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RECEIVED for review June 29, 1962. Accepted November 28, 1962. Division of Petroleum Chemistry, General Sessions, ACS, Washington, D. C., March, 1962. Work sponsored by the Gulf Research & Development Co. as part of the research program of the Multiple Fellowship on Petroleum.

Pyrolysis of *n*-Butane in a Differential Flow Reactor

SAMUEL SANDLER and M. ALI LANEWALA[1]
University of Toronto, Department of Chemical Engineering Toronto, Ont., Canada

The thermal decomposition of *n*-butane has been studied in the very low conversion region, 0.05 to 5%, in an isothermal flow reactor. The analytical problem was solved by the very successful application of a gas liquid chromatographic technique. An inherent weakness in the usual procedure of extrapolating relatively high conversion data to estimate incipient conversion mechanisms is demonstrated by the results. On the basis of the measured product distributions at these low conversions, it is possible to confirm earlier suggestions concerning the reaction mechanism and kinetics.

THERMAL decomposition of light hydrocarbons has been studied extensively from the theoretical as well as the industrial point of view. Considerable work has been done on the pyrolysis of *n*-butane because of the intermediate complexity of the product mixtures obtained. Moreover, the conversion to useful chemical intermediates of the excess quantities of this material produced during certain seasons has been a spur to research in this area.

Most of the early work was carried out in the low temperature region between 450° and 650° C. and has been carefully reviewed by Steacie (*10*). In the investigations involving determinations of the initial products of decomposition, conflicting results were recorded because of the necessity for extrapolating relatively high conversion data to obtain a measure of the product distributions in the incipient conversion region. The few low conversion data reported by Crawford and Steacie (*3*), suffer from incomplete analyses.

The present work demonstrates an approach which may be used to overcome these difficulties and to obtain a better estimate of the reaction mechanism and kinetics.

EXPERIMENTAL

The reactor used in this study was a 1.3-cm. I.D. Vycor tube, 96% silica, with an effective volume of 17.15 cc., mounted coaxially in the central zone of a 16-inch furnace. Integral parts of the reactor assembly were inlet and outlet quartz capillary tubes which functioned, respectively, for

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[1] Present address, Department of Chemical Engineering, New York University, New York 53, N. Y.

gas preheating and reaction quenching. With these conditions, no detectable decomposition took place in the preheater capillary, and the reaction products were removed through the exit capillary and cooled quickly enough to allow an accurate estimate of the residence time to be made.

Temperatures were measured by a pair of Chromel-Alumel thermocouples connected in series to obtain a larger output signal and calibrated at the boiling point of water and the melting points of lead and tin. These were tied along the outer wall of the reactor in its central zone. In this region, temperature variations of only ±0.1% at 900° K. were noted. The probable temperatures of the gas stream were calculated from the outer-wall temperatures by means of heat balances using an appropriate heat transfer coefficient for the gas film at the inside wall of the reactor. At low rates of flow and low conversions (0.04 to 0.50%), outer-wall temperatures and calculated gas stream temperatures were nearly identical. The pressures used in this study were ambient pressures only (around 750 mm. of Hg). *n*-Butane (C.P.-grade) was used without further purification. The presence of traces of isobutane and some C_4 olefins was revealed by gas chromatographic analysis of 16-cc. samples (Figure 1). These amounts were subtracted from the quantities obtained during the analysis of the reaction products.

The reactor effluent was analyzed by gas liquid chromatography using a ¼-inch copper column, 30 feet in length and packed with 30–60 mesh firebrick impregnated with 40% by weight of dimethylsulfolane (*6*). The column was placed in an ice water bath at 0° C. and was connected to a thermal conductivity detector cell utilizing thermistor elements for high sensitivity.

Good separations were obtained for most of the components. A few, however, although not completely resolved, were still sufficiently well separated to make an analysis possible (Figure 2). By using the statistical procedure developed by Bartlet and Smith (*1*), it was possible to correct for the effect of peak overlap.

Because helium was used as the eluent gas, output signals for hydrogen were very weak and direct measurements could not be made. The hydrogen content was therefore calculated from the amounts of butenes and the excess of ethylene over ethane. A hydrogen balance over the products of the reaction and over the *n*-butane decomposed as calculated from the carbon balance showed that this procedure was quite sound.

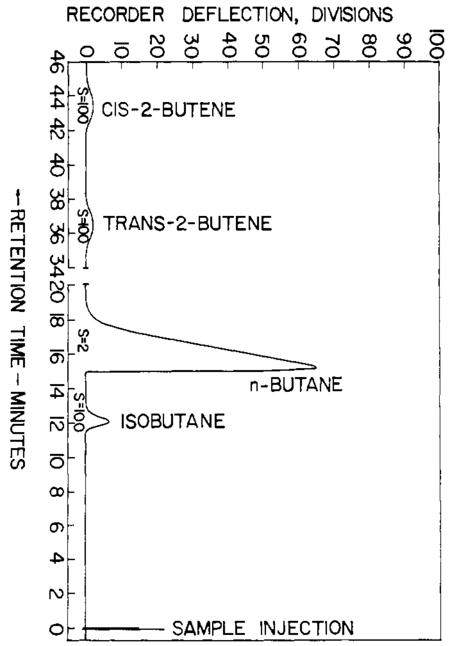

Figure 1. Chromatogram of *n*-butane feed

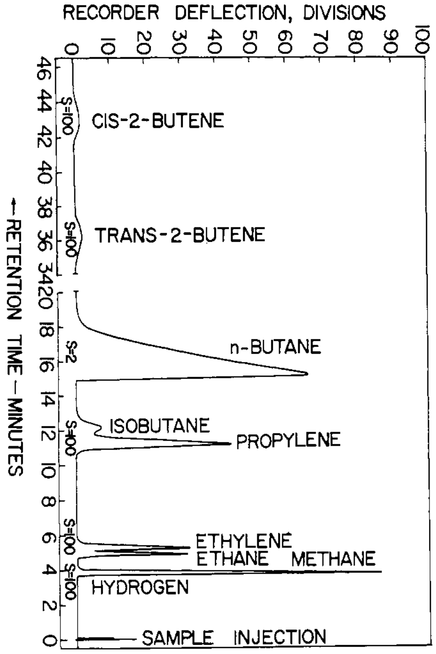

Figure 2. Chromatogram of reactor effluent at 0.4% *n*-butane conversion

RESULTS

The values of the activation energies and frequency factors at different residence times are summarized in Table I. The average activation energy is 51 kcal./gram-mole. However, considering the uncertainty regarding the actual reaction temperature, the heat transfer calculations suggest that 46 kcal. is the more probable value. The values for the pyrolyses of *n*-butane, which appear in the literature, range from 43 to 74 kcal. with the lower values being reported generally for work done with flow type reactors (*2, 4, 5, 8, 9*).

Figure 3 is a plot of the number of moles of the various components produced per 100 moles of butane decomposed (product selectivities) against per cent conversion, for a conversion range of 0.05 to 7%. Work at these low conversions has the advantages of avoiding the complicating side reactions, allowing better estimates of residence time and reaction temperature to be made and avoiding the necessity for any great extrapolation of the product selectivities to zero conversion. The curves in Figure 3 justify this approach. The selectivity plots have a definite curvature, indicating that any extrapolation of results obtained at high conversion conditions would be approximate only. This is probably the most important reason for the apparent lack of agreement of the results reported by different investigators. Table II illustrates this by a comparison between published and present work, the former being obtained by extrapolation of literature selectivity data at conversions from 5 to 25%, while the latter are the results of the minor extrapolation of the data taken at conversions of 0.05 to 7%. The important products at incipient conversion are methane, propylene, ethane, ethylene, and hydrogen. Butenes were detected and measured at conversions higher than 0.5% and small quantities of propane were formed at conversions over 1%.

The results indicate that the radical decomposition reaction involving the ethyl radical and forming ethylene and

Table I. Activation Energy and Frequency Factor Values

Temp. Range, ° K.	Residence Time, Sec.	Frequency Factor Sec.$^{-1}$ x 10^{-10}	Activation Energy Kcal./Gram-Mole
700-884	5.15	0.8	46
794-884	1.00	13.7	52
874-999	0.28	19.5	54

Table II. Comparison of Incipient Conversion Product Selectivities

	Initial Product Selectivities, %	
Product	Previous results	Present work
Methane + propylene	36-124	138-148
Ethane + ethylene	22-72	53-62
Hydrogen	...	2-6
Hydrogen + butenes	0-20	...
Hydrogen + butadienes	0-4	...

Table III. Reaction Multipliers at Incipient Conversion

	Temperature Ranges, ° C.		
Reaction	400-425	500-525	600-625
	Reaction Multipliers		
$C_4H_{10} \rightarrow CH_4 + C_3H_6$	0.74	0.72	0.69
$C_4H_{10} \rightarrow C_2H_6 + C_2H_4$	0.24	0.24	0.25
$C_4H_{10} \rightarrow H_2 + 2C_2H_4$	0.02	0.04	0.06

hydrogen proceeds even at very low conversions and low temperatures (over 400° C.). This is in contrast to the suggestion in the original Rice mechanism that this reaction occurs appreciably only at high temperatures (*7*). The reaction $C_2H_5\cdot \rightarrow C_2H_4 + H\cdot$ may therefore be considered as a primary process. The preponderance of ethylene over ethane has been observed previously by other investigators (*2, 3, 8*), but their results were obtained at conversions well above those used in the present work.

On the basis of these results it is postulated that the reactions given in Table III are involved in the initial stages of the thermal decomposition of *n*-butane. The reaction multipliers, which indicate the fraction of the total conversion proceeding according to the suggested reaction in any given temperature range, are also indicated in this table.

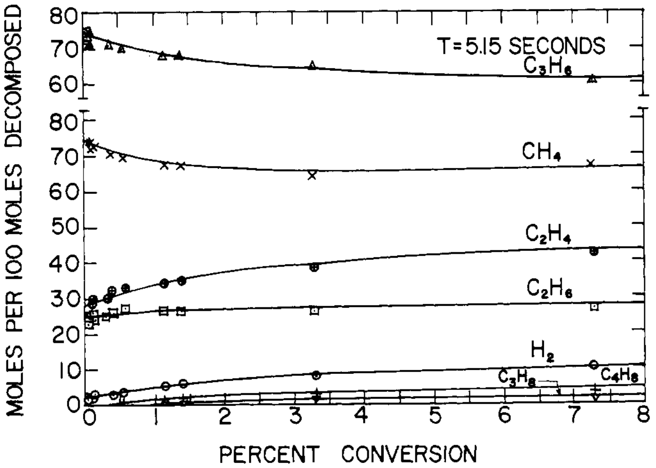

Figure 3. Effect of per cent conversion on product selectivities

Residence time, 5.15 seconds

As a complement to this study, several experiments concerned with the effect of dilution of the *n*-butane with an inert gas (helium) were performed. Over a range of butane concentrations from 0.25 to 1 mole fraction, the fraction of *n*-butane decomposed was remarkably constant, indicating that the reaction scheme involved is essentially a first order process. Again, as was evident with a temperature increase (Table III), the ratio of ethylene to ethane increased as the mole fraction of *n*-butane in the helium dilution studies was decreased at constant temperature and conversion.

CONCLUSIONS

The results of this investigation show that three primary reactions are involved in the gas phase pyrolysis of *n*-butane at temperatures down to the lowest studied. The procedure of extrapolating the results for conversions above 1 or 2% to zero conversion gives a relatively poor approximation. The previously reported low values of the apparent activation energy of this reaction (*2, 4, 8*) are supported by the present work; these low values may be obtained because of the heat transfer characteristics of flow systems.

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RECEIVED for review June 18, 1962. Accepted November 13, 1962. Part 39 of an investigation of the mechanism of the oxidation, decomposition, ignition, and detonation of fuel vapors and gases. Financial assistance was received in the form of a Grant-in-Aid from the President's Advisory Committee on Scientific Research of the University of Toronto.