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Effect of Reaction Temperature on Product Distribution in the Catalytic Cracking of a Neutral Distillate

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The time-on-stream theory of catalyst decay has been applied to catalytic cracking data obtained using a La-Y zeolite catalyst in a fixed-bed reactor. In this way the effect of temperature on the kinetics of minor product formation in the cracking of a neutral distillate was investigated over a temperature range of 482–524°C.

Over a wide range of feed conversion, the yields of C_5^+ gasoline and coke decrease with increasing temperature, while the yields of butene, *n*-butane, propylene, propane, ethylene, ethane and methane increase.

The activation energy for the formation of primary gaseous products was found to be about 60 kcal/mole, while the activation energy for the formation of gasoline is about 50 kcal/g mole. It appears that the average bond broken to produce a C_5^+-410°F fraction molecule is weaker than that cracked to produce propylene, butene and *n*-butane.

NOMENCLATURE

A	Feed
b	Proportionality constant of the equation $\tau = bPt_f$
C_{so}	Initial concentration of active sites
k_j	Rate constant for the reaction of the *j*th species in a mixture (hr^{-1})
k_{z0}	Initial rate constant for formation of the product *z* (hr^{-1})
K_{Aj}	Adsorption equilibrium constant for *j*th species in the total feed A
k_0	Overall initial rate constant for the catalytic cracking of feed (hr^{-1})
P	Catalyst-to-oil ratio (g/g)
t_f	Total duration of an experimental run
W	Refractoriness parameter in Eqs. (2) and (4)
X_{Aj}	Mole fraction of the *j*th species in the feed
$\overline{X}_A$	Time-averaged fractional conversion of feed
X_A	Instantaneous fractional conversion of feed
α_j	Initial selectivity for formation of the *j*th product
ϵ_A	Average volume expansion correction factor
θ	Fraction of active sites remaining unpoisoned
τ	Space time

INTRODUCTION

Comparative kinetic and selectivity studies in catalytic cracking are generally difficult because of complex interactions between the process variables (temperature, feed composition, pressure, catalyst composition, etc.). This type of study is made even more difficult to interpret in meaningful terms by the decay of catalyst activity which occurs during the cracking reaction. Nevertheless some qualitative information on the effect of reaction temperature on product selectivities has been reported in the literature (*1*,*2*). Unfortunately, due to the lack of a comprehensive kinetic model to describe the catalytic cracking of gas oils, even the quantitative

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studies have usually been limited to investigations of the effect of temperature on C_5^+ gasoline formation alone (*3,4*). No thorough studies to obtain quantitative data on the effect of temperature on the selectivities for the other products of catalytic cracking have been reported.

This paper deals with changes in product selectivities due to variations in reaction temperature. In order to observe the effect of temperature on product selectivity without the masking influence of catalyst decay, all comparisons have been made on the basis of the "optimum performance envelope" (OPE) of the reacting system (*5,6*). The OPE of a reacting system which is subject to catalyst decay is obtained by plotting the time-averaged yield of a product versus the time-averaged conversion for various catalyst-to-oil ratios. The resulting selectivity loops form an envelope which is coincident with the experimental runs performed at short catalyst times-on-stream. This envelope, it has been shown (*3,5*), represents instantaneous selectivity behavior.

In order to obtain quantitative data from the selectivity curve which is represented by the OPE, the concept of initial product selectivity or ultimate product efficiency (UPE) was introduced (*6*). The UPE is given by the slope of the OPE at zero conversion. Thus

$$\alpha_j = \left.\frac{dX_{Aj}}{dX_A}\right|_{X_A=0} = \frac{k_{j_0}}{k_0}. \quad (1)$$

Using Eq. (1), the initial selectivity (or UPE) for formation of the *j*th product, α_j, can be obtained by graphical means while k_0, the overall rate constant for the catalytic cracking of the same feed at the same conditions, can be obtained by fitting our model for catalytic cracking to conversion data. The model has been reported previously (*4,7*) and is given by

$$\tau k_0 \theta = \int_0^{X_A} \left(\frac{1+\epsilon_A X_A}{1-X_A}\right)^{1+W} dX_A \quad (2)$$

and

$$\overline{X}_A = \frac{1}{t_f}\int_0^{t_f} X_A \, dt, \quad (3)$$

where θ decay function (*8*)
W refractoriness parameter
ϵ_A average volume expansion
τ space time.

The space time is defined as:

$$\tau = bPt_f,$$

where P catalyst-to-oil ratio
t_f duration of an experimental run
b ratio of the density of the vaporized feed to the density of the catalyst.

Therefore Eq. (2) can be written as:

$$bPt_f k_0 \theta = \int_0^{X_A} \left(\frac{1+\epsilon_A X_A}{1-X_A}\right)^{1+W} dX_A. \quad (4)$$

Since α_j and k_0 can be determined from experimental data, it follows that the initial rate constants k_{j_0} for the formation of all the primary products of catalytic cracking can be evaluated. This fact is exploited in the present study to obtain initial rate constants for the formation of all the primary products of catalytic cracking at three different temperatures.

EXPERIMENTAL METHODS

The preparation of the feedstock, the equipment used in this study and the methods of product analyses were described previously by John and Wojciechowski (*9*). The feed used in this investigation was A0W1 and was described in the above publication in some detail.

RESULTS

The effect of temperature on product selectivity was evaluated on the basis of the optimum performance envelope of the reacting system. The construction of the OPE from data obtained from a fixed-bed

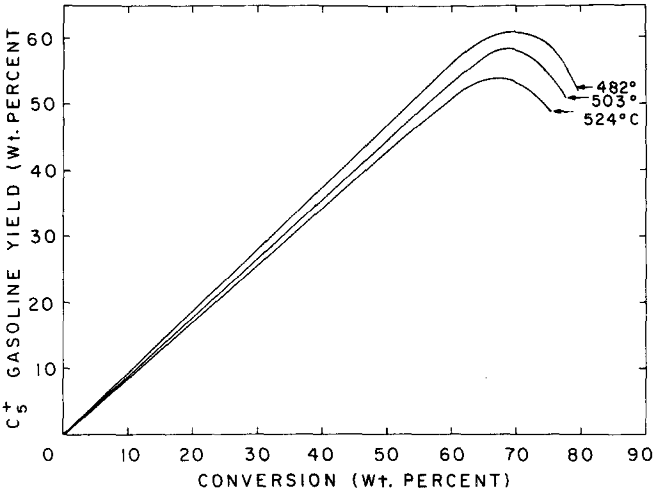


FIG. 1. Effect of reaction temperature on the OPE for gasoline.

reactor has been described elsewhere (*5,6,9*).

Figure 1 shows that the yield of C_5^+ gasoline decreases with increasing reaction temperature over the range of conversions studied. At the same time Fig. 5 shows that as the yield of gasoline decreases with increasing reaction temperature, the olefinicity of the gasoline tends to increase. This trend is repeated for all the gaseous products. Figures 2 and 3 indicate that the yields of propylene and *n*-butane increase with increasing temperature throughout the range of conversions investigated. In the case of butene, Fig. 4 shows that there is a tendency for the selectivity curves to cross at conversion levels above 72.0%. Below this level of conversion, Fig. 4 indicates that the butene yield increases with increasing reaction temperature.

The effect of increasing cracking temperature on the formation of secondary reaction products is shown in Figs. 6–11. In the conversion range studied, it can be seen that increasing the reactor temperature increases the yields of all the secondary products except coke. At a given con-

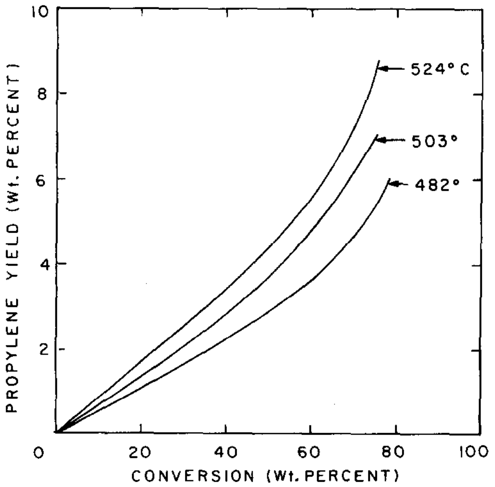


FIG. 2. Effect of reaction temperature on the OPE for propylene.

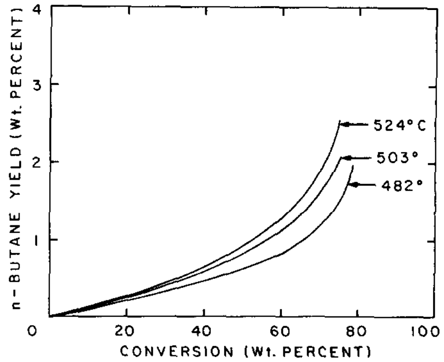


FIG. 3. Effect of reaction temperature on the OPE for *n*-butene.

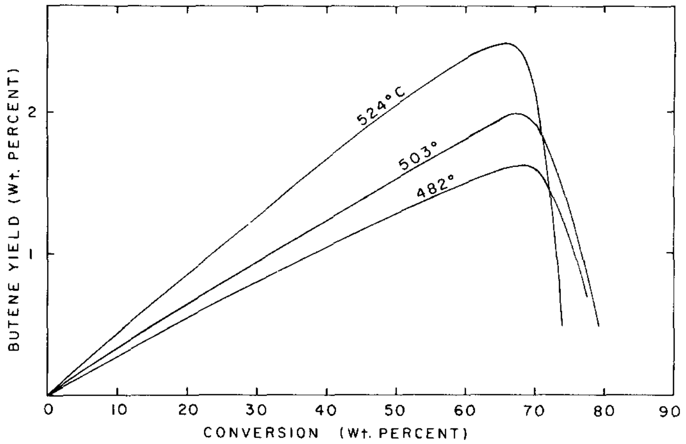


FIG. 4. Effect of reaction temperature on the OPE for butene.

version level, less coke is produced as the reaction temperature is increased.

In summary, these results indicate that increasing the cracking temperature increases the yields of all C_1–C_4 gases and decreases the yields of gasoline and coke. It is worth noting that the trends shown in Figs. 1–11, which are established on the basis of the OPE of the fixed-bed reactor, agree qualitatively with the results reported by Arden *et al.* (*2*) and also by Murphree (*1*) who obtained their data from studies in fluid-bed reactors. Thus the OPE is shown to provide a means of conducting studies of cracking patterns in a fixed-bed reactor and, by proper interpretation, of predicting the behavior which can be expected in fluidized bed reactors.

Estimates of the initial selectivity for formation of the primary products were obtained graphically from the slopes of the lines drawn tangent to the optimum performance envelopes. The results which are listed in Table 1 show that the initial selectivity for formation of the C_5^+ gasoline fraction decreases with increasing temperature while the initial selectivities for the

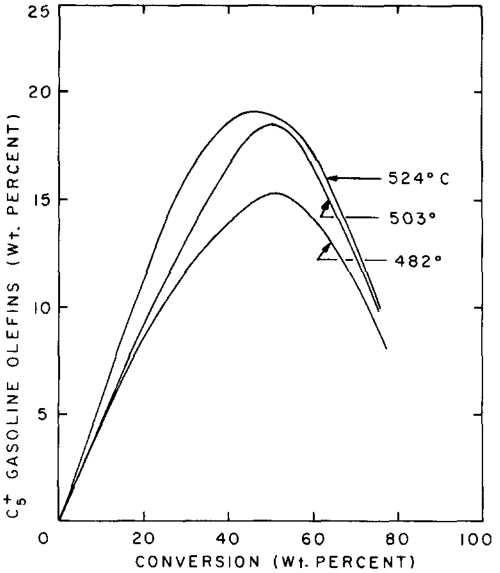


FIG. 5. Effect of reaction temperature on the OPE for C_5^+-410°F gasoline olefins.

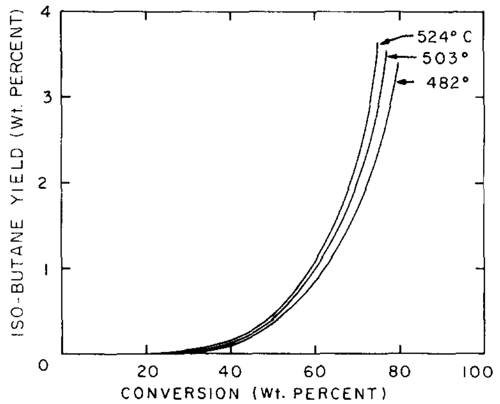


FIG. 6. Effect of reaction temperature on the OPE for isobutane.

TABLE 1

EFFECT OF TEMPERATURE ON THE INITIAL RATE CONSTANT FOR CRACKING (*10*) AND ON THE INITIAL SELECTIVITIES FOR FORMATION OF PROPYLENE, *n*-BUTANE, BUTENE AND C_5^+ GASOLINE FROM A0W1

Reaction temp (°C)	Overall rate constant k_0 (hr^{-1})	Initial selectivity α_j			
		Propylene	*n*-Butane	Butene	C_5^+ gasoline (*10*)
524	53.8×10^7	0.090	0.015	0.042	0.840
503	23.4×10^7	0.070	0.013	0.033	0.876
482	9.6×10^7	0.055	0.008	0.030	0.900

formation of the primary gaseous products all increase as the reaction temperature is increased. A more accurate estimate of the initial selectivity for product formation could have been obtained by fitting a comprehensive model of catalytic cracking to the experimental data. However, such a model has not been fully developed.

A simplified model, which describes the feed conversion and gasoline formation, has been used to obtain estimates of the rate constant for cracking the feed as well as the rate constant for formation of gasoline and will be reported elsewhere (*10*). There the initial selectivity for gasoline formation was found to vary from 0.90 to 0.85 when temperature was raised from 482 to 524°C. This trend agrees qualitatively with Weekman's results (*3*) which showed a range of initial gasoline selectivity between 0.820 and 0.700 for mid-continental gas oil when temperature was raised from 482 to 538°C.

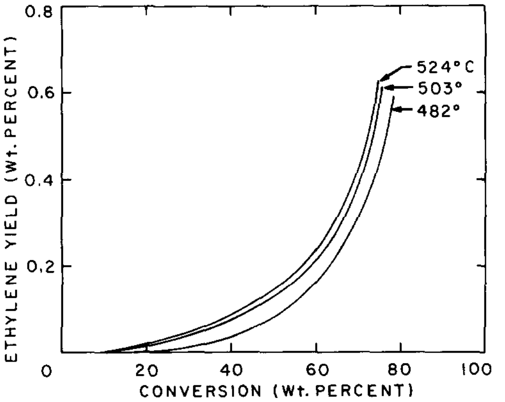


FIG. 8. Effect of reaction temperature on the OPE for ethylene.

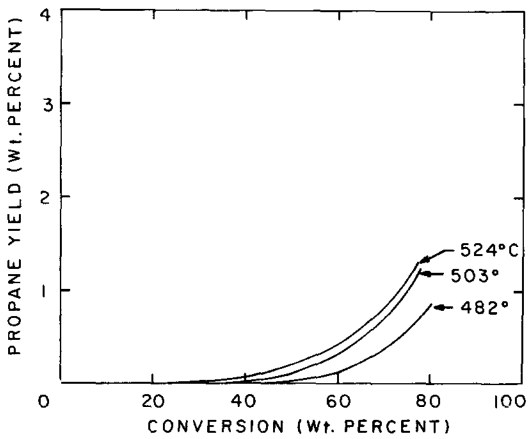


FIG. 7. Effect of reaction temperature on the OPE for propane.

The initial rate constant for formation of propylene, butene and *n*-butane can be evaluated using Eq. (1). These compounds along with C_5^+ gasoline were identified as primary products in the catalytic cracking of extracted neutral distillate (*9*). Estimates of the initial rate constants for formation of the primary products are listed in Table 2.

The Arrhenius plot shown in Fig. 12 is

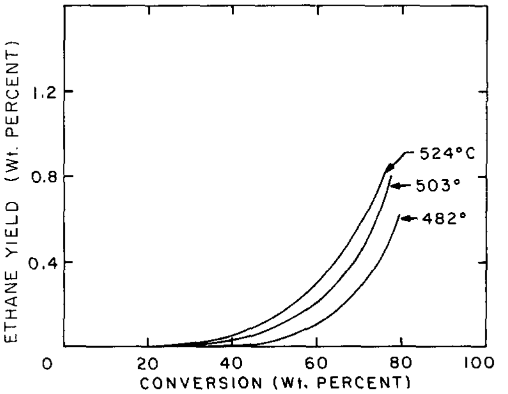


FIG. 9. Effect of reaction temperature on the OPE for ethane.

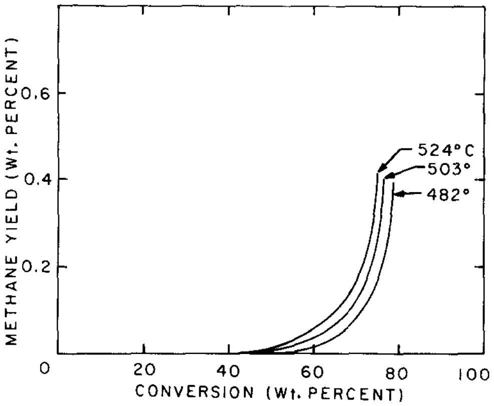


FIG. 10. Effect of reaction temperature on the OPE for methane.

prepared from values of the initial rate constants reported in Table 2. Estimates of the preexponential factor of the initial rate constants, A_e, and the apparent activation energy, E_e, obtained from the Arrhenius plots are given in Table 3.

DISCUSSION

Wojciechowski (*4*) has shown that in the catalytic cracking of complex mixtures of hydrocarbons the observed rate constants are not the simple constants observable in elementary chemical reactions. For gas oil cracking it was shown that the first order rate constant can be written as (*10*)

$$k_{z_0} = C_{s_0} \sum_{j=1}^{n} k_{jz} K_{Aj} X_{Aj_0}, \qquad (5)$$

TABLE 2

EFFECT OF REACTION TEMPERATURE ON THE INITIAL RATE CONSTANT FOR FORMATION OF PROPYLENE, BUTENE, *n*-BUTANE AND C_5^+ GASOLINE (*10*) FROM A0W1

Reaction temp (°C)	Initial rate constants (hr^{-1})			
	Propylene	Butene	*n*-Butane	C_5^+ gasoline (*10*)
524	4.84×10^7	2.26×10^7	0.81×10^7	45.20×10^7
503	1.64×10^7	0.77×10^7	0.30×10^7	20.60×10^7
482	0.53×10^7	0.29×10^7	0.08×10^7	8.65×10^7

where C_{s_0}	initial concentration of catalyst active sites
K_{Aj}	adsorption equilibrium constant
k_{jz}	rate constant for reaction of the *j*th fraction of the feed to product *z*
X_{Aj_0}	initial mole fraction of the *j*th species in the feed
n	number of species which react to produce the compound *z* in the initial cracking event.

In the special case when

$$k_{1z}K_{A1} \approx k_{2z}K_{A2} \approx \cdots \approx k_m K_{Am}$$

or if the feed consists of one compound

$$k_{z_0} = C_{s_0} k K_A. \qquad (6)$$

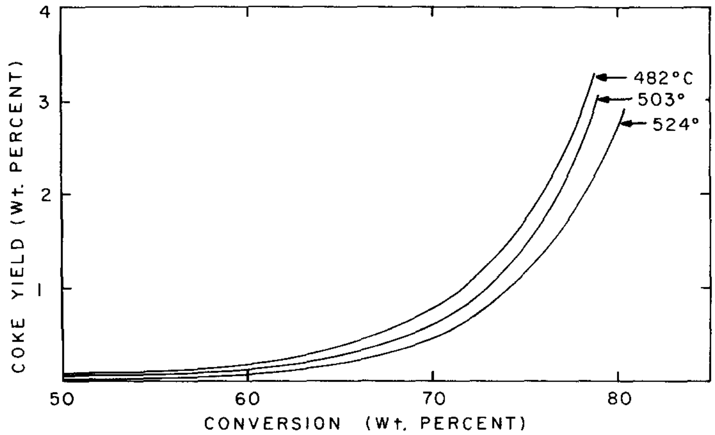


FIG. 11. Effect of reaction temperature on the OPE for coke.

TABLE 3

KINETIC PARAMETERS FOR THE FORMATION OF PRIMARY PRODUCTS FROM AOW1

Primary products	A_e (hr^{-1})	E_e (kcal/mole)
Propylene	8.92×10^{24}	63.0
Butene	2.29×10^{23}	58.4
n-Butane	1.04×10^{25}	66.0
C_5^+ gasoline (*10*)	3.74×10^{21}	46.8

In this study we assume that there exists an average value kK_A which can be used in Eq. (6) to represent the behavior of a mixture of hydrocarbons. The rate constant k in the above is then a first order kinetic rate constant, which can be defined in terms of some average of the pertinent thermodynamic functions:

$$k = \frac{k_bT}{h} \exp\left(\frac{\Delta S_r}{R}\right) \exp\left(\frac{-\Delta H_r}{RT}\right), \quad (7)$$

where k_b Boltzman constant

ΔS_r and ΔH_r entropy and heat of activation.

Although the heat of activation is not strictly equal to the energy of activation, Condon (*11*) has reported that they seldom differ by more than 0.5 kcal.

The equilibrium adsorption constant K_A is written as:

$$K_A = \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(\frac{-\Delta H_a}{RT}\right),$$

where ΔS_a and ΔH_a are the entropy and heat of adsorption. It follows that Eq. (6) may be written as

$$k_{z_0} = C_{s_0} \frac{k_bT}{h} \exp\left(\frac{\Delta S_r + \Delta S_a}{R}\right) \exp - \left(\frac{\Delta H_r + \Delta H_a}{RT}\right). \quad (8)$$

Thus, the preexponential factor can be defined as:

$$A_e = C_{s_0} \frac{k_bT}{h} \exp\left(\frac{\Delta S_r + \Delta S_a}{R}\right) \quad (9)$$

and the experimental activation energy may be defined as

$$E_e = \Delta H_r + \Delta H_a.$$

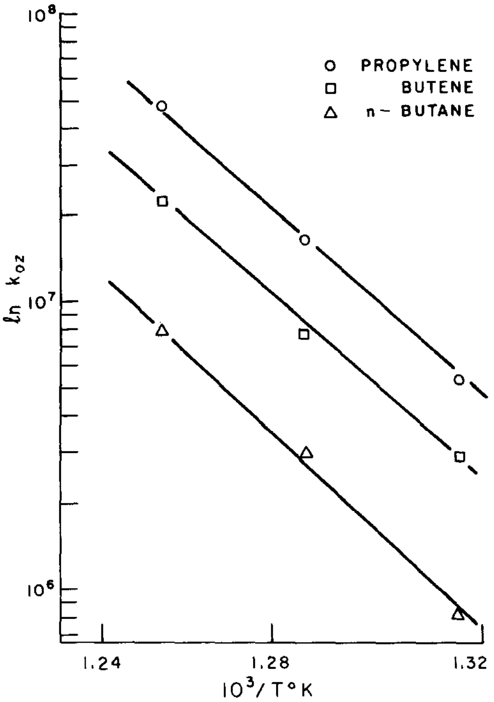


FIG. 12. Arrhenius plots of the initial rate constants for formation of propylene, butene and *n*-butane.

Equation (9) suggests that the relationship between the preexponential factor, A_e, for the formation of a given product is complex and dependent on such factors as the concentration of active sites and the entropy of adsorption. Furthermore it appears from Eq. (5) that in the catalytic cracking of a complex feed, the value of A_e may also depend on the distribution of concentrations of the various reacting species. Therefore the experimentally observed values of A_e are not easy to interpret as to their thermodynamic significance. Fortunately, in evaluating activation energies from the same rate constants, the effects of incidental factors are less important.

Apparent Activation Energies of the Primary Products

An examination of the estimated activation energies reveals that the apparent activation energies of the rate constants for formation of propylene, butene and *n*-butane are of the order of 60 kcal/mole. The formation of propylene and butene involve the β scission of a C–C bond on a secondary carbonium ion:

$$\mathrm{R{-}CH_2{-}CH_2} \vdots \mathrm{CH_2{-}\overset{+}{C}H{-}CH_3} \rightarrow$$

$$\mathrm{CH_2{=}CH{-}CH_3 + R{-}CH_2{-}\overset{+}{C}H_2}, \quad \text{(a)}$$

$$\mathrm{R{-}CH_2} \vdots \mathrm{CH_2{-}\overset{+}{C}H{-}CH_2{-}CH_3} \rightarrow$$

$$\mathrm{CH_2{=}CH{-}CH_2CH_3 + R{-}\overset{+}{C}H_2}, \quad \text{(b)}$$

$$\mathrm{R\,\overset{+}{C}H_2 + H^- \rightarrow R\,CH_3}. \quad \text{(c)}$$

Since different σ bonds are broken in the formation of propylene and butene, the result in Table 3 suggests that inner bonds on a straight chain crack with somewhat lower activation energy. Fragments smaller than C_3 apparently are not formed at all. If fragments less than C_3 could be formed just as easily as propylene or butene then the alternative beta scission would occur in Eq. (b) and methane would be observed as a primary product

$$\mathrm{R{-}CH_2{-}CH_2{-}\overset{+}{C}H{-}CH_2} \vdots \mathrm{CH_3} \rightarrow$$

$$\mathrm{CH_2{=}CH{-}CH_2CH_2{-}R + \overset{+}{C}H_3},$$

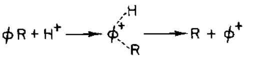
$$\mathrm{\overset{+}{C}H_3 + H^- \rightarrow CH_4}.$$

In our work it has been shown (9) that methane is clearly a secondary reaction product.

The formation of *n*-butane is the net result of two reaction steps. The first is the breaking of the C–C bond followed by a single step transfer of a hydride ion to the carbonium center [Eqs. (b) and (c)]. The apparent activation energy, 66 kcal/mole, obtained for the formation of *n*-butane is only a little higher than those estimated for propylene and butene whose formation involved only C–C bond scission. It seems at this time that the bond breaking step is probably also rate determining in the formation of *n*-butane and that the activation energy for hydride ion addition is lower than that required for beta scission. Support for this view comes from the work of Parravano *et al.* (*12*) who reported that the activation energy for hydrogen exchange between CH_4 and CD_4 on an acidic catalyst is only 13 kcal/mole.

The observed activation energy for the gasoline forming reactions is 49.5 kcal/mole. This significant difference in the activation energies of the rate constants for the formation of gaseous products and of the gasoline range products may arise due to the fact that gasoline range compounds are formed from a variety of compounds with various cracking characteristics. A detailed analysis of the feedstocks used in this study shows that they contain alkyl and napthenic aromatics. The available data on the catalytic cracking of these compounds indicate that the cracking reaction of alkyl aromatics is very selective for the removal of the entire side chain

(*13,14*). One of the mechanisms suggested for this reaction postulates that the dealkylation reaction is an electrophilic substitution on the benzene ring due to the great affinity of the benzene ring for protons.



$$\phi R + H^+ \longrightarrow \phi^+\langle{}^{H}_{R} \longrightarrow R + \phi^+$$

In the case of cumene for example a range of values has been reported for the activation energy of the rate determining step in cumene cracking. Campbell and Wojciechowski (*15*) obtained 19.5 kcal/mole; Horton and Maatman (*16*) reported 23.4 kcal/mole, while Prater and Lago (*17*) reported 40 kcal/mole. These data, added to the fact that the feedstocks used in this study contained alkyl benzenes, allow for the possibility that the value of 45 kcal/mole for the gasoline forming reactions may be an average for the two reaction mechanisms, namely C–C bond scission and electrophilic substitution.

Another explanation for the difference in the activation energies for the C_5^+ gasoline and gas forming reactions may be that the strength of the σ bonds on the straight and branched chain hydrocarbons, which make up most of the feed, become weaker with increasing distance from the terminal carbon. The results in Table 3 regarding the apparent activation energies for the C_3 and C_4 forming reactions show some support for this conclusion. It is possible that substantial difference in average bond strength exists between the bonds broken to form C_3 and C_4 compounds and those broken to form C_5 to C_{14} hydrocarbons (C_5^+ gasoline).

Regardless of the mechanism through which the gasoline range compounds are formed, a difference of 10 kcal/mole between the activation energies for gasoline formation and the formation of the primary gas products accounts for the fact that with increasing temperature the initial selectivity for the formation of gasoline decreases, while the selectivities of all the other primary products increase (Table 1).

TABLE 4

EFFECT OF TEMPERATURE ON THE INITIAL SELECTIVITY FOR FORMATION OF OLEFINS

Reaction temp (°C)	Initial selectivity for formation of C_5^+ olefins (wt%)	Overall initial selectivity for formation of C_3, C_4 and C_5^+ olefins (wt%)
482	48.0	56.4
503	48.0	58.0
524	57.0	70.0

Although the initial selectivity for total gasoline formation decreases with increasing reaction temperature, estimates of the initial selectivity for formation of gasoline range olefins indicate that the latter increases with increasing temperature. The results reported in Table 4 are obtained graphically from Fig. 5 and appear to indicate that the split between olefins and the other products of the primary cracking step is a function of temperature. The initial selectivity for olefin formation increases significantly with temperature.

Since olefins react readily on acidic surfaces, it follows that the rate of secondary reactions should increase with increasing temperature. The results shown in Figs. 6–11 indicate that this is indeed the case. It is seen that the selectivity for formation of all the secondary reaction products, except coke, follows the same trend as that observed for the formation of olefins in the primary cracking step.

Unlike the other products of secondary reactions, the selectivity for coke formation decreases with increasing reaction temperature. This result is consistent with a mechanism of coke formation which is based on the abstraction of hydride ions by olefins from compounds strongly adsorbed on the surface of the catalyst. If the rate of hydride ion transfer from the coke precursors decreases relative to the rate of cracking, the yield of the hydrogen deficient material which becomes coke will decrease and the concentration of olefins in the product will increase at any given feed conversion. This explanation suggests that the activation energy for hydride ion transfer is less than it is for cracking, in keeping with reported observations (*12*).

We have previously (*9*) suggested that the fact that the gasoline fraction is composed of approximately 50% olefins at 503°C indicates that the cracking event consists of the departure of an olefin from an adsorbed carbonium ion followed promptly by hydrogenation and desorption of the residual moiety. From Fig. 5 and Table 4 we see that the probability of recracking the residual moiety before desorption increases markedly at high temperature. Such an effect would be expected if recracking without desorption involves a step whose activation energy and frequency factor are both higher than those of the β scission reaction. We are at present not prepared to speculate on the exact nature of the step which is responsible for our observations.

CONCLUSIONS

The concepts of optimum performance envelope and ultimate product efficiency have been applied to the study of the effect of temperature on product distribution.

It has been shown that the apparent activation energies for formation of C_3 and C_4 compounds are significantly higher than those for the formation of gasoline range hydrocarbons. We are led to believe that the gasoline range products are on an average the result of the cleavage of weaker bonds or are produced from certain molecules whose cracking reactions proceed via a different transition state from those reactions which produce the other primary products.

We note that the proportion of olefins in the products increases rapidly at high temperatures indicating the emergence of a new dominant reaction step under such conditions.

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