

# The Role of Bimolecular Mechanism in the Skeletal Isomerisation of *n*-Butene to Isobutene

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Several methods were used to evaluate the potential role of bimolecular mechanism in skeletal isomerisation of *n*-butene to isobutene. Dimers of *n*-butene were prepared and their reaction monitored. Product distributions of these reactions were compared with those obtained with *n*-butene. Comparison was performed with different catalysts at 1 bar total pressure in an apparatus which makes both continuous flow and pulse experiments possible. Compositions of products of the reactions of *n*-butene and of dimers were found to be very different on catalysts selective to isobutene. On highly acidic catalysts, which form isobutene nonselectively and show a high formation of by-products ( $C_3^-$  and  $C_5^-$ ), distributions were similar. Skeletal isomerisation is *suppressed* by a higher pressure of butene while the rate of formation of by-products *increases* with increasing pressure. Optimum temperatures of dimerisation and of skeletal isomerisation differ considerably. All these results indicate that bimolecular mechanism is responsible mainly for the by-products. It is concluded that the skeletal isomerisation of *n*-butene to isobutene runs via a monomolecular mechanism whereas the by-products are formed by cracking of dimers of *n*-butene. Another source of the by-products seems to be dimers arising from isobutene, the latter being first formed by a monomolecular skeletal isomerisation of *n*-butene. The formation of by-products is suppressed when 10-membered ring zeolite is used as a catalyst. © 1996 Academic Press, Inc.

## I. INTRODUCTION

Since isobutene is very suitable raw material for the production of the much demanded octane booster methyl tertiary butyl ether, the skeletal isomerisation of *n*-butene to isobutene enjoys increasing popularity. A selection of recent papers and patents documents this clearly (1–10). This reaction is interesting also from the point of view of the fundamental theory of catalysis. According to conclusions made some time ago (11), the  $C_4$ -hydrocarbons should not isomerise skeletally at all, since upon a “monomolecular” isomerisation, a primary carbenium ion formation is unavoidable. The primary ion is generally considered to be so unstable that an appreciable yield of  $C_4$ -skeletal isomerisation is very doubtful. When catalysts were discov-

ered [see e.g. Ref. (3)] which can induce this isomerisation, the authors suggested that the isomerisation observed is a multistep process: butene  $\rightarrow$  octene(s)  $\rightarrow$  isomerisation of octene(s)  $\rightarrow$  cracking octene  $\rightarrow$  isobutene. This “bimolecular” mechanism can operate throughout with secondary and tertiary carbenium ions.

The problem of which mechanism is prevailing, or solely operating, during the skeletal isomerisation is by no means only a matter of academic interest. The catalysts known at the moment are not yet optimal and, for example, a decrease in the temperature of their operation is very desirable. A further improvement of the catalyst requires some knowledge of the active centers. The question is then: Should the active centers allow a faster dimerisation, because this is the main way to isobutene, or should this way be suppressed, because dimerisation induces side reactions to propene and pentenes, hydrogen redistribution reactions, and formation of carbonaceous deposits? Therefore the idea of the “bimolecular” mechanism has been tested by investigations reported in this paper.

If the bimolecular mechanism is to be the prevailing one in formation of isobutene, several conditions have to be fulfilled:

- (1) dimerisation of *n*-butene must be possible and must occur at a sufficient extent also at the temperature of reaction;
- (2) the product distribution obtained from *n*-butene reaction on the one side and from any of the octenes [primary dimers of *n*-butene (3,4-dimethyl-2-hexene or 3,4-dimethyl-1-hexene) (and further 3,4-dimethyl-2(1)-hexene), 5-methyl-3(2)-heptene, 3(2)-octene] should show a great similarity;
- (3) octenes produced by primary dimerisation of *n*-butene have to undergo a fast isomerisation, or otherwise they would not yield isobutene by cracking.

Preliminary experiments (5) performed with halogenated aluminas threw serious doubts on the possible universality of the bimolecular mechanism and results of research presented below strengthen the doubts.

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## II. EXPERIMENTAL

### A. Catalytic Measurements

The reaction was followed in continuous flow with a fixed bed reactor, at the pressure of 1 bar. Temperature was measured by a thermocouple situated very close to the catalyst. Under standard reaction conditions the total flow through the system was 20 ml/min. The flow was controlled by thermal mass flow controllers (Bronkhorst NL). When experiments with *n*-butene and isobutene were performed, the mixture of these gases (5% of hydrocarbons) with nitrogen was used. One gram of catalyst was used in each experiment. Two ways were used to introduce liquid reactants into the reactor: (i) in the case of the experiments with octenes and butanols, nitrogen was saturated by saturated vapours of these compounds at 295 K, and (ii) liquid octenes, octanols, and butanols (10  $\mu$ l) were injected directly into the reactor. No difference in the product distributions of reactants was observed when using these two ways. Nitrogen was dried by molecular sieve A.

Products were analysed by a gas chromatograph (HP 5890) equipped with a flame ionisation detector and a column filled with KCl-treated alumina (length, 50 m; diameter, 0.53 mm).

The temperature-programmed gas chromatography, used for analysis of products of dimerisation of butenes, started at 373 K and temperature was increased at 3.5 K/min for 23 minutes, then at 1.5 K/min up to 473 K, and finally it was kept constant. For *n*-butene dimerisation experiments, the partial pressure of *n*-butene in nitrogen was 60 kPa and the flow used was 15 ml/min. Dimerisation of isobutene is much easier than that of *n*-butene so the partial pressure of isobutene in nitrogen used was only 5 kPa and the flow was 22 ml/min. Peaks of octenes appeared in chromatographic record between the 28th and 36th minute. Table 1 shows the retention times of different octenes.

TABLE 1  
Octenes Identified by Chromatography

Octene	Retention time [min]	Octene	Retention time [min]
2,4,4-Trimethyl-2-pentene	28.11	Methylheptene	32.13
2,3,4-Trimethyl-2-pentene	28.75	Methylheptene	32.30
3,4-Dimethyl-2-hexene	29.28	Methylheptene	32.43
3,4-Dimethyl-2-hexene	29.57	Methylheptene	33.09
Methylheptene	29.63	3-Octene + methylheptene	33.53
2,3,4-Trimethyl-1-pentene	30.65	3-Octene	34.05
Methylheptene	31.10	Methylheptene	34.37
3,4,4-Trimethyl-1-pentene	31.77	2-Octene	35.24
2,4,4-Trimethyl-1-pentene	31.92	2-Octene	35.94

Identification of products of dimerisation was performed by an addition of different individual octenes to the products in the effluent. This was done for the reactions in the temperature range 370–420 K. At higher temperatures secondary isomerisations occur. The number of various products from the reaction of octenes at the reaction temperature of skeletal isomerisation of *n*-butene is so high that the quantitative determination and identification of individual products was impossible.

### B. Evaluation of Data

The data evaluation was performed as in Ref. (5). The relative concentration of any compound in an effluent was defined by Eq. [1]. This concentration can be taken as a measure of the activity and selectivity. The sum in the denominator comprises all gases detected by GC, whereas  $N_i$  stands for the integrated GC-signal due to the compound "*i*":

$$C_i = \left[ N_i / \sum N_i \right] \times 100\%. \quad [1]$$

In this way, the balance is expressed in terms of carbon atoms.

The main by-products are propene and pentenes. The composition of the butene mixture in the effluent reaches mostly the thermodynamic value. The difference between all catalysts used, or with a given catalyst between various reactants, manifests itself mainly by the amount of by-products in the effluent. Therefore, the ratio  $(C_3^- + C_5^-)/C_4^-$  is used below to compare product patterns of different reactants.

On all catalysts used, there is always a thermodynamic equilibrium reached among all linear butenes at temperature at which skeletal isomerisation sets in. The product distribution does not differ when we start from any of butenes or from their mixture. Under this condition, the conversion of *n*-butenes can be conveniently defined by Eq. [2]:

$$X = \left[ \sum N_{i(i \neq \text{linear butenes})} / \sum N_i \right] \times 100\%. \quad [2]$$

The sum in the denominator comprises all compounds detected, whilst that in the numerator is over all products except linear butenes.

### C. Catalyst Preparation

H<sub>3</sub>PO<sub>4</sub>/SiO<sub>2</sub> catalyst was prepared as described in Ref. (15). Aerosil 200 was boiled with an amount of diluted phosphoric acid such that the final catalysts contained 65 wt% of P<sub>2</sub>O<sub>5</sub>. Water was slowly evaporated and the catalyst was calcined in oxygen at 773 K for 16 h. The relative concentration of isobutene obtained with this catalyst (used for skeletal isomerisation of *n*-butene) was always higher than 35%. Halogenated aluminas were prepared as in Ref. (5). Fluorinated alumina was prepared by a treatment of  $\gamma$ -alumina (Akzo) with trifluoroacetic acid (Janssen

Chimica, 99%, added to the feed as a saturated vapour at 295 K) for 30 min at 623 K. Chlorinated alumina was prepared by the treatment of  $\gamma$ -alumina by saturated vapour (295 K) of butylchloride (Baker, 99%) for 1 h at 623 K. Molecular sieves SAPO 11 and MnAPO 11 were kindly supplied by Professor J. H. C. van Hooff, TU Eindhoven. Borosilicate B-ZSM-5 was synthesized by R. Klik, UFCH, Czech Academy of Sciences, Prague. This borosilicate contained 300 ppm of aluminum in the framework.

#### D. Reactants

The following gases were used as reactants: 1-butene (AGA GAS BV, 99.4%), *cis*-2-butene (Fluka, 99%), and isobutene (Messer Griesheim, 99%). The octenes and octanols used were 2,4,4-trimethyl-1-pentene (2,4,4-TMP, Merck, 99%), 2,3,4-trimethyl-2-pentene (2,3,4-TMP, Aldrich, 98%), 1-octene (Janssen Chimica, 98%), 3-octanol, and 5-methylheptan-3-ol. 3,4-Dimethyl-2-hexene (DMH) was synthesized by a Wittig reaction. This compound was purified by GC and the purity achieved (gas chromatograph) was 98%. The structure was checked by NMR. Methylheptenes and *n*-octenes were prepared from alcohols by distillation from the solution with phosphoric acid. 3-Octanol (Aldrich, 99%) reacted under these conditions to the mixture of 3-octene and 2-octene. The mixture contained 5% of undesired products, i.e., the more branched octenes. 5-Methylheptan-3-ol was prepared from 5-methylhept-3-one (Aldrich, 97%) by reaction with  $\text{NaBH}_4$ . The structure of the product was checked by NMR. Reaction of 5-methylheptan-3-ol with phosphoric acid is less selective. It yields four main compounds (probably 5-methyl-3(2)-heptenes, 76%) and four other octenes in smaller amounts.

### III. RESULTS

#### A. Product Composition as a Function of Pressure

If skeletal isomerisation of *n*-butene runs by a bimolecular mechanism one can expect that a higher partial pressure of butene would lead to a faster formation of octenes and thus to a faster isomerisation. The dependence of the product distribution on the partial pressure of *n*-butene has therefore been determined with chlorinated alumina as a catalyst. Partial pressures of 3.4 and 41 kPa were used, respectively. The total flow was in both cases 20 ml/min. To eliminate the problem of deactivation of the catalyst, the pressure was repeatedly switched from 3.4 to 41 kPa and back during the measurement.

The results are shown in Fig. 1a. A higher pressure of *n*-butene leads to a decrease of relative concentration of isobutene among products. Contrary to this, the amount of by-products (propene, pentenes, and isobutane) increases significantly with increasing pressure (Fig. 1b).

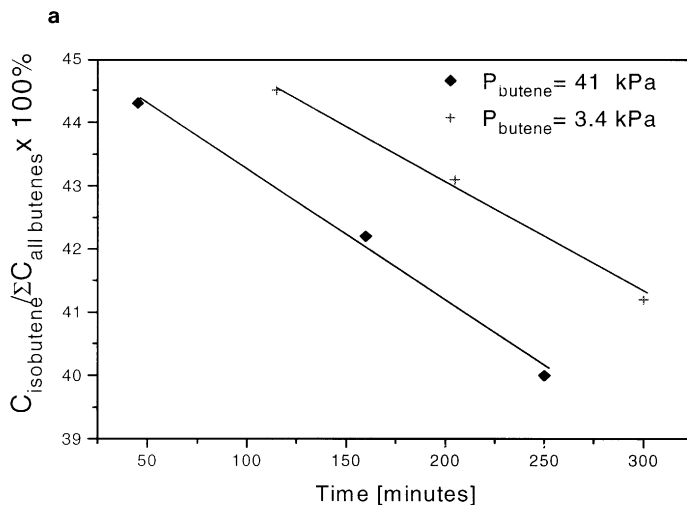


FIG. 1a. Isomerisation of *n*-butene. The influence of partial pressure of *n*-butene on the relative concentration of isobutene. Catalyst: 1 g of chlorinated alumina.  $T = 623 \text{ K}$ . Flow 20 ml/min. Both the relative concentration of isobutene and the conversion decrease with time on stream due to self-poisoning. Conversion of *n*-butene (*n*-butene pressure 3.4 kPa) after 205 min on stream (45.4%) is almost identical with the conversion (*n*-butene pressure 41 kPa) after 250 min (44.7%).

#### B. Dependence of the Catalyst Activity on Temperature

The maximum possible selectivity to isobutene is of course limited by thermodynamics. The exact value of the equilibrium content of isobutene amongst all butenes is, however, also important for the discussion on the prevailing mechanism. Several authors used in their discussion of results somewhat obsolete equilibrium data, with apparently lower values for isobutene, and when a higher value was observed experimentally (4, 5), the logical conclusion was made that the bimolecular mechanism was responsible for the values higher than the "thermodynamic" ones, due

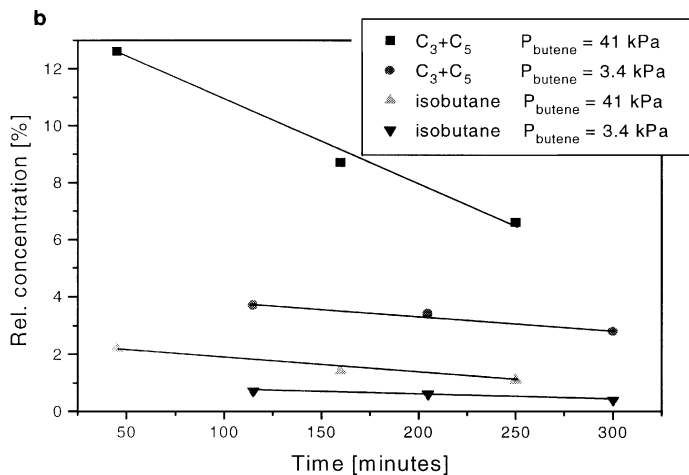


FIG. 1b. The influence of partial pressure of *n*-butene on the formation of by-products. 1 g of chlorinated alumina.  $T = 623 \text{ K}$ . Flow 20 ml/min. Relative concentration as a function of the time on stream.

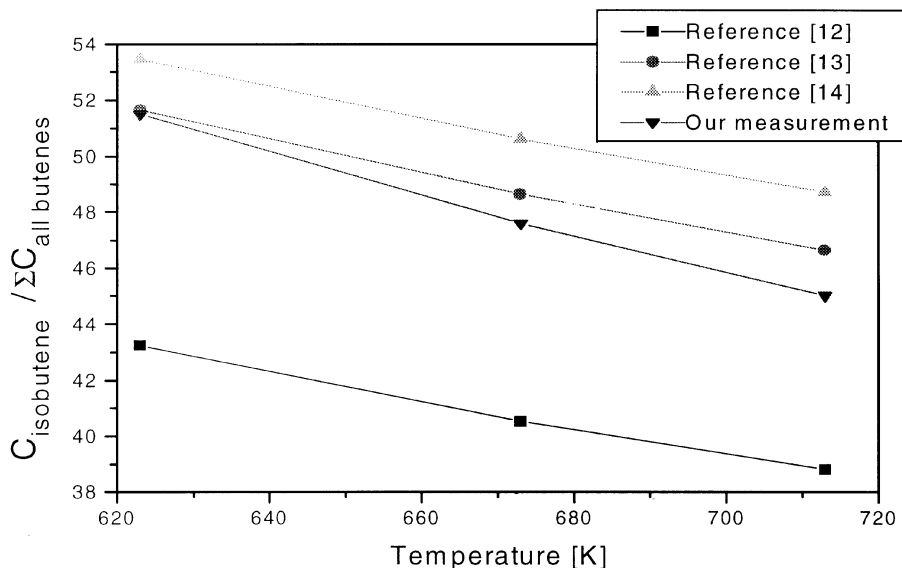


FIG. 2. Equilibrium composition of the mixture of butenes according to different authors. Our measurements are an average of the values measured with different reactants.

to the approaching of the equilibrium “from the other side.” However, the most recent and more reliable data (13, 14) show higher equilibrium values for isobutene; values which in reality have not been exceeded in the previous experiments (4, 5).

It was not our intention to establish a new set of thermodynamic data. We have merely checked the steady-state values obtained with the reaction of following reactants: *n*-butene, isobutene, 3,4-dimethyl-2-hexene, and a mixture of methylheptenes. The average values obtained between 623 and 713 K with the most active catalysts used (SAPO 11, MnAPO 11, H<sub>3</sub>PO<sub>4</sub>/SiO<sub>2</sub>) are shown in Fig. 2 together with the data from the literature (12–14).

The composition of the individual products approached the thermodynamic equilibrium and the best agreement was observed with the data collected by the National Bureau of Standards (13). In no case, with any catalyst studied here, were these (13) thermodynamic values surpassed in catalytic experiments. Thus, the maximum selectivities obtained do not bring about the necessity to postulate the bimolecular mechanism.

The steady-state *trans*-2-butene/*cis*-2-butene ratio has been determined in a total of 280 measurements on different catalysts (phosphoric acid on SiO<sub>2</sub>, TiO<sub>2</sub>, MoO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, . . . , SAPO 11, MeAPO's 11, alumina) and with different reactants in the feed (*n*-butene, isobutene, butanols, octenes, octanols) at 713 K. Activities of the catalysts used were very different (relative concentration of isobutene was 3–42%), but the *trans/cis* ratio value was 1.35 ± 0.01. However, this value does not agree with any published data (12–14), which vary between 1.38 and 1.45.

The extent of dimerisation also depends on temperature. Thermodynamic data for octenes are scarce, but some cal-

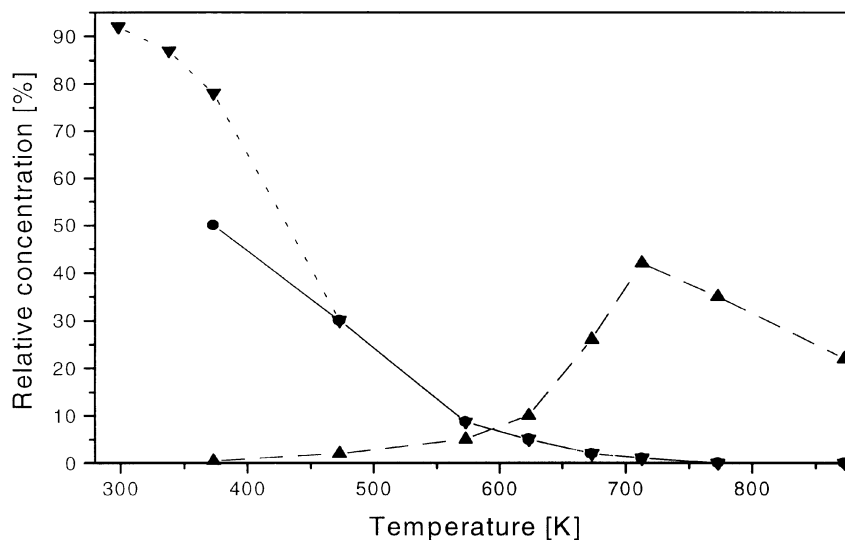
culations have already been made. For example, Szabo (3) calculated the equilibrium between *n*-butene and *n*-octene and established that the amount of dimers at equilibrium decreases strongly with increasing temperature.

It has been found here that the dimerisation of isobutene is an easy reaction at low temperatures, contrary to the dimerisation of *n*-butene. We monitored the formation of dimers as a function of temperature on the H<sub>3</sub>PO<sub>4</sub>/SiO<sub>2</sub> catalyst. The result is shown in Fig. 3. The relative concentration of dimers (mostly 2,4,4-trimethylpentenes and 2,3,4-trimethylpentenes) in the gas phase was 51% at 373 K. Measurements at low temperature were complicated by the fact that the boiling point of trimethylpentenes is about 400 K so they condensed in the reactor during the experiment. However, a rough estimate of dimerisation extent can be made by the assumption that all carbon atoms “missing” in a GC signal compared to a blank experiment are dimers remaining in the reactor.

Obviously, dimerisation is strongly suppressed at high temperature. It should be noted that the temperature range at which skeletal isomerisation occurs on H<sub>3</sub>PO<sub>4</sub>/SiO<sub>2</sub> catalysts is above 670 K. As maximum, only about 1% of octenes are formed at this temperature, under the reaction conditions used for skeletal isomerisation of *n*-butene.

### C. A Comparison of the Product Distributions of the Reactions of Butenes and Octenes

Only a few octenes can be formed from *n*-butene by one-step dimerisation; 3,4-dimethyl-1(2) hexene, 5-methyl-3(2)-heptene can arise by dimerisation via a carbenium ion while 3-methyl-2(1) heptene, 3(2)-octene, as well as the above-mentioned two octenes, can be formed by dimerisation via a coordinative insertion mechanism (16). However, 2,4,



**FIG. 3.** A comparison of isobutene dimerisation with skeletal isomerisation of *n*-butene. 1 g of  $\text{H}_3\text{PO}_4/\text{SiO}_2$  used as the catalyst. 5% of isobutene in nitrogen. Flow rate 20 ml/min. (●) Isobutene dimerised [%] (analysis of mixture in the loop of GC valve only). (▼) Isobutene dimerised [%] (analysis of mixture corrected by adding of the decrease of the number of carbon atoms detected by GC). (▲) Isobutene formed by isomerisation from *n*-butene [%].

4-trimethyl-1(2)-pentene is the only possible primary dimer of isobutene.

Mooiweer *et al.* (1) propose a bimolecular mechanism of isobutene formation from *n*-butene, through dimerisation to 3,4-dimethylhexene, subsequent isomerisation to 2,4-dimethylhexene, and cracking to one molecule of isobutene and one molecule of *n*-butene. The isomerisation step has to be fast. A logical consequence of the mechanism suggested is that if any of the mentioned octenes should be an intermediate in the skeletal isomerisation of *n*-butene, very similar product distribution patterns should be observed when under similar reaction conditions, either *n*-butene or its primary dimers are used as reactants in the feed.

All dimers which can be formed directly from *n*-butene were synthesized or purchased. Different catalysts were used to compare the product distributions in reactions of *n*-butene, isobutene, and the octenes. The most convenient conditions for skeletal isomerisation were always chosen to reach the maximum activity and selectivity of the catalyst. The main features (only) of the catalysts used are presented in Table 2.

To compare the product distribution of *n*-butene and the cracking pattern of different octenes, the ratio  $(C_3^- + C_5^-)/C_4^-$  ( $C_4^-$  stands for all butenes taken together) has been evaluated. Propene and pentenes are namely the main by-products of the skeletal isomerisation of *n*-butene. There is only a very small difference in the composition of butenes on various catalysts when different reactants are used (see above). However, the amount of by-products varies significantly with the catalyst used, so we consider this ratio as the most sensitive way to characterize the similarities (or differences) among the product distributions arising from various compounds in the feed.

Conversion of octenes was almost complete on all catalysts (close to the thermodynamic equilibrium with butenes). The  $\text{H}_3\text{PO}_4/\text{SiO}_2$  catalyst slowly deactivated during the experiment and a lower conversion could also be obtained (higher than 40%). No significant changes were observed in product distributions of octene reactions at high (fresh catalyst) or low (after self-poisoning by carbonaceous deposits) conversion with this catalyst.

The product distributions obtained showed that  $\text{H}_3\text{PO}_4/\text{SiO}_2$  is a selective catalyst. When *n*-butene is used as the reactant, the relative concentration of isobutene is here 35% and the total amount of by-products only 3%. Compared to this, any dimer of *n*-butene produces about 16% of isobutene and 50% of by-products (about equal amounts of propene and pentenes, see Fig. 4). There are large similarities among the product distributions of the *n*-butene, isobutene, and 2,4,4-trimethylpentene (2,4,4-

**TABLE 2**

**Catalysts Used to Compare Cracking Patterns of Octenes with the Product Distribution in the *n*-butene reaction (1 g of Catalyst)**

Catalyst	Reaction temperature [K]	Structure	Relative concentration of isobutene [%]
$\text{H}_3\text{PO}_4/\text{SiO}_2$	713	Crystalline phosphates	35
Chlorinated $\gamma$ -alumina	623	Amorphous	40
MnAPO 11	623	Molecular sieve	40
SAPO 11	713	Molecular sieve	35
Fluorinated $\gamma$ -alumina	623	Amorphous	25
Borosilicate ZSM-5	623	Zeolite	20

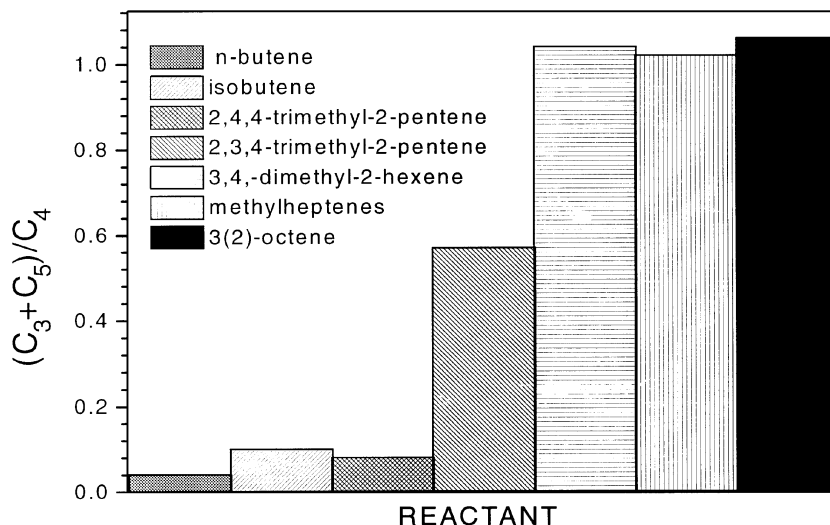


FIG. 4. Content of by-products in reaction of different reactants, on H<sub>3</sub>PO<sub>4</sub>/SiO<sub>2</sub> catalysts,  $T = 713$  K. 1 g of catalyst. Total flow 20 ml/min.

TMP) reactions. The low amount of by-products in the case of 2,4,4-TMP in comparison with other octenes shows that the *isomerisation* of TMP to other octenes and the following cracking of them to by-products is *not fast*. However, the situation is different when a strongly acidic, nonselective catalyst is used. The nonselective catalysts show a fast isomerisation of octenes. The formation of all octenes (among them the dimers of isobutene and *n*-butene) probably approaches the thermodynamic composition before cracking so that the product distributions arising from all reactants are rather similar (Fig. 5). Fluorinated alumina is a typical example of a nonselective catalyst (5). Let us mention here that alumina treated by trifluoroacetic acid contains strong

Brønsted acid sites which are expected to be responsible for “ionic” dimerisation and, consequently, for formation of by-products (5).

The results of experiments on MnAPO 11, SAPO 11, B-ZSM-5, and chlorinated alumina are shown in Figs. 6 and 7. When dimers of *n*-butene are cracked, a large amount of propene and pentenes is present on all catalysts used. In contrast to this, the number of by-products is low on selective catalysts when *n*-butene has reacted. There is a large difference between these two patterns.

Of particular interest is the reaction of 2,3,4-trimethyl-1-pentene (2,3,4-TMP). This compound occurs in significant concentrations among the dimers as a product of

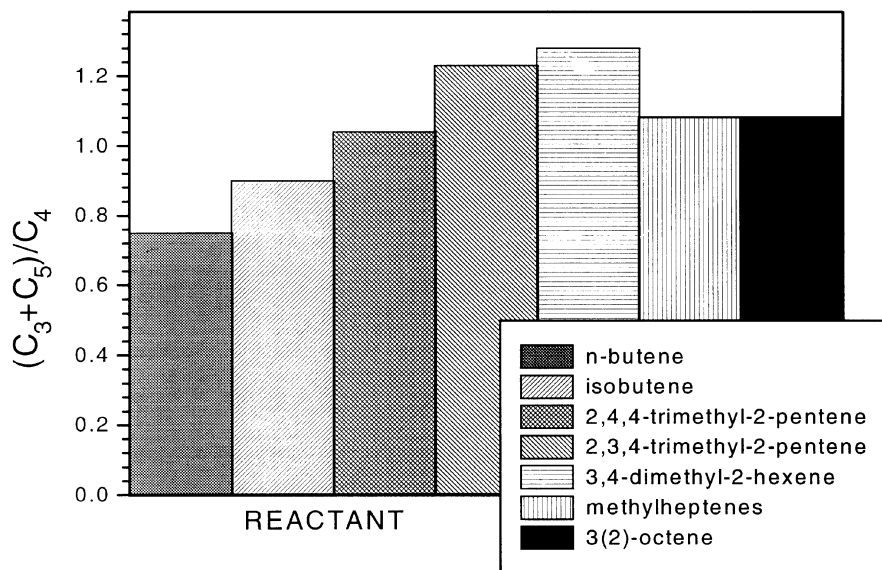


FIG. 5. Content of by-products in reaction of different reactants on fluorinated alumina.  $T = 623$  K. 1 g of catalyst.

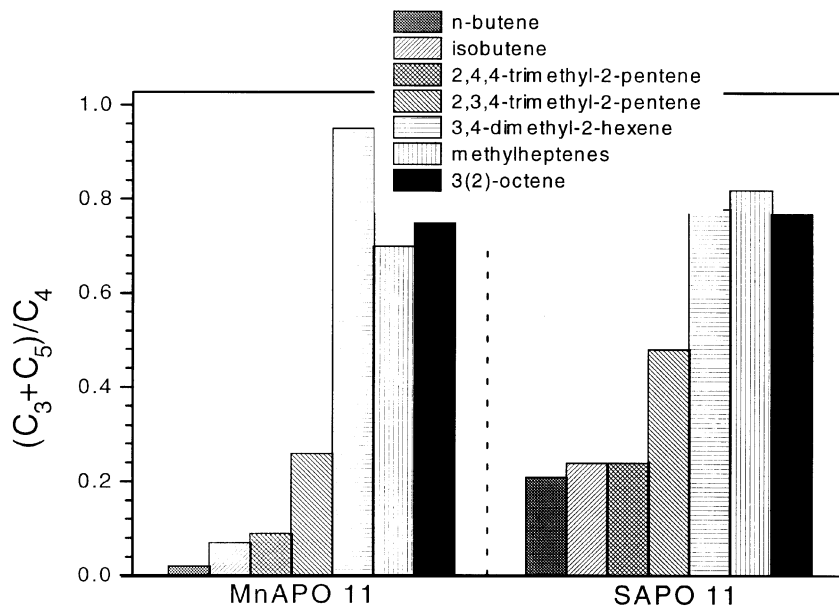


FIG. 6. Content of by-products in reaction of different reactants on MnAPO 11 and SAPO 11.  $T = 713$  K. 1g of catalyst.

isomerisation of 2,4,4-trimethylpentene (in its turn a dimer of isobutene). The ratio  $(C_3^- + C_5^-)/C_4^-$  in the reaction of 2,3,4-TMP lies in between the ratio for 2,4,4-TMP and that for the other octenes. This indicates that only a part of this compound is cracked to propene and pentenes, while the rest reacts first to 2,4,4-TMP before cracking. This is important for the selectivity of all catalysts, because 2,3,4-TMP is probably always present on nonzeolitic catalysts.

Reaction of isobutene and trimethylpentenes on B-ZSM-5 containing 300 ppm of alumina produces less by-products than the reaction of *n*-butene and its dimers. The

B-ZSM-5 used by us is a rather acidic catalyst so a higher amount of by-products can be expected with different reactants. The different behavior of this catalyst, compared to fluorinated alumina, is caused by the "shape selectivity" of the zeolite. The external surface of the zeolite is poisoned very quickly during reaction, so that the total number of acid sites and the acidity strength decrease (17). Diffusion of isobutene and highly branched trimethylpentenes into the 10-membered ring channels is very slow, and consequently the highly branched molecules react mostly on the outer surface, where the acidity of the catalyst on stream is

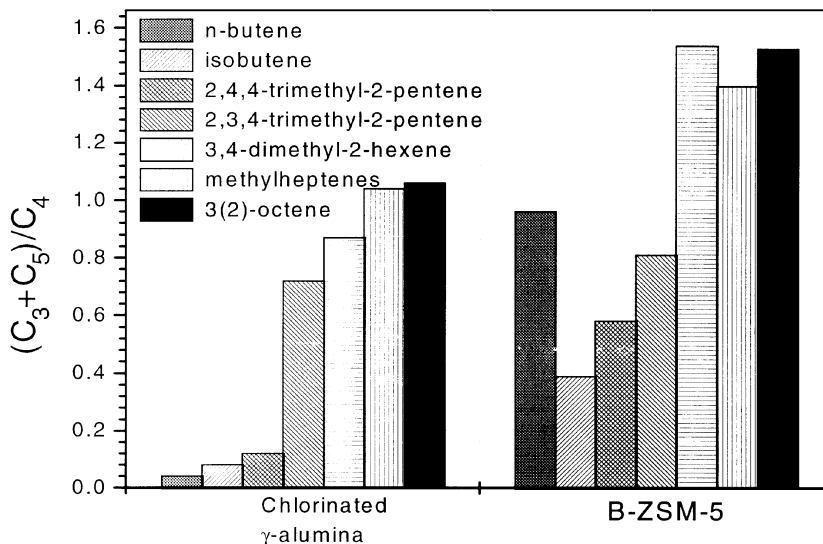


FIG. 7. Content of by-products of different reactants on chlorinated alumina and B-ZSM-5.  $T = 623$  K.

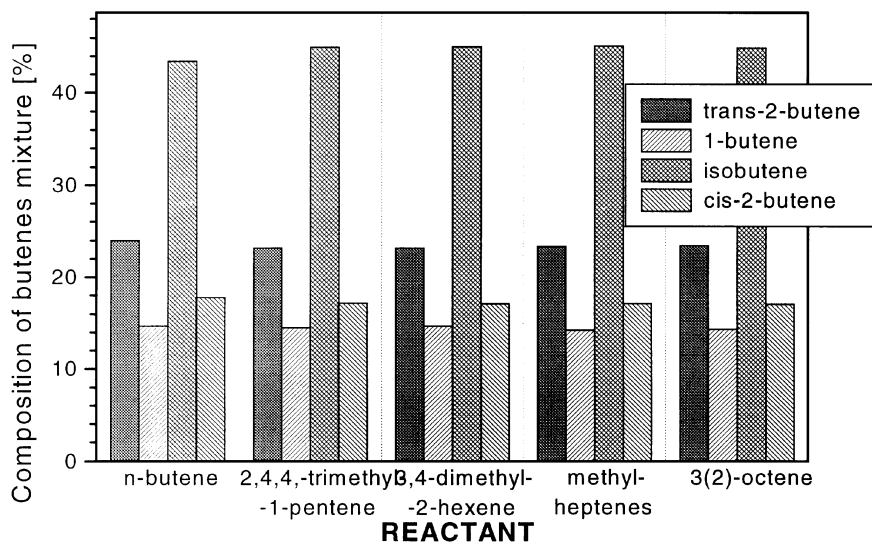


FIG. 8. Composition of butenes mixture with SAPO 11 as a catalyst at 713 K when different reactants are used (1 g of catalyst).

quickly lowered by self-poisoning and the overall reaction is then rather selective.

The maximum concentration of isobutene is limited by the thermodynamics. Some authors (4, 5) suppose that a bimolecular mechanism can help to escape this limitation. They suppose that *n*-butene dimerises and products of dimerisation isomerise fast to octene which is cracked to isobutene, producing a concentration of isobutene higher than the thermodynamic value. However, with any octene—dimer of *n*-butene—used here, we never observed that the concentration of isobutene was higher than the thermodynamic value from Ref. (13). When cracking of octenes is monitored, the distribution of butenes just approaches the thermodynamic composition but does not exceed it (Fig. 8). Only trimethylpentenes can indeed produce larger amounts of isobutene than the equilibrium values on the less active catalysts. Trimethylpentenes cannot be universal intermediates because their bulky molecules cannot be formed in a restricted space of some shape selective catalysts (see below).

#### D. Dimerisation

Analysis of catalytically formed dimers of *n*-butene and *cis*-2-butene was performed with the  $\text{H}_3\text{PO}_4/\text{SiO}_2$  catalyst. Products of dimerisation of *n*-butene are shown in Table 3a. Although the reactants in the feed were free of isobutene, the majority of the dimers are trimethylpentenes. This indicates strongly that a skeletal isomerisation of *n*-butene to isobutene occurs already at 373 K. Only one dimer of *n*-butene was detected and identified in a low concentration (0.09%), namely the 3,4-dimethyl-2-hexene (3,4-DMH). No linear octenes and no methylheptenes were found in significant amounts. Dimerisation of *n*-butene on  $\text{H}_3\text{PO}_4/\text{SiO}_2$  catalyst at 373 K is very slow.

The concentration of octenes depends on temperature, as can be seen in Fig. 9. It is influenced both by thermodynamic limitations and by secondary reactions (isomerisation to other octenes).

Significant amounts of trimethylpentenes were found when *n*-butene reacted. A reasonable explanation seems to be that skeletal isomerisation is present already at low temperature and that the subsequent dimerisation of isobutene is easy. To check this, we allowed isobutene to react on  $\text{H}_3\text{PO}_4/\text{SiO}_2$  catalyst, at 373 K. The composition of the products is shown in Table 3b. About 45% of isobutene reacts to its dimers at this temperature, in sharp contrast to *n*-butene.

The presence of large amounts of 2-methyl-2-butene, 2-methyl-1-butene, and hexenes is interesting (see the product pattern shown in Table 3b). Although the extent of the skeletal isomerisation of isobutene to linear butenes is low

TABLE 3a

Reaction of *n*-Butene (60 kPa in Nitrogen, Flow 15 ml/min) on  $\text{H}_3\text{PO}_4/\text{SiO}_2$  Catalyst at 373 K and on SAPO 11 at 423 K (1g of Catalyst)

	$\text{H}_3\text{PO}_4/\text{SiO}_2$ [%]	SAPO 11 [%]	Used SAPO 11 [%]
Linear butenes	98.7	98.4	99.8
2-Methyl-2(1)-butene	0.12	0.01	—
Other pentenes	—	—	—
2,3,4-TMP	0.71	0.13	0.008
2,4,4-TMP	0.21	0.17	—
3,4-DMH	0.09	0.08	0.013
Identified methylheptenes	—	0.36	0.076
3(2)-Octenes	—	—	—



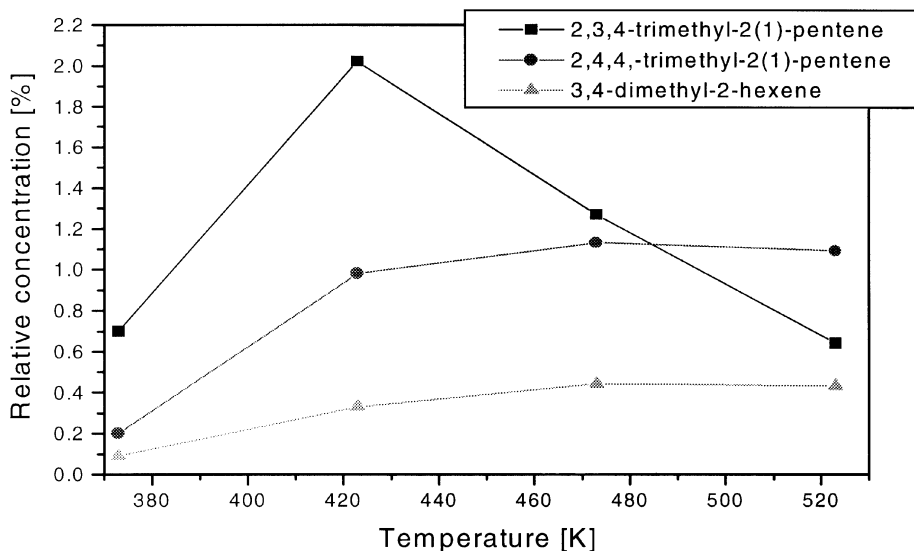


FIG. 9. Relative concentration of different octenes as a function of temperature. *n*-butene reaction on  $\text{H}_3\text{PO}_4/\text{SiO}_2$  catalyst. Flow 15 ml/min. Partial pressure of *n*-butene 60 kPa.

(0.87%), already about 8.7% of by-products are present. Only traces of other pentenes were found next to the two mentioned methylbutenes.

Reaction from isobutene to by-products is reversible. We reacted the mixture of propene (2 kPa) and 2-methyl-1-butene (10 kPa) in nitrogen on  $\text{H}_3\text{PO}_4/\text{SiO}_2$  catalyst at 423 K. Relative concentration of isobutene among products was 3.6% while only 0.03% of linear butenes were present. In particular, dimerisation of propene is easy under the conditions used; almost all propene present reacted to hexenes. All octenes identified during this reaction chromatographically were trimethylpentenes.

Dimerisation of isobutene on SAPO 11 was followed at 423 K. Except for temperature, the conditions used were the same as with  $\text{H}_3\text{PO}_4/\text{SiO}_2$  catalyst. The results are shown in

TABLE 3b

Reaction of Isobutene (5 kPa in Nitrogen, Flow 22 ml/min) on the  $\text{H}_3\text{PO}_4/\text{SiO}_2$  Catalyst at 373 K and on SAPO 11 at 423 K (1 g of Catalyst)

	$\text{H}_3\text{PO}_4/\text{SiO}_2$ [%]	SAPO 11 [%]	Used SAPO 11 [%]
Isobutene	43.2	89.6	97.0
Linear butenes	0.87	1.93	1.60
Propene	0.08	—	—
Hexenes	3.58	0.59	—
2-Methyl-1(2)butene	5.02	0.44	—
Other pentenes	—	—	—
2,3,4-TMP	15.3	2.23	0.29
2,4,4-TMP	29.4	3.78	1.02
Other products	Isobutane, octanes, 3,4,4-TMP	—	—

Table 3b. Next to a fresh sample, another sample of SAPO 11 was also used. The latter catalyst was first used in skeletal isomerisation of *n*-butene at 713 K (monitored before the dimerisation experiment at 423 K), so that the outer surface of the molecular sieve SAPO 11 was poisoned by carbonaceous layers deposited by the reaction at higher temperatures. This can be reasonably expected, since the sites on the open surface of the  $\text{H}_3\text{PO}_4/\text{SiO}_2$  catalyst also deactivated quickly (15).

The samples of SAPO 11 did not dimerise isobutene to trimethylpentenes. While about 45% of dimers (in the gas phase) were observed on  $\text{H}_3\text{PO}_4/\text{SiO}_2$ , only 6.9% were observed on fresh SAPO 11, and only 1.2% were observed in the effluent with the “used” SAPO 11 in the reactor. However, there is almost no difference in the relative concentration of isobutene in the effluent when a fresh and used SAPO 11 catalysts are used for skeletal isomerisation of *n*-butene at 713 K. No by-products ( $\text{C}_3^-$ ,  $\text{C}_5^-$ ) were seen with the “used” SAPO 11.

When *n*-butene reacted on SAPO 11 the pattern of dimers was different compared to the reaction on  $\text{H}_3\text{PO}_4/\text{SiO}_2$  catalyst. A very small amount of trimethylpentenes was observed, especially on the “used” SAPO 11. Methylheptenes became the dominant products. No linear octenes were detected (Table 3a).

Dimerisation of *n*-butene on fluorinated alumina was performed at 373 K, too. The partial pressure of *n*-butene in nitrogen was 60 kPa and the total flow was 15 ml/min. Under these conditions 1.19% of dimers were detected. The number of compounds formed was too large for full identification of individual components by the available equipment.

## IV. DISCUSSION

Various arguments have been put forward in the literature to support the idea of a bimolecular mechanism:

- (1) a higher content of isobutene among butenes than predicted by thermodynamics;
- (2) the apparent ease of the secondary carbenium ion formation;
- (3) detection of dimers and polymers with the active catalyts.

However, as we mentioned in the Introduction, there are more points on which the operation of a bimolecular mechanism could be tested. This testing is done in the following discussion.

#### A. Product Distribution as a Function of Temperature and Partial Pressure

Skeletal isomerisation of *n*-butene is limited by thermodynamic factors. It is therefore desirable to prepare a catalyst working at as low as possible a temperature. If measurements represented a true equilibrium, the maximum relative concentrations of isobutene would be 51.5% at 623 K, 47.7% at 673 K, and 45.0% at 713 K. No catalyst produced isobutene in a concentration higher than the thermodynamic values in Ref. (13).

If skeletal isomerisation runs via dimerisation of *n*-butene to octenes, one would expect that the temperatures at which dimerisation and skeletal isomerisation occur to high extent should be not very distant from each other. Experiments with dimerisation of isobutene to trimethylpentenes on  $\text{H}_3\text{PO}_4/\text{SiO}_2$  catalyst showed that dimerisation strongly decreases with increasing temperature. On the other hand, the optimal temperature for skeletal isomerisation of *n*-butene on this catalyst is rather high, 713 K. The best temperature for dimerisation and the optimal temperature for skeletal isomerisation are obviously very different

Simon *et al.* (2) measured the order of skeletal isomerisation of *n*-butene to isobutene on ZSM-22 catalyst and they found that the reaction was of the first order. The dependence of the product pattern of reaction of *n*-butene on partial pressure was measured in this paper, too. The higher partial pressure of *n*-butene should increase the rate of dimerisation to octenes and if octenes were indeed the main intermediates of skeletal isomerisation their faster formation should lead to faster formation of isobutene. However, a negative effect of the increase in partial pressure *n*-butene was observed for the skeletal isomerisation of *n*-butene to isobutene. Contrary to this, the relative concentration of all by-products (propene, isobutane, pentenes) was significantly higher when a higher pressure of *n*-butene in the feed was used. This result indicates that not the production of isobutene but the formation of by-products runs via

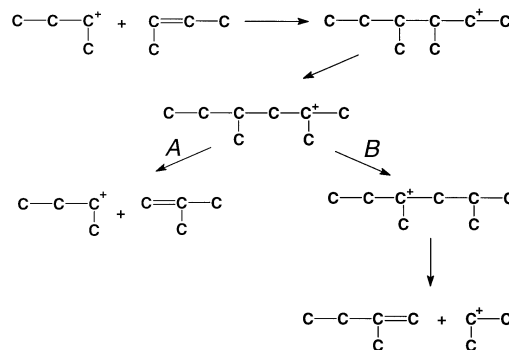


FIG. 10. Possible pathways of bimolecular mechanism via 3,4-dimethyl-2-hexene (schematic).

a bimolecular mechanism. The bimolecular pathway contributes then only very little to the isobutene formation. Other considerations (sections B and C below) support this conclusion. See also the note added in proof.

#### B. Comparison of Reactions of *n*-Butene and Octenes

Reactions of *n*-butene and its dimers were studied on different catalyts. When the possible dimers of linear butenes are subjected to cracking at the isomerisation reaction temperature, a large amount of by-products appears with all catalyts. However, the reaction of *n*-butene on  $\text{H}_3\text{PO}_4/\text{SiO}_2$ , MeAPO 11 and on chlorinated alumina is quite selective to isobutene, showing a low formation of by-products. This indicates that the main reaction pathway in skeletal isomerisation is not that via the dimers of *n*-butene. Mooiweer *et al.* (1) suggested that the reaction pathway in skeletal isomerisation of *n*-butene runs via the mechanism showed in Fig. 10 under "A." The experiments performed here with cracking of 3,4-dimethyl-2-hexene on selective catalyts showed that the reaction can also proceed through route "B," with a comparable probability. The isomerisation and the cracking of other octenes is not a selective reaction either; higher amounts of propene and pentenes are always observed. The only exception is the reaction of 2,4,4-TMP; this cracking, which in principle can run through a tertiary carbenium ion, is rather selective.

The experiments with dimerisation of isobutene showed that this reaction, possibly running via tertiary carbenium ion, is very easy, much easier than the reactions via secondary carbenium ion (isomerisation, cracking). There is probably a thermodynamic equilibrium between isobutene and its dimers at 423 K on the catalyts used, while dimerisation of *n*-butene is still very slow under the same conditions.

Cracking of 2,4,4-TMP, as mentioned above, is rather selective. The amount of by-products is about the same as the amount of propene and pentenes in *n*-butene reactions. A likely explanation seems to be a cracking reaction proceeding via 2,3,4-TMP. At 373 K about 15% of 2,3,4-TMP is present when isobutene is dimerised. Methyl shift in TMPs

is very fast and 2,3,4-TMP can be easily formed from 2,4,4-TMP.

It is probable that 2,3,4-TMP is formed by secondary reaction of isobutene at reaction temperature of skeletal isomerisation, too. Fortunately for the selectivity of the highly selective catalysts, the methyl shift in TMPs is easier than the cracking of 2,3,4-TMP to propene and pentenes. Cracking is apparently the rate-determining step in a formation of by-products by the secondary reaction of isobutene.

The situation is different when an acidic catalyst not selective to isobutene, is used. With these catalysts, containing strong Brønsted acid sites, there are two possibilities how to influence the selectivity:

(1) a dimerisation of *n*-butene via secondary carbenium ion is more probable on these catalysts (as shown earlier, all dimers of *n*-butene crack unselectively to a large amount of propene and pentenes);

(2) more severe reaction conditions used in the reaction with these catalysts accelerate the cracking reaction of 2,3,4-TMP to by-products compared to isomerisation, making the former reaction faster than isomerisation.

The influence of strong Brønsted acid sites on the formation of by-products (by a bimolecular mechanism) was noticed already earlier [see Refs. (5, 16)] and the experiments reported here confirm and explain those observations.

### C. Dimers Formed from *n*-Butene and Isobutene

Dimers formed in *n*-butene and isobutene reactions were analysed with SAPO 11 and H<sub>3</sub>PO<sub>4</sub>/SiO<sub>2</sub> catalysts at reaction temperatures 373–423 K. When *n*-butene reacts on the H<sub>3</sub>PO<sub>4</sub>/SiO<sub>2</sub> catalyst the main dimers are trimethylpentenes. Only a small amount of 3,4-dimethylhexene was detected. When isobutene reacts under the same conditions, a large amount of trimethylpentenes is observed. This means that dimerisation via a tertiary carbenium ion is very easy but dimerisation via a secondary carbenium ion is slow under the same reaction conditions. The concentration of the only identified dimer of *n*-butene (3,4-dimethyl-2-hexene) never exceeds a few tenths of a percent in the whole temperature range monitored, 373–723 K.

About 75% of isobutene reacts to trimethylpentenes at 373 K on the H<sub>3</sub>PO<sub>4</sub>/SiO<sub>2</sub> catalyst. The only compounds present among the products are 2,4,4-trimethyl-2(1)-pentene (2,4,4-TMP), 2,3,4-trimethyl-2(1)-pentene (2,3,4-TMP), hexenes, and 2-methyl-2(1)-butene. Composition of the products indicates the only possible way of formation of by-products and this is shown in Fig. 11 (by the bold print). For the sake of the following discussion, labeled molecules are used in schemes although no labeled molecules were used in this study. The reaction shown is dimerisation of isobutene and the cracking of TMP via tertiary carbenium ion. The fact that only 2-methyl-2(1)-butenes are present

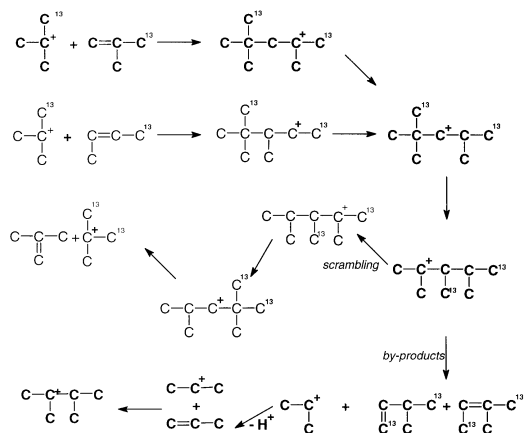


FIG. 11. Possible secondary reactions of isobutene (on open surface catalysts only).

and no other pentenes have been detected in the investigation reported here seems to exclude the formation of by-products via a methathesis-like mechanism not involving octenes.

The fact that 2,4,4-TMP can easily isomerise to 2,3,4-TMP is important for the selectivity of the catalyst. Because dimerisation of isobutene is easy, 2,4,4-TMP and 2,3,4-TMP are always present (being formed—at least—on the outer surface of zeolitic materials). If cracking was the only reaction of 2,3,4-TMP, only propene and pentenes would be formed. However, the product pattern of the 2,3,4-TMP reaction showed that a direct cracking of this compound is slower than its isomerisation to 2,4,4-TMP when selective catalysts are used. On the nonselective catalysts (like fluorinated alumina or ZSM-5) the situation is different and the mechanism shown in Fig. 11 could have been responsible for the significant amount of by-products.

This paper is totally devoted to *n*-butene isomerisation, but some information concerning the *n*-butane isomerisation might also be of interest. Although skeletal isomerisation of *n*-butane is different from butene isomerisation (different very acidic catalysts, different pressure dependence, different product distribution) the question as to whether a monomolecular or a bimolecular mechanism is operating arises here, too. The problem was attacked (19, 20) by experiments with labeled compounds. Two very recent studies lead to very different conclusions. Garin *et al.* (19), working with a pulse reactor and short contact times, found the skeletal isomerisation of *n*-butane running via a monomolecular mechanism on the ZrO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup> catalyst. Adeeva *et al.* (20), working with a batch reactor and longer contact times, found extended intermolecular scrambling of carbon labels and concluded that the prevailing mechanism is a bimolecular one.

In principle it should be possible to perform similar experiments to those in Refs. (19, 20) also with *n*-butene,

using  $^{13}\text{C}$ -labeled *n*-butene in the feed. This would produce labeled isobutene and labeled TMP, which after repeated isomerisation and cracking steps would produce again isobutene according to the scheme in Fig. 11. The products obtained after a sufficient long reaction time, as usual in a batch experiment, can (in principle) contain more labeled atoms per molecule of isobutene than the original *n*-butene (see Fig. 11). However, this latter fact must not be taken then as evidence that isobutene is produced mainly bimolecularly, via octenes. Isobutene, "monomolecularly" produced from single labeled *n*-butene, could have been "enriched" in the label in the way indicated by Fig. 11. This was one of the reasons why we have chosen the approach reported on by this paper and why experiments with labeled compounds have not been performed by us. The different results obtained by Refs. (19) and (20) support our choice of the experimental approach.

Dimerisation of isobutene on SAPO 11 is strongly suppressed compared to dimerisation on the freely exposed surface of the  $\text{H}_3\text{PO}_4/\text{SiO}_2$  catalyst. SAPO 11 contains POH groups and OH groups at the intersection of P-Al-Si and Si-Al domains (21). The acidity of these groups is higher than that of those on  $\text{H}_3\text{PO}_4/\text{SiO}_2$  catalyst, so if the acidity were the only decisive factor, one would expect some dimerisation on SAPO 11. The explanation of the phenomenon observed is probably as follows. The 10-membered ring channels of a molecular sieve are too small to accommodate trimethylpentene and thus this molecule is not formed there. The dimerisation of isobutene can proceed probably only on the outer surface, which can be "self-poisoned" by carbonaceous deposits, during the running reaction.

A similar conclusion can be drawn from the results concerning the *n*-butene reaction on SAPO 11. The concentrations of 2,3,4-TMP, 3,4-dimethylhexene, and especially 2,4,4-TMP are very low. The dominant peaks in the gas chromatogram are various methylheptenes. The less branched methylheptenes are formed preferentially. No linear octenes are formed, probably due to the low stability of  $\pi$ -complexed *n*-butene on the surface. This complex is necessary for the coordinative dimerisation mechanism leading to linear octenes (16). The dimerisation of *n*-butene proceeds apparently only via a secondary carbenium ion and thus yields branched molecules.

The low concentration of octenes seen in the reaction of butenes on SAPO 11 shows that this catalyst exhibits a "shape selectivity." The formation of trimethylpentenes (by dimerisation of *n*-butene or by codimerisation of *n*-butene with isobutene) is probably prevented completely inside the pores, the formation of the other less branched octenes being simultaneously suppressed. The structure of SAPO 11 can entirely stop the secondary formation of by-products via isobutene (Fig. 11) reaction and decrease their direct formation via dimers of *n*-butene. This shape selec-

tivity obviously occurs on all one-directional 10-membered ring zeolites like SAPO 11 (15), MeAPO 11 (18), ZSM-22 (2), and ZSM-23 (22). It probably plays the same role even on zeolites with two-directional channels like ferrierite (1), where the 10-membered ring channels are crossed by narrow 8-membered ring channels. The low selectivity of ZSM-5 (15) shows that the larger cavities formed at the intersections of two 10-membered ring channels are too large to prevent the formation of by-products via dimerisation. Large amounts of propene pentenes, and isobutane are formed on strongly acidic sites of this catalyst.

## V. CONCLUSIONS

(1) Skeletal isomerisation of *n*-butene to isobutene proceeds mainly by a monomolecular mechanism. Cracking patterns of octenes, all possible primary dimers of *n*-butene, showed that these compounds could not be intermediates of the skeletal isomerisation on selective catalysts. Copolymers of isobutene and butene (trimethylpentenes) are too large to be formed in some active and selective catalysts (10-membered ring molecular sieves).

(2) Bimolecular mechanism is mainly responsible for the formation of by-products. There are two possible bimolecular mechanisms of formation of propene and pentenes. These are the primary one, via direct formation of octenes from *n*-butene, and the secondary one, via the secondary dimerisation of isobutene formed monomolecularly from *n*-butene to trimethylpentenes.

(3) The selectivity of a catalyst is low if strong Brønsted acid sites are present. These sites induce extensive dimerisation and the subsequent skeletal isomerisation of octenes. Cracking of octenes formed is not a selective pathway to isobutene.

(4) The 10-membered ring zeolites exhibit a suitable shape selectivity. A secondary reaction mechanism of formation of by-products (via isobutene) is probably impossible with them; the primary reaction mechanism leading to by-products via *n*-butene is strongly suppressed.

(5) Experiments with labeled compounds cannot always be considered as definitive evidence of bimolecular mechanism.

*Note added in proof:* One of the referees suggested a reaction scheme comprising several different mechanisms, each operating under different reaction conditions:

(i) at low conversion, there is the monomolecular mechanism, possibly accompanied by a dimerisation/cracking mechanism;

(ii) at high conversion a bimolecular mechanism prevails in the form of codimerisation/cracking: *n*-butene + isobutene  $\rightarrow$  trimethylpentenes  $\rightarrow$  two isobutenes.

One would expect that a sudden *n*-butene pressure increase should lead to the higher concentration of isobutene

amongst the products, but the opposite is true. The intermediates of the codimerisation mechanism cannot be formed in the 10-membered ring zeolites with one-directional channels, but these are the most active and selective catalysts. Thus, the mechanism (ii) can be disregarded.

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