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Reactions of Olefins on Zeolites: The Change of the Product Distribution with Time on Stream in the Reaction of Butene-1 on Calcined $NaNH_4$–Y

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The reaction of butene-1 on NaH–Y zeolites with various degrees of exchange has been investigated in a flow reactor at reaction temperatures of 250–400°C and at olefin partial pressures of 14–70 Torr as a function of time on stream. The results indicate that isobutane, propylene, and *n*-butane as main products have distinct induction periods, which are time-shifted toward each other. The duration of the induction periods increases (a) with decreasing exchange level of the catalyst, (b) with decreasing partial pressure of butene-1, and (c) with increasing reaction temperature. The observed maxima can be explained only by the participation of coke precursors in the reaction sequence, which are formed at the beginning of the reaction on the surface of the catalyst. Because alicyclic and aromatic compounds could be identified in the reaction mixture, it can be suggested that the coke precursors possess cyclic structures. A formal reaction scheme may be proposed, which leads to the formation both of the hydride transfer products and of the cracking products via mono- and polycyclic intermediates. In a hypothetical reaction sequence it is shown that the formation of the cracking products may occur by paring reactions of alkylated cyclic coke precursors.

INTRODUCTION

The reactions of olefins on solid acid catalysts such as zeolites or silica–alumina result in the formation of polymerization and cracking products with high amounts of paraffinic hydrocarbons (*1*–*6*). The reactions are accompanied by a rapid deactivation of the catalyst during the reaction which is caused by the deposit of highly unsaturated polymeric material on the catalyst surface. Investigations by Venuto and Hamilton (*7*) and by Eberly *et al.* (*8*) have shown that the coke formed consists mainly of alkylated fused aromatics and hydroaromatics. It was established that the coke tendency is strongly dependent on the nature of the reactants (*8*) and on the structure of the catalysts (*9*).

The main products of the reaction of lower olefins at reaction temperatures above 100°C are isobutane and isopentane, whatever the starting olefin may have been. For example, these compounds are predominant in the reaction of ethylene (*6*), propylene (*3*), butene (*1*, *2*), and hexene (*4*) on deammoniated ammonium-exchanged Y and propylene (*5*) on silica–alumina.

Although it is commonly accepted that the reactions of olefins on acid catalysts are proton catalyzed, the mechanism of these reactions is not known in detail. Örhalmi and Fejes (*3*) have explained the formation of isobutane and isopentane in the reaction of propylene on HY by the cracking of methylpentyl carbenium ions as intermediates with intramolecular hydride transfer. At the same time, unsaturated carbenium ions such as $C_2H_3^+$ and CH^+ were assumed which could be responsible for coke formation. On the other hand, investigations by Bolton and Weeks (*2*) have demonstrated that the reactions of [4-^{13}C]butene-1 on HY lead to isobutane and isopentane with carbon-13 enrichment with regard to the start-

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ing olefin. These results cannot be reconciled with a simple dimerization–cracking mechanism. It has been assumed, therefore, that these products are breakdown products of polymeric material, which is tightly bound to the catalyst surface. Shephard *et al.* (*4*) have proposed that an intermolecular hydride-transfer mechanism is responsible for the formation of paraffins from propylene. It has been supposed that hydride transfer proceeds via cyclic compounds—presumably coke precursors which are adsorbed on the catalyst—as evidence was cited that preadsorption of tretalin increases the relative amount of saturated hydrocarbons.

Nevertheless, the existing studies do not provide unambiguous information regarding the question, which products result from coke precursors or from the interaction of olefins with coke precursors. The nature of the coke precursors remains unclear, too. As the accumulation of coke precursors and coke on the catalyst increases during the reaction, it can be supposed that one can get more information about the reaction mechanism by studying the reaction in a flow reactor as a function of time on stream. Weeks *et al.* (*1*) have observed an induction period for all products from the reaction of butene-1 on HY. But this induction period might be attributed to the physical adsorption of the reactants, because the reaction temperature of 125°C is below the critical temperatures of the resulting compounds. Therefore, the purpose of this work was to study the reaction of butene-1 on deamminated ammonium–Y at reaction temperatures above 250°C, at low butene partial pressures ($p_{\text{butene-1}} < 70$ Torr, 1 Torr = 133.3 N m^{-2}), and at low residence time ($\tau = 0.39$ g catalyst · s · cm^{-3}), as a function of time on stream in a flow reactor. It could be expected that the composition of the reaction mixture and its change with time on stream can give further information about the reaction sequence of the reaction of olefins on solid acid catalysts.

EXPERIMENTAL

Catalysts

The starting material for the preparation of the catalysts was a commercial NaY zeolite (Linde Type 30-200) in powder form. After washing with distilled water the catalyst base was exchanged with a measured amount of 0.001–0.1 *m* ammonium nitrate solution under reflux conditions for 17 h. The sodium ammonium form (denotation: NaNH$_4$(x)–Y, where x is the exchange degree) was filtered, thoroughly washed with distilled water, and carefully predried at 80°C. The exchange degree was determined by back-titration of the ammonium in the filtrate. For exchange degrees above 50%, the exchange procedure was repeated several times. In order to maintain a constant water content (24%) over a long period, the NaNH$_4$–Y was stored over a saturated ammonium chloride solution. All experiments were carried out with 1.00 g (according to 0.76 g dry matter) of the catalyst.

Apparatus and Procedure

The reactor consisted of a glass tube (d = 15 mm) with an internal glass frit for the catalyst and a glass coil to preheat the feed. The apparatus was mounted in a fluidized sand bath (Techne Type SBS 4), the temperature of which could be adjusted to ±1°K. The reaction temperature was measured by a thermocouple placed in the catalyst bed. The gas flow was regulated by needle valves and controlled by flow meters. Prior to the reaction, the catalyst was activated in the reactor in a stream of dry nitrogen (1 liter/h) at 350°C for 17 h. After calcination, a mixture of nitrogen and butene-1 (Messer-Griesheim 99.5%) was passed over the catalyst at atmospheric pressure with a total gas velocity of 7 liters/h. Different partial pressures of the olefin were obtained by changing the ratio butene-1/nitrogen. In all experiments, the residence time based on dry matter of the catalyst was 0.39 g catalyst · s · cm^{-3}.

Because of the low partial pressure of the butene-1, all reaction products were gaseous, even at room temperature, and sampling could be carried out with a gas-tight syringe.

Analyses

The product was injected into two gas chromatographs, with flame ionization detectors (Hewlett–Packard 5711) connected with two electronic integrators (Hewlett–Packard 3380). The separation of the reaction mixture was made with a 4-m × ¼-in. glass column with 20% di(2-ethylhexyl)sebaccinate/sebaccine acid on Chromosorb at 70°C and a 4-m × ¼-in. glass column with 33% dimethylsulfolane on Chromosorb at 25°C. With this chromatographic equipment, all interesting compounds—aside from butene-1/isobutene—could be separated within 8 min, which determined the intervals of sampling. In some cases, the butenes were separated by a 4-m × ¼-in. column with diethylene glycol/AgNO$_3$ on Chromosorb at 25°C. By these analysis, it could be established that under the reaction conditions the *n*-butenes are approximately in thermodynamic equilibrium. Therefore, it was possible to calculate the proportion of isobutene under the chromatographic peak of the butene-1 from the thermodynamic equilibrium of the linear butenes.

The identification of the cyclic compounds and of the C$_8$ isomers were carried out with a 50-m squalane capillary column at 70°C by comparing them with known kovats indices (*10*). In some cases, aromatic compounds were characterized by a gas chromatograph–mass spectrometer combination (HP 5992).

RESULTS

Product Distribution

Although the relative quantities of the individual compounds are strongly dependent on reaction temperature, on butene partial pressure, on exchange level of the catalyst, and on time on stream, the same hydrocarbons were found in all experiments. An example of the product distribution is given in Table 1. The main products are propylene, isobutane, isopentane, and butane, with a high proportion of isobutane, while the fraction of dimers of the butenes was found to be less than 4% in all experiments. The ratio olefins/paraffins decreases with increasing length of the carbon chain. While the ratio propylene/propane amounts to 10, the C$_8$ hydrocarbons consisted exclusively of paraffins, especially methylheptanes and dimethylhexanes. This tendency can be attributed to the lower diffusivity and higher reactivity of the higher olefins, which first react to relatively inert paraffins, before they can desorb from the catalyst. Similarly, higher reactivity may be the reason that branched olefins react more readily than linear olefins to the

TABLE 1

Example of the Product Distribution of the Reaction of Butene-1 on Calcined NaNH$_4$(25)–Y[a]

Product	wt%	mole%
Ethylene, ethane	0.5	1.0
Propane	0.7	0.9
Propylene	7.4	10.2
Isobutane	20.1	20.1
Isobutene	4.5[b]	4.7
n-Butane	6.6	6.6
Butene-1	9.3[b]	9.6
Butene-2	32.0	33.2
Isopentane	7.9	6.3
Methylbutenes, *n*-pentane	3.8	3.1
Isohexanes	2.1	1.4
Isoheptanes	1.2	0.7
Isooctanes	2.7	1.4
Toluene	0.3	0.2
Xylenes	0.8	0.5

Additional products in small amounts: alkylated benzenes, mono-, di-, and trimethylated naphthalenes, dimethylcyclohexanes, trimethylcyclopentanes.

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[a] Reaction conditions: $T = 350°\mathrm{C}$, $p_{\mathrm{butene}} = 40$ Torr, $\tau = 0.39$ g catalyst · s · cm^{-3}, sampling after 16 min on stream.

[b] Calculated from the thermodynamic equilibrium of the *n*-butenes.

corresponding paraffins by hydride transfer. As shown by the distribution of the C_4 compounds in Table 1, the ratio isobutane/isobutene is clearly higher than the ratio *n*-butane/*n*-butenes. Besides aliphatic compounds from C_1 to C_8, cyclic compounds were also found in the reaction mixture. Toluene and xylenes reached a level of up to 3% in some experiments at high temperatures, while benzene and ethyl benzene were only detected in traces (<0.03%). Furthermore, highly alkylated benzenes with methyl, ethyl, and propyl side chains and mono-, di-, and trimethylated naphthalenes were detected by gc/ms analysis. By their kovats indices saturated cyclic compounds such as dimethylcyclohexanes and trimethylcyclopentanes were also identified by capillary gas chromatography. Although the quantities of cyclic compounds were very low, they may play an important role as coke precursors.

Change of Product Distributon with Time on Stream

With time on stream not only the overall activity of the catalyst decreases, but also the product distribution changes. This will be demonstrated by tracing three of the major components in the reaction mixture:

(1) *n*-butane as a measure for hydride-transfer activity of the catalyst,
(2) the sum of propylene and propane (abbreviated C_3) as a measure for the cracking activity, and
(3) isobutane.

Isobutene and the corresponding hydride-transfer product isobutane are cracking products rather than skeletal isomerization products of the linear butenes, because in all experiments, the behavior of isobutane, with regard to time and pressure dependence, is similar to the behavior of isopentane so that it can be assumed that these compounds are formed from similar intermediates. This is also confirmed by the investigations of Bolton and Weeks (*2*) and by Maurel *et al.* (*12*) who reported very low rate constants for the skeletal isomerization of butane on a bifunctional catalyst. So the yield of isobutane is a measure for cracking activity plus hydride-transfer activity of the catalyst.

The influence of time on stream on the distribution of the three key compounds at a butene partial pressure of 70 Torr is shown in Fig. 1. (The logarithmic time scale is chosen only for convenience.) The rapid loss of activity can be seen by the decreasing quantities of the cracking products C_3 and isobutane. After 50 min the amount of these compounds has fallen to one-third of the initial value at 9 min. In contrast, the behavior of *n*-butane differs clearly, because *n*-butane exhibits a weak induction period at the beginning of the reaction, in which its quantity rises from 8.5 to 9%. Moreover, the decrease after reaching the maximum is not so pronounced as that of the cracking products, because *n*-butane drops within 40 min by only 30%.

By lowering the partial pressure of the olefin to 25 Torr (Fig. 2) the different reaction behavior is even more pronounced. The C_3 quantity decreases continuously with time on stream, while there are induction periods both for *n*-butane and for isobutane, which are time-shifted toward each other. By comparison with the experiment at 70 Torr (Fig. 1), it can be seen that the maximum for *n*-butane has drifted toward higher time and the decrease of activity is generally slower at the lower partial pressure.

At a partial pressure of 14 Torr (Fig. 3) all compounds present distinct induction periods; even the C_3 fraction reaches its maximum only after 15 min and the *n*-butane maximum has drifted beyond the observation time of 300 min. Simultaneously, it was observed that a great deal of the feed was absorbed on the catalyst at the initial stage of reaction, because the injection of constant volumes (150 μl) of the reaction mixture into the gas chromatograph showed that the sum of the responses of the elec-

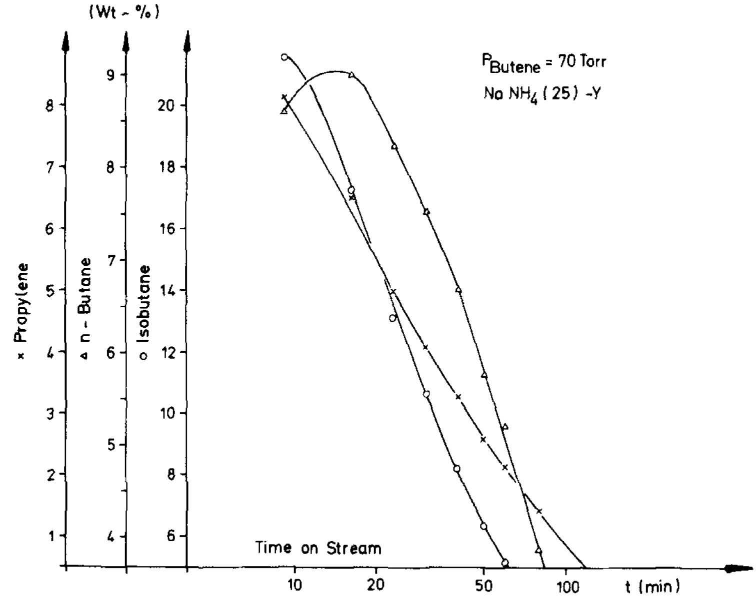

FIG. 1. Change of the product distribution with time on stream at a butene-1 partial pressure of 70 Torr.

tronic integrator of all compounds was about 30% lower at the beginning of the reaction than at higher time on stream. This is shown by the dashed line in Fig. 3. This induction period for the product effluent can only be attributed to chemisorption, because physisorption of butene is impossible at temperatures of 350°C.

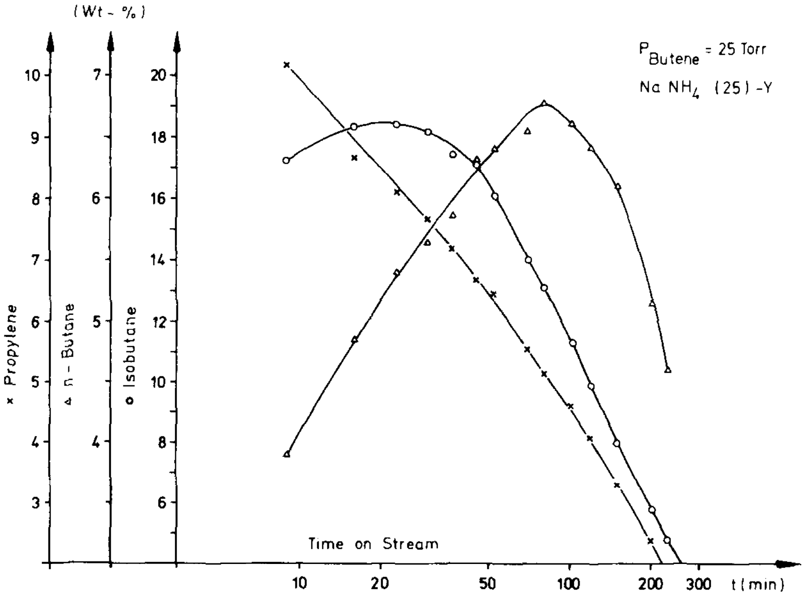

FIG. 2. Change of the product distribution with time on stream at a butene-1 partial pressure of 25 Torr.

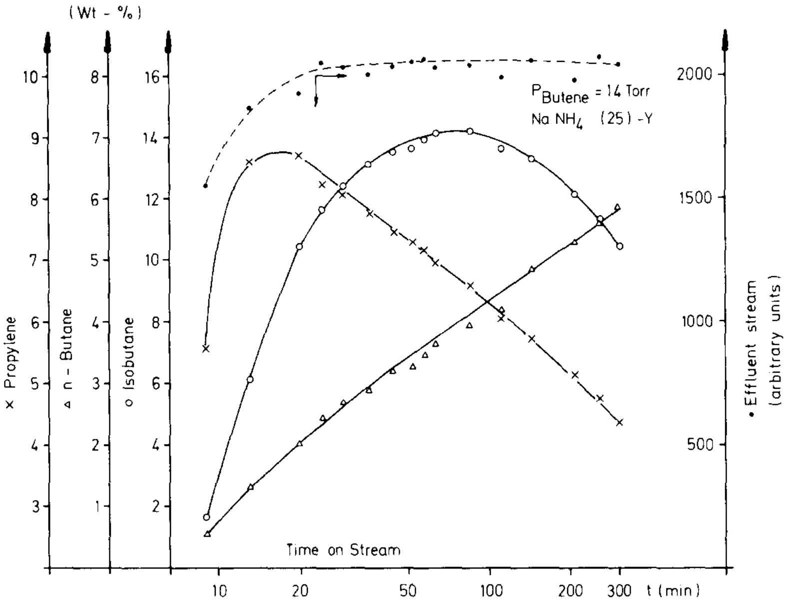

FIG. 3. Change of the product distribution and adsorption of butene on the catalyst (---) with time on stream at a butene partial pressure of 14 Torr.

Influence of Exchange Level

Both the duration of the induction periods and the degree of conversion are dependent on the exchange degree of the catalyst. At low exchange degrees (Fig. 4) the induction periods drift to much higher time and the maxima are weaker. With a zeolite of an exchange level of 6% (NaNH$_4$(6)–Y) even at a partial pressure of

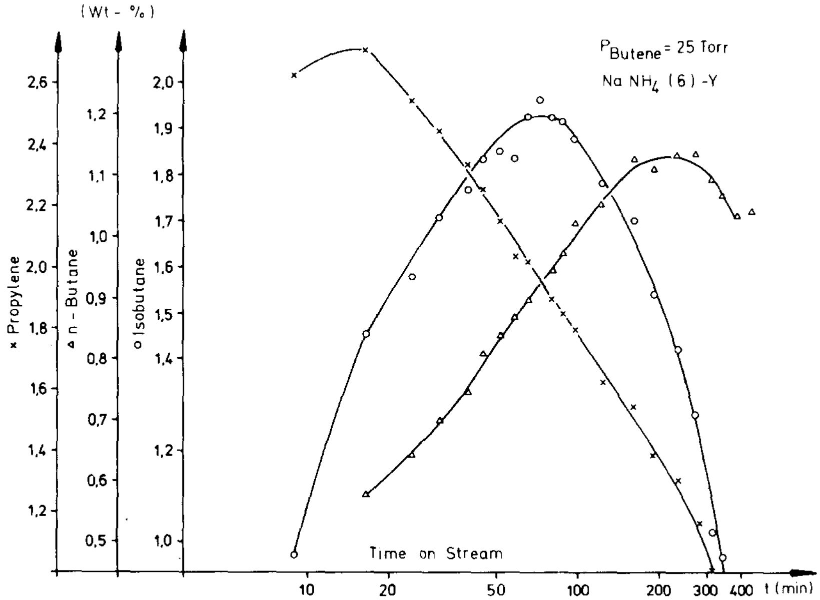

FIG. 4. Change of the product distribution with time on stream with a low-exchanged NaH–Y catalyst (p_{butene} = 25 Torr).

25 Torr a maximum for C_3 can be observed (Fig. 4), and the maximum for *n*-butane drifts from 100 min with the $NaNH_4(25)$–Y catalyst (Fig. 2) to 250 min with the $NaNH_4(6)$–Y catalyst. The loss of activity at low exchange levels has different consequences for the three compounds. In comparison with the maximum values in Fig. 2 the C_3 portion falls to one-quarter, the *n*-butane to one-sixth, and the isobutane even to one-tenth.

In Fig. 5 the dependence of the induction period and of the maximum amounts of *n*-butane on the exchange degree is shown. At high exchange degrees only short induction periods for *n*-butane are observed and it could be established that at exchange levels above 70% the induction period for isobutane disappears. A similar observation was made by Karge and Ladebeck (*12*), who observed an induction period for the conversion of ethylene on mordenite catalysts only for the weakly acidic LaM and BeM, and not for the strongly acidic HM. From Fig. 5 it follows that even at low exchange degrees the catalyst shows activity for cracking and hydride transfer, which is in contrast to the results of Galuszka *et al.* (*13*) who have shown by temperature-programmed desorption of butene-1 from HY that polymerization, cracking, and hydride transfer occur only at exchange degrees greater than 12%. At exchange degrees greater than 40% the conversion of the butenes reaches a limiting value of roughly 85%. This high degree of conversion may be the reason why higher exchange levels of the zeolite do not influence the conversion of the olefin under these reaction conditions.

Influence of Reaction Temperature

The dependence of the reaction temperature on the conversion and the induction periods at various pressures is summarized in Table 2. The influence of temperature is opposite to the influence of the exchange level. At higher temperatures the conversion increases and the induction periods drift to longer times. Also, deactivation of the catalyst is more rapid at lower temperature, although conversions are much lower. It takes about 150 min to decrease the amount of C_3 to one-half of the initial value at a reaction temperature of 400°C, while the same effect is obtained within 50 min at

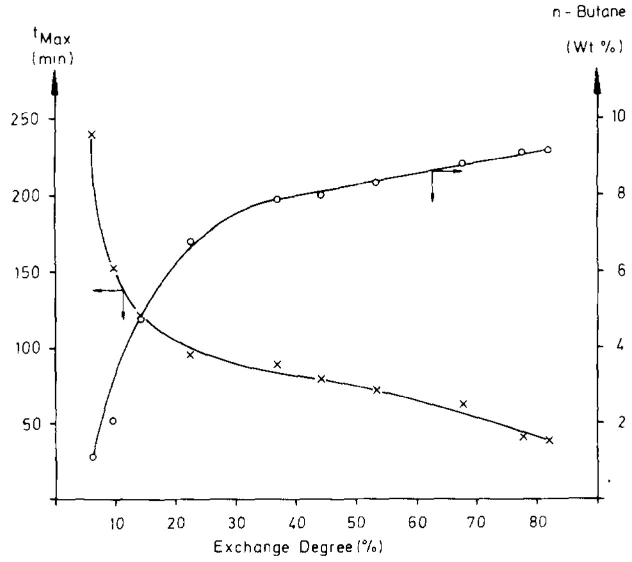

FIG. 5. Duration of the induction period and maximum value for *n*-butane as a function of exchange degree of the zeolite (p_{butene} = 25 Torr).

TABLE 2

Influence of the Reaction Temperature on the Induction Periods of *n*-Butane and Isobutane at Various Butene Partial Pressures[a]

	Temperature (°C)								
	400	400	400	350	350	350	300	300	250
p_{butene} (Torr)	70	40	25	70	40	25	40	25	25
$t_{\mathrm{max,butane}}$ (min)	36	70	114	16.5	50	90	25	35	33
Butane$_{\mathrm{max}}$ (wt%)	9.9	8.9	9.5	9.0	7.6	6.8	5.5	5.1	4.3
$t_{\mathrm{max,isobutane}}$ (min)	—[b]	26	55	—[b]	—[b]	22	—[b]	—[b]	—[b]
Isobutane$_{\mathrm{max}}$ (wt%)	23.6	20.3	22.4	21.5	20.0	19.0	16.3	16.7	16.7

[a] Reaction conditions: $\tau = 0.39$ g catalyst · s · cm^{-3}; catalyst: calcined $NaNH_4(25)$–Y.

[b] No maximum observed, wt% after 9 min on stream.

250°C under equal conditions (25 Torr). This may be due to the high adsorption of butene at low temperatures at the beginning of the reaction. At 250°C and 25 Torr butene partial pressure more than 50% of the butene feed was adsorbed on the catalyst at the initial stage of the reaction.

DISCUSSION

The appearance of different induction periods for the reaction products from the reaction of olefins on solid acids has not been observed until now. There may be several reasons for this. First, the time dependence of these reactions has been hardly investigated, and second, the present results demonstrate that distinct induction periods are only visible, if the reactions are carried out at high reaction temperatures, at low olefin partial pressures and with a catalyst which is not too acidic.

The induction periods for the paraffins *n*-butane and isobutane clearly demonstrate the important role of the coke precursors for the extent of hydride-transfer reactions. At the beginning of the reaction substances must be built up on the catalyst surface, which are able to act as a hydrogen source for the olefins. This is supported by the relatively high amount of adsorbed butene at the initial stage of the reaction, which is particularly pronounced in the experiments at low olefin pressures and at low temperatures. Therefore, the maxima for paraffin formation can be ascribed to two opposite effects:

(1) the increasing amount of coke precursors with time on stream, which builds up a high hydrogen transfer potential,
(2) the general decrease of carboniogenic activity with time on stream.

In order to obtain a maximum, the accumulation of available hydrogen must occur at a higher rate than the deactivation of the catalyst. The time lag between the maxima of *n*-butane and isobutane could be attributed to the fact that the decrease of activity affects the formation of *n*-butane less strongly than the formation of cracking products such as isobutane, because cracking products are formed in sequential reactions in many steps. The sensitivity of cracking products to the number of active centers is confirmed by the more rapid decrease of the amounts of C_3 and isobutane with time on stream, compared with the decrease of *n*-butane (Fig. 1). This leads to a drift of the induction periods to earlier times for the saturated cracking products like isobutane or isopentane. The time lag between the maxima of *n*-butane and isobutane could alternatively be explained by different sites at which these reactions take place. So the sites of cracking may be poisoned more rapidly than the sites of hydride transfer (*14*). By reducing the olefin partial pressure or the exchange level of the zeolite catalyst both the rate of building up hydrogen-delivering compounds and the rate of deactivation of the catalyst are lowered, which causes a drift of the maxima to longer induction periods. At low reaction temperatures polymerization is favored over cracking and hydride transfer. This is indicated by the large extent of chemisorption of butene when the reaction starts. The polymerization products block the pores of the zeolite so that deactivation is more rapid at low reaction temperatures, resulting simultaneously in a short induction period. Although the polymerization products possess a high hydride-transfer potential, hydride transfer is disfavored, because diffusion of the reactants is strongly restricted by pore blocking. That deactivation at low reaction temperatures is attributed to pore blocking rather than to chemisorption of highly condensed aromatics on active sites of the zeolite is confirmed by the color of the catalyst after reaction. At high temperatures, the catalysts were black after reaction, while at low temperatures they had a brownish color, which may be a hint to the low aromaticity of the coke.

Initially, it was surprising that there was found a distinct reproducible maximum for the C_3 hydrocarbons at the beginning of the reaction at very low butene partial pressures (Fig. 3), respectively at low exchange levels (Fig. 4). At roughly the same time on stream maxima for the sum of C_5 hydrocarbons and for the sum of i-C_4 hydrocarbons were also obtained. These induction periods cannot be explained by the reaction scheme discussed above. Therefore, it must be assumed that—at least in part—cracking products are derived from coke precursors and not only from dimers or trimers of the butene. This assumption is supported by the product distribution. In no experiment were aliphatic compounds found with more than 8 carbon atoms. For that reason an oligomerization of butenes to linear trimers appears to be unlikely. But, assuming a dimerization–cracking mechanism for the molar quantities the following must be valid: $C_3/C_5 = C_2/C_6 = C_7/C_1 = 1$. Table 1 shows that this assumption does not correspond to the experimental results. Therefore, other intermediates must be responsible for the formation of the cracking products.

The induction periods even for unsaturated cracking products indicate that there must be a close connection between cracking and coke-formation reactions. It is more likely that the coke precursors are cyclic hydrocarbons rather than aliphatic oligomers of the butenes, because possible coke precursors such as alkylated benzenes or naphthalenes and alkylated cyclopentanes and cyclohexanes were identified by gc/ms analysis and by kovats indices. Therefore, a new formal reaction scheme (Fig. 6) for cracking and coke formation is proposed. The olefins—either the butenes themselves

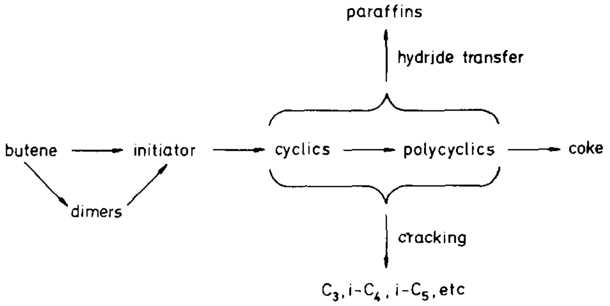

FIG. 6. Formal reaction scheme for the reaction of butene on NaH–Y.

or the dimers—react first to an unknown initiator which can start the cyclization reaction. Although the mechanism of the cyclization reactions is not well understood up to now, it is generally assumed that ring formation occurs by an intramolecular reaction of long-chain dienes catalyzed by Brønsted sites (*15, 16*). Nevertheless, from experiments carried out with butadiene on dehydroxylated NaH–Y we have provided some evidence that cyclization may also proceed by Diels–Alder addition catalyzed by Lewis sites (*17*). So it may be speculated that dienes—formed by hydride transfer during the reaction—undergo a Diels–Alder addition with olefins, leading first to monocyclics, which may grow rapidly to polycyclics by further Diels–Alder additions.

It is proposed (Fig. 6) that from both the monocyclics and the polycyclics the observed cracking products should be formed. It is well known that alkylated cyclohexanes and aromatics can undergo so-called "paring reactions" under (hydro)cracking conditions (*18–20*). These reactions lead to the formation of high amounts of isobutane with lower yields of isopentane and propane under preservation of the ring structure. Similar product distributions are obtained in the reaction of butene-1 on calcined NaNH$_4$–Y (Table 1). Both the observed induction periods for the formation of the cracking products and the similarity of the product composition could be explained by the hypothesis that the formation of cracking products in the reaction of lower olefins proceeds to a great deal by the paring reaction of substituted cyclic compounds. A possible reaction scheme for these reactions is shown in Fig. 7. The main reactions are rearrangements by alkyl shifts and ring contractions leading to i-propyl and t-butyl groups, which can easily be split off. This mechanism is in accordance with the experimental observation that the relative amount of propylene and propane in the reaction mixtures increases with increasing reaction temperatures, indicating that splitting off an i-propyl group becomes faster than the migration of a methyl group. It is probable that the paring reactions are not restricted to monocyclic compounds, but proceed also with oligocyclic coke precursors which are strongly adsorbed on the catalyst.

The discrepancies between the relatively low amounts of coke formed during the time on stream and the high amounts of cracking products may be easily explained by an alkylation–rearrangement–dealkylation mechanism shown in Fig. 8: the cyclics are alkylated by olefins and then undergo a reverse paring reaction leading to methylated and ethylated cyclics which can crack again in the way shown in Fig. 7. This mechanism receives support from

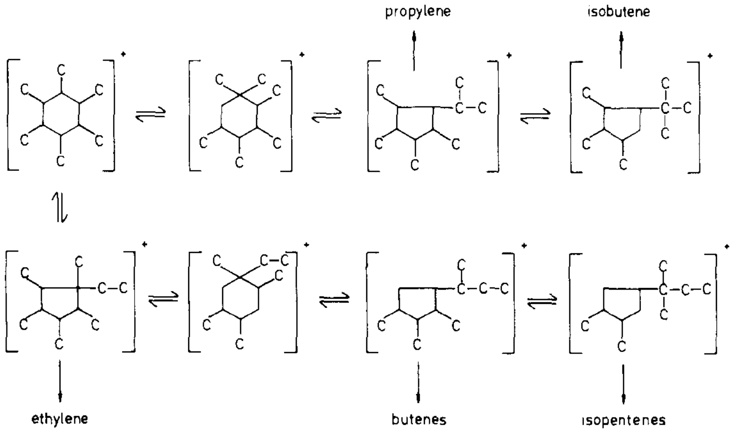

FIG. 7. Possible cracking mechanism of highly alkylated cyclic hydrocarbons ("paring reactions").

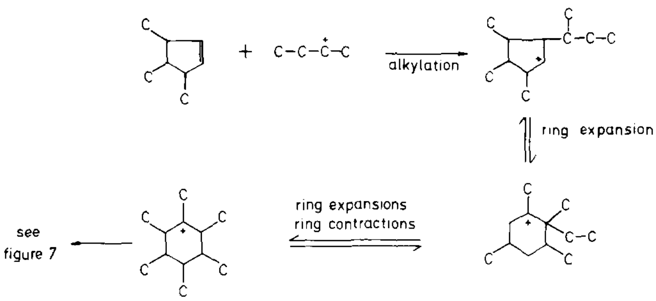

FIG. 8. Alkylation of cyclic hydrocarbons with butene.

investigations by Langlois and Sullivan (*20*) who have reported fast isomerization reactions of i-butylcyclohexane under hydrocracking conditions. Furthermore such reactions are known from alkylation reactions of cyclics with olefins in sulfuric acid (*21*) and hydrogen fluoride (*22*). The fast isomerization reaction could also offer an explanation for the fact that in the reactions of different olefins on solid acids isobutane is always a main cracking product (*1–6*), because the structure of the alkylating olefins plays a minor role for the structure of the formed cracking products if fast isomerization reactions precede cracking. Thus, it is postulated that the ring structure acts like a co-catalyst together with an acidic site of the zeolite for the formation of the cracking products.

The olefinic cracking products and the starting olefin can partly react to paraffins by abstracting hydrogen from the cyclic compounds via carbenium ions (e.g., investigations of Shephard *et al.* (*4*) have shown that cyclic compounds such as tetralin have a high hydride-transfer potential). At the same time the cyclic coke precursors become more hydrogen deficient and the extent of hydride transfer determines the aromaticity of the coke, which is higher at high reaction temperatures than at low reaction temperatures.

CONCLUSIONS

The different time-drifted induction periods for the reaction products in the reaction of butene-1 on NaH–Y at temperatures above 250°C can only be explained by the important role of coke precursors in the reaction sequence. First of all, this is valid for the hydride-transfer reactions which lead to a high amount of paraffins, but a short induction period for the unsaturated cracking products and a product distribution which does not correspond to a simple dimerization–cracking mechanism suggest the participation of coke precursors in the cracking reactions, too. The cyclic compounds in the reaction mixture could be a hint that the coke precursors possess cyclic structures. A detailed mechanism is proposed in which cyclic coke precursors act like a cocatalyst for the initiation of cracking reactions.

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REFERENCES

1. Weeks, T. J., Angell, C. L., Ladd, I. R., and Bolton, A. P., *J. Catal.* **33**, 256 (1974).
2. Bolton, A. P., and Weeks, T. J., *Trans. Faraday Soc.* **70**, 1676 (1974).
3. Örhalmi, O., and Fejes, P., *in* "Proceedings, Symposium on the Mechanisms of Hydrocarbon Reactions" (F. Marta and D. Kallo, Eds.), p. 457. Elsevier, Amsterdam, 1975.
4. Shephard, F. E., Rooney, J. J., and Kemball, *J. Catal.* **1**, 379 (1962).
5. Eberly, P. E., *J. Phys. Chem.* **17**, 1717 (1967).
6. Liengme, B. V., and Hall, W. K., *Trans. Faraday Soc.* **62**, 3229 (1966).

7. Venuto, P. B., and Hamilton, L. A., *Ind. Eng. Chem. Prod. Res. Develop.* **6,** 190 (1967).

8. Eberly, P. E., Kimberlin, C. N., Miller, W. H., and Drushel, H. V., *Ind. Eng. Chem. Process Des. Develop.* **5,** 193 (1966).

9. Rollmann, L. D., and Walsh, D. E., *J. Catal.* **56,** 139 (1979).

10. ASTM Special Technical Publication No. 343, Compilation of GC Data, American Society of Testing and Materials, Philadephia.

11. Chevalier, F., Guisnet, M., and Maurel, R., *in* "Proceedings, 6th International Congress on Catalysis, London, 1976" (G. C. Bonds, P. B. Wells, and F. C. Thompkins, Eds.), p. 478. The Chemical Society, London, 1977.

12. Karge, H. G., and Ladebeck, J., *Acta Phys. Chem.* **24**(1–2), 161 (1978).

13. Galuszka, J., Baranski, A., and Ceckiewicz, S., *Trans. Faraday Soc.* **74,** 146 (1978).

14. Karge, H. G., private communication.

15. Poutsma, M. L., *in* "Zeolite Chemistry and Catalysis," ACS Monographs 171 (J. A. Rabo, Ed.), p. 437, Amer. Chem. Soc., Washington, D. C., 1976.

16. Gates, C. G., Katzer, J. R., and Schuit, G. C. A., "Chemistry of Catalytic Processes." McGraw–Hill, New York, 1979.

17. Langner, B. E., and Meyer, S., paper to be presented at the "Symposium on Catalyst Deactivation, Oct. 11–14, 1980, Antwerp."

18. Sullivan, R. F., Egan, C. J., Langlois, G. E., and Sieg, R. P., *J. Amer. Chem. Soc.* **83,** 1156 (1961).

19. Egan, C. J., Langlois, G. E., White, R. J., *J. Amer. Chem. Soc.* **84,** 1204 (1962).

20. Langlois, G. E., and Sullivan, R. F., *Advan. Chem. Ser.* **97,** 38 (1970).

21. Pines, H., and Ipatieff, V. N., *J. Amer. Chem. Soc.* **67,** 1631 (1945).

22. Schneider, A., *J. Amer. Chem. Soc.* **76,** 4938 (1954).