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Can Macroscopic Parameters, Such as Conversion and Selectivity, Distinguish between Different Cracking Mechanisms on Acid Catalysts?

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***n*-heptane cracking has been carried out for very short time periods on an established reaction mechanism which includes the following group of stream reactions on different zeolites: Initiation reactions (protolytic cracking), charge isomerization, chain isomerization, hydride transfer, β-scission–alkylation, desorption–adsorption, and hydrogen transfer–cyclization. It has been observed that a given experimental distribution of products can be explained by more than just one reaction scheme. This does not allow one to clearly distinguish the fraction of reactant which disappears via monomolecular initiation reactions with respect to bimolecular hydride transfer reactions.** © 1997 Academic Press

INTRODUCTION

Paraffin cracking has been, and still is, one of the most widely used test reactions employed to investigate cracking mechanisms (1–11). From recently reported literature it appears that the cracking of a paraffin occurs via two mechanisms which work in a concerted manner (2, 4–7, 12–15), such that it is believed that the initiation step in the cracking of paraffins on solid acids is a monomolecular one which involves the attack of a Brönsted acid site, to either a C−C or a C−H bond. This attack yields a penta-coordinated carbonium ion which evolves by protolysis giving either a shorter paraffin and the complementary adsorbed carbenium ion, or H_2 while leaving behind a carbenium ion of the original reactant.

The smaller carbenium ion adsorbed on the surface can either desorb as an olefin, or start a second cracking mechanism which involves a hydride transfer step from a reactant molecule, followed by the β-scission of the subsequent carbenium ion generated on the reactant (bimolecular cracking process). There is no doubt that the adsorbed carbenium ions formed may isomerize before cracking takes place so that one does not need to invoke a different mechanism to explain reactant isomerization.

As well as these reactions there are others that contribute to make the olefin/paraffin ratio observed different to one expected to take place from a simple cracking process, namely disproportionation and hydrogen transfer reaction, the latter being responsible for forming more paraffins than expected at the expense of olefins to yield hydrogen-deficient products, aromatics, and coke (1, 14, 15).

On the other hand, some disproportionation reactions also increase the proportion of paraffins due to the fact that two molecules of reactant yield three molecules of product. According to the literature, the disproportionation reaction can occur either by oligomerization of olefins followed by cracking (3, 6, 15), or via the attack of a carbenium ion on a reactant paraffin followed by protolytic cracking (2, 16).

Up until now the contributions of each one of the mechanisms has been established either approximately by considering the selectivities of certain products (17), or in a more exact manner by establishing reaction schemes which are able to correlate with the product distribution. Following the second approach Lukjanov *et al.* (6) determined the rate constants for protolytic cracking and hydride transfer for *n*-hexane cracking by comparing the dependence of the experimental product distribution obtained at different contact times, with theoretical values predicted by a mathematical model. Other significantly valuable work by Zhao *et al.* (1) established the conservation equations by making use of the initial selectivities of the reaction products. However, in both cases some hydrogen transfer reactions take place in the reaction scheme that are not independent. Hence, the validity of the numerical parameters obtained is limited.

If the dependent reactions are eliminated a model would be obtained that, while fitting the experimental results with the same precision, the relative participation of the uni- and bimolecular mechanisms would change.

Moreover, in work previously done (1, 18) the conservation equations were not applied to the intermediate carbenium species, such that a system of linear equations which contained more unknowns that equations was produced.

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In order to resolve this, certain equations must be employed and certain unjustified optimizations need to be carried out.

In the present work we have developed a systematic procedure to establish the independent reactions which generate a valid reaction scheme for the cracking of *n*-heptane from the initial selectivities calculated at very short times on stream, i.e. in the absence of deactivation. Our procedure enables one to avoid assuming and applying optimization techniques.

In this way one is able to show if it is possible to fit the experimental data to a reaction scheme and to certify if this is the only possible route through which the catalytic cracking process occurs.

EXPERIMENTAL

Material

n-heptane (99+%) was obtained from Aldrich and was used without further purification. N_2 (99.999% purity) was used as the carrier gas.

USY-24.46 (unit cell 24.46 Å), USY-24.31 (unit cell 24.31 Å), ZSM-5, and beta catalysts were prepared using standard synthesis procedures. Details of the preparation and characterization of the samples are presented elsewhere (19). The final samples were pelletized, crushed, and sieved, such that particles with 0.30–0.50 mm were used.

Reaction Procedure

The experiments were carried out at 500°C and atmospheric pressure in a fixed bed continuous glass reactor. The reactor was heated in an electric furnace. The catalyst was diluted with SiO_2 (BASF) and the length of bed was maintained constant. The N_2/Reactant molar ratio was always 9. The flow of hydrocarbon was 7.7×10^{-6} mol s^{-1}. The reactor exit was connected to a multisampling computer controlled heated valve equipped with a hydrocarbon detector at the outlet of the valve in order to detect the moment when the hydrocarbon fills the first loop. This moment is considered to be the zero reaction time, and the sample is kept in the first loop automatically. The rest of the loops were automatically filled at programmed time on stream. After the experiment was finished the samples were separated in a 100 m. Supelco-Petrocol capillary column and in a Porapack Q + silica packed column and analyzed by GC using two detectors (TCD and FID). The contact time was varied between 1.47 and 91.63 kg s m^{-3} by changing the weight of catalyst.

THEORY

In this section we will introduce the basic theoretical concepts that will be employed in this work. We define product yield as the number of moles obtained of a given product per mole of reactant fed. Product selectivity (S_j) is the number of moles of the product j per mole of reactant converted. The reaction selectivity (RS_i) is defined as the rate of reaction i divided by the rate of reactant disappearance. Finally, the reaction network, represents the set of R reactions which are considered in order to explain the formation and distribution of products observed experimentally.

In agreement with the above definitions and the mass balance equations, the selectivity of a reaction product or in general to any of the species present in the network can be calculated by means of the equation

$$\sum_{i=1}^{R} \nu_{ij} RS_i = S_j, \qquad [1]$$

where ν_{ij} represents the stoichiometric coefficient for the species j ($j = 1, 2, \ldots, k, \ldots, S$, k being the reactant species) in the reaction i ($i = 1, 2, \ldots, R$). This expression can also be applied to the reactant, i.e., $j = k$, if one takes into account that in this case S_k should be -1, defining what has been named in this the paper as the reactant reaction selectivity ($\mathrm{RRS} = \sum \nu_{ik} RS_i = S_k = -1;\ i = 1, 2, \ldots, R$).

In matrix terminology, Eq. [1] can be written as

$$\Gamma^T \boldsymbol{RS} = \boldsymbol{S}, \qquad [2]$$

where Γ is the $R \times S$ matrix of the stoichiometric coefficients, $\boldsymbol{RS}$ is the reaction selectivity vector, and $\boldsymbol{S}$ is the species selectivity vector.

If one knows, or can propose, a reaction scheme and certain conditions are fulfilled, it is possible to calculate from the selectivities obtained experimentally the selectivities for each one of the reactions. Thus, in this way it is possible to see how the selectivities are modified with changing the reaction conditions. The conditions referred to above are obvious in mathematical terms and are primarily that the Γ matrix should be square and nonsingular. Thus, the nonsingularity of the matrix depends on the fact that the set of reactions which conform to the network are all independent. It is, therefore, necessary to carefully select the reactions or the steps involved in order to avoid any one being a linear combination of the others. Aris and Mah (20) and, more recently, Smith and Missen (21) have proposed a procedure to determine the maximum number of independent reactions which exist in a given reaction network. These researchers have proposed generating matrix, $\mathbf{A}$, with as many columns as chemical species that are involved in the reaction network and as many rows as elements that exist in the system. A chemical species is a chemical entity which can be distinguished from another by either its molecular formula, molecular structure (in the case of isomers), or by the phase in which it is present. Meanwhile, the list of elements may include any atom or isotope present in the system (even if it is an inert one), as well as the electric charge in the case of ionic species. The coefficients a_{ij}, of this matrix are the number of elements of type *i* contained in the species *j*. Hence, the authors (20, 21) conclude that the maximum number of independent reactions is always given by the expression:

$$\text{Number of reactions} = \text{Number of species} - \text{Range } \mathbf{A}. \qquad [3]$$

In order to clarify further we have applied Eqs. [1]–[3] to a particular case in Appendix A.

Our objective will be, therefore, to establish one or several networks for the reaction of *n*-heptane cracking which fulfill Eq. [3]. In this way it will be possible to obtain the selectivities to each one of the reactions by solving Eq. [2].

RESULTS AND DISCUSSION

Initial Product Selectivity and Reaction Network

Figure 1 shows the yields versus conversion for selected products obtained in the cracking of *n*-heptane on different catalysts. From them and following the methodology described elsewhere (22) the initial selectivities at zero conversion level were determined by measuring the slope of

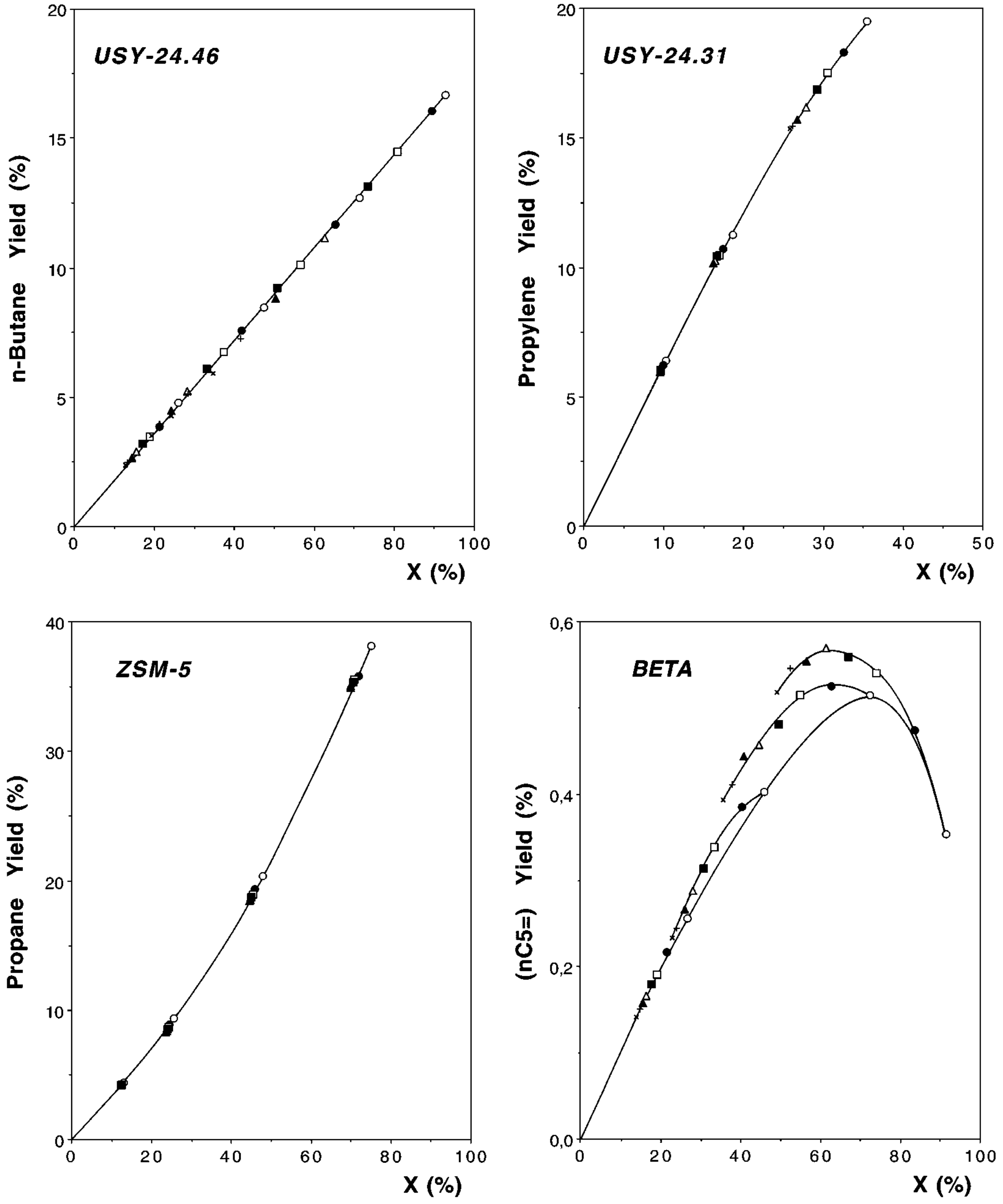


FIG. 1. Experimental selectivity curves for *n*-heptane cracking over different catalysts. Molar yield (%) of product vs conversion *X* (%). (TOS [s] → ○, 0; ●, 6; □, 18; ■, 39; △, 90; ▲, 180; +, 330; ×, 600).

TABLE 1

Initial Molar Selectivities and Product Type for *n*-Heptane Cracking

	USY 24.46		USY 24.31		BETA		ZSM5	
Product	IS_j	Type	IS_j	Type	IS_j	Type	IS_j	Type
Hydrogen	-	-	0.0517	1+2 S	0.0969	1+2 S	0.1845	1+2 S
Methane	0.0135	1+2 S	0.0922	1+2 S	0.0331	1+2 S	0.0461	1+2 S
Ethane	0.0199	1+2 S	0.1505	1+2 S	0.0309	1+2 S	0.2043	1 S
Ethylene	0.0429	1+2 S	0.0645	1+2 S	0.0995	1+2 S	0.2377	1+2 S
Propane	0.4741	1+2 S	0.3136	1+2 S	0.4368	1+2 S	0.3392	1+2 S
Propylene	0.6237	1 U	0.6224	1 U	0.5781	1 U	0.7186	1 U
n-Butane	0.1799	1 S	0.1756	1 S	0.2106	1 S	0.1721	1 S
i-Butane	0.2773	1+2 S	0.1449	1+2 S	0.2085	1+2 S	0.0286	1+2 S
nC4$^{=}$	0.2011	1 U	0.2606	1 U	0.2079	1 U	0.2617	1 U
i-Butene	0.1327	1 U	0.1736	1 U	0.1515	1 U	0.1674	1 U
n-Pentane	0.0173	1 U	0.0368	1 U	0.0217	1 U	0.0176	1 U
i-Pentane	0.0288	1+2 U	0.0417	1 S	0.0186	1+2 S	0.0033	1+2 S
nC5$^{=}$	0.0087	1 U	0.0114	1 U	0.0102	1 U	0.0155	1 U
bC5$^{=}$	0.0193	1 U	0.0297	1 U	0.0226	1 U	0.0347	1 U
n-Hexane	-	-	0.0011	1 U	0.0013	1+2 U	0.0000	2 U
bC6	0.0005	1+2 U	0.0033	1 U	0.0012	1+2 U	0.0000	2 U
nC6$^{=}$	-	-	-	-	-	-	0.0000	2 U
bC6$^{=}$	-	-	-	-	0.0005	1+2 U	0.0000	2 U
bC7	-	-	-	-	0.0022	1 U	0.0032	1+2 S
C7$^{=}$	-	-	-	-	-	-	-	-
Benzene	0.0000	2 S	-	-	0.0021	1+2 S	0.0000	2 S
Toluene	0.0017	1+2 S	0.0032	1+2 S	0.0123	1+2 S	0.0000	2 S
bC8	-	-	-	-	-	-	0.0000	2 S
ArC8H10	0.0024	1+2 U	0.0006	1+2 S	0.0047	1+2 S	0.0000	2 S
bC9	-	-	-	-	-	-	-	-
ArC9H12	0.0000	2 U	0.0000	2 U	0.0013	1+2 S	0.0000	2 S
ArC10H14	-	-	-	-	-	-	-	-
Coke CnHm*	(0.0000)	2 S	(0.0000)	2 S	(0.0000)	2 S	-	-
Coke CnHm**	0.0000		0.0000		0.0000		-	
$\Sigma\ IS_j \cdot C_j$	7.0011		7.0006		6.9995		7.0006	
$\Sigma\ IS_j \cdot H_j$	16.0002		16.0012		16.0002		15.9990	

Product Type: 1, primary; 2, secondary; S, stable; U, unstable.

* Coke Weight Selectivity; ** Coke Molar Selectivity with n/m=0.8

IS_j, Initial Molar Selectivity for Product j; C_j,H_j Number of Carbon or Hydrogen Atoms respectively in Product j.

the tangent at the origin (Table 1). By looking at the product distribution obtained, we have constructed a reaction scheme which produces all the species obtained through reaction steps whose participation have been accepted previously (3, 6, 15). These reaction steps are given in Fig. 2 (reactions 1^* to 59^*) and steps can be ordered into groups in the following way:

A. *Initiation reactions or monomolecular protolytic cracking.* This group is formed by the set of reactions 1^* to 6^*, in which one paraffin and one primary carbenium ion which should rapidly isomerize through reactions 7^* to 9^* and 11^* to a more stable secondary carbocation, are always produced.

Recently (23), a pathway for monomolecular cracking which directly produces secondary carbenium ions has been presented. With the reaction scheme proposed in this work, it is possible to arrive at these types of reactions by a simple linear combination of pairs of the reactions: $2^* + 11^*$, $3^* + 9^*$, $4^* + 8^*$, $5^* + 7^*$, by considering this, it would not be necessary to consider the charge isomerization reactions producing secondary carbenium ions from primary ones. The process described does not modify by any means the calculations since one chemical species is eliminated for each discarded reaction, and the equations generated with the new reactions are a linear combination of the previous ones.

B. *Reactions of charge isomerization,* 7^*–12^*. These reactions are responsible not only for the transformation of primary to secondary carbenium ions, but also for the adaptations of the carbenium ions for other reactions, such as those involved in β-scission–alkylation.

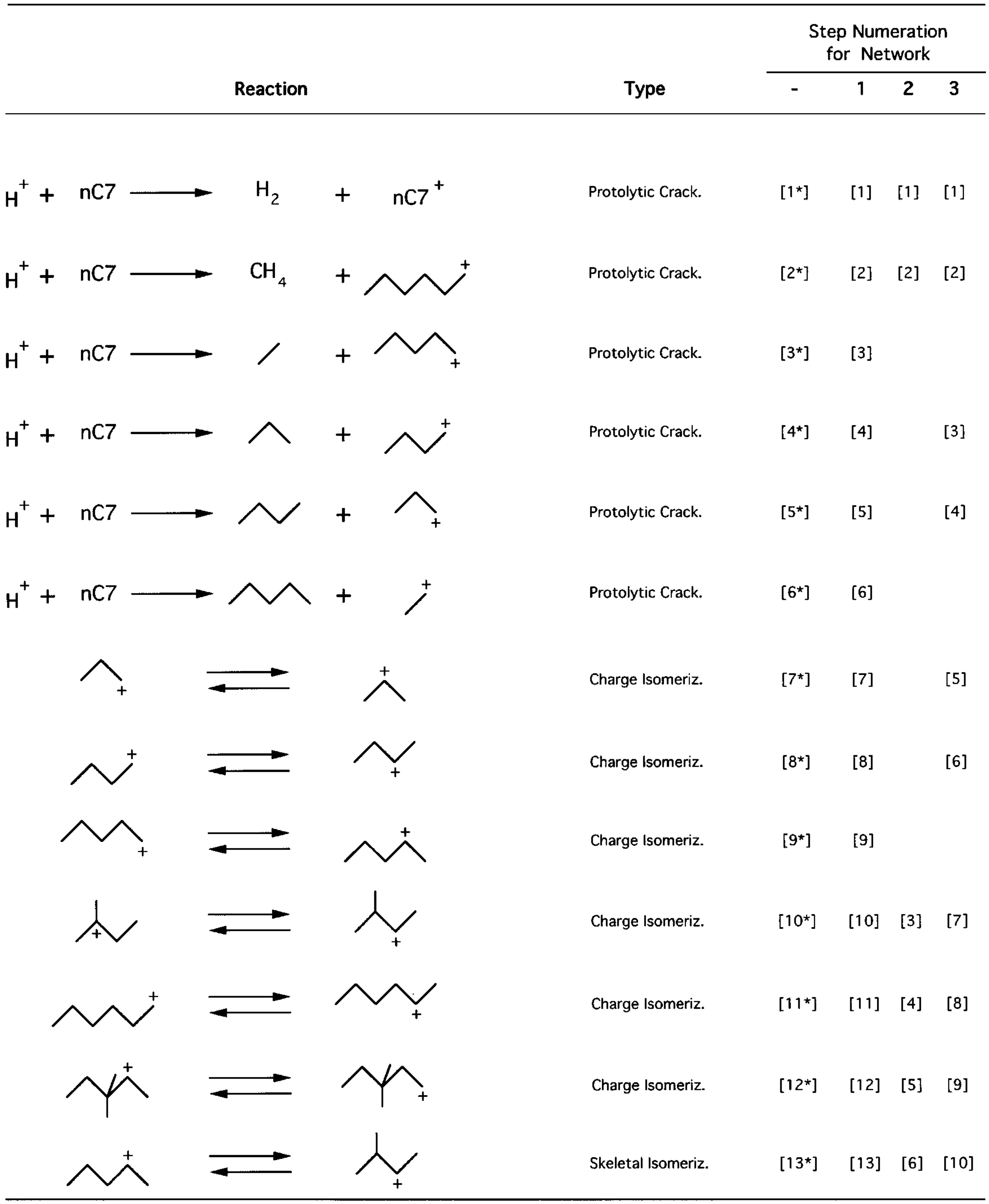


FIG. 2. Possible reaction steps for *n*-heptane cracking on zeolites and numeration of those in each network considered.

C. *Reactions of chain isomerization,* 13*–19*, *which account for the formation of branched isomers.* We have not included the direct isomerization of the nC_4^+ species, to iso-C_4^+ species since it is not favored thermodynamically at the temperatures at which catalytic cracking is carried out. It is accepted that under these conditions C_4 branching occurs via a bimolecular mechanism involving the formation of intermediates of more than six carbon atoms which crack (12, 15, 16, 24, 25). In our case the isobutyl carbenium ion would be formed from the *n*-butyl one with the participation of C_7 species through the following linear combination of reactions: $-32^* - 15^* + 16^* + 33^*$.

D. *Reactions of hydride transfer,* 23*–30*. These are chain propagation reactions and basically produce paraffins

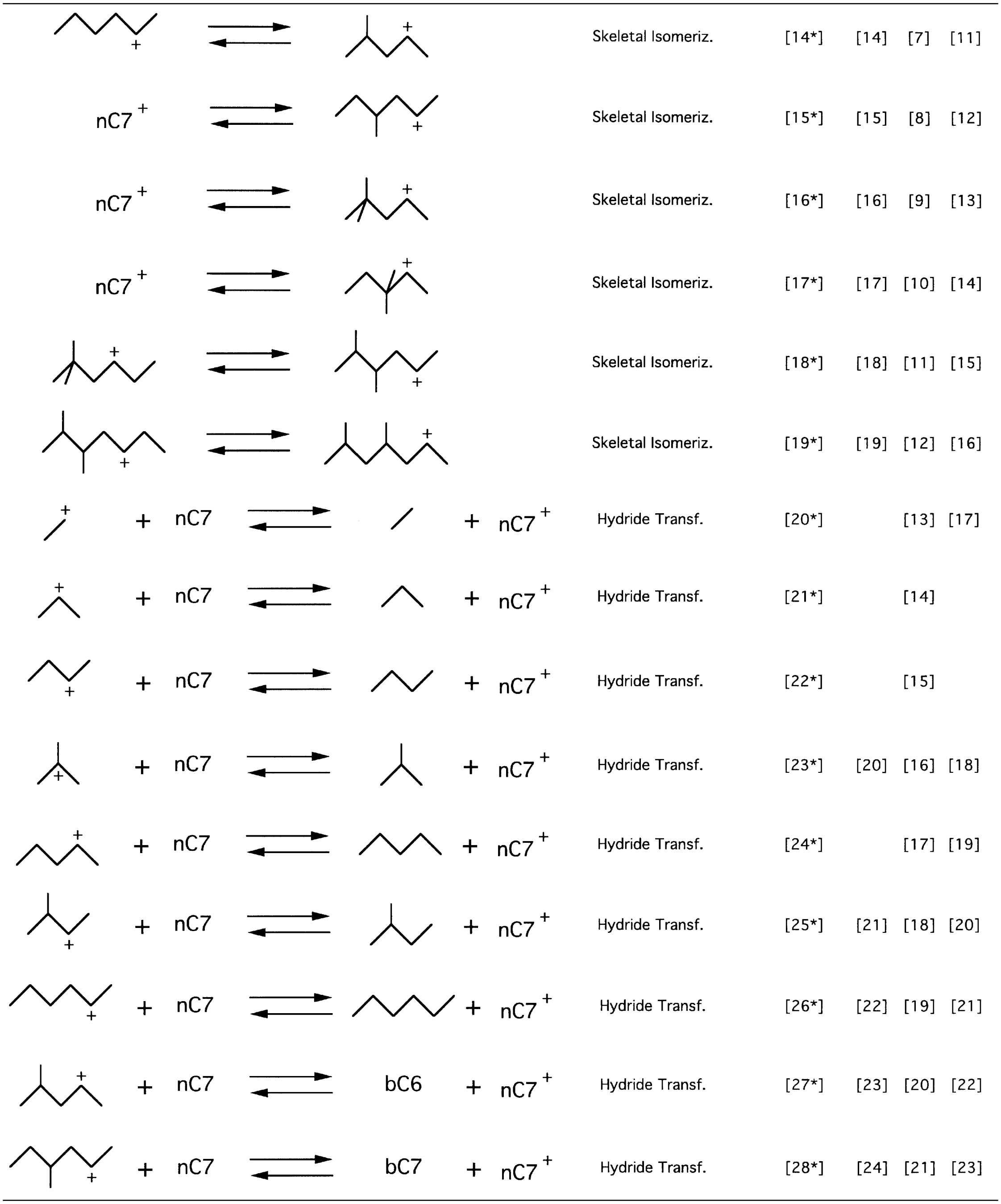
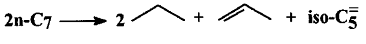


FIG. 2—*Continued*

shorter than the feed. They also generate branched paraffin species.

E. *β-scission–alkylation reactions,* 31*–39*. The forward reaction represents the classical carbenium ion cracking mechanism, while the reverse reaction represents a dimerization between carbenium ions and olefins which do intervene in one type of disproportionation reaction. In this way one disproportionation such as



can be obtained through the reactions

$$2\times 21^* + 15^* + 32^* + 16^* + 33^* + 42^* - 35^* + 18^* + 36^* - 2\times 41^* + 45^*$$

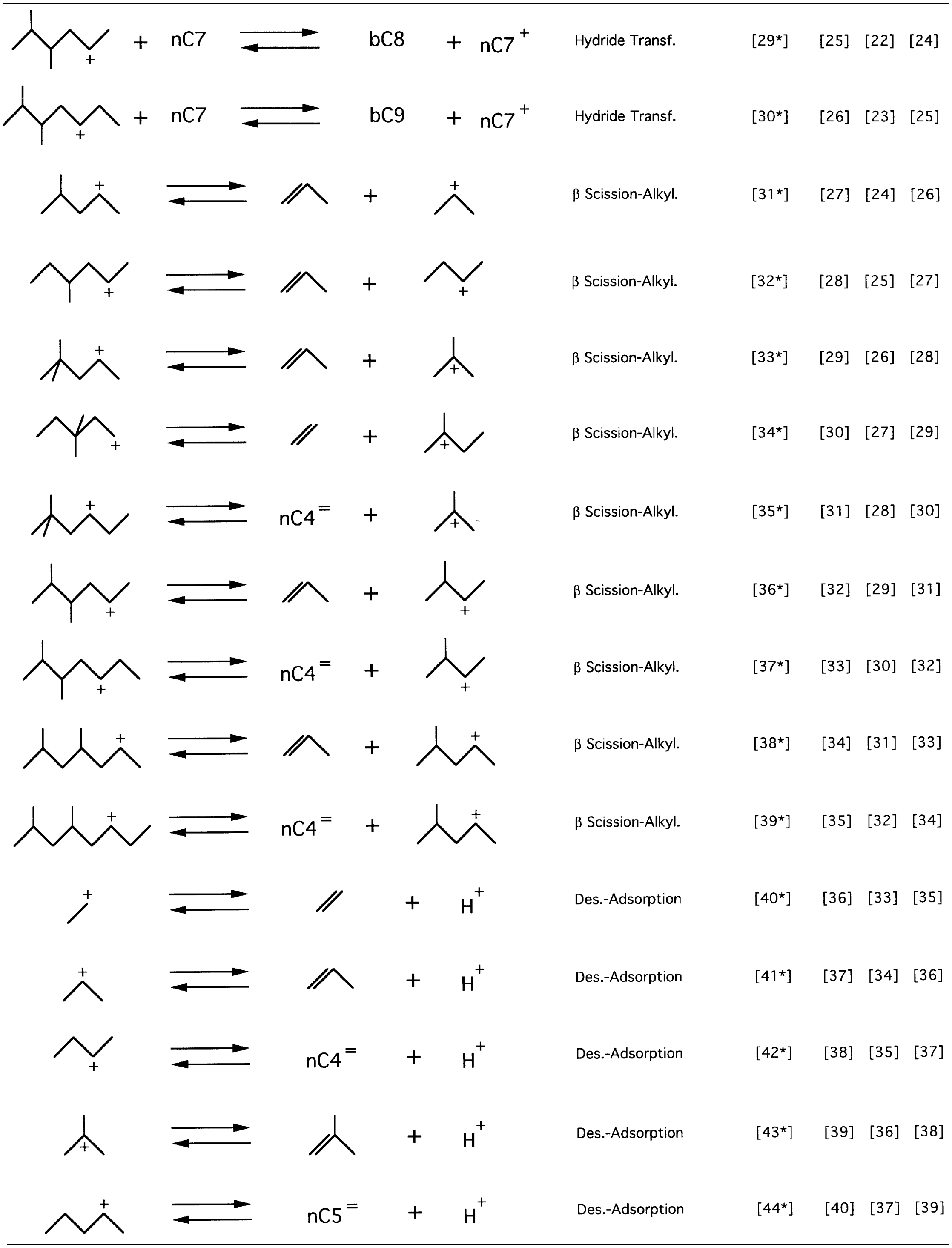
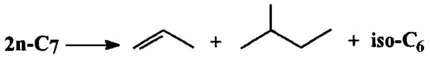


FIG. 2—*Continued*

while another can be obtained such as



can be obtained by

$$36^* + 25^* - 35^* + 18^* + 16^* + 33^* - 41^* - 31^* + 27^* + 15^* + 32^* + 42^*.$$

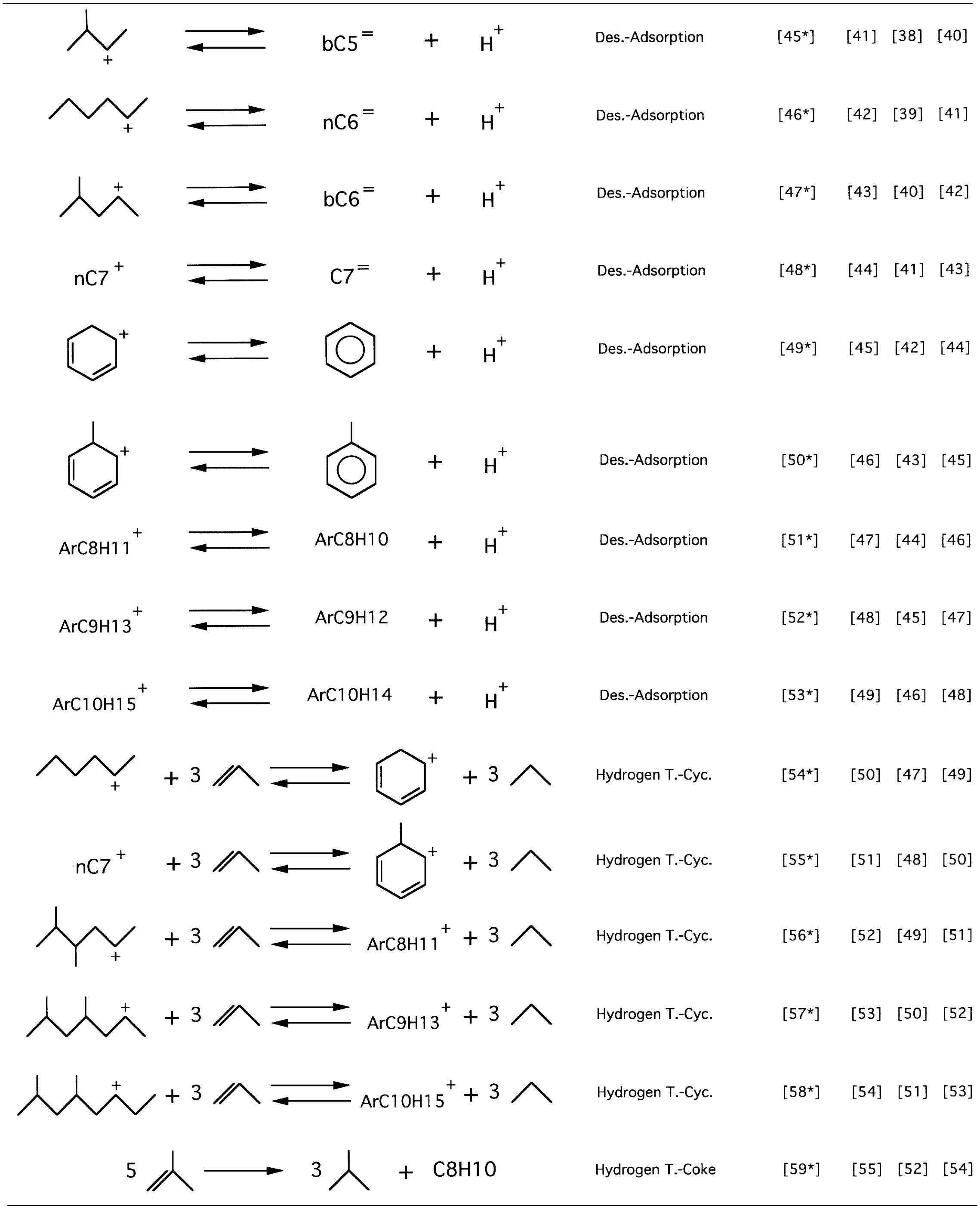


FIG. 2—*Continued*

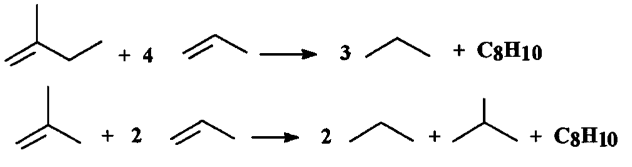
F. *Reactions of desorption–adsorption*, 40*–53*. These represent the liberation and the occupation, respectively, of the active sites of the catalyst. One should in this case write as many reactions of this type as olefins and aromatics that appear in Table 1.

G. *Reactions of hydrogen transfer and cyclization*, 54*–59*, *which are responsible for the formation of aromatics and coke.* They transfer hydrogen from some particular species to forming in this way excess paraffins (C_nH_{2n+2}) from olefins (C_nH_{2n}), utilizing the hydrogen yielded during the formation of less hydrogenated species such as aromatics and coke (C_mH_n, $n < m$).

The reactions considered in the last group should only be considered as representative of the conservation equations and not as true reaction steps. We have used them to explain the formation of aromatics and coke, emphasizing that three molecules of hydrogen, which saturate three olefins, are transferred for each molecule of aromatic formed. The formation of aromatics could occur via olefin oligomerization reactions (26) and/or via cyclization of olefinic carbenium ions (27). Nevertheless, independent of the reaction mechanism that takes place, it is possible to state that the real steps in the formation of aromatics can be obtained by a linear combination of those presented in Fig. 2.

With respect to coke formation, reaction 59^*, we have only intended to establish a chemical reaction which explains the stoichiometric C/H ratio observed by elemental analysis of the coke deposited on the catalysts whose ratio is approximately $C/H = 0.8$. Thus reaction 59^* indicates only this and not that the coke molecule can be described as C_8H_{10}.

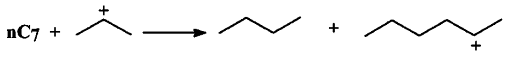
As is well known that coke is a polymeric product with a complex and ill-defined molecular formula; which in the case of paraffin cracking is formed via olefins produced during the cracking process (28). Equation 59^* also indicates that by addition of 8 atoms of carbon and 10 of hydrogen to the coke already deposited on the catalyst, three molecules of hydrogen need to be transferred for the formation of paraffins. It is possible to arrive at the same result when starting from other olefins to form the coke:



Reaction Network Analysis

If one analyzes the 59 reactions listed in Fig. 2, it can be seen that it is not possible to obtain the selectivity for each reaction with the experimental results available. Indeed, in our system there are 58 chemical species, whereas there are only three elements, i.e. carbon, hydrogen, and electric charge. In this case the calculated range of matrix **A**, which contains three rows and 58 columns, is 3. This means that in agreement with Eq. [3], only 55 independent reactions can exist and consequently there are reactions in Fig. 2 which must be obtained by a lineal combination of the others. This is certainly so, for instance in order for reaction 21^* to produce propane via a bimolecular mechanism it must be a result of $4^* + 8^* - 15^* - 32^* + 41^*$. Consequently, the system of linear equations which would be generated using Eq. [2] will not have a solution. The same occurs with reactions 20^*, 22^*, and 24^*. This, therefore, generates the following question: Does it means that reaction 21^* does not occur? The answer to this is that reaction 21^* can occur and very probably will occur. However, if reactions 4^*, 8^*, 15^*, 32^*, and 41^* also occur, it is evident that it is not possible to distinguish, with the experimental data available, between propane coming via a monomolecular mechanism from that coming from a bimolecular mechanism. This conclusion appears logical since, as there is no distinction between the two types of propane, we think that the reaction network should not be considered as something which strictly represents the mechanism through which the reaction occurs, but rather as a scheme which allows one to follow the formation of all the chemical species, taking into account that any real step will be obtained as a linear combination of the steps present in the network. For instance, should the hydrogen transfer reaction be developed as it has been established in Fig. 2? Probably not. However, it becomes clear that the real steps of hydrogen transfer can be obtained by a linear combination of the independent reactions written in the network.

On the other hand, in Fig. 2 we have not included the disproportionation or dimerization–cracking steps of the type:



which have been used in other work (1, 2). This does not mean to say that they do not occur, but that they were not included because they can be obtained as a linear combination of those reactions given in Fig. 2. As an example, the above disproportionation reaction can be obtained as a combination of $31^* + 41^* + 5^* + 7^* - 14^*$. Hence it is clear that the network used to establish the conservation equations has to involve only independent reactions and then thus calculated reaction selectivities will be valid if those reactions are the only ones produced.

Following this strategy and because there are 58 species, we have established a reaction network which in agreement with Eq. [3] is formed of 55 independent reactions. We have intended in this scheme, named as network #1, to include all possible protolysis reactions. The reactions which intervene in this network, as well as the number assigned to each one, is given in Fig. 2.

Therefore, it is possible to obtain a set of 58 linear equations similar to Eq. [1] from the selectivities of each reaction product, assuming that the selectivity of the ionic species is zero (since they do not appear as reaction products). In this system of equations there are only 55 unknown parameters and this implies that we should exclude the three equations which are the linear combination of the others. In our case, we have eliminated the equations which apply to *n*-heptane, isobutene, and to acid sites. Obviously, it is necessary to check *a posteriori* with the solution obtained, in order to see if these equations were correct.

However, it should be taken into account that network #1 is not the only scheme which can explain the product distribution in the cracking of *n*-heptane. For instance, it can also be assumed that protolytic cracking only produces hydrogen and methane, whereas, ethane, propane, n-butane, and n-pentane only come from hydrogen transfer. In this case, it would not be necessary to consider the presence of the propyl, n-butyl, and n-pentyl primary carbenium ions, and consequently, only 55 species would intervene in the network. In other words, if one is able to find a reaction scheme with $55 - 3 = 52$ independent reactions in which 55 species are present another possible network which may explain the product distribution can be obtained. This alternative scheme exists and we have named it network #2 as represented in Fig. 2.

In the same way that we accomplished the results above, other similar reaction schemes can also be established. However, in order to be valid the set of reactions must be independent and in agreement with the method of Smith and Missen (21), the number of species minus the number of equations should be three since this is the range of matrix **A**. In this way, network #3, which is formed of 54 reactions and 57 species, represents an intermediate situation between network #1 and network #2, i.e., the intermediate situation between a minimum and a maximum contribution of the bimolecular hydride transfer reactions.

Initial Reaction Selectivity from the Reaction Network

In Table 2 the numbers assigned to the different species participating in the networks that we have constructed are given. In all the cases, we have omitted the equations corresponding to the reactant, isobutene, and Brönsted sites. These equations have been used to check the validity of the calculated selectivity values.

As an example, the initial selectivity values of the reactions for n-heptane obtained from network #1 are given in Table 3. The presence of some negative reaction selectivities is surprising. However, this is not so surprising if one takes into account that in reactions such as skeletal isomerization, hydride transfer, β-scission–alkylation, or desorption–adsorption, which are reversible, the reverse reaction can predominate over the forward reactions.

In Table 4, the monomolecular reaction selectivity (MRS) and the bimolecular reaction selectivity (BRS) for the three networks considered here are given. MRS and BRS are defined

$$\mathrm{MRS} = \sum_{i=1}^{R} \nu_{ikM}\, RS_i \qquad [4]$$

$$\mathrm{BRS} = \sum_{i=1}^{R} \nu_{ikB}\, RS_i \qquad [5]$$

where ν_{ikM} and ν_{ikB} represent the stoichiometric coefficients for the disappearance of the reactant (k) in reaction i, through the mono and bimolecular mechanism, respectively.

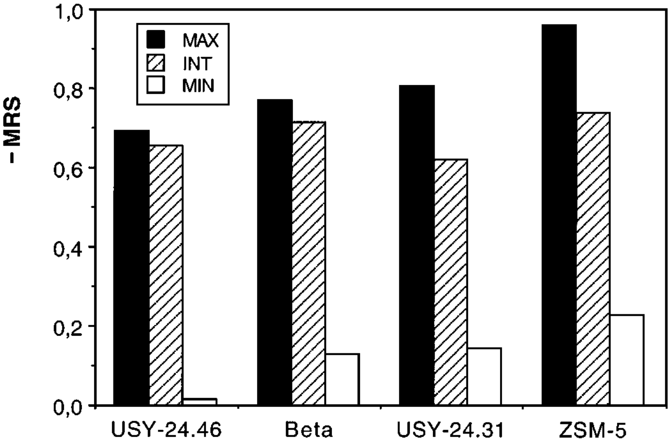


FIG. 3. Influence of catalyst over MRS in n-heptane cracking.

In Table 4, the effective hydrogen transfer selectivity (EHTS) is also given. It is defined as

$$\mathrm{EHTS} = \sum_{i=1}^{R} \mathrm{NEHT}_i\, RS_i \qquad [6]$$

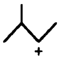
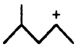
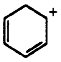
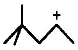
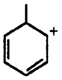
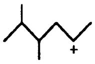
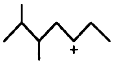
where NEHT_i, the number of effective hydrogen transfers of reaction i, is defined as the number of hydrogen molecules which are transferred in reaction i.

From Eqs. [4] and [5] it can be seen that $\mathrm{MRS} + \mathrm{BRS} = \mathrm{RRS} = -1$ must occur. The MRS values for each one of the three networks and four catalysts are given in Fig. 3. Any network will give MRS values that lie between two extreme situations which are represented by: Network #1 which corresponds to a situation with a maximum contribution of the monomolecular cracking (MRS MAX) and, consequently, a minimum contribution of the bimolecular cracking (BRS MIN); and network #2 corresponding to a minimum contribution of the monomolecular cracking (MRS MIN) or the equivalent to a maximum contribution of the bimolecular cracking (BRS MAX). This gap between the maximum and minimum MRS values generates an UNCERTAINTY BAND whose size will depend on: operation conditions, catalyst, and reactant. The UNCERTAINTY BAND will always exist except in very special cases such as the cracking of isobutane (15). In most of the cases the real situation will be one that is in between the two extreme situations described above and can be represented by all the reactions in Fig. 2.

One can see in Fig. 3 that the size of the UNCERTAINTY BAND is quite large, making it impossible to determine the real contribution of the two mechanisms. If one takes into account the nature of the catalyst, it appears that the stronger the strength of the acid sites and the lower their density and the smaller size of the pores, then the maximum and minimum values for the MRS will increase. This indicates that for higher acid strength, lower density of

TABLE 2

Numeration for Molecular and Ionic Participant Species in Proposed Reaction Networks

Species	*[Netw.#1,2,3]*	*Species*	*[Netw.#1]*	*[Netw.#2]*	*[Netw.#3]*
Hydrogen	*1*	H^+ (Acid Sites)	*For Check*	*For Check*	*For Check*
Methane	*2*		*28*	*28*	*28*
Ethane	*3*		*29*	–[a]	*29*
Ethylene	*4*		*30*	*29*	*30*
Propane	*5*		*31*	–	*31*
Propylene	*6*		*32*	*30*	*32*
n-Butane	*7*		*33*	*31*	*33*
i-Butane	*8*		*34*	–	–
$nC4^{=}$	*9*		*35*	*32*	*34*
i-Butene	*For Check*		*36*	*33*	*35*
n-Pentane	*10*		*37*	*34*	*36*
i-Pentane	*11*		*38*	*35*	*37*
$nC5^{=}$	*12*		*39*	*36*	*38*
$bC5^{=}$	*13*		*40*	*37*	*39*
n-Hexane	*14*		*41*	*38*	*40*
bC6	*15*	$nC7^+$	*42*	*39*	*41*
$nC6^{=}$	*16*		*43*	*40*	*42*
$bC6^{=}$	*17*		*44*	*41*	*43*
n-Heptane	*Reactant*		*45*	*42*	*44*
bC7	*18*		*46*	*43*	*45*
$C7^{=}$	*19*		*47*	*44*	*46*
Benzene	*20*		*48*	*45*	*47*
Toluene	*21*		*49*	*46*	*48*
bC8	*22*	$ArC8H11^+$	*50*	*47*	*49*
ArC8H10	*23*		*51*	*48*	*50*
bC9	*24*		*52*	*49*	*51*
ArC9H12	*25*	$ArC9H13^+$	*53*	*50*	*52*
ArC10H14	*26*		*54*	*51*	*53*
Coke	*27*	$ArC10H15^+$	*55*	*52*	*54*

[a] – *Not used in the Network.*

TABLE 3

Reaction Selectivities (RS_i) in n-Heptane Cracking on Zeolite Catalysts According to Network 1

	Catalyst			
Reaction #	*USY 24.46*	*USY 24.31*	*BETA*	*ZSM5*
1	0.00000	0.05170	0.09690	0.18450
2	0.01350	0.09220	0.03310	0.04610
3	0.01990	0.15050	0.03090	0.20430
4	0.46180	0.30220	0.37560	0.33920
5	0.17990	0.17560	0.21060	0.17210
6	0.01730	0.03680	0.02170	0.01760
7	0.17990	0.17560	0.21060	0.17210
8	0.46180	0.30220	0.37560	0.33920
9	0.01990	0.15050	0.03090	0.20430
10	0.02560	0.02770	0.07780	0.22010
11	0.01350	0.09220	0.03310	0.04610
12	0.02560	0.02770	0.07780	0.22010
13	0.01120	0.13910	0.02070	0.18880
14	0.01350	0.09110	0.02970	0.04610
15	-0.17725	-0.05330	-0.11935	-0.03075
16	0.45655	0.26510	0.35795	0.03025
17	0.02560	0.02770	0.07780	0.22010
18	0.04858	-0.05325	-0.00323	-0.16368
19	0.03488	0.04155	0.04938	0.20723
20	0.27730	0.14490	0.20850	0.02860
21	0.02880	0.04170	0.01860	0.00330
22	0.00000	0.00110	0.00130	0.00000
23	0.00050	0.00330	0.00120	0.00000
24	0.00000	0.00000	0.00220	0.00320
25	0.00000	0.00000	0.00000	0.00000
26	0.00000	0.00000	0.00000	0.00000
27	0.04788	0.12935	0.07608	0.25333
28	-0.17725	-0.05330	-0.12155	-0.03395
29	0.45655	0.26510	0.35795	0.03025
30	0.02560	0.02770	0.07780	0.22010
31	-0.04858	0.05325	0.00323	0.16368
32	0.04618	-0.05385	-0.00793	-0.16368
33	-0.03488	-0.04155	-0.04938	-0.20723
34	0.03488	0.04155	0.04808	0.20723
35	0.00000	0.00000	0.00000	0.00000
36	0.01730	0.03680	0.02170	0.01760
37	0.22778	0.30495	0.28668	0.42543
38	0.28455	0.24890	0.25405	0.30525
39	0.13068	0.17345	0.15268	0.16533
40	0.00870	0.01140	0.01020	0.01550
41	0.01930	0.02970	0.02260	0.03470
42	0.00000	0.00000	0.00000	0.00000
43	0.00000	0.00000	0.00050	0.00000
44	0.00000	0.00000	0.00000	0.00000
45	0.00000	0.00000	0.00210	0.00000
46	0.00170	0.00320	0.01230	0.00000
47	0.00240	0.00060	0.00470	0.00000
48	0.00000	0.00000	0.00130	0.00000
49	0.00000	0.00000	0.00000	0.00000
50	0.00000	0.00000	0.00210	0.00000
51	0.00170	0.00320	0.01230	0.00000
52	0.00240	0.00060	0.00470	0.00000
53	0.00000	0.00000	0.00130	0.00000
54	0.00000	0.00000	0.00000	0.00000
55	0.00000	0.00000	0.00000	0.00000

acid sites, and smaller pore diameter the monomolecular mechanism becomes relatively favored, as in the case of ZSM-5 which has an MRS value close to one.

When the network of an intermediate situation is considered (INT in Fig. 3), correlations different from those described above can occur. Therefore, the participation of the mono- and bimolecular cracking mechanism established from certain network intermediates between the two extremes of the UNCERTAINTY BAND should be considered with reservations.

In the case of the hydrogen transfer reactions the same does not occur since the EHTS is independent of the steps through which the hydrogen is transferred and only depends on the experimental selectivities of aromatics and coke. This is due to the fact that if one accepts that aromatics and coke are formed from the olefins generated in the cracking process, three hydrogen molecules are transferred for each molecule of the aromatic formed and also for every eight carbon and 10 hydrogen atoms which are deposited as coke. In fact, during the cracking of alkanes the EHTS can also be obtained, without making use of the reaction selectivities, by means of the following equation:

$$\mathrm{EHTS} = \sum_{\substack{j=1 \\ UD_j>1,}}^{S} S_j(UD_j - 1) \qquad [7]$$

where UD_j is the UNSATURATION DEGREE of product j with respect to the paraffin with the same number of carbon atoms. UD_j can be calculated with the expression

$$UD_j = \frac{2(\mathrm{C}_j + 1) - \mathrm{H}_j}{2}. \qquad [8]$$

In this equation C_j and H_j are the number of carbon and hydrogen atoms, respectively, in product j.

From the results given in Table 4, it is possible to see that while hydrogen transfer occurs with zeolite beta is almost nonexistant with ZSM-5. Meanwhile, as is expected, the lower unit cell size of the USY zeolite causes these reactions to become more restricted.

The limitations encountered in the case of n-heptane to calculate the contribution of the mono- and bimolecular cracking mechanism from the observed product distribution should also apply to all other alkanes that contain at least six carbon atoms (29). In the case of isobutane the difference between the initiation and propagation reactions can unambigously be established and a reaction scheme for the cracking of this molecule using the same terms as those in Fig. 2 is already reported (15). In this work, it was shown that H_2 and CH_4 could only be produced by the initiation steps. All remaining paraffinic products are only produced by propagation reactions.

TABLE 4

Initial Molar Selectivities of Reactant for Monomolecular and Bimolecular Mechanism, and Effective Hydrogen Transfer in *n*-Heptane Cracking over Zeolite Catalysts

				Catalyst			
	Network	*Value*	*Reaction # i*	*USY-24.46*	*USY-24.31*	*BETA*	*ZSM-5*
- MRS	1	MAX	1-6	0.6924	0.8090	0.7688	0.9638
- BRS	1	MIN	20-26	0.3066	0.1910	0.2318	0.0351
- RRS	1			0.9990	1.0000	1.0006	0.9989
Calc. i-C4$^=$ S	1		39,55	0.1307	0.1735	0.1527	0.1653
H^+ S	1		1-6,36-49	$-2.178\cdot10^{-8}$	$-4.109\cdot10^{-8}$	$1.141\cdot10^{-7}$	$-1.304\cdot10^{-8}$
EHTS	1		50-55	0.0123	0.0114	0.0612	0.0000
- MRS	2	MIN	1-2	0.0135	0.1439	0.1300	0.2306
- BRS	2	MAX	13-23	0.9855	0.8561	0.8706	0.7683
- RRS	2			0.9990	1.0000	1.0006	0.9989
Calc. i-C4$^=$ S	2		36,52	0.1307	0.1735	0.1527	0.1653
H^+ S	2		1-2,33-46	$1.921\cdot10^{-8}$	$3.341\cdot10^{-8}$	$-7.584\cdot10^{-8}$	$-1.303\cdot10^{-8}$
EHTS	2		47-52	0.0123	0.0114	0.0612	0.0000
- MRS	3	-	1-4	0.6552	0.6217	0.7162	0.7419
- BRS	3	-	17-25	0.3438	0.3783	0.2844	0.2570
- RRS	3			0.9990	1.0000	1.0006	0.9989
Calc. i-C4$^=$ S	3		38,54	0.1307	0.1735	0.1527	0.1653
H^+ S	3		1-4,35-48	$-3.108\cdot10^{-8}$	$-1.007\cdot10^{-7}$	$5.268\cdot10^{-8}$	$2.254\cdot10^{-7}$
EHTS	3		49-54	0.0123	0.0114	0.0612	0.0000
Exp. i-C4$^=$ S				0.1327	0.1736	0.1515	0.1674

The methodology presented here is applied to the case of the cracking of isobutane on two USY catalysts with 24.46 and 24.25 Å unit cell sizes at several reaction temperatures. As in the case of *n*-heptane, we have omitted equations that define the selectivities to the reactant, isobutene, and acid centers from the system. The results in Table 5 show that it is possible to match the selectivities corresponding to the three species named above with the calculated reaction selectivities. It can also be seen in Table 5 that when the reaction temperature increases the contribution of the bimolecular reactions decreases with an increase in the number of unimolecular reactions. The hydrogen transfer reactions decrease with the reaction temperature and, as can be expected, are of less importance on the USY zeolite which possesses a lower unit cell size.

TABLE 5

Initial Molar Selectivities of Reactant for Monomolecular and Bimolecular Mechanism and Effective Hydrogen Transfer in *i*-Butane Cracking over Zeolite Catalysts

	Catalyst					
	USY-1 (24.46 Å)			*USY-2 (24.25 Å)*		
	400 °C	*450 °C*	*500 °C*	*400 °C*	*450 °C*	*500 °C*
- MRS	0.3619	0.4420	0.6020	0.0822	0.2069	0.5890
- BRS	0.6384	0.5583	0.3971	0.9182	0.7930	0.4119
- RRS	1.0003	1.0003	0.9991	1.0004	0.9999	1.0009
Calc. i-C4$^=$ S	0.0528	0.0735	0.1291	0.0316	0.0825	0.1961
H^+ S	$3.725\cdot10^{-9}$	$5.960\cdot10^{-8}$	$-1.490\cdot10^{-8}$	$2.235\cdot10^{-8}$	$2.980\cdot10^{-8}$	$-1.118\cdot10^{-8}$
EHTS	0.1659	0.1380	0.0924	0.1614	0.1158	0.0105
Exp. i-C4$^=$ S	0.0550	0.0734	0.1300	0.0315	0.0822	0.1950

CONCLUSIONS

Contrary to that which has been claimed, it is not possible to establish a unique reaction mechanism for *n*-heptane cracking from selectivity data. Indeed, when we tried to separate (differentiate) the mono from the bimolecular cracking reactions, we found a large UNCERTAINTY BAND in which the selectivities for the monomolecular cracking can change.

The existence of this UNCERTAINTY BAND does not enable one to establish the effect of the different reaction variables and catalyst on the reaction mechanism.

Only in those cases in which it is possible to clearly distinguish between the products that come from the mono- or bimolecular cracking mechanism, is it possible to build a single reaction mechanism and, consequently, establish the selectivities for each one of the set of reactions which represent the reaction mechanism.

APPENDIX A

The methodology described in the theory section can be applied to an imaginary scheme of *n*-pentane cracking and product selectivity data, which have been selected solely with an illustrative purpose.

In this imaginary scheme we postulate the reactions

$$C_5H_{12} \rightarrow C_2H_4 + C_3H_8 \qquad i = 1$$

$$C_5H_{12} \rightarrow CH_4 + C_4H_8 \qquad i = 2$$

$$C_3H_8 + C_4H_8 \rightarrow C_7H_{16} \qquad i = 3$$

$$2\ C_5H_{12} \rightarrow C_7H_{16} + C_3H_8 \qquad i = 4$$

$$2\ C_5H_{12} \rightarrow 2C_3H_8 + C_4H_8 \qquad i = 5,$$

where there are five reactions and six species: $CH_4 \equiv A_1$; $C_2H_4 \equiv A_2$; $C_3H_8 \equiv A_3$; $C_4H_8 \equiv A_4$; $C_5H_{12} \equiv A_5 \equiv A_k$; and $C_7H_{16} \equiv A_6$. Let us suppose that the selectivities of the reaction products are: $S_1 = 0.1$; $S_2 = 0.3$; $S_3 = 0.55$; $S_4 = 0.05$; $S_6 = 0.35$, which are in agreement with the mass balance; the set of Eqs. [1] in this case is

$$RS_2 = 0.1$$

$$RS_1 = 0.3$$

$$RS_1 - RS_3 + RS_4 + 2\ RS_5 = 0.55$$

$$RS_2 - RS_3 + RS_5 = 0.055$$

$$-RS_1 - RS_2 - 2\ RS_4 - 2\ RS_5 = -1$$

$$RS_3 + RS_4 = 0.35,$$

where more equations than unknowns exist. This set of equations is only consistent if one eleminates an equation and resolves RS_i such that the eliminated equation should be satisfied. It can be seen that it is not possible to resolve the set of equations because the matrix of coefficients Γ is always singular; its determinant is zero, independent of the selectivity values.

This behavior can be explained in terms of matrix **A** whose coefficients a_{ij} are the number of i elements contained in species j. In this case,

$$\mathbf{A} = \begin{array}{c} \\ \mathrm{C} \\ \mathrm{H} \end{array} \begin{array}{c} \begin{array}{cccccc} A_1 & A_2 & A_3 & A_4 & A_5 & A_6 \end{array} \\ \begin{bmatrix} 1 & 2 & 3 & 4 & 5 & 7 \\ 4 & 4 & 8 & 8 & 12 & 16 \end{bmatrix} \end{array}.$$

As can be seen the range of **A** is 2 and, in accordance with Eq. [3], the maximum number of independent reactions that one can generate with the six species is four and not five, as we had supposed initially.

The conclusion is that only with a network of independent reactions is it possible to calculate reaction selectivities from product selectivity data.

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