JOURNAL OF CATALYSIS 144, 377–394 (1993)

# The Varying Effects of $N_2$, $H_2$, $CO_2$, and CO as Diluents in 2-Methylpentane Cracking on HY

YINGXIAN ZHAO AND B. W. WOJCIECHOWSKI[1]

*Department of Chemical Engineering, Queen's University, Kingston, Ontario, Canada K7L 3N6*

Received March 25, 1993; revised June 16, 1993

The effects of dilution by $N_2$, $H_2$, $CO_2$, and CO on 2-methylpentane cracking over ultrastable zeolite HY have been studied at 400°C. It was found that all these diluents slow down the rate of feed conversion, shorten the kinetic chain length, and reduce the selectivity ratios of both paraffin to olefin and isomerization to cracking. However, different diluents show different degrees of influence on these values. To explain this we propose that the various diluents "passivate" the strength of the active sites to a different degree. A quantitative description and a detailed comparison of activity and selectivity for this reaction in the presence of these various diluents are presented.

## INTRODUCTION

There continues to be a great deal of research on the cracking of paraffins on aluminosilicate catalysts (*1–14*) to which we have recently contributed by describing, in quantitative terms, a chain process which explains the mechanism of paraffin cracking (*15*). In our view this mechanism consists of three steps:

(1) initiation of the reaction, in which a feed paraffin is adsorbed onto a Brønsted acid site to form a carbonium ion and is then protolyzed into a smaller paraffin (or hydrogen) and a new carbenium ion, which stays on the acid site;

(2) propagation of the reaction chain, in which a carbenium ion acts as an active Lewis acid site and reacts with a feed molecule (by hydride transfer or disproportionation) to produce a paraffin and a new carbenium ion which can in turn act as a new site;

(3) termination of the reaction chain, in which a carbenium ion desorbs as an olefin or forms "coke."

A kinetic model describing this chain mechanism has been applied to several paraffin cracking reactions on HY zeolite (*16*). A quantitative method of treating product selectivity has also been presented (*17*). Here we investigate the effects of four diluents, $N_2$, $H_2$, $CO_2$, and CO, on the activity and selectivity of this reaction. Some of these diluents are nonpolar, while others are polarizable and potentially active in the chemistry of the reaction.

## THEORY

### *Kinetics*

A kinetic model suitable to this system has been described previously (*15*). The model accounts for monomolecular and bimolecular cracking, both of which are active in 2-methylpentane cracking. It assumes that the same locations on the surface catalyze both mechanisms, that the surface reaction is rate controlling, and that it yields the rate equation

$$\frac{dX}{d\tau} = \frac{A_1\left(\dfrac{1-X}{1+\varepsilon X}\right) + A_2\left(\dfrac{1-X}{1+\varepsilon X}\right)^2}{1 + B\left(\dfrac{1-X}{1+\varepsilon X}\right)} [1 + Gt]^{-N}, \quad (1)$$

---

[1] To whom correspondence should be addressed.

0021-9517/93 $5.00

where $X$ is the instantaneous fractional conversion of reactant, $\tau$ is the space time, $G$ is the deactivation rate constant, $N$ is the decay exponent, and $\varepsilon$ is the volume expansion coefficient. The constants $A_1$, $A_2$, and $B$ are functions of rate and equilibrium constants of various processes in the mechanism:

$$A_1 = \frac{\Sigma k_i K_A + \Sigma k_{jR} \Sigma K_j n_j [C_A]_0}{1 + \Sigma K_j n_j [C_A]_0} [\mathrm{SH}]_0 \tag{2}$$

$$A_2 = \frac{-\Sigma k_{j\mathrm{R}} \Sigma K_j n_j [C_A]_0}{1 + \Sigma K_j n_j [C_A]_0} [\mathrm{SH}]_0 \tag{3}$$

$$B = \frac{(K_A - \Sigma K_j n_j)[C_A]_0}{1 + \Sigma K_j n_j [C_A]_0}. \tag{4}$$

The $A_1$ parameter is related to the sum of the rates of reaction occurring via monomolecular and bimolecular chain processes, while $A_2$ is related to the sum of the reaction rates of bimolecular processes alone.

### *Selectivity*

A suitable methodology for determining the initial selectivity of products from experimental product yields and conversion data has been presented previously (*19, 20*). For each reaction product, the time-averaged yield sampled from $t = 0$ to $t_f$ is plotted against the average conversion of feed, $\overline{X}_{t_f}$. Each of the plots can be enveloped by a single curve, the optimum performance envelop (OPE), which describes the selectivity behaviour of that product as catalyst decay approaches zero. The initial selectivity of a product, given by the slope of the OPE at the origin, is nonzero for a primary product and zero for a secondary or subsequent product. Primary products are those which are formed directly from the feed molecule without any detectable gas phase intermediate.

## EXPERIMENTAL

The 2-methylpentane was obtained from Aldrich and used without further purification. The only impurity present was 3-methylpentane (0.55%). The $N_2$, $H_2$, $CO_2$, and CO (UHP grade) were obtained from Linde and used as diluents.

Ultrastable HY zeolite (USHY) was prepared from NaY (BDH Chemicals) by repeated exchange with 0.5*M* $NH_4NO_3$ solution at 20°C for 24 hr. Between exchanges, the catalyst was dried at 110°C for 24 hr., then calcinated in air at 500°C for 2 hr. After 10 such exchanges the catalyst was steamed at 200°C for 24 hr. The powder was pelletized, crushed, and sieved to obtain the 60–80 mesh material used in our runs. On analysis, the catalyst was found to be 99.8% $Na^+$ exchanged. The unit cell size was 24.536 (Å) (X-ray diffraction); each unit cell contained 35 Al atoms. The bulk Si/Al ratio was 2.5 (X-ray fluorescence). The framework Si/Al ratio was 4.49 ($^{29}$Si MAS–NMR) and the surface area was 540 $m^2/g$ ($N_2$ BET).

All experiments were performed in a fixed-bed plug-flow glass reactor (60 × 1.7 cm I.D.) which had an independently controlled three-zone heater and a 0.15-m catalyst bed containing catalyst diluted with sand in order to minimize thermal effects. Time on stream was varied between 2 and 20 min. At various times catalyst-to-reactant ratios between 0.013 and 0.11 were used. Details of experimental apparatus and methodology have been presented previously (*21*). Blank runs were carried out to determine the extent of thermal cracking.

The identification of the products was performed using a Finnigan 1020 GC/MC. Gaseous products were analyzed by a Carle SX 1156 gas chromatograph which also allowed for hydrogen determination. Liquid products were analyzed by a Varian 3700 gas chromatograph with a 60-m SE54 capillary column and a flame ionization detector. Products up to $C_7$ were eluted at 15°C followed by a temperature ramp of 5°C/min up to 300°C. At the end of each run, the reactor was purged with dry $N_2$ for 30 min and the purge gases were also collected in the burette. All unpurged residues were regarded as coke. The catalyst was then regenerated by passing dry, carbon-dioxide-free air through the reactor at 500°C for 8 hr. Regeneration gases were passed through a second reactor containing an oxidation catalyst to ensure their complete combustion to carbon dioxide and water. The water produced was trapped in two drierite tubes in series and the carbon dioxide in two ascarite tubes. The amount of coke produced during the reaction was calculated from the weight of water and carbon dioxide trapped during regeneration.

## RESULTS AND DISCUSSION

### ACTIVITY

The kinetic model presented in the theory section accounts for monomolecular and bimolecular processes and is based on the assumption that the same locations are active in the two processes and that the surface reaction is rate controlling. Figure 1 shows that for the reaction of 2-methylpentane on USHY at 400°C in all cases, whether without or with $N_2$, $H_2$, $CO_2$, or CO as a diluent at dilution ratios from 1 to 3, experimental data are well fitted by this model. Optimum values of kinetic parameters for various reaction systems are given in Table 1.

We know that the rate of a catalytic reaction depends on the strength, distribution, activity, and concentration of active sites on the catalyst surface, as well as the concentration of the reactant in the gas phase. The introduction of a diluent gas into a reaction system decreases the concentration of reactant but may or may not change the concentration, decay rate, or strength distribution of active sites.

#### *Cumulative Conversion*

The various curves of cumulative conversion $\overline{X}_{t_f}$ as a function of time on stream at different catalyst-to-feed ratios are presented in Fig. 1. We find that, in general, the addition of $N_2$ or $H_2$ at a 1 : 1 ratio lowers the early slopes of the conversion curves as shown in Fig. 1. The limiting conversions decrease with increasing dilution ratio and curves continue to become flatter in the early stage as shown in Figs. 1c and 1e.

The fact that the limiting conversion does not vary a great deal with $N_2$ or $H_2$ dilution suggests that the dilution decreases the decay rate as well as the reaction rate (*17*). In the case of $CO_2$ as a diluent one may see that both the limiting conversion and the early slope of the conversion curve decrease at a dilution ratio of 1 : 1 (Fig. 1f) and the trend continues with increasing dilution ratio (Fig. 1g). In the case of CO the above tendency is even more pronounced. For example, at a catalyst/oil ratio of 0.11 and a time on stream of 20 min, the cumulative conversion declines sharply from 42% to 29% to 24% with increasing dilution ratio from 0 (Fig. 1a) to 1 : 1 (Fig. 1h) to 3 : 1 (Fig. 1i).

The behaviour of conversion curves plotted in this way allows an alternative approach to the quantitative evaluation of initial catalyst activity and the rate of decay. The slope at the origin of the $\overline{X}$ vs $t_f$ curve is given by

$$\left(\frac{d\overline{X}}{dt_f}\right)_{t_f\to 0} = bP\left(\frac{dX}{d\tau}\right)_{\tau\to 0} = bP\left(\frac{A_1 + A_2}{1 + B}\right) = bP\left(\frac{\Sigma k_i K_A}{1 + K_A[C_A]_0}\right). \qquad (5)$$

This in turn represents the initial rate of reaction modified by the adsorption parameter $B$. As long as we take it that the $A$ parameters do not vary significantly with dilution, it is the parameter $B$ which governs change in this slope. A smaller slope indicates a less negative value of $B$, which agrees with Table 1. The $A$ parameters, however, do vary somewhat with dilution. In the case of dilution the slope at the origin of the $\overline{X}$ vs $t_f$ curve is given by

$$\left(\frac{d\overline{X}}{dt_f}\right)_{t_f\to 0} = \frac{1}{1+\beta}\left(\frac{d\overline{X}}{dt_{f\beta}}\right)_{t_{f\beta}\to 0} = \frac{bP}{1+\beta}\left(\frac{A_{1\beta} + A_{2\beta}}{1 + B_\beta}\right) = bP\left(\frac{\Sigma k_i K_A}{1 + \beta + K_A[C_A]_0}\right). \qquad (6)$$

The level of the plateau in $\overline{X}$ at a given

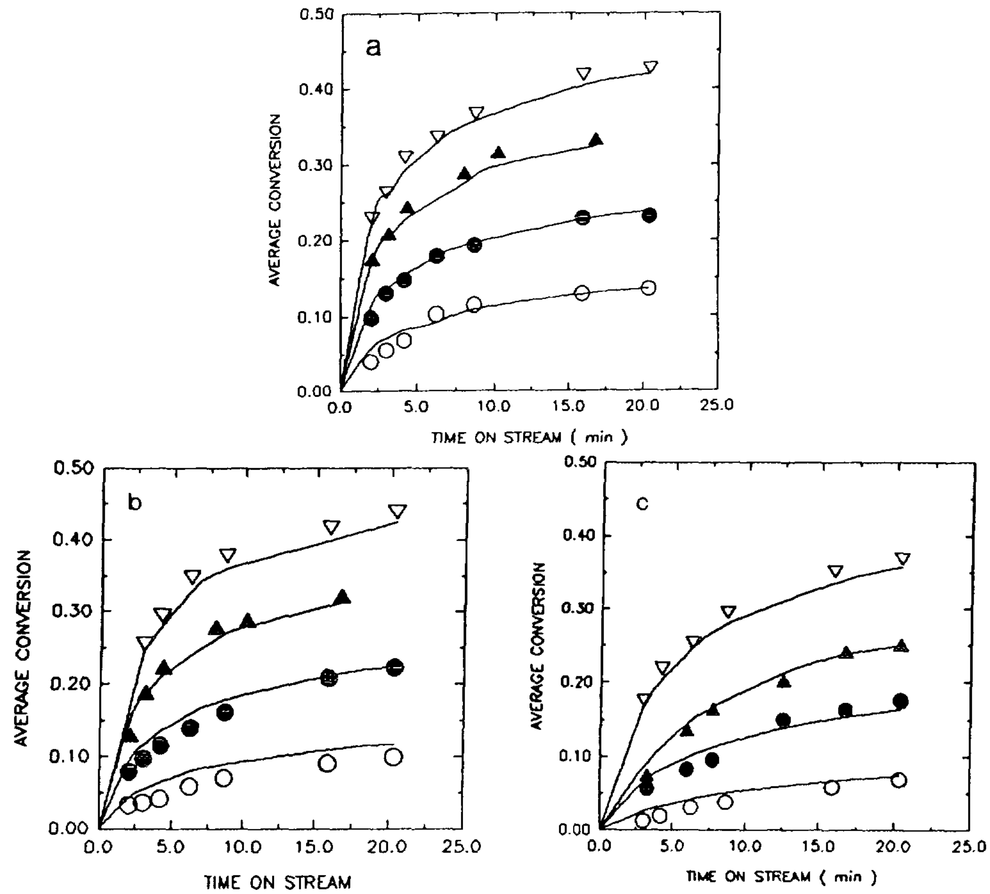

FIG. 1. Theoretical curves and experimental points of average conversion vs time on stream for 2-methylpentane cracking on HY at 400°C. Reactant molar composition: (a) pure feed, (b) $N_2$/feed = 1, (c) $N_2$/feed = 3, (d) $H_2$/feed = 1, (e) $H_2$/feed = 3, (f) $CO_2$/feed = 1, (g) $CO_2$/feed = 3, (h) CO/feed = 1, (i) CO/feed = 3. Catalyst-to-feed weight ratio: (▽) 0.11; (▲) 0.068; (●) 0.035; (○) 0.013.

catalyst/oil ratio is a function of the decay, adsorption, and decay constants. It is not easy to write down the specific form of that dependence but one can say that if dilution does not change the $\overline{X}$ level significantly then the constants which define $\overline{X}$ have not been changed or have been changed in some compensating manner.

One would also expect that the results in Fig. 1 reflect the dependence of the conversion rate on the concentration of feed in the gas phase, since any diluent reduces the concentration of reactant. The higher the dilution ratio, the slower should be the conversion rate. We note, however, that the same dilution ratio, using different diluents, reduces the reaction activity to a different extent in the following order:

$$CO > CO_2 > N_2 \approx H_2. \quad (7)$$

This difference must be a function of the physical and chemical properties of the diluents. Among the four diluent gases, CO is a polar molecule with a permanent dipole moment, while $H_2$, $N_2$, and $CO_2$ are nonpolar molecules but with polarizability in the order $H_2 \leq N_2 < CO_2$. We can therefore expect the ability to adsorb on ionic acid sites to increase as follows:

$$H_2 \approx N_2 < CO_2 < CO. \quad (8)$$

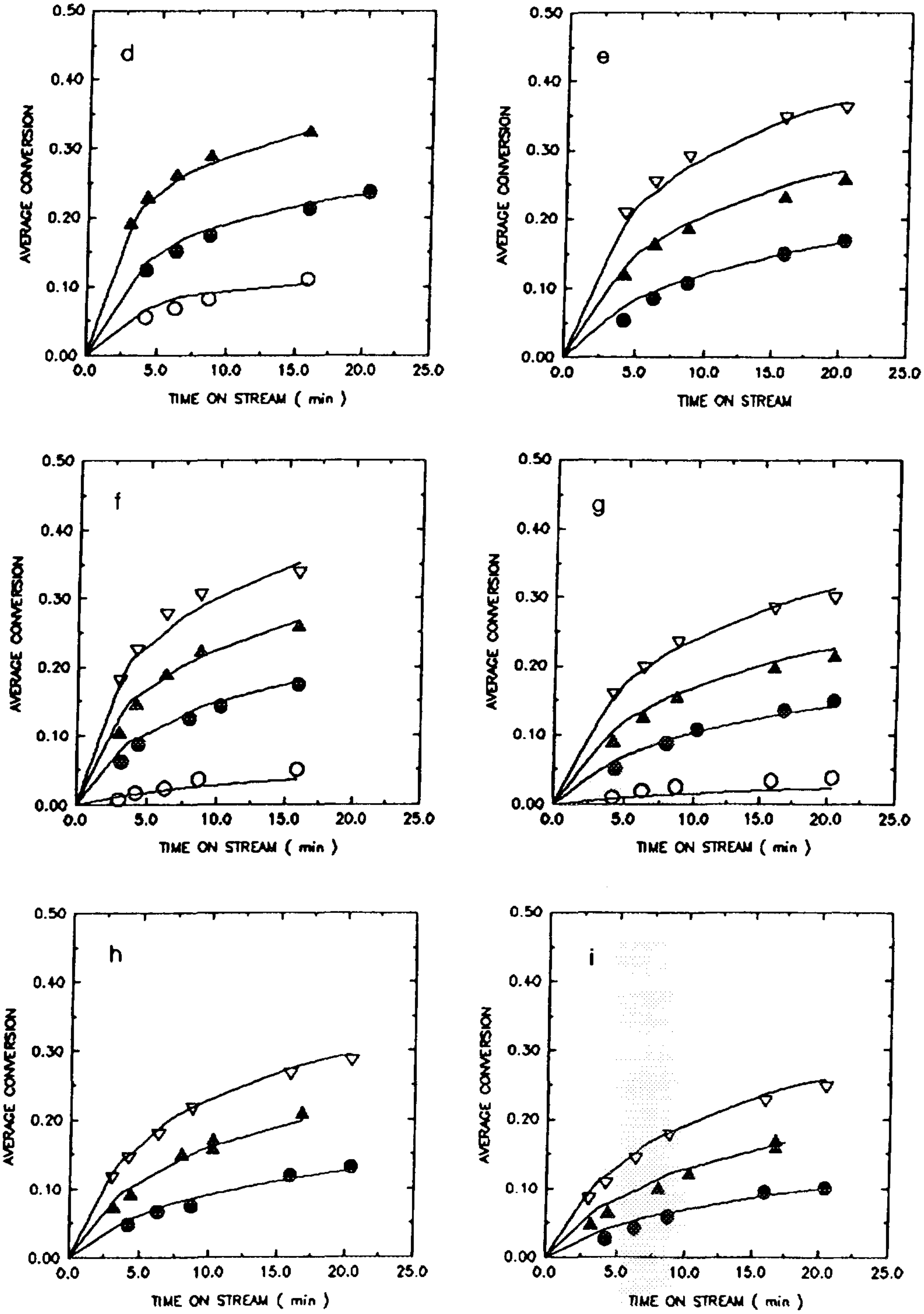

FIG. 1—*Continued*

TABLE 1

Optimum Values of Kinetic Parameters for 2-Methylpentane Cracking on HY at 400°C

| Kinetic parameter | Gases (dilution ratio) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Pure feed (0) | $N_2$ (1) | $N_2$ (3) | $H_2$ (1) | $H_2$ (3) | $CO_2$ (1) | $CO_2$ (3) | CO (1) | CO (3) |
| $A_1$ ($min^{-1}$) | .267 | .308 | .498 | .316 | .521 | .304 | .337 | .292 | .295 |
| $A_2$ ($min^{-1}$) | −.084 | −.077 | −.063 | −.081 | −.065 | −.073 | −.066 | −.062 | −.056 |
| $B$ | −.902 | −.850 | −.663 | −.863 | −.657 | −.753 | −.525 | −.549 | −.356 |
| $G$ ($min^{-1}$) | .262 | .232 | .208 | .254 | .211 | .209 | .199 | .194 | .189 |
| $N^a$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $\varepsilon^b$ | .309 | .166 | .094 | .161 | .093 | .181 | .104 | .202 | .116 |

[a] $N$ is fixed at a value of 1 (*16, 20*).

[b] $\varepsilon$ is calculated using experimental selectivity data (*16, 20*).

It seems then that we must attribute some of the loss of activity to "passivation" of active Brønsted sites by the polar interactions of the diluent with active sites, as well as to the simple effect of dilution. We propose that the interaction of $H_2$ and $N_2$ with an active site is weak and does not change the rate parameters significantly, since they cause little loss of limiting conversion, while that of CO is strongest since it causes a large loss in limiting conversion. That of $CO_2$ falls between these two cases.

A further possible reason for the loss of activity is the polar interaction between diluents and surface carbenium ions, those which are active in bimolecular chain processes in this reaction. As an electron acceptor (Lewis acid) a carbenium ion can interact with an electron donor (Lewis base). This interaction alters the acid strength, or "passivates" the bimolecular reaction sites, resulting in a drop of conversion due to decreased chain propagation. $H_2$ and $N_2$, with no active free electrons, are not expected to take part in such interctions. CO is a known electron donor while $CO_2$, with four pairs of free electrons, may also act as a donor. Both can inhibit chain propagation reactions by passivating active carbenium ions on the surfaces, causing a reduction in total conversion.

### *Initial Reaction Rates*

To examine the effects of dilution on the initial conversion rate in another way we can consider the variation in the value of $(A_1 + A_2)/(1 + B)$ with dilution using Table 1, since this is a measure of the monomolecular rate $dX/d\tau$ at $t \rightarrow 0$ and $x \rightarrow 0$, i.e., the instantaneous initial rate (Eq. (1)). Figure 2

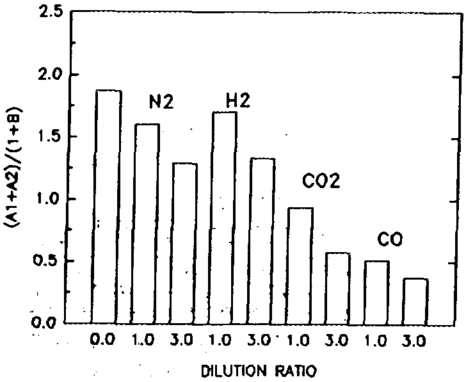

FIG. 2. A comparison of the initial rate for pure 2-methylpentane cracking with the rate in the presence of diluent $H_2$, $N_2$, $CO_2$, or CO at dilution ratio of 1 or 3.

shows the value of $(A_1 + A_2)/(1 + B)$ without and with $N_2$, $H_2$, $CO_2$, and CO as a function of the diluent at the dilution ratios 1 : 1 and 1 : 3. The rate of pure feed conversion is the highest. For each diluent it decreases with an increase in dilution ratio. For the various diluent gases at the same dilution ratio the magnitude of this initial rate is in the order:

$$H_2 \geq N_2 \gg CO_2 \gg CO. \qquad (9)$$

Here we clearly see the effects of both simple dilution by hydrogen and nitrogen and dilution plus passivation by the other two diluents, on a clean catalyst surface. The more polar the diluent, the stronger the passivation of the active sites, and the smaller the initial rate of reactant conversion as we saw in Fig. 1.

*Monomolecular and Bimolecular Processes*

We have argued that the mechanism of 2-methylpentane cracking on HY consists of monomolecular and bimolecular processes in which the active sites are Brønsted acid sites on the pristine catalyst and carbenium ions on these Brønsted sites, respectively (*15*, *17*). We must therefore investigate the effects of dilution on these two different but related processes. To do that we derive the following equation using Eqs. (2) and (3):

$$\frac{(A_1 + A_2)}{-A_2} = \frac{\Sigma k_i K_A}{\Sigma k_{jR} \Sigma n_j K_j [C_A]_0}. \qquad (10)$$

The right hand side in Eq. (10) is the rate ratio of monomolecular processes to bimolecular processes at a steady state coverage by surface species. If the adsorption and reaction rate constants do not change upon the addition of a diluent, Eq. (10) becomes

$$\left(\frac{A_1 + A_2}{-A_2}\right)_\beta = \frac{\Sigma k_i K_A (1 + \beta)}{\Sigma k_{jR} \Sigma n_j K_j [C_A]_0^0}, \qquad (11)$$

where $\beta$ is the dilution ratio and $[C_A]_0^0$ is the initial concentration of feed without dilution (*22*).

In a previous study (*22*) we applied Eq. (11) to the case of $N_2$ as a diluent at ratios from 1 : 1 to 5 : 1 and concluded that $N_2$ diluted the concentration of reactant and promoted the desorption of carbenium ions as olefins but did not significantly change the constants of adsorption and reaction. From Fig. 3 we see that by this measure $H_2$ has almost the same effect as $N_2$. In the case of $CO_2$ and CO the situation is significantly different. First, at the dilution ratio of 1 : 1 this ratio is slightly larger than that for $N_2$ or $H_2$. Second, on increasing the dilution ratio from 1 : 1 to 3 : 1 this ratio for CO or $CO_2$ increases much less than that for $N_2$ or $H_2$. The result can be explained by considering the balance of the effects of passivation on monomolecular reaction sites (i.e., Brønsted sites) and on bimolecular reaction sites (i.e., carbenium ions).

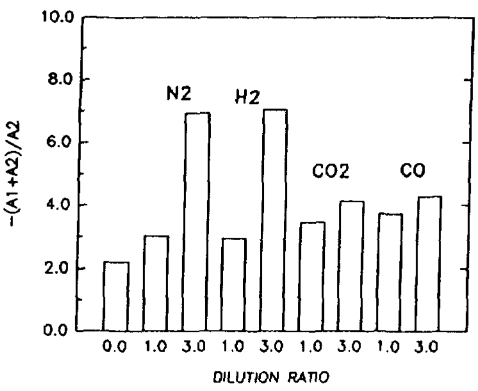

FIG. 3. A comparison of the rate ratio of monomolecular process to bimolecular process for pure 2-methylpentane cracking with the ratio in the presence of $H_2$, $N_2$, $CO_2$, or CO as a diluent at dilution ratio of 1 or 3.

Both CO and $CO_2$ as simple diluents would have the same effect as that seen for $N_2$ and $H_2$ in Fig. 3. What makes the effect of CO and $CO_2$ different is that at 1 : 1 ratio both gases seem to slow down bimolecular reactions more than by simple dilution. The result is that $|A_2|$ decreases more than expected and the ratio $(A_1 + A_2)/(-A_2)$ is larger than for $N_2$ and $H_2$. We think this occurs because the polar diluents interact with surface ions, both protons and carbenium ions, to make them less reactive. Table 1 supports this conjecture; we see $|A_2|$ decreasing much more for the polar gases, while $A_1$ remains almost constant.

As we increase the diluent ratio to 1 : 3 we see that $(A_1 + A_2)/(-A_2)$ increases markedly for $H_2$ and $N_2$, indicating a rapid suppression of bimolecular reactions by the dilution effect. For the polar gases this suppression of bimolecular reactions seems to be smaller or, alternatively, there is a significant suppression of monomolecular reactions represented by $(A_1 + A_2)$. This in fact is the case, as shown in Fig. 2 and in Table 1. It seems therefore that polar diluents have the following effects on the rates of surface processes:

(1) A simple diluent effect which reduces the probability of bimolecular collisions and hence of both the initiation and chain propagating reactions.

(2) A passivation effect on both protons and carbenium ions which also slows down the rates of both initiation and propagation reaction but to a different extent.

### *Parameter B and G*

The value of the kinetic parameter *B* quantifies the competition for adsorption sites between product olefins and the feed. The smaller (i.e., more negative) the value, the stronger the adsorption of products vis-à-vis the reactant. From Table 1 we see that dilution increases the *B* value. For the same diluent the larger the dilution ratio, the larger the *B* value. For various diluents at the same dilution ratio (1 : 1 or 3 : 1) the values follow the order

$$\text{pure feed} < N_2 \approx H_2 < CO_2 < CO. \quad (12)$$

That is to say that the adsorption of product (i.e., carbenium ions) becomes weaker vis-à-vis the reactant (i.e., carbonium ions).

There is also a tendency for the decay parameter *G* to decrease with dilution ratio (Table 1). Since catalyst decay results from the formation of coke, which in turn seems to involve bimolecular reactions between adjacent carbenium ions (*22*), we interpret the decrease in *G* as being related to the reduction of surface coverage by active carbenium ions. Furthermore, passivation of carbenium ions by interaction with a polar diluent molecule makes them less reactive in the coke-making reaction.

## SELECTIVITY

Tables 2 and 3 present the initial selectivity data for 2-methylpentane cracking over HY at 400°C, without and with $N_2$, $H_2$, $CO_2$, or CO as a diluent, at the dilution ratio of 1 : 1 or 3 : 1. For each case, the initial products include $C_1$–$C_5$ paraffins, $C_2$–$C_6$ olefins, three $C_6$ isomeric paraffins, coke, and hydrogen.

### *Product Formation Probability*

Table 3 shows that total molar selectivities increase due to the addition of all diluents indicating that the molecule is breaking up into more fragments. For the same dilution ratio the order of total molar selectivities is $CO > CO_2 > N_2 > H_2$. To investigate the changes in selectivity distribution in more detail we divide all products, excluding coke, into three classes:

(a) $C_1$–$C_5$ paraffins and hydrogen;
(b) $C_2$–$C_6$ olefins;
(c) $C_6$ isomeric paraffins.

The variations of their PFPs (i.e., normalized molar selectivities) with dilution are shown in Fig. 4. We see that for the same diluent both (a) and (b) increase with dilution and that at the same dilution the PFPs of (a) or (b) follow the order

$$CO > CO_2 > N_2 \geq H_2 > \text{pure feed}. \quad (13)$$

The PFPs of (c) decrease with dilution ratio and for various diluents at the same dilution ratio in the order

$$\text{pure feed} > H_2 \geq N_2 > CO_2 > CO \quad (14)$$

In other words, different diluents inhibit isomerization to a different extent. This is the root reason that the total molar selectivity increases.

According to our proposed chain mecha-

TABLE 2

Initial Weight Selectivities for 2-Methylpentane Cracking on HY Zeolite at 400°C

| Products | Gases (dilution ratio) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Pure feed (0) | $N_2$ (1) | $N_2$ (3) | $H_2$ (1) | $H_2$ (3) | CO (1) | CO (3) | $CO_2$ (1) | $CO_2$ (3) |
| Hydrogen | .0004 | .0002[a] | .0001[b] | .0002 | .0001 | .0004 | .0003 | .0005 | .0003 |
| Methane | .0030 | .0047 | .0076 | .0057 | .0087 | .0038 | .0059 | .0054 | .0069 |
| Ethane | .0021 | .0023 | .0029 | .0031 | .0051 | .0033 | .0055 | .0048 | .0067 |
| Propane | .0955 | .1021 | .1091 | .0970 | .1018 | .1360 | .1507 | .1078 | .1198 |
| Butanes | .0824 | .0869 | .0933 | .0802 | .0820 | .0741 | .0796 | .0756 | .0821 |
| Pentanes | .0883 | .0894 | .0928 | .0848 | .0930 | .0795 | .0865 | .0816 | .0911 |
| Hexanes | .5476 | .5241 | .4833 | .5431 | .5028 | .4740 | .4161 | .5114 | .4613 |
| Ethylene | .0066 | .0076 | .0108 | .0082 | .0163 | .0130 | .0156 | .0116 | .0163 |
| Propylene | .0976 | .1088 | .1192 | .0990 | .1032 | .1376 | .1578 | .1107 | .1251 |
| Butenes | .0117 | .0127 | .0193 | .0191 | .0227 | .0176 | .0229 | .0188 | .0275 |
| Pentenes | .0065 | .0079 | .0106 | .0112 | .0168 | .0076 | .0105 | .0142 | .0165 |
| Hexenes | .0487 | .0475 | .0465 | .0476 | .0461 | .0416 | .0409 | .0470 | .0427 |
| Coke | .0086 | .0063 | .0039 | .0068 | .0052 | .0123 | .0101 | .0095 | .0063 |
| Totals | 0.9990 | 1.0006 | 0.9994 | 1.0060 | 1.0038 | 1.0008 | 1.0024 | 0.9989 | 1.0026 |

[a] 0.00024.
[b] 0.00015.

nism for paraffin cracking (*22*), olefins are the products of chain termination (carbenium ion desorption); isomeric paraffins are the products of the chain propagation (hydride transfer between feed molecules and carbenium ions); and paraffins whose number of carbons is less than that of the feed molecule may be produced by the protolysis of the feed molecule or by chain propagation (dimerization cracking).

As we have already pointed out, one function of a diluent is to reduce the concentration of feed and thus slow down the rate of bimolecular chain propagation, hence the drop of the PFPs of $C_6$ isomeric paraffins. Since the rate of chain termination is independent of the concentration of feed in the gas phase, the rise in the PFPs of olefins as the bimolecular processes slow down is also expected. For the smaller paraffins, dilution reduces their PFPs by slowing the rate of bimolecular reactions but also enhances their PFPs by increasing the proportion of conversion due to chain initiation in the overall reaction processes. Here we see the values increase slightly due to these offsetting trends.

To explain the difference in the effects of different diluent gases we must consider the interaction between a diluent and the active site in more detail. As we outline in the preceding section, CO and $CO_2$ may be easier to attach to an ionic site than $H_2$ and $N_2$. It is this interaction that we believe reduces the surface residence time of carbenium ions and hence inhibits the propagation of reaction chains as well as promoting the formation of olefins.

The increase in the PFPs in Fig. 4b and the sharp drop of the PFPs in 4c for CO as a diluent, in contrast to $N_2$ or $H_2$, is so pronounced that we may even want to call CO an inhibitor of the isomerization reaction. Unfortunately the whole issue of interpreting catalyst properties using the PFPs is greatly complicated, if not made impossible, by the confusion caused by the presence of the chain processes. Each PFP represents

TABLE 3

Initial Molar Selectivities for 2-Methylpentane Cracking on HY Zeolite at 400°C

| Products | Gases (dilution ratio) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Pure feed (0) | $N_2$ (1) | $N_2$ (3) | $H_2$ (1) | $H_2$ (3) | CO (1) | CO (3) | $CO_2$ (1) | $CO_2$ (3) |
| Hydrogen: $H_2$ | .0172 | .0105 | .0063 | .0086 | .0043 | .0172 | .0129 | .0215 | .0129 |
| Paraffins: $C_1$ | .0161 | .0253 | .0409 | .0306 | .0468 | .0204 | .0317 | .0290 | .0371 |
| $C_2$ | .0060 | .0066 | .0083 | .0089 | .0146 | .0095 | .0158 | .0138 | .0192 |
| $C_3$ | .1867 | .1996 | .2132 | .1896 | .1990 | .2658 | .2946 | .2107 | .2342 |
| $C_4$ | .1222 | .1289 | .1383 | .1189 | .1216 | .1099 | .1180 | .1121 | .1217 |
| $C_5$ | .1055 | .1068 | .1108 | .1013 | .1111 | .0950 | .1033 | .0975 | .1088 |
| $C_6$ | .5476 | .5241 | .4833 | .5431 | .5028 | .4740 | .4146 | .5114 | .4613 |
| sum | 1.0013 | 1.0018 | 1.0012 | 1.0010 | 1.0020 | .9918 | .9924 | .9960 | .9952 |
| Olefins: $C_2$ | .0203 | .0233 | .0332 | .0252 | .0501 | .0399 | .0479 | .0356 | .0501 |
| $C_3$ | .1998 | .2228 | .2441 | .2028 | .2113 | .2818 | .3231 | .2267 | .2562 |
| $C_4$ | .0180 | .0195 | .0296 | .0293 | .0349 | .0270 | .0352 | .0289 | .0422 |
| $C_5$ | .0080 | .0097 | .0130 | .0137 | .0206 | .0093 | .0129 | .0174 | .0203 |
| $C_6$ | .0499 | .0486 | .0476 | .0487 | .0472 | .0426 | .0419 | .0481 | .0437 |
| sum | .2960 | .3239 | .3675 | .3197 | .3641 | .4006 | .4610 | .3567 | .4125 |
| Coke[a] | .0086 | .0065 | .0039 | .0068 | .0052 | .0123 | .0101 | .0095 | .0063 |
| Totals | 1.3059 | 1.3319 | 1.3726 | 1.3275 | 1.3695 | 1.4027 | 1.4635 | 1.3622 | 1.4140 |

*Note*. Molar selectivity = (Weight selectivity) × Mol. wt. of feed/Mol. wt. of product.

[a] The coke selectivity is in terms of weight, not in moles.

a molar selectivity composed of the contribution of one or more modes of formation for that product. To see a more fundamental cause for these effects we must examine the probabilities of conversion by each of the many processes occuring on the surface. It is the changes in these Reaction Pathway Probabilities (RPPs) which may reveal the cause of the changes induced by dilution or, for that matter, by catalyst formulation.

### *Reaction Path Probability (RPP)*

The reaction network for 2-methylpentane cracking on HY consists of a series of individual elementary reactions, as shown in Table 4. The mathematical model of this mechanism (i.e., matrix expression) and the computer procedure used to evaluate the RPPs have been presented previously (*17*). The RPPs of all individual reaction pathways for our systems can be calculated using this methodology. We apply the same model as in (*17*) to all the cases with various diluents at different dilution ratios. The results are presented in Fig. 5. The RPPs of pathway $X_{20}$, $X_{21}$, $X_{31}$, $X_{40}$, and $X_{41}$ are not shown since they are 0 at all dilutions. We see that for monomolecular initiation, the RPPs of paths $X_{01}$, $X_{02}$, and $X_{03}$ increase with dilution but to a different extent for various diluents. $X_{04}$ varies slowly with dilution while the change in $X_{00}$ is opposite to that for the other protolysis modes.

For propagation the RPPs of $X_{23}$, $X_{30}$, and $X_{60}$ decrease while $X_{32}$ and $X_{50}$ increase with dilution ratio, but to different extents for various diluents. At the same time $X_{22}$ increases with $N_2$ and decreases with CO or $CO_2$ with increasing dilution ratio. All the above-mentioned changes can be attributed to changes in the number and strength distribution of surface active sites due to the addi-

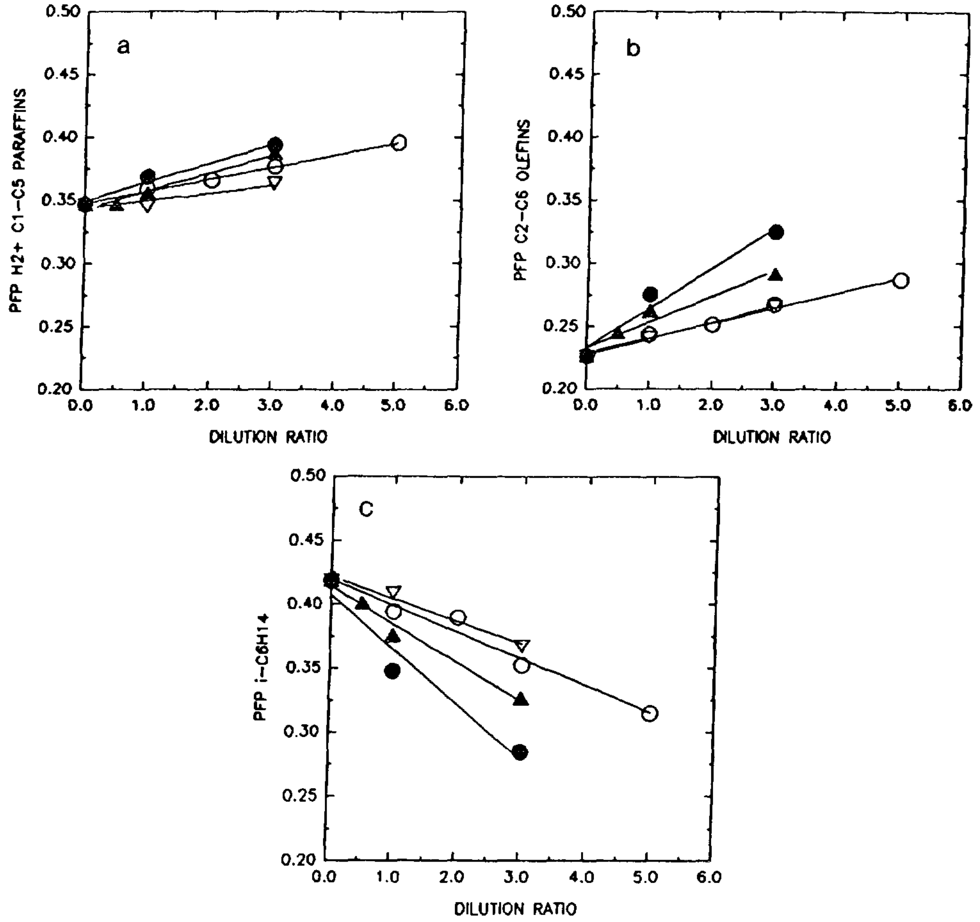

FIG. 4. Product formation probability in 2-methylpentane cracking vs dilution ratio: (a) $H_2$ + $C_1$–$C_5$ paraffins, (b) $C_2$–$C_6$ olefins, (c) $C_6$ isomeric paraffins. Diluent symbols: (▽) $H_2$, (○) $N_2$, (▲) $CO_2$, (●) CO.

tion of various diluents at various ratios. We can now compare chain initiation to chain propagation probabilities.

From Fig. 6 we see that the total of the RPPs of initiation reactions increases with increasing dilution ratio for all diluents and follows the order

$$\mathrm{CO} > \mathrm{CO_2} > \mathrm{H_2} \approx \mathrm{N_2} > \text{pure feed}, \quad (15)$$

while the total of RPPs of the propagation reactions changes in reverse order. More detailed consideration of the individual chain propagating reactions is left for consideration in the future when more examples of this type of information become available.

*Bond Cracking Probability (BCP)*

To compare the probabilities of protolysis of various C–C and C–H bonds we have defined

$$\mathrm{BCP}_i = \frac{\mathrm{RPP}_{X_{0i}}}{\sum \mathrm{RPP}_{X_{0i}}}. \quad (16)$$

The calculated BCP values with no diluent show the protolysis of bonds in the feed molecule obeys the following order of preference (*17*):

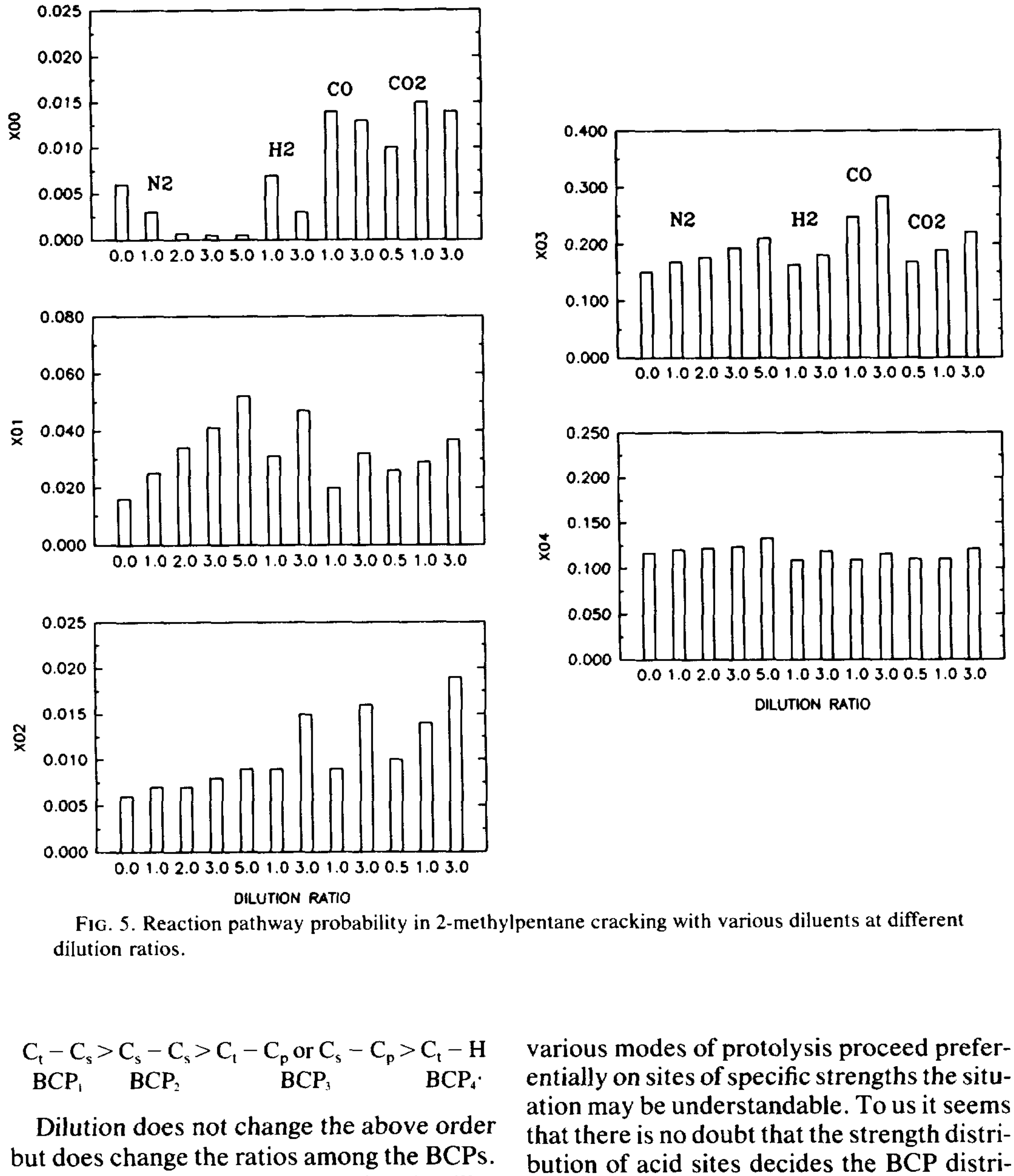

FIG. 5. Reaction pathway probability in 2-methylpentane cracking with various diluents at different dilution ratios.

$C_t - C_s > C_s - C_s > C_t - C_p$ or $C_s - C_p > C_t - H$
$BCP_1 \quad BCP_2 \quad BCP_3 \quad BCP_4$.

Dilution does not change the above order but does change the ratios among the BCPs. From Fig. 7 we see that increasing the dilution ratio caused $BCP_1$ to stay constant in the cases of $N_2$, $H_2$, and $CO_2$ as a diluent and to increase in the case of CO. $BCP_2$ decreased and $BCP_3$ increased to a different extent for the various diluents. $BCP_4$ decreased with $N_2$ as a diluent and increased then decreased with $H_2$, CO, and $CO_2$. The reasons for these changes are not immediately clear. However, if one agrees that the various modes of protolysis proceed preferentially on sites of specific strengths the situation may be understandable. To us it seems that there is no doubt that the strength distribution of acid sites decides the BCP distribution. There is also no doubt that the available acid strength distribution of the pristine catalyst itself is not the same as that available for the protolysis reaction at steady state in the absence of diluent, and that this distribution will change due to the introduction of a diluent, at least because more sites are made available by the enhanced desorption. That is to say that the level of dilution and the kind of diluent used results in a

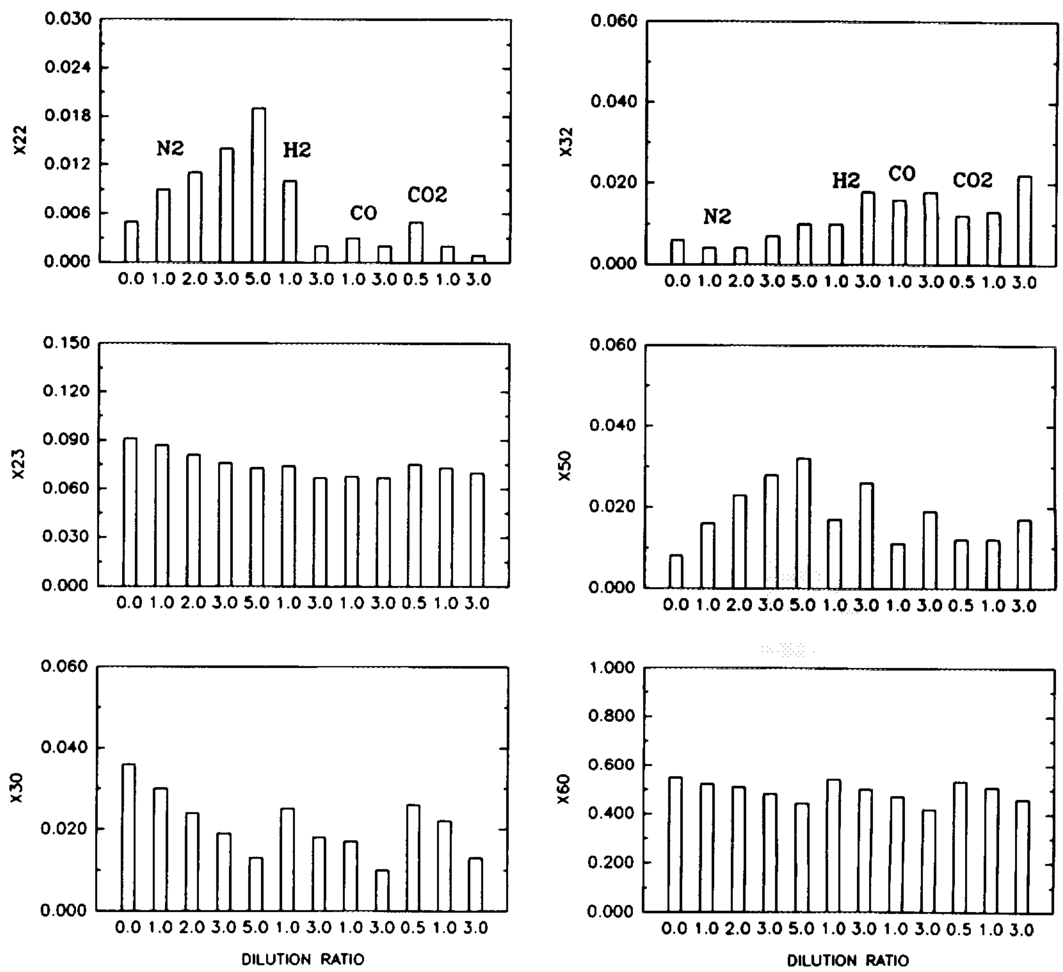

FIG. 5—*Continued*

specific site strength distribution of the uncovered, "pristine" sites. By the same token it changes the strength distribution of the sites covered by carbonium ions. This in turn governs the proportions of the various BCPs and of the chain carrying processes. The complex behaviour observed is not immediately obvious and its detailed interpretation awaits further investigations.

### *Kinetic Chain Length (KCL)*

We have defined the kinetic chain length (KCL) as the ratio of overall reaction rate to initiation reaction rate. Its value may be calculated from the RPP data (*17*). Figure 8 shows the KCLs of 2-methylpentane cracking on HY varies with the dilution ratio. One can see that the KCL becomes shorter with increasing dilution ratio for all diluents. For the same dilution ratio the order of KCL is $H_2 = N_2 > CO_2 > CO$. This result confirms that dilution slows down the rate of overall reaction by impeding the propagation of reaction chains more than it does the rate of initiation. The converse should also be true: high pressure cracking should proceed via chain propagation to a larger extent. This influences the selectivity for products in a manner analogous to that described above; i.e.,

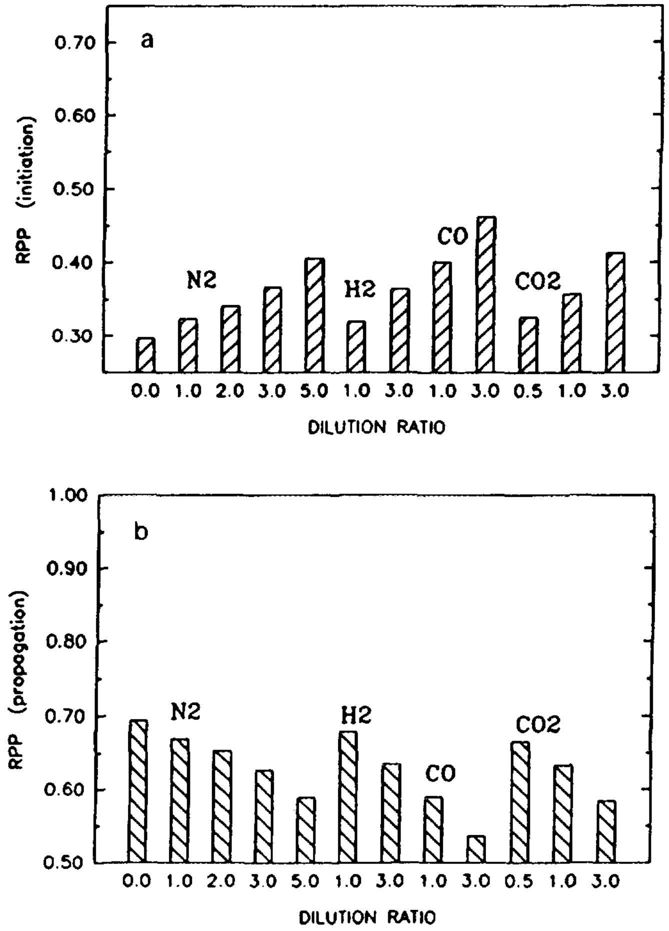

FIG. 6. Reaction pathway probability of initiation and propagation reactions in 2-methylpentane cracking with various diluents at different dilution ratios: (a) initiation; (b) propagation.

higher pressure should increase the selectivity for paraffins, isomers, and coke.

### *Competitive Events on Carbenium Ions*

As the active sites of chain propagation processes, carbenium ions play a very important role in the reaction mechanism. Examining the various competitive events occurring on them can help to unravel more of the causes for the observed effects of dilution on the reaction mechanism. Here we specifically discuss the fates of $C_2^+$, $C_3^+$, and $C_6^+$ carbenium ions, since they are the dominant surface species in this reaction system (*22*).

From the reaction network presented in Table 4 we see that there are two kinds of fates awaiting $C_2^+$ or $C_3^+$ ions, desorption as ethylene or propylene or reaction with a feed molecule (hydrogen transfer or disproportionation), and that there are three fates awaiting $C_6^+$ ions, desorption as $C_6$ olefins, hydrogen transfer with a feed molecule, and $\beta$-cracking. We can observe the probability of each of these fates.

For example, by defining (*17*)

$$OC_2 = \frac{d_2}{d_2 + X_{20} + X_{21} + X_{22} + X_{23}} \qquad (17)$$

$$OC_3 = \frac{d_3 - X_{b63}}{d_3 - X_{b63} + X_{30} + X_{31} + X_{32}} \qquad (18)$$

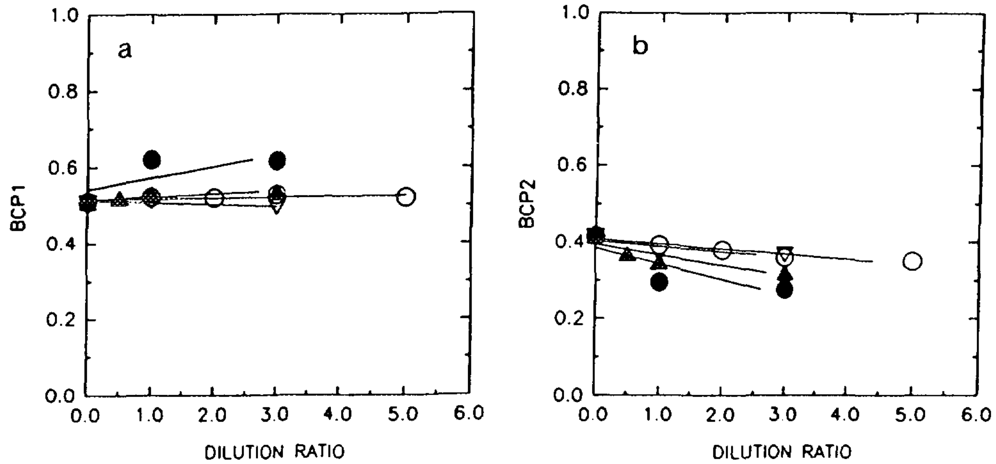

FIG. 7. Bond cleavage by protolysis probability vs dilution ratio: (a) BCP1: $C_t$–$C_s$ bond, (b) BCP2: $C_s$–$C_s$ bond, (c) BCP3: $C_t$–$C_p$ or $C_2$–$C_p$ bond, (d) BCP4: C–H bond. Diluent: (▽) $H_2$, (○) $N_2$, (▲) $CO_2$, (●) CO.

$$OC_6 = \frac{d_6}{d_6 - X_{b63} + X_{60}}, \qquad (19)$$

we calculate the probability that an ion will desorb as an olefin rather than suffering any of the other fates.

Using the values of RPPs and $d_j$ in Eqs. (17), (18), and (19), the values of $OC_2$, $OC_3$, and $OC_6$ in various cases have been calculated and are shown in Fig. 9. One can see that the value of $OC_2$ is 18% at no dilution and increases rapidly with dilution ratio for all diluents; the value of $OC_3$ is 82% at no dilution and also increases with the dilution ratio. At any given dilution CO causes the largest increase of both $OC_2$ and $OC_3$. This confirms that dilution promotes the desorption of $C_2^+$ or $C_3^+$ ions and tells us that the $C_2^+$ ion is more sensitive to dilution than $C_3^+$ ions as well as that CO causes more desorption than do the other diluents.

For $C_6H_{13}^+$ ions we have calculated that $X_{b63} = 0$ for all cases discussed here. Figure 9c shows that the value of $OC_6$ is 8.4% at no dilution and increases slightly with dilution ratio for all diluents. This behaviour indicates that the $C_6^+$ carbenium ion is stable to both β-cracking and desorption as an olefin and prefers to attract an $H^-$ from a feed molecule (isomerization) in the reaction of 2-methylpentane over USHY at 400°C. The reason that the PFP for isomerization is reduced so much (see Fig. 4) is therefore not so much the desorption of $C_6$ carbenium ions as a decrease in their population due to the large decrease in the bimolecular, chain propagating, hydrogen transfer processes. These in turn are inhibited by the increase in the desorption of $C_2$ and $C_3$ carbenium ions as discussed above. The desorption of these ions leaves less

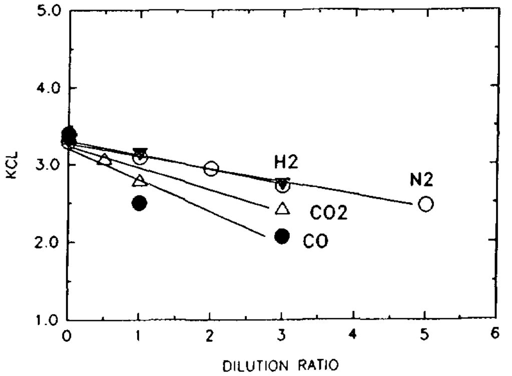

FIG. 8. Plots of kinetic chain length as a function of dilution ratio. Diluent: (▼) $H_2$, (○) $N_2$, (△) $CO_2$, (●) CO.

TABLE 4

Reaction Mechanism of 2-Methylpentane on HY Zeolite

| Reaction pathway | | Type | RPP symbol |
|---|---|---|---|
| $C_6H_{14}$ + HS | → $H_2 + C_6H_{13}S$ | Initiation | $X_{00}$ |
| $C_6H_{14}$ + HS | → $CH_4 + C_5H_{11}S$ | | $X_{01}$ |
| $C_6H_{14}$ + HS | → $C_2H_6 + C_4H_9S$ | | $X_{02}$ |
| $C_6H_{14}$ + HS | → $C_3H_8 + C_3H_7S$ | | $X_{03}$ |
| $C_6H_{14}$ + HS | → $C_4H_{10} + C_2H_5S$ | | $X_{04}$ |
| $C_6H_{14} + C_2H_5S$ | → $C_2H_6 + C_6H_{13}S$ | Propagation | $X_{20}$ |
| $C_6H_{14} + C_2H_5S$ | → $C_3H_8 + C_5H_{11}S$ | | $X_{21}$ |
| $C_6H_{14} + C_2H_5S$ | → $C_4H_{10} + C_4H_9S$ | | $X_{22}$ |
| $C_6H_{14} + C_2H_5S$ | → $C_5H_{12} + C_3H_7S$ | | $X_{23}$ |
| $C_6H_{14} + C_3H_7S$ | → $C_3H_8 + C_6H_{13}S$ | | $X_{30}$ |
| $C_6H_{14} + C_3H_7S$ | → $C_4H_{10} + C_5H_{11}S$ | | $X_{31}$ |
| $C_6H_{14} + C_3H_7S$ | → $C_5H_{12} + C_4H_9S$ | | $X_{32}$ |
| $C_6H_{14} + C_4H_9S$ | → $C_4H_{10} + C_6H_{13}S$ | | $X_{40}$ |
| $C_6H_{14} + C_4H_9S$ | → $C_5H_{12} + C_5H_{11}S$ | | $X_{41}$ |
| $C_6H_{14} + C_5H_{11}S$ | → $C_5H_{12} + C_6H_{13}S$ | | $X_{50}$ |
| $C_6H_{14} + C_6H_{13}S$ | → $C_6H_{14} + C_6H_{13}S$ | Isomerization | $X_{60}$ |
| $C_6H_{13}S^+$ | → $C_3H_6 + C_3H_7S^+$ | $\beta$-Cracking | $X_{b63}$ |
| $C_6H_{14}$ | → $m_kC_xH_y + m_hH_2$ | Coke formation | $X_{Kc}$ |
| $C_2H_5S^+$ | → $C_2H_4$ + HS | Termination | $d_2$ |
| $C_3H_7S^+$ | → $C_3H_6$ + HS | | $d_3$ |
| $C_4H_9S^+$ | → $C_4H_8$+ HS | | $d_4$ |
| $C_5H_{11}S^+$ | → $C_5H_{10}$ + HS | | $d_5$ |
| $C_6H_{13}^+$ | → $C_6H_{12}$ + HS | | $d_6$ |

*Note.* $X_{0i}$ is the probability of feed consumption via the *i*th mode of protolysis mode of initiation; $X_{jn}$ is the probability of feed consumption via the reaction of a feed molecule with the surface ion $C_jH_{2j+1}S^+$ forming a paraffin molecule $C_nH_{2n+2}$ and a new surface ion $C_{6+j-n}H_{2(6+j-n)+1}S^+$; $X_{60}$ is the probability of feed consumption via the production of isomers of the feed molecule; $X_{Kc}$ is the probability of feed consumption by the formation of coke; $X_{b63}$ is the molar selectivity for propylene ($C_3$) production from the $\beta$-scission of $C_6H_{13}S^+$ ($C_6$) ion; $d_j$ is the molar selectivity for olefin $C_jH_{2j}$ production from the desorption of $C_jH_{2j+1}S^+$ in a termination reaction.

opportunity for the hydrogen transfer reactions which are necessary to form hexyl carbenium ions.

## CONCLUSIONS

Our investigation of the effects of four diluents ($N_2$, $H_2$, $CO_2$, and CO) on the reaction of 2-methylpentane on USHY at 400°C indicates that the addition of an inert diluent to a heterogeneous catalytic reaction system has multiple effects on the reaction:

(1) The diluent reduces the concentration of the gas-phase reactants in the case of all of diluents. This leads to a decrease in the rate of reaction, a decrease in the rate decay, and an increase in the contribution of monomolecular (initiation) reactions to overall conversion.

(2) The diluent changes the number and acid strength distribution of Brønsted sites available for initiation by changing the fraction of these sites left unoccupied by diluent, reactant, or product molecules.

(3) The diluent influences the reactivity of ions on the surface if the diluent is an active electron donor or acceptor. This changes the RPPs of all processes in ways which are superimposed on the effects of

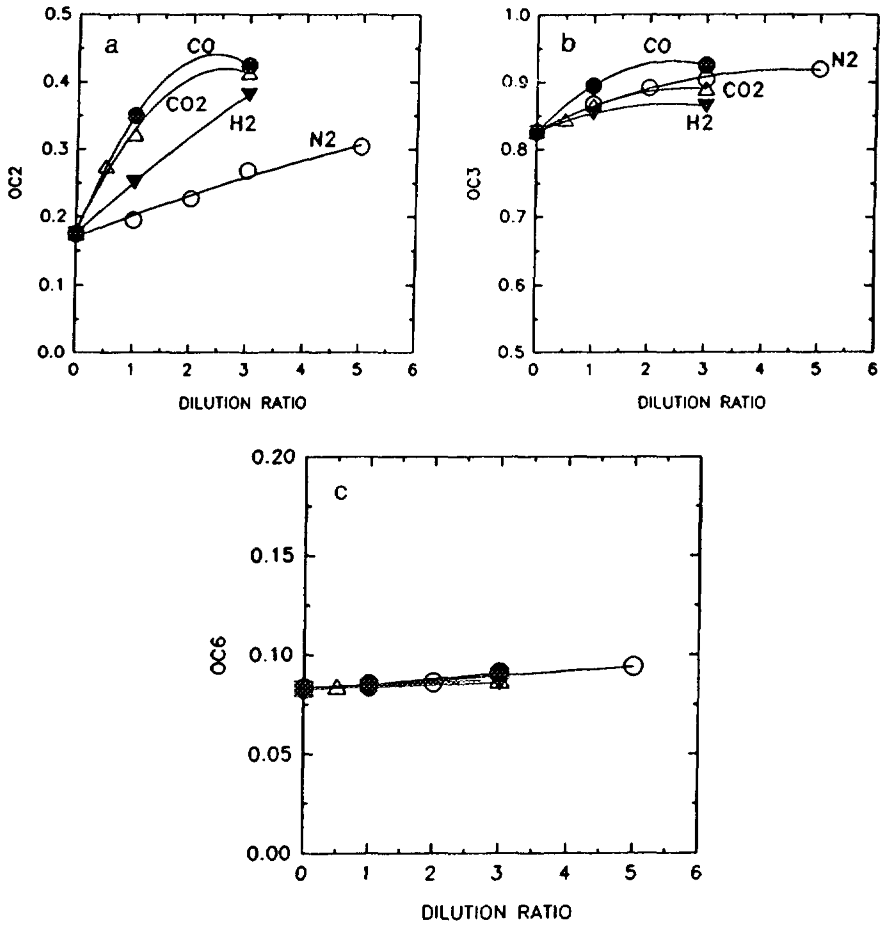

FIG. 9. Desorption probability of carbenium ions vs dilution ratio: (a) OC2: for $C_2^+$ carbenium ion, (b) OC3: for $C_3^+$ carbenium ion, (c) OC6: for $C_6^+$ carbenium ions. Diluent: (▽) $H_2$, (○) $N_2$, (△) $CO_2$, (●) CO.

concentration-driven population changes which arise with any diluent.

As a result of dilution the 2-methylpentane cracking rate decreases and the ratio of monomolecular to bimolecular reactions increases. The decay rate also decreases. For $N_2$ and $H_2$ these changes are attributable to simple concentration changes due to the dilution of the reactant. We believe that these two gases are indeed inert.

For $CO_2$ and CO the effects are more complicated as these diluents passivate both monomolecular and bimolecular reaction sites, as well as diluting the concentration of the feed.

The influence of dilution on the selectivity of this reaction is most easily characterized by the molar selectivity ratios of product paraffin to olefin and of isomerization to cracking products. Both these ratios decrease with dilution which inhibits the propagation of reaction chains and promotes chain termination.

We have seen no products which could be attributed to a chemical reaction between any of the above diluents and the feed.

## APPENDIX: NOMENCLATURE

| | |
|---|---|
| $X$ | instantaneous fractional conversion of feed |

| | |
|---|---|
| $\overline{X}$ | average fractional conversion |
| $b$ | reactant to catalyst density ratio (dimensionless) |
| $\tau$ | space time (min) |
| $t$ | catalyst time-on-stream (min) |
| $t_f$ | total run time of the experiment (min) |
| $\varepsilon$ | volume expansion coefficient |
| $G$ | aging parameter ($\mathrm{min}^{-1}$) |
| $N$ | aging exponent (dimensionless) |
| $P$ | catalyst to oil weight ratio (dimensionless) |
| $A_1, A_2, B$ | kinetic parameters |
| $[\mathrm{SH}]_0$ | concentration of active sites (initial) |
| $\beta$ | diluent gas to feed mole ratio |
| $[C_\mathrm{A}]_0$ | initial concentration of reactant (mol/liter) |
| $n_i$ | the mole numbers of the $i$th product when 1 mol of feed completely reacted |
| $K_\mathrm{A}$ | adsorption constant of reactant |
| $K_j$ | adsorption constant of the $j$th product |
| $k_i$ | rate constant of the $i$th mode of monomolecular reaction |
| $k_{jR}$ | rate constant of carbenium ion $\mathrm{C_jH_{2j+1}S^+}$ undergoing the $R$th mode of bimolecular reaction. |
| PFP | product formation probability |
| RPP | reaction pathway probability |
| $X_{0i}$ | RPP symbol of initiation processes |
| $X_{ji}$ | RPP symbol of propagation processes |
| BCP | bond cleavage by protolysis probability |
| KCL | kinetic chain length |
| OC | olefin desorption probability |

## REFERENCES

1. Brenner, A., and Emmett, P. H., *J. Catal.* **75,** 410 (1982).
2. Haag, W. O., and Dessau, R. M., "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. III, p. 305. Dechema, Frankfurt-am-main, 1984.
3. Corma, A., Monton, J. B., and Orchilles, A. V., *Appl. Catal.* **23,** 255 (1986).
4. Lombardo, E. A., Gaffney, T. R., and Hall, W. K., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 1, p. 412. Chem. Inst. of Canada, Ottawa, 1988.
5. Abbot, J., and Wojciechowski, B. W., *J. Catal.* **113,** 353 (1988).
6. Abbot, J., and Wojciechowski, B. W., *J. Catal.* **115,** 1 (1989).
7. Engelhardt, J., and Hall, W. K., *J. Catal.* **125,** 472 (1990).
8. Abbot, J., *Appl. Catal.* **57,** 105 (1990).
9. Abbot, J., and Head, J. D., *J. Catal.* **125,** 187 (1990).
10. Voogd, P., and Bekkum, H. V., *Appl. Catal.* **59,** 311 (1990).
11. Santilli, D. S., *Appl. Catal.* **60,** 137 (1990).
12. Wielers, A. F. H., Vaarkamp, M., and Post, M. F. M., *J. Catal.* **127,** 51 (1991).
13. Krannila, H., Haag, W. O., and Gates, B. C., *J. Catal.* **135,** 115 (1992).
14. Shertukde, P. V., Marcelin, G., Sill, G. A., and Hall, W. K., *J. Catal.* **136,** 446 (1992).
15. Zhao, Y. X., Bamwenda, G. R., Groten, W. A., and Wojciechowski, B. W., *J. Catal.* **140,** 243 (1993).
16. Groten, W. A., and Wojciechowski, B. W., *J. Catal.* **140,** 262 (1993).
17. Zhao, Y. X., Bamwenda, G. R., and Wojciechowski, B. W., *J. Catal.* **142,** 465 (1993).
18. Groten, W. A., Ph.D. Thesis, Queen's University, Kingston, 1991.
19. Ko, A. N., and Wojciechowski, B. W., *Prog. React. Kinet.* **12**(4), 201 (1983).
20. Wojciechowski, B. W., *Catal. Rev. Sci. Eng.* **9**(1), 79 (1974).
21. Abbot, J., and Wojciechowski, B. W., *J. Catal.* **107,** 451 (1987).
22. Zhao, Y. X., and Wojciechowski, B. W., *J. Catal.* **142,** 499 (1993).