

Relative Reactivities of Alkanes in Catalytic Cracking Reactions

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A microtechnique was developed for measuring relative reactivities of various alkanes in their catalytic cracking reactions over heterogeneous catalysts under mild conditions, 200–400°C. With the technique, a small quantity of a catalyst, 0.01–0.05 g, is placed in the evaporator of a gas chromatograph. Injection of a small quantity of a liquid hydrocarbon, 0.05–0.2 μ l, in the evaporator brings about the cracking reaction. The reaction products and the unreacted feed enter the chromatographic column and are analyzed. The proposed method allows repetitive cracking of various feeds over the same load of a catalyst. The kinetic treatment of the experimental data accounts for a gradual catalyst deterioration with time. The technique was used to measure relative reactivities (with respect to the reactivity of 2-methylnonane) of various alkanes in the C₈–C₁₇ range. The comparison provided the data for the analysis of alkane reactivities as a function of their carbon atom number and the number and types of substituents, as well as the temperature and catalyst composition effects. © 1990 Academic Press, Inc.

INTRODUCTION

The studies of the catalytic cracking reactions of pure hydrocarbons span more than 50 years (1–3). In spite of an enormous progress in understanding of these reactions, they continue to attract interest, both with respect to their intimate mechanism (4–6) and the reaction kinetics (7–9).

This article provides information on relative reactivities of various alkanes in their catalytic cracking reactions in the presence of several cracking catalysts under mild conditions.

Significant information on this subject has already been accumulated. It was discovered long ago that alkane reactivities strongly depend on the types and the number of various C–H bonds in their molecules (1, 3). The tertiary C–H bonds have the highest reactivity and the primary C–H bonds have the lowest reactivity. The relative C–H bond reactivities in CH, CH₂, and CH₃ groups at 550°C decrease approxi-

mately as 20:2:1 (3). The most detailed studies on the reactivities of various alkanes were reported by Nace (10). The cracking rate constants over a zeolite-based catalyst at 382°C were found to decrease in the order: tetramethylpentadecane (3300) > *n*-C₁₆ (1000) > *n*-C₁₄ (984) > *n*-C₁₇ (738) > *n*-C₁₈ (680) > *n*-C₁₂ (660) > tetramethylnonane (164) > *n*-C₈ (36). These data indicate that, in general, *n*-alkane reactivity increases with the increase of the carbon atom number. This conclusion was later confirmed in a detailed kinetic study of Abbot and Wojciechowski (7).

We developed a simple and rapid microtechnique for the measurement of the relative reactivities of various saturated and olefinic hydrocarbons in the catalytic cracking reactions in the 250–400°C temperature range. The technique requires very small quantities of reactants (usually 0.1 μ l) and thus allows the reactivity evaluations for numerous compounds which are usually expensive but available in small quantities from the companies supplying hydrocarbon samples for the GC analysis. Reactivities of over 40 alkanes are discussed in this paper.

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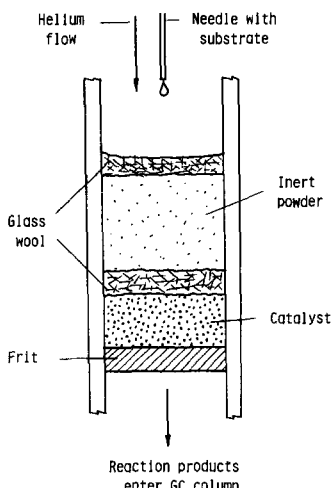


FIG. 1. Scheme of microreactor.

These data provided the basis for a more comprehensive analysis of the factors affecting alkane reactivities in the catalytic cracking reactions.

EXPERIMENTAL

A gas chromatograph (Hewlett-Packard 5880A) was used both as a cracking microreactor and an analytic tool. The glass evaporator of the chromatograph served, after a slight modification, as the reactor. Its scheme is shown in Fig. 1. A small amount of a cracking catalyst, from 0.01 to 0.05 g, was placed on the frit of the evaporator. It was covered with a small amount (ca. 0.03 g) of an inert powder (10% OV-1 on 80/100 mesh SW-AW DMCS) which is traditionally used for sample evaporation in gas chromatography. The evaporator was placed in the injector assembly of the chromatograph, capped with a rubber septum, and purged with the helium flow at 200°C for 10–24 h.

To carry out a cracking reaction, the assembly was heated to a particular temperature, and 0.05 to 0.2 μl of a feed was injected into the space above the catalyst. The feed was carried by the helium flow, evaporated over the inert material, and contacted the catalyst layer. The unreacted feed and the cracked products immediately entered the

chromatographic column and their relative quantities were measured.

This technique allowed successive testings of numerous hydrocarbons with a single load of a catalyst. A special procedure was used to account for a gradual deterioration of the catalyst activity with time (see below). The upper reaction temperature with this technique is limited by the maximum temperature of the injection port of a chromatograph (400°C in our case). The quantities of catalysts and the reaction temperatures are easily adjusted to reach feed conversions in the 10–30% range. The total duration of each experiment (cracking reaction itself plus the analysis time) ranged from 15 to 30 min depending on the carbon atom number (C_n) of the substrate.

The chromatograph was equipped with a flame ionization detector and was operated in the split injection mode with a split ratio of 100:1. The column used was 50 m, 0.2-mm i.d. fused silica capillary coated with the 0.5- μm film of cross-linked methyl silicone. Helium was used as a carrier gas at a flow rate of 1 ml/min. The column temperature was programmed to increase from 40 to 300°C at a rate of 5°C/min. Peak integration was carried out with a Hewlett-Packard lab automation system. The calibration factors for all peak areas (those of reactants and cracked products) were assumed equal.

The following catalysts were tested: Silica-alumina AAA, calcined overnight at 540°C; rare earth-exchanged Y zeolite (Linde SK500), 100–170 mesh; industrial catalyst FSS-1 (Filtrol), steam-equilibrated (the active ingredient is the rare earth-exchanged Y zeolite); hydrocracking catalyst, contains 4% Ni, 14% Mo, on 1:1 alumina/Y-zeolite.

All hydrocarbons studied were supplied by Wiley Organics Co.

KINETIC TREATMENT OF EXPERIMENTAL DATA

Reaction Conversions

Each cracking experiment with the microreactor gave the peak area values for the

unreacted feed (A_{feed}) and for each of the cracked products (A_{prod}). No compounds with C_n higher than C_n of the feed hydrocarbons were produced when the cracking reactions were carried out under mild conditions. The chromatographic analysis allowed identification of all major reaction products. The chemistry of the cracking reactions of various alkanes under mild conditions will be discussed in a separate article.

Reaction conversions were calculated as

$$\text{Conversion } C = A_{\text{prod}} / (A_{\text{prod}} + A_{\text{feed}}) \quad (1)$$

Kinetic Treatment

Abbot and Wojciechowski, in a series of articles (11, 5, 7, 8), developed a comprehensive kinetic scheme for the description of the catalytic reactions between gaseous substrates and solid catalytic surfaces (the time-on-stream theory). The scheme accounts for several intrinsic features of such reactions. It predicts that conversion in the catalytic cracking reactions rapidly levels off with increase in duration of the catalyst exposure to a substrate. Two most important factors encountered in the kinetic analysis of such reactions are (a) competition between substrates and reaction products for the adsorption sites on the catalyst surface, and (b) catalyst aging. Our reaction arrangement apparently allows separation of these two problems. Two factors account for it:

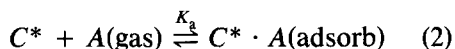
1. The duration of each cracking experiment in our case (estimated from the volume rate of the helium flow through the catalyst layer) had the order of a few seconds. These contact times were much shorter than typical times on stream, from 50 to 1000 sec, encountered in classic kinetic experiments of this type (5, 7, 8). Short reaction times allowed us to neglect catalyst deactivation during each separate feed injection.

2. Most of our cracking experiments were carried out at very high catalyst/substrate ratios, 50–200 (the amount of a catalyst 0.01–0.05 g; the amount of a feed 0.1–0.2 μl). A typical commercial cracking catalyst contains ca. 20% of the rare earth-ex-

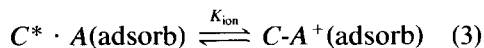
changed Y zeolite with the specific surface area of 400–500 m^2/g . (The zeolite is embedded in the silica–alumina matrix, which by itself can act as a mild cracking catalyst.) An amount of 0.025 g of such a catalyst provides 2–2.5 m^2 of the catalytically active surface. An amount of 0.1 μl of a C_{10} alkane contains ca. 3×10^{17} molecules. Thus, in a typical cracking experiment, a 500–1000 \AA^2 area of a catalytically active surface was available for adsorption and reactions of each substrate molecule. These high available surface areas allowed an assumption that, under our reaction conditions, saturation of the catalyst surface with substrate molecules was not achieved and one could neglect competition between the substrate and reaction products for adsorption centers.

Although the general kinetic dependencies for catalytic cracking reactions with heterogeneous catalysts are established (12), relative significance of various cracking stages remain uncertain. The following scheme for the kinetic description of catalytic cracking represents generally accepted reaction stages. In the scheme, active centers (marked C^*) are highly acidic sites on the catalyst surface that are capable of ionizing alkanes.

1. Equilibrium adsorption of a substrate molecule on the active centers



2. Formation of carbenium ions from the adsorbed species

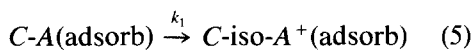


3. Reversible transformations of carbenium ions (skeleton isomerization reactions)

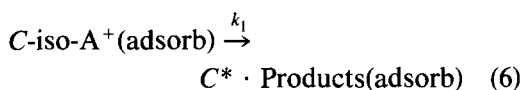


It is known from the literature (3, 12, 13), and our experiments confirmed, that the skeletal isomerization reactions of carbenium ions at increased temperatures pro-

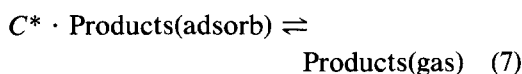
ceed at very high rates. As a result, the probability of a substrate molecule, after ionization in Reaction (3), skeletal isomerization in Reaction (4), deionization in Reaction (3), and desorption in Reaction (2), of retaining its original structure is very low. For this reason, a combination of Reactions (3) and (4) can be regarded, from a kinetic point of view, as a single irreversible process



4. Irreversible transformations of carbenium ions (cracking)



5. Reversible desorption of the cracked products



Our data indicate that Reaction (7) is well pronounced at low temperatures. It manifests itself in a significant peak tailing in gas chromatograms due to slow product desorption from the catalyst surface. However, high ratios between the catalyst surface and the amount of substrates allow a suggestion that Reaction (7) does not control the overall reaction kinetics.

The cracking scheme, as represented by Reactions (2), (5), (6), and (7), is much too complex to be of any practical use in comparing alkane reactivities in cracking reactions under our conditions, even if the steady-state approach is applied to derive expressions for all concentrations of transient species. Several simplifications were introduced to make the scheme more tractable. The use of these simplifications is justified in our case because the only kinetic effect examined is the relative consumption parameters of alkane substrates in the cracking reactions. First, an assumption was made that the substrate adsorption equilibrium (Reaction (2)) is established

very rapidly and, in practical terms, is not affected by subsequent reactions. Application of the steady-state condition and the assumption that $C^* > A(\text{gas})$ gives the following equation for the concentration of the adsorption species:

$$[C^* \cdot A(\text{adsorb})] \sim K_a [C^*][A(\text{gas})], \quad (8)$$

The only reaction responsible for the disappearance of substrate molecules from the gas phase is Reaction (5):

$$-d[C^* \cdot A(\text{adsorb})]/dt = k_1 [C^* \cdot A(\text{adsorb})]. \quad (9)$$

Substitution of Eq. (8) in Eq. (9), and the use of the definition of the reaction conversion as the fraction of the original substrate concentration consumed at time t

$$\text{Conversion } C = [A(\text{gas})_0 - A(\text{gas})_t]/[A(\text{gas})_0] \quad (10)$$

gives, after integration of Eq. (9) from $t = 0$ to t , the final kinetic relationship,

$$\ln[1/(1 - C)] = k_1 K_a [C^*] t. \quad (11)$$

This approach describes the reactivity of a particular hydrocarbon in a catalytic cracking reaction as a function of two parameters, the equilibrium constant of the hydrocarbon adsorption on the active sites, K_a , and the rate constant of the ionization of the adsorbed hydrocarbon molecule, k_1 .

The proposed reaction scheme does not take into consideration coke formation, and, as a result, somewhat underestimates conversions in the cracking reactions. Direct measurements of coke yields under our experimental conditions were not possible due to minuscule coke yields. Separate studies of alkane catalytic cracking in a bigger reactor showed that these reactions in the 250–350°C range produce relatively low yields of aromatic compounds and coke, not exceeding a few percent of the total product yields.

Accounting for Catalyst Instability

Most of heterogeneous catalysts used for cracking hydrocarbons are kinetically un-

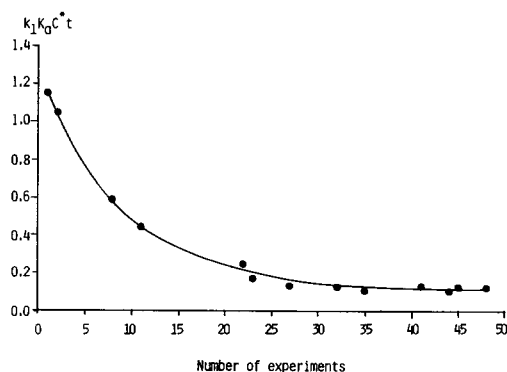


FIG. 2. Aging of FSS-1 catalyst at 350°C. Substrate - 2-methylnonane.

stable. They rapidly lose cracking activity when exposed to hydrocarbon vapor at increased temperatures. This instability was pronounced in all our experiments. One example is shown in Fig. 2. The figure gives the results of a series of experiments in which 2-methylnonane (0.1 μ l) was repeatedly cracked, intermittently with other C_{10} alkanes, over 0.050 g of commercial FSS-1 catalyst at 350°C. Figure 2 shows the $k_1K_a[C^*]t$ values (calculated from 2-methylnonane conversions using Eq. (11)) in 48 successive experiments. A steady, quasiexponential decrease in catalyst activity is obvious from the plot. The deactivation is strongly pronounced at higher temperatures, but it is relatively small at temperatures in the 200–250°C range.

This decrease in activity must be accounted for when reactivities of various hydrocarbons are compared on the basis of their cracking conversions in successive reactions with the same load of a catalyst. The following procedure was adopted for the correction. 2-Methylnonane was chosen as a reference substrate. As follows from the data presented below, this isoalkane exhibits intermediate relative reactivity in cracking reactions. Plots similar to that shown in Fig. 2 were drawn for each series of experiments, and the $k_1K_a[C^*]t$ values for each feed (calculated from conversions with Eq. (11)) were normalized to the expected

$(k_1K_a[C^*]t)_{2-MeC_9}$ values for 2-methylnonane at this experimental point. The normalized relative reactivity parameters were thus $(k_1K_a)_{feed}/(k_1K_a)_{2-MeC_9}$. This normalization assumed approximately the same t values (the contact times for plugs of feed vapor passing through a catalyst bed) for each injection. To justify this last assumption, the volumes of feeds were kept the same for each successive injection.

Experimental Confirmation of the Reaction Scheme

The kinetic scheme used in this paper to evaluate reactivities of various alkanes in catalytic cracking reactions is based on the assumption that the conversions in the cracking reactions do not depend on the reactant concentration (in our case, on the reactant feed volumes)—see Eq. (11). This assumption was tested under several sets of conditions. Unfortunately, large variations in the feed volumes are impractical under our experimental setup: if low feed volumes are used, conversion estimates lose precision (some reaction products are formed in yields too low to be detected) and, if very high feed volumes are used, the measurement of the unreacted feed quantity becomes unreliable due to detector overload.

Table 1 compares conversions and corrected $(k_1K_a)[C^*]t$ values in the cracking of 2-methylnonane at various catalyst loads at

TABLE 1

Effect of Feed Volume on Reaction Kinetics and Cracking of 2-Methylnonane over FSS-1 Catalyst

| Temp. (°C) | Cat. (g) | Feed (μ l) | Conversion (%) | Correction factor | $(k_1K_a)[C^*]t$ |
|------------|----------|-----------------|----------------|-------------------|------------------|
| 350 | 0.010 | 0.10 | 8.81 | 1 | 0.092 |
| | | 0.15 | 3.63 | 1.94 | 0.072 |
| | | 0.10 | 3.91 | 2.30 | 0.092 |
| | | 0.20 | 3.66 | 2.79 | 0.103 |
| 350 | 0.025 | 0.10 | 60.5 | 1 | 0.929 |
| | | 0.10 | 36.0 | 2.08 | 0.929 |
| | | 0.05 | 27.8 | 2.86 | 0.803 |
| 250 | 0.053 | 0.10 | 41.4 | 1 | 0.534 |
| | | 0.20 | 35.9 | 1 | 0.445 |

350 and 250°C. The correction factors used for calculating the $(k_1K_a)[C^*]t$ values were estimated as described above, as the ratios of the $(k_1K_a)[C^*]t$ values for the 0.10- μ l 2-methylnonane feed volume for the first injection and for a particular subsequent injection of the feed. The data agree with the first-order kinetic law (implied in Eq. (11)) and justify the use of this equation for reactivity comparisons. The data in Table 1 also allow the precision estimation in this type of experiments, ca. $\pm 15\%$.

Two other parts of the reaction scheme amenable to experimental verification are the assumptions that the substrate diffusion into catalyst grains under our conditions is very fast and that the adsorption equilibrium (Reaction (1)) is established rapidly. Our data on the cracking of linear and branched α -olefins support these assumptions. Reaction studies of a series of C_6 – C_{10} α -olefins over aged catalysts at 150–250°C showed that even at these reduced temperatures the olefins are isomerized into equilibrium mixtures of internal olefins.

RELATIVE REACTIVITIES OF ALKANES IN CRACKING REACTIONS

Normal Alkanes

Table 2 contains the data on relative reactivities on several n -alkanes in catalytic cracking over FSS-1 catalyst at 350°C. Obvious from the data is a rapid increase in n -alkane reactivity with the increase in C_n .

| C_n : | C_8 | C_{10} | C_{12} | C_{14} | C_{16} | C_{17} | C_{18} |
|----------------|-------|----------|----------|----------|----------|----------|----------|
| Nace, 482°C | 0.05 | — | 1.0 | 1.49 | 1.52 | 1.12 | 1.03 |
| Present, 350°C | 0.05 | 0.22 | 1.0 | 4.3 | 9.4 | 8.8 | — |

Whereas both sets of the data show the same trends in n -alkane reactivities, including the apparent leveling-off at C_{17} , the results of the present study at 350°C show a much stronger reactivity dependence on the carbon atom number. A large difference in temperature between these sets of data can ac-

TABLE 2

Reactivities of n -Alkanes in Catalytic Cracking Reactions over FSS-1 Catalyst at 350°C, Normalized to the Reactivity of 2-Methylnonane

| Alkane | Relative reactivity $(k_1K_a)/(k_1K_a)_{2MeC_9}$ | Renormalized reactivity [Reactivity ($n - C_{10}$) = 1] |
|------------------|---|--|
| n -Octane | 0.014 | 0.23 |
| n -Decane | 0.06 | 1 |
| n -Dodecane | 0.27 | 4.5 |
| n -Tetradecane | 1.16 | 19.5 |
| n -Hexadecane | 2.54 | 42.3 |
| n -Heptadecane | 2.38 | 39.7 |

Cracking conversions for alkanes with the highest C_n become too high to afford dependable reactivity determination.

n -Alkanes predominantly form secondary carbenium ions in Reaction (5):



It is reasonable to assume that the average energy requirements for the CH_2 group ionization in alkanes of various lengths (represented by k_1 values in Eq. (5) and (11)) are similar. In such a case, the observed large differences in n -alkane reactivities can be attributed to the differences in their equilibrium adsorption constants K_a .

Data in Table 2 can be compared with the data published by Nace (10) on the relative reactivities of n -alkanes in their catalytic cracking over a zeolite-based catalyst at 482°C (after renormalization of all data to the n - C_{12} reactivity):

count for the differences in relative reactivities.

2-Methyl-Substituted Alkanes

Table 3 gives the relative reactivities of several 2-methyl-substituted alkanes in the cracking reactions with FSS-1 catalyst at

TABLE 3

Reactivities of 2-Methyl-Substituted Alkanes in Catalytic Cracking Reactions over FSS-1 Catalyst at 350°C, Normalized to the Reactivity of 2-Methylnonane

| Alkane | Relative reactivity (k_1K_a)/(k_1K_a) _{2MeC₉} | Renormalized reactivity (k_1K_a) _{2MeC_n} / (k_1K_a) _{n-C_n} |
|---------------------|--|---|
| 2-Methylheptane | 0.18 | 12.9 |
| 2-Methyloctane | 0.49 | ca. 16 |
| 2-Methylnonane | 1 | 16.6 |
| 2-Methyldecane | 2.04 | 17.3 |
| 2-Methylundecane | 2.76 | 10.2 |
| 2-Methyltetradecane | 5.48 | ca. 3 |
| 2-Methylhexadecane | 8.23 | 3.4 |

350°C. The general effect is similar to that for *n*-alkanes: the reactivity strongly increases with the increase in C_n , although the increase is not as strong as for *n*-alkanes. Table 3 also contains the ratios of the reactivities of 2-methyl-substituted alkanes and *n*-alkanes with the same carbon atom numbers. If one takes into account a relatively low precision of the estimations, it is possible to state that the reactivity ratio remains approximately constant, ca. 15, for the C_n range of 8–11. This ratio reflects a higher reactivity of the tertiary C–H bond in 2-methyl-substituted alkanes in the carbenium ion formation reaction (represented by the k_1 constant in Reaction (5)) compared to the reactivity of secondary C–H bonds in *n*-alkanes. The rate ratio corresponds to E_{act} of ~14 kJ/mol. The reactivity ratio de-

creases to ca. 3 for C_n in the 15–17 range, apparently due to the cumulative effect of many CH₂ groups on the overall alkane reactivity.

Reactivities of Isoalkanes

Table 4 lists relative reactivities of a series of isoalkanes in the C₈–C₁₃ range cracked over FSS-1 catalyst at 350 and 250°C. The third column in the table gives renormalized reactivities of the isoalkanes at 350°C, with the reactivity of each 2-methyl-substituted isoalkane C_n being taken equal to 1.

The data for C₁₀ and C₁₁ monomethyl-substituted alkanes show that a shift of a methyl group from the second position in a chain toward the center of the chain always results in a small, ca. 30–40%, decrease in isoalkane reactivity. Reactivities of monomethyl-substituted alkanes apparently reflect relative stabilities of carbenium ions they form in reactions with acidic catalysts. Carbenium ion stability should depend on two parameters, the total inductive effect of the substituents attached to the charge-bearing atom and the hyperconjugative effect. In a carbenium ion R₁R₂R₃C⁺, the combined electron donor effect of R₁, R₂, and R₃ (which reduces the positive charge on C⁺ and increases ion stability) can be represented as the sum of the Taft inductive factors σ^* (14). These sums for various monomethyl-branched C₁₀ and C₁₁ alkanes are:

| | | | | |
|-----------------------|----------------------|----------------------|----------------------|----------------------|
| C ₁₀ range | 2-Me-C ₉ | 3-Me-C ₉ | 4-Me-C ₉ | 5-Me-C ₉ |
| σ^* | -0.20 | -0.28 | -0.28 | -0.26 |
| C ₁₁ range | 2-Me-C ₁₀ | 3-Me-C ₁₀ | 4-Me-C ₁₀ | 5-Me-C ₁₀ |
| σ^* | - | -0.30 | -0.30 | -0.29 |

Judging by the σ^* values, All mono-methyl-substituted alkanes in a particular C_n range, except for 2-methyl-substituted isomers, should produce carbenium ions of similar stabilities and thus can be expected to have similar k_1 values in Reactions (5). If their adsorption constants K_a are similar too, one

can also expect similar overall reactivities of these isoalkanes in catalytic cracking reactions—the conclusion supported by the data in Table 4.

On the basis of the inductive parameters alone, 2-methyl-substituted alkanes should exhibit the lowest reactivity among all

TABLE 4

Reactivities of Various Isoalkanes in Catalytic Cracking Reactions over FSS-1 Catalyst at 350 and 250°C, Normalized to the Reactivity of 2-Methylnonane

| Alkane | 350°C | | 250°C |
|-------------------------------|---|--|---|
| | Rel. react. $(k_1K_a)/$ $(k_1K_a)_{2MeC_9}$ | Renorm. react. $(k_1K_a)/$ $(k_1K_a)_{2MeC_{n-1}}$ | Rel. react. $(k_1K_a)/$ $(k_1K_a)_{2MeC_9}$ |
| C ₇ | | | |
| 2-Methylhexane | — | — | 0.066 |
| 3-Methylhexane | — | — | 0.050 |
| C ₈ | | | |
| 2-Methylheptane | 0.18 | 1.0 | 0.22 |
| 3-Methylheptane | 0.22 | 1.22 | — |
| 2,4-Dimethylhexane | 0.38 | 2.40 | 0.38 |
| 2,5-Dimethylhexane | 1.25 | 7.85 | — |
| 3,4-Dimethylhexane | — | — | 0.22 |
| C ₉ | | | |
| 2-Methyloctane | 0.49 | — | ca. 0.5 ^a |
| 4-Methyloctane | — | — | ca. 0.9 |
| C ₁₀ | | | |
| 2-Methylnonane | 1 | 1 | 1 |
| 3-Methylnonane | 0.75 | 0.75 | — |
| 4-Methylnonane | 0.72 | 0.72 | — |
| 5-Methylnonane | 0.57 | 0.57 | — |
| 2,2-Dimethylnonane | — | — | 0.07 |
| 2,3-Dimethyloctane | 0.96 | 0.96 | 0.77 |
| 2,6-Dimethyloctane | 1.96 | 1.96 | 2.01 |
| 2,7-Dimethyloctane | 2.76 | 2.76 | 2.56 |
| 3,5-Dimethyloctane | 1.18 | 1.18 | 0.31 |
| 3,6-Dimethyloctane | 2.53 | 2.53 | 1.70 |
| 3-Ethyloctane | 0.32 | 0.32 | 0.12 |
| 3,4,5-Trimethylheptane | — | — | 0.28 |
| C ₁₁ | | | |
| 2-Methyldecane | 2.04 | 1 | 3.06 |
| 3-Methyldecane | 1.28 | 0.62 | — |
| 4-Methyldecane | 1.38 | 0.67 | — |
| 3-Ethylonane | 0.54 | 0.26 | — |
| C ₁₂ | | | |
| 2-Methylundecane | 2.76 | 1 | 4.76 |
| 2,6-Dimethyldecane | 6.21 | 2.25 | — |
| C ₁₃ | | | |
| 2-Methyldodecane ^a | ca. 3.4 | 1 | — |
| 2,6-Dimethylundecane | — | ca. 2.6 | — |
| | 8.9 | | |

^a Estimate, see Table 3.

mono-methyl-substituted isomers. However, an additional factor, the hyperconjugative effect of the second methyl group, apparently significantly increases carbenium ion stability of these isomers.

Reactivities of both studied 3-ethyl-sub-

stituted isoalkanes were only ca. 0.4–0.5 of those of 3-methyl-substituted alkanes with the same C_n (Table 4). This difference emphasizes the role of hyperconjugation in the overall carbenium ion stabilization. In the absence of hyperconjugation, one could ex-

pect 3-ethyl-substituted alkanes to be more reactive than their methyl-analogs judging by the -0.10 difference in their σ^* values.

Reactivities of dimethyl-substituted alkanes are usually higher than those of their monomethyl-substituted analogs. Two reasons for these differences can be proposed, an increased stability of carbenium ions due to the σ^* decrease and the availability of multiple stable ionization states for the molecules with two tertiary carbon atoms. In the case of 2,7-, 2,6-, and 3,6-dimethylalkanes, the tertiary carbon atoms are separated enough to assume the absence of any significant additional inductive affects. Such molecules are 2.0–2.5 times more reactive than corresponding monomethyl-substituted compounds. These differences underline the significance of multiple stable ionized states for the overall alkane reactivity. On the other hand, 2,3-, 2,4-, 3,4-, and 3,5-dimethylalkanes have the same or lower relative reactivities than the reactivities as their monomethyl-substituted analogs, thus suggesting a possible steric interference. The same reason apparently accounts for a relatively low reactivity of 3,4,5-trimethylheptane. 2,2-dimethyloctane does not have any tertiary atoms. Its reactivity at 250°C is much lower than that of 2-methylnonane.

Temperature Effects on Alkane Reactivity

Data shown in Tables 1–3 allow a comparison of relative alkane reactivities at different temperatures. It appears that when compounds with the same carbon atom numbers are compared (Table 4), the reactivity ratios usually remain approximately constant in the 250–350°C range (two exceptions are *n*-decane and 3-ethylnonane). Figure 3 compares relative reactivities of various 2-methyl-substituted alkanes at 250 and 350°C. The temperature decrease apparently results in larger differences in the isoalkane reactivities, probably because the adsorption parameters (K_a values) of molecules with higher C_n values become higher—apparently the same effect that determines reactivities of *n*-alkanes with different C_n (Table 2).

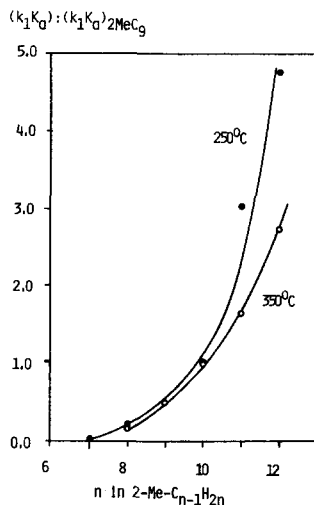


FIG. 3. Relative reactivities of 2-methyl-substituted alkanes in cracking over FSS-1 catalyst at 250 and 350°C.

Catalyst Effects on Alkane Reactivity

Table 5 gives relative alkane reactivities in their cracking reactions with amorphous silica–alumina at 350°C. Conversions in these reactions were much lower than those in the reactions over the commercial cracking catalyst, which makes the reactivity data much less precise. General reactivity patterns obvious in Table 5 are similar to those in Tables 1–3: the reactivities of *n*-alkanes are much lower than those of isoalkanes, dimethyl-substituted alkanes are more reactive than mono-methyl-substituted alkanes, etc. There are several pronounced differences, however, between the zeolite-based catalyst and silica–alumina. The first catalyst is much more effective in cracking heavy *n*-alkanes, and the difference between reactivities of *n*-decane and 2-methylnonane with this catalyst is much more pronounced.

Table 6 gives relative reactivities of alkanes in their cracking over pure aged Y zeolite and the zeolite-based hydrocracking catalyst. Pure unequilibrated Y zeolite is extremely active in hydrocarbon cracking reactions under mild conditions. However, its

TABLE 5

Reactivities of Various Alkanes in Catalytic Cracking Reactions over Amorphous Silica-Alumina at 350°C, Normalized to the Reactivity of 2-Methylnonane

| Alkane | Relative reactivity (k_1K_a)/(k_1K_a) _{2MeC9} |
|---------------------------------|---|
| C ₁₀ | 0.38 |
| <i>n</i> -Decane | 1 |
| 2-Methylnonane | 1.29 |
| 2,3-Dimethyloctane | 1.93 |
| 2,6-Dimethyloctane | 3.74 |
| 2,7-Dimethyloctane | 1.84 |
| 3,5-Dimethyloctane | 1.42 |
| 3,6-Dimethyloctane | 0.36 |
| 3-Ethylloctane | |
| C ₁₂ | 2.34 |
| 2-Methylundecane | 6.36 |
| 2,6-Dimethyldecane | |
| <i>n</i> -C _{<i>n</i>} | 0.38 |
| <i>n</i> -Decane | 1.85 |
| <i>n</i> -Hexadecane | 2.17 |
| <i>n</i> -Heptadecane | |
| 2-Me-C _{<i>n</i>-1} | 0.45 |
| 2-Methylhexane | 1.11 |
| 2-Methylheptane | 1 |
| 2-Methylnonane | 1.45 |
| 2-Methyldecane | 2.34 |
| 2-Methylundecane | 15.1 |
| 2-Methylhexadecane | |

TABLE 6

Reactivities of Various Alkanes in Catalytic Cracking Reactions over Aged Y Zeolite and Hydrocracking Catalyst at 350°C, Normalized to the Reactivity of 2-Methylnonane.

| Alkane | Relative reactivity Aged Y zeolite | (k_1K_a)/ (k_1K_a) _{2MeC9} Hydrocracking catalyst |
|-----------------------------|--|---|
| C ₈ | | |
| <i>n</i> -Octane | 0.10 (0.14) | 0.11 (0.28) |
| 2-Methylheptane | 0.69 (1.0) | 0.38 (1.0) |
| 2,2-Dimethylhexane | 0.05 (0.07) | ca. 0 (ca. 0) |
| 2,3-Dimethylhexane | 0.43 (0.62) | 0.22 (0.58) |
| 2,4-Dimethylhexane | 0.63 (0.91) | 0.30 (0.79) |
| 2,5-Dimethylhexane | 0.78 (1.13) | 0.66 (1.60) |
| 3,3-Dimethylhexane | 0.07 (0.10) | ca. 0 (ca. 0) |
| 3,4-Dimethylhexane | 0.78 (1.13) | 0.18 (0.47) |
| C ₁₀ | | |
| <i>n</i> -Decane | 0.28 (0.28) | 0.12 (0.12) |
| 2-Methylnonane | 1.0 (1.0) | 1.0 (1.0) |
| 2,2-Dimethyloctane | 0.15 (0.15) | 0.13 (0.13) |
| 2,6-Dimethyloctane | — | 1.56 (1.56) |
| 2,7-Dimethyloctane | 1.41 (1.41) | 2.32 (2.32) |
| 3,3-Dimethyloctane | 0.09 (0.09) | 0.15 (0.15) |
| 3,5-Dimethyloctane | — | 1.07 (1.07) |
| 3,6-Dimethyloctane | 0.66 (0.66) | 1.64 (1.64) |
| 3-Ethylloctane | 0.73 (0.73) | 0.62 (0.62) |
| 3,4,5-Trimethyl- Heptane | 0.36 (0.36) | 1.17 (1.17) |

Note. Numbers in parentheses: renormalized reactivity (k_1K_a)/(k_1K_a)_{2MeC_{*n*-1}}.

activity greatly decreases with successful cracking steps. In general, the data presented in Table 6 are similar to those for the commercial cracking catalyst:

1. With both catalysts, *n*-alkanes are less reactive than monomethyl-substituted alkanes, although the differences are not as large as those for FSS-1 catalyst.

2. Isoalkanes with quaternary carbon atoms exhibit very low reactivities.

3. Dimethyl-substituted alkanes with spatially separated methyl groups have reactivities higher than those of monomethyl-substituted alkanes. However, isoalkanes with two vicinal methyl groups have reactivities close to those of monomethyl-substituted alkanes.

4. Reactivities of 3-ethyl-substituted alkanes are lower than those of methyl-substituted alkanes.

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