

A Kinetic Investigation of the Formation of Benzene on Heating Long-Chain ($n\text{-C}_7\text{-}n\text{-C}_{18}$) Saturated Aliphatic Alcohols on Ferric Oxide

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It has been shown that on heating long-chain ($n\text{-C}_6\text{-}n\text{-C}_{18}$) saturated aliphatic alcohols with excess ferric oxide, the following products were formed through rate processes: (i) olefin, by alcohol dehydration; (ii) benzene, indicating extensive rearrangement of the carbon skeleton of the reactant; and (iii) carbon dioxide, from complete reactant oxidation. Product yields were small, and reactions are identified as desorption of surface intermediates produced during oxidation of chemisorbed hydrocarbon radicals by the ferric oxide. Particular interest was directed to the benzene formation reaction since this was a somewhat unexpected product. The kinetic characteristics observed for this process from $n\text{-C}_7\text{-}n\text{-C}_{18}$ alcohols were closely similar—all the reaction activation energies were close to 25 kcal mole⁻¹, and the product yields increased somewhat with chain length. Benzene production from stearic acid and $n\text{-octylamine}$ was very similar to the reactions of the alcohols. A reaction mechanism to account for these observations is proposed.

Numerous investigations of the kinetics of chemisorption and subsequent desorption of simple molecules on diverse solid phases have been reported in the literature. Such studies have characterized the properties of chemisorbed radicals, some of which are undoubtedly intermediates in heterogeneous catalysis. Kinetic investigations of surface processes involving more complex molecules have been undertaken less frequently, probably due to the difficulties inherent in the measurement of small volumes of low vapor pressure reactants. It was found possible (1, 2), however, to study the kinetics of desorption of product $\text{C}_6\text{-C}_8$ hydrocarbons on heating organic compounds chemisorbed on metallic oxides. From the results, it was concluded that the decomposition of certain organic acids on nickel oxide proceeded through salt formation (2); this was consistent with later work (3, 4). Alcohols, reacting under the same conditions, yielded product olefins (1, 2). For example, $n\text{-hexanol}$ heated with nickel oxide gave $n\text{-1-hexene}$ as the almost exclusive hydrocarbon product, but on ferric oxide a mixture of product hydrocarbons was detected (1).

The present article reports an investigation of the surface rearrangement reactions of chemisorbed organic radicals, derived from alcohols, on ferric oxide. Qualitative and quantitative measurements were made of hydrocarbon product formation on heating saturated $n\text{-C}_7\text{-}n\text{-C}_{18}$ alcohols (and certain other compounds) on samples from a single preparation of ferric oxide. Preliminary work showed that all reactants yielded benzene as the most abundant (or, indeed, only significant) product in the $\text{C}_6\text{-C}_8$ hydrocarbon boiling range. The greater part of the present study was concerned with the determination of the mechanism of formation of this somewhat unexpected product.

EXPERIMENTAL

Kinetic measurements, for the rate of product formation from the reaction of each organic substance studied, were made using samples from a single batch of reactant mixture. Each reactant material was prepared by mixing ~ 0.2 g of the organic compound with ~ 50 g of ferric oxide and warming the mixture to $\sim 60^\circ$; a 0.200-g sample from this preparation was taken for each

rate measurement made. A detailed description of the subsequent reaction procedure has been given previously (1); this may be outlined as follows: A 0.200-g sample of reactant mixture was weighed into each reaction tube, evacuated 3 hr at $\sim 10^{-6}$ torr and sealed. The reactant was held at room temperature during evacuation so that excess of the organic constituent was removed from the sample tube and thus kinetic studies were concerned with the reaction of that fraction of the organic material which had remained at the oxide surface on completion of the evacuation process. The reactant was then heated to a known temperature for a measured time during which the volatile products were condensed at -195° . While chilled, the latter were sealed off, and, after warming, were subsequently analyzed by gas-liquid chromatography using the radioactive ionization detector. Yields and kinetic data are reported as g^{-1} of reactant mixture.

Except where otherwise stated, reactant mixtures were prepared from a single batch (~ 700 g) of Hopkins and Williams "Ferric oxide-calcined." This was heated in air at $\sim 500^\circ$ with mixing, before use, to remove possible organic impurities. $\alpha\text{-Fe}_2\text{O}_3$ (hematite) was the only phase detected by X-ray diffraction measurements. The surface area, from nitrogen adsorption at -195° and application of the BET equation, was found to be $10.5 \pm 1.0 \text{ m}^2 \text{ g}^{-1}$. Gravimetric analysis of the oxide (solution in acid, precipitation as hydroxide, and ignition) gave 99.0% Fe₂O₃.

The purest available grades of organic reactants were used.

RESULTS

Blank Experiments

When the ferric oxide was heated under reaction conditions, it gave no detectable yield (i.e., $< 0.3 \times 10^{16}$ mol. g^{-1}) of benzene or other C₅-C₈ hydrocarbon. Ferric oxide, moistened with benzene, gave no detectable hydrocarbon yield at $< 350^\circ$, and the total benzene yield on heating to $> 450^\circ$ was 4×10^{16} mol. g^{-1} , which is small compared with yields from the other reactant mixtures.

Preliminary Measurements

Preliminary work was concerned with the identification of the products obtained in these reactions. Careful gas-liquid chromatographic analyses, using silicone oil and dinonylphthalate liquid phases showed that the desorption reactions ($200\text{--}300^\circ$) of *n*-decanol and *n*-octadecanol from ferric oxide both yielded benzene as the most abundant product in the C₄-C₈ hydrocarbon boiling range. Smaller amounts ($\sim 10\%$ that of benzene) of toluene and a C₅ isomer, almost certainly *n*-pentane, were also found. Above 300° the relative yield of toluene increased and small amounts of further compounds were detected at retention distances characteristic of saturated and unsaturated C₅ and C₆ hydrocarbon isomers.

The Benzene Production Reaction

Benzene production, as a predominant reaction at $200\text{--}300^\circ$, was unexpected and it was, therefore, considered appropriate to use the present experimental technique to study the formation of this product. Reactants studied included *n*-C₇-*n*-C₁₈ alcohols to investigate the influence of chain length, a secondary alcohol (2-octanol) and, to determine the effect of change of functional group, *n*-octylamine and stearic acid.

Two typical sets of kinetic data for the benzene formation reaction, obtained in the present work, are shown as Arrhenius plots in Figs. 1a and b. Each point represents a product yield measurement divided by reaction time. Measurements were almost entirely concerned with the early stages of reaction, for which results showed that the product yields were directly proportional to time; this observation has been reported in previous similar studies (1, 2). Readings were taken over the maximum temperature range for which satisfactory rate measurements could be obtained. All the kinetic data found in the present study are summarized in Table 1, which includes total benzene yields, the activation energy for benzene production, and, to allow quantitative comparisons between different reactants, the temperature at which the reaction reached a *defined rate*, which is taken, for use

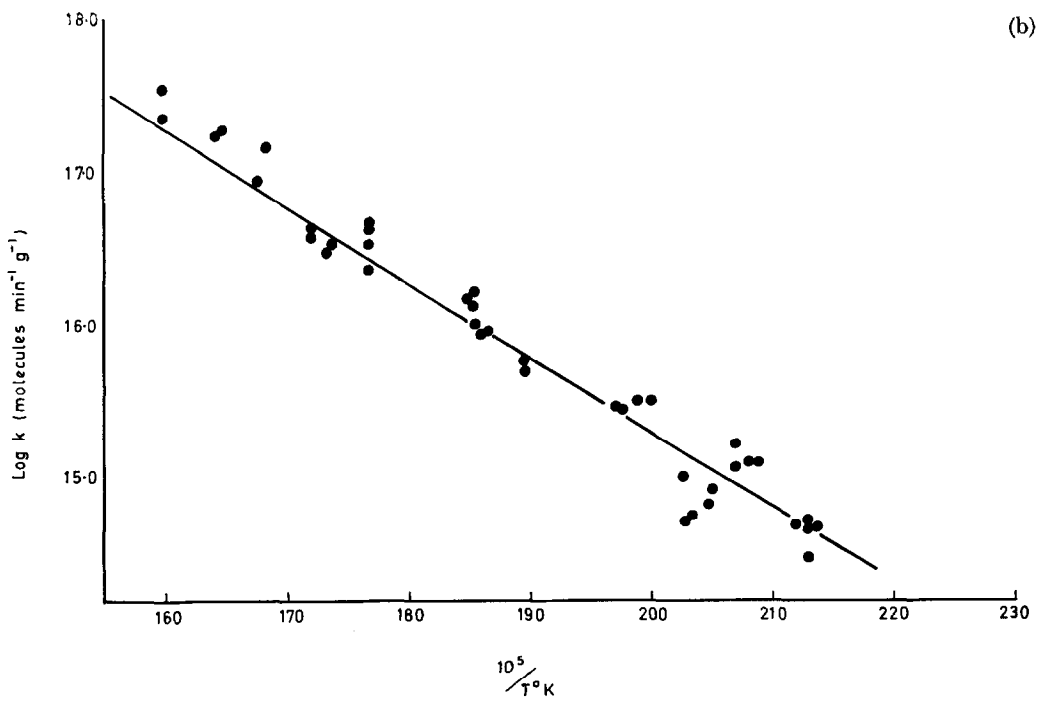
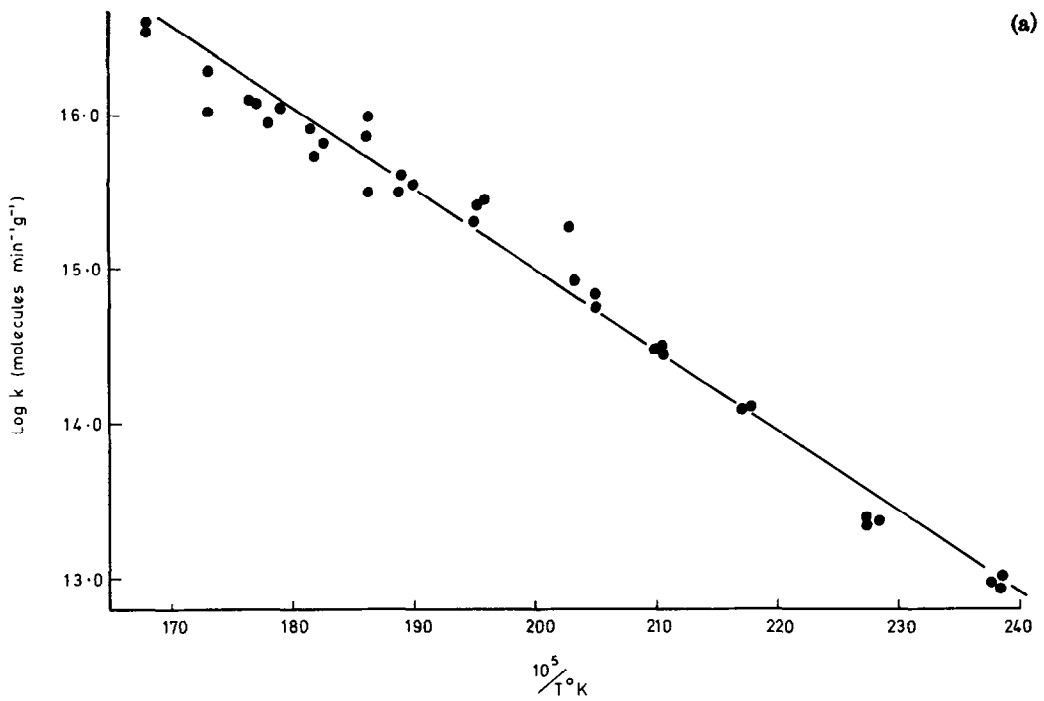


FIG. 1. Arrhenius plots for the benzene desorption reactions on heating small amounts of normal alcohols with ferric oxide. Each point represents a single product yield determination from reaction after a measured time at a known temperature. (a) *n*-Octanol, (b) *n*-Hexadecanol.

TABLE 1
SUMMARY OF KINETIC DATA OBTAINED FOR THE BENZENE FORMATION REACTION
ON HEATING ORGANIC COMPOUNDS WITH FERRIC OXIDE

Compound	Total benzene yield ($\times 10^{16}$ mol. g ⁻¹)	Activation energy (kcal mole ⁻¹)	Temperature range studied (°C)	Temperature of defined reaction rate (1.0×10^{16} mol. min ⁻¹ g ⁻¹)
<i>n</i> -Hexanol	~100	—	—	~320°
<i>n</i> -Heptanol	80	23.2	230–370°	290.7°
<i>n</i> -Octanol	60	24.2	180–320°	279.0°
<i>n</i> -Decanol	60	25.7	180–300°	263.2°
<i>n</i> -Dodecanol	120	23.7	180–300°	267.0°
<i>n</i> -Tetradecanol	160	25.9	170–300°	266.0°
<i>n</i> -Hexadecanol	150	25.5	190–350°	261.8°
<i>n</i> -Octadecanol	180	24.2	190–360°	273.0°
2-Octanol	~30	20–25	275–360°	~340°
<i>n</i> -Octylamine	>100	20–25	280–370°	~280°
Stearic acid	250	25.4	190–350°	272.3°

in the present article, as 1.0×10^{16} mol./g⁻¹ min⁻¹ (Fig. 2).

Products Other than Benzene

Information, some of it qualitative, from chromatographic product analyses is sum-

marized under reactant headings below ("small" and "very small" refer to yields corresponding to 2–10% and <2% that of benzene).

Cyclohexanol. The total cyclohexene product yield and the rate of formation were,

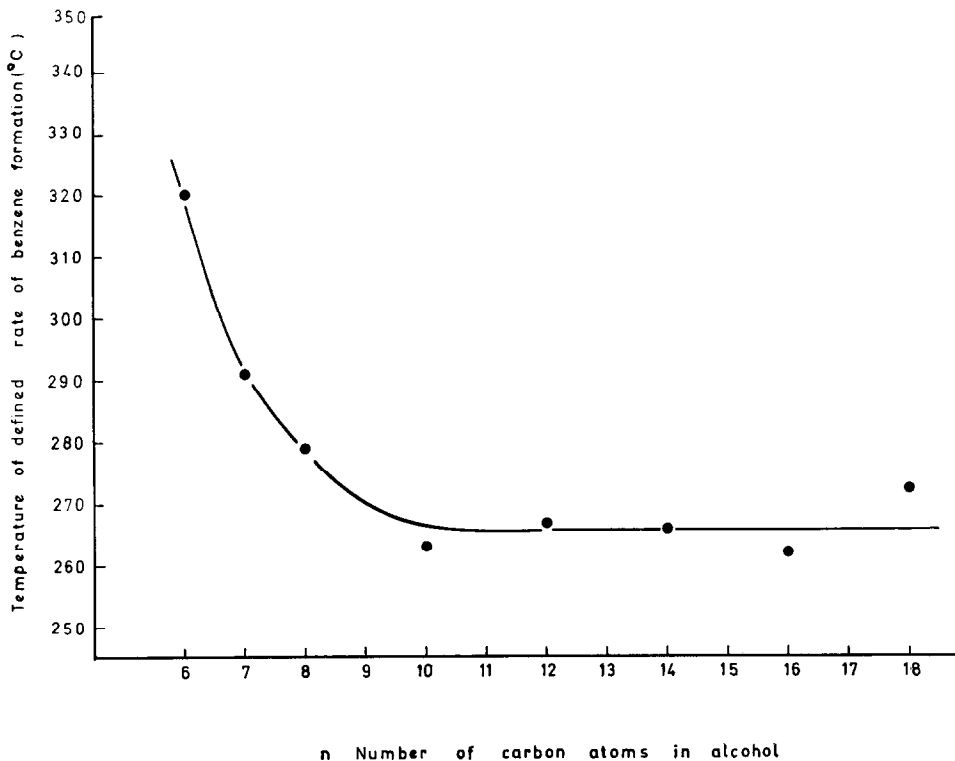


FIG. 2. Plot of temperature of defined reaction rate for benzene formation (1.0×10^{16} mol. min⁻¹ g⁻¹) against length of carbon chain (*n*) in the chemisorbed alcohol.

within experimental error, identical with values previously reported (1). The formation of this product proceeded at the defined rate at 188°. Small benzene yields were again (1) detected from reaction above 300°.

***n*-Hexanol.** *n*-1-Hexene was the predominant hydrocarbon product. The total yield was slightly greater than that previously reported (1) for a different oxide preparation. Again appreciable yields of several further hydrocarbons were detected, though the proportions relative to the olefin found in the present work were slightly less than before (1). The present study showed that benzene formation could be detected above ~300° and the temperatures of defined reaction rates for *n*-1-hexene and benzene production were 250° and ~320°, respectively.

***n*-Heptanol.** The total yield of *n*-1-heptene ($\sim 50 \times 10^{16}$ mol. g⁻¹) was somewhat less than that of benzene and no systematic variations with changes in reaction time or temperature (230-370°) were found. Small amounts of C₅ hydrocarbons and even smaller yields of C₆ compounds were also detected.

***n*-Octanol.** Kinetic measurements for *n*-1-octene formation (total yield 60×10^{16} mol. g⁻¹) showed that the activation energy for this reaction was 25.0 ± 2.0 kcal mole⁻¹, and the defined reaction rate was attained at 225°. Toluene yields were ~10% those of benzene, though the proportion increased above 350°. C₅ and C₆ hydrocarbon products were detected in small, or very small, yields from reaction above 300°.

Other alcohols studied. The yield of product toluene from *n*-decanol was ~10% that of benzene and was relatively greater above 300°; very small yields of C₅ and C₆ hydrocarbons were detected above 300°. *n*-Dodecanol gave benzene as the predominant product, but significant yields (~0.2 those of benzene) of *n*-pentane were found, together with small amounts of toluene. *n*-Tetradecanol, *n*-Hexadecanol, and *n*-Octadecanol gave benzene as the only significant product in the boiling range studied, with small or very small yields of pentane and toluene, the proportion of the latter increasing above 300°. 2-Octanol gave a yield of *n*-1-octene which was about twice that of

benzene; toluene was sought but not found, and yields of C₅ hydrocarbon isomers were 10-30% that of benzene.

Other reactants. *n*-Octylamine. Small yields of toluene and of C₅ and C₆ hydrocarbon isomers were detected. *Stearic acid*. Benzene was the predominant product recognized, yields of C₆ and C₇ hydrocarbons were small or very small. *Dodecane*. This reactant yielded benzene above ~250° and at 350° the amount of product benzene was ~30% of that from dodecanol. Very small amounts of C₄ and C₅ hydrocarbons were also detected.

Effect of Variation of the Oxide Phase

***n*-Decanol and ferric oxide.** The reaction of *n*-decanol on a different preparation of ferric oxide (Hopkins and Williams: "Precipitated, Red," previously ignited in air and with a surface area 48 m² g⁻¹) was very similar to that described above. The total benzene yield (120×10^{16} mol. g⁻¹) was greater from this sample, which had the larger surface area; the activation energy (190-350°) was 24.0 kcal mole⁻¹ and the temperature of defined reaction rate was 255.0°.

***n*-Octanol and ferric hydroxide.** Two samples of hydrated ferric oxide were prepared by the addition of (i) ammonia and (ii) sodium hydroxide to ferric chloride solutions. Precipitates were washed and dried at (i) 100° and (ii) 160°. These contained (i) 62.5% and (ii) 78.8% ferric oxide. A small amount of *n*-octanol was added and the benzene desorption reaction studied as previously. The large yield of ammonia and/or water precluded the possibility of making kinetic measurements. Results gave definite evidence of benzene formation, however, though the total yield was relatively small, $10-20 \times 10^{16}$ mol. g⁻¹. Small amounts of further products, probably *n*-pentane and C₄ hydrocarbons, were also detected.

Stearic acid and nickel oxide. This reactant mixture also yielded product benzene, though the amounts formed were smaller than those from reaction on ferric oxide, yields were ~10% at 250° rising to 25% above 320°.

Gas Desorption from, and Alcohol Oxidation on Ferric Oxide

On heating ferric oxide, to which no organic reactant had been added, in an evacuated constant volume system with a -80° trap, oxygen desorption at 250° and 300° was 250 and 600×10^{16} mol. g⁻¹, respectively. On similar heating of the alcohol-containing reactant mixtures used in kinetic studies, the initial total gas yield was greater (1000×10^{16} mol. g⁻¹) but diminished at longer time intervals or on the introduction of a -195° trap, suggesting the oxidation of hydrocarbon radicals. Chromatographic measurements showed that carbon dioxide was formed; yields from reactions for 10 min at 300° and 25 min at 380° were 80 and 600×10^{16} mol. g⁻¹, respectively. Meaningful kinetic data for gas evolution 280 – 350° could not be obtained, but, qualitatively results were consistent with the onset of hydrocarbon oxidation, detectable above $\sim 280^{\circ}$.

DISCUSSION

Since most (if not all) of the present organic reactants may be distilled in vacuum unchanged, we conclude that the chemical processes studied here occurred *after* dissociative chemisorption of the reactant on ferric oxide, and that, on heating, the excess organic constituent was rapidly volatilized from the reaction zone. The results indicated that these surface processes were complex. At least three different reactions were observed which occurred in successively slightly higher temperature ranges in the sequence: (i) alcohol dehydration, to yield olefin, and sometimes double-bond migration also occurred (1); (ii) benzene formation, accompanied by cracking; and (iii) hydrocarbon radical oxidation to carbon dioxide. It is also probable that there was desorption of unchanged alcohol.

Blank experiments showed that benzene desorption did not occur on heating the prepared sample of ferric oxide and that benzene chemisorption on this phase was small. The results found for reactions of *n*-hexanol and cyclohexanol were very similar to previously reported observations (1) though there were minor differences between

the reactions on the different oxide preparations. The present results showed that both these reactants yielded benzene above 300° .

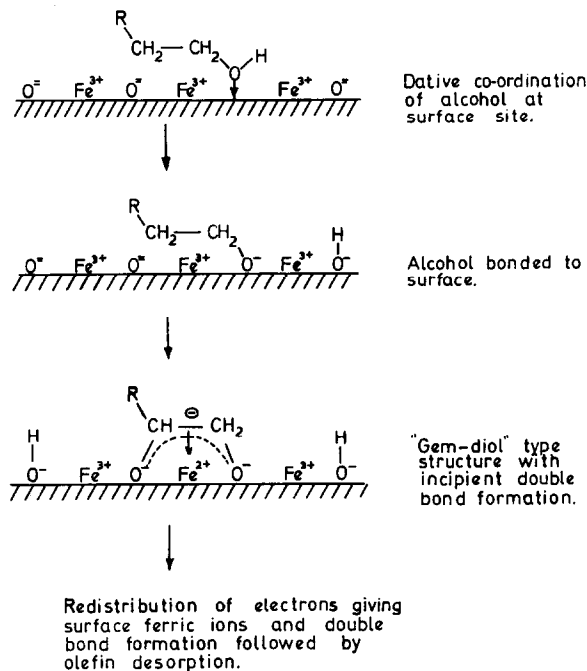
Product yields. Using approximate values for the area of oxide surface occupied by each chemisorbed reactant molecule and the measured area of the oxide, product yields may be expressed as fractional surface coverage. The total benzene and olefin yields were 0.03–0.06 monolayer each and that of carbon dioxide ~ 0.2 . These products thus correspond to the occupation of 26–32% of the oxide surface. In addition, chemisorbed alcohol may be desorbed unchanged and surface hydroxyl groups may be retained to at least 200° (5). Oxygen evolution from ferric oxide, to which alcohol had not been added, was ~ 0.1 monolayer.

High-temperature reaction. The results gave clear evidence that a fraction of the chemisorbed organic reactant was oxidized to carbon dioxide under the conditions used to study the kinetics of benzene formation [see also ref. (6)]. This is consistent with the observed oxygen desorption from ferric oxide in the same temperature range.

The olefin formation reaction. The present study showed that olefin desorption from C₆ alcohols proceeded at 100 – 260° and also that the reactions of *n*-heptanol, 1- and 2-octanol yielded olefin at temperatures below those at which benzene production became significant. The activation energy values for the formation of *n*-hexene [28 kcal mole⁻¹ (7)] and *n*-octene (25 kcal mole⁻¹) from the alcohols were similar but appreciably greater than that for cyclohexanol dehydration [19 kcal mole⁻¹ (1)].

Alcohol chemisorption on the oxide may be expected to proceed through initial dative bond formation, probably with accommodation of the oxygen atom at an unoccupied superficial oxide ion site. Since (i) hydrocarbons are oxidized under reaction conditions and (ii) ferric hydroxide undergoes dehydration at reaction temperatures, we propose Scheme I to represent the sequence of steps in olefin formation. The initial step is transfer of the alcohol proton to an oxide ion; alternatively, initial rupture of the C O bond can yield the same species. Proton transfer from the second carbon atom to an

SCHEME I



oxide ion then yields a surface *gem*-diol type structure which may also be represented as a π -complex formed between an adsorbed olefin and surface orbitals derived from appropriate crystal field splitting of the $3d$ orbitals of the cation. Resonance involving both structures would be expected to stabilize the surface intermediate and a subsequent activation process involving redistribution of electrons results in olefin desorption. The mechanism of this process may show points of similarity with the dehydration of alcohols on alumina (7).

The benzene formation reaction. The present observations show that the kinetics of benzene production were largely independent of (i) variations in alcohol chain length (n -C₈- n -C₁₈) and (ii) replacement of the -OH group, -NH₂ (octylamine) or -COOH (stearic acid). The benzene yield did, however, increase somewhat with chain length. Results (Fig. 2) also showed an increase in benzene production rate from n -hexanol to n -octanol, and thereafter there was a slight reduction in rate from C₈ to C₁₈, if due account is taken of the

increased yield from the longer chain compounds. Change in substituent position to the 2-position in n -octyl alcohol reduced the benzene yield.

The above results, together with the observations on cracking and oxidation reactions, may be accounted for by the following mechanism. The formation of the *gem*-diol type structure (Scheme I) is the first step in a continuing hydrogen removal process which is the initial process in hydrocarbon oxidation. Successive reactions of this type lead to the generation of an adsorbed radical which is, in effect, a conjugated multiolefin. The hydroxyl groups, simultaneously produced, may be removed by water formation (5) so that the outer plane of the lattice array thereafter consists predominantly of cations. Such an array may be expected to exhibit properties somewhat similar to those of metals on which adsorption of unsaturated organic compounds as π -complexes has been postulated (8, 9); Dollimore and Tonge have postulated π -complex adsorption of cinnamyl alcohol at the cations on manganese dioxide (10).

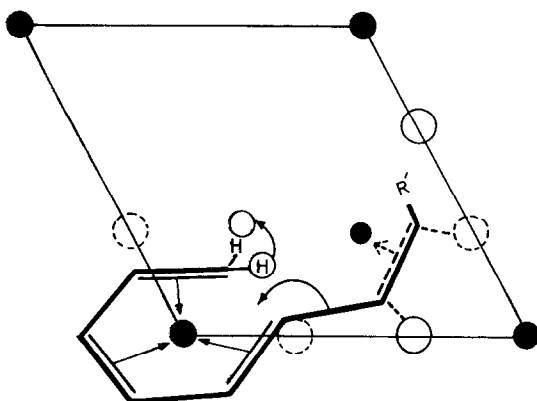


FIG. 3. Scale drawing for the postulated rate-determining step in the benzene formation reaction on the 111 face for the rhombohedral description of the hematite lattice. The conjugated unsaturated chain, formed by oxidation of the hydrocarbon, tends to form an aromatic ferrocene-type complex, which, after transferring a proton and making an appropriate redistribution of electrons, yields benzene. Open circles, oxygen ions in the surface plane; solid circles, ferric ions just below the surface; dashed circles, oxygen ions appreciably below the surface plane.

Appropriate disposition of the chemisorbed conjugated multiolefin on ferric oxide may thereafter result in a stereochemical configuration suitable for aromatic compound formation as shown for the 111 face in the rhombohedral description of the hematite lattice (11) in Fig. 3. Conjugation of the three double bonds, shown here, tends towards an aromatic nucleus since the surface cation may be expected to stabilize a ferrocene-type adsorbed complex. Thereafter, a single proton transfer, accompanied by appropriate electron redistribution, results in aromatic ring formation and subsequent desorption of benzene from the unstable "ferrocene" intermediate which may be formed on only one side of the surface cation. The aromatic ring is thus regarded as resulting from a preferred surface configuration which is stabilized through adoption of ferrocene-type bonding.

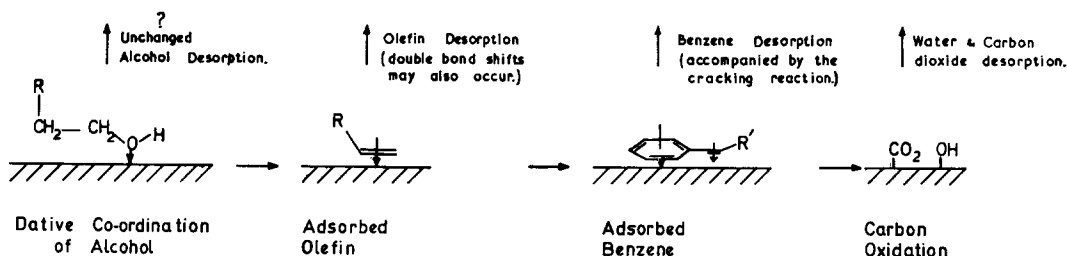
A variation of the above scheme, in which there is proton transfer to the β -carbon atom, can explain the formation of the precursor to toluene product. Subsequent reactions of the hydrocarbon radical R' (Fig. 3) with

gain or loss of hydrogen may yield saturated or olefinic cracking products.

The mechanism described above accounts for the following observations: (i) There was a relatively low frequency factor for benzene formation from n - C_6 and n - C_7 alcohols (Fig. 2, Table 1) since here the complete aromatization process must take place about a single cation and (a) the probability of this event must differ from that found when a second point of surface attachment is possible, also (b) ring closure involves different bond redistribution processes. The almost equal rates of benzene production for reactants with more than eight carbon atoms is consistent with the intermediate proposed (Fig. 3). (ii) Variations in the functional group present in the organic reactant did not significantly influence the energy of activation for benzene production. This is in accordance with the supposition that such groups are removed prior to the aromatic ring formation step. (iii) The reaction of n -heptanol did not yield product toluene. Proton transfer to the β -carbon atom was not possible here. (iv) The reaction of n -dodecanol gave a relatively large pentane yield. This may result from oxidation of the carbon atom α to the aromatic ring, together with hydrogenation at the β -position followed by desorption of the hydrocarbon radical. (v) Dodecane reacted on ferric oxide to yield benzene. To explain this reaction it may be assumed that hydrocarbon oxidation preceded volatilization to yield one of the intermediates in Scheme I, above, which thereafter reacted by the mechanism proposed for the alcohols. (vi) 2-Octanol gave a relatively low benzene yield. This is attributed to preferred initial adsorption in the 2- and 3-positions so that ring closure of the conjugated olefin subsequently formed is inhibited by the terminal methyl groups.

The production of benzene from the reactions of alcohols with hydrated ferric oxide is consistent with the above mechanism, in which the formation of, and subsequent desorption reactions of, surface hydroxyl groups did not prevent aromatic ring formation. The low benzene yields here are attributed to a reduction in the probability of initial bonding of the alcohol to the hy-

SCHEME II



droxyl-covered surface, during the initial period when reactant may be rapidly distilled from the heated zone.

General reaction scheme. The above mechanisms describe reactions whereby the observed products are desorbed from intermediates formed during the progressive oxidation of surface adsorbed hydrocarbon radicals. These processes may be diagrammatically summarized as shown in Scheme II.

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