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Superacid Catalysis of Light Hydrocarbon Conversion

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SUMMARY

The new catalyst Fe- and Mn-promoted sulfated zirconia is remarkably active for the low-temperature (even room temperature) isomerization of *n*-butane to give isobutane in the near absence of side products. Thus this catalyst offers excellent potential for practical application in this process. The catalyst is so active that it even converts smaller alkanes, including propane and ethane.

The ethane conversion is orders of magnitude slower than the butane conversion, and the prospects for practical application with ethane are apparently negligible. However, the results for ethane conversion provide strong evidence that the alkane conversions proceed (at least under some conditions) by protonation of the alkane with the catalyst; thus the catalyst is comparable to superacids, and the chemistry is analogous to that occurring in superacid solutions. This insight will be useful in further improvement of the catalyst and the potential process for butane isomerization.

The catalyst is active for alkane cracking at temperatures of typically 200-300 °C, and evidence, summarized here, indicates that numerous reactions of alkanes begin as the catalyst protonates the alkane reactant. The kinetics data for this family of reactions fall on a linear compensation effect plot; such data for reactions that do not proceed via such a mechanism do not fall near the line representing the compensation effect. Thus the analysis of the kinetics data provides a good diagnostic tool for understanding the fundamental chemistry of the acid-catalyzed hydrocarbon conversions.

I. Ethane conversion in the presence of Fe- and Mn-promoted sulfated ZrO_2: evidence of autocatalysis and oligocondensation chemistry

Introduction. Light alkanes in liquid superacids react at temperatures <273 K, giving heavier hydrocarbons via carbenium ion and carbonium ion intermediates (Olah et al., 1973). In the presence of Fe- and Mn-promoted sulfated ZrO_2 (FMSZ), propane reacts similarly, being converted largely into butane at 473 K (Cheung et al., 1995A), and *n*-butane is catalytically isomerized and disproportionated even at 298 K (Hsu et al, 1992; Cheung et al., 1995B). The propane product distribution and the high catalytic activity for *n*-butane conversion suggest superacid chemistry (Olah et al., 1973). Although FMSZ was called a superacid (Lin and Hsu, 1992), the acid strength is still debated (Adeeva et al, 1995; Tabora and Davis, 1995). One of our goals was to probe the acidic character of FMSZ (and, for comparison, acidic USY zeolite) by investigating its reactivity and catalytic activity with a relatively unreactive alkane (ethane).

Experimental Methods. FMSZ (Cheung et al., 1995ABC), containing approximately 1 wt% Fe, 0.5 wt% Mn, and 1.8 wt% S, was made by incipient wetness impregnation of sulfated $Zr(OH)_4$ with aqueous $Fe(NO_3)_3$ then aqueous $Mn(NO_3)_2$ and calcined in static air at 923 K. The BET surface area and pore volume were about 90 m^2/g and 0.2 mL(NTP)/g, respectively.

Ethane conversion was carried out in a once-through packed-bed flow reactor under the following conditions: temperature, 473-723 K; pressure, 101 kPa; ethane partial pressure, 5-20 kPa; mass of FMSZ, 0.5-1.5 g; feed (ethane + N_2) flow rate, 10-80 mL(NTP)/min.

Results and Discussion. The products of the ethane reaction were H_2, methane, ethene, butane, and traces of aromatics; at 473 K they were predominantly *n*-butane and ethene.

n-Butane selectivity decreased from 30% (at 0.01% conversion) at 473 K to 10% (at 0.1% conversion) at 673 K. In the temperature range 473-623 K, the conversion to *n*-butane, ethene, and methane decreased with increasing time on stream (TOS). At temperatures >623 K, the conversion into *n*-butane decreased monotonically with increasing TOS, but the conversion to ethene and to methane decreased and then increased with TOS (suggesting autocatalysis), followed by another declining period. The length of the first declining period for ethane conversion decreased with increasing temperature and ethane partial pressure. H_2 was observed only at temperatures >673 K; at 723 K, production of H_2 was characterized by a period of increasing conversion followed by a slow decline with TOS.

At 723 K, 20 kPa ethane partial pressure, and 5.5×10^{-6} mol/(s · g) space velocity, the number of ethane molecules converted/sulfate group was >1 after 18 h TOS; ethane conversion was then catalytic. Catalysis was not demonstrated at lower temperatures.

Initial ethane conversion rates were estimated by extrapolating conversions in the first declining period to zero TOS. At 723 K and 20 kPa alkane partial pressure, the rate of ethane conversion in the presence of FMSZ [4×10^{-8} mol/(s · g)] is lower than that of propane conversion [determined by extrapolating published data (Cheung et al., 1996), 4×10^{-6} mol/(s · g)]. The products formed from ethane [or propane (Cheung et al., 1995A)] at 473 K are nearly the same as those reported (Olah et al., 1973) for reaction in superacid solution.

Adopting the analogy to superacid chemistry for the reactions in the presence of FMSZ, we suggest reaction cycles whereby ethane is first protonated to form $C_2H_7^+$, which collapses to either H_2 and $C_2H_5^+$ or methane and CH_3^+. Then $C_2H_5^+$ is deprotonated to give ethene (CH_3^+ deprotonation is energetically unfavorable). The initial decrease in conversion with TOS is attributed to deactivation of acidic sites. Oligocondensation to give *n*-butane is inferred to proceed as ethane combines with adsorbed $C_2H_5^+$ to form $C_4H_{11}^+$, which is deprotonated to give butane. Autocatalysis is postulated to set in as $C_2H_5^+$ and CH_3^+ function as chain carriers. Thus, ethane is converted into ethene, along with methane (Figure 1). The conversions to ethene and to methane ultimately decrease with TOS as the number of these chain carriers declines, e.g., because carbonaceous deposits form on FMSZ.

This carbocation chemistry accounts for the ethane reactivity with FMSZ, being consistent with Olah's results (Olah et al., 1973), except that Olah did not observe autocatalysis, presumably because products were analyzed only following the batch reactor experiment. The behavior suggestive of autocatalysis in ethane conversion was not observed for propane (Cheung et al., 1995A) or *n*-butane (Cheung et al., 1995ABC). The difference may be associated with the higher reactivities of propane and butane and the correspondingly shorter initial declining periods.

Presuming that the carbocation chemistry inferred here for ethane conversion in the presence of FMSZ also pertains to *n*-butane isomerisation catalyzed by FMSZ, we suggest that the initial increase in conversion of butane in a flow reactor can be attributed to build-up of $C_4H_9^+$, which reacts with *n*-butane to form $C_8H_{19}^+$, which rearranges and splits into 2-methylpropane + $C_4H_9^+$. In contrast, Adeeva et al. (1994) proposed a classical bifunctional carbenium ion mechanism for *n*-butane isomerisation catalyzed by FMSZ, whereby $C_4H_9^+$ reacts with butene (formed by butane dehydrogenation) to give $C_8H_{17}^+$, which undergoes β-scission to form $C_4H_9^+$ and 2-methyl-1-propene, with subsequent hydrogen transfer giving 2-methylpropane; correspondingly, Adeeva *et al.*.[6] concluded that acidic sites in FMSZ were only moderately strong.

The oligocondensation (giving butane) observed in the ethane reaction with FMSZ was not observed with USY zeolite replacing FMSZ, although ethene was formed in comparable amounts with each material, provided that the space velocity was adjusted to give comparable ethane conversions. Furthermore, no evidence of autocatalysis was observed with USY zeolite; ethane conversion decreased monotonically with TOS. Thus, in ethane conversion with USY zeolite, there is no evidence of the classical bifunctional carbenium ion mechanism for butane formation analogous to that postulated by Adeeva et al. (1994) for butane isomerisation.

Consequently, we infer that butane formation from ethane in the presence of FMSZ proceeds via a mechanism different from the classical bifunctional mechanism. Rather, carbocation chemistry analogous to that occurring in superacid solutions accounts for butane formation from ethane. The implication is that FMSZ incorporates extremely strong acidic sites, consistent with Lin and Hsu's (1992) postulate. To reconcile this inference with the observation (Adeeva et al., 1995) that the acidic groups in FMSZ are only moderately strong, we postulate that the strongest acid groups constitute only a small minority that were not observed by Adeeva.

The inference that the ethane conversion in the presence of FMSZ proceeds via routes analogous to carbocation superacid chemistry does not exclude the possibility of butane isomerisation proceeding (perhaps simultaneously) via the classical carbenium ion route.

II. PROTOLYTIC CRACKING OF LOW-MOLECULAR-WEIGHT ALKANES IN THE PRESENCE OF IRON- AND MANGANESE-PROMOTED SULFATED ZIRCONIA: EVIDENCE OF A COMPENSATION EFFECT

Introduction. Activation of low-molecular-weight alkanes by superacids at subambient temperatures in solution was investigated by Olah et al. (1968, 1969, 1973), who demonstrated the involvement of penta-coordinated carbocations (carbonium ions). Formation of carbonium ions, which incorporate 2-electron-3-center bonds, was proposed to result from protonation of either C-C or C-H bonds, giving highly reactive carbocations, presumably transition states, which collapse to yield either cracking or dehydrogenation products, as shown in Scheme 1.

Gas-phase products of the reactions (alkanes and H_2) were analyzed by gas chromatography and/or mass spectrometry, and the tri-coordinated carbenium ions formed by carbonium ion collapse were analyzed in solution by nuclear magnetic resonance spectroscopy. The data are qualitative.

Quantitative data characterizing alkane conversion proceeding via transition states inferred to be adsorbed carbonium ions were reported by Haag and Dessau (1984), who used zeolites or silica-alumina to catalyze 3-methylpentane cracking, determining selectivity and rates of product formation in the temperature range of 623-823 K. Haag and Dessau (1984) used the following simplified picture to represent an equilibrated structure of four different carbonium ions, with any of the C-C and C-H bonds possibly being protonated (Scheme 2).

This family of carbonium ions was proposed to collapse with equal probability into three pairs of products, each consisting of an alkane or H_2 and an adsorbed carbenium ion. Consistent with this hypothesis, the formation rate was virtually the same for each of the three alkane products in the limit of zero conversion. At higher conversions, the reaction proceeded increasingly by the classical bimolecular mechanism involving hydride transfer and oligomerization/β-scission steps (Brouwer, 1980), producing more alkanes than alkenes.

Following the Haag-Dessau work, Krannila et al. (1992) investigated conversion of *n*-butane catalyzed by the zeolite HZSM-5 at about 770 K. They confirmed that the formation rate of each of the alkane products (methane and ethane) and of H_2 was almost the same and nearly equal to the rate of formation of each of the alkene products (ethene, propene, and butenes); furthermore, the apparent activation energies for formation of the product pairs (H_2 and butene; methane and propene; ethane and ethene) were determined to be the same within about $\pm 10\%$.

Numerous other recent product distribution data (Kwak et al., 1994) (Narbeshuber et al., 1995; Cheung et al., 1995, 1996) are consistent with these results and support the hypothesis of the formation of carbonium ions from alkanes at low conversions in the presence of solid acids and the simplified representation of how these transition states collapse to produce alkanes (or H_2) and carbenium ions, which are subsequently deprotonated to give alkenes.

The goal of the present investigation was to gain insight into acid-catalyzed cracking and dehydrogenation reactions involving carbonium ions by analyzing data characterizing the rates of reaction of low-molecular-weight alkanes, namely propane, *n*-butane, and 2, 2-dimethylpropane. The catalyst was chosen to be one of the most active known for cracking and related reactions of alkanes, namely, iron- and manganese-promoted sulfated zirconia. This catalyst was found to be extremely active for *n*-butane isomerization at 298 K, and was thus inferred to be a superacid (Hsu et al., 1992).

Some of the data presented here are new, and some have already been reported (Cheung et al., 1995, 1996).

The Compensation Effect. The temperature dependence of reaction rate constants in heterogeneous catalysis can be commonly described by the Arrhenius equation:

$$k = A\, e^{(-E/RT)} \qquad (1)$$

where k is the rate constant, E the apparent activation energy, A the pre-exponential factor, T the absolute temperature, and R the gas constant. The compensation effect (Constable, 1925; Cremer, 1955; Galwey, 1977) arises when an increase in log A is offset by a corresponding increase in E such that the rate remains constant for a given group of rate processes. For example, this effect may describe a linear relationship between log A and E for a family of reactions on one catalyst or for a particular reaction taking place on a family of catalysts:

$$\log A = \log k + E[\log(e)]/RT \qquad (2)$$

$$B \equiv \log(k\beta);\ \hat{e} \equiv [\log(e)]/R\beta \text{ at } T = \beta \text{ and } k = k\beta \qquad (3)$$

where $k\beta$ is the isokinetic rate constant and β isokinetic temperature.

Commonly, rates are measured as a function of temperature, and compensation effects are presented as a dependence of the normalized rate r (that measured under a particular set of conditions); then the compensation effect is represented as

$$r = A'\, e^{(-E/RT)} \qquad (4)$$

The compensation effect has been observed frequently in catalysis, among other fields, and most of the interpretations offered for it in surface catalysis were summarized in a review by Galwey (1977). There is no single explanation for the effect; the proposed explanations include the following, among others:

(1) The effect is a consequence of the heterogeneity of catalytically active surface sites, so that rates and activation energies are different on different sites; Galwey (1977) cited work showing how differences in the distribution of surface sites for a family of reactions can account for a linear compensation effect plot.

(2) The effect is an indication of a linear relationship between the entropy of adsorption and the enthalpy of adsorption for a family of reactions; a discussion of the enthalpy and entropy relationships based on transition state theory and statistical mechanics was given by Conner (1982). Patterson and Rooney (1994) extended the development of Conner (1982) by including a consideration of the adsorption that precedes the surface reaction.

(3) The effect is an indication of an equivalent reaction mechanism proceeding via similar reaction intermediates for each reaction in a family.

(4) However, concerns have been raised about whether some apparent compensation effects are no more than indications of experimental errors.

Experimental Methods. *Catalyst Preparation.* Rust-colored iron- and manganese-promoted sulfated zirconia, containing 1 wt% iron, 0.5 wt% manganese, and 1.8 wt% sulfur, was made by stepwise incipient wetness impregnation of the precursor sulfated zirconium hydroxide (Magnesium Elektron, Inc.) with iron and manganese nitrate solutions, respectively, followed by calcination in static air at 773 K in a tubular reactor with once-through flow, as described elsewhere (Cheung et al., 1995). The BET surface area and pore volume of the material were roughly 90 m^2/g and 0.2 mL(NTP)/g, respectively.

Catalytic Reaction Experiments. The pretreatment conditions and apparatus are described elsewhere (Cheung et al., 1995). Reactions were performed in a once-through plug flow reactor with the catalyst placed on a coarse frit. The gas feed contained propane (Matheson or Liquid Carbonic), *n*-butane (Liquid Carbonic), or 2,2-dimethylpropane (Liquid Carbonic). The alkane content of the feed stream was 1-5 mol%, with the remainder being diluent N_2 (Liquid Carbonic, 99.997%). The reaction conditions were as follows: temperature, 473-723 K; pressure, 101 kPa; mass of catalyst, 0.05-2.0 g; reactant partial pressure, 25, 250 and 1000 Pa; total (alkane + N_2) feed flow rate, 20-80 mL(NTP)/min. Hydrocarbon products were analyzed by an on-line gas chromatograph (Hewlett-Packard 5890A) equipped with an Al_2O_3/KCl PLOT column and a flame-ionization detector.

Results. Interpretation of the data is complicated by rapid catalyst deactivation; data representing most of the rates of reaction for the fresh catalyst were obtained by extrapolating low, nearly differential, declining conversions to zero on-stream time. In most cases, conversions of reactants were < 10% to assure satisfactory extrapolation; the errors in the extrapolated conversions (and the rates determined from them) were sometimes as much as ±50%.

The data examined here are the following: overall rates of conversion of propane, *n*-butane, and 2,2-dimethylpropane; rates of formation of methane from each of the three reactants; rates of formation of ethene from propane and from *n*-butane; and rates of formation of ethane from *n*-butane. The conversion vs. time-on-stream (TOS) profiles for all of these reactions are simple monotonically declining functions. (However, data for some products, including propene formed from *n*-butane and from propane and 2-methylpropane formed from *n*-butane, were not considered because the conversion vs. TOS profiles are other than monotonically decreasing functions, and there is not a sufficiently rigorous method for estimation of extrapolated reaction rates.)

Orders of each reaction in the reactant were determined experimentally to be about 1 except for the conversion of propane, which has a reaction order of 1.5 in the temperature range of 523-623 K; the reaction order for conversion of *n*-butane is lacking because of the complication of competing reactions, as discussed below.

The Arrhenius parameters E and A' determined at various reactant partial pressures are summarized in Table 1. In most cases, the values of these Arrhenius parameters were estimated from 3-4 data points with linear regression coefficients > 0.99. The pre-exponential factors A were normalized to a partial pressure of 25 Pa by using the experimentally determined orders of reaction. A plot of log *A'* at that partial pressure as a function of *E* yields the nearly linear relationship shown in Figure 2; this is an indication of a compensation effect.

A summary of the parameters determined from the plot, including the statistical values, is shown in Table 2. The isokinetic temperature and isokinetic rate were determined to be 860 ± 70 K and $(2 \pm 1) \times 10^{-8}$ mol/(s · g of catalyst), respectively. To show how well the data agree with the compensation effect, the rate observed for each reaction rate at the isokinetic temperature is compared in Table 3 with the prediction of the isokinetic rate determined from the compensation effect plot.

Discussion. *Interpretation of Compensation Effect.* The experimentally determined Arrhenius parameters for all the investigated reactions except the excluded reactions stated above fall near a straight line on the compensation effect plot (Figure 2), with a linear regression coefficient of 0.984. Thus there is a substantial data set indicative of the compensation effect.

The reactions giving data that fall on the linear plot of Figure 2 include (overall) conversion of propane, *n*-butane, and 2,2-dimethylpropane at low conversions; formation of methane from each of these three reactants; formation of ethene from propane and *n*-butane; and formation of ethane from *n*-butane. In contrast, reactions that led to products other than those stated immediately above, such as propene, butenes, and 2-methylpropane, did not give data that were extrapolatable. Thus these reactions are not classified as part of the family of reactions represented in Figure 2; the products of the reactions that are not represented on Figure 1 were likely formed in secondary reactions or reactions that do not involve carbonium ion transition states. These latter reactions were characterized by conversion versus TOS profiles different from those of the reactions associated with the linear compensation effect plot.

Thus we infer that the linear compensation effect plot (Figure 2) distinguishes a family of reactions proceeding via protonation and simple carbonium ion collapse from reactions that do not; this is the major point. Evidence supporting the carbonium ion mechanism is summarized in the following section.

The data are not sufficient to distinguish several plausible explanations for the observed compensation effect. The plausible explanations include the following:

(1) Protonation of the alkane reactant may occur at various C-C and C-H bonds, giving families of similar transition states having different reactivities. Olah et al. (1968, 1969, 1973) hypothesized that any C-H or C-C bond in an alkane can be protonated, but it is not possible from the distribution of observed products to identify which of these bonds are protonated. The suggestion that transition states are formed by protonation of various bonds in reactant alkanes is related to the third of Galwey's explanations of the compensation effect, listed above.

(2) The heterogeneity of the surface acidic sites may lead to different rates of reaction on different catalytic sites; this is the first of Galwey's interpretations. Microcalorimetric measurements of ammonia adsorption showed that unpromoted sulfated zirconia has acidic sites of various strengths (Yaluris et al., 1996), suggesting that the iron- and manganese-promoted sulfated zirconia is also characterized by a distribution of sites. Corma et al. (1993) invoked similar reasoning in proposing that the heterogeneity of the acidic and/or basic sites is responsible for the compensation effect observed for various hydrocarbon reactions catalyzed by acidic or basic zeolites.

(3) Galwey's second point about adsorption effects cannot be ruled out. Haag's observations (1994) of kinetics of alkane cracking catalyzed by the zeolite HZSM-5 provide an example. Haag (1994) explained an observed compensation effect by resolving the kinetics into a fast adsorption of the reactant followed by a rate-determining cracking of the adsorbed intermediate; the intrinsic activation energy for cracking of each adsorbed alkane (*n*-butane, *n*-hexane, *n*-octane, *n*-nonane, *n*-decane) was almost the same.

Narbeshuber et al. (1995) reported similar results for conversion of propane, *n*-butane, *n*-pentane, and *n*-hexane catalyzed by HZSM-5; they further concluded that the intrinsic activation energy was independent of which of the C-C bonds in a reactant was cleaved.

Evidence of Carbonium Ion Mechanisms of a Family of Reactions Catalyzed by Promoted Sulfated Zirconia. As reported earlier (Cheung et al., 1996), at propane conversions <0.2% and at 623 K, the molar ratios of methane to ethene and methane to propene were equal 1 and 2, respectively. These results are consistent with the hypothesis that methane and ethene formed from the same transition state, $C_3H_9^+$, which is the carbonium ion formed by protonation of propane. Thus, the reactions of propane to give methane and ethene belong to the family represented on the compensation plot in Figure 2. Presumably, there were two pathways for cleavage of the carbonium ion to yield methane and ethene, and one pathway for cleavage of the carbonium ion to give H_2 and propene. The product distribution data imply that all three pathways are approximately equally probable for this presumed transition state at very low conversion.

In the catalytic conversion of *n*-butane (Cheung et al., 1995), the ethane to ethene molar ratio in the product approached 1 after 1 h TOS at temperatures in the range of 623-723 K. Thus the reaction of *n*-butane to give ethane and ethene is consistent with the hypothesis of formation of carbonium ions by protonation of the reactant, followed by collapse to give the observed products; correspondingly, this reaction is one of the family represented on the compensation plot (Figure 2). In contrast, the methane to propene molar ratio in the products formed from *n*-butane exceeded unity under all the observed conditions. Evidently, secondary reactions of reactive propene occurred, and this reaction is not part of the family represented in Figure 2. The even more reactive butenes were observed only occasionally and underwent secondary reactions; thus the reactions to form butenes cannot be identified as part of the family represented in Figure 2.

Conversion of 2,2-dimethylpropane catalyzed by the promoted sulfated zirconia (Cheung et al., 1995) gave methane as the only gas-phase product observed even at conversions as low as 1%. The products are explained by the protonation of the reactant by the catalyst and the collapse of the carbonium ion to give methane and *t*-butyl cation. Consistent with this hypothesis, the rate data for methane formation and for 2,2-dimethylpropane conversion are represented in Figure 2 and are part of the family of reactions proceeding by protonation of alkane reactants and decomposition of the resulting carbonium ions. 2-Methylpropene was formed only at long TOS (> 2 h), and its yield was much lower than that of methane, suggesting that the *t*-butyl cation, the carbenium ion formed by cleavage of the protonated reactant, $C_5H_{13}^+$, was either converted into products other than 2-methylpropene (such as coke) or remained (in some form) adsorbed on the catalyst. Thus the data for the reaction forming 2-methylpropene do not belong on Figure 2.

Complications in Carbonium Ion Formation and Collapse. As mentioned above, the compensation effect could be an indication of protonation of alkanes at various C-C and C-H bonds. Theoretical calculations have shown that the transition states for H-D exchange, cracking, and dehydrogenation involve carbonium ions with different energies, and the reactions are all concerted (Lercher et al., 1994; Kazansky et al., 1994; Kazansky et al., 1994).

Thus, although some of the results for propane, *n*-butane, and 2,2-dimethylpropane conversion in the presence of the promoted sulfated zirconia catalyst are consistent with the Haag-Dessau hypothesis of protonation of the alkane reactant by the catalyst followed by collapse of the resulting "equilibrated" carbonium ion into three pairs of alkane (or H_2) and alkene with approximately equal probability, the issues of which bonds are protonated and to what degree are not yet resolved. If cracking of 2,2-dimethylpropane were to be examined by the Haag-Dessau model, then there should be two pathways for cleavage of $C_5H_{13}^+$ to give methane and 2-methylpropene and one pathway for cleavage of $C_5H_{13}^+$ to give ethane and propene. In contrast, only methane was observed in the presence of the promoted sulfated zirconia catalyst, which suggests that the patterns of carbonium ion formation and collapse are not yet well understood.

Conclusions. Iron- and manganese-promoted sulfated zirconia was used to catalyze reactions of alkanes; data include reaction rates and product distributions at low conversions. A compensation effect was observed, and it is suggested to be characteristic of the family of reactions (overall conversion of propane, *n*-butane, and of 2,2-dimethylpropane; formation of methane from each of the three reactants; formation of ethene from propane and from *n*-butane; and formation of ethane from *n*-butane) proceeding via carbonium ion collapse. The rate and product distribution data are consistent with the identification of carbonium ions as transition states. Consistent with the interpretation, data for reactions that are not expected to proceed via carbonium ion transition states do not fall on the linear compensation effect plot.

NOTATION

A = pre-exponential factor for rate constant, units of rate constant

A' = pre-exponential factor for rate, units of rate

β = isokinetic temperature, K

δ_L = standard deviation of the linear compensation effect relationship

δ_B = standard deviation of B

$\delta_{\hat{e}}$ = standard deviation of $\hat{e}$

E = apparent activation energy

e = 2.71......

k = reaction rate constant

k_β = isokinetic rate constant

n = reaction order

P = reactant partial pressure

r = reaction rate, mol/(g of catalyst s)

R = gas constant

T = temperature, K

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Table 1. Arrhenius parameters for alkane conversions in the presence of iron- and manganese-promoted sulfated zirconia.

Reaction	E, kcal/mol	log A' [A' in units of mol/(s · g)]	Partial pressure, Pa	Temperature, K	No. of data points	Linear Regression coefficient
n-butane conversion	2.2	-5.94	250	673-723	2	-----.
methane from *n*-butane	13.3	-3.49	250	623-723	3	0.996
ethane from *n*-butane	12.6	-3.64	250	623-723	3	0.990
ethene from *n*-butane	11.1	-4.52	250	623-723	3	0.990
2,2-dimethyl propane conversion	12.0	-4.60	25	623-723	4	0.999
methane from 2,2-dimethyl propane	17.3	-2.83	25	623-723	3	0.996
propane conversion	14.7	-1.29	1000	473-623	4	0.996
methane from propane	25.2	0.44	1000	523-723	3	0.999
ethene from propane	25.1	0.04	1000	523-723	3	0.999

Table 2. Isokinetic parameters[a] and their standard deviations[b] derived from different reactant partial pressures.

Partial pressure, Pa	B	$\hat{e}$	Linear regression coefficient	δ_L	δ_B	$\delta_{\hat{e}}$	β, K	k_β, mol/(s · g)
25	-7.72	0.255	0.984	0.381	0.34	0.019	860	1.91×10^{-8}

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[a] See text for definitions.

[b] Definitions of standard deviations:

δ_L, standard deviation of the linear relationship
δ_B, standard deviation of B
$\delta_{\hat{e}}$, standard deviation of $\hat{e}$

Table 3. Existence of isokinetic conditions.

Correlation	log k_β[a] at 25 Pa[a]	Uncertainty in log k_β
Compensation effect plot	-7.72	0.34
n-butane conversion	-7.50	0.10
methane from *n*-butane	-7.88	0.35
ethane from *n*-butane	-7.85	0.33
ethene from *n*-butane	-8.35	0.30
2,2-dimethylpropane conversion	-7.66	0.32
methane from 2,2-dimethylpropane	-7.24	0.45
propane conversion	-7.45	0.38
methane from propane	-7.59	0.65
ethene from propane	-7.96	0.65

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[a] Units of k_β: mol/(s · g)

List of Figures

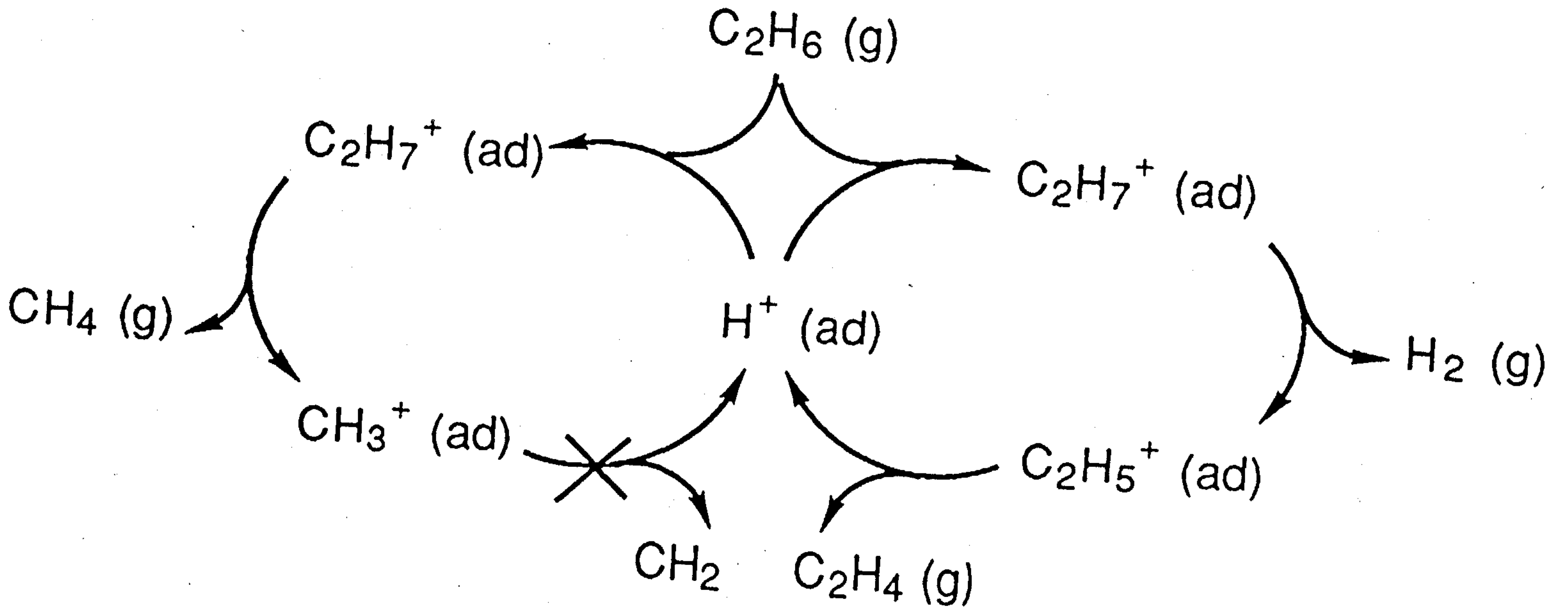


Figure 1

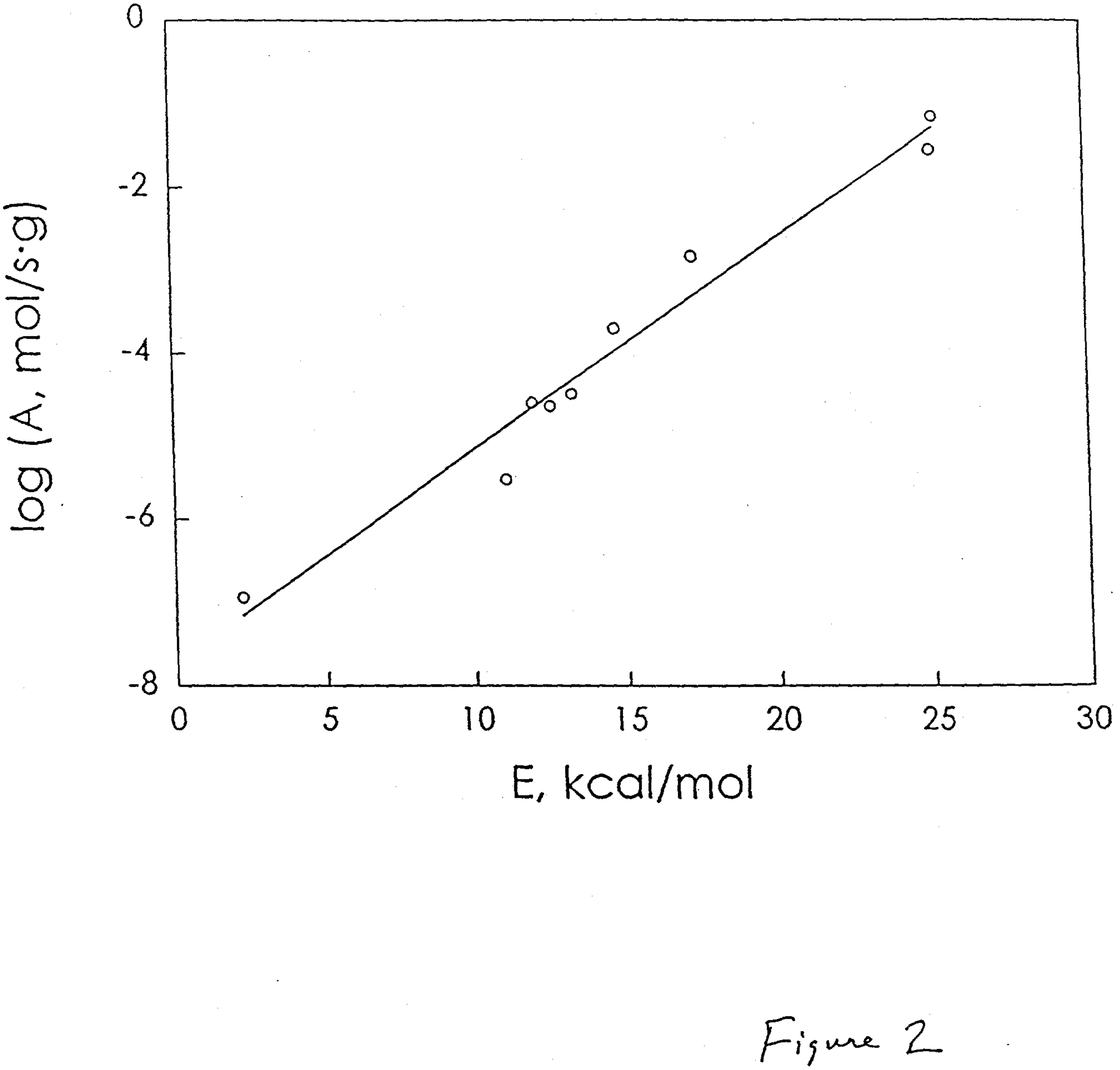
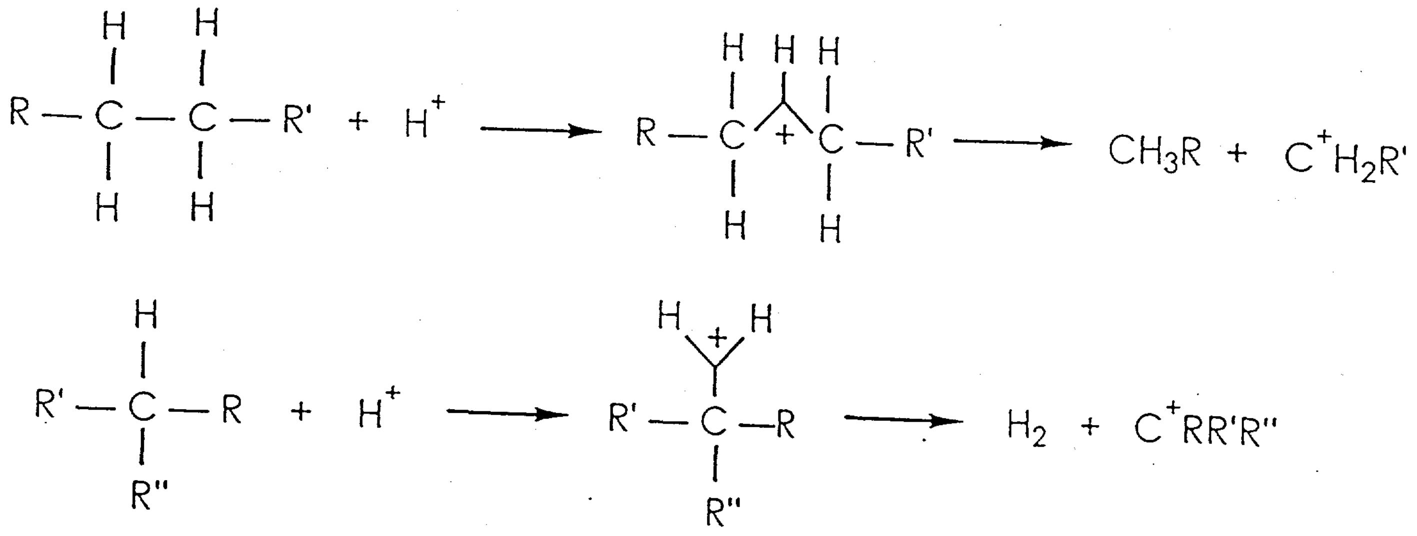


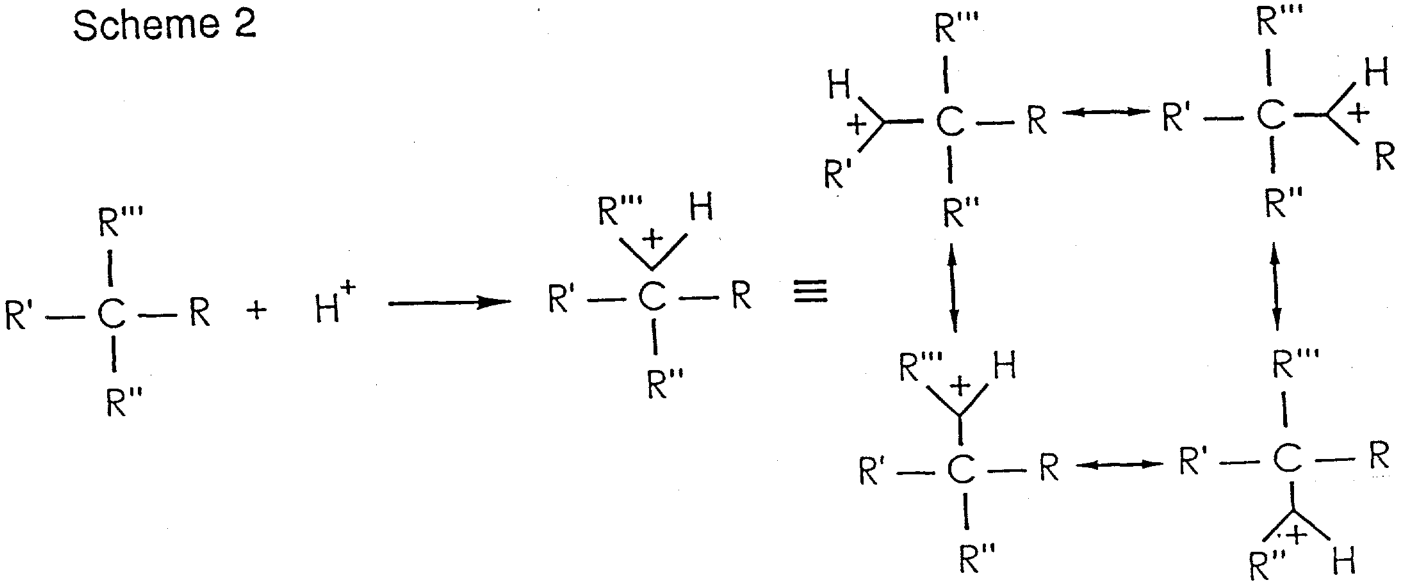
Figure 2

Scheme 1



R, R' and R'' = alkyl

Scheme 2



R, R' and R'' = alkyl or H