Comments on "Skeletal Isomerization of Butene: On the Role of the Bimolecular Mechanism"
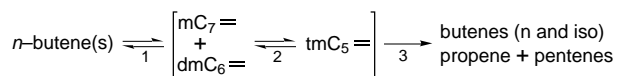
M. Guisnet,*,† P. Andy,† N. S. Gnep,† C. Travers,‡ and E. Benazzi‡

*Laboratoire de Catalyse en Chimie Organique, UMR 6503, UFR Sciences, Université de Poitiers,
40 avenue du Recteur Pineau, 86022 Poitiers Cedex, France, and Institut Français du Pétrole,
1 et 4 avenue du Bois-Préau, BP 311, 92852 Rueil-Malmaison Cedex, France*

Sir: In a recent paper Houzvicka and Ponec (1997) examined the various mechanisms of skeletal isomerization of butene proposed in the literature. Among them, the mechanisms which we proposed in the case of ferrierite catalysts, (i) bimolecular with fresh HFER samples (Guisnet et al., 1996a) and (ii) pseudomonomolecular (involving anchored carbocations as sites) with aged HFER samples (Guisnet et al., 1995, 1996b), are rejected by these authors owing to a misinterpretation of our proposals and of those of Meriaudeau et al. (1996). The previously reported observations in favor of these mechanisms are summarized here, and complementary results are presented.

Mechanism of Butene Isomerization over a Fresh HFER Sample

n-Butene isomerization was investigated at 350 °C on a HFER sample (Si/Al = 13.8). On the fresh catalyst (Guisnet et al., 1996a) *n*-butene isomerization is accompanied by a significant formation of propene and pentenes but only a very small amount of octenes. This suggests a dimerization−cracking mechanism (generally called a bimolecular mechanism) in which the desorption of octenes (*n*-butene dimers, i.e., methylheptene ($mC_7^=$), dimethylhexene ($dmC_6^=$), and trimethylpentene ($tmC_5^=$) isomers) is limited by the narrow pores of HFER (Guisnet et al., 1996a; Mooiweer et al., 1994).

$$n\text{–butene(s)} \underset{1}{\rightleftarrows} \begin{bmatrix} mC_7^= \\ + \\ dmC_6^= \end{bmatrix} \underset{2}{\rightleftarrows} tmC_5^= \overset{3}{\longrightarrow} \begin{array}{l} \text{butenes (n and iso)} \\ \text{propene + pentenes} \end{array}$$

Indeed as emphasized by various authors (Houzvicka and Ponec, 1997; Mooiweer et al., 1994) triple-branched hydrocarbons (such as $tmC_5^=$) cannot diffuse into the narrow pores of HFER and the diffusion of double-branched molecules ($dmC_6^=$) is slowed down. However, contrary to what is stated by Houzvicka and Ponec (1997), the octene intermediates of bimolecular butene isomerization can be formed in the HFER pores. Indeed a molecular modeling study carried out by Mooiweer et al. (1994) shows that even trimethylpentenes fit at the intersections of the 8- and 10-membered ring channels. Therefore, although octenes are observed in traces, or even are not observed ($tmc_5^=$), they can be intermediates in *n*-butene skeletal isomerization and all the steps (reactions 1−3) of bimolecular isomerization can occur inside the HFER pores.

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* Author to whom correspondence is addressed. Telephone: 33 5 49 45 39 05. Fax: 33 5 49 45 34 99. E-mail: michel.guisnet@cri.univ-poitiers.fr.
† Université de Poitiers.
‡ Institut Français du Pétrole.

In agreement with this bimolecular mechanism, the isobutene formed from conversion of *n*-butene with one ^{13}C atom over a fresh HFER sample is a mixture of molecules containing two ^{13}C atoms, one ^{13}C atom, and no ^{13}C atom (Meriaudeau et al., 1996). It is therefore clear that, at least with fresh HFER, the dimerization−cracking mechanism is responsible not only for the formation of byproducts as claimed by Houzvicka and Ponec (1997) but also for the skeletal isomerization of *n*-butenes.

Mechanism of Butene Isomerization over an Aged HFER Sample

However, the main observation emphasized in our previous paper (Guisnet et al., 1995; 1996b) was that, while as expected from deactivation by coke deposits, the rate of formation of propene and pentenes decreases with an increase in time-on-stream (TOS), the rate of skeletal isomerization increases with TOS and then decreases, with the maximum rate being obtained after 4−10 h of reaction depending on the contact time. Carbonaceous compounds (coke) are formed which block the access of the zeolite pores as shown by adsorption experiments (Guisnet et al., 1995, 1996b). Figure 1 which summarizes these observations suggests the following:

(1) The formation of propene and pentenes, through the dimerization cracking mechanism (demonstrated in the case of fresh HFER), occurs inside the zeolite pores. Indeed, coke deposits which block the access of these pores strongly inhibit the formation of these products (Figure 1).

(2) A new mode of isobutene production superposes on the dimerization cracking (bimolecular) mode found on the fresh HFER sample. Coke deposits should decrease the formation of isobutene from the bimolecular mechanism, whereas an increase is actually observed.

(3) In this new mode of isobutene production, coke molecules are more than likely the active sites. Indeed this new mode can take place neither in the zeolite pores (which are blocked by coke deposits) nor on the acid sites located on the outer surface of the crystallites. The number of these outer sites is very small compared to the total number of acid sites, less than 3% of the total number (estimated from the crystallite size). The activity of the outer surface of the crystallites for a facile acid model reaction—isooctane cracking—was furthermore found to be negligible. Moreover, as with the fresh catalyst these outer acid sites should intervene in addition to the inner sites; no increase in isobutene production should be observed with deactivation of the inner acid sites by coke deposits.

Therefore, a mechanism involving as active sites carbocations formed from coke molecules blocked inside

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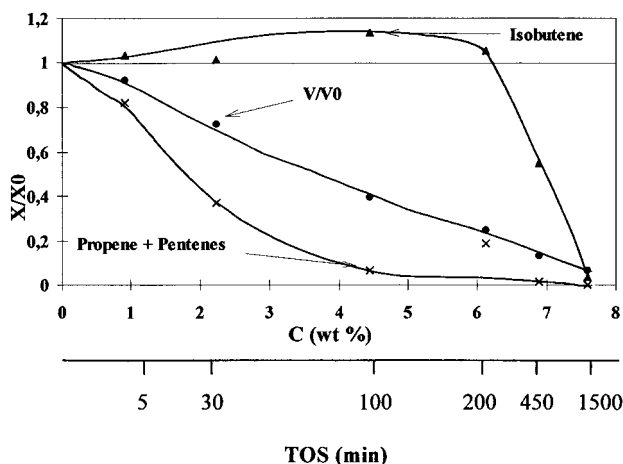
Figure 1. Influence of coke content on the residual activity of HFER for the various transformations of n-butenes at 623 K (into isobutene and into propene + pentenes) and on the residual capacity for nitrogen adsorption (V/V_0).
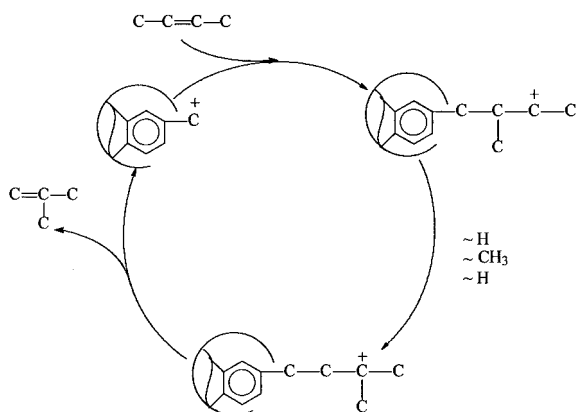

Figure 2. Pseudomonomolecular mechanism of n-butene isomerization into isobutene over aged HFER samples.

the pores close to the outer surface of the crystallites (pore mouth catalysis) was proposed (Guisnet et al., 1995, 1996b; Guisnet, 1997) (Figure 2).

In our first paper (Guisnet et al., 1995) tertiary carbenium ions were suggested as the active species. However, analysis of the carbonaceous compounds (coke) recently led us to propose benzylic carbocations instead of these tertiary carbenium ions. Indeed coke mainly consisted of methylaromatics (Guisnet et al., 1996b), which are precursors of benzylic carbocations, and not of branched alkenes, precursors of tertiary carbenium ions. However, with both active species, the new mechanism was pseudomonomolecular; i.e., only one n-butene molecule is involved in the formation of isobutene (Figure 2). In agreement with this, isobutene formed from transformation of n-butene with one ^{13}C atom over an aged (after 20 h reaction) HFER sample contains only one ^{13}C atom (Meriaudeau et al., 1996).

The positive effect which carbenaceous deposits have on isobutene production was contested by Houzvicka and Ponec (1997) on the basis of pulse experiments. Indeed a decrease and not an increase in isobutene production was observed. We have confirmed this result by carrying out a large number of product analyses at short time-on-stream (Figure 3).

This decrease, which was not observed in our first paper (Guisnet et al., 1995) because the analysis by GC were carried out at intervals of 50 min (duration of analysis), is not in disagreement with our previous
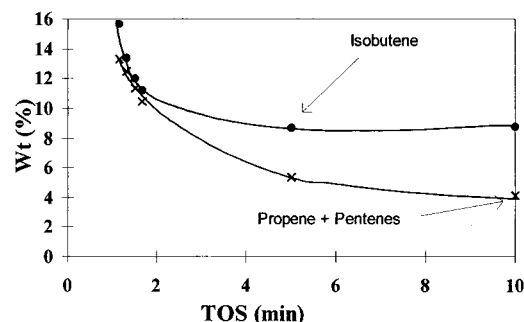

Figure 3. Influence of time-on-stream (TOS) on the conversion of n-butenes into isobutene and into propene + pentenes. Operating conditions: $P_{n\text{-butenes}} = 0.1$ bar; WHSV (weight hourly space velocity) = 20.6. [Short values of time-on-stream (1.5−10 min)].

proposals. First, it confirms that coke deposits deactivate both the formation of propene and pentenes and that of isobutene which occur through the dimerization-cracking mechanism. However, the decrease in isobutene yield found at very short time-on-stream is followed by a significant increase at longer time-on-stream (Guisnet et al., 1995, 1996b; Meriaudeau et al., 1996) due to the formation and the blockage of coke molecules in pores located near the outer surface of the HFER crystallites.

Conclusions

Contrary to what is concluded by Houzvicka and Ponec (1997), n-butene isomerization over *fresh* HFER samples can occur, and mainly occurs, through a bimolecular mechanism involving successive dimerization, isomerization, and cracking steps. This is suggested by the selectivity of butene transformation (Guisnet et al., 1996a) and by the possibility for octene intermediates to be formed and accommodated in the zeolite pores as shown by molecular modeling (Mooiweer et al., 1994), and this is proven by the intermolecular exchange of ^{13}C between butene molecules found during isomerization (Meriaudeau et al., 1996).

The initial decrease in isobutene formation found by Houzvicka and Ponec (1997) and confirmed by us is not an argument against the mechanism involving anchored carbocations as active sites found on *aged* HFER samples. Indeed this decrease is followed at longer time-on-stream by a significant increase in isobutene production (Guisnet et al., 1995, 1996b; Guisnet, 1997; Meriaudeau et al., 1996). The active sites are benzylic carbocations formed from the methylaromatic components of coke blocked in the pores at the vicinity of the outer surface of the crystallites. The isomerization is pseudomonomolecular (involving only one butene molecule), which is in perfect agreement with the absence of intermolecular ^{13}C exchange found by Meriaudeau et al. (Meriaudeau et al., 1996) during n-butene isomerization.

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