Homogeneous Gas-Phase Pyrolyses Using a Wall-less Reactor. I. Neopentane[1]

Jay E. Taylor, David A. Hutchings,[2] and Kenneth J. Frech[3]

Contribution from the Department of Chemistry, Kent State University, Kent, Ohio 44240. *Received November 23, 1968*

Abstract: A wall-less gas-phase reactor has been developed for homogeneous pyrolytic studies. The reactor described is of general utility for first-order reactions and gives a precision which is significantly higher than is generally observed in gas-phase kinetics. In contrast to studies made at lower temperatures in a conventional reactor, the rate of decomposition of neopentane is found to be first order from 650 to 800°. The activation energy is 80.5 kcal/mole, and the *A* factor is $10^{16.9}$. A host of products form; these include hydrogen, methane, ethane, ethylene, propylene, allene, methylacetylene, isobutylene, 2-methyl-1-butene, 2-methyl-2-butene, isoprene, and neohexane (trace). The initial rate-determining reaction is the unimolecular decomposition of neopentane to form *t*-butyl and methyl radicals. Hydrogen, ethane, and some methane appear to form by radical combinations; other methane by methyl abstraction of hydrogen; isobutylene by decomposition of the *t*-butyl radical; ethylene, propylene, and allene by degradation of isobutylene; and the other products by a variety of reactions. The ratio of methane to ethane formed varies with dilution of neopentane, the ratio approaching zero at high dilutions. The previously reported three-halves order is likely the result of a surface effect which forms the products methane and isobutylene by an alternate mechanism.

Gas-phase reactions, though theoretically ideal for the fundamental study of molecular interactions, are made much less significant because of the uncertainties due to surface effects. The heterogeneous effects which may be introduced include catalysis and energy transfer either to or from the wall. Previous attempts to evaluate surface effects have been generally inconclusive. These have included conditioning of the reactor wall, variation in amount of surface, etc. The ineffectiveness of these techniques has been discussed by Rice.[4] The disposition of this article is to describe a general means for total elimination of surface effects, and to provide a means for direct comparison of reactions under heterogeneous and homogeneous conditions.

Other techniques for the study of homogeneous gas-phase reactions which have been developed include the shock tube, the cool flame, crossed molecular beam, and ionic reactions in the mass spectrometer. None of these is adaptable to general application.

At 500–570° in a static reactor the pyrolysis of neopentane[5,6] has been indicated to be a three-halves order reaction. The activation energy of 51.5 kcal/mole is significantly less than the bond dissociation energy. The value of 60 kcal/mole was reported by Hinshelwood[7] in the presence of nitric oxide. The use of nitric oxide and the incompleteness of the analysis reduce the creditability of this work. In view of the complex order and the low activation energy, a mechanism encompassing hydrogen abstraction by a methyl radical from neopentane has been proposed as the significant step following a dissociation of the neopentane molecule. Methane and isobutylene are the products.

$$C(CH_3)_4 + \cdot CH_3 \longrightarrow \cdot CH_2C(CH_3)_3 + CH_4 \qquad (1)$$

$$\cdot CH_2C(CH_3)_3 \longrightarrow \cdot CH_3 + CH_2{=}C(CH_3)_2 \qquad (2)$$

Using a shock-tube reactor, Tsang[8] has determined the activation energy for neopentane pyrolysis as 78.2 kcal/mole with an *A* factor of $10^{16.1}$ in the range of 1100°K with toluene present. A complete analysis is not reported by Tsang. He indicates, however, that ethane is formed and that the methane to isobutylene ratio is 0.6.

In principle, the wall-less reactor, as developed for this project, encompasses a flowing stream of hydrocarbon inside a protective cylinder of inert flowing gas. No contact of the hydrocarbon with the containing surface is permitted during the course of the reaction. The hydrocarbon enters the reactor at a low temperature and is brought rapidly and precisely to the reaction temperature by mixing with a zone of superheated gas. Plug flow is maintained over the significant range since the length of movement of the gas is only one to three times that of the diameter of the tube. The flow is downward to avoid turbulence due to gravity effects. A cooled sampling tube is mounted on a three-dimensional microscope stage permitting movement to any part of the reaction zone. The products are analyzed with a vapor-phase chromatograph.

Upon inserting a surface through which the gas stream may flow without significant resistance, it is possible to make a direct comparison of a reaction under both homogeneous and heterogeneous conditions.

The pyrolysis of neopentane has been examined in detail over a temperature range of 650–800°. The comparison with the work of Tsang is reasonable, though the data presented here are much more extensive. Both our data and those of Tsang contrast sharply with the earlier workers.

---

[1] Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

[2] (a) NASA Trainee, 1964–1967; (b) Goodyear Fellow, 1967–1968.

[3] Research Division, The Goodyear Tire and Rubber Co., Akron, Ohio.

[4] F. O. Rice and K. F. Herzfeld, *J. Phys. Colloid Chem.*, **55**, 975 (1951).

[5] J. Engel, A. Combe, M. Letort, and M. Niclause, *Compt. Rend.*, **244**, 453 (1957).

[6] K. H. Anderson and S. W. Benson, *J. Chem. Phys.*, **40**, 3747 (1964).

[7] M. C. Peard, F. J. Stubbs, C. N. Hinshelwood, and C. J. Danby, *Proc. Roy. Soc.* (London), **A214**, 330 (1952).

[8] W. Tsang, *J. Chem. Phys.*, **44**, 4283 (1966).

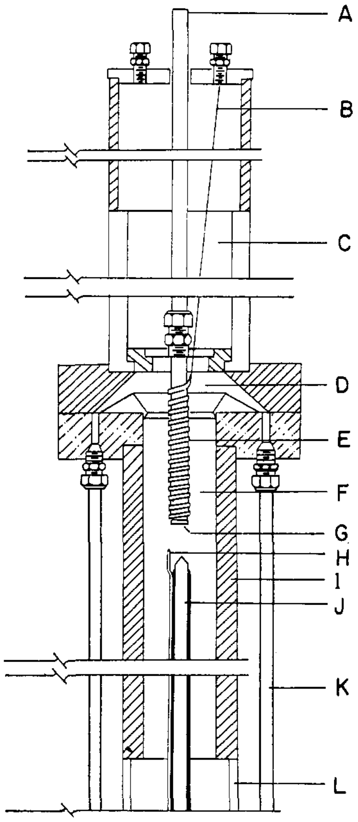

Figure 1. Wall-less reactor: A, hydrocarbon inlet; B, resistance heater lead; C, refractory filling; D, inert gas entry; E, compensating heater; F, inert gas stream; G, tip heater; H, thermocouple; I, 1.5-in. i.d. reactor tube; J, sampling probe; K, inert gas inlet; L, extension on reactor to prevent turbulence. The reactor is encompassed in a 7-in. i.d. three-zone tube furnace mounted vertically.

Experimental Section

The wall-less reactor as used for the bulk of this work is shown in Figure 1. Nitrogen metered by an appropriate flowmeter enters at K and D and flows downward through the reaction chamber F. The reactant neopentane is mixed with nitrogen and flows into A entering the reaction chamber at G. The neopentane is kept about 300–400° below reaction temperature by an air-cooled inlet tube, the details of which are shown in Figure 2. A heater is wrapped around the inlet tube M–T to offset the heat loss of the inner cooled chamber. The sample tube U–W is cooled and insulated so that its temperature is maintained well below reaction temperature. The temperature of the reaction zone is carefully monitored by means of a thermocouple H (Figure 1) attached to the sample tube. The lower extremity of the sample tube is mounted below the furnace on a three-dimensional microscope stage. Thus, the location of the sample tube is measurable with an accuracy approximating ±0.1 mm.

The total reactor is enclosed in a three-zone Lindberg furnace, 7 in. i.d., with an effective heating zone of 24 in. It is vertically mounted with the top opening plugged with firebrick.

The furnace temperature is maintained to ±1°. Inside the reactor the temperature control is significantly better due to the damping effect of the stainless steel walls. There is, however, cooling by the inlet tube which is offset by the inlet heater. In a typical measurement of temperature at the center of the reactor, the temperature at the center of the mouth of the inlet tube G is 709°; at 0.5 cm downstream, 736°; 1 cm, 740°; 2 cm, 743°; 2.5 cm, 744°. No variation in temperature is detected from 2.5 to 10+ cm. On the average, the wall is 3° warmer than the center.

The reactant neopentane flows from a 150-ml, 1-in. i.d., precision bore syringe which is activated by a synchronous motor and reduction gear. Change gears are incorporated to permit a variation in flow. The neopentane is then mixed with nitrogen metered by a flowmeter such that the mixture contains about 5% of the hydrocarbon. The mixture then flows into A. The neopentane used was Phillips research grade. There were no detectable impurities at the dilution under which the reaction was run.

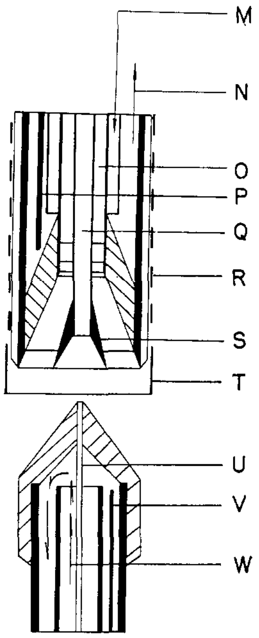

Figure 2. Detailed construction of hydrocarbon inlet and sampling probe: M–T, inlet system; U–W, sampling system; M, air inflow; N, air outflow; O, inert gas diluent inlet; P, thermocouple; Q, hydrocarbon plus inert gas inlet; R, resistance wire heater over insulation; S, cone-shaped mixing tip; T, mixing zone; U, capillary sampling tube; V, thermocouple inside air-outlet tube; W, air-inlet tube.

A 6-ft Polypak column was used for the major separations of neopentane products. Others, including a 15-ft, 20% UCON column, and silicone columns, were used for more specific analyses.

With a 1.5-in. i.d. reactor at a temperature of 800°, a detectable concentration of hydrocarbon (*e.g.*, neopentane) diffuses to the outer wall in roughly 0.30 sec. This approaches the reaction time limitation for this reactor at this temperature. The lower molecular weight reaction products, particularly hydrogen and methane, diffuse at a greater rate. In order to determine the total amounts of both products and reactants, the gas stream is sampled at a number of points horizontally across the stream, and a concentration curve is drawn for each product and reactant (see Figure 3). Each point on the curve is taken at 5 cm downstream and represents the concentration of the indicated substance at that distance (or reaction time) downstream. A check on the laminar character of the flowing hydrocarbon stream is also provided by this sampling technique.

The consistency of these concentration curves, of which Figure 3 is a typical example, clearly indicates that the flow is laminar. In view of the relatively short traversal distance with respect to the diameter of the tube, plug flow may also be assumed.

The total cross-sectional analysis, as described above, was not done for all experiments. It was found that the flow characteristics were quite reproducible and that it was possible to make a standardized correction for the variation in rates of diffusion of the several products. This was done with the bulk of data herein reported.

A significant gravity effect is noted when a pure hydrocarbon is injected through the inlet tube. In fact, a downward trajectory of the hydrocarbon stream is noted if the reactor is horizontal and a diffuse spreading of the stream appears if the flow is upward. This resulted in the choice of the vertical setting with the downward flow of the gas stream. With the diluted hydrocarbon stream the gravity effect should be greatly reduced.

Lateral diffusion of the reactant effects a dilution of the reactant stream; however, since the lateral diffusion is concurrent with and effectively independent from the stream flow, the reaction time is not affected by the rate of diffusion.

Because of the dilution of the flowing stream, with time the reactor is readily adaptable only to first-order reactions.

In treating first-order reactions by this technique the concentrations of the reactant and all detectable products are determined

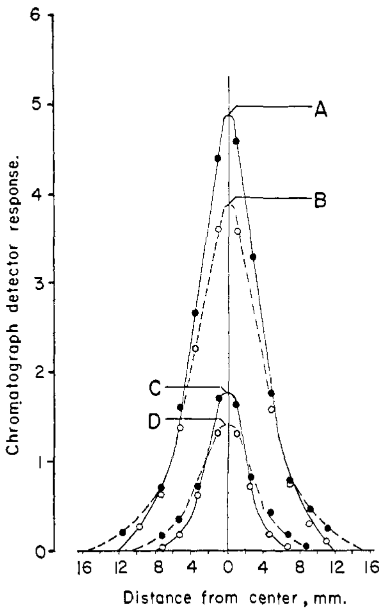

Figure 3. Cross-sectional distribution of products 5 cm from nozzle at 759° with a center tube input of 5% neopentane and a linear flow rate of 28.3 cm/sec. The concentration in the center stream is 1% total hydrocarbon at 5 cm: A, ethane + ethylene; B, methane; C, C_5 olefins; D, propylene + allene. The reactor wall is 19.1 mm, from the center.

at each point of analysis. It is thereby possible to determine the molar per cent reaction from which the first-order rate constant is calculated.

Reaction time is determined from the linear rate of flow downstream and the perpendicular distance traversed.

The reproducibility of methane and ethane analyses on the gas chromatograph is ±2% and for higher molecular weight substances is ±1%. A Barber-Coleman instrument was used for all of the work described. The reproducibility of samples taken from the center of reactant stream is ±3% and from the edge of the stream ±5%. The per cent conversion is determined by summing the products in accordance with their respective contributions to the reaction. Thus, ethylene, propylene, allene, and isobutylene are each assumed to form from an equivalent of neopentane. Methyl radicals form methane by a variety of reactions. Ethane is assumed to arise from the combination of two methyl radicals. Under homogeneous conditions the total methane + ethane is closely equivalent to the sum of isobutylene + 2 × (allene + propylene) and 3 × ethylene.

In order to make a run, the probe temperature is established at about 300°, and the nozzle temperature at 300° below reaction temperature. Following the alignment of the sampling probe, the blanket stream flow is carefully adjusted and the hydrocarbon injection syringe turned on along with the mixing diluent. A sample is withdrawn with the aid of a gas-tight syringe through U (Figure 2). After injecting the sample into a gas chromatograph, the hydrocarbon feed is shut off and the flow of blanket gas reduced to one-tenth of its rate at the time of sampling. The above process is repeated with different settings as dictated by the requirements of the particular study.

Data are taken with this reactor by either of two procedures.

(1) **Precise Analysis.** The reaction products are analyzed at a series of distances (times) downstream. The rate constant is determined from the slope of the plot of −log % conversion *vs.* time. This allows for any uncertainties in the rate of heating of the reactant as it emerges from the inlet tube. A typical curve is given in Figure 4. Activation energies are determined by repetition of the above procedure at a series of temperatures.

(2) **Thermal Scan Technique.** The sampling tube is set at a given distance (8–10 cm) from the edge of the inlet tube. Determinations of per cent conversions are made at a range of temperatures with the assumption of a first-order reaction, and the activation energy is calculated. The reaction time is corrected for variation in flow due to the temperature changes since the flow rates are established at room temperature. Relative rate constants only are obtainable, but the value for E_{act} is quite good. Since the extent of completion of the reaction increases with increasing temperature, a small effect upon the activation energy may be noted due to partial product decomposition. This technique has been particularly useful for comparative homogeneous-heterogeneous rate data which are to be reported in a following paper.

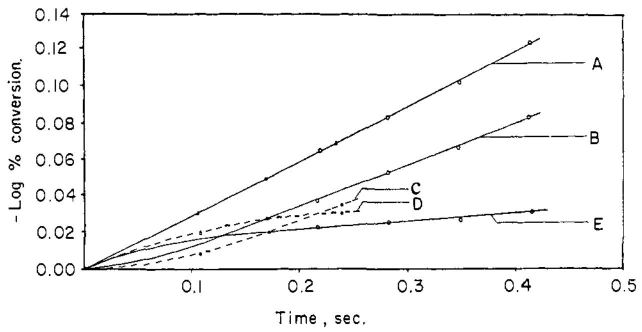

Figure 4. Neopentane rate data taken at 755° (hydrocarbon injection rate of 5.8 cc/min (5% in N_2) (○) and 0.97 cc/min (0.833% in N_2) (△); bulk flow rate is constant): A, over-all rate of neopentane decomposition; B, ethylene + ethane at the lower hydrocarbon concentration; C, ethylene + ethane at the higher hydrocarbon concentration; D, methane at the higher hydrocarbon concentration; E, methane at the lower concentration.

Discussion

Under homogeneous conditions, the products of pyrolysis of neopentane include hydrogen, methane, ethane, ethylene, propylene, allene, methylacetylene, isobutylene, neopentane, 2-methyl-2-butene, 2-methyl-1-butene, isoprene, and neohexane (trace) with the major products being methane, ethane, isobutylene, and hydrogen. 1-Butene may also be present, but it is not separable from isobutylene with the chromatograph columns in current use.

The over-all rate of decomposition of neopentane is first order, but the products form by more complex kinetics (see Figure 4). The data for curve A are determined from total product analyses at the indicated reaction times.

Particularly interesting is the variation of methane to ethane ratios with time. The plot of log concentration of neopentane which has been converted to ethane curves upward and the corresponding curve for methane approaches a limiting slope with dilution. The plot of log concentration of neopentane converted to secondary products *vs.* time shows an upward curvature similar to that observed for ethane formation. Over the range of 650–800° the energy of activation is 80.5 kcal/mole (see Figure 5). The Arrhenius pre-exponential factor is $10^{16.9}$. These values are in fair agreement with those of Tsang. However, because of the uncertainty of temperature measurement in the shock-tube technique, our values appear to be the more accurate.

Based on the observed data the following reaction sequence is proposed. The estimated bond energies are also given when available.[9]

$$C(CH_3)_4 \rightleftharpoons \cdot CH_3 + \cdot C(CH_3)_3 \qquad \Delta H = +80 \text{ kcal} \qquad (3)$$

From these radicals the major products are formed by at least two routes.

---

[9] J. A. Kerr, *Chem. Rev.*, 66, 465 (1966), is the major source of bond energies.

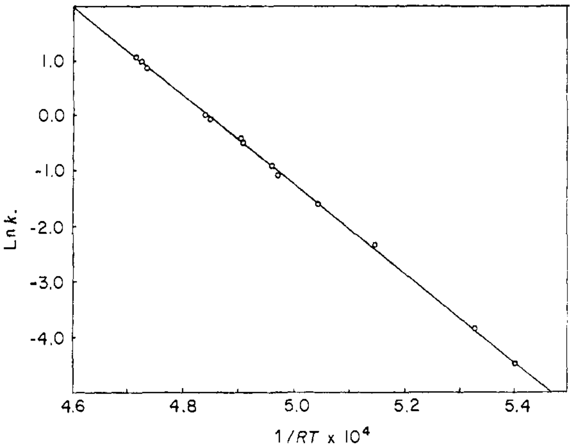

Figure 5. Arrhenius plot of neopentane pyrolysis. The rate constant is in sec^{-1}.

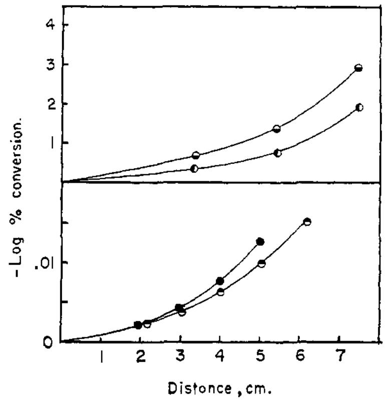

Figure 6. A plot of time *vs.* the reciprocal log of molar per cent of neopentane converted to the indicated products: ◓, ethylene; ●, C$_5$ olefins; ◐, allene; and ◒, propylene (temperature 796°; 1 cm = 0.0232 sec residence time; 5% hydrocarbon input).

Radical decomposition

$$\cdot C(CH_3)_3 \rightleftharpoons \cdot H + CH_2{=}C(CH_3)_2 \qquad \Delta H = +42 \text{ kcal} \qquad (4)$$

Radical–radical combinations

$$2\cdot CH_3 + M \longrightarrow C_2H_6 + M \qquad \Delta H = -88 \text{ kcal} \qquad (5)$$

$$2\cdot H + M \longrightarrow H_2 + M \qquad \Delta H = -104 \text{ kcal} \qquad (6)$$

$$\cdot H + \cdot CH_3 + M \longrightarrow CH_4 + M \qquad \Delta H = -104 \text{ kcal} \qquad (7)$$

The minor products or reactions are presumed to form as follows.

Radical abstractions in addition to eq 1

$$CH_2{=}C(CH_3)_2 + \cdot CH_3 \text{ (or } \cdot H) \longrightarrow CH_2{=}C(CH_3)CH_2\cdot + CH_4 \text{ (or } H_2) \qquad (8)$$

$$\cdot C(CH_3)_3 + \cdot CH_3 \text{ (or } \cdot H) \longrightarrow CH_2{=}C(CH_3)_2 + CH_4 \text{ (or } H_2) \qquad \Delta H = -62 \text{ kcal} \qquad (9)$$

Radical couplings

$$CH_2{=}C(CH_3)CH_3\cdot + \cdot CH_3 \rightleftharpoons CH_2{=}C(CH_3)CH_2CH_3 \qquad (10)$$

$$\cdot CH_2C(CH_3)_3 \text{ (from (14))} + \cdot CH_3 \rightleftharpoons CH_3CH_2C(CH_3)_3 \qquad (11)$$

Radical additions to double bonds

$$\cdot H + CH_2{=}C(CH_3)_2 \rightleftharpoons \begin{cases} \cdot C(CH_3)_3 & \Delta H = -42 \text{ kcal} \\ \cdot CH_2CH(CH_3)_2 & \Delta H = -35 \text{ kcal} \end{cases} \qquad (12)$$

$$\cdot H + CH_2{=}CHCH_3 \rightleftharpoons \cdot CH_2CH_2CH_3 \qquad \Delta H = -39 \text{ kcal} \qquad (13)$$

$$\cdot CH_3 + CH_2{=}C(CH_3)_2 \rightleftharpoons \begin{cases} \cdot CH_2C(CH_3)_3 & \Delta H = -23 \text{ kcal} \\ CH_3CH_2\underset{\cdot}{C}(CH_3)_2 & \end{cases} \qquad (14)$$

Radical decompositions

$$\cdot CH_2CH_2CH_3 \rightleftharpoons CH_2{=}CH_2 + \cdot CH_3 \qquad \Delta H = +26 \text{ kcal} \qquad (15)$$

$$\cdot CH_2CH(CH_3)_2 \rightleftharpoons CH_2{=}CHCH_3 + \cdot CH_3 \qquad \Delta H = +24 \text{ kcal} \qquad (16)$$

$$CH_3CH_2\underset{\cdot}{C}(CH_3)_2 \rightleftharpoons CH_3CH{=}C(CH_3)_2 + \cdot H \qquad (17)$$

$$CH_2{=}C(CH_3)CH_2\cdot \rightleftharpoons CH_2{=}C{=}CH_2 + \cdot CH_3 \qquad (18)$$

The most likely sources of isoprene are the two C$_5$ olefins which can be dehydrogenated by initial abstraction of hydrogen.

It appears that (3) is both the thermodynamically and kinetically significant step. The bond dissociation energy for neopentane is estimated at ΔH = 80 kcal/mole at 25° by subtracting the ΔH_f values of the *t*-butyl and methyl radicals from that of neopentane. Correspondingly, E_a = 80.5 kcal/mole. If it is assumed that the activation energy for the reverse combination is nearly zero, the equality of the activation energy and bond energy suggests that bond dissociation is the primary step which is followed by a series of fast secondary reactions by the radical fragments. The maintenance of the first-order character of the primary reaction in the temperature range of 650–800° even with broad deviations in the methane to ethane ratios (Figure 4) further demonstrates the fundamental nature of reaction 3.

Reactions 1, 2, and 3, as suggested by earlier workers, appear to be quite significant at the low temperatures as indicated by the three-halves order and the lower values for the observed activation energies. Reaction 1 does not appear to be at all important under homogeneous conditions.

This change in mechanism with temperature is not without precedent since the kinetic order for propylene changes from three-halves to unity with an increase in temperature.[10] In view of the lack of homogeneous three-halves order, the basis for this change in order with both neopentane and propylene is probably an effect of surface since the low-temperature runs[5–7] are made in a static reactor with relatively long reaction times. The methyl and *t*-butyl radical intermediates may be of such stability at the lower temperatures that the rate of their diffusion to the reactor wall in the static reactor is equal to or greater than the homogeneous reaction rate. The contribution by a heterogeneous reaction could then become highly significant. Since accurate rates in the homogeneous reactor cannot be determined at 500–570° due to the time limitation, a direct comparison with the earlier data at corresponding temperatures is not feasible.

The variation of methane to ethane ratios with dilution (Figure 4) is indicative of the sources of these products. Ethane appears to be formed exclusively by the reaction of two methyl radicals (eq 5), whereas

---

(10) A. Amano and M. Uchiyama, *J. Phys. Chem.*, 68, 1133 (1964).

methane occurs as a result of the interaction of hydrogen plus methyl radical (eq 7) or by any of several abstraction reactions such as (8), (9), or (1). At higher concentrations the methyl radical reacts with the most available reactive component which may be another radical or an olefin. At high dilutions the alternative is a methyl–methyl radical interaction. High dilution should provide a corresponding increase in the per cent concentration of methyl radicals based on neopentane. The actual per cent of momentary radical concentration has not been determined, but it does not appear to be high under any conditions.

Ethylene appears not to be formed by dehydrogenation of ethane since the C–H bond energy is 98 kcal/mole. A more favorable route is the degradation of isobutylene. See reactions 12, 13, 15, and 16. A possible, though unlikely, alternative is the abstraction of hydrogen from ethane by $\cdot$H or $\cdot CH_3$; this is deemed unlikely in view of the lack of evidence for reaction 1.

A graph of the log concentrations of ethylene, allene, propylene, and pentenes with time all curve upward similar to ethane (see Figure 6). Thus, the dependence of the formation of these products on secondary reactions as in (8), (10), and (12)–(18) is definitely indicated.

The formation of 2-methyl-1-butene is clearly indicative of a methyl–methallyl radical combination (eq 9). The reactions for formation of 2-methyl-2-butene and isoprene are less clearly defined.

As noted in the Experimental Section, there is significant diffusion of both reactants and products as they flow downstream. This has led to some interesting observations pertaining to the apparent rates of diffusion of the several products. Comparison of the square root of molecular weight and apparent diffusion rate indicates that the distributions of methane and propylene plus allene are about normal; ethane plus ethylene diffuse more rapidly and the methylbutenes and isoprene diffuse more slowly. Obviously this is not a confrontation of Graham's law. Those products which form by the interaction of two like radicals, *e.g.*, ethane from two methyl radicals, form to a greater extent in the outer stream where the competing reactions 8–11 and 14 are less likely to occur, thus the apparent high diffusion rate. In contrast, those products formed from two different radicals (except hydrogen atom because of its independently high diffusion rate) generally form to a greater extent in the center of the stream where the dual concentrations are highest. Accordingly, the diffusion rate appears to be somewhat low.

The wall-less reactor provides a means of obtaining highly reproducible and completely homogeneous data as evidenced in particular by the equality of the bond dissociation and activation energies for neopentane. This technique provides a means of determining appropriate bond dissociation energies directly by determining the activation energy. Further, a source of unequivocal kinetic data suitable for theoretical treatment may now become available. The most interesting facet of this work is to be presented in a paper to follow where an absolute comparison of homogeneous and heterogeneous rate data is made over a wide range of temperatures.

Acknowledgment. The authors wish to acknowledge the valuable assistance of Paul M. Norton, Machinist, Frederick Hoppstock of Goodyear Tire & Rubber Co., and Alan G. Welsh of this department.