

a year earlier than the results at lower pressure, using the somewhat less satisfactory experimental procedure referred to previously. It is evident that equations (3) and (4) in conjunction with equations (5) and (6) may be used to obtain the heat capacity of either compound at any temperature and pressure in the range studied. Probably extrapolation to pressures of several atmospheres would give results adequate for many purposes.

The calculated heats of vaporization in Table II provide a further excellent check of the consistency of equations (5) and (6). The calculated values of the heats of vaporization of 2,2-dimethylbutane were obtained by use of a slightly modified version of eq. (6) derived from Osborne and Ginnings⁶ 25° heat of vaporization and the variation of $C_p^1 - C_p^0$ with temperature, thus providing calculated values of the heats of vaporization at 22.9 and 49.7° which are essentially independent of the heats of vaporization measured in this Laboratory.

Acknowledgments.—We wish to thank Mr. R. M. Gooding of this Station for the time and care spent in the purification of the compounds. We also appreciate the assistance given by Mr. Harold Coleman to Mr. Gooding in the determination of purity and physical constants. The valuable suggestions made by Dr. S. S. Todd during the progress of this work and his assist-

ance in making some of the measurements are gratefully acknowledged. The authors appreciate the encouragement and helpful advice given by Dr. H. M. Huffman.

Summary

The heat capacities of the vapors of *n*-hexane and 2,2-dimethylbutane have been measured at several pressures in the temperature range 33 to 470° K.

The experimental values of the heat capacities of the vapors in the ideal gas state deviate from the following empirical equations by less than 0.1%

$$n\text{-Hexane: } C_p^0 = 4.280 + 0.10573T - 1.9948 \times 10^{-5}T^2$$

2,2-Dimethylbutane:

$$C_p^0 = -2.558 + 0.13724T - 5.339 \times 10^{-5}T^2$$

The heats of vaporization of the two compounds have been measured and are represented with an accuracy of approximately $\pm 0.1\%$ in the range from 25° to the normal boiling points by the equations

$$n\text{-Hexane: } \Delta H_{\text{vap.}} = 8571 + 6.372T - 0.03298T^2$$

$$2,2\text{-Dimethylbutane: } \Delta H_{\text{vap.}} = 8149 + 2.37T = 0.0252T^2$$

Second virial coefficients which represent the low temperature, low pressure behavior of the vapors have been obtained from the thermal measurements.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES, HOUSTON REFINERY, SHELL OIL COMPANY, INCORPORATED]

Kinetics and Mechanism of the Thermal Decomposition of *n*-Heptane¹

BY W. G. APPLEBY, W. H. AVERY^{1a} AND W. K. MEERBOTT

Introduction

During the past decade a large number of papers has appeared in the literature which deal with the thermal decomposition of paraffin hydrocarbons. Because of the labor involved in the analysis of the decomposition products, very few investigations have been reported in which complete enough analytical data were obtained to permit conclusions of general validity to be drawn regarding the kinetics and mechanism of the decomposition of the normally liquid paraffins.

If the Rice free radical chain theory predicts the products formed in the decomposition of paraffins, then no saturated compounds other than hydrogen, methane, ethane and propane should be formed in the pyrolysis at atmospheric pressure of paraffin hydrocarbons. This, in turn, would imply that the amount of unreacted paraffin remaining after pyrolysis of a liquid paraffin could be

(1) The work described here was carried out during 1942. Publication has been delayed by the pressure of other work during the war.

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determined from the weight of the liquid product remaining after suitable treatment for removing olefins. The hypothesis that, after treatment of the liquid sample to remove olefins, only unchanged charging stock should remain can be supported by determination of the refractive index of the treated sample. This line of reasoning has been tested by Dintses and co-workers.² Pure normal octane was pyrolyzed to 20% decomposition in a copper reactor. The liquid and gaseous product showed on "most careful analysis" no saturated hydrocarbons other than methane, ethane and propane. Further tests were made on fractions of Baku gasoline (containing 60% naphthenes) that had been treated with concentrated sulfuric acid before pyrolysis. In every case, treatment of the liquid product of the reaction with sulfuric acid left a material identical in refractive index and other physical properties with the original charging stock.

(2) A. I. Dintses and A. V. Frost, *J. Gen. Chem., U. S. S. R.*, **3**, 747 (1933); **4**, 610 (1934); A. I. Dintses and A. V. Zherko, *ibid.*, **6**, 68 (1936).

Examination of the data of Frey and Hepp^{2a} and Marschner³ provides striking confirmation of Dintses' work. The importance of Dintses' recognition of the simplification of the analytical problem that would result if no higher paraffins were produced by pyrolysis is apparent. It suggests that kinetic data may be obtained in a very short time for the cracking of compounds of great complexity; and that studies of such refractory problems as the order of hydrocarbon reactions and the effect on hydrocarbon reaction rates of the presence of impurities or other added material might be determined with the minimum of analytical equipment.

In order to obtain data for tests of Rice's theory and the proposals of Dintses and Frost, a study of *n*-heptane decomposition was undertaken.

Experimental

Pure *n*-heptane was obtained from the California Chemical Company. Its properties compare with those from the literature.⁴

	F. p., °C.	B. p., °C.	n_{20}^D	d_{20}^4
Our sample	-90.65	98.41	1.3877	0.6838
Literature	-90.60	98.43	1.3877	0.6837

No further purification was carried out.

The investigation was made using a preheater-reactor system in which liquid normal heptane was pumped into the preheater zone for vaporization and heating to reaction temperature prior to entering the reaction zone. The entire reaction zone was encased in electrical heating elements which were manually controlled so that temperature variations during an experiment did not exceed $\pm 1^\circ$.

The brass reactor used in most of the experiments listed in Table I, where it is designated as reactor no. 1, had a volume of 29.6 ml. at 580°. The reactor designated reactor no. 2 in Table I, with a volume of 31.2 ml. at 580°, contained four connected reaction chambers instead of one to indicate whether or not such a change in design influenced the reaction as a result of the difference in the surface-volume ratio and diffusion effects. Reactor no. 3 consisted of reactor no. 1 filled with brass turnings to give a surface-volume ratio more than fivefold greater than that of no. 1. The volume of this reactor was 27.0 ml. at 580°. Reactor no. 4 was the same as reactor no. 2 with a volume of 30.2 ml. at 580°.

After the desired preheater-reactor temperature profile was approximately established, the system was given a five-minute pretreatment with hydrogen sulfide. This pretreatment served to stabilize the reactor surface so that reproducible experiments could be obtained. Experiments first performed with untreated brass and carbon steel reactors indicated that these surfaces were influencing the reaction, but that on treatment with hydrogen sulfide the experiments became immediately reproducible. This pretreatment was carried out prior to each experiment reported here. At all times between experiments the unit was kept under about 20 p. s. i. of nitrogen to prevent leakage in of air.

The product analytical method was based on the fact that the afore-mentioned authors as well as Gault and Hessel⁵ reported no paraffins higher boiling than the butanes^{5a} and no products higher boiling than the reactant for the decomposition of hexanes, octanes, dode-

cane and hexadecane.⁵ These experimental data, which are in accord with the predictions of the free radical chain theory of Rice,⁶ indicate that the only products to be expected from *n*-heptane decomposition would be

Gaseous	Liquid (at 20°, atmospheric pressure)
H ₂	C ₂ H ₄
CH ₄	C ₂ H ₆
C ₂ H ₄	C ₃ H ₆
C ₂ H ₆	C ₄ H ₈
C ₃ H ₆	C ₅ H ₁₀
C ₃ H ₈	C ₆ H ₁₂
C ₄ H ₈	C ₇ H ₁₆
C ₄ H ₁₀	
C ₇ H ₁₆ (small amounts)	

Analysis of the gas sample was carried out by means of an adaptation of a technique developed in these laboratories.⁷ The method involves, essentially, the expansion of a sample of the gas into an evacuated system consisting of a measuring buret, a Toepler pump, a cold trap and a modified Orsat apparatus for analysis of hydrogen, methane and olefins. Some details of the apparatus are shown in Fig. 1. The gas sample is circulated through the cold trap B (at -195°) by means of the Toepler pump until equilibrium is reached. Thereafter, the gaseous material (hydrogen and methane) is pumped into the buret for analysis. Succeeding fractions are taken off similarly at the temperatures of molten ethyl chloride (ethene, ethane, propene, propane), molten *n*-propyl bromide (ethane, propene, propane, butene, butane) and solid carbon dioxide-acetone (propene, propane, butene, butane). In these experiments, propane and butane were found to be present only in insignificant amounts which simplified the computation of the product composition. The residue after removal of the carbon dioxide-acetone fraction consisted of *n*-heptane and was measured by expansion into the Toepler pump.

Computation of the product composition was carried out by assuming initially that all of the olefins in the carbon dioxide-acetone fraction were butenes. Thus, by the method referred to above,⁷ a first approximation to the butenes content of the *n*-propyl bromide fraction could be made. This value could then be used for a second approximation, etc. The second approximation, for the analyses reported here was always accurate enough. The calculated value of butenes in the *n*-propyl bromide fraction was used to calculate the propene content of this fraction from the total olefin content shown by bromination. This value could then be used⁷ to calculate the propene content of the carbon dioxide-acetone fraction and thence the butenes content of this fraction. Application of this method to the other compounds present gave the complete analysis. Tests of this method on a synthetic blend containing all of the expected gaseous products showed that the concentration by volume of each could be determined within about ± 1 .

Analysis of the liquid product presented greater difficulties since, in addition to unreacted *n*-heptane and C₅ and C₆ olefins, the liquid contained small amounts of the lighter gases. Whether this was significant or not depended on the amount of gaseous products formed. Normally such an analysis would involve ordinary stabilization by precision distillation techniques, but for the small volume of product samples taken in this work an approximation to such methods had to be employed. The relative volatilities of the several components⁸ of the liquid mixture are indicated below for -50°. The data indicate

(2a) F. E. Frey and H. J. Hepp, *Ind. Eng. Chem.*, **25**, 441 (1933).

(3) R. F. Marschner, *ibid.*, **30**, 554 (1938).

(4) A. P. I. Research Project 44, National Bureau of Standards, Selected Values of Hydrocarbons, June 30, 1945.

(5) H. Gault and F. A. Hessel, *Ann. Chim.*, Series 10, **2**, 319 (1924).

(5a) Butanes were found only in minute amounts.

(6) F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Maryland, 1935.

(7) L. S. Echols, Jr., and E. Gelus, submitted for publication in *Ind. Eng. Chem., Anal. Ed.*

(8) A. P. I. Research Project 44, "Selected Values of Properties of Hydrocarbons," June 30, 1945.

Component	Vapor pressure at -50°, mm.
C ₂ H ₄	7800
C ₂ H ₆	4130
C ₃ H ₆	680
C ₄ H ₈	95
Normal heptane	0.2

that a flash distillation of the light gases away from the normal heptane should be possible at -50°. In the light of this, the technique described in the next paragraph was worked out for the liquid product.

A small sample (about 0.2 to 0.3 g.) of the liquid product was placed in the sample tube C (Fig. 1). This sample tube was then attached to the ground joint A of the Toepler pump system and about one-third to one-half of the sample was distilled into the Toepler trap B, which was kept immersed in liquid nitrogen. Sample tube C was kept at room temperature during this operation. After the proper amount of the sample had been trapped in B, stopcock E was turned off, sample tube D was placed on A and the system (with stopcock E now open) was pumped free of any air or other fixed gases which were present. The liquid nitrogen was then removed from B and placed on D and the sample in B was condensed in D. After all of the sample had been transferred from trap B to sample tube D, stopcock E was closed. The liquid nitrogen was removed from D to trap B and the sample in D was allowed to come to room temperature. After the sample had come to room temperature, sample tube D was immersed slowly in another liquid nitrogen container so as to crystallize the liquid from the bottom upward, thereby eventually condensing any material in the vapor phase in the surface layer of the liquid. Now stopcock E was opened and, with the trap B still in liquid nitrogen, a bath of acetone and solid carbon dioxide, maintained at -50°, was rapidly substituted for the liquid nitrogen bath on sample tube D. The sample in D (at -50°) was exposed thus to trap B (at -195°) for five minutes after which stopcock E was closed and the sample in D was allowed to come to room temperature again. Thereafter, the above procedure was repeated two or three times, after which stopcock E was closed and the material in trap B was analyzed by the method of multi-isothermal distillation as described above for the gas sample.

Analysis of synthetic blends of *n*-heptane, *n*-butane, 1-butene, propylene, propane, ethylene and ethane by the above procedure showed that about 95 to 100% of all the normally gaseous constituents could be removed by the above procedure. Analysis of the liquid product, by the above method, disclosed the amounts of normally gaseous olefins and saturates dissolved in the liquid. This value of gaseous olefins was used to correct the total olefins in the liquid (as determined from the bromine number of the total liquid product; the assumption that olefins higher than C₄H₈ were C₅ and C₆ olefins in equal amounts was used in computing their amount) and yields a value of higher olefins in the liquid product. In experiments at conversions below 5%, where the gas yield was low, the volume of gases dissolved in the liquid product amounted to a large fraction of the total product. This method of liquid analysis was too inaccurate to give a satisfactory over-all product distribution under these conditions, and no data are therefore included for conversions in the range of 0 to 5%.

The complete data for the experiments are shown in Table I. It is estimated that the values of first order rate constant are probably accurate to within about ±0.2 in experiments M-59 and 61 and about ±0.1 in experiment M-64. These values are the square roots of the sum of the squares of errors arising from (1) uncertainty (±1°) in temperature measurements and (2) uncertainty in the analysis of the liquid and gaseous products. The value of the rate constant in experiment M-69 deviates from the other values considerably more than is indicated by the estimated experimental error. This experiment involved the lowest possible pump rate

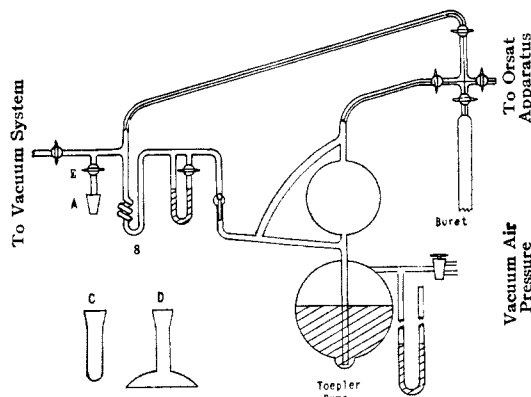


Fig. 1.—*n*-Heptane decomposition apparatus for analysis of liquid product.

(0.15 ml. of *n*-heptane per minute) and, as indicated by the rather poor weight recovery of 97%, is therefore probably more in error than the others in Table I.

A fraction of the liquid product from several of the experiments listed in Table I was extracted with 98% by weight sulfuric acid, containing 3% silver sulfate, to remove olefins. In agreement with the findings of Dintses and Frost, the olefin-free product, in every case, showed the same value of refractive index as the *n*-heptane charge. These results support the earlier suggestion that the thermal decomposition of paraffin hydrocarbons can be studied simply and quickly by a determination of the amount of product left after stabilization and extraction to remove olefins. Thus, such problems as the kinetics of decomposition, cross-activation in mixtures, the influence of products on decomposition, etc., can be determined with less time and with much simpler equipment than had been thought necessary in the past.

Discussion of Results

Kinetics.—The study of reaction rates in a flow system requires a mathematical formulation different from that required for a static system. The formulation for flow systems has been presented by Hulburt⁹ and this work will form the basis for the treatment of the data presented here.

Hulburt's equation (20) for first order kinetics, neglecting diffusion, can be written

$$\ln \frac{(1)}{1-f} - \frac{(v-1)}{v} f = \frac{KP}{S} \quad (1)$$

at constant temperature, where

- f = conversion of normal heptane
- v = moles products per mole reacted
- K = constant
- P = pressure
- S = feed rate, moles *n*-heptane per second per ml. reactor volume.

Thus, at constant conversion level and temperature, pressure and feed rate are directly related for a first order reaction. We can estimate the order of the reaction by comparing the feed rate at 8.7 atmospheres and 24.4 per cent. reaction (experiment M-47, Table I) with the feed rate at one atmosphere and 24.4 per cent. reaction. The former from Table I is 9.45×10^{-6} while the latter, from a curve of conversion *versus* feed rate 580°, is 1×10^{-6} . The ratio, 9.45, is very close

(9) H. M. Hulburt, *Ind. Eng. Chem.*, **36**, 1012 (1944).

TABLE I
 THERMAL DECOMPOSITION OF *n*-HEPTANE

Experiment no. M	59	61	57	58	62	67	
Reactor no.	1	1	1	1	1	1	
Temperature, °C.	580	580	580	580	580	580	
Pressure, mm.	767	776	769	769	776	766	
<i>n</i> -Heptane feed rate { moles/sec./ml. reactor space × 10 ⁶	5.90	5.90	2.62	2.61	1.77	1.17	
Fraction reacted {	From <i>n</i> -heptane disappeared	0.069	0.069	0.126	0.127	0.150	0.216
	From product H ₂ + saturates	.066	.064	.113	.110	.155	.209
Moles product per mole <i>n</i> -Heptane reacted	2.43	2.52	2.53	2.40	2.72	2.56	
Weight recovery, %	98.8	99.0	99.1	98.5	99.5	98.0	
Products % by volume of total	H ₂	2	1	1	2	0	
	CH ₄	18	18	17	18	17	
	C ₂ H ₄	30	33	30	30	31	
	C ₂ H ₆	16	16	16	15	17	
	C ₃ H ₆	16	14	15	12	15	
	C ₃ H ₈	1	1	1	2	2	
	C ₄ H ₈	11	14	8	12	12	
C ₄ H ₁₀	3	0	1	1	0	1	
Higher olefins	4	3	10	9	4	6	
First order rate constant { sec. ⁻¹ × 10 ²	From <i>n</i> -heptane disappearance	3.06	3.04	2.64	2.68	2.23	2.14

to the theoretically required ratio of pressures, 8.7. As will be discussed later, the first order rate constant decreases with conversion up to about 15 to 20% conversion. Thus, the first order dependence indicated here applies to the reaction at conversions above this range.

The homogeneity of the reaction was tested by experiments with a packed reactor (M-70 and 71, Table I) in which the surface-volume ratio was increased by more than fivefold. The first order constant was increased by about 36%. However, no increase was observed in experiments M-30 and 35, where the unpacked reactor no. 2, with an increased surface-volume ratio by virtue of its four-hole design, was used. It can be concluded, therefore, that in the experiments listed in Table I other than M-70 and 71, the reaction was essentially homogeneous in the vapor phase.

The decrease in first order rate constants with conversion at 580° is in agreement with the results of other investigators^{1,10,11} using hydrocarbons from ethane through octane. It is worth mentioning that, since the decrease in rate constants with increase in conversion is in the direction to be expected by neglecting axial diffusion effects in equation (1), a rough estimate of the mass transfer by diffusion in experiment M-64 was made. The result was less than one-tenth of the mass transfer difference required to cause the difference in rate constants between experiments M-59 and M-64. It must be concluded, therefore, that the thermal decomposition of normal heptane is not a simple first order process. As has been suggested by Echols and Pease¹⁰ and Dintses and Frost^{1,11} equation (1), in its derivation, should contain

(10) L. S. Echols, Jr., and R. N. Pease, *THIS JOURNAL*, **61**, 208 (1939); *ibid.*, **61**, 1024 (1939).

(11) A. I. Dintses, *Uspekhi Khimii*, No. 3, **7**, 404-435 (1938).

some appropriate "product" term representing the inhibition effect. For a free radical chain decomposition mechanism, this product effect, for the product distribution shown in Table I, is probably caused by the presence of propene.¹⁰⁻¹⁴ Eshevs-kaya¹³ has made the interesting proposal that only propene, among the *n*-olefins, can produce a large radical of any stability with the methyl radical and that no stable radical can be produced by addition of the ethyl radical to the normal olefins. It is possible, however, that inhibition comes about by the removal of a hydrogen from propene with the consequent replacement of the chain carrying radicals by the more stable allyl radical.¹⁵

The rate constant-conversion trend at 580° indicates that an equilibrium in the inhibition may be reached somewhere in the neighborhood of 15-20% conversion, where the first order rate constant no longer changes markedly with per cent. conversion. This equilibrium rate constant should be more useful in the application of this type of data to engineering design than values at lower per cent. conversion. It is even possible that a consistent and generally applicable system of rate constants and temperature and pressure coefficients could be assembled for a wide range of molecular weights and structures on the basis of "equilibrium" first order kinetics, provided data were available covering a wide enough conversion range.

The activation energy of normal heptane de-

(12) J. E. Hobbs, C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **167A**, 447 (1938).

(13) M. Eshevs-kaya, *J. Gen. Chem., U. S. S. R.*, **9**, No. 23, 2162 (1939); translation in *Refiner Natural Gasoline Mfr.*, **19**, No. 8, 264 (1940).

(14) E. W. R. Steacie and H. O. Folkens, *Canadian J. Res.*, **B17**, 105 (1939).

(15) F. O. Rice and O. L. Polly, *J. Chem. Phys.*, **6**, 273 (1938).

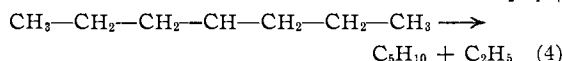
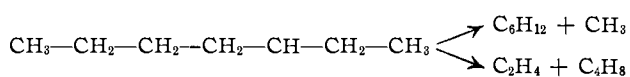
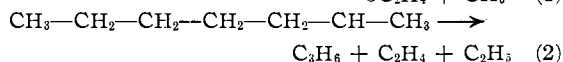
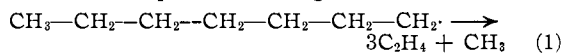
TABLE I (Continued)

30 ^b	64	34 ^b	69	47	65	66	70 ^a	71 ^a
2	1	2	1	4	1	1	3	3
580	580	580	580	580	552	629	579	580
760	765	768	766	(8.71 atm.)	776	767	764	765
1.11	0.78	0.74	0.58	9.45	0.78	8.70	2.86	2.86
0.211	.262	.267	.359	0.244	.123	0.175	0.140	0.142
.....	.262364	.299	.142	.196	.138	.142
assumed		assumed						
2.56	2.73	2.73	2.62	3.04	2.94	3.01	2.66	2.76
.....	98.2	97.0	102.3	100.4	100.2	99.1	99.3
.....	2	1	1	1	4	1	1
.....	18	18	16	18	18	18	18
.....	31	29	24	30	31	30	30
.....	16	17	19	16	14	16	16
.....	16	16	15	13	14	13	15
.....	1	2	2	3	1	1	2
.....	11	8	13	10	10	12	11
.....	1	2	2	2	1	1	0
.....	5	7	8	7	7	8	7
2.02	2.02	1.91	2.34	2.64	0.72	14.6	3.36	3.38

^a Packed reactor. ^b Liquid product not analyzed for dissolved gases. This would not cause serious error, however, at the high percentage conversion involved.

composition can be calculated from the data of Table I after an approximate correction for the effect of conversion level on the first order rate constant. The values of k at 552 and 629° were plotted *versus* conversion and curves parallel to that at 580° were drawn through these points. Thus, it was possible to obtain estimated rate constants at 552 and 629° more nearly consistent with the values at 580° by taking values from these curves at 15% conversion. These values were 0.55×10^{-2} at 552°, 2.40×10^{-2} at 580°, and 14.7×10^{-2} at 629°. The activation energy calculated therefrom was 65 kcal. This value is in good agreement with the value obtained by Rice and Johnson¹⁶ in their study of *n*-heptane decomposition in a higher temperature range by means of the Paneth technique of metallic mirror removal.

Mechanism of the Reaction.—The free radical chain decomposition of normal heptane should proceed⁶ through the formation of four radicals which decompose according to the schemes

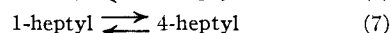
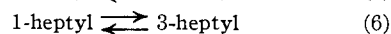
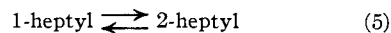


It was assumed in the earlier applications of the free radical chain theory⁶ that decompositions such as (3a) and (3b) proceed at the same rate.

(16) F. O. Rice and W. R. Johnson, *THIS JOURNAL*, **56**, 214 (1934).

It was pointed out later,¹⁷ however, that those decompositions involving the production of radicals of higher carbon number than methyl proceed faster because of the resonance energy of the higher radicals. In (3b), according to the theory, the decomposition proceeds through the formation of a *n*-propyl radical, which decomposes to give $\text{C}_2\text{H}_4 + \text{CH}_3$. Consequently, we may conclude that (3b) will proceed faster than (3a) and, on the basis of the estimates by Rice and Kossiakoff¹⁷ of the resonance energy of a *n*-propyl radical, and the assumption that about half of this energy will be developed in the transition state, we can calculate that (3b) will be about fourfold faster than (3a). It was also postulated by Rice and Kossiakoff that radicals of six carbon atoms and higher may undergo isomerization prior to reaction. In the case of *n*-heptane all of the above heptyl radicals probably can exist in equilibrium with each other.

In order to calculate the relative rates of reactions (1)–(4) above, it is necessary to obtain equilibrium constants for the reactions



Rice and Kossiakoff¹⁷ estimated the resonance energy of a *n*-propyl radical to be about 5 kcal., which should correspond roughly to the energy of 1-heptyl radical and represent the difference in resonance energy between the primary and secondary radicals above. If one-half of this energy is developed in the transition state the Boltzmann

(17) F. O. Rice and A. Kossiakoff, *ibid.*, **65**, 590 (1943).

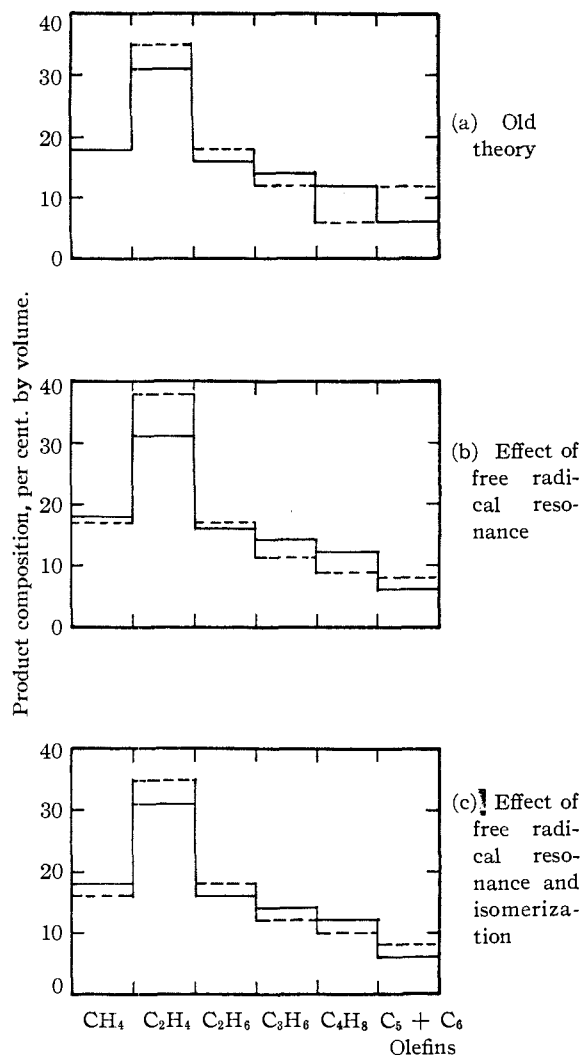


Fig. 2.—*n*-Heptane decomposition comparison of experimental and theoretical product distributions.

factor at 580° for these reactions will be 4.4. The statistical factor for (5) and (6) will be $4/6$ and for (7) $2/6$. Thus, we obtain $K_5 = K_6 = 3$ and $K_7 = 1.5$. On the basis of these hypotheses, then, we obtain the theoretical distribution of decomposition products shown (dotted line), with the experimental values (solid line) at low percentage decomposition, in Fig. 2. For sake of comparison, the theoretical product distribution neglecting, (a) the radical isomerization and resonance energy effects and (b) the isomerization effects are also shown. It is clear from the results that excellent agreement between theory and experiment is obtained when radical stabilization by resonance and isomerization are taken into account and that the agreement is somewhat less good if either or both of these hypotheses is neglected. We may conclude, therefore, that the Rice free radical chain theory,⁶ as amended by Rice and Kossiakoff,¹⁷ will predict very satisfactorily the product

distribution to be expected from the thermal decomposition of normal heptane.

Eshevskaya¹³ has shown experimentally that, as the Rice theory predicts, it is possible to calculate the percentage conversion of 2,2,4-trimethylpentane from the amount of saturate gases produced. It was found in the work reported here also, as the data of Table I show, that the values of normal heptane conversion so calculated are in excellent agreement with the values calculated from the measured disappearance of *n*-heptane. This information should be particularly useful under circumstances where only gaseous products are obtained or can be analyzed.

Rice's prediction that increase of temperature should result in an increase of the concentration of unsaturates and hydrogen and a decrease of ethane is not too clearly substantiated by the data of Table I except in the case of hydrogen and ethane (experiments M-62, 65, and 66). It must be pointed out, however, that this observation is based on a comparison of product compositions at different levels of conversion. While this procedure should be valid for small differences in conversion level, it would be desirable to determine the effect of temperature at the same conversion level.

Increase of the pressure should cause an increase of the concentration of saturates via increased reaction of chain carrying radicals with substrate molecules as against decomposition. Also, the concentration of olefins should decrease with increased pressure through increased polymerization. These results were obtained as shown by a comparison of the data of experiment M-64 at one atmosphere with that of experiment M-47 at 8.7 atmospheres.

Acknowledgment.—The experimental work involved in the development of the technique of analysis of the liquid product was carried out by Mr. A. F. Sartor.

Summary

The thermal decomposition of *n*-heptane has been studied by a flow method in the temperature range 550 to 630° at pressures of 1 and 8.7 atmospheres. Complete analysis of the reaction product has been made by use of a method of multiisothermal distillation for determination of the gaseous product, combined with olefin analysis of the liquid product. In agreement with the predictions of the Rice theory and experimental observations of Dintzes, only traces are found of saturated products having more carbon atoms than propane. The important simplifications in the analytical requirements for kinetic studies of higher hydrocarbons that this fact permits is emphasized.

The composition and concentration of the decomposition products are in excellent agreement with the Rice theory as amended by Rice and Kossiakoff.

The rate of the decomposition is of the modified

first order type where inhibition by products causes the first order rate constant to decrease with increase of conversion. The activation en-

ergy, calculated from the temperature variation of the first order rate, is 65,000 cal.

HOUSTON, TEXAS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF TRINITY COLLEGE]

Ternary Systems. VIII. Potassium Iodate, Iodic Acid and Water

BY STERLING B. SMITH

Some forty years ago Meerburg¹ conducted a phase rule investigation of the solubility relations in the ternary system, potassium iodate, iodic acid and water at 30°. Since that time potassium biiodate has been accepted as a primary standard for use in alkalimetric and iodimetric titrations.

Inasmuch as the purification of the biiodate by recrystallization from aqueous solution hinges upon the congruent solubility of this salt in water, Meerburg's work has been extended to cover a range of temperatures from 0 to 50°.

Experimental

Isotherms at 0, 25 and 50° have been completed by analyzing the solutions and residues obtained by rotating mixtures of the three components in a thermostat until equilibrium is established.

The procedure differed from that of Meerburg in that he warmed his original complexes to 50-60°, obtaining homogeneous solutions, and then slowly cooled them to the temperature of the investigation. The prepared mixtures were then rotated in a thermostat until equilibrium was established, often requiring several weeks.

In this work, the original complexes were prepared using the compounds which exist as solid phases after equilibrium has been established. This cut down to forty-eight hours the time required to establish equilibrium and also obviated the appearance of metastable solid phases.

The analytical procedure also differed slightly. Meerburg titrated his samples with standard thiosulfate solution in the presence of excess potassium iodide both before and after the addition of sulfuric acid. In this work the acid content was first determined by titration with standard alkali and total iodate determined in the same sample by titration with standard thiosulfate solution in the presence of excess potassium iodide and hydrochloric acid.

The experimental results are given in the following abbreviated table. Values are given only for the isothermally invariant points and the point of congruent solubility. The values at these invariant points are the average of two or more closely agreeing results, the solid phases being the same in each instance but present in widely different proportions.

Kolthoff and van Berk² in advocating the use of potassium biiodate as a standard substance in volumetric analysis stated that "it should not be dried at too high temperatures, as the iodic acid in the potassium biiodate loses its water of constitution and is transformed into the corresponding anhydride. When dried at 200°, this takes place quantitatively."

A series of drying experiments was run at $105 \pm 3^\circ$ to determine the loss in water when the biiodate was dried at the usual temperatures. It was found that the sample reached a constant weight at the end of three days. Analysis of the resultant product showed an iodine

(1) Meerburg, *Chem. Weekblad*, **1**, 474 (1904); *Z. anorg. Chem.*, **45**, 324 (1905).

(2) Kolthoff and van Berk, *THIS JOURNAL*, **48**, 2799 (1926).

TABLE I^a

Point in figure	SOLUBILITY DATA		Solid phases
	Solution % HIO ₃	% KIO ₃	
	Temperature, 0°		
	None	4.51	KIO ₃
	0.35	4.47	KIO ₃ , KIO ₃ ·HIO ₃
	1.30	1.68	KIO ₃ ·HIO ₃
	5.76	0.13	KIO ₃ ·HIO ₃ , KIO ₃ ·2HIO ₃
	73.69	.39	KIO ₃ ·2HIO ₃ , HIO ₃
	73.56	None	HIO ₃
	Temperature, 25°		
	None	8.39	KIO ₃
	0.61	8.46	KIO ₃ , KIO ₃ ·HIO ₃
	.77	4.90	KIO ₃ ·HIO ₃
	7.68	0.61	KIO ₃ ·HIO ₃ , KIO ₃ ·2HIO ₃
	75.51	.42	KIO ₃ ·2HIO ₃ , HIO ₃
	75.56	None	HIO ₃
	Temperature, 50°		
A	None	13.21	KIO ₃
B	1.34	13.58	KIO ₃ , KIO ₃ ·HIO ₃
S	3.74	4.64	KIO ₃ ·HIO ₃
C	11.02	1.85	KIO ₃ ·HIO ₃ , KIO ₃ ·2HIO ₃
D	78.72	1.17	KIO ₃ ·2HIO ₃ , HIO ₃
E	78.78	None	HIO ₃

^a For supplementary tables order Document 2389 from the American Documentation Institute, 1719 N St., N. W., Washington 6, D. C., remitting 50¢ for microfilm or 50¢ for photocopies.

pentoxide content of 87.67%, corresponding to a theoretical value of 87.63% for the compound 2KIO₃·I₂O₅.

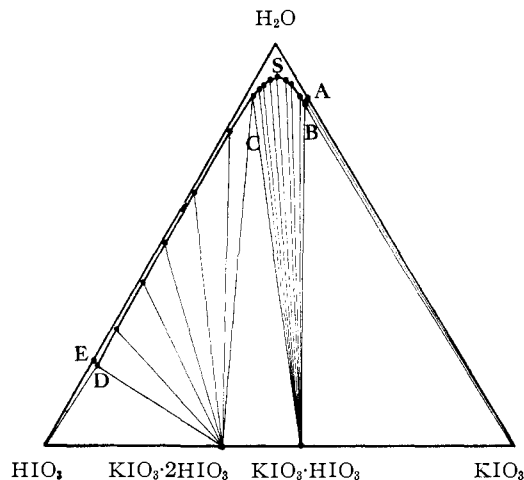


Fig. 1.—Temperature 50°.