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The Kinetics of the Desorption of Aromatic Hydrocarbons during the Thermal Decomposition of Organic Radicals Adsorbed on the Surface of Nickel Oxide

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A study has been made of the kinetics of benzene and toluene formation reactions on heating, *in vacuo*, small amounts of organic compounds, all of which contained a single aromatic nucleus, in the presence of excess nickel oxide. Results showed that only small amounts of product hydrocarbons, comparable to a fraction of a monolayer of adsorbed material, were given and an experimental method, designed to enable quantitative study of the kinetics of these reactions, is described. Acidic compounds, benzoic acid, phthalic acid, etc., yielded benzene with an energy of activation 46 ± 3 kcal/mole and it is suggested that a nickel salt is formed at the surface of the oxide as an intermediate in the hydrocarbon formation reaction. The formation of benzene from adsorbed benzyl alcohol and 2-phenylethanol occurred with an energy of activation 31 ± 2 kcal/mole and these results are interpreted in terms of intermediates consisting of ligands coordinated with surface atoms of the solid. Mechanisms of benzene and toluene formation from the reactions of adsorbed surface species are discussed.

In the literature of heterogeneous catalysis two general approaches to the characterization of intermediate radicals adsorbed at the surface of solid catalysts have been widely used. One such approach is to distinguish between possible intermediates using suitable kinetic and/or isotopic exchange measurements for the reaction as a whole. The other approach is to obtain information about the nature of the adsorbed species from measurements of some physical property of the catalyst which is modified when molecules are adsorbed (electrical conductivity, infrared spectra, etc.). Both approaches have yielded information about the mechanisms of catalytic reactions but in some instances the approaches give results which lead to different conclusions. Kemball (*1*) has pointed out, however, that the species adsorbed over the greater part of the surface of the catalyst may be unreactive and a labile species, present only in small concentration, may be the active intermediate in a catalytic reaction. It was considered of interest, therefore, to investigate directly the reactivity of species adsorbed on the surface of a solid since such information is relevant to the establishment of reasonable reaction mechanisms to account for complex catalytic processes. Many studies of adsorption reactions have appeared in the literature but a relatively smaller number of studies of the reactivity or desorption reactions of possible adsorbed intermediates has been published. A similar approach was previously used in a study of the cracking of hydrocarbons chemisorbed on nickel metal, where nickel carbide was postulated (*2*) as an intermediate, and it was shown (*3*) that the presence of this intermediate was consistent with the chemical properties of nickel carbide studied under similar reaction conditions.

More recently (*4*) a study has been made of the kinetics of hydrocarbon formation reactions on heating *in vacuo* C_6 and C_7 alcohols chemisorbed on iron oxide or on nickel oxide to investigate the reactivity of species adsorbed at an oxide surface. The present article reports an extension of this work in which a study has been made of the kinetics of formation of aromatic hydrocarbons when aromatic molecules containing a variety of functional groupings (acid, aldehyde, alcohol, and others) were desorbed on heating *in vacuo* from different samples of a single preparation of nickel oxide. Attention was confined to the aromatic hydrocarbon product.

EXPERIMENTAL

A single sample of nickel oxide, B.D.H. Ltd. Laboratory Reagent Grade, "Low in Fe and Co, a variable mixture of NiO and Ni_2O_3" was used throughout the work. Five hundred grams was heated to about 650°C for 30 min in an open dish with constant stirring, stirred while cooling, and stored in a tightly stoppered glass jar. Samples for study ($\sim$30 g) were withdrawn and heated to 150°C for 10 min and, when cold, a small amount (0.2–0.3 g) of the organic reactant was added. With solid reactants the mixture was crushed in a pestle and mortar. Small samples ($\sim$0.5 g) were placed at the sealed ends of tubes 30 cm long and 9 mm diameter, two constrictions were pulled in each tube, and a right angle bend made between them. The open end of the tube was then sealed onto a conventional pumping system and evacuated to around 10^{-6} for 3–4 hr, with a liquid air trap between sample and pumps. The sample, in the evacuated glass envelope, was then detached from the vacuum system by rapid application of a hot flame at the constriction further from the sample. Each sample was later heated in a horizontal furnace at known temperature for a measured time with the emergent end immersed in liquid nitrogen to condense volatile products. The second constriction was then rapidly sealed off and the solid subsequently weighed. The condensed material in the portion of the tube between the two sealed constrictions was warmed to room temperature, inserted in the supply of argon to a Pye Argon Chromatograph, both thin glass constrictions broken, and the sample analyzed over a dinonyl phthalate or silicone oil supported on Celite column. For kinetic studies a new sample of reactant mixture was used for every time–temperature reading. A more detailed account of the experimental procedure has been reported elsewhere (*4*). The response of the argon detector to each hydrocarbon studied, identified by the retention distance on each of the columns mentioned above, was calibrated by injecting measured volumes of mixtures of known composition.

At low percentage reaction it was found that the volume of product hydrocarbon formed at constant temperature was directly proportional to reaction time [this is comparable to the determination of rate constants used by Anderson and Baker (*5*) and a similar procedure is used in the present work]. In kinetic studies two or three readings were taken at each of five or more temperatures and the slopes of the volumes of product against time plots were used to determine the Arrhenius energies of activation. In order to make comparisons of rates of reactions for different organic reactants, zero order rate constants found in this way were divided by the average total volume of product formed on completion of reaction. This was measured in desorption experiments made at temperatures somewhat higher than those at which meaningful kinetic measurements could be made.

The sources of the chemicals used were as follows: phenylacetic acid, phenylbenzoate, phthalic acid, phthalide, benzophenone, and 2-phenylethanol—B.D.H. Ltd. Laboratory Reagent grade; benzoic acid, phthalic anhydride, nickel chloride (hydrated)—"Analar" chemicals; benzyl alcohol, B.P. grade, and benzaldehyde, specially pure—both supplied by Bush Ltd.; and diphenyl ether, nickel hydroxide, and nickel metal supplied by Hopkins and Williams Ltd.

RESULTS

Examination of Nickel Oxide

Most of the results reported in the present article were obtained for the desorption of organic compounds from a single sample of nickel oxide. Properties of the oxide were as follows:

Chemical composition. Mean of three gravimetric determinations gave 77.7% Ni to be compared with 78.58% for stoichiometric NiO.

X-ray study. All the X-ray diffraction lines for the NiO fcc structure were observed; there was no evidence of any other crystalline phase.

Surface area. Measurements of the adsorption of nitrogen at —195°C and application of the BET equation gave surface area 8.0 m^2/g.

Blank desorption reaction. Two blank desorption reactions on samples of oxide, to which no organic compound had been added, treated by the standard experimental procedure, gave no detectable hydrocarbon products.

Preliminary Experiments

Small amounts of benzene and toluene were added to the oxide at room temperature and samples were subsequently evacuated and subjected to the normal reaction procedure between 200–500°C. Small amounts of these hydrocarbons were detected in the desorption products. These results show that it is necessary to evacuate above room temperature to remove physically adsorbed hydrocarbon from the oxide, but no evidence of any rate process in this desorption reaction could be found. It is concluded that product benzene or toluene, once formed, is readily desorbed from the oxide at reaction temperature. Any rate process detected above 200°C cannot be

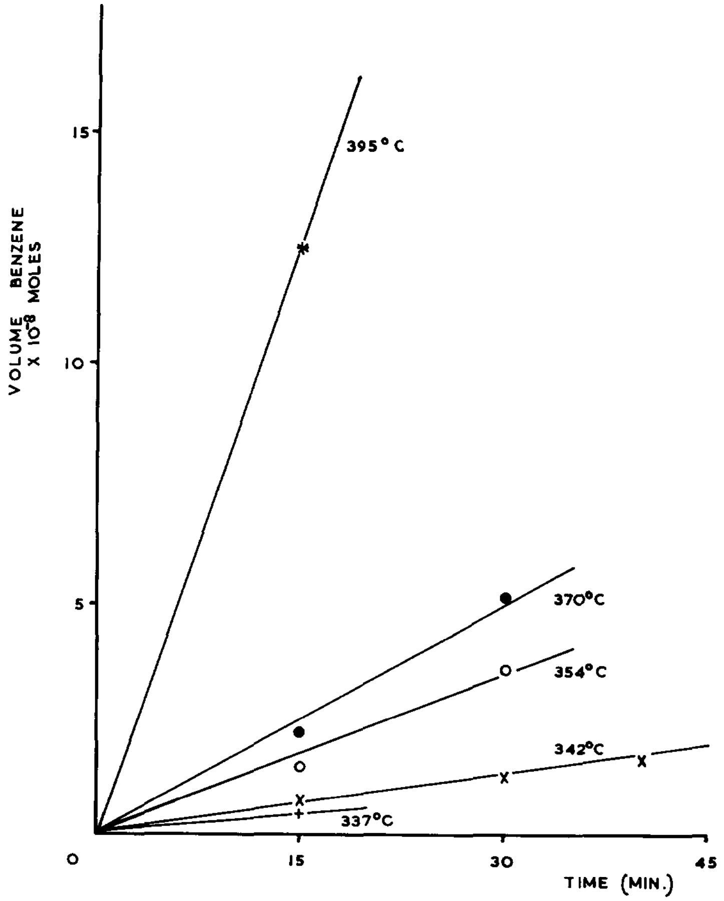

FIG. 1. Plot of volumes of product benzene against time for reaction of benzoic acid on nickel oxide at various temperatures.

ascribed to desorption reactions of benzene or of toluene from the oxide.

Desorption of Benzene from Benzoic Acid Adsorbed on Nickel Oxide

Zero order rate constants, determined from the slope of volume of product against time plots, corresponding to small percentage reaction, were divided by the total volume of product formed on completion of reaction.

Plots of the volumes of product benzene against time for reaction of benzoic acid on nickel oxide at several temperatures are given in Fig. 1. The mean of two determinations gave 4.67×10^{-6} moles of benzene per gram of NiO total product after reaction at 520°C. These results fit the Arrhenius equation (Fig. 2) from which the energy of activation 47.0 kcal/mole was found. A second set of experiments was made, identical in all respects to those above except that a few drops of water were added during the mixing of the reactants; no change in the rate of the benzene formation reaction was observed.

Desorption of Benzene and Toluene from Other Systems Studied

The benzene and toluene formation reactions on heating different organic compounds with samples of a single preparation of nickel oxide were studied using the experimental technique described above. Some experiments were also made using solid phases other than nickel oxide. A summary of all results of the present study is given in Table 1, which lists the energy of activation found and the total volume of product formed on completion of reaction. The logarithm of the rate constant (min^{-1}) divided by the total volume of product at 625°K has also been listed to provide a measure of relative reaction rates in different systems at a convenient temperature.

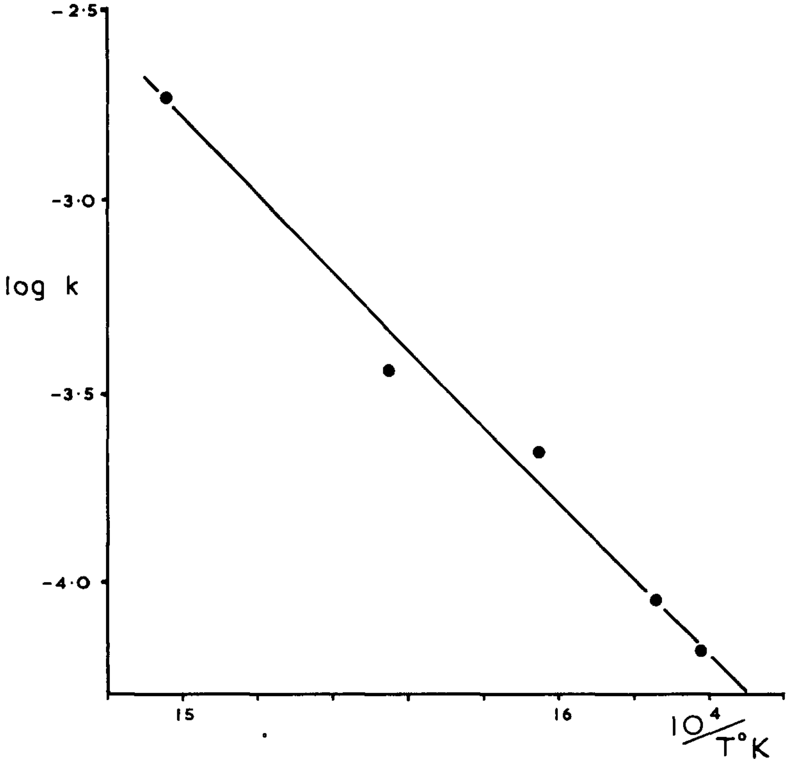

Fig. 2. Arrhenius plot for data given in Fig. 1.

TABLE 1

SUMMARY OF RESULTS FOR THE KINETICS OF DESORPTION OF BENZENE AND TOLUENE ON HEATING ORGANIC COMPOUNDS ON NICKEL OXIDE, NICKEL HYDROXIDE, NICKEL METAL, AND ANHYDROUS NICKEL CHLORIDE

		Benzene			Toluene		
Organic reactant	Solid	Energy of activation (kcal/mole)	log k at 625°K	Total number of molecules formed $\times 10^{-16}$ (per gram NiO)	Energy of activation (kcal/mole)	log k at 625°K	Total number of molecules formed $\times 10^{-16}$ (per gram NiO)
Benzoic acid	NiO	47.0	−4.10	280	—	—	—
Benzoic acid	Ni	43.9	−1.00	13.0	—	—	—
Phenyl benzoate	NiO	46.5	−3.20	3.5	—	—	—
Benzaldehyde	NiO	47.0	−3.14	3.5	—	—	—
Phthalic acid	NiO	48.8	−2.80	83	—	—	—
Phthalic anhydride	NiO	48.0	−2.75	83	—	—	—
Phthalide	NiO	45.1	−2.47	50	31.2	−2.28	2.6
Phenylacetic acid	NiO	20.3	−2.07	3.9	31.2	−2.21	3.3(5)
Benzyl alcohol	NiO	29.0	−1.48	307	18.9	−0.10	8.9
2-Phenylethanol	NiO	33.4	−0.48	22	25.0	−0.90	30
Benzyl alcohol	$Ni(OH)_2$	31–35	+0.30	280	15	−0.03	112
Diphenyl ether	NiO	14.8	−2.09	2.4	—	—	—
Benzophenone	NiO	4.1	—	57	—	—	—
Benzyl alcohol	$NiCl_2$	18.0	+0.20	350	10.3	−0.64	520

Further remarks about particular systems are as follows.

Phenyl benzoate and benzaldehyde. Results for both compounds were closely comparable and rate constants for both substances fell very near a single line on the Arrhenius plot.

Phthalic acid and phthalic anhydride. Results for both compounds were closely similar; the points mentioned in the preceding paragraph may be repeated here.

Phenylacetic acid. As with benzoic acid, no differences in the kinetics of hydrocarbon formation were detected between two series of experiments in one of which the reactants were mixed dry and the other in which a few drops of water were added before mixing.

Benzyl alcohol. An identical study of this system has been reported previously (*4*) but it was considered desirable to repeat the measurements using the batch of oxide as used throughout the present studies. Results obtained in both sets of experiments are in agreement except that the energy of activation for toluene formation found here (18.9 kcal/mole) is slightly lower than that reported previously (22 kcal/mole).

2-Phenylethanol. In addition to benzene and toluene, styrene, but no detectable ethylbenzene, was formed by a reaction which was similar to the other hydrocarbon formation reactions. The energy of activation was 13.7 kcal/mole, 48×10^{16} molecules were formed on completion of the reaction, and $\log_{10}k$ at 625°K was -0.87.

Samples of reactant mixture containing added 2-phenylethanol were analyzed for carbon content by combustion analysis (a) following the normal evacuation procedure and (b) after heating 30 min at 500°C under reaction conditions. The former sample was found to contain 0.348% C, equivalent to some 2.2×10^{19} molecules 2-phenylethanol/g NiO and, if it is assumed that each adsorbed molecule occupies $40\ \text{Å}^2$ on the surface, this corresponds to about 9 m^2/g surface area of the oxide. The latter sample (b) contained 0.148% C. It is concluded, therefore, that an amount of alcohol corresponding to approximately a monolayer remained on the oxide after evacuation and, since only 1.0×10^{18} molecules of hydrocarbon product were detected, appreciable desorption of unchanged alcohol also probably occurred.

Nickel benzoate and nickel phthalate. Small amounts of these salts were mixed with the oxide and reacted in the usual way. Volumes of products detected were too small to enable kinetic studies to be made.

Nickel hydroxide and benzyl alcohol. Results in Table 1, obtained using the standard experimental procedure, were obtained with a sample of nickel hydroxide which was boiled 20 min with excess benzyl alcohol, filtered, and dried at 130°C for 3 hr. No change in the X-ray diffraction pattern of the solid phase before and after heating with benzyl alcohol could be detected. Kinetic results were less reliable than for the other systems studied, hence the energy of activation was less accurately determined because relatively large amounts of water were desorbed during reaction.

Nickel chloride and benzyl alcohol. Hydrated nickel chloride was boiled with excess benzyl alcohol, filtered, dried at 130°C for 2 hr and the hydrocarbon desorption reaction studied by the standard procedure. X-ray studies showed that the treated salt had a structure different from the original hydrate but no further change was observed after the reaction.

Benzophenone. Results for this compound were not comparable with those of the other substances investigated. A slow rate process was detected between 90° and 350°C which occurred only in the latter stages of reaction and varied only slightly with temperature. Extrapolation of this rate process to zero reaction time gave a measure of the volume of product hydrocarbon rapidly desorbed immediately on heating and an Arrhenius-type plot of volumes initially desorbed gave the energy of activation listed in Table 1.

DISCUSSION

The preliminary ignition of the oxide sample was designed to remove organic impurities and prepare a homogeneous sample. Since no hydrocarbon products were detected in the blank experiments, using oxide alone and made according to the usual reaction procedure, it was concluded that reaction products observed did not result either from contamination under reaction conditions or from an impurity in the oxide. Preliminary studies showed that oxide to which pure hydrocarbon had been added, treated according to the usual reaction procedure, rapidly desorbed small amounts of unchanged hydrocarbon when heated; this was not a rate process in the temperature range over which kinetic studies were made.

Benzene and toluene are clearly not the only products formed in the reactions reported above but attention has been confined to these since they were most readily studied. The object of the study was to decide whether the kinetics of formation of these compounds from a number of different organic compounds would enable conclusions to be reached about the relative reactivity of various groupings at the surface of nickel oxide.

Clearly the reactions leading to hydrocarbon formation from the molecules studied must involve several steps, but two general types of mechanism can be suggested. The rate process observed may result from either (a) the breakdown of organic radicals adsorbed on the surface of the oxide, simultaneously a fraction of the adsorbed material may be distilled unchanged from the reaction zone, on heating or (b) adsorption followed by catalytic (or homogeneous) breakdown of gaseous material before it diffuses from the heated reaction zone. The results for benzophenone are consistent with model (b) where the apparent energy of activation is lower than that usually observed for chemical reactions. These results are interpreted as showing that, immediately after heating, an appreciable vapor pressure of benzophenone is established in the reactant powder and a part was adsorbed and underwent catalytic decomposition with some benzene formation or homogeneous decomposition reactions. Distillation from the reaction zone was rapidly completed, however, and the initial reaction stopped. There was no evidence that any comparable reaction occurred with any of the other compounds studied and subsequent general discussions exclude benzophenone from consideration.

The results of the kinetic studies summarized in Table 1 are believed, therefore, to be the thermal decomposition of radicals adsorbed on the surface of the oxide. Such adsorbed radicals are not necessarily formed at room temperature during mixing of the reactants but may be formed during heating to reaction temperature, excess organic material being distilled from the heated zone. This mechanism is consistent with the observation that the maximum amount of products detected from reactions of different substances on 1 g of oxide (3×10^{16}–3×10^{18} molecules) was always appreciably less than the number of molecules of benzene (2.6×10^{19}) or toluene (2.3×10^{19}) required to form a complete monolayer, assuming the area occupied by adsorbed species to be those given by Schreiner and Kemball (*6*). See also the analysis of carbon content of nickel oxide, after treatment with 2-phenylethanol and evacuation, mentioned above.

The formation of benzene and/or toluene from the reactants studied must involve hydrogen transfer to the reaction intermediate hence hydrogen must be available at the surface. The amount present must, however, be small since aliphatic hydrocarbon products were not observed.

The energy of activation for benzene formation is very nearly equal for those compounds listed between benzoic acid and phthalide in Table 1. The most satisfactory explanation for this is that the nickel salt of either benzoic or phthalic acid, depending on the organic reactant, is formed at the oxide surface as an intermediate and subsequent thermal decomposition yields benzene. Excess organic reactant is distilled unchanged from the hot zone. This conclusion is supported by work at present in progress on the thermal decomposition of nickel benzoate and of nickel phthalate; these salts yield product benzene with energies of activation of 44.0 and 47.5 kcal/mole, respectively (*7*). The results of the present work may be explained, therefore, by a mechanism involving two reactions. On heating, the volatile organic compounds react with the oxide surface to form the nickel salt of an organic acid and excess is distilled unchanged. The presence of water added to the reaction mixture, expected to facilitate dispersal of the organic reactant, does not influence the rate or the amount of reaction products and is, therefore, probably rapidly removed initially. The second reaction, occurring at elevated temperature, possibly involves coalescence of the initially formed surface compound yielding aggregates of nickel salts which then decompose independently of the presence of the oxide and the energy of activation for decomposition is similar to that found for the bulk salt.

The close similarity of results for benzaldehyde and phenylbenzoate suggests that these compounds form similar amounts of the same intermediate with the surface. The relatively low yield of benzene found may result from a high degree of dispersal of the low concentration of reactant on the surface so that adsorbed phenyl radicals have a reduced chance of combining with a hydrogen atom before undergoing some other reaction (e.g., dimerization). Results for benzaldehyde showed that toluene was not formed; therefore it is concluded that benzaldehyde is adsorbed to form an intermediate similar to those found for the other "acidic" compounds rather than the type of radical postulated for benzyl alcohol (see below).

The identical kinetics of the benzene formation reaction from phthalic acid and the anhydride on nickel oxide suggest a common intermediate, almost certainly nickel phthalate. No satisfactory kinetic measurements could be made for the reaction of benzoic acid on nickel hydroxide since relatively small amounts of benzene ($\sim 7 \times 10^{15}$ molecules) and large amounts of water were formed. It seems probable that any surface salt was readily hydrolyzed and distilled from the reaction zone. The reaction of benzoic acid on nickel metal was very similar to that on nickel oxide, which is to be expected since the metal was undoubtedly covered with a layer of oxide. The different yields of benzene may result from different surface areas and reactivities of the two solid phases.

The energy of activation for the benzene formation reaction from adsorbed phthalide is comparable to that found for the reaction of other "acidic" compounds on nickel oxide and it is suggested that the initial step in the reaction is hydrogen dissociation at the $>CH_2$ group to yield an intermediate which is readily converted to the same adsorbed species which has been suggested for the thermal decomposition of phthalic acid. In contrast, the formation of toluene from the same compound is more readily explained by a mechanism in which an initial decarboxylation reaction yields an adsorbed intermediate which is similar to that believed to occur in the reactions of adsorbed alcohols (see below). A similar mechanism of toluene formation is suggested for the decomposition of phenylacetic acid, kinetic results for both compounds being closely comparable. Here, however, the reaction yielding benzene has a lower energy of activation than those found for all other "acidic" compounds and this may result from the thermal decomposition of the nickel salt of an acid in which the carboxyl group is not attached directly to the aromatic ring. In support it may be mentioned that the energy of activation for the thermal decomposition of nickel acetate has been found (*8*) to be 22.75 ± 2 kcal/mole. In the benzene formation reaction a similar initial step to that postulated in the formation of benzene from adsorbed phthalide may be suggested; subsequent reactions here do not yield "adsorbed nickel phthalate" since the carboxyl group is not joined to the aromatic nucleus.

The reactions of alcohols on nickel oxide contrasted with those of the "acidic" substances mentioned above in having somewhat lower energies of activation of hydrocarbon formation. Also it may be significant that appreciable amounts of benzene and toluene were formed in the desorption of benzyl alcohol from nickel hydroxide whereas benzoic acid, desorbed from the same solid, yielded very small amounts of benzene only.

The results for alcohols are interpreted by a mechanism in which it is believed that adsorbed alcohol is bonded to the surface by coordination of the oxygen atom of the alcohol with a nickel atom in the solid surface, in contrast with the "surface salt" intermediate postulated for "acidic" substances. Such a surface ligand may dissociate on heating to yield water and an adsorbed species, which, in the case of 2-phenylethanol, may be desorbed unchanged as styrene or react further to form toluene and benzene. Direct desorption of the dehydration product of benzyl alcohol is not possible, however, and either hydrogen must be added to form toluene or loss of carbon occurs with the formation of an adsorbed species which may subsequently add hydrogen to form benzene. These conclusions are consistent with the observation that a greater proportion of toluene results from the reaction of benzyl alcohol on nickel hydroxide than on the oxide. With the former solid, more surface hydrogen, probably as hydroxyl radicals, is available, leading to an increased probability of toluene formation. Also this mechanism is consistent with the results for dehydrated nickel chloride, coordination of a ligand with a surface atom may be expected but salt formation would appear less probable on the surface of this salt of a strong acid. The energy of activation and yields of product may be expected to be influenced by the properties of the solid to which the ligands are attached, thus accounting for the differences in magnitude of the kinetic results between oxide and chloride. It seems probable that cracking (i.e., removal of a carbon atom from the aromatic nucleus) reactions of the type postulated in the present paragraph may occur in the vicinity of a single or small number of metal atoms at the surface of the oxide or chloride by a mechanism which is somewhat different to that discussed (*2*, *9*) for the cracking reactions of hydrocarbons adsorbed on the surface of reduced nickel metal.

2-Phenylethanol gave styrene as the most abundant product and the energy of activation was 13.7 kcal/mole; the increases in energy of activation of toluene formation compared to that of styrene formation, and of benzene compared to toluene were 11.3 and 8.4 kcal/mole, respectively. Similarly the latter value for benzyl alcohol was found to be 10.1 kcal/mole. Results for nickel hydroxide were not sufficiently accurate to enable meaningful comparisons to be made. The increase in energy of activation associated with the removal of a carbon atom from the side chain is therefore close to 10 kcal/mole and it is concluded that the formation of benzene from 2-phenylethanol involves two successive reactions each involving the removal of a single carbon atom.

The low energy of activation found for the formation of benzene from diphenyl ether in the presence of excess oxide may result from a reaction similar to that giving toluene from adsorbed benzyl alcohol; here a dissociation reaction occurring at the oxygen atom would yield an adsorbed phenyl radical. Difficulty in coordination of this large molecule with the surface metal atom and consequent instability of the adsorbed intermediate may account for the low yield and relatively low energy of activation for the formation of the product benzene.

CONCLUSIONS

The present results show that several different compounds of the series studied react with the nickel oxide surface to give hydrocarbon products at comparable rates, suggesting that common adsorbed radicals are formed as intermediates. Yields of hydrocarbon were always less than those theoretically possible from reaction of a monolayer of reactant. The results, with the exception of those of benzophenone, suggest that reactions yielding product hydrocarbons proceeded by two general mechanisms. One class of compounds, acids, or substances capable of being converted to acids fairly readily, gave kinetics similar in some respects to those believed to occur in the thermal decomposition of nickel salts. It is possible that acid initially adsorbed on the surface of the salt coalesces to form small fragments of the nickel salt prior to thermal decomposition. The results with alcohol were more readily explained by the formation of ligands coordinated to the surface metal atoms of the solid.

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