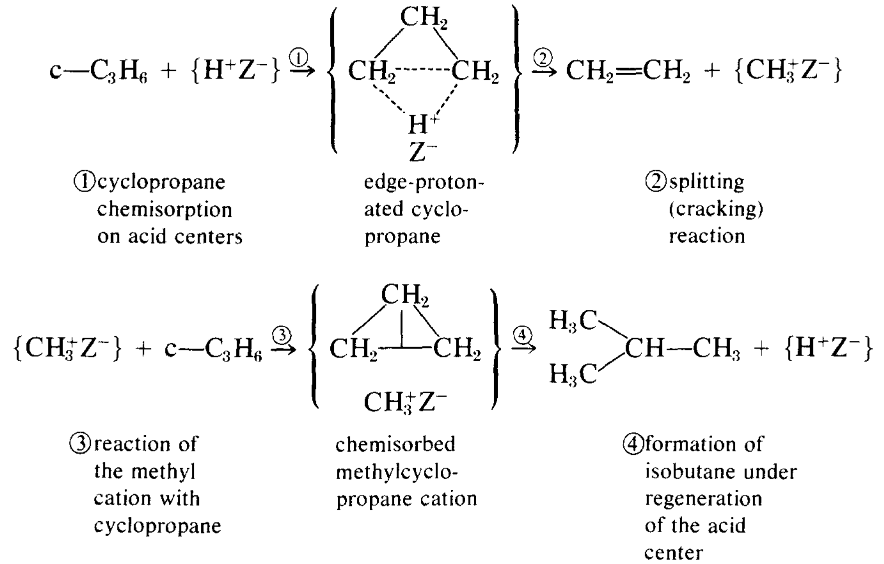
JOURNAL OF CATALYSIS 63, 501–504 (1980)

Reactions of Cyclopropane over Zeolite Catalysts

The skeletal isomerization of cyclopropane to propylene is a widely used test reaction for the investigation of the performance of catalytic reactors (*2–4*) and the activity of acid-type solid catalysts (*5–10*). The reaction mechanism has been extensively studied (*11–15*), as have the further reactions of the product propylene over silica–alumina (*16, 17*) and zeolites (*18–21*).

Infrared spectroscopy was applied first by Tam *et al.* (*1*) to study chemisorption and reactions of cyclopropane in zeolite frameworks. They measured the ir spectra of cyclopropane and products on HY using self-supporting wafers and determined the composition of the desorbed products by mass spectroscopy. A characteristic ir absorption band at 2889 cm^{-1} was assigned to the tertiary ≡C—H group. In agreement with this observation the desorbed gases contained isobutane. Tam *et al.* suggested the following mechanism (Mechanism I):



①cyclopropane chemisorption on acid centers

edge-protonated cyclopropane

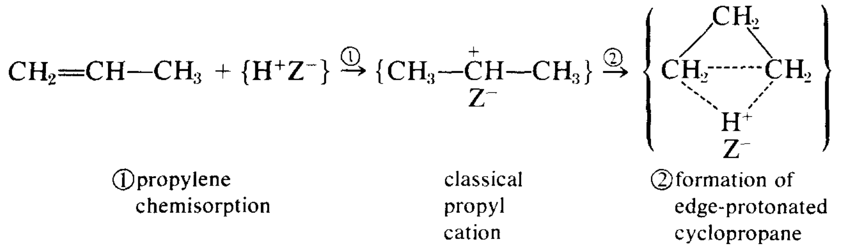
②splitting (cracking) reaction

③reaction of the methyl cation with cyclopropane

chemisorbed methylcyclopropane cation

④formation of isobutane under regeneration of the acid center

The same mechanism has been applied to interpret the experimental results obtained by Liengme and Hall (*19*). According to Tam *et al.*, edge-protonated cyclopropane could be produced from propylene by the reaction sequence (Mechanism II):



①propylene chemisorption

classical propyl cation

②formation of edge-protonated cyclopropane

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and following this the protonated cyclopropane reacts as indicated in Mechanism I.

Mechanisms I and II of Tam *et al.* (*1*) raise the following difficulties:

—Provided that isobutane is produced via Mechanism I, ethylene should be present among the products as a consequence of reaction ②. Actually no ethylene could be observed. (The failure to find ethylene was explained by evacuation losses.)

—The production of methyl cations in step ② is very improbable from a thermodynamic point of view; preference should be given to the more stable cations like the classical propyl cations (*22*).

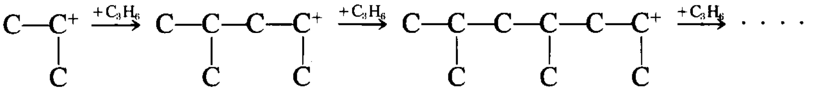
—Step ② in mechanism II should therefore be ruled out (*23*), although there are some indirect observations showing that similar reactions in solutions might actually occur (*24*).

In an attempt to rationalize the contradictions in the paper by Tam *et al.*, we have carried out further experiments. The skeletal isomerization of cyclopropane has been investigated in a static reactor over NaY (*7, 25*), NaCaY (50% Na^+ exchanged for Ca^{2+}) and NaHY zeolites. Infrared spectra of cyclopropane over NaHY wafers under reaction conditions agreed exactly with those published by Tam *et al.* so it is valid to compare the systems.

Product compositions as a function of reaction time (as measured by gc analysis) are shown in Fig. 1a and b for the NaCaY and NaHY catalysts, respectively. After passing the maximum on the kinetic curve for propylene (Fig. 1a), isobutane and, in lower concentration, 2-methylbutane could be detected among the gaseous products. 2-Methylpentane is also present as a trace component. The amount of C_2 and C_1 hydrocarbons in the products was nil.

From the kinetic point of view propylene behaves clearly as a reaction intermediate in the overall reaction of cyclopropane into isobutane; therefore, when unraveling this transformation one can rely upon the extensive literature concerning cationic polymerization of propylene.

As far as the reactions of propylene over acidic catalysts are concerned, it is generally agreed that under mild conditions (i.e., below 473 K) the dimeric 2-methylpentyl cation is formed (*16–21, 26*), which may either lose a proton giving the respective olefin or react with another propylene molecule leading to the trimeric carbonium ion:



$$\mathrm{C{-}\underset{\overset{|}{C}}{C}^{+}} \xrightarrow{+C_3H_6} \mathrm{C{-}\underset{\overset{|}{C}}{C}{-}C{-}\underset{\overset{|}{C}}{C}^{+}} \xrightarrow{+C_3H_6} \mathrm{C{-}\underset{\overset{|}{C}}{C}{-}C{-}\underset{\overset{|}{C}}{C}{-}C{-}\underset{\overset{|}{C}}{C}^{+}} \xrightarrow{+C_3H_6} \cdots \qquad (1)$$

How far in the zeolitic framework this process might actually proceed has never been clearly established. Above a certain size molecules become trapped in the structure (reverse molecular sieve action) impeding analysis unless the catalyst is destroyed. At low temperatures carbonium ions undergo isomerization with retention of the carbon skeleton.

At elevated temperature, but still below 473 K, the oligomerization of propylene might not continue undisturbed because complex cracking and hydrogen transfer steps take over, blurring the kinetic picture. Among the reaction products over NaHY catalysts, isobutene, 2-methylbutene (their amounts decreasing; see Fig. 2), and a few saturated hydrocarbons like propane, isobutane, 2-methylbutane, 2-methypentane, and heptanes could be identified (Fig. 3). Meanwhile the pore structure becomes increasingly filled with products of great complexity, known as "coke."

Starting from cyclopropane most of these hydrocarbons, with the possible exception of the major product, isobutane, escape detection unless long reaction times are used.

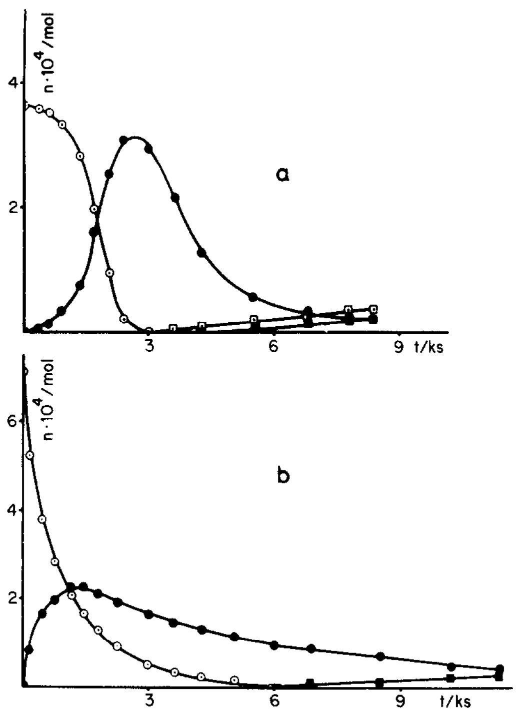


FIG. 1. Kinetic curves of cyclopropane over zeolites. (a) The amount of cyclopropane, ⊙; propylene, ●; isobutane, ⊡; and 2-methylbutane, ■, vs reaction time. Reaction temperature, 523 K; mass of catalyst, 5 × 10^{-4} kg; reactor volume, 221.3 cm^3. (b) The amount of cyclopropane, ⊙; propylene, ●; and isobutane, ■, vs reaction time. Reaction temperature, 398 K; mass of catalyst, 3 × 10^{-4} kg; reactor volume, 230.6 cm^3.

Although the complex oligomerization–isomerization–cracking process of propylene on zeolites has received deserved attention in the past 20 years, experimental sophistication has not yet reached the degree necessary to explain all the details of the relevant steps. According to Poutsma (*27*) the olefins are produced from the respective alkyl cations by β-scission. Their H^- ion transfer reactions result in paraffins and coke precursors. The most interesting, still unresolved, question seems to be whether the C_4 and C_5 olefins and the C_4, C_5, and C_6 paraffins originate from a C_6 or $C_{>6}$ carbonium ion precursor. Considering the stabilities of the ethyl and methyl cations thermodynamics rules out the C_6 carbonium ion as a parent molecule and this receives strong experimental support; on the other hand the simple product pattern cannot either be easily deduced from the trimeric carbonium ion skeleton [see Eq. (1)], even when allowance is made for intramolecular H^- ion transfer. This could be the reason why some Russian authors made an attempt to derive the C_4–C_6 hydrocarbons from the dimeric ion, although an explicit mechanism has never been published (*28*).

On the basis of the results cited above it can be judged that the production of isobutane from cyclopropane over acidic zeolite

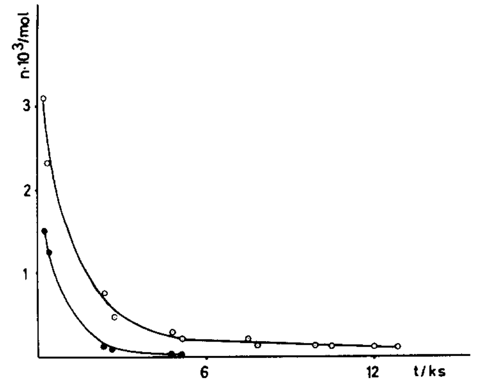


FIG. 2. The amount of isobutene, ⊙, and 2-methylbutene, ●, depending on reaction time in the oligomerization reaction of propylene over NaHY zeolite catalyst. Reaction temperature, 473 K; mass of catalyst, 2 × 10^{-3} kg; reactor volume, 225.0 cm^3.

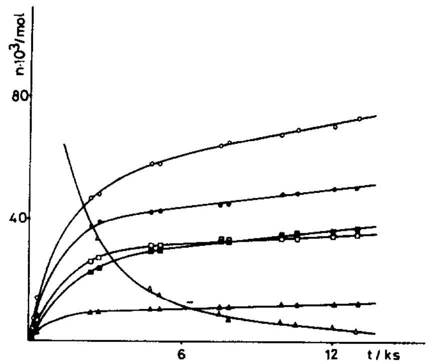


FIG. 3. The paraffinic products (propane, ■; isobutane, ○; 2-methylbutane, ●; 2-methylpentane, □; and heptanes, ▲) in the oligomerization–isomerization–cracking reaction of propylene (△) over a NaHY zeolite catalyst. The reaction conditions are the same as for Fig. 2.

catalysts does not follow Mechanism I suggested by Tam *et al.* (*1*). Similar difficulties are encountered with their Mechanism II when it is applied to the results of Liengme and Hall (*19*). In our opinion isobutane is only one, though major, representative of a more complex reaction mixture formed from propylene as an intermediate of cyclopropane isomerization by the known oligomerization-isomerization-cracking process.

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Received May 29, 1980