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Paraffin Disproportionation Catalyzed by Aluminum Chloride/Sulfonic Acid Resin

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The disproportionation of *n*-butane and of *n*-pentane was investigated as reactant vapors flowed over beads of a solid superacid catalyst (an aluminum chloride/sulfonic acid resin) at 1 atm and 70–143°C. *n*-Butane reacted in the presence of HCl to give equimolar ratios of propane and pentanes; the butane isomerization reaction took place simultaneously, occurring at an order-of-magnitude-higher rate than the disproportionation. The observed *i*- to *n*-pentane ratios were less than the equilibrium ratios predicted from literature data. The conversion of *n*-pentane under similar conditions yielded products ranging from methane to hexanes. The main products were propane and isobutane, which indicates that extensive β-scission occurred. The results are broadly consistent with classical carbenium-ion mechanisms involving hydride and methyl shifts and C–C bond-forming and -breaking steps, although some details of the mechanism of the *n*-butane disproportionation remain unexplained.

INTRODUCTION

Paraffin conversion catalyzed by extremely strong acids (superacids) proceeds by several simultaneous reactions, including isomerization, β-scission (cracking), alkylation, and disproportionation (*1, 2*). The foundations for understanding the chemistry of paraffin conversion were laid more than 40 years ago by Whitmore, Ipatieff, Schmerling, Pines, and others (*1*). Yet many of the details of paraffin conversions proceeding through carbenium-ion intermediates have been learned only recently, some of the key results having been obtained in experiments with superacid solutions and NMR spectroscopy (*3, 4*). Opportunities for further understanding are provided by solid superacids (*5–7*), which allow simple flow-reactor studies with paraffins as gas-phase reactants at low temperatures and pressures. Primary products of paraffin conversion can be determined from the exceedingly low conversions measurable with modern, highly sensitive gas chromatographs.

The classical mechanism of acid-catalyzed paraffin disproportionation (Fig. 1) involves the C–C bond-forming reaction between a carbenium ion and an olefin, followed by rearrangements of the resulting alkylate and a β-scission step (*1, 8*). Disproportionation is the least well characterized of the reactions of paraffins, there being few quantitative results in the literature. Here we report data characterizing disproportionation of two simple paraffins, *n*-butane and *n*-pentane. The *n*-butane disproportionation [which is accompanied by the order-of-magnitude-faster isomerization (*9*)] has been found to occur stoichiometrically in the presence of a solid superacid catalyst, giving propane and pentanes in equimolar amounts.

Paraffin disproportionation has typically been observed to be accompanied by extensive β-scission of the higher-molecular-weight intermediates, giving products with fewer carbon atoms than the reactant. The

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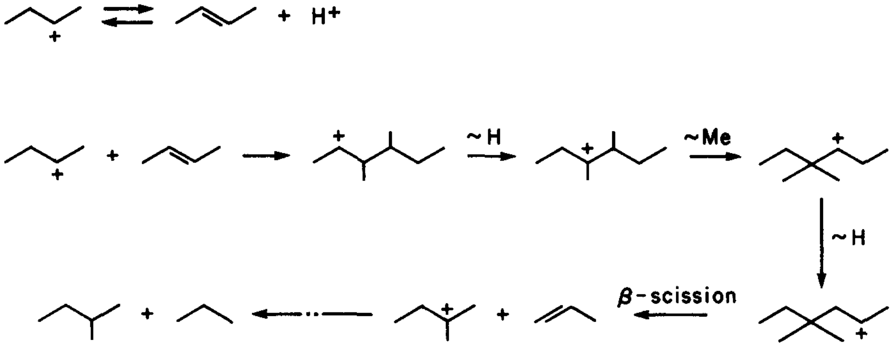


FIG. 1. Classical mechanism of acid-catalyzed paraffin disproportionation.

main products are normally isobutane and propane. Methane and ethane are usually not formed in more than trace amounts, unless the conditions are severe ($T \gtrsim$ 120°C) (*1*). Formation of disproportionation products, along with (poly)cyclic compounds, which are highly unsaturated and possibly contain halogenated species (*1, 10*), has been observed in most studies of paraffin conversion catalyzed by acidic halides. Pines and Wackher (*11*) studied *n*-butane conversion catalyzed by $AlCl_3$–HCl and determined that, in the absence of olefins, no reaction occurred. Upon addition of 0.01% of *n*-butenes at 100°C, reaction started. When higher concentrations of olefin were used, paraffin disproportionation occurred. Ipatieff and Schmerling (*12*) studied the isomerization of *n*-pentane catalyzed by $AlCl_3$–HCl. At 125°C, methane, ethane, propane, butanes, and hexane were formed; H_2 at 100 atm suppressed the formation of these products.

Solid superacid catalysts used for paraffin conversion include aluminum chloride/SiO_2–Al_2O_3 (*7*) and aluminum chloride/sulfonic acid resin (*5, 13*), among others. Tanabe and Hattori (*6*) investigated the reaction of *n*-butane and the reaction of isobutane in the presence of SbF_5 supported on oxides (e.g., Al_2O_3, TiO_2–SiO_2) at 20°C. The products consisted primarily of propane and isobutane; *n*-pentane, isopentane, and hexanes were formed to a lesser extent. Ono *et al.* (*14–17*) investigated *n*-pentane conversion occurring in the presence of $AlCl_3$–metal sulfate, $AlCl_3$–metal chloride, and $AlBr_3$–metal sulfate mixtures.

Disproportionation of paraffins has also been observed to occur at higher temperatures in the presence of aluminosilicates. There is a patent (*18*) illustrating the disproportionation of propane catalyzed by silica–alumina at temperatures $\gtrsim$425°C and catalyzed by H-mordenite at temperatures $\gtrsim$315°C. Another patent (*19*) illustrates the disproportionation of *n*-pentane at temperatures $\gtrsim$200°C catalyzed by H-mordenite, of isopentane at temperatures $\gtrsim$235°C catalyzed by H-mordenite, and of *n*-pentane catalyzed by rare-earth X and Y zeolites at temperatures $\gtrsim$235°C. This patent also illustrates the disproportionation of isobutane, of *n*-pentane, and of isopentane catalyzed by H-ZSM-4 at unspecified temperatures. Another patent (*20*) provides more complete characterization of the disproportionation of *n*-pentane catalyzed by H-ZSM-4, e.g., at 238°C.

The *n*-butane disproportionation reaction also occurs in the presence of nonacidic catalysts, e.g., Pt–Au films (*21*). Formation of *n*-pentane in significant amounts accompanied the formation of *i*-butane, propane, ethane, and methane. The disproportionation was also catalyzed by highly coked Pt films. The reaction scheme suggested to explain these results includes paraffin dehydrogenation, olefin disproportionation, and olefin hydrogenation.

The disproportionation of paraffins is catalyzed efficiently by a mixture of particles of Pt–Li/Al_2O_3 with WO_3/SiO_2 (*22*). The data were explained by a scheme involving olefin formation and hydrogenation on the Pt surface and disproportionation of olefins on the WO_3 surface. Hydrogenolysis of the C_{5+} products was suggested to account for the observation that C_{5-} yields exceeded C_{5+} yields.

EXPERIMENTAL

The reaction experiments were performed in stainless-steel packed-bed flow reactors operating at 1 atm. The dimensions of the tubular reactors were: length, 12.7 cm; internal diameters, 0.7 and 1.09 cm. To keep dead volume and response time to a minimum, all the lines connected to the reactor were 0.038-cm-i.d. tubing.

The feed was made up of research-grade *n*-butane or *n*-pentane (Phillips Petroleum), electronic-grade HCl (Linde), and dry-grade helium (Linde). The flow rates were regulated with mass flow controllers [Matheson (*n*-butane, He); Brooks (HCl)]. Liquid *n*-pentane was fed with a syringe pump into a mixing–vaporizing section upstream of the reactor. The He stream passed through a column containing a 4A molecular sieve (Linde) to remove traces of water.

The reactor was placed in a modified gas chromatograph oven, equipped with constant-load and set-point heaters. The temperature range of the experiments was 25 to 143°C. Temperature control was better than ±0.2°C. A 0.79-mm-o.d. stainless-steel sheathed copper–constantan thermocouple (Omega Engineers) was positioned in the reactor, and the temperature was monitored continuously during an experiment.

Analyses of the feed and product streams were performed with an on-line gas chromatograph (Antek 300) equipped with a flame ionization detector. A single-loop (0.25-cm^3) six-port gas sampling valve (Valco) was used to introduce samples into a 213-cm-long, 0.23-cm-i.d. stainless-steel column packed with *n*-octane on Porasil C (100–200 mesh, Waters Associates) maintained at room temperature.

The catalyst was prepared by subliming $AlCl_3$ onto beads of macroporous sulfonic acid ion-exchange resin (Amberlyst 15, Rohm and Haas). The resin had been treated to remove impurities (such as surfactants) remaining from its synthesis; the treatment consisted of washes with deionized water, methanol, and NaOH and HCl solutions. According to a procedure developed from that of Magnotta and Gates (*23*), a sample of the treated H^+-form resin was dried at 120°C under vacuum for at least 3 days and then placed in one chamber of a synthesis reactor, the other (upstream) chamber being filled with dry $AlCl_3$ (anhydrous, Fisher certified). All handling of $AlCl_3$ was done in a glove box under N_2. The synthesis reactor was fed with a stream of N_2 purified by flow through a dry ice–acetone trap followed by a column of 4A molecular sieve desiccant. A mineral oil bubble trap was used to isolate the reactor from impurities. The temperature of the chamber containing $AlCl_3$ was kept in the range 115 to 120°C, while the chamber containing resin was held at 125 to 130°C. The synthesis time was 2 to 3 weeks.

The resulting solid superacid was formed by the reaction of $AlCl_3$ with the ion-exchange resin; HCl was a product (*13*, *23*). The resin samples taken from the synthesis reactor were placed in sealed flasks under dry N_2 and stored in a desiccator, where they remained in a nearly anhydrous state (*9*). Samples were loaded under dry N_2 into the reactor for catalysis experiments.

The resin samples were analyzed (Galbraith Laboratories, Knoxville, Tenn.), the average compositions (wt%) being: S, 9.4; Al, 6.2; and Cl, 11.5. Carbon, oxygen, and hydrogen were the remaining elements in the resin.

Further details of the experiments are available in a thesis (*24*).

RESULTS

Conversion of n-Butane

The products detected in the *n*-butane conversion experiments were (in order of decreasing yield) isobutane, propane, isopentane, *n*-pentane, methane, and ethane. Neither olefins nor neopentane were detected. Methane and ethane were detected only during the initial periods of reaction. The molar ratio of propane to pentanes was always nearly equal to one for a range of space velocities (Fig. 2), temperatures (70–143°C), and times on stream (Fig. 3).

Conversions of *n*-butane to each of the products are shown as functions of inverse space velocity in Fig. 4. The data were obtained with a catalyst sample that had been partially deactivated by operating for about 5 hr—the deactivation rate had become so low as to be negligible. The nonlinearity of the curves in Fig. 4 for the disproportionation products suggests a phenomenon akin to autocatalysis, perhaps resulting from the buildup of cationic chain carriers; such behavior has been observed previously (*25*). The plot of conversion to isobutane vs inverse space velocity, on the other hand, is a straight line passing through the origin, indicating that differential conversions were observed for the isomerization reaction. For disproportionation, the results suggest that for values of inverse space velocity $<5 \times 10^5$ g · s · mol^{-1}, it is a good approximation to consider the conversions differential, but at higher values of inverse space velocity, the approximation is less good, the estimated rates being roughly 20% too low.

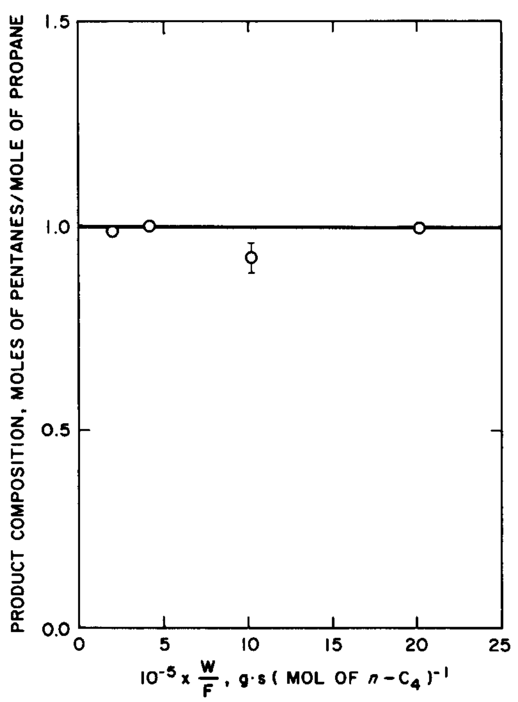


FIG. 2. Product distribution in *n*-butane conversion catalyzed by aluminum chloride/sulfonic acid resin: the dependence of the pentanes : propane ratio on inverse space velocity. T = 143°C; $P_{n\text{-}C_4}$ = 0.37 atm; P_{HCl} = 0.05 atm.

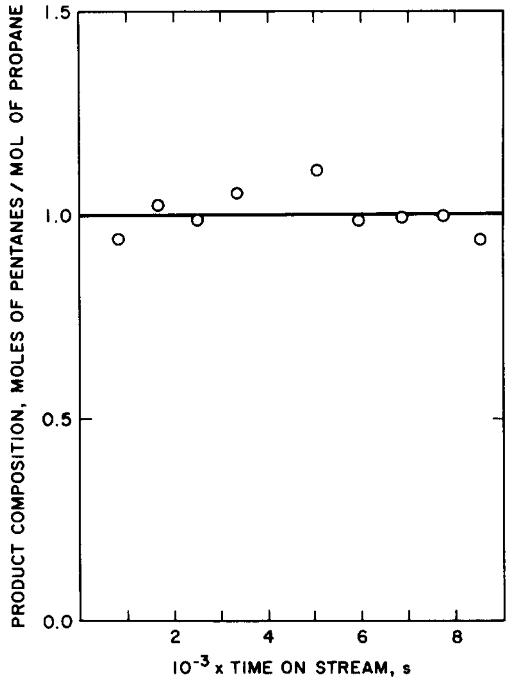


FIG. 3. Production distribution in *n*-butane conversion in a flow reactor: time dependence of the pentanes : propane ratio. T = 100°C; $P_{n\text{-}C_4}$ = 0.33 atm; P_{HCl} = 0.22 atm; $F/W = 1.87 \times 10^{-6}$ mol n-$C_4 \cdot g^{-1} \cdot s^{-1}$.

Conversions of *n*-butane to the various products are shown in Fig. 5 as a function of time on stream in the flow reactor. The

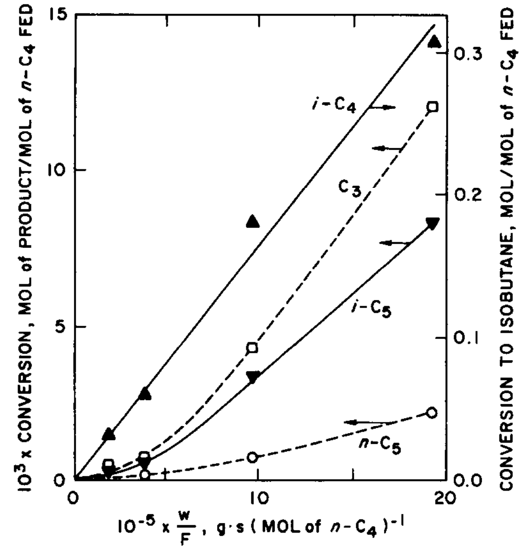


FIG. 4. Product formation in n-butane conversion: dependence on inverse space velocity (W/F). The catalyst was aged, and deactivation during the course of the experiments was negligible. T = 143°C; $P_{n\text{-}C_4}$ = 0.37 atm; P_{HCl} = 0.05 atm.

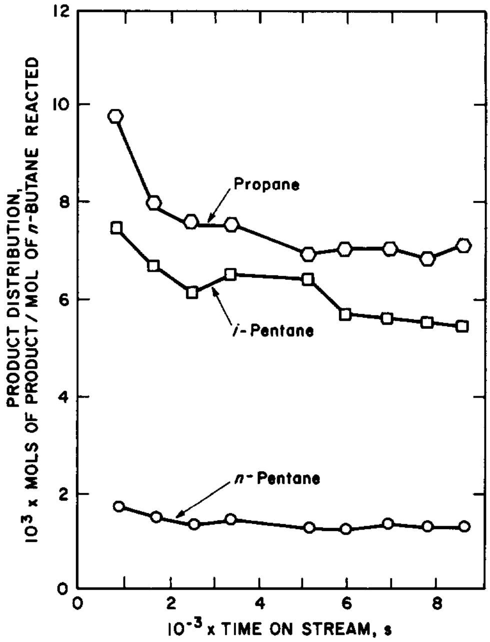


FIG. 5. Product distribution during n-butane conversion in a flow reactor. T = 100°C; $P_{n\text{-}C_4}$ = 0.33 atm; P_{HCl} = 0.22 atm; $F/W = 1.87 \times 10^{-6}$ mol n-$C_4 \cdot g^{-1} \cdot s^{-1}$.

decreasing conversions indicate the magnitude of the catalyst deactivation (*24*).

The rates of formation of these products at 100°C (approximated by assuming differential conversions—before and after introduction of HCl into the n-butane feed—are summarized in Table 1. The data indicate that the disproportionation rate increased

TABLE 1

Rates of Formation of Products during n-Butane Conversion at 100°C: The Effect of HCl in the Feed

10^{-4} × Time on stream (s)	10^{10} × Rate of product formation[a]					
	Methane	Ethane	Propane	Isobutane	Isopentane	n-Pentane
No HCl flow						
1.43	—	—	0.9	345	0.8	—
Start of HCl flow						
1.52						
1.53	6.2	1.6	11.6	2350	5.8	1.4
1.66	3.8	—	22.2	2917	20.0	4.2
1.76	2.2	—	21.5	2800	18.5	Trace

[a] The conversions to disproportionation products were approximately differential; the data in this table are average rates calculated by dividing the conversion by the inverse space velocity. The average rates are given in units of moles of product/(g of catalyst · s). The catalytic activity was not constant, as indicated by the time dependence of the average rates. Before introduction of HCl, the value of $P_{n\text{-}C_4}$ was 0.41 atm. After introduction of HCl: $P_{n\text{-}C_4}$ = 0.32 atm; P_{HCl} = 0.22 atm. $F/W = 1.98 \times 10^{-6}$ mol of n-C_4/(g of catalyst · s).

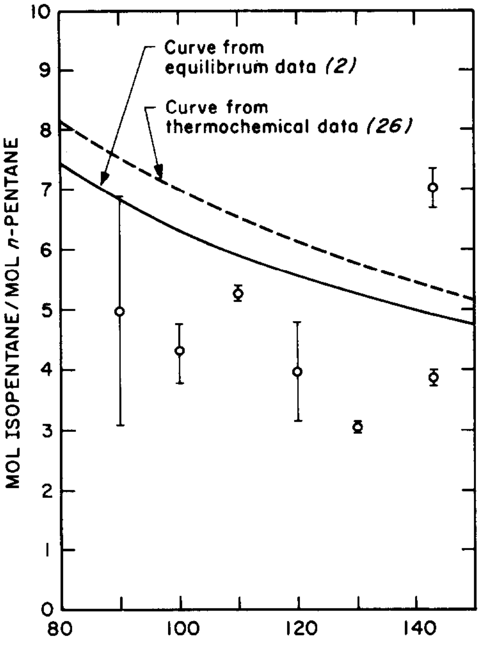


FIG. 6. *n*-Butane conversion catalyzed by aluminum chloride/sulfonic acid resin: observed and calculated equilibrium *i*- to *n*-pentane molar ratios. Reaction conditions varied widely.

about 24 times upon introduction of HCl into the feed, whereas the increase in the isomerization rate was less than tenfold (*9*).

The observed *i*- to *n*-pentane ratios are compared in Fig. 6 with values calculated from equilibrium data. Each experimental point is the mean of all the results (at all conversions) at a particular temperature. The results show that the iso to normal ratios are less than the equilibrium values [although one relatively unreliable point (measured at a very low conversion) appears to contradict the pattern].

Conversion of n-Pentane

The observed products of the *n*-pentane conversion were isopentane, isobutane, propane, *n*-butane, all the hexane isomers, and traces of methane and ethane. No olefins were observed. Table 2 is a summary of the estimated rates of formation of the products in the range 70 to 140°C. Since deactivation of the catalyst was rapid (even with HCl in the feed), the rates are only rough (order-of-magnitude) estimates; the quantitative product distributions, however, are indicated by the data of Table 2.

The *n*-pentane disproportionation, in contrast to the *n*-butane disproportionation, was not stoichiometrically simple. The molar ratio of butanes to hexanes was roughly

TABLE 2

Approximate Rates of Formation of Products during *n*-Pentane Conversion

Temperature (°C)	10^{10} × Rate of product formation[a]								
	Propane	Isobutane	*n*-Butane	Isopentane	2,2-DMB[b]	2,3-DMB[b]	2-MP[c]	3-MP[c]	*n*-Hexane
70	4.9	220	1.6	177	2.4	7.2	18.3	8.3	0.8
80	4.8	133	1.3	128	0.8	4.3	12.6	6.3	—
100	5.8	93	1.4	101	—	3.3	9.3	4.5	—
140	19.8	167	7.0	180	—	5.0	15.0	7.8	2.7

[a] Data are approximate because the catalyst was undergoing deactivation. The catalyst had been used for 7 hr for *n*-butane conversion and lost roughly half of its initial activity at the start of these experiments. The catalyst continued to lose activity at unknown rates during the sequence of *n*-pentane conversion experiments, which proceeded from the lowest temperature to the highest. Rates are average values determined by dividing conversion by inverse space velocity. The units of rate are moles of product/(g of catalyst · s). $P_{n\text{-}C_5} = 0.25$ atm; $P_{HCl} = 0.11$ atm. $F/W = 1.60 \times 10^{-6}$ mol of *n*-pentane/(g of catalyst · s).

[b] DMB = dimethylbutane.

[c] MP = methylpentane.

TABLE 3

Distributions of Butane and Hexane Isomers Formed during *n*-Pentane Conversion[a]

Temp (°C)	Product ratio											
	Isobutane / *n*-Butane		2,2-Dimethylbutane / Total hexanes		2,3-Dimethylbutane / Total hexanes		2-Methylpentane / Total hexanes		3-Methylpentane / Total hexanes		*n*-Hexane / Total hexanes	
	Obsd	Equil.[b]	Obsd	Equil.[c]	Obsd	Equil.[c]	Obsd	Equil.[c]	Obsd	Equil.[c]	Obsd	Equil.[c]
70	136	3.5	0.1	0.7	0.2	0.1	0.5	0.1	0.2	0.1	0.002	0.02
80	104	3.3	0.03	0.7	0.2	0.1	0.5	0.1	0.3	0.1	—	—
100	64.5	2.7	—	—	0.2	0.1	0.5	0.1	0.3	0.1	—	—
140	23.7	2.0	—	—	0.2	0.1	0.5	0.2	0.3	0.1	0.09	0.08

[a] Reaction conditions are given in Table 2.

[b] Equilibrium ratios for C_4 are vapor-phase values calculated from data in Ref. (*2*).

[c] Equilibrium ratios for C_6 are vapor-phase values calculated from data in Ref. (*26*).

5 : 1, a result accounted for by the susceptibility of hexanes to extensive β-scission. The observed isomer distributions are collected in Table 3, and the calculated equilibrium values (*27*) are shown for comparison. Most of the product ratios shown in the table are different from those at equilibrium; for example, the *i*- to *n*-butane ratio are greater than the equilibrium values.

DISCUSSION

Product Distributions

Most noteworthy is the result that the disproportionation of *n*-butane takes place as a stoichiometrically simple reaction:

$$2\ C_4H_{10} \rightarrow C_3H_8 + C_5H_{12}. \qquad (1)$$

In previous studies, products of acid-catalyzed paraffin disproportionation have been observed in nonstoichiometric ratios, usually with preferential formation of the low-molecular-weight products.

The data of Ono *et al.* (*16*), however, indicate that in *n*-pentane conversion catalyzed by aluminum chloride–metal chloride mixtures suspended in liquid reactant, a stoichiometric disproportionation to hexanes and isobutane occurred with some of the catalysts. In the conversion of *n*-pentane vapors catalyzed by $AlCl_3$–$CuCl_2$, disproportionation products formed preferentially, isobutane being the predominant product. The present results for *n*-pentane conversion follow the generally observed pattern, the lower-molecular-weight products like propane and isobutane being more abundant than the higher-molecular-weight products. The formation of all the hexane isomers, however, had not been reported before.

As shown in Fig. 6, the *i*- to *n*-pentane ratios observed in the *n*-butane conversion were consistently less than the calculated equilibrium ratios. This pattern appears to be general. The data of Tanabe and Hattori (*6*) similarly show less-than-equilibrium *i*- to *n*-pentane ratios for both *n*-butane and isobutane conversion at 20°C in the presence of various solid superacids. One of their results obtained at <5% conversion even shows an *i*- to *n*-pentane ratio less than one. In the isobutane (*19*) and *n*-butane (*20*) conversions catalyzed by H-ZSM-4, the *i*- to *n*-pentane ratios were also less than the calculated equilibrium values. This pattern remains to be explained, since the classical alkylation–β-scission mechanism for disproportionation (Fig. 1) leads to the preferential formation of branched hydrocarbons. The data might be interpreted as suggesting the importance of the simple

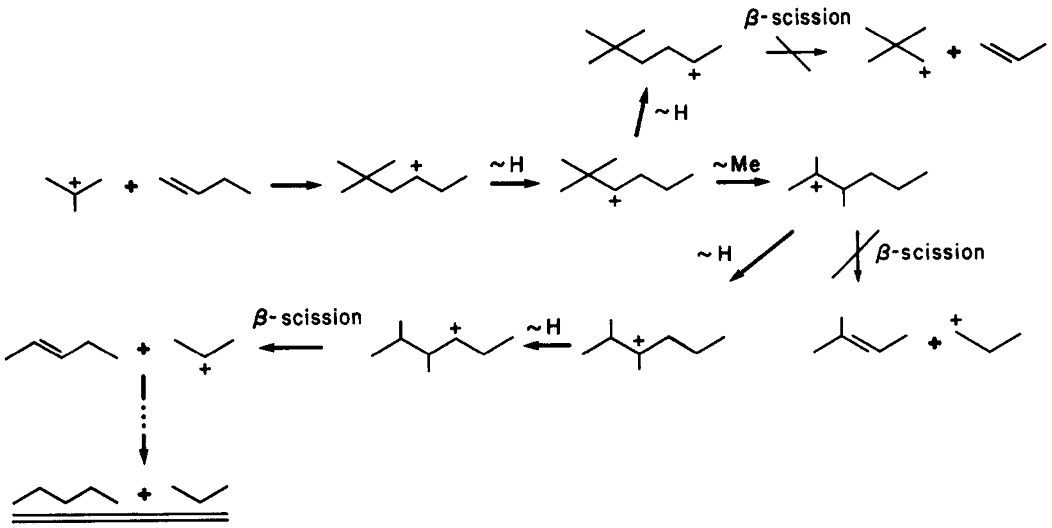


FIG. 7. Disproportionation reaction pathways proceeding via the reaction of *t*-butyl cation with 1-butene.

pathway shown in Fig. 7 (giving *n*-pentane) in comparison with the more complex pathways shown in Fig. 8 (ultimately giving *i*-pentane and *n*-pentane), but this suggestion is speculative.

In the conversion of *n*-pentane, in contrast to the conversion of *n*-butane, the branched products (e.g., isobutane) were formed preferentially (Table 3). This pattern is consistent with the classical disproportionation mechanism shown in Fig. 1.

Catalyst Deactivation

The observation of a higher deactivation rate for *n*-pentane than for *n*-butane conversion is in agreement with industrial experience (*28*, *29*). Deactivation of metal halide catalysts during hydrocarbon conversion has been ascribed to cyclic hydrocarbons, usually those containing five-membered rings and conjugated double bonds (*2*). Formation of such Lewis bases from C_4 and C_5

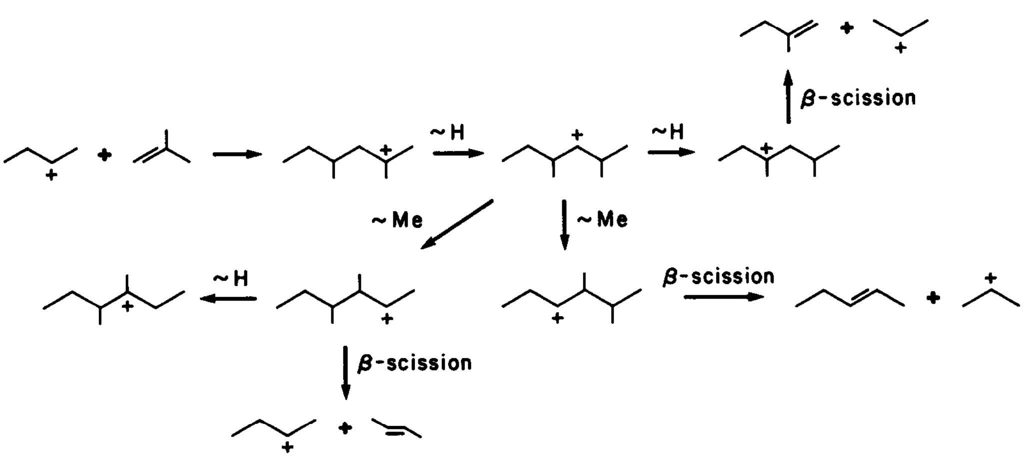
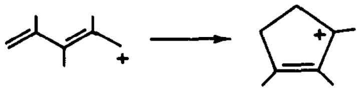
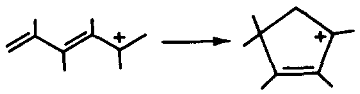


FIG. 8. Disproportionation reaction pathway proceeding via the reaction of *s*-butyl cation with isobutene.

hydrocarbons proceeds through alkylation products. For C_4 conversion, we may explain the ring formation in terms of Pines's mechanism of "conjunct polymerization" of olefins (*2*), which proceeds through a primary carbenium ion:


(2)

The higher rate of catalyst deactivation accompanying C_{5+} hydrocarbon conversion might be explained by the formation of alkylation products which undergo the cyclization via secondary, not primary, carbenium ions:


(3)

Reaction Pathways

The reaction pathways occurring during paraffin conversion are summarized in Fig. 9. The predominant pathways depend on the reaction conditions and the number of carbon atoms in the reaction, and the product distributions are usually complex.

An advantage of *n*-butane as a model reactant is the simplicity of the product distribution that can be obtained. With this reactant under relatively mild conditions, only pathways I, III, and IV are significant. Under the conditions of this work, the isomerization pathway (I) predominates, and increased severity leads to increased rates of disproportionation and deactivation of the catalyst (*24*).

In the conversion of *n*-pentane, C_5 carbenium ions form, and these react readily according to the scheme of Fig. 9, the important restriction being that pathway II is virtually excluded because it would require formation of a highly unstable primary carbenium ion. With C_6 and higher-molecular-weight paraffins, this restriction is lifted, and highly complex product distributions are the rule.

The effect of olefins in the reactant is expected to be an increase in the rate of disproportionation and catalyst deactivation relative to isomerization, and this expectation is confirmed by experimental results (*11*, *25*). Benzene and H_2 are effective in suppressing the reactions accompanying isomerization of lower-molecular-weight paraffins, but they are ineffective in C_{7+} conversion, since pathways II and VII occur via facile unimolecular steps.

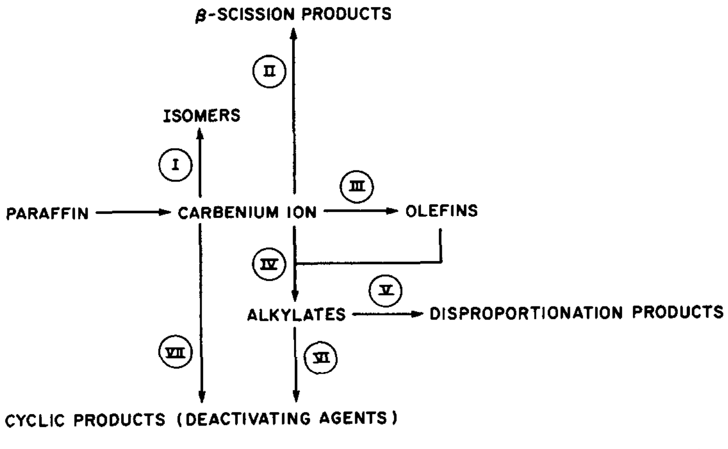


FIG. 9. Schematic representation of reaction pathways in paraffin conversion catalyzed by strong acids.

ACKNOWLEDGMENTS

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