JOURNAL OF CATALYSIS 4, 697–703 (1965)

The Thermal Decomposition of Nickel Phthalate

A. K. GALWEY

From the Department of Chemistry, The Queen's University of Belfast,
Northern Ireland

Received March 16, 1965; revised May 4, 1965

The kinetics of the thermal decomposition of nickel phthalate have been studied. In the temperature range 300–450°C the main products were carbon dioxide, benzene, and benzoic acid. Carbon dioxide formation obeyed the second order equation, that of benzoic acid followed the zero order rate law. The energies of activation for the formation of product carbon dioxide, benzene, and benzoic acid were found to be 46.2 ± 1.0; 47.0 ± 1.5; and 45 ± 2 kcal mole^{-1}, respectively. Other products identified were nickel metal, and trace amounts of nickel oxide, diphenyl, and phthalic acid.

A reaction mechanism to account for the results is proposed.

A study of the kinetics of formation of aromatic hydrocarbons on heating organic compounds in the presence of a large excess of nickel oxide was recently reported (*1*). Results were interpreted as indicating the formation of nickel salts of organic acids as reaction intermediates at the oxide surface. Nickel phthalate was postulated as one such intermediate. An examination of the literature yielded no information about the reactivity or stability of this salt, though a method of preparation has been described (*2*). It was therefore considered to be of interest to study the reactions occurring on heating the pure salt in the absence of added oxide to determine whether the mechanism of reaction postulated previously (*1*) was tenable.

EXPERIMENTAL AND RESULTS

Nickel Phthalate

The salt was prepared (*2*) by the addition of basic nickel carbonate ("low in Co and Fe") to a boiling aqueous solution of phthalic acid until effervescence ceased (both reagents B.D.H. Laboratory Reagent Grade). The solution was filtered hot, evaporated, and the resulting viscous paste was dried by heating to ~180°C. The green solid was crushed and samples from this single stock used throughout the present study. The salt was slightly hygroscopic and dissolved completely in water.

Analysis of this product showed it to contain 21.79% Ni (gravimetric determination by dimethylglyoxime complex); 41.31% C and 2.85% H (by combustion analysis). These values may be compared with 26.34%, 43.12%, 1.81%, and 24.37%, 39.90%, 2.51% calculated for $C_6H_4(COO)_2Ni$ and the monohydrate, respectively. The reactant, therefore, probably contained some water and part of the phthalic acid was probably contained in the solid as impurity or as the acid salt. X-Ray diffraction photographs for the salt (a) as prepared and (b) after heating in vacuum 3 min at 300°C were identical and showed four very diffuse diffraction halos and no sharp lines. It is concluded, therefore, that the reactant studied contained no crystal lattice and, although it is somewhat more ordered than a liquid, it must be regarded as approaching the vitreous state.

Products of Decomposition and Reaction Kinetics

Attention was largely directed to the study of those compounds the kinetics of formation of which could be studied directly. No attempt was made to identify and estimate the yields of every possible reaction product. Experimental methods will be described at appropriate places in the text below.

Carbon dioxide. Gas chromatographic analysis of the products of the decomposition reaction which were not condensed at —80°C indicated carbon dioxide to be the main gaseous product. No traces of ethane or propane were detected using the argon ionization detector, which is more sensitive to the detection of these compounds than to carbon dioxide (*3*).

Kinetic measurements of the carbon dioxide formation reaction were made in a constant volume vacuum apparatus in which the pressure of products not condensed at —80°C was measured using a McLeod gauge. Weighed samples were initially outgassed 2–3 hr at $\sim 10^{-6}$ mm and rapidly heated to reaction temperature, maintained constant ± 1C°. Quantitative measurements showed that complete decomposition of 1 mole of salt at 327–390°C yielded 1.56 moles of carbon dioxide.

The carbon dioxide formation reaction was strongly deceleratory throughout. Plots of fractional decomposition (α) against time for reaction at four different temperatures are shown on Fig. 1. These results, and those from other similar experiments were tested for obedience to zero, first, second, and third order kinetic equations, the "contracting cube" formula, and other equations characteristic (*4*) of the thermal decomposition of solids. Results fitted the second order equation to a very satisfactory degree of accuracy, $0.2 < \alpha < 0.9$; appropriate plots of the data on Fig. 1 are shown on Fig. 2. The data for the experiment at 390°C were unsatisfactory since thermal equilibrium was not attained before appreciable decomposition had occurred. An Arrhenius plot for second order rate constants 290–360°C gave an energy of activation 46.2 ± 1.0 kcal/mole.

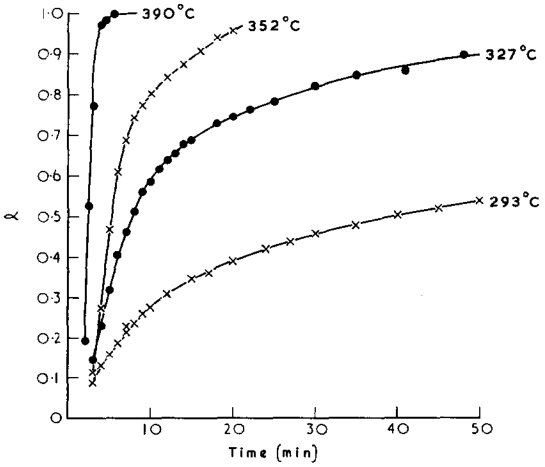

FIG. 1. Plots of the fractional decomposition (α) against time for the carbon dioxide formation reactions from the isothermal decomposition of nickel phthalate at four different temperatures.

No evidence of any initial acceleratory period was found; measurements for the first part of reactions at 196° and 240°C showed that there was an initial ($0 < \alpha < 0.1$) deceleratory reaction with an energy of activation ~35 kcal/mole. This reaction was somewhat faster than the main reaction, and, again, no evidence of any initial acceleratory reaction was found.

Two experiments using comparatively large (~3-mm diameter) brittle fragments of reactant gave reaction kinetics identical, within experimental error, to that found for the normal reactant which consisted of the range of particle sizes given by lightly crushing the original brittle preparation. Three pairs of experiments were made in which the salt was decomposed at 330–360°C after crushing (*i*) alone, (*ii*) with added nickel powdered metal, and (*iii*) with added nickel carbide. All six second order rate constants measured for these reactants were close to twice those found for decomposition of the stock material at the same temperature. No changes in reaction rate attributable to the presence of the additives was observed.

Permanent gases. A small yield of a gaseous product was not condensed at —195°C. The volume of this product increased with decomposition temperature 327–390°C, but was always <10% of the volume of the product carbon dioxide. It is believed that this product was *carbon monoxide* formed in a side reaction or possibly (*5*) by reaction of carbon dioxide with nickel metal.

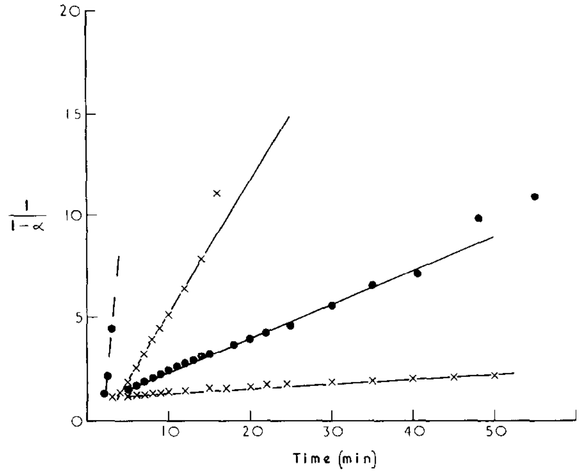

FIG. 2. Second order plots for data given in Fig. 1.

Benzene. Gas chromatographic analysis of the products of the decomposition, over silicone oil or dinonylphthalate columns, each supported on celite, showed that decomposition of each mole of salt yielded 0.014 moles of benzene. No other C_5, C_6, or C_7 compound was detected. Gas chromatographic analysis of a cyclohexane extract of the sublimate of this reaction over a silicone oil column at 100°C yielded a single peak at the same retention distance as that found for diphenyl. Naphthalene was sought but not detected in the products.

The kinetics of benzene formation was studied at 218–500°C by gas chromatographic measurements of the quantity of benzene distilled in a known interval of time from reaction of a sample of nickel phthalate sealed in an evacuated tube and held at a constant reaction temperature. This technique has been described in detail elsewhere (*6*). It has been assumed, in the consideration of these results, that the benzene formation reaction obeyed the same kinetic equation as that found for carbon dioxide formation. Analysis of the data showed that rate constants for both benzene and carbon dioxide formation fell on a single line on the Arrhenius plot, the best value for benzene formation being 47.0 ± 1.5 kcal/mole. The scatter of results for the former reaction was slightly greater than for the latter, as expected from the accuracy with which the measurement of volumes of the different products could be measured.

Benzoic acid. The thermal decomposition reaction in vacuum yielded a sublimate on the reaction vessel wall immediately outside the heated zone. An infrared spectrum of a solution of the sublimate from reaction at 360°C was almost identical with a similar solution of benzoic acid, from which it is concluded that this was a main reaction product. An X-ray examination of the small amount of sublimate from reaction at 283°C indicated the formation of small amounts of phthalic acid at this temperature. Reaction at above ~320°C yielded a yellow-colored sublimate, indicating the distillation of further organic products.

Kinetic studies of the formation of acid were made by interruption of the reaction, at known times, and titration of the sublimate with standard decinormal alkali. If it is assumed that benzoic acid was the only acidic product, the results show that decomposition of 1 mole of salt at 327–390°C yielded 0.39 mole of benzoic acid. Kinetic measurements were not very reliable but the data could be approximated to a zero order process up to $\alpha \sim 0.6$; above this value readings showed considerable scatter. Zero order rate constants gave an energy of activation 44.4 ± 2.0 kcal/mole. A plot of values of α for the acid-forming reaction against corresponding values for the carbon dioxide formation reaction is shown in Fig. 3. This data shows that the relative rate of the reactions which yield the two different products is independent of temperature.

Phenol. Determination of phenol by precipitation as the tribromo derivative from a water solution of the sublimate showed that decomposition of 1 mole of salt at 400°C yielded 0.083 mole of phenol. The sublimate for this determination was collected in a tube of the type used for the study of the benzene formation reaction since it is believed that phenol was distilled to the —80°C trap in the apparatus used to study the other rate processes.

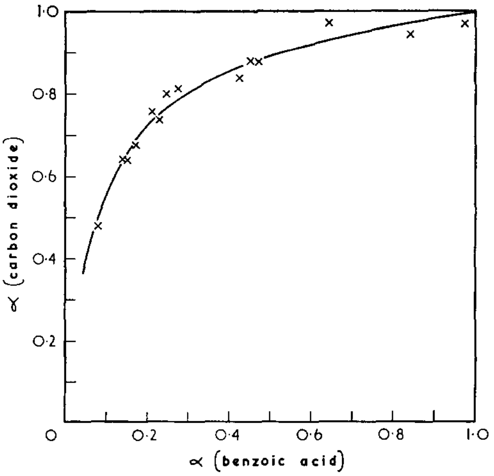

FIG. 3. Fractional decomposition values for the acid formation reaction plotted against corresponding values for the carbon dioxide formation reaction from the thermal decomposition of nickel phthalate at a number of temperatures.

Solid products. X-ray examinations were made of the solid residue from decomposition at a number of different temperatures and corresponding to different values of α. The most prominent lines in the diffraction patterns obtained were very close to a prominent line in patterns similarly obtained for nickel metal, nickel carbide, and nickel oxide. Critical examination of photographs for the product phase from completed reactions suggested nickel metal to be the main product, but small amounts of the carbide and oxide were probably also present. The diffraction lines were somewhat diffuse, indicating small crystallite size, though the product clearly had a considerably greater degree of crystallinity than the reactant.

The residue from the completed reaction was 32.2% of the weight of the reactant and combustion analysis showed it to contain 28.3% C and 0.77% H, which may be expressed, in atomic proportions, as Ni, 1.00; C, 1.75; H, 0.56; and, by difference, O, 0.14. The reactant did not melt during decomposition. From measurements of the volume of nitrogen adsorbed at —195°C by the solid products from decomposition, and application of the BET equation, it was found that the surface area of the residue was 160 $m^2\ g^{-1}$.

Subsidiary Experiments

Some experiments were made in which hydrocarbon formation during decomposition of the salt in 30 mm of hydrogen was studied using a mass spectrometer. Benzene was detected and there was no evidence of cyclohexane formation, though the latter product was not expected (*7*). Condensation outside the heated zone indicated substantial water formation and gas chromatographic analyses of the sublimate indicated the presence of diphenyl.

Some experiments were made in which phthalic acid or phthalic anhydride was sublimed at 300°C (and above) in the presence of residue from a completed nickel phthalate decomposition reaction. At 400°C the volume of gaseous products approached that found from decomposition of salt containing the same weight of acid. The yields of gaseous products from these sublimations were, however, somewhat irreproducible and varied with reaction temperature. Reaction was a rate process but substantially slower than the decomposition of the salt at the same temperature. Sublimation of benzoic acid under the same conditions gave a smaller ($<\sim 5\%$) yield of carbon dioxide. Sublimation of phthalic acid or anhydride, in the absence of a metallic residue, showed that some slight decomposition occurred at 300–400°C, but the yield was only 10–20% of that found when the metallic residue was present.

Discussion

Products of Reaction

The quantitative measurements given above may be summarized

$$o\text{-}C_6H_4(COO)_2Ni \rightarrow 1.56\ CO_2 + 0.10\ CO + 0.39\ C_6H_5COOH + 0.083\ C_6H_5OH + 0.014\ C_6H_6 + [Ni + C_{1.75} + H_{0.56} + O_{0.14}]$$

The bracketed products refer to the residue. Water has not been included in the equation since the yield in the products was not determined. Small amounts of phthalic acid were sublimed; this has not been included in the above equation since the yield was small. The above equation does not account for $C_{1.28}H_{0.52}O_{-0.22}$ from each molecule decomposed; the negative value for oxygen may be ascribed to experimental errors and deviations from stoichiometry of the reactant.

The solid product consisted largely of a nickel-carbon mixture with smaller amounts of oxide. Calculations using the measured surface area indicate that if the crystallites of the solid consisted of cubes of equal size the edge of each cube would be about 75 Å. This model is consistent with the data from X-ray measurements which indicated a finely divided product. The retention of some hydrogen in the solid is interpreted as showing that some of the carbon was present as a high molecular weight polymer, not distilled at reaction temperature, probably strongly adsorbed at the surfaces of the nickel crystallites.

Reaction Kinetics

The reactant did not melt during decomposition, hence kinetic equations characteristic of the decomposition of solids (*4*) could be expected to be obeyed. However, since no initial acceleratory reaction was observed, a mechanism based on nucleation and growth of a product phase was not tenable. Furthermore, deceleratory reactions characteristic of solids, the first order equation, "contracting cube" equation did not fit the results. It has been shown above, however, that the second order equation provides a satisfactory fit to the kinetic data. Since this equation has found application in the study of reactions occurring in the homogeneous phase it is concluded that the nickel phthalate structure is so disordered that reaction may be considered to proceed in an amorphous matrix approaching the vitreous state. Thus the reactant structure may be regarded as an amorphous cross-linked polymer comprised of bidentate ligands in which some interchange of bonding, or spatial rearrangement of ligands, can probably occur at reaction temperature. Reaction is believed to result from the formation of an activated transition complex through a bimolecular process involving two reaction species. This yields carbon dioxide, which is rapidly evolved as product gas, benzoic acid, which may not so readily diffuse from the reaction site, nickel metal, and a hydrogen-depleted aromatic radical. It is suggested that the energy of activation for this reaction was the energy necessary to rupture the bond between the metal atom and the carboxyl group of the acid. Each decomposition may be followed by the decomposition of a number of "molecules" in the immediate vicinity of the original transition complex to yield a small nickel crystallite at the surface of which the hydrogen-depleted aromatic nuclei may be adsorbed. Subsequent disproportionation reactions yield the observed benzene, which may rapidly volatilize, giving the same kinetics as those for the carbon dioxide formation reaction, and diphenyl. Reaction of such radicals with adsorbed oxide or hydroxide species yielded the phenol. It is clear, however, that a disproportionation reaction of the type discussed must yield a high proportion of carbon. This may limit the growth of any crystallite and result in the high surface area carbon containing nonvolatile product, the nature of which was discussed in the preceding section. The carbon dioxide formation reaction is believed, therefore, to result from a continued bimolecular nucleation process in the amorphous matrix but the growth of any nucleus was rapidly inhibited by the deposition of carbonaceous material at the surface.

Benzoic acid was sublimed from the reactant by a process having the same energy of activation as that found for the other products studied, but the rate law obeyed was different. It is suggested that volatilization of this product from the reaction matrix was difficult in the early stages of reaction but was facilitated by the opening of channels in the solid as reaction proceeded. This qualitatively explains the somewhat lower reaction order and is consistent with the observation that benzoic acid underwent little decomposition when sublimed under reaction conditions. It is improbable that nickel benzoate was formed as a reaction intermediate since (*8*) this salt melted during decomposition and yielded nickel carbide as the solid product.

Crushing nickel metal or nickel carbide with the reactant did not increase decomposition rate as might be expected if metal or carbide surface catalyzed the decomposition of the acid, as shown by the subsidiary experiments, and if extensive mobility of the acid radical was possible before decomposition. Thus gaseous phthalic anhydride is not formed as a reaction intermediate, in contrast to the decomposition of basic ferric phthalate where the anhydride was found (*9*) to be the predominant volatile product. The increase in reaction rate resulting from crushing the reactant is not attributed to a change in the reaction mechanism, since no change in energy of activation was detected, but to cold-working of the solid, causing a reduction of the void space in the reactant which had been occupied by water during preparation of the salt. This increases the effective concentration of the reactant and thus the rate of decomposition.

Reactions of Adsorbed Aromatic Radicals

The absence of product C_2–C_7 hydrocarbons (other than benzene) showed that extensive hydrocarbon interconversion and cracking reactions did not occur on the nickel metal. Also the formation of single carbon atoms, and thus bulk nickel carbide, was not appreciable. It is known (*10*) that benzene cracked to yield methane quantitatively in the presence of excess nickel metal and hydrogen. It is reasonable to suppose that in the present system the concentration of adsorbed hydrogen was very low, but it must also be concluded that hydrogen was not readily adsorbed since appreciable quantities of diphenyl were detected from reaction in the presence of excess gaseous hydrogen. Hydrocarbon products were benzene, diphenyl, carbonaceous material retained on the residue, and substances which were not characterized but which may have included terphenyl. It is therefore concluded that the nickel-containing residue from these reactions was not an effective cracking catalyst but it may promote dimerization and possibly polymerization of aromatic nuclei to yield diphenyl and possibly higher homologs.

Nickel Oxide–Phthalic Acid Reaction

The energy of activation for the benzene formation reaction reported above agrees well with that found (*1*) for the formation of the same product on heating small amounts of phthalic acid or phthalic anhydride with excess nickel oxide. Reanalysis of the kinetic data for the early stages of the formation of benzene from nickel phthalate by an identical method to that used previously (*1*) gave the value of $\log_{10}k$ ($\min^{-1}$) at 625°K as —2.60. This compares well with the values —2.80 and —2.75 found for reactions of phthalic acid and anhydride on nickel oxide. Quantitative comparisons indicate that, if the yield of benzene from a given weight of reactant salt was equal for both studies, then the amount of benzene from reactions in the presence of oxide results from about two monolayers of nickel phthalate on the oxide surface. The degree of dispersion of the reactant in the two studies may be different and it is possible that coalescence of nickel phthalate initially dispersed over the oxide surface may yield particles of salt which subsequently decompose independently of the oxide. In the presence of oxide some hydrogen may be transferred between aromatic nuclei and not all results in reduction of the oxide phase.

It is concluded, therefore, that the present results are entirely consistent with the mechanism proposed to account for results in the previous (*1*) study.

ACKNOWLEDGMENTS

The author would like to thank Professor C. Kemball, F.R.S. for providing facilities for mass spectrometric analysis and Miss I. Woodward for advice on the interpretation of X-ray diffraction photographs.

REFERENCES

1. GALWEY, A. K., *J. Catalysis* **4,** 34 (1965).
2. EPHRAIM, F., *Ber. Deut. Chem. Ges.* **51,** 644 (1918).
3. GALWEY, A. K., *Talanta* **9,** 1043 (1962).
4. JACOBS, P. W. M., AND TOMPKINS, F. C., *in* "Chemistry of Solid State" (W. E. Garner, ed.), Chap. 7. Butterworths, London, 1955.
5. GALWEY, A. K., *J. Catalysis* **2,** 176 (1963).
6. GALWEY, A. K., *Proc. Intern. Congr. Catalysis, 3rd, 1964, Amsterdam,* **2,** 791 (North-Holland Publ. Co., 1965).
7. BEECK, O., AND RITCHIE, A. W., *Discussions Faraday Soc.* **8,** 159 (1950).
8. GALWEY, A. K., *J. Chem. Soc.,* in press.
9. GALWEY, A. K., *J. Chem. Soc.,* p. 4235 (1965).
10. GALWEY, A. K., *Proc. Roy. Soc. (London)* **A271,** 218 (1963).