon of dissolved air.

that the reactions are not simple.[5] The marked difference between the xylenes and the isomeric ethylbenzene is significant in view of statements in the patent literature[6] that xylene may be substituted for ethylbenzene in the preparation of styrene

$$C_6H_5{-}C_2H_5 \longrightarrow C_6H_5{-}C_2H_3 + H_2$$
$$C_6H_5(CH_3)_2 \longrightarrow C_6H_5{-}C_2H_3 + H_2$$

While we are not prepared to say that some styrene is not formed from ortho or meta xylene, it is nevertheless obvious that the over-all rate of reaction is far less in the case of xylene than in the case of ethylbenzene. Rates of reaction must be roughly as 1 to 10 or 100. Thus, the rather radical shifting of groups necessary to form styrene from xylene is at best not easy. There is, of course, no reason to believe that the xylenes give styrene exclusively. On the other hand, this is the most important reaction with ethylbenzene, as will be later shown.

Ethylcyclohexane which has roughly the possibilities of reaction of cyclohexane plus those of ethylbenzene dissociates at 550° at a rate considerably greater than that of either of these compounds. Pentene-2 dissociates faster than cyclohexane at 550°, which suggests that hexylene (the metamer of cyclohexane) would also dissociate more rapidly.

Experiments on *n*-Heptane, Ethylbenzene, Pentene-2, and Cyclohexane.—More detailed data (including static measurements) were obtained on *n*-heptane, ethylbenzene, pentene-2 and cyclohexane. In the static experiments, measurements of pressure change were made simultaneously on two reaction bulbs one of which had been cleaned with concentrated nitric acid and water while the other was rinsed out with 20% aqueous potassium chloride solution. The latter treatment is known to alter markedly the surface properties of the glass.[7] The absence of any effect whatever on the dissociations of the four hydrocarbons leads to the conclusion that these reactions are purely homogeneous. A chain mechanism also appears to be excluded.

The general nature of the static measurements may be seen from the curves of Fig. 1. The order of the rates is the same as that already found in the flow experiments (Table I). *n*-Heptane, ethylbenzene, and pentene-2 undergo normal pressure increases with limits of approximately 150, 50, and 90%, respectively. Cyclohexane is abnormal in the sense that there is a well-marked initial period of negligible pressure change. This is believed to be due to an isomerization, as will be later indicated. The subsequent pressure increase is finally about 100%. Detailed data on the four compounds follow.

***n*-Heptane.**—There is no reason to doubt that the primary reactions of all paraffins at temperatures below 700° are dissociations into a lower

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(5) See Hurd, "Pyrolysis," The Chemical Catalog Co., New York, 1929, pp. 103–104.

(6) For example, Ostromislenski and Sheppard, U. S. Patent 1,541,175.

(7) Pease, THIS JOURNAL, **51**, 1839 (1929); **52**, 5106 (1930).

paraffin (or hydrogen) and the complementary monoolefins. For *n*-heptane, six such simultaneous reactions are theoretically possible, neglecting the formation of isomeric olefins. No attempt was made to apportion by analysis the *n*-heptane decomposing among these six reactions, but it was demonstrated that gaseous olefins and paraffins were formed in quantity and in about equal amount. The data to be presented refer to the total

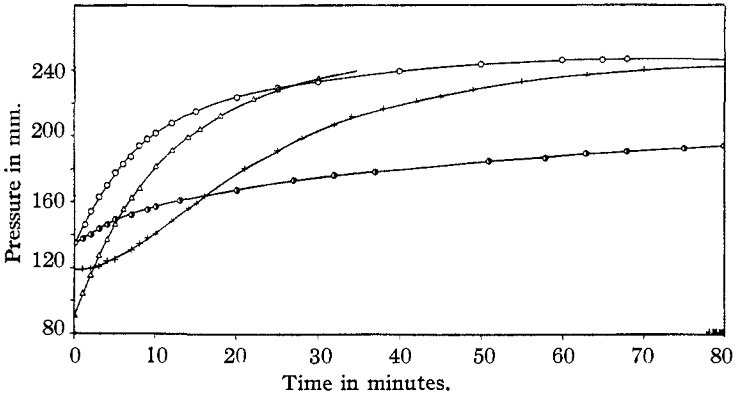

Fig. 1.—Rates of dissociation: +, cyclohexane; △, *n*-heptane; ◑, ethyl benzene; O, pentene-2; all 550°.

TABLE II

DISSOCIATION OF *n*-HEPTANE

Run	Temp., °C.	Init. press., mm.	t_{25}, sec. Obs.	t_{25}, sec. "High-press"	$k \times 10^3$ (sec.$^{-1}$) Obs.	$k \times 10^3$ (sec.$^{-1}$) Calcd.
63	530	41	(310)			
64		88	(240)			
65		139	190			
66		162	190			
69		163	210	200	1.4	1.6
70	540	58	(250)			
71		99	140			
74		141	140			
72		151	130			
42		154	130			
43		156	130			
75		197	130	130	2.2	2.3
53	550	49	(110)			
46		59	(90)			
54		63	(100)			
52		90	80			
48		192	80	80	3.6	3.2
76	560	53	(60)			
57		61	(70)			
58		140	70			
56		149	70	70	4.1	4.3

of n-heptane dissociating. If the dissociations to one molecule each of lower paraffin and olefin are the only reactions occurring, the total pressure increase should be exactly 100%, and would measure the rate of disappearance of n-heptane. Actually the pressure increase approached a figure somewhat nearer 150%, pointing to secondary reactions. In spite of this we have assumed that the time for the first 25% of the pressure increase may be taken as the time for 25% reaction. Values of t_{25} in seconds are given in Table II as a function of temperature and initial pressure.

Although the values at the lower pressures are at best only approximate, there appears to be a definite tendency for the rate to fall off with the pressure. This is in accord with observations on other unimolecular reactions.[8] "High-pressure" values of t_{25} have been selected with which to calculate first-order constants. These are given in the next to last column of Table II, and in the last column appear values calculated from the equation

$$\log_{10} k = -\frac{46{,}500}{2.3\,RT} + 9.85$$

Comparison of this equation with those for ethane and propane reveals some interesting features. These equations are[9]

$$\text{Ethane} \quad \log_{10} k_1 = -\frac{73{,}200}{2.3\,RT} + 15.12$$

$$\text{Propane} \quad \log_{10} k_1 = -\frac{61{,}800}{2.3\,RT} + 13.44$$

Both constants of these equations increase regularly as the series is ascended. It would evidently be possible to set up equations for the intermediate members and deduce over-all rates of dissociation for these. It may be noted that judging from the behavior of normal and isobutane,[10] the equations for isomers will be much the same.

The parallelism between the two constants of the above equations leads to a very simple but as yet unexplained relation. Their ratio is nearly constant, being 4.84, 4.60 and 4.72 × 10^3 for ethane, propane and n-heptane, respectively. Similar relationships have been noted before in other series.[11] Burk[12] has been led by the speculations of Polanyi and Wigner[13] to an equation for the rates of dissociation of the paraffin hydrocarbons which yields

$$\log_{10} k = -\frac{\epsilon}{2.3\,RT} + \log_{10}(n-2)v$$

In this equation, ϵ and v are constants for the whole series while n is the number of carbon atoms in the molecule. This is not in accord with the

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(8) *E. g.*, azomethane, Ramsperger, THIS JOURNAL, **49**, 1495 (1927).

(9) Marek and McCluer, *Ind. Eng. Chem.*, **23**, 878 (1931).

(10) Pease and Durgan, THIS JOURNAL, **52**, 1262 (1930).

(11) *E. g.*, Syrkin, *Z. anorg. Chem.*, **199**, 28 (1931).

(12) Burk, *J. Phys. Chem.*, **35**, 2446 (1931).

(13) Polanyi and Wigner, *Z. physik. Chem.*, **A139**, 439 (1928).

experimental data. Further discussion of this point will be taken up in a later paper.

Ethylbenzene.—The predominant gaseous product from the dissociation of ethylbenzene at 550–600° and small conversions is hydrogen (Table III). By analogy with ethane one would expect the reaction to be

$$C_6H_5C_2H_5 \longrightarrow C_6H_5\text{—}CH\text{=}CH_2 + H_2 \qquad (1)$$

yielding styrene as the other product. We did not determine styrene quantitatively, but it was found that samples of treated ethylbenzene on standing left a quantity of hard glassy material which was undoubtedly polymerized styrene. The occurrence of small amounts of unsaturated substances suggests the complementary reaction

$$C_6H_5C_2H_5 \longrightarrow C_6H_6 + C_2H_4 \qquad (2)$$

The methane and ethane may arise from reactions such as

$$2C_6H_5C_2H_5 \longrightarrow C_6H_5\text{—}CH_2\text{—}CH_2\text{—}C_6H_4CH_3 + CH_4 \qquad (3)$$

$$2C_6H_5C_2H_5 \longrightarrow C_6H_5\text{—}C_6H_4\text{—}C_2H_5 + C_2H_6 \qquad (4)$$

$$C_6H_5C_2H_5 + H_2 \longrightarrow C_6H_6 + C_2H_6 \qquad (5)$$

The pure dissociation reactions would give a total pressure increase of 100%. Actually the limit which was approached was nearer 50%. This is evidently due to the occurrence of reactions (3)–(5) which would give no pressure increase. It is unlikely that polymerization of styrene plays a part since simple distillation of partially polymerized styrene causes de-polymerization. Recombination of styrene and hydrogen is probably impeded by a large steric factor. We have calculated first order rate constants on the assumption that the first 12.5% of pressure increase corresponds to 12.5% reaction. This undoubtedly gives too low values for the constants by a factor of something less than 1.5 to 2, but our data do not permit more precise analysis. Pertinent data and values of k are given in Table IV. In the last column are values of k calculated from the equation

TABLE III

GASES FROM DISSOCIATION OF ETHYLBENZENE

Run	Temp., °C.	Contact time, sec.	Cc. of gas per 100 cc. vapor in.	Gaseous products, %			
				H_2	CH_4	C_2H_6	Unsats.
10	555	16	0.8	74.5	6.0	16.5	3.0
9		40	2.3	68.2	16.4	10.1	5.3
8		70	4.7	63.6	22.4	7.2	6.8
5	580	10	2.0	70.3	18.3	6.6	4.8
4		12	2.4	69.6	17.1	7.9	5.4
3		15	2.8	68.3	17.0	9.3	5.4
6		33	5.0	64.4	15.1	13.5	7.0
14	605	59	23.3	49.3	27.6	12.0	11.1
12		63	24.1	48.2	26.8	13.4	11.6

$$\log_{10} k = -\frac{70{,}000}{2.3\,RT} + 15.01$$

The constants for this equation are almost the same as those for the dissociation of ethane

$$\log_{10} k = -\frac{73{,}200}{2.3\ RT} + 15.12$$

The dissociation of ethylbenzene to styrene and hydrogen must, therefore, be very like the dissociation of ethane to ethylene and hydrogen. It is remarkable that the substitution of the phenyl group for a hydrogen atom should make so little difference. One may, perhaps, predict that this type of relationship holds for other alkyl groups on the benzene ring.

TABLE IV

VALUES OF k FOR ETHYLBENZENE

Run	Temp., °C.	p_0, mm.	$t_{12.5}$ (sec.) Obs.	$t_{12.5}$ (sec.) Accepted	$k \times 10^4$ (sec.$^{-1}$) Obs.	$k \times 10^4$ (sec.$^{-1}$) Calcd.
109	540	133	840	840	1.6	1.6
94	550	102	470			
96		136	410			
97		147	470			
98		178	470			
95		236	500	470	2.8	2.8
103	560	99	230			
102		147	230			
99		163	290			
100		179	300			
101		197	300	300	4.5	4.6
106	580	91	100			
104		104	90			
107		127	110			
105		137	110	110	12.1	12.3

Pentene-2.—A glance at the curve for pentene-2 in Fig. 1 shows that the primary reaction must be one of dissociation. The curve rises perfectly regularly from the start to something short of 100% pressure increase.[14] Polymerization is, therefore, not an important primary reaction as it is for ethylene at a few atmospheres' pressure and 350–500°.[15]

The nature of the dissociation reactions is not entirely clear. By analogy with the paraffins one would expect reactions like

$$\begin{aligned} CH_3CH_2CH{=}CHCH_3 &\longrightarrow CH_4 + CH_2{=}CH{-}CH{=}CH_2 \\ &\longrightarrow C_2H_4 + C_3H_6 \end{aligned}$$

No doubt these occur, but reactions of these types do not account for the production of the next lower mono-olefin, which has been found to be an important product.[16] This type of reaction

$$m\,CH_3CH_2CH{=}CHCH_3 \longrightarrow n\,CH_3CH_2CH{=}CH_2 + ?$$

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[14] This curve should not be confused with that for cyclohexane, which reveals an apparent induction period.

[15] Pease, THIS JOURNAL, **53**, 613 (1931).

[16] $C_3H_6 \longrightarrow C_2H_4$: Frey and Smith, *Ind. Eng. Chem.*, **20**, 948 (1928); Hurd and Meinert, THIS JOURNAL, **52**, 4978 (1930); Schneider and Frolich, *Ind. Eng. Chem.*, **23**, 1405 (1931). *iso*-$C_4H_8 \longrightarrow C_3H_6$: Hurd and Spence, THIS JOURNAL, **51**, 3561 (1929). —$C_5H_{10} \longrightarrow C_4H_8$: Norris and Reuter, *ibid.*, **49**, 2526 (1927).

seems to require either a bimolecular reaction, or a dissociation into free radicals. The bimolecular reaction could conceivably be of first order

$$\mathrm{R{-}C{=}C{-}C \longrightarrow R{-}C{-}C{-}C}\quad\text{(slow)}$$
$$\mathrm{R{-}C{-}C{-}C + R{-}C{=}C{-}C \longrightarrow R{-}C{=}C + R{-}C{=}C{-}C{-}C}\quad\text{(fast)}$$

Hurd and Spence have suggested an activation of this sort to account for polymerization in isobutylene.

In analyzing the data of the static experiments we have assumed that the first 25% of pressure increase corresponds to 25% of the pentene reacting. Data appear in Table V. "High-pressure" values of t_{25} have been assigned, and values of $k_{1\,\mathrm{obs.}}$ calculated from these. In the last column appear values of k_1 calculated from the equation

$$\log_{10} k_1 = -\frac{61{,}000}{2.3\,RT} + 13.33$$

TABLE V

VALUES OF k_1 FOR PENTENE-2

Run	Temp., °C.	p_0, mm.	t_{25}, sec. Obs.	"High-press."	$k \times 10^4$ (sec.$^{-1}$) Obs.	Calcd.
112	525	135	714			
113		165	696			
114		214	660	650	4.4	4.4
132	540	72	378			
131		152	353			
130		217	324	320	9.0	8.9
116	550	51	264			
117		119	258			
115		135	240			
118		208	210	210	13.7	14.1
125	560	48	150			
123		64	162			
124		74	138			
119		92	162			
121		121	147			
122		153	151			
120		201	133	130	22.1	21.9

Cyclohexane.—The behavior of cyclohexane is unusual in that the pressure measurements reveal a well-marked apparent induction period. This might indicate a chain reaction, a close balance between a dissociation and a polymerization, or a slow isomerization. Accepting the last as the correct explanation it becomes of importance to determine what isomer is formed. Approximate thermodynamic calculations favor methylcyclopentane rather than hexylene, or compounds like ethylcyclobutane. In the absence of sensitive tests for small amounts of ethylcyclopentane in cyclohexane, the following indirect procedure was adopted. Any possible isomer would produce a lowering of the freezing point of cyclohexane, but only a hexylene would absorb bromine. However, more volatile secondary products, which might have dissolved in the cyclohexane collected after treatment, could also absorb bromine. Samples of cyclohexane which had been passed through the flow apparatus at short contact times showed the expected freezing point depressions and bromine absorptions. These samples were then partially evaporated in a stream of nitrogen to remove the more volatile secondary products. With only 10% evaporation the bromine absorption became negligible, while a substantial freezing point depression remained. This eliminates hexylene as a possible intermediate, and makes methylcyclopentane the more probable.

The primary product subsequently dissociates giving a 100% pressure increase (Fig. 1). With respect to the nature of the final products we are in much the same position as in the case of pentene-2. This much could be definitely shown. In flow experiments at 650°, over 10% of the cyclohexane reacting could be recovered as butadiene (in the form of the solid tetrabromide).[17] This points to the reaction

$$C_6H_{12} \longrightarrow C_4H_6 + C_2H_6$$

as one to be considered. Further, there was no evidence whatever of dehydrogenation to benzene as an important reaction. About 0.4 mole of hydrogen was recovered for each mole of cyclohexane reacting, but nitration yielded only traces of nitrobenzene. If this hydrogen is all due to benzene formation, only 15% of the cyclohexane reacting is converted to benzene. We feel certain that if dehydrogenation occurs at all as a primary reaction of cyclohexane, it is unimportant as compared to the indicated isomerization. Cyclohexane (or methylcyclopentane) is much more closely related to the corresponding mono-olefin. In considering the dissociation of isobutylene, Hurd and Spence[18] say ". . . Three such 'activated olefin molecules,' by combination, would produce a cyclohexane derivative which, at the elevated temperature of formation (up to 700°), would be stripped into benzene derivatives." Our data do not bear out this contention. It would appear that the cyclohexane ring has not the necessary stability to permit such a sequence of reactions.

If the reaction of cyclohexane is of the type

$$A \xrightarrow{k_1} B \qquad\qquad B \xrightarrow{k_2} 2C$$

as indicated by the form of the curves (Fig. 1), the rate equations are

$$-\frac{dp_A}{dt} = k_1p_A \qquad\qquad +\frac{dp_B}{dt} = k_1p_A - k_2p_B$$

$$+\frac{dP}{dt} = {}^1/_2\,\frac{dp_C}{dt} = k_2p_B$$

These lead to the expression[19]

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(17) Compare Frolich, Simard and White, *Ind. Eng. Chem.*, **22**, 240 (1930).

(18) Hurd and Spence, THIS JOURNAL, **51**, 3572 (1929).

(19) The case is analogous to that of successive radioactive transformations. See Rutherford Chadwick and Ellis, "Radiations from Radioactive Substances," Macmillan, New York, 1930, p. 10 *et seq.*

$$\Delta P = \frac{p_{0\mathrm{A}}}{(k_2 - k_1)}\left[k_1(e^{-k_2 t} - 1) - k_2(e^{-k_1 t} - 1)\right]$$

It will be noted that k_1 and k_2 enter symmetrically and cannot be distinguished. Calculations based on this expression indicated that k_1 and k_2 must be nearly equal—as indeed also appears from the form of the curves (Fig. 1). In view of these facts, the somewhat simpler expression which results from setting k_1 equal to k_2 was used. In this case

$$\Delta P = p_{0\mathrm{A}}\,[1 - e^{-kt}\,(kt + 1)]$$

This equation can be used to calculate k by making successive approximations. For a 25% pressure increase

$$\frac{\Delta P}{p_{0\mathrm{A}}} = 0.25 = 1 - e^{-kt_{25}}\,(kt_{25} + 1)$$

or (Equation I)

$$e^{-kt_{25}}\,(kt_{25} + 1) = 0.75$$

Values of k calculated from this expression are given in Table VI.

Values of k may also be obtained from the rate at the inflexion point, the relation being

(Equation II)

$$k = \left[\frac{d(\Delta P)}{dt}\right]_{\text{inflex.}} \frac{e}{p_{0\mathrm{A}}}$$

Such values are also given in Table VI.

Values of k calculated from the equation

(Equation III)

$$\log_{10} k = -\frac{69{,}000}{2.3\,RT} + 15.41$$

are given in the last column of Table VI.

TABLE VI

VALUES OF k_1 FOR CYCLOHEXANE

					$k \times 10^3$ (sec.$^{-1}$) from			
Run	Temp., °C.	p_0, mm.	t_{25} sec.	$d(\Delta P)/dt$ inflex. mm./sec.	Eq. I	Eq. II	Accepted	Eq. III
90	526	238	2100	0.024	0.45	0.27	0.35	0.36
86	555	119	720	.066	1.3	1.5		
85		246	560	.189	1.7	2.1	1.8	1.7
79	578	97	240	.109	4.0	3.1		
83		104	270	.168	3.5	4.4		
80		162	190	.295	5.1	5.0		
81		246	200	.45	4.8	5.0	5.0	5.1

Discussion

Considerations advanced in the body of the paper lead to some general conclusions as to the behavior of pure hydrocarbons. These are as follows.

1. The reactions studied all appear to be normal first-order, homogeneous gas reactions.

2. The average energy of activation for paraffin hydrocarbons drops as the series is ascended. This is in part compensated by a corresponding drop in the value of the other constant of the rate equation, so that at the

lower temperatures the higher members dissociate somewhat more rapidly. The two constants are directly proportional to each other.

3. A side-chain on the benzene ring has nearly the same properties as the paraffin of the same number of carbon atoms. There is no evidence that side chains have a high degree of mobility on the benzene ring.

4. The cyclohexane ring has by no means the stability of the benzene ring. It is broken up on reaction, and probably first yields a smaller cycloparaffin ring. Cycloparaffins have more in common with the metameric mono-olefins than with the corresponding benzene compounds.

A summary of constants for the rate equation

$$\log_{10} k = -\frac{E}{2.3\,RT} + I$$

is given in Table VII. It will be noted that the proportionality between E and I holds even outside the paraffin series.

TABLE VII

SUMMARY OF RATE CONSTANTS

Substance	E (cal.)	I ($\log_{10}$ sec.$^{-1}$)	$E/I \times 10^{-3}$
Ethane[9]	73,200	15.12	4.9
Propane[9]	61,800	13.44	4.6
n-Heptane	46,500	9.85	4.7
Ethylbenzene	70,000	15.01	4.7
Pentene-2	61,000	13.33	4.6
Cyclohexane	69,000	15.41	4.5

Summary

1. Flow and static experiments have been made on the dissociation of several hydrocarbon vapors.

2. In the neighborhood of 600°, the order of stability of the nine hydrocarbons studied is *o*-xylene, toluene, benzene, *m*-xylene, ethylbenzene, cyclohexane, pentene-2, ethylcyclohexane, *n*-heptane.

3. The dissociations of ethylbenzene, cyclohexane, pentene-2, and *n*-heptane are pseudo-unimolecular, homogeneous gas reactions.

4. Regularities in the constants of the rate equations are pointed out.

5. Ethylbenzene resembles ethane rather closely in its behavior.

6. Cycloparaffins (cyclohexane) are probably to be compared with the metameric mono-olefins. The rings have far less stability than benzene. There is no evidence that benzene is an important reaction product.

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