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The Consequences of Steam Dilution in Catalytic Cracking

II. Effect of Steam Dilution on the Selectivity and Mechanism in 2-Methylpentane Cracking over USHY

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The effect of steam dilution in shaping the selectivity of 2-methylpentane cracking has been studied at 400, 450, and 500°C using a USHY zeolite. The results show that the presence of steam enhances isomerization of the feed and suppresses the production of cracked products. This and other evidence leads us to believe that steam dilution enhances the chain propagating reactions in the mechanism of catalytic cracking. At the same time, steam inhibits chain termination by desorption. The net result is that the presence of steam increases kinetic chain length and the paraffin-to-olefin ratio. The effects of steam dilution are surprisingly strong at lower temperatures but become less significant as temperature rises. All these effects are interpreted in terms of their influence on the elementary steps of the chain mechanism and are principally rendered in terms of a new measure: the reaction path probabilities (RPPs). These describe the likelihood that a feed molecule will be converted by a given reaction. Probabilities of all the reactions of the various ions present in the chain mechanism of 2-methylpentane cracking are quantified by formulating appropriate secondary functions using the RPPs derived from our experimental data. These various "internal" probabilities are used to quantify just how likely are each of the many alternative reactions of a given ion, as reaction conditions change. They allow us to track the effect of changes in reaction conditions, or in catalyst formulation, in unprecedented detail. Moreover, they give a detailed picture of the behavior of elementary processes in this reaction. We present and discuss examples of the quantitative information which our methods make available, and the mechanistic interpretations which flow from this information. In particular, we apply these measures in a study of the effects of steam when it is added to cracking 2-methylpentane in various proportions. It appears that catalytic cracking is much more susceptible to the effects of dilution than has previously been suspected.

INTRODUCTION

In this work we describe a new and potentially important direction in studies of the mechanism of hydrocarbon cracking over zeolite catalysts, a topic which is under active investigation in a number of laboratories (1–10). Our previous reports on 2-methylpentane cracking over USHY and on the effects of various diluents on this reaction have confirmed the presence of a chain mechanism in the cracking of this paraffin, and in the cracking of paraffins in general (11, 12). They have also shown that there are previously unsuspected interactions between the active sites and diluent molecules (13, 14). This stimulated our interest in investigating the interactions between "inert" electron donors and acceptors, when these are used as diluents added to the feed during the cracking reaction. As we will show, such studies have helped us to illuminate some fundamental aspects of acid catalysis on zeolites.

The role of steam as a modifier and stabilizer of zeolite catalyst activity in "steaming" is well known. Catalyst steaming is thought to *reduce* and narrow the strength distribution of acid sites on the surface of cracking catalysts (15–20). However, the influence of steam as a diluent on the kinetics and selectivity of cracking reactions has been largely ignored. This is surprising, since steam is an unavoidable contaminant in commercial cracking operations.

In our first paper on the consequences of steam dilution in catalytic cracking, we reported an investigation on the effects of steam dilution on the kinetics and activation energy of 2-methylpentane cracking over USHY (21). In this second report we comment on the effects of steam dilution and of reaction temperature on the initial selectivity of 2-methylpentane cracking on USHY, and on other more detailed aspects of the mechanism of this reaction.

THEORY

Chain Mechanism

We have recently proposed a chain mechanism for paraffin cracking (12, 22). This consists of three main steps:

1. chain initiation by the direct protolysis of C–C and C–H bonds of feed molecules on Brønsted acid sites;

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TABLE 1

Reaction Mechanism of 2-Methylpentane on HY Zeolite

Reaction pathway	Type	RPP symbol
$C_6H_{14} + HS \rightarrow H_2 + C_6H_{13}S$	Initiation	X_{00}
$C_6H_{14} + HS \rightarrow CH_4 + C_5H_{11}S$	(protolysis)	X_{01}
$C_6H_{14} + HS \rightarrow C_2H_6 + C_4H_9S$		X_{02}
$C_6H_{14} + HS \rightarrow C_3H_8 + C_3H_7S$		X_{03}
$C_6H_{14} + HS \rightarrow C_4H_{10} + C_2H_5S$		X_{04}
$C_6H_{14} + C_2H_5S \rightarrow C_2H_6 + C_6H_{13}S$	Propagation	X_{20}
$C_6H_{14} + C_2H_5S \rightarrow C_3H_8 + C_5H_{11}S$	(dispropor-	X_{21}
$C_6H_{14} + C_2H_5S \rightarrow C_4H_{10} + C_4H_9S$	tionation)	X_{22}
$C_6H_{14} + C_2H_5S \rightarrow C_5H_{12} + C_3H_7S$		X_{23}
$C_6H_{14} + C_3H_7S \rightarrow C_3H_8 + C_6H_{13}S$		X_{30}
$C_6H_{14} + C_3H_7S \rightarrow C_4H_{10} + C_5H_{11}S$		X_{31}
$C_6H_{14} + C_3H_7S \rightarrow C_5H_{12} + C_4H_9S$		X_{32}
$C_6H_{14} + C_4H_9S \rightarrow C_4H_{10} + C_6H_{13}S$		X_{40}
$C_6H_{14} + C_4H_9S \rightarrow C_5H_{12} + C_5H_{11}S$		X_{41}
$C_6H_{14} + C_5H_{11}S \rightarrow C_5H_{12} + C_6H_{13}S$		X_{50}
$C_6H_{14} + C_6H_{13}S \rightarrow C_6H_{14} + C_6H_{13}S$	Isomerization	X_{60}
$C_6H_{13}S^+ \rightarrow C_3H_6 + C_3H_7S^+$	β-cracking (chain transfer)	X_{b63}
$C_6H_{14} \rightarrow m_kC_xH_y + m_hH_2$	Coke formation	X_{kc}
$C_jH_{2j+1}S^+ \rightarrow C_jH_{2j} + HS$	Termination (desorption)	d_j

Note. X_{0i} is the RPP of feed conversion via the *i*th mode of protolysis, X_{jn} is the RPP of feed conversion via the reaction of a feed molecule with $C_jH_{2j+1}S^+$ to form a paraffin C_nH_{2n+2} and a new surface ion $C_{6+j-n}H_{2(6+j-n)+1}S^+$, X_{kc} is the RPP of feed conversion by the formation of coke X_{b63} is the molar selectivity for propylene from the β-scission of $C_6H_{13}S^+$ (C_6) ions d_j is the molar selectivity for C_jH_{2j} olefin production from $C_jH_{2j+1}S$ by desorption.

2. chain propagation by hydrogen transfer and other disproportions between feed molecules and carbenium ions on the catalyst surface;
3. chain termination by the desorption of carbenium ions.

A full set of elementary reactions in 2-methylpentane cracking on USHY, including some ancillary processes, is presented in Table 1. In order to quantify this mechanism, we collect experimental selectivity data.

Selectivity

1. *Optimum Performance Envelope (OPE)*

Well-defined initial selectivities must be used in evaluating the quantitative aspects of the cracking reaction mechanism. This is not a simple matter in practice and must be done correctly if one is to avoid confusing secondary reactions with initial processes. The contribution of thermal products must be identified and removed in order to quantify the initial overall process of *catalytic cracking* in a given hydrocarbon. A methodology for determining the initial selectivity of products from experimental product yields and conversion data has been presented previously (23) and has stood the test of time (24–28). The method involves plotting the time-averaged yield of each product against the time-averaged conversion. According to theory (23), each resultant plot is enveloped by a single curve, called the optimum performance envelope (OPE), which describes the selectivity behavior of that product under conditions of zero decay.

The selectivity "types" of the various products can be determined from the shape of the OPEs by noting the initial slope and subsequent curvature, as shown in Fig. 1. The initial selectivity of a product, given by the slope of the OPE at the origin, is non-zero for a primary product and zero for secondary or subsequent products. Primary products are those gas-phase products which are formed from the feed molecule without any detectable gas-phase intermediates. OPEs which exhibit a maximum with conversion belong to unstable products; those which increase linearly with conversion belong to stable products; and those which curve up belong to products which arise in both primary and secondary reactions.

For any product, the slope of the OPE at the origin represents the ratio of the rate of formation of that primary product to the total rate of conversion of the feed. Therefore the molar selectivity of a product is a measure of the ratio of two corresponding rates of reaction in units of moles per unit time:

$$\mathcal{F}_i = \frac{r_i}{r_t} \quad [1]$$

where

$\mathcal{F}_i$ is the molar selectivity of the ith product
r_i is the molar rate of formation of the ith product
r_t is the molar conversion rate of the feed.

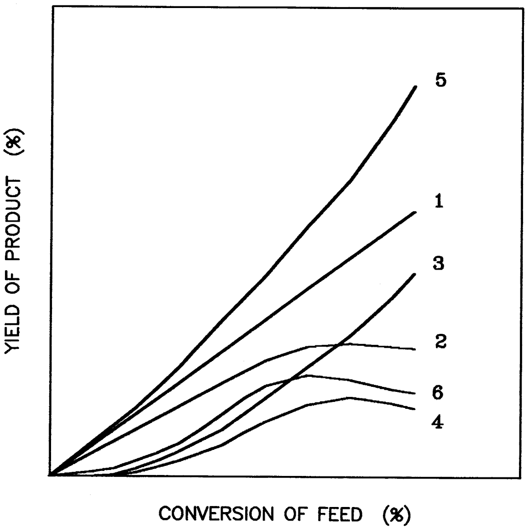

FIG. 1. OPEs and selectivity types: (1) stable primary product; (2) unstable primary product; (3) stable secondary product; (4) unstable secondary product; (5) stable primary plus secondary product; (6) unstable primary plus secondary product.

2. *Initial Molar Selectivity ($\mathcal{F}$)*

In our experiments we measure the weight yields of products and the weight conversion of the feed, and thus we can directly obtain the initial weight selectivities (F_{wi}) of products from their OPE curves. Initial molar selectivities ($\mathcal{F}_i$) of the products are then calculated from their weight selectivities by using the relationship

$$\mathcal{F}_i = F_{wi}\left(\frac{MW_f}{MW_i}\right), \qquad [2]$$

where

MW_f	is the molecular weight of feed
MW_i	is the molecular weight of the ith product
F_{wi}	is the weight selectivity of the ith product.

It is clear that the sum of the initial weight selectivities of all products in any reaction must be one, in order to meet the requirement of mass balance. On the other hand, the sum of the initial molar selectivities of all products in a cracking reaction, which indicates the extent of "volume expansion" in the reaction, may be other than one. Summing of the initial weight selectivities therefore provides a check on the quality of the experimental data and can reveal the presence of unanalyzed products. The total molar selectivity in turn supplies the volume expansion factor necessary for kinetic-parameter evaluation in terms of a mechanistic rate expression. This factor was used in our previous report on the kinetics of this reaction.

The preliminary verification of experimental data by summing the initial weight selectivities is of great importance in determining if the experimental results are quantifiable by the subsequent mathematical procedures. Experimental results with bad mass balances are uninterpretable by our procedures— or, in fact, by any other means. In our procedures this is made amply clear by the fact that, if the mass balances are bad, the requisite selectivity equations cannot be solved for any sensible mechanism.

3. *Product Formation Probability (PFP)*

By normalizing the molar selectivity of all products, we introduce a new measure: the product formation probability (PFP). The PFP of a given product is defined by

$$\mathrm{PFP}_i = \frac{\mathcal{F}_i}{\sum \mathcal{F}_i} = \frac{r_i}{\sum r_i}, \qquad [3]$$

where PFP_i is the PFP of the ith product. The PFP is therefore directly derived from selectivity measurements. Since products may arise from more than one reaction, the PFP is not a fundamental measure of the events taking place in a reaction.

Reaction Path Probability (RPP)

Since the production of any product, even in the initial stages of a cracking reaction, may involve several contributing elementary reactions, the initial molar selectivity of a product is the sum of contributions from all contributing processes, rather than a representation of the product-forming rate of just one elementary reaction. This point cannot be overemphasized as to its importance in unravelling the true mechanism of any reaction. In a sound mechanistic approach to catalytic cracking, it therefore becomes necessary to introduce another measure of product formation, one defined at the level of the various elementary reaction paths. We have introduced such a concept and call the corresponding measure the reaction path probability (RPP).

1. *The Definition of RPP*

The RPP of an elementary reaction is defined as the fraction of total conversion which proceeds via that one elementary reaction. According to this definition, for the ith reaction path involving a protolysis reaction, which we will denote with a leading 0 subscript (that is, $0i$), we write the RPP ($= X$) as

$$X_{0i} = \frac{r_{0i}}{r_t} = \frac{r_{0i}}{\sum r_{0i} + \sum r_{jR}} \qquad [4]$$

and for a propagation reaction path (with subscript jR), its RPP is

$$X_{jR} = \frac{r_{jR}}{r_t} = \frac{r_{jR}}{\sum r_{0i} + \sum r_{jR}}, \qquad [5]$$

where

X	is the symbol for the RPP;
r	is the symbol for the rate;
$0i$	represents the ith mode of protolysis which gives the paraffinic product C_iH_{2i+2} containing i carbons and a residual carbenium ion;
jR	represents the Rth mode of bimolecular disproportionation reaction involving a carbenium ion $C_jH_{2j+1}^+S^-$ containing j carbons and a feed molecule. These produce a product paraffin containing R carbons C_RH_{2R+2}, and a new carbenium ion.

Obviously, the sum of all RPPs for all conversion processes must be equal to one:

$$\sum X_{0i} + \sum X_{jR} = \frac{\sum r_{0i} + \sum r_{jR}}{r_t} = 1. \qquad [6]$$

Since an RPP presents a measure of the relative rates of elementary reactions, it represents an important mechanistic parameter and will supply a crucial measure in our mechanistic quantification of this, or any other, cracking reaction.

2. *Kinetic Chain Length (KCL)*

We define kinetic chain length as the ratio of the rate of feed conversion to the total rate of all initiation reactions; that is,

$$\begin{aligned}\mathrm{KCL} &= \frac{r_t}{\sum r_{0i}}\\ &= \frac{\sum r_{0i} + \sum r_{jR}}{\sum r_{0i}}\\ &= \frac{\sum X_{0i} + \sum X_{jR}}{\sum X_{0i}}\\ &= \frac{1}{\sum X_{0i}}.\end{aligned} \qquad [7]$$

3. *Bond Cracking Probability (BCP)*

To compare the probabilities of protolysis of various C–C and C–H bonds, we define the "internal" bond cracking probability (BCP) for a given protolysis reaction as

$$\mathrm{BCP}_{0i} = \frac{r_{0i}}{\sum r_{0i}} = \frac{X_{0i}}{\sum X_{0i}}; \quad \sum \mathrm{BCP}_{0i} = 1. \qquad [8]$$

The BCP_{0i} is the (internal) probability of cleaving bond i by the appropriate protolysis processes as a fraction of all possible protolysis reactions. Its value is calculated using X_{0i} values, confirming the importance of obtaining experimental data which will allow the calculation of reliable values of the RPPs.

4. *Isomerization Probability (IP)*

According to the chain mechanism, isomerization in paraffin cracking is an integral part of the overall process of feed conversion and proceeds via a step which is part of the chain propagation suite of reactions. We define the isomerization probability of "originating parent" ions (that is, ions derived from the feed molecule before rearrangement) as

$$\mathrm{IP} = \frac{\text{formation rate of product isomers}}{\text{formation rate of parent ions}}. \qquad [9a]$$

In the case of 2-methylpentane cracking, the IP is calculated from

$$\begin{aligned}\mathrm{IP} &= \frac{r_{60}}{r_{00} + r_{20} + r_{30} + r_{40} + r_{50} + r_{60}}\\ &= \frac{X_{60}}{X_{00} + X_{20} + X_{30} + X_{40} + X_{50} + X_{60}}.\end{aligned} \qquad [9b]$$

5. *Ion Desorption Probability (IDP)*

Since a carbenium ion may be involved in various competitive events, we quantify the relative contribution of the desorption reaction to the fates which can befall a given carbenium ion. In 2-methylpentane cracking, for example, the C_2 carbenium ion may desorb as an olefin or participate in various disproportionation reactions (see Table 1). To quantify the competition between desorption and disproportionation involving C_2 ions, we define

$$\begin{aligned}\mathrm{IDP}_2 &= \frac{r^{\mathrm{d}}_{\mathrm{C_2H_4}}}{r^{\mathrm{d}}_{\mathrm{C_2H_4}} + r_{20} + r_{21} + r_{22} + r_{23}}\\ &= \frac{\mathcal{F}_{\mathrm{C_2H_4}}}{\mathcal{F}_{\mathrm{C_2H_4}} + X_{20} + X_{21} + X_{22} + X_{23}},\end{aligned} \qquad [10]$$

where $r^{\mathrm{d}}_{\mathrm{C_2H_4}}$ represents the rate of formation of ethylene by the desorption of an ethyl carbenium ion.

Other measures of probability can be derived; all depend on the quality of the experimental data. Careful experimental work will allow a wealth of understanding that cannot be derived from inadequate data.

EXPERIMENTAL

The feed consisted of 2-methylpentane (99+%) obtained from Aldrich and was used without further purification. Distilled water and the feed, at the designed ratio, were separately pumped into the reactor, vaporized, and mixed, before the mixed stream entered the catalyst bed.

HY zeolite was prepared from NaY (BDH Chemicals) by exchanging 10 times with 0.5*M* NH_4NO_3 solution at 20°C for 24 h, drying at 110°C for 24 h and then calcinating at 500°C for 2 h after each exchange. The HY zeolite was then converted to ultrastable HY (USHY) by steaming at 400°C for 24 h.

All experiments were performed in a fixed-bed plug-flow glass reactor. Details of the apparatus and methodology have been described previously [29]. Before the main experimental runs were carried out, we conducted two preliminary sets of runs: one set of blank runs to determine the extent of thermal cracking; and one of replicate runs to examine the stability of USHY at the reaction conditions of high temperature and in the presence of steam as diluent.

All products were identified by GC/MS and analyzed quantitatively using a Carle chromatograph (for gases) or capillary chromatograph (for liquids). Mass balances were performed on the raw data, and runs whose mass balances were off by more than 3% were rejected. This level of accuracy was adequate for the construction of useable OPE plots.

RESULTS AND DISCUSSION

Selectivity

Initial weight selectivities for 2-methylpentane cracking over USHY at three temperatures and four steam dilution ratios were measured from weight OPE curves and are listed in Table 2. Table 3 presents the molar selectivities calculated from the data in Table 2 using Eq. [2].

TABLE 2a

Initial Weight Selectivity for 2MP Cracking at 400°C with Steam Dilution

	H_2O/feed molar ratio			
Products	0.00	0.07	0.73	1.46
Hydrogen	0.0004	0.0002	0.0001	0.0000
Methane	0.0030	0.0003	0.0007	0.0010
Ethane	0.0021	0.0006	0.0009	0.0017
Propane	0.0955	0.0412	0.0473	0.0515
i-butane	0.0595	0.0618	0.0704	0.0782
n-butane	0.0229	0.0084	0.0103	0.0146
i-pentane	0.0814	0.0641	0.0754	0.0826
n-pentane	0.0069	0.0035	0.0044	0.0052
2,2-DMbutane	0.0000	0.0057	0.0054	0.0050
2,3-DMbutane	0.0853	0.1830	0.1716	0.1570
3-Mpentane	0.4151	0.4806	0.4575	0.4385
n-hexane	0.0472	0.0539	0.0486	0.0445
Total paraffin (mass)	0.8193	0.9033	0.8926	0.8798
Ethylene	0.0066	0.0029	0.0037	0.0049
Propene	0.0976	0.0357	0.0388	0.0507
Butenes	0.0117	0.0066	0.0107	0.0115
Pentenes	0.0065	0.0034	0.0104	0.0120
Hexenes	0.0487	0.0433	0.0414	0.0397
Total olefin (mass)	0.1711	0.0919	0.1050	0.1188
Coke	0.0086	0.0063	0.0046	0.0032
Total (mass)	0.9990	1.0015	1.0022	1.0018

As shown in Table 3, the primary products are similar at all dilution ratios. The only new product in the presence of steam is 2,2-dimethylbutane. In each case, the primary products include skeletal isomers of 2-methylpentane, C_1–C_5 paraffins, C_2–C_6 olefins, coke, and hydrogen. At higher conversions, hydrocarbons with carbon number >6 appear as secondary products.

The procedure of drawing the slopes in order to obtain the initial selectivities is somewhat arbitrary but is guided by well-defined constraints: first of all, the slopes must be believable by inspection; second, their sum must be close to one; and finally, the atomic mass balance of the products must close. Iterating between these constraints, one arrives within fairly narrow bounds of acceptable initial selectivities which are then used as inputs into our calculations. The whole procedure can be quantified and automated to some extent, but remains semi-qualitative.

The selectivity values are obviously affected by the temperature and dilution ratio. Some preliminary quantitative information is available at this stage from the raw data. For example, the selectivity for feed isomers shows a significant increase with increasing dilution ratio from 0.00 to 0.07, and then decreases with this ratio from 0.07 to 1.46 at all temperatures. This shows that a small amount of steam can significantly enhance isomerization of the feed, an effect which is reduced at higher steam dilution ratios and higher temperatures. In contrast, the total selectivity for olefinic products shows a significant decrease as the dilution ratio increases from 0.00 to 0.07, and then increases with further steam addition, indicating that a small amount of steam inhibits desorption (proton release) of surface carbenium ions.

We note that the sum of molar selectivities of the paraffinic products is very near one at all dilution ratios and temperatures. This supports the proposed chain mechanism shown in Table 1 (12), where it can be seen that each conversion reaction results in the formation of a product paraffin. This "check-sum" presents a new measure of data reliability; if the sum of paraffin selectivities is found to be other than one, we may well wonder why.

According to the simple β-cracking hypothesis, the sum of olefin selectivities was also expected to be one, but we see that it need not be that at all. In fact, olefins in this reaction arise mainly by desorption. If they arise exclusively in this way, then the reciprocal of their molar selectivity will be equal to the kinetic chain length of the reaction. Thus, if the reaction proceeds by protolysis alone, with no chain propagation, the total olefin selectivity will be one, as will the kinetic chain length. As the chain length increases, the selectivity for olefins decreases. In principle this decrease goes to zero at infinite chain length, i.e., if there is only a sequence of propagation reactions, and no desorption, after initiation.

TABLE 2b

Initial Weight Selectivity for 2MP Cracking at 450°C with Steam Dilution

	H_2O/feed molar ratio			
Products	0.00	0.07	0.73	1.46
Hydrogen	0.0008	0.0005	0.0003	0.0002
Methane	0.0028	0.0008	0.0012	0.0019
Ethane	0.0016	0.0009	0.0015	0.0019
Propane	0.1510	0.0905	0.1012	0.1119
i-butane	0.0609	0.0714	0.0842	0.0884
n-butane	0.0214	0.0169	0.0208	0.0263
i-pentane	0.0870	0.0796	0.0842	0.0934
n-pentane	0.0055	0.0037	0.0053	0.0072
2,2-DMbutane	0.0000	0.0037	0.0048	0.0056
2,3-DMbutane	0.0690	0.1651	0.1488	0.1209
3-Mpentane	0.3045	0.3517	0.3250	0.3063
n-Hexane	0.0460	0.0476	0.0394	0.0371
Total paraffin (mass)	0.7505	0.8324	0.8167	0.8011
Ethylene	0.0068	0.0060	0.0082	0.0112
Propene	0.1695	0.1042	0.1145	0.1232
Butenes	0.0161	0.0068	0.0119	0.0134
Pentenes	0.0080	0.0055	0.0092	0.0137
Hexenes	0.0420	0.0413	0.0350	0.0321
Total olefin (mass)	0.2424	0.1638	0.1788	0.1936
Coke	0.0074	0.0040	0.0029	0.0026
Total (mass)	1.0003	1.0002	0.9984	0.9973

TABLE 2c

Initial Weight Selectivity for 2MP Cracking at 500°C with Steam Dilution

Products	H_2O/feed molar ratio 0.00	0.07	0.73	1.46
Hydrogen	0.0023	0.0010	0.0005	0.0003
Methane	0.0031	0.0029	0.0032	0.0045
Ethane	0.0030	0.0025	0.0034	0.0038
Propane	0.2170	0.2029	0.2181	0.2243
i-butane	0.0820	0.0948	0.0978	0.0994
n-butane	0.0217	0.0207	0.0266	0.0272
i-pentane	0.0950	0.1078	0.1171	0.1205
n-pentane	0.0033	0.0088	0.0094	0.0107
2,2-DMbutane	0.0000	0.0036	0.0033	0.0030
2,3-DMbutane	0.0382	0.0523	0.0453	0.0404
3-Mpentane	0.1210	0.1398	0.1148	0.1017
n-hexane	0.0210	0.0331	0.0282	0.0243
Total paraffin (mass)	0.6076	0.6702	0.6677	0.6601
Ethylene	0.0124	0.0146	0.0167	0.0185
Propene	0.2900	0.2376	0.2401	0.2439
Butenes	0.0394	0.0290	0.0308	0.0324
Pentenes	0.0032	0.0074	0.0079	0.0094
Hexenes	0.0410	0.0393	0.0376	0.0356
Total olefin (mass)	0.3860	0.3279	0.3331	0.3398
Coke	0.0065	0.0028	0.0021	0.0018
Total (mass)	1.0001	1.0009	1.0029	1.0017

This simple picture is distorted by the presence of β-cracking reactions which produce olefins without consuming paraffins. Moreover, a number of successive β-cracking events can take place in large carbenium ions. In such cases these events result in more than one olefin being formed from one ion before desorption takes place. This could, in principle, lead to a paraffin-to-olefin ratio smaller than one; or, looking at it from another perspective, to a total olefin selectivity greater than one. We therefore come to the realization that desorption and β-cracking belong to the same set of *decomposition* reactions. The upshot of these various considerations is that olefin selectivity can be anything ranging from more than one to zero. It is dangerous to use the P/O ratio *a priori* as a measure of any feature of the reaction.

Reaction Path Probability (RPP)

The RPPs of all elementary reactions for 2-methylpentane have been calculated by using the reaction network in Table 1, the experimental molar selectivity data in Table 3, and established mathematical procedures (12). The results are presented in Table 4.

1. A General View and the Kinetic Chain Length

The total RPP value of the initiation processes (i.e., $\sum X_{0i}$) decreases as dilution ratios increase from 0 to 0.07, and then increases with dilution ratio from 0.07 to 1.46. The total RPP of all chain propagation reactions (i.e., $\sum X_{jR}$) shows the opposite change, as it must if the sum of all RPPs is to be equal to one.

According to the definition given in Eq. [7], the kinetic chain length (KCL) is the ratio of overall rate of feed conversion to the rate of the sum of all the initiation reactions. A value of KCL = 2, for example, indicates that the initiation and propagation processes contribute equally to the overall conversion of the feed, whereas a value of one indicates that only initiation is taking place. The actual values of KCL at various temperatures and steam dilution ratios have been calculated from the RPP data and are shown in Fig. 2.

As shown in Fig. 2, changes in KCL with dilution ratio are significant at 400°C, observable at 450°C, and negligible at 500°C. At 400°C the dominant processes are the chain propagation reactions, with a KCL of 3.38 at zero dilution, 7.09 at a dilution ratio of 0.07, and 5.21 at a ratio of 1.46. Thus at low temperature and dilution, propagation contributes six times as much conversion as does the protolysis reaction, a significant departure from the predictions of the β-cracking mechanism. In view of the very different product selectivities resulting from initiation and propagation reactions, this has a major impact on the overall selectivity of cracking.

The chain initiation reaction becomes more important as temperature is raised. At 500°C the rate of initiation reactions is about twice that of propagation reactions, as

TABLE 3a

Initial Molar Selectivity for 2MP Cracking at 400°C with Steam Dilution

Products	H_2O/feed molar ratio 0.00	0.07	0.73	1.46
Hydrogen	0.0172	0.0086	0.0024	0.0000
Methane	0.0161	0.0016	0.0038	0.0054
Ethane	0.0060	0.0017	0.0026	0.0049
Propane	0.1867	0.0805	0.0925	0.1007
i-butane	0.0882	0.0916	0.1044	0.1160
n-butane	0.0340	0.0125	0.0153	0.0216
i-pentane	0.0972	0.0766	0.0901	0.0987
n-pentane	0.0082	0.0042	0.0053	0.0062
2,2-DMbutane	0.0000	0.0057	0.0054	0.0050
2,3-DMbutane	0.0853	0.1830	0.1716	0.1570
3-Mpentane	0.4151	0.4806	0.4575	0.4385
n-hexane	0.0472	0.0539	0.0486	0.0445
Total paraffin (moles)	1.0013	1.0005	0.9992	0.9984
Ethylene	0.0203	0.0089	0.0114	0.0151
Propene	0.1998	0.0731	0.0794	0.1038
Butenes	0.0180	0.0101	0.0164	0.0177
Pentenes	0.0080	0.0042	0.0128	0.0147
Hexenes	0.0499	0.0443	0.0424	0.0406
Total olefin (moles)	0.2960	0.1407	0.1624	0.1919
Coke	0.0086	0.0063	0.0046	0.0032
Total (moles)	1.3059	1.1474	1.1662	1.1935

TABLE 3b

Initial Molar Selectivity for 2MP Cracking at 450°C with Steam Dilution

Products	H_2O/feed molar ratio			
	0.00	0.07	0.73	1.46
Hydrogen	0.0344	0.0215	0.0129	0.0065
Methane	0.0151	0.0043	0.0065	0.0102
Ethane	0.0046	0.0026	0.0043	0.0054
Propane	0.2951	0.1769	0.1978	0.2187
i-butane	0.0903	0.1059	0.1248	0.1311
n-butane	0.0317	0.0251	0.0308	0.0390
i-pentane	0.1039	0.0951	0.1006	0.1116
n-pentane	0.0066	0.0044	0.0063	0.0086
2,2-DMbutane	0.0000	0.0037	0.0048	0.0056
2,3-DMbutane	0.0690	0.1651	0.1488	0.1209
3-Mpentane	0.3045	0.3517	0.3250	0.3063
n-hexane	0.0460	0.0476	0.0394	0.0371
Total paraffin (moles)	1.0012	1.0038	1.0020	1.0010
Ethylene	0.0209	0.0184	0.0252	0.0344
Propene	0.3471	0.2134	0.2345	0.2523
Butenes	0.0247	0.0104	0.0183	0.0206
Pentenes	0.0098	0.0068	0.0113	0.0168
Hexenes	0.0430	0.0423	0.0358	0.0329
Total olefin (moles)	0.4455	0.2913	0.3250	0.3569
Coke	0.0074	0.0040	0.0029	0.0026
Total (moles)	1.4541	1.2291	1.3300	1.3605

shown by the KCL value of ∼1.50 at all dilution ratios at 500°C. Under these conditions the product distribution we observed approaches that expected from the β-cracking model, a model which was previously expected to hold under all reaction conditions. However, even at the highest reaction temperature the product distribution shows a significant departure from the perfect β-cracking model, and it does this, not because of "side reactions," but because of processes which participate in the main-line chain mechanism of 2-methylpentane cracking at all conditions.

Once again we note an important fact. Initiation and propagation reactions belong to the same class of processes: disproportionations. This class includes all disproportionations between surface-resident ions and gas phase paraffins. There are therefore only two types of processes active in catalytic cracking: disproportionations and decompositions. It is the large number of possible variants in each type of process that makes possible the variety of products and mechanisms which arise in the cracking of various pure feeds.

2. *Monomolecular Initiation and BCP*

In our previous study of the effects of "inert" gases such as nitrogen or hydrogen as diluents, we found that the total RPP of all protolysis reactions increases with the addition of each diluent. This is to be expected in the case of a diluent whose only role is to dilute the concentration of the feed. Dilution reduces the rates of all reactions, but it reduces the rates of higher order reactions more. On the simplest level of interpretation we see that, since protolysis reactions are first order in feed concentration while propagation reactions are second order in reactant concentration, an inert diluent suppresses chain propagation (13, 14) more than it suppresses chain initiation.

In the case of steam dilution, by contrast, we find that the total RPP of the initiation reactions shows a large drop as the dilution ratio rises from zero to 0.07 at the lower temperature. It then rebounds slowly as the dilution ratio increases from 0.07 to 1.46. This anomaly in the dilution range from zero to ∼0.07 must indicate that a small amount of steam increases the surface residence times of some of the carbenium ions, by inhibiting their desorption. This increases surface coverage by carbenium ions, thereby lowering the number of pristine Brønsted sites and hence inhibiting protolysis while promoting disproportionations. To do this, steam must raise the acidity of the available Brønsted sites; but why does this reduce their contribution to the overall product distribution? To examine this issue in more detail we look at the chain mechanism in more detail and at the occurrence of each protolysis reaction in turn by calculating their BCPs.

From RPP data we see immediately that, of all the processes of protolysis, the path X_{03} has the largest RPP; the

TABLE 3c

Initial Molar Selectivity for 2MP Cracking at 500°C with Steam Dilution

Products	H_2O/feed molar ratio			
	0.00	0.07	0.73	1.46
Hydrogen	0.0989	0.0430	0.0215	0.0129
Methane	0.0167	0.0156	0.0172	0.0242
Ethane	0.0086	0.0072	0.0097	0.0109
Propane	0.4241	0.3966	0.4263	0.4384
i-butane	0.1216	0.1406	0.1450	0.1474
n-butane	0.0322	0.0307	0.0394	0.0403
i-pentane	0.1135	0.1288	0.1399	0.1439
n-pentane	0.0039	0.0105	0.0112	0.0128
2,2-DMbutane	0.0000	0.0036	0.0033	0.0030
2,3-DMbutane	0.0382	0.0523	0.0453	0.0404
3-Mpentane	0.1210	0.1398	0.1148	0.1017
n-hexane	0.0210	0.0331	0.0282	0.0243
Total paraffin (moles)	0.9997	1.0017	1.0019	1.0002
Ethylene	0.0381	0.0448	0.0513	0.0568
Propene	0.5938	0.4865	0.4916	0.4994
Butenes	0.0605	0.0445	0.0473	0.0498
Pentenes	0.0039	0.0091	0.0097	0.0115
Hexenes	0.0420	0.0402	0.0385	0.0364
Total olefin (moles)	0.7383	0.6252	0.6384	0.6540
Coke	0.0065	0.0028	0.0021	0.0018
Total (moles)	1.7445	1.6297	1.6424	1.6560

TABLE 4

Reaction Path Probabilities for 2-Methylpentane Cracking on USHY at Various Levels of Steam Dilution

H_2O/feed	0.00	0.07	0.73	1.46	0.00	0.07	0.73	1.46	0.00	0.07	0.73	1.46
Temp. (K)	673	673	673	673	723	723	723	723	773	773	773	773
X_{00}	0.006	0.003	0.001	0.000	0.026	0.014	0.006	0.001	0.092	0.039	0.020	0.012
X_{01}	0.016	0.002	0.004	0.005	0.015	0.004	0.006	0.010	0.017	0.016	0.017	0.024
X_{02}	0.006	0.002	0.003	0.005	0.005	0.003	0.004	0.005	0.009	0.007	0.010	0.011
X_{03}	0.151	0.080	0.092	0.101	0.266	0.148	0.168	0.186	0.418	0.397	0.416	0.427
X_{04}	0.117	0.054	0.063	0.081	0.117	0.122	0.140	0.155	0.133	0.161	0.175	0.179
$\sum X_{0i}$	0.296	0.141	0.163	0.192	0.429	0.291	0.324	0.357	0.669	0.620	0.638	0.653
X_{20}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
X_{21}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
X_{22}	0.005	0.007	0.006	0.007	0.005	0.006	0.016	0.015	0.021	0.010	0.009	0.009
X_{23}	0.091	0.038	0.046	0.059	0.090	0.098	0.099	0.106	0.074	0.106	0.115	0.114
X_{30}	0.036	0.000	0.000	0.000	0.029	0.029	0.030	0.033	0.007	0.000	0.011	0.011
X_{31}	0.000	0.003	0.009	0.009	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000
X_{32}	0.006	0.043	0.050	0.046	0.015	0.002	0.003	0.007	0.031	0.027	0.029	0.030
X_{40}	0.000	0.041	0.042	0.040	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
X_{41}	0.000	0.000	0.000	0.000	0.000	0.000	0.005	0.007	0.000	0.000	0.000	0.000
X_{50}	0.008	0.000	0.000	0.000	0.005	0.000	0.000	0.000	0.013	0.006	0.007	0.013
X_{60}	0.548	0.723	0.683	0.645	0.419	0.568	0.518	0.470	0.181	0.229	0.192	0.169
$\sum X_{jR}$	0.694	0.855	0.836	0.806	0.563	0.705	0.671	0.638	0.327	0.378	0.363	0.346
X_{kC}	0.009	0.006	0.005	0.003	0.008	0.004	0.003	0.002	0.004	0.002	0.001	0.001
X_{b63}	0.000	0.000	0.000	0.000	0.017	0.000	0.000	0.000	0.070	0.006	0.000	0.000

second most probable path is X_{04}, while paths X_{00}, X_{01}, and X_{02} are less important. To compare the internal probabilities of various protolysis events, BCP_{0i} values have been calculated at various steam dilution ratios and at each of the three temperatures.

The results indicate that the protolysis of bonds in the 2-methylpentane molecule obeys the following order of preference:

$$C_t - C_s > C_s - C_s > C_t - C_p \quad \text{or} \quad C_t - H$$
$$BCP_{03} > BCP_{02+04} > BCP_{01} > BCP_{00}.$$

This order does not vary with steam dilution or temperature, but the BCPs themselves do vary with dilution ratio and with temperature. From Fig. 3 we see that:

—BCP_{00} decreases with increasing dilution ratio at each temperature;

—BCP_{01} at 400 and 450°C and $BCP_{02\text{–}04}$ at 400°C decrease with the dilution ratio from 0 to 0.07, then rebound when dilution ratio goes from 0.07 to 1.46;

—BCP_{03} and BCP_{04} appear less sensitive to the effect of steam dilution.

Our observations almost certainly reflect changes in the acid strength distribution of active sites as a result of dilution. It is to be expected that sites of different acidity will act preferentially in promoting the various modes of protolysis, with the stronger sites contributing more to the more difficult reactions. Exactly what is causing the change in acid site distribution is less clear. The effect on the increased acid strength is masked by the fact that the number of available protolysis sites is simultaneously decreased by an increase in surface coverage by carbenium ions. If the level of surface coverage is changed by any means at all, the sites remaining uncovered will have a new distribution of acidities, unless the additional coverage is

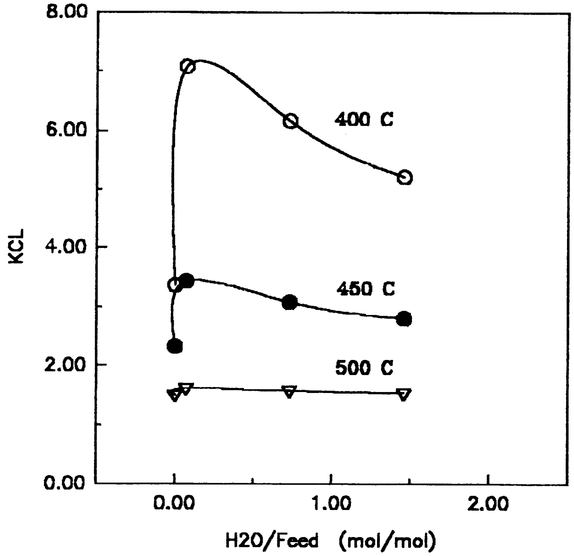

FIG. 2. KCL vs steam dilution ratio at various temperatures: 400°C (○); 450°C (●); and 500°C (∇).

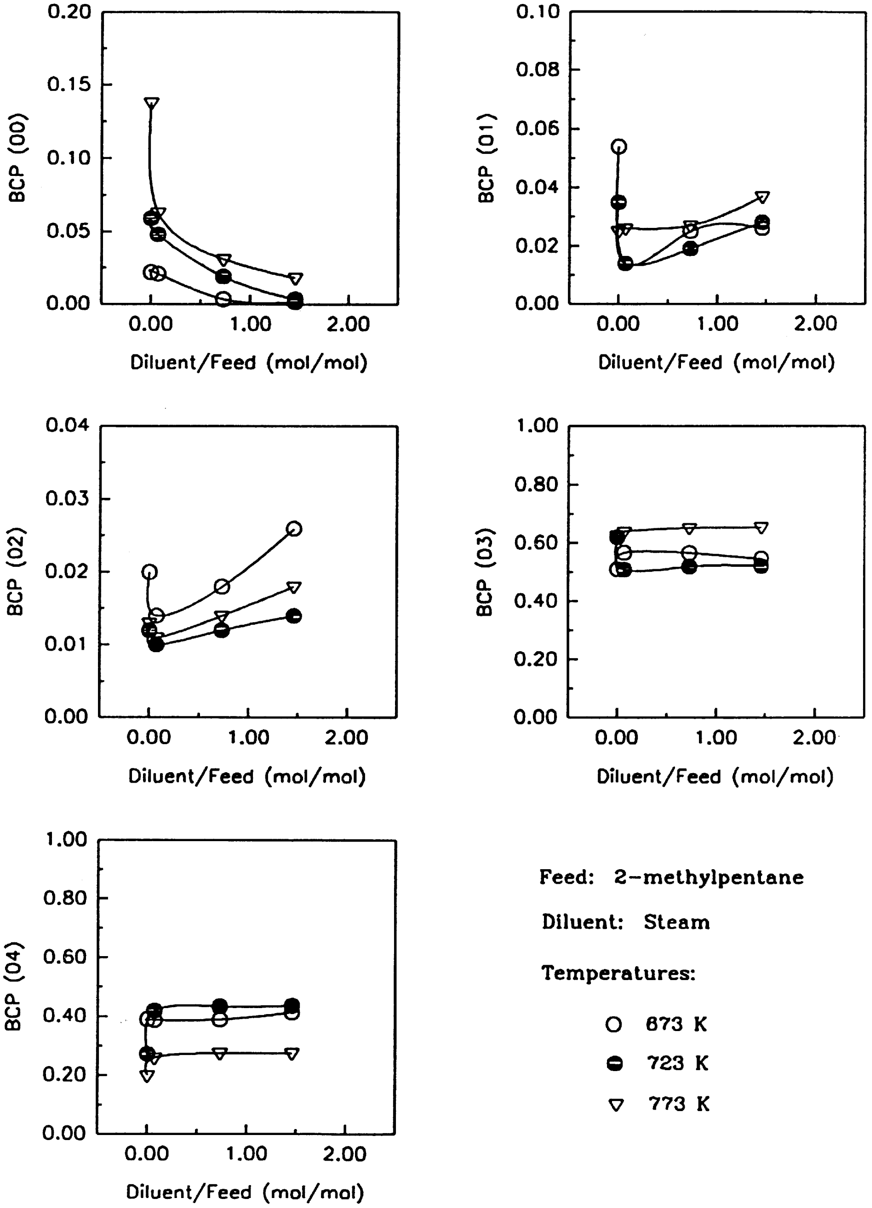

FIG. 3. BCP vs steam dilution ratio at various temperatures: 400°C (○); 450°C (●); and 500°C (▽).

deducted from the previously uncovered site distribution in exactly the proportions required to preserve the previous distribution. This seems highly unlikely, so that, as steam changes the acid properties of sites, its effect is distorted by changes in the number of pristine sites present at steady state.

If we take it that the order of preference in the BCPs indicates that the least probable protolysis (corresponding to BCP_{00}) occurs on the strongest acid sites, then we must conclude that, for whatever reason, the remaining acid sites have a distribution with relatively fewer strong sites available for protolysis. The primary C–C bond cracking is also enhanced while the remaining probabilities stay relatively constant. Both observations indicate a flatter distribution of pristine acid sites available for protolysis, not a decrease in their absolute strength.

3. Bimolecular Propagation and IP

From Table 4 we see that the total of the RPPs of propagation increases as the dilution ratio rises from zero to 0.07 and then drops slowly as the ratio increases from 0.07 to 1.46. Of all the propagation processes, X_{60} is the most probable path for the reaction to take and has the largest RPP. The data in Table 4 show that path X_{60} dominates all paths at lower temperatures and continues to dominate the propagation paths at higher temperatures. The results also show that steam can significantly enhance isomerization of the feed at lower temperatures and low dilutions.

It is important to remember that, according to the chain mechanism of cracking, isomerization is an integral part of the overall conversion process. There is no need to invoke special "isomerization sites." This is not so much a matter of choice as it is of closing mass balances and arriving at a soluble set of selectivity equations for the RPPs. The mathematics and physical realities of mass balances require that isomerization be treated as an integral part of the conversion mechanism.

The dominance of the isomerization reactions is such that it will be informative to focus on the reactions of C_6^+ carbenium ions, the active ionic species in the majority of the reactions leading to isomerized products. Besides skeletal rearrangement followed by hydride transfer, there are two potential fates awaiting C_6^+ ions: desorption as C_6 olefins; and β-cracking to form smaller olefins and carbenium ions.

A high IP value indicates that there is a strong tendency for C_6^+ ions to abstract a hydride from a feed molecule relative to the total rate of formation of parent carbenium ions. The probability of isomerization IP_6 was calculated using Eq. 9b. Figure 4 shows that the values of IP_6 increase with the first increments of steam dilution, indicating that the addition of small amounts of steam to the reactant mixture encourages hydrogen transfer between an isomerized C_6^+ carbenium ion and a feed molecule. The effect is persistent and does not change with further additions of steam.

At the same time an examination of X_{bij} values shows that steam is a strong inhibitor of the β-cracking of C_6^+ ions. The increase of IP_6 with steam dilution is therefore much larger at 500°C than at 400°C. At the higher temperature β-cracking was becoming important in the dry reaction, while it is completely suppressed by the presence of steam. The parent carbenium ions are therefore forced either to desorb as olefins or to abstract a hydride and desorb as isomers of the feed. The presence of steam alters the active sites so as to encourage hydride transfer over β-cracking or desorption of C_6^+ carbenium ions. If β-cracking is a more energetic reaction than hydride transfer, then steam is seen to favour the less energetic reaction, hydride transfer. By the same token, desorption must also be more demanding than hydride abstraction. The two observations can be rationalized under one hypothesis, if we remember that both β-cracking and desorption are decomposition reactions and then adopt the following explanation.

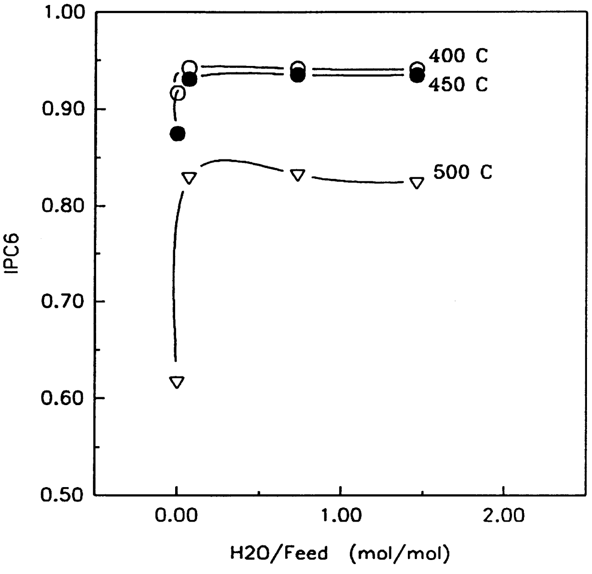

FIG. 4. IP vs steam dilution ratio at various temperatures: 400°C (○); 450°C (●); and 500°C (▽).

Steam strengthens the pristine acid sites and weakens the conjugate Brønsted bases. The two effects constitute one *dichotomy* (there are a number of such dichotomies which are important to the interpretation of cracking mechanisms). As a consequence of this dichotomy, desorption of carbenium ions and β-cracking are both inhibited. The weak bases have more difficulty in abstracting a proton from the carbenium ion or speeding the decomposition of adsorbed carbenium ions. The carbenium ions thereby have an increased time of residence on the surface and so cover more of the sites. The sites remaining uncovered are therefore fewer and have a different site acidity distribution, resulting in slower protolysis reactions and a somewhat altered set of BCPs.

In the above we have recognized that β-cracking and desorption of olefins are alternative modes of carbenium ion decomposition. In a sense, therefore, **the proton on a pristine acid site is a carbenium ion with carbon number zero.** Although this is an unconventional viewpoint, it can help to see various interconnections in the chain mechanism of catalytic cracking.

4. *Termination and IDP*

As we have discussed, the desorption of carbenium ions to yield olefins is responsible for the terminating chain processes. This fate may befall an ion which might otherwise have undergone a propagation reaction or β-cracking. If it does, the ion gives up a proton to the Brønsted base on the catalyst and departs as an olefin.

In the case of C_6^+ ions, we have seen that steam dilution encourages hydride transfer to the ion and inhibits β-cracking. We can also examine the probability of proton release for this ion in terms of IPD_6. From Fig. 5, we see that the value of the ion desorption probability, IDP_6, remains relatively constant between 400 and 450°C. At 500°C IDP_6 increases slightly with steam dilution. Thus at the highest temperature the total suppression of β-cracking causes the internal probabilities of the reactions of C_6^+ ions

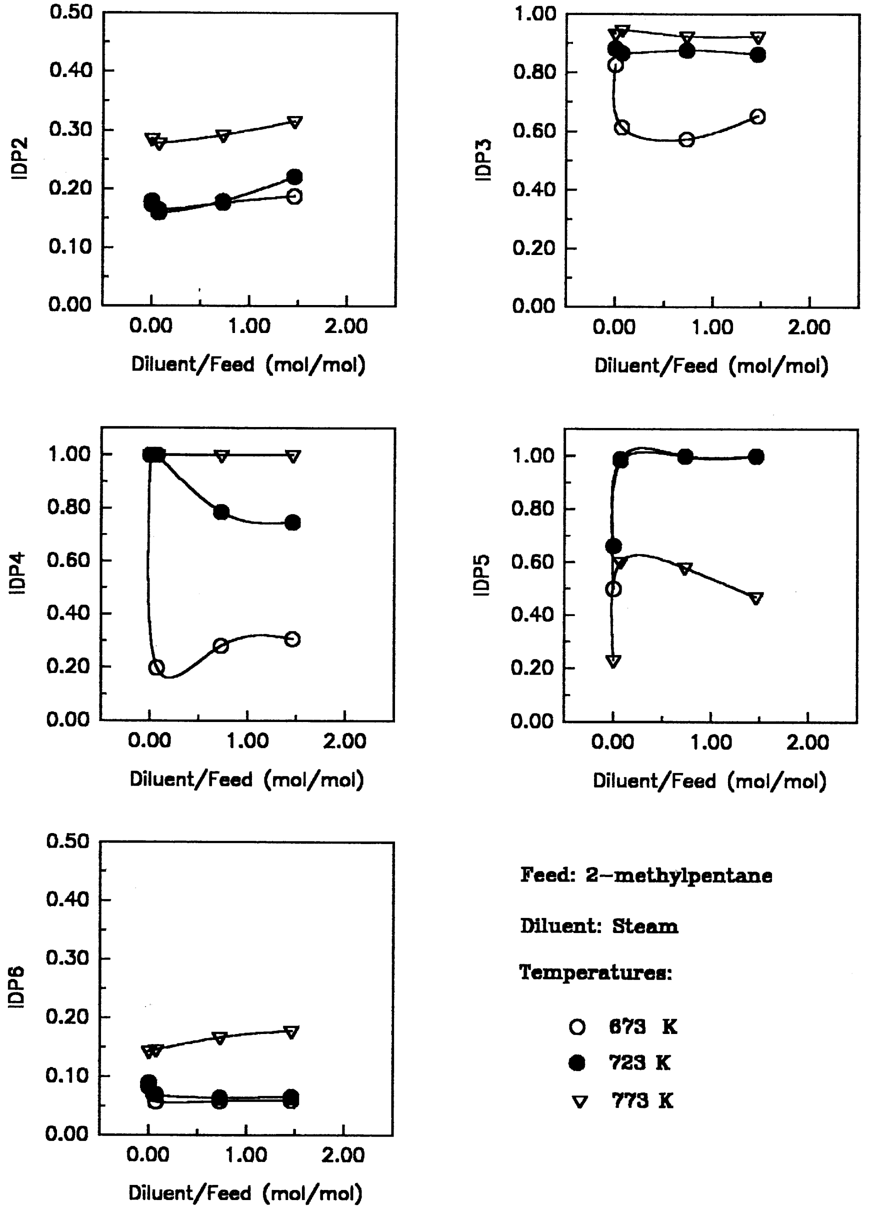

FIG. 5. IDP vs steam dilution ratio at various temperatures: 400°C (○); 450°C (●); and 500°C (∇).

to rearrange so that there is a slight increase in IDP_6. The fact that the total of the internal probabilities must be one leads to confusion of this kind and it is therefore advisable to extract the actual rates of the individual reactions and examine the effects of steam at that level. We will do that after we have examined the remaining selectivity effects in terms of probabilities.

5. *Formation of Hydrogen and Coke*

(a) *Coke formation.* The RPP value of the path forming coke, X_{kc}, also decreases with both increasing dilution ratio and increasing temperature, indicating that the formation of initial coke is inhibited by both these influences. We have proposed elsewhere that catalytic (poisonous) coke is the result of surface disproportionations of adjacent carbenium ions (30, 31). In this context, temperature increases lead to reduced catalytic coke because, under high temperature conditions, the surface is less densely covered by adsorbed carbenium ion species.

The explanation for the inhibition of coke formation by steam is more complicated. As we have seen, steam tends to increase surface coverage. If surface coverage were the sole parameter affecting coke formation by surface disproportionation of ions, then the presence of steam should increase the coke make. According to previous discussion, ions on weak conjugate bases are *more* reactive in disproportionating with gas phase molecules. It now seems that the same ions are *less* reactive in ion–ion disproportionations, reactions which we suspect are responsible for second-order decay in the cracking of pure components. We should remember that this means that ion–ion disproportionations are relatively less likely than the other fates an ion can suffer.

(b) *Hydrogen formation.* It is generally acknowledged that initial molar hydrogen can be formed by the protolysis of C−H bonds in feed molecules and by the elimination of molecular hydrogen from surface species in association with the hardening of coke. Comparing the RPP values of the path X_{00} in Table 4 to the total molar selectivity of hydrogen reported in Table 3, we find that the ratios of $X_{00}/\mathcal{F}_{H_2}$ are approximately 35% at 400°C and 93% at 500°C, at all the dilution ratios. This indicates that at 400°C most of the hydrogen is produced in association with coke formation, whereas at 500°C more than 90% is formed by protolysis of the C−H bonds in the feed.

In other words, dehydrogenation of surface "precoke" species is the dominant source of molecular hydrogen at 400°C, while the protolysis of C−H bonds in the feed molecule dominates the production of hydrogen at 500°C. This agrees with the observation that more coke is formed at the lower temperatures (32–34). However coke is formed, at all conditions the formation of coke involves hydrogen depletion of the residual surface species. Now we see that much of this hydrogen depletion of the surface species, in a process known as "hardening," results in the formation of molecular hydrogen rather than in the transfer of hydrogen to unsaturated products.

The presence of steam seems to have no affect on hydrogen production modes at 400 or 500°C. The result at 450°C is more complicated and we will not attempt to explain it now. A clearer picture will emerge when we consider the rates of the various reactions including coking.

Temperature Effects in Cracking Selectivity in the Presence of Steam

The Influence of Temperature on Protolysis

In a recent paper on the roles of steam as a diluent in hydrocarbon cracking (21), we presented a phenomenological approach to the effects of temperature on the activity and kinetics of 2-methylpentane cracking over USHY, with and without steam dilution. We obtained an apparent activation energy of 150 kJ/mol and an apparent order of 1.92 for the overall reaction of the feed conversion (21). Now that we have RPP values, we can take a look at the effects of temperature on the various elementary reactions in this reaction system. We begin by discussing the effects of temperature on the protolysis processes.

The initial rates of various protolysis reactions have been calculated by first distributing the total rate of initiation, obtained from optimum kinetic parameters (12), to the various protolysis paths, by means of the equation (34)

$$\begin{aligned} r_{0i} &= X_{0i} \cdot r_t \\ &= \left(\frac{X_{0i}}{\sum X_{0i}} \right) \cdot \frac{A_1 + A_2}{1 + B}, \end{aligned} \qquad [11]$$

where A_1, A_2, and B are optimum kinetic parameters (11) and the X_{0i} RPPs refer to initiation reactions only. The propagating and coking reaction rates are calculated using an appropriately modified form of this equation. The calculated rates of all protolysis reactions in 2-methylpentane cracking at different temperatures and with various steam dilution ratios are presented in Table 5.

Theoretically, the rate of the *i*th protolysis reaction may be expressed by

$$r_{0i} = k_{0i}[SH][C_A]. \qquad [12]$$

Putting this rate constant in the Arrhenius form and expressing the concentration of feed as a function of the

TABLE 5

Initial Rates (min^{-1}) for the Protolysis Reactions in 2-Methylpentane Cracking on USHY at Various Levels of Steam Dilution

H_2O/feed	0.00	0.07	0.73	1.46	0.00	0.07	0.73	1.46	0.00	0.07	0.73	1.46
Temp. (K)	673	673	673	673	723	723	723	723	773	773	773	773
IRR												
r_{00}	0.038	0.032	0.004	0.001	1.26	0.465	0.113	0.010	23.7	4.98	1.43	0.416
r_{01}	0.101	0.021	0.031	0.019	0.725	0.133	0.113	0.103	4.39	2.04	1.22	0.921
r_{02}	0.038	0.021	0.024	0.019	0.242	0.100	0.075	0.052	2.32	0.893	0.715	0.422
r_{03}	0.954	0.845	0.723	0.375	12.9	4.92	3.15	1.92	108	50.7	29.7	16.4
r_{04}	0.739	0.570	0.495	0.301	5.66	4.05	2.63	1.60	34.3	20.5	12.5	6.87
$\sum r_{0i}$	1.87	1.49	1.28	0.713	20.7	9.67	6.08	3.68	173	79.1	45.6	25.1
r_{60}	3.46	7.64	5.37	2.39	20.3	18.9	9.72	4.85	46.7	29.2	13.7	6.49
r_{kc}	0.056	0.067	0.036	0.012	0.387	0.133	0.056	0.021	1.03	0.255	0.104	0.038

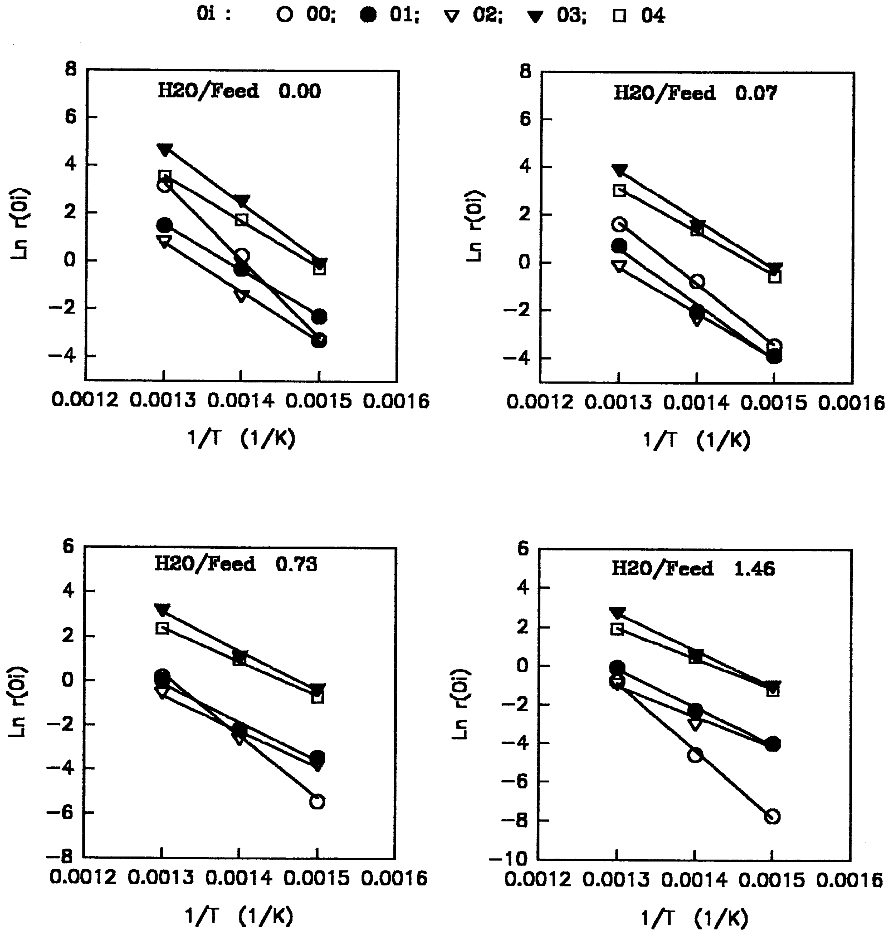

FIG. 6. Arrhenius plots of protolysis reactions in 2-methylpentane cracking on USHY and with steam dilution.

dilution ratio in the way described in Ref. (11), we have

$$r_{0i} = A_{0i} e^{-E_{0i}/RT} [SH] \frac{[C_A]_{\beta=0}}{1+\beta}, \qquad [13]$$

where

E_{0i}	is the Arrhenius activation energy of the ith reaction;
$[C_A]_{\beta=0}$	is the concentration of pure feed (at $\beta = 0$);
β	is the molar steam/hydrocarbon ratio in the feed.

Changing Eq. [13] into its logarithmic form gives the expression:

$$\ln(r_{0i}) = -\frac{E_{0i}}{RT} + \ln A_{0i} + \ln[SH] + \ln[C_A]_{\beta=0} - \ln(1+\beta). \qquad [14]$$

Using the above equation, the rates of the various protolysis reactions have been calculated and plotted in Fig. 6. From the slopes of the plots in Fig. 6 we have calculated the Arrhenius parameters of all the protolysis reactions. These and the activation energies of isomerization and coking are reported in Table 6. Other such parameters can be obtained from the data reported in Table 4.

It should be pointed out that the activation energies calculated from the slopes of these Arrhenius plots include the effects of temperature on the concentration of the active sites ([SH]); these effects would show up due to the term ln[SH] in Eq. [14]. Any such effects would imply that the number of active sites changes with temperature at cracking temperatures, and for now we will discount such a possibility. The trends in the lines on Fig. 6 and the numbers in Table 6 clearly show a decrease in both the frequency factor and activation energy with steam dilution. This is a typical compensation effect, in which a reduction in activation energy brings with it a reduction in the entropy of activation. This effect represents another dichotomy affecting the mechanism of catalytic cracking.

At the outset we observe that, in the set of initiation reactions, the rates show correct and systematic behavior with temperature at all dilution ratios. This is so despite the observation discussed previously that some RPPs go up and some go down with temperature, and it underlines the

TABLE 6

Activation Energies of Protolysis, Isomerization, and Coking Reactions in 2-Methylpentane Cracking at Various Levels of Steam Dilution

E_{0i} kJ/mol	H_2O/feed (mol/mol)			
	0.00	0.07	0.73	1.46
E_{00}	279	218	255	259
A (min^{-1})	1.6E + 20	2.8E + 15	2.5E + 17	9.5E + 16
E_{01}	163	156	158	167
A (min^{-1})	4.6E + 11	3.2E + 10	4.3E + 10	1.6E + 11
E_{02}	177	161	146	133
A (min^{-1})	2.0E + 12	6.2E + 10	3.9E + 9	3.2E + 8
E_{03}	205	176	160	163
A (min^{-1})	7.9E + 15	3.6E + 13	1.6E + 12	1.4E + 12
E_{04}	166	155	140	135
A (min^{-1})	5.8E + 12	6.4E + 11	3.4E + 10	9.8E + 9
E_{60}	113	58	41	44
A (min^{-1})	2.5E + 9	2.7E + 5	8.0E + 3	6.1E + 3
E_{kc}	127	58	46	50
A (min^{-1})	4.8E + 8	2.0E + 3	1.2E + 2	8.6E + 1

limitations of even the RPPs as a means of interpreting catalyst behavior. Needless to say, the selectivities observed experimentally and their consequent PFPs are even further removed from fundamental significance by the very fact that certain products arise from more than one reaction. The set of reactions contributing to the yield of a given product will not, as a rule, have the same temperature dependence for each member of the set.

Figure 6 shows that good linearity is obtained for the individual rates on the Arrhenius plot, encouraging us to interpret the activation energies calculated from these plots and shown in Table 6. We note right away that the addition of steam to the reactant causes a drop in all E_{0i} indicating that steam dilution changes the interaction between the Brønsted proton and the feed molecule. We also note that the protolysis of the C−H bond leading to H_2 formation requires the highest activation energy at all dilution ratios, while the activation energies for the C−C bonds are similar for all bond orders.

Perhaps the most striking change in the Arrhenius parameters is seen in those connected with coking. Steam reduces the activation energy for coking but it reduces the frequency factor for this reaction even more dramatically. This decrease is large enough to explain the observed reduction in coking selectivity. This implies that the entropy of reaction for ion–ion disproportionation is decreased by the presence of steam to a remarkable extent. Why this should be so is not clear.

The abruptness of the change in the behavior of this system at low steam addition ratios seems to be confirmed from all aspects. Clearly a significant change in surface interactions is introduced by small amounts of steam. At higher dilutions, this effect becomes submerged in the effects of straight dilution by the chemically inert steam and in changes of the average strength of covered and of pristine sites (both of which depend on surface coverage), making it hard to separate the effects.

The changes in activation energy we have already ascribed to changes in the distribution of acid strength on the sites available for protolysis at various levels of dilution. This effect we see as follows:

— the activation energy for any one protolysis reaction on any site will depend on the acid strength of that site;

— the observed activation energy of a protolysis is a weighted average of the activation energies on the various sites capable of catalyzing a given reaction;

— the activation energy of a protolysis reaction is reduced if site "activity" is increased;

— there is a pre-existing distribution of acidities of the pristine acid sites;

— of the available sites, some are covered by carbenium ions and some are not, leaving behind a new distribution of site energies for the sites capable of protolyzing the feed molecule;

— it is the strongest sites which are most likely to be covered by a carbenium ion; the number, and hence the distribution, of the available acid sites changes as surface coverage is changed by the presence of steam;

— activation energies in the case of heterogeneous site-energy distributions will always be a function of surface coverage, as well as of the pre-existing distribution of site energies.

Even with the large and carefully collected data set reported here, we feel that the activation energies and frequency factors are not sufficiently well defined to say much more than what we have already said above. It will take much more data of this kind to document the behavior of cracking mechanisms to the point where even semi-quantitative predictions can be made.

The Chain Reaction Mechanism at Various Dilution Conditions

We have proposed a formalism and an associated mathematical treatment for quantifying the behavior of catalytic cracking reactions as chain processes. In earlier publications (11–14, 22, 35–38) this powerful concept has allowed us to interpret the mechanisms of cracking for a variety of reactants. In the case of 2-methylpentane it has also provided us with a broad and consistent picture of the effects of various influences the cracking of this molecule. Temperature effects have been studied and found to follow the behavior expected on the basis of the Arrhenius equation in every detail.

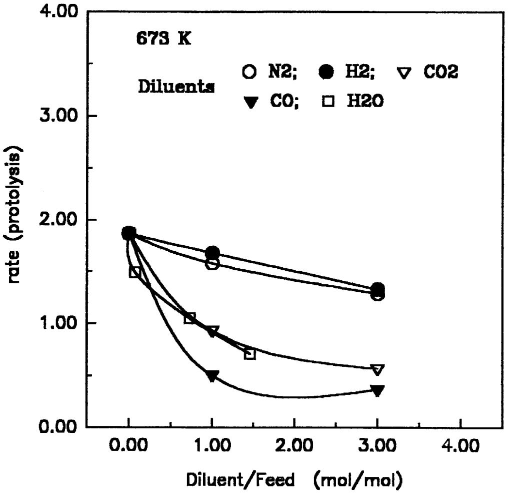

FIG. 7. Protolysis rate vs dilution ratio at 400°C with various diluents.

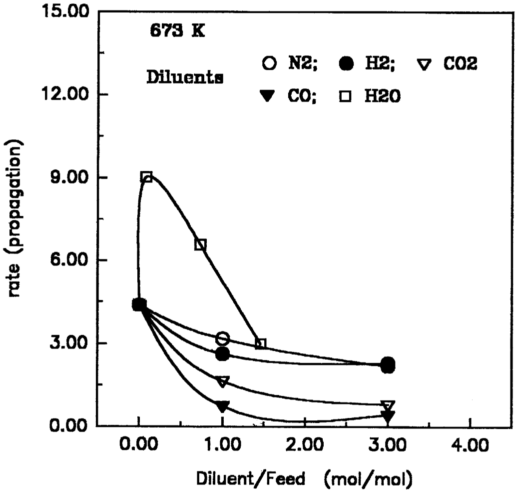

FIG. 8. Propagation rate vs dilution ratio at 400°C with various diluents.

The effects of N_2, H_2, CO_2, and CO used as diluents were found to vary from diluent to diluent. The effect of both N_2 and H_2, for instance, is simply the dilution of the feed concentration. This slows down the rates of feed conversion via both monomolecular (protolysis) and bimolecular (propagation) reactions. However, bimolecular reactions suffer a larger decrease (13, 14) in reaction rate, due to the fact that their rates depend on the second power of feed concentration. As a result, the observed cracking selectivities are affected, even by these chemically “inert” diluents.

The role of the polar molecule CO and of the polarizable CO_2 is both a simple dilution, as described above, and a “passivation” of both monomolecular and bimolecular reaction sites. This new effect causes an additional drop in the rate of feed conversion (14). What the “passivation” effect might be in terms of changes in the nature of the interaction of the feed with the active sites is not immediately clear. Comparison of the effects of these diluents with the effects of steam as a diluent may help to clarify the effects observed when a polar or polarizable diluent is present in hydrocarbon cracking.

Figure 7 shows the changes in the rate of initiation with dilution ratio, using different diluents. We see that H_2O, like CO and CO_2, causes a larger decrease in this rate than do the inert diluents.

Figure 8 shows the changes in the rate of propagation with dilution ratio, using various diluents. In this case the effects of H_2O dilution are markedly different from those of CO and CO_2. Steam alone causes an increase in the rate of propagation at the lowest dilution ratios we have studied, while CO and CO_2 cause a decrease. Although we did not study the effects of very small additions of CO and CO_2, there is no indication that the unusual behavior of steam shown in Fig. 8 is duplicated in these two diluents. We interpret this as an indication that CO and CO_2 “passivate” the sites of bimolecular reactions, while steam promotes bimolecular processes but only up to a point. Larger additions of steam do not continue to augment this effect and in fact seem to have a larger inhibitory effect than do the other two gases.

Figures 9 to 12 present more evidence for the unusual effect of steam addition at low temperatures. At the higher temperatures this behavior is much less pronounced but the distinction between steam and the other diluents persists.

A Proposed Mechanism of the Action of Diluents in Catalytic Cracking

In earlier work we reported on the effects of steaming on the catalyst itself (39). We found that cracking selectivity and activity in 2-methylpentane was largely unaffected by the extraction of extraframework aluminum from a given

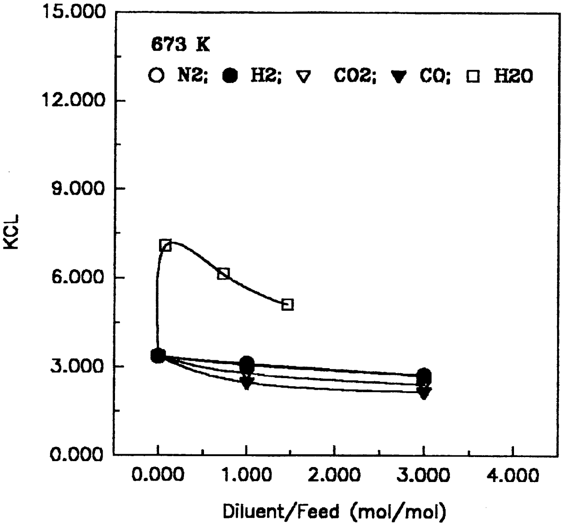

FIG. 9. KCL vs dilution ratio at 400°C with various diluents.

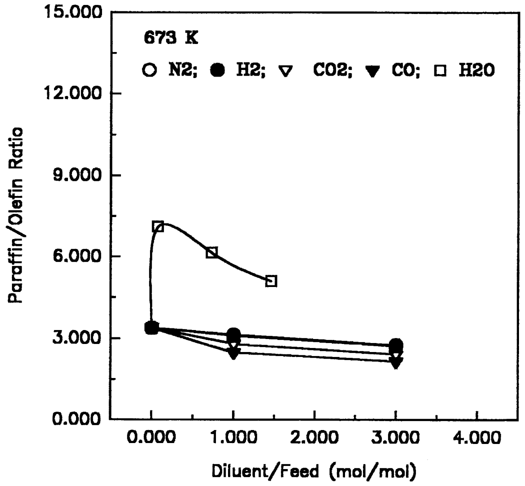

FIG. 10. Paraffin/olefin ratio in product vs dilution ratio at 400°C with various diluents.

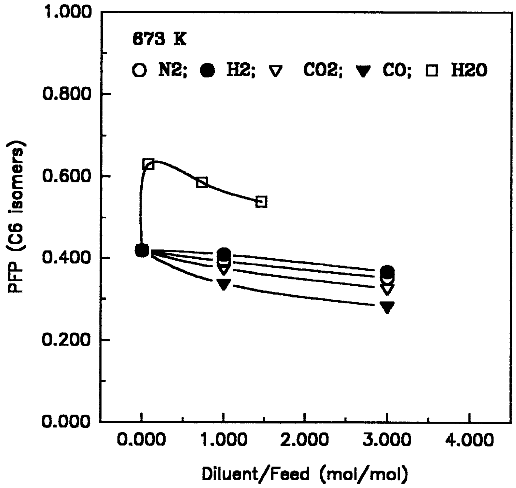

FIG. 12. PFP of isomers vs dilution ratio at 400°C with various diluents.

steamed catalyst. The rise in activity could be assigned to the unblocking of a small portion of *average* sites so that the output selectivity was not affected. Sites on the catalyst were obviously not altered by the rather intrusive procedure of removing amorphous alumina which is formed by the steaming.

At the same time, catalysts steamed to various degrees showed clear changes in activity and selectivity, even without EFAI extraction. We have reported (39) that, as the extent of steaming was increased, selectivity in 2-methylpentane cracking tended to shift so as to produce more isomers and paraffins. This is also the effect that steam as a diluent has on cracking. We know that increased steaming leads to fewer sites and that a lower site density connotes higher acidity per site (40, 41). It is therefore consistent to believe that steam dilution also causes acidity to increase, at least at the conditions where the shift to isomerization is most pronounced. In order to formulate a comprehensive explanation of this phenomenon as well as of the effects of the various diluents, all the observations must be encompassed in one mechanistic set of postulates. The explanation which will suffice to account for all these disparate observations and, in particular, for the varying effects of the diluents tested to date, may go as follows.

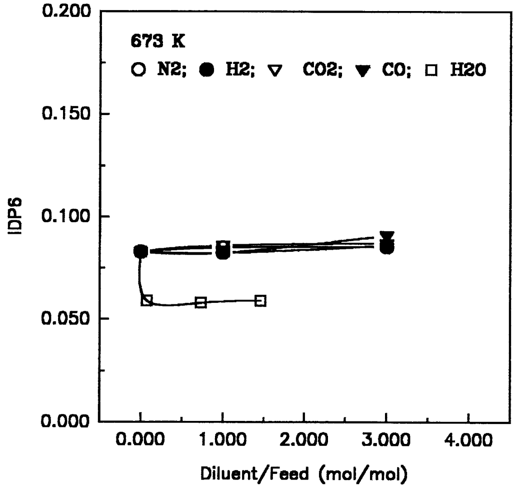

FIG. 11. IDP_6 vs dilution ratio at 400°C with various diluents.

A diluent has at least one of two distinct modes of influencing the cracking process. The first effect involves a purely physical dilution of the feed. This effect lowers the rates of all reactions involving gas phase species and appears in the presence of all diluents. Since some of the catalytic cracking conversion processes are first order in feed concentration (protolysis reactions), while others are second order (propagation reactions), dilution as a purely physical effect will decrease the rates of the latter reactions to a greater extent and will result in selectivity changes. How big the selectivity changes are will depend on the relative contributions of the two types of reactions in the mechanism of cracking for the specific feed used. For example, if a mechanism involves very short chains, little effect will be observed. Thus at higher temperatures, where the chain lengths are shorter, the "physical" effect should be minimized, as it will also be in the cracking of linear paraffins, which mostly crack by protolysis.

This simple picture is somewhat complicated by the changes in surface coverage in the presence of diluent, due to the lower partial pressure of all hydrocarbon species in the gas phase and the consequently lower surface coverage. These changes in coverage will change the average acidity of the uncovered (pristine) sites and consequently their average activity, as well as that of the covered sites. Details of these effects have not been studied for the inert diluents H_2 and N_2.

The second effect involves some form of "chemical" interaction between a polar or polarizable diluent and the catalyst sites and is superimposed on the first. Whether such an interaction could arise without involving competitive adsorption is not clear. The adsorption of the diluents studied, in sufficient amounts to cause any effect at reaction temperatures, is surprising and needs to be better understood. We must leave the exact source of this interaction for future clarification, but its results have been observed in considerable detail.

The milder "chemical" effects are due to CO and CO_2, each of which cause a decrease in the sum of the rates of both protolysis and of chain propagation. We propose that the reason for this additional effect is a "passivation" of the active sites. By this we mean that the uncovered active sites become less capable of promoting protolysis in the presence of these diluents. Such an effect suggests a weakening in the acid strength of the active sites and an increase in the strength of the conjugate bases which hold the carbenium ions during propagation reactions. These two effects would result in a *decrease* in the rates of protolysis and an increase in the rate of desorption. Both effects shorten the kinetic chain length, as was observed by experiment (13, 14). The changes in product distribution are simply a consequence of this change in the proportion between initiation and propagation reactions.

The chemical effect of steam dilution is exactly the opposite to the above. Steam *increases* the acidity of the pristine (unoccupied) sites and lowers the basicity of the associated Brønsted bases. Carbenium ions tend to desorb less readily from the weaker conjugate bases and thus surface coverage is increased on the stronger sites. The result is that protolysis is slowed down by the reduction in unoccupied sites, but the occupation of sites by undesorbed carbenium ions is increased. The consequence of these two associated effects (which represent another dichotomy) is an increase in the chain length, a decrease in olefin yield, and even an increase in the overall rate of reaction, under appropriate circumstances.

It is not surprising that an increase in the overall rate can be observed when more sites are available for propagation, since propagation reactions in chain mechanisms are faster than initiation reactions. The observed positive effect of steam on the rate of the overall reaction is just a matter of speeding up the propagation reactions, which steam seems to do, despite the accompanying presence of the "physical" dilution affect. The "physical" effect eventually overcomes the rate-enhancing benefits of the "chemical" effect of steam at higher dilution ratios. At small dilution ratios the physical effect is small and is obviously overcome by the chemical effect.

It should be pointed out that there is a potential for confusion in calling the second effect "chemical." None of the "chemically" active diluents lead to the formation of any new products. Chemically, they are quite inert in the reaction. They are chemically active only as modifiers of catalyst activity and selectivity.

Since the chemical effect reaches its full potential at low dilution ratios, one can reasonably suspect that some form of saturation plays a role here, indicating that perhaps the chemical effect is the result of an adsorption-like interaction, however unlikely it may seem. Therefore in our view there may exist other diluents, more powerful than steam, which could for example almost totally (but not quite totally) suppress initiation reactions, yielding a much different overall "cracking" reaction. The products of this reaction would be highly paraffinic and would consist mainly of isomers of the feed. In fact, for all practical purposes, this would be an isomerization catalyst.

There may also be more powerful CO_2-type diluents which will reduce site activity to the point where protolysis alone is operating and the chain length is one. Such a diluent could give a product with a paraffin-to-olefin ratio of one or less, at the expense of low rates of overall reaction. There seems to be no prospect of developing a diluent which would drive the paraffin-to-olefin ratio to zero. On the other hand, one can conceive of diluents which raise the paraffin-to-olefin ratio to large values on a given catalyst without changing the temperature. This procedure could provide an added degree of flexibility to those already available for product quality control in commercial operations and, in particular, may provide a method of increasing isomer yield.

The effects being observed with diluents in catalytic cracking echo similar effects in the gas phase pyrolysis of small paraffins, some of them similar to the paraffins being cracked as model feeds on acid catalysts. This was an active area of research some 50 or 60 years ago, when the mechanism of "limiting inhibition" by diluents such as nitric oxide was being vigorously debated (42). The gas phase cracking (pyrolysis) reaction proceeds via a free-radical chain mechanism whose essential steps are initiation, chain transfer, propagation, and termination. In these earlier studies, surprising results were observed in a number of such reactions in the presence of various diluents. The effect most frequently observed was a reduction of the overall rate of conversion to a value which was independent of further additions of diluent. It was even suspected that other diluents may increase the rate of the chain reaction. After some 30 years of debate, it was shown that the diluents (inhibitors in this case) interfere in the initiation reactions of the ongoing chain process without producing any new products (43–45). Deja vu all over again.

CONCLUSIONS

Our investigation of the influence of steam dilution on the mechanism of 2-methylpentane cracking over USHY at temperatures between 400 and 500°C shows:

1. no oxygenated products are formed by the addition of steam;
2. selectivity is changed in such a way that isomerization is greatly enhanced;
3. hydrogen transfer is enhanced;
4. paraffin/olefin ratio is significantly increased;
5. olefin production is reduced;
6. at 400°C a small amount of steam reduces the rates of all the protolysis processes but increases the rates of disproportionation processes. At 500°C even low levels of steam dilution reduce the rates of both protolysis and propagation processes;
7. steam increases the kinetic chain length (KCL) by suppressing the rate of termination in the chain reaction. This automatically reduces the rate of initiation, encourages disproportionation reactions and increases the paraffin/olefin ratio;
8. steam reduces the activation energy of all elementary reactions in the cracking process;
9. steam does not change the order of bond cracking probabilities (BCP) in protolysis, but it does decrease the probability of hydrogen and methane formation by protolysis;
10. steam decreases the rate of coke formation and inhibits the β-cracking of C_6^+ carbenium ions.

The observed results suggest the existence of an electron donor/acceptor interaction between water molecules and the acid sites on the catalyst at cracking-reaction temperatures. There is no reason to believe that the effects of steam dilution represent an extreme example of this type of behavior.

The effects of steam dilution on hydrocarbon cracking will depend on the dilution ratio and the mechanism operating in the cracking of the specific molecule. For 2-methylpentane cracking at low temperatures, a small amount of steam diluent causes a large change in isomerization selectivity and in the overall reaction rate.

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