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Monomolecular and Bimolecular Mechanisms of Paraffin Cracking: n-Butane Cracking Catalyzed by HZSM-5

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The cracking of n-butane catalyzed by the zeolite HZSM-5 has been characterized by measurements of the conversion determined with a flow reactor at temperatures of 426–523°C and n-butane partial pressures of 0.01–1.00 atm. The primary products, each formed in a first-order reaction, are H_2 + butenes; methane + propylene; and ethane + ethylene. In the limit approaching zero conversion, each compound in each stated pair was formed at approximately the same rate as the other. Propane and a small amount of isobutane were formed as secondary products in second-order reactions. The results are consistent with the occurrence of two simultaneous mechanisms: (1) a monomolecular mechanism proceeding through the pentacoordinated carbonium ion formed by protonation of the n-butane at the two position and (2) a bimolecular hydride transfer proceeding through carbenium ion intermediates. The former proceeds almost to the exclusion of the latter in the limit approaching zero n-butane conversion. The limiting product distribution characterizes the intrinsic selectivity of the collapse of the carbonium ion; at 496°C, the relative rates of decomposition of the carbonium ion to give H_2 + butenes, methane + propylene, and ethane + ethylene are 30 ± 6, 36 ± 4, and 34 ± 5, respectively, with the corresponding activation energies all being approximately 140 kJ/mol. These results provide the first demonstration of stoichiometric dehydrogenation accompanying paraffin cracking. © 1992 Academic Press, Inc.

INTRODUCTION

Many mechanistic details of paraffin cracking have eluded researchers because of the complexity of the reaction networks, which, besides β-scission, often include isomerization, disproportionation, and conversion of olefinic cracking products by protonation and hydrogen transfer reactions. Catalyst deactivation is usually rapid. Distributions of primary cracking products have only seldom been distinguished.

Some of the most clearly interpretable data characterizing the pathways of paraffin cracking have been obtained with solid acid catalysts used in the presence of low concentrations of olefins. Haag and Dessau (*1*) observed that cracking of n-hexane and of 3-methylpentane proceeded by two simultaneous pathways: (1) the classical bimolecular hydride transfer mechanism involving β-scission of tricoordinated carbenium ions and (2) a monomolecular path proceeding via pentacoordinated carbonium ions formed as the acidic catalyst protonates the paraffin; the carbonium ion reacts by breaking C–C and C–H bonds to give the primary products, including H_2, paraffins, and olefins. The occurrence of these pathways has been confirmed by measurements of product distributions, e.g., in cracking of 2-methylpentane and 2,3-dimethylbutane catalyzed by acidic zeolites (*2, 3*) and of n-heptane catalyzed by fluorided γ-Al_2O_3 (*4*). The bimolecular path is predominant under most conditions, but the monomolecular path becomes predominant with catalysts having low hydrogen transfer activity and/or when olefin concentrations approach zero. There is increasing evidence for penta-

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coordinated carbonium ion intermediates in catalytic cracking (*5*), and they could play a role in commercial cracking of petroleum, perhaps accounting for the formation of methane and ethane.

The goal of the research described here was to investigate the cracking of a paraffin under conditions chosen to maximize the role of an easily characterizable monomolecular mechanism. Butanes are appealing reactants because they give simple product distributions; for example, isobutane has been observed at low conversions (*6–9*) to crack with little isomerization to give products that nearly match the distribution expected from decomposition of the carbonium ion resulting from isobutane protonation, but some catalyst deactivation occurs. *n*-Butane has also been observed to give a simple cracking product distribution explained by the decomposition of the carbonium ion formed by its protonation (*7*). *n*-Butane was selected for this research because (a) it is not a good hydride donor and therefore might be expected to undergo cracking with less catalyst deactivation than isobutane and (b) because it was expected that its protonation might occur at the most highly substituted carbon (C_2), thereby giving only a single kind of carbonium ion as a reaction intermediate. The cracking product distribution data would then be expected to provide evidence of the intrinsic reactivity pattern of the carbonium ion.

In contrast to large-pore zeolites, medium-pore zeolites such as HZSM-5 have reduced hydrogen transfer activity as a result of steric inhibition of the bulky bimolecular transition state (*10*). Consequently, HZSM-5 favors the monomolecular cracking path. This zeolite also catalyzes cracking of small paraffins with minimal coke formation and catalyst deactivation. HZSM-5 was therefore chosen for this work.

Experiments were performed with a once-through flow reactor to determine steady-state values of the product distributions and kinetics of the cracking. Products were analyzed for hydrocarbons and hydrogen.

EXPERIMENTAL METHODS

n-Butane was obtained from Matheson and used without purification; it was found by gas chromatography to contain 0.11 wt% isobutane and 0.15 wt% propane as impurities (these were taken into account in the calculation of conversions). The crystalline ZSM-5 catalyst, consisting of particles about 0.05 μm in size and having a Si/Al atomic ratio of 35, was prepared at Mobil and received in the ammonium form. It was converted into the hydrogen form by calcination at 550°C.

The reactor was a Pyrex or a quartz tube, 1 cm in inside diameter and 40 cm in length. It was charged with either 103 or 506 mg of catalyst crystallites, dispersed in quartz wool to minimize the pressure drop, and placed on a porous silica frit in the central heated zone. The temperature was varied from 426 to 523°C, measured with a thermocouple in a well near the center of the catalyst bed, and controlled within ±1°C; most of the experiments were performed at 496°C. The reactor pressure was approximately atmospheric. Pressure was measured with Validyne DP15-38 transducers upstream and downstream of the catalyst bed.

The feed *n*-butane was mixed with a stream of dry, purified N_2, giving butane partial pressures in the range 0.01 to 1.00 atm (101 kPa). The total flow rate through the reactor was held at either 70 or 117 ml/min, measured at NTP. The products flowed through a heated exit line to an on-line gas chromatograph (Hewlett–Packard 5750) equipped with two packed columns. The hydrocarbons were analyzed with a 10-ft VZ-10 column and a flame ionization detector (He carrier gas). Hydrogen was analyzed with a 15-ft Porapak Q column and a thermal conductivity detector (N_2 carrier gas). Samples were injected simultaneously into the two columns (held at 50°C) with a Valco multiport sampling valve.

At the beginning of each catalysis experiment, the reactor was purged with flowing

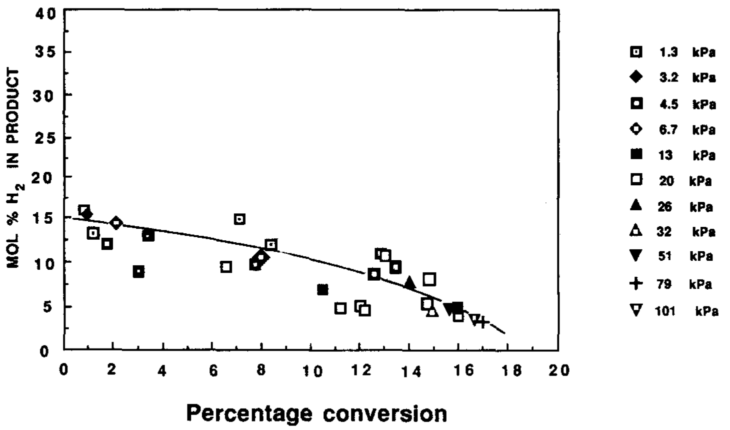


FIG. 1. Formation of H_2 in *n*-butane cracking catalyzed by HZSM-5 at 496°C. H_2 is a primary product.

N_2 prior to the start of feed flow. Data were collected for conversions of butane up to 17%.

RESULTS

The cracking of *n*-butane catalyzed by HZSM-5 proceeded cleanly and without measurable catalyst deactivation. Reaction in the absence of catalyst was undetectable. Conversions to each of the products were measured at various temperatures, reactant partial pressures, and reactant flow rates. Most of the measurements were made at low conversions, as one of the principal goals was to minimize the influence of secondary reactions and characterize the cracking to give primary products.

The products observed in the conversion of *n*-butane catalyzed by HZSM-5 were hydrogen, methane, ethylene, ethane, propylene, propane, the butene isomers, and (in small yields) isobutane. Representative product distribution data for reaction at 496°C are plotted in Figs. 1–3, where the yields of the H_2, methane, and ethane, respectively, are shown as a function of conversion at various partial pressures of *n*-butane in the feed. Almost all the data fall

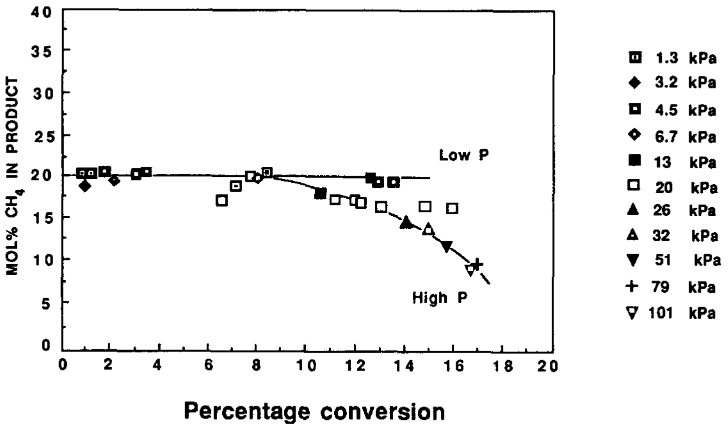


FIG. 2. Formation of methane in *n*-butane cracking catalyzed by HZSM-5 at 496°C. Methane is a primary product.

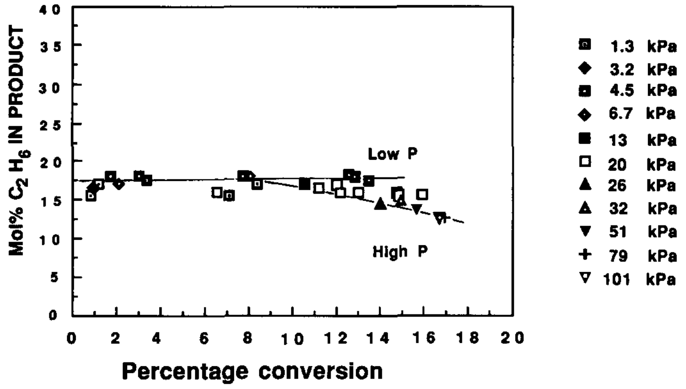


FIG. 3. Formation of ethane in *n*-butane cracking catalyzed by HZSM-5 at 496°C. Ethane is a primary product.

in envelopes between the lines characterizing the lowest and the highest *n*-butane partial pressures in the feed. The yield of each of these three products decreased with increasing conversion.

The data of Fig. 4 characterize the formation of propane at 496°C. The pattern is different from that of Figs. 1–3; the conversion extrapolated to zero conversion is zero. The data for isobutane fall on a plot (not shown) similar to that for propane, but the yields are an order of magnitude less.

The data for each product have been extrapolated to zero conversion, as shown on the figures. The product distribution at 496°C, determined by such extrapolations, is shown in Table 1. Product distribution data for conversions of zero and 17% are compared in Table 2; the contrast is sharp. For example, the yield of H_2 decreased from 15 to 6 mol%, and the yield of propane increased from 0 to 40% as the conversion increased from 0 to 17%.

The data of Table 2 also include the H/C ratios of the feed and products, calculated from the composition data. The internal consistency of the results is good and within the estimated experimental error. The re-

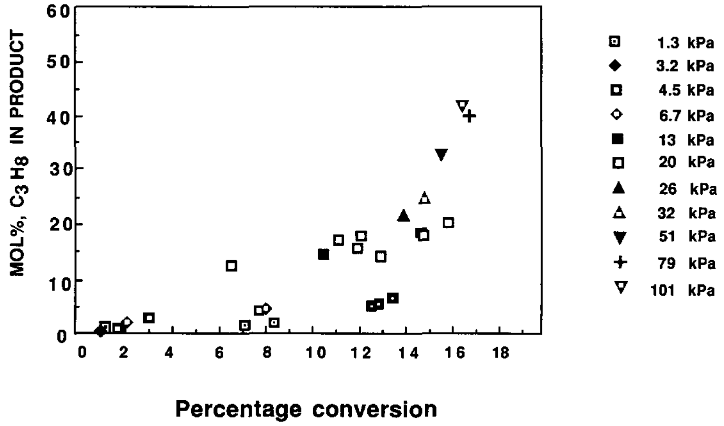


FIG. 4. Formation of propane in *n*-butane cracking catalyzed by HZSM-5 at 496°C. Propane is a nonprimary product.

TABLE 1

Initial Distribution of Products in *n*-Butane Cracking Catalyzed by HZSM-5 at 496°C

Saturates		Olefins		Total
Product	Selectivity[a]	Product	Selectivity[a]	Selectivity[a]
H_2	15 ± 3	C_4H_8	15 ± 3	30 ± 6
CH_4	20 ± 2	C_3H_6	16 ± 2	36 ± 4
C_2H_6	17 ± 2	C_2H_4	17 ± 3	34 ± 5
Total	52 ± 7	Total	48 ± 8	100

[a] Mol% of product, extrapolated to zero conversion.

sults are consistent with the absence of coke formation.

The full set of conversion data for each of the primary products is well approximated by first-order kinetics, as demonstrated, for example, by the plots (not shown) of reaction rate (determined from *apparently* differential conversions—plots of conversion vs inverse space velocity were approximately linear) as a function of *n*-butane partial pressure. The rate constants and reaction orders (determined for each product by a least-squares analysis of the data) are summarized in Table 3.

TABLE 2

Distribution of Products in Cracking of *n*-Butane Catalyzed by HZSM-5 at 496°C

Product	Percentage[a] of product extrapolated to zero conversion	Percentage[a] of product at 17% conversion[b]
H_2	15	6
CH_4	20	9
C_2H_6	17	13
C_3H_8	0	40
C_2H_4	15	14
C_3H_6	16	10
C_4H_8[c]	17	8
Total	100	100
H/C ratio[d]	2.52	2.55

[a] Mol%.

[b] Partial pressure of *n*-butane in reactant = 101 kPa.

[c] All isomers.

[d] Molar ratio; value for *n*-butane = 2.50.

TABLE 3

Kinetics of *n*-Butane Cracking Catalyzed by HZSM-5

Product	Reaction order[a]	Rate constant at 496°C	Activation energy (kJ/mol)
Hydrogen	0.7	0.103 ± 0.005[b]	149[c]
But-1-ene	1.0	0.183 ± 0.018[b]	145
cis-But-2-ene	1.0	0.018 ± 0.013[b]	146
trans-But-2-ene	0.9	0.041 ± 0.003[b]	134
Isobutylene	0.9	0.023 ± 0.015[b]	139
Methane	0.9	0.214 ± 0.010[b]	142
Propylene	0.9	0.170 ± 0.008[b]	156
Ethane	1.0	0.188 ± 0.008[b]	134
Ethylene	0.9	0.214 ± 0.010[b]	139
Propane	2.0	0.005 ± 0.0008[d]	133
Isobutane	1.7	0.0005[d]	133[c]

[a] Determined with a precision of ±0.1.

[b] Calculated on the basis of first-order kinetics; units, ml (at reaction conditions)/(min · g · kPa).

[c] Based on only two points.

[d] Based on the assumption of second-order kinetics; units, ml (at reaction conditions)/(min · g · kPa^2).

In contrast, second-order kinetics provides a good representation of the data for formation of the secondary products, propane and isobutane (but the data for the latter are relatively imprecise) (Table 3).

The kinetics measurements were made in the temperature range 426–523°C. Some of the first-order rate constants are plotted in the Arrhenius plot of Fig. 5. The activation energies calculated from the slopes of such plots are summarized in Table 3.

DISCUSSION

Lack of Intracrystalline Mass Transport Influence

Haag *et al.* (*10*) measured first-order rate constants for cracking of paraffins that are larger and more reactive than *n*-butane (including the branched 3-methylpentane) catalyzed by HZSM-5 crystallites larger than those used in this work; rate constants were measured for various sizes of zeolite crystallites, and effectiveness factors of unity were observed (*10*). Therefore, it is concluded that the rates of conversion of the smaller, less reactive *n*-butane were not influenced by intracrystalline transport.

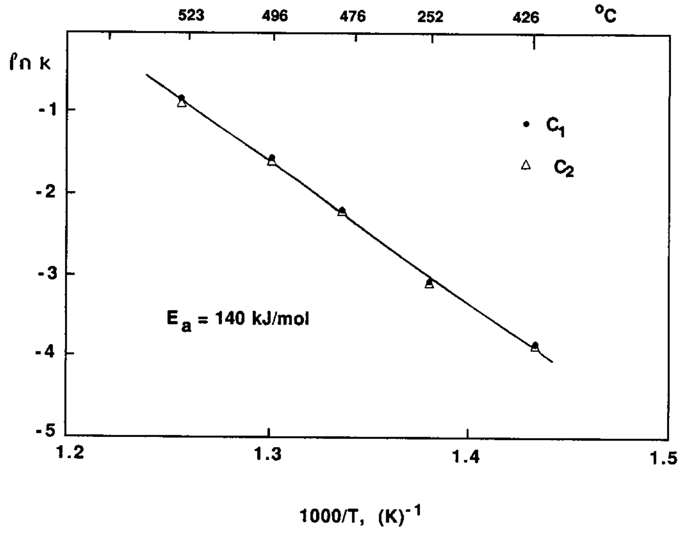
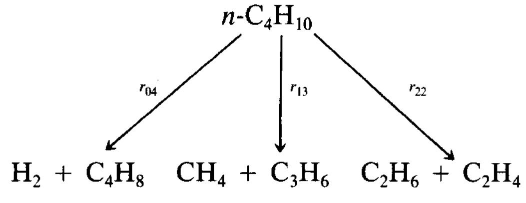


FIG. 5. Arrhenius plot: temperature dependence of the first-order rate constants for formation of methane and ethane. The average activation energy is about 140 kJ/mol. Activation energies for the individual products are summarized in Table 3. The units of the rate constant k are ml (at NTP)/(min · g · kPa). (The rate constants of Table 3 are defined in a slightly different way.)

Monomolecular Cracking of n-Butane via Pentacoordinated Carbonium Ions

The extrapolations of the data of Figs. 1–3 demonstrate that hydrogen, methane, and ethane are primary products, and the data of Fig. 4 demonstrate that propane is not a primary product. Similar plots for the other products demonstrate that all except isobutane are primary.

The data extrapolated to zero conversion (Table 1) establish precisely the stoichiometry of the primary reactions: The yields of hydrogen and butenes are nearly equal to each other, the yields of methane and propylene are nearly equal to each other, and the yields of ethane and ethylene are nearly equal to each other. Furthermore, all the yields are approximately the same. Therefore, the network of primary reactions is summarized as follows:



The data extrapolated to zero conversion give the following estimates for the relative rates of these primary reactions:

r_{04}: 30 ± 6

r_{13}: 36 ± 4

r_{22}: 34 ± 5

The stoichiometry of the n-butane cracking catalyzed by HZSM-5 at low conversions agrees with the observations of pulse reactor experiments carried out under similar conditions (*7*) (but there were no measurements of the hydrogen product in the earlier experiments). The observation of hydrogen as a product in paraffin cracking confirms the early results of Garten (*11*), which were confirmed by Brenner and Emmett (*12*) and other investigators (*2, 8, 13, 14*). The present results are qualitatively consistent with the earlier results and for the first time demonstrate the stoichiometry of dehydrogenation during cracking and show that the dehydrogenation and cracking are parallel reactions. Furthermore, the activation energy for dehydrogenation is nearly

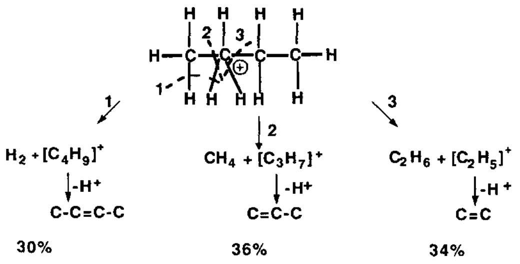
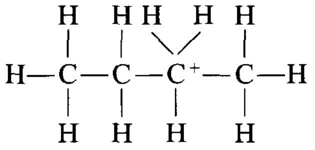


FIG. 6. Schematic representation of *n*-butane cracking by the monomolecular pathway: collapse of the carbonium ion.

equal to that for cracking. As expected from this pattern in paraffin conversion, the cracking of hexanes has been shown to be accompanied by the formation of C_6 olefins (*2, 3*), but the isomer distributions have not been determined.

The identifications of the primary and secondary products bear out the inferences of Haag and Dessau (*1*) regarding the occurrence of the monomolecular and bimolecular mechanisms in cracking, in particular verifying the inference that the former becomes predominant in the limit as the olefin concentration approaches zero. According to the Haag–Dessau hypothesis (which may be oversimplified), the monomolecular mechanism proceeds as the reactant paraffin is protonated at the most highly substituted carbon atom, in the case of *n*-butane giving the following structure:



There are three pathways for decomposition of this carbonium ion (Fig. 6). The splitting off of H_2 gives butenes (pathway 1); the splitting off of CH_4 gives propylene (pathway 2); and the splitting off of C_2H_6 gives ethylene (pathway 3). The relative rates of the three reactions (approximated as the mean of the relative rates of formation of H_2 and butenes or of methane and propylene, or of ethane and ethylene, respectively) are inferred to represent the intrinsic selectivity for the collapse of the carbonium ion. Since the concentration of the carbonium ion in the zeolite is immeasurably small, we can determine only relative rates of the reactions.

Hydrogen, methane, and ethane are products characteristic of the monomolecular and not the bimolecular cracking mechanism, and the most precise data were obtained for methane and ethane. All three of these products are formed at approximately the same rate and with approximately the same activation energy (Fig. 5, Table 3). These results indicate a statistical decomposition of the carbonium ion (Fig. 6) with no significant difference in the energy barriers. Since the carbenium ions formed from the collapse of the carbonium ion are much different in energy (being both secondary and primary carbenium ions; Fig. 6), we might infer, on the basis of an assumed Polanyi relationship, that the barriers for collapse of the carbonium ion to the different carbenium ions would be different. But since they are not, we suggest that the barriers are very small and that the carbonium ion has nearly the energy of each transition state.

If, in the limit of conversions approaching zero, the stoichiometry were exactly as represented above (Fig. 6), the extrapolated rate of formation of each product in a pair (e.g., ethane and ethylene) would be equal. But the product distribution data extrapolated to zero conversion (Table 1) show that the rate of ethylene formation was slightly greater than that of ethane, and that of propylene was slightly less than that of methane. These results therefore suggest that other reactions occurred at significant rates, even in the limit for which the data could be precisely extrapolated to zero conversion.

The other kinetically significant reactions include (a) further reactions of the primary products and (b) bimolecular cracking initiated by hydrogen transfer from the reactant butane to the product olefins. We now discuss these in turn.

Subsequent Reactions of the Primary Products

The hydrogen and olefins formed as primary products undergo fast subsequent reactions. The decrease in the hydrogen content of the product with increasing conversion (Fig. 1) is consistent with the inference that the cracking occurred by a different mechanism (a bimolecular mechanism, discussed below). At the higher reactant partial pressures, the selectivities to methane, ethane, and hydrogen all decline similarly, consistent with the bimolecular mechanism (*1*). However, at the low reactant partial pressures, this pattern does not hold; the methane and ethane selectivities are nearly constant, and the lower hydrogen selectivity is therefore taken as evidence that it is converted.

A likely reaction to account for the hydrogen conversion is the acid-catalyzed hydrogenation of olefins (*4*), as expected from the principle of microscopic reversibility. The secondary reactions of the olefins are thus inferred to include the following: (1) fast skeletal isomerization of *n*-butenes to isobutylene (indicated by the observation of all the butene isomers in the product), (2) cracking of *n*-butenes to ethylene, and (3) interconversion of olefins by an oligomerization-cracking path (*15*), exemplified by the conversion of butenes, mostly to propylene, consistent with thermodynamic data:

$$2C_4^= \rightleftharpoons [C_8^=] \rightleftharpoons C_3^= + C_5^= \quad (1)$$

$$C_4^= + C_5^= \rightleftharpoons [C_9^=] \rightleftharpoons 3C_3^= \quad (2)$$

$$\text{Sum:} \quad 3C_4^= \rightarrow 4C_3^= \quad (3)$$

Bimolecular Cracking of n-Butane via Carbenium Ions

With increasing conversion, increasing reactant partial pressure, and decreasing temperature, bimolecular cracking becomes increasingly significant. Bimolecular cracking involves hydrogen transfer from *n*-butane to carbenium ions formed from product olefins. The secondary butyl cation that is formed can undergo classical β-scission to give ethylene. This reaction is much slower than β-scission of longer-chain carbenium ions because one of the products is a primary carbenium ion. Therefore, a reaction of the secondary butyl cation that occurs more rapidly at higher olefin concentrations involves an oligomerization-cracking sequence similar to the one discussed above.

As the conditions approach those of the limiting case of cracking by the bimolecular mechanism only (which was not observed in this work), the cracking is envisioned to take place as follows:

$$\text{C—C=C} \xrightarrow{H^+} \text{C—C}^+\text{—C} \quad (4)$$

$$\text{C—C—C—C} + \text{C—C}^+\text{—C} \rightarrow \text{C—C—C}^+\text{—C} + \text{C—C—C} \quad (5)$$

$$\text{C—C—C}^+\text{—C} \xrightarrow{-H^+} \text{C—C=C—C} \quad (6)$$

$$\text{Sum:} \quad C_4H_{10} + C_3H_6 \rightarrow C_4H_8 + C_3H_8 \quad (7)$$

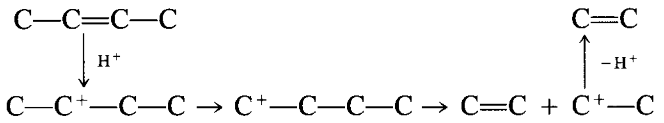
If reaction (7) takes place three times and reaction (3) once, the sum is

$$3C_4H_{10} \rightarrow 3C_3H_8 + C_3H_6 \quad (8)$$

The ratio of propane to propylene at 17% conversion (4, Table 2) is not greatly different from the ratio of 3 predicted by this simple accounting. A more exact agreement is not expected because of the occurrence of some monomolecular cracking at 17% conversion.

Similar arguments explain the yields of ethane and ethylene at the high conversion; these products are formed by both monomolecular and bimolecular mechanisms. The latter is envisioned to occur as follows.

Ethylene can be formed by monomolecular cracking of butene:



$$\begin{tikzcd} C{-}C{=}C{-}C \arrow[d, "H^+"] & & & C{=}C \\ C{-}C^+{-}C{-}C \arrow[r] & C^+{-}C{-}C{-}C \arrow[r] & C{=}C\ + & C^+{-}C \arrow[u, "-H^+"'] \end{tikzcd} \tag{9}$$

Ethane is then formed from ethylene in a reaction analogous to Eq. (7).

Comparison with Cracking of Isobutane

Data comparable to those presented here have been reported for cracking of isobutane (*9*); the catalyst was the same and the reaction conditions nearly identical. The isobutane conversions were low ($<1\%$) and the rate approximately the same as that reported here for *n*-butane. The primary products formed from isobutane at low conversions were methane and propylene (in nearly equimolar proportions) and isobutylene (presumably formed by dehydrogenation, but analyses for H_2 were not performed). These products are consistent with the Haag–Dessau hypothesis that the reaction proceeded by protonation of the isobutane, giving carbonium ions that decomposed into the observed products. In this respect, the results are very similar to those presented here.

However, there are some differences: (1) The isobutane conversion was accompanied by noticeable catalyst deactivation (except when the conversions were very low, $<1\%$), whereas the *n*-butane conversion was not, even at conversions of 17%, and (2) in the isobutane conversion, propane gave the appearance of being a primary product, whereas it was evidently not a primary product of the *n*-butane conversion.

These differences between isobutane and *n*-butane can be explained by the higher isobutylene concentrations formed from the isobutane and the fact that isobutane is a better hydride donor than *n*-butane, consistent with the greater stability of the *t*-butyl cation than that of secondary butyl cations. It has been suggested (*9*) that propane might have been formed from isobutane as a result of hydride transfer from isobutane.

Empirical Cracking Kinetics

The kinetics data of Table 3 represent the full conversion range up to 17%, whereby reaction takes place by both mechanisms of cracking, predominantly the monomolecular mechanism at low conversions and increasingly the bimolecular mechanism at the higher conversions. Although the kinetics is complex when both cracking mechanisms take place simultaneously (*1*), the results of the simple analysis presented here provide a good representation of the data. We emphasize, however, that this representation of the kinetics is only empirical, as it lumps the conversions by several parallel pathways that are not yet quantitatively resolved. The results are broadly consistent with the patterns observed before (*8*) in terms of the reaction orders of the primary and nonprimary products.

ACKNOWLEDGMENT

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