1152. *The Thermal Decomposition of Nickel Benzoate and of the Nickel Salt of Cyclohexanecarboxylic Acid*

By A. K. Galwey

A study of the kinetics of formation of carbon dioxide from the isothermal decomposition of nickel benzoate in a vacuum has shown that reaction was zero-order ($0{\cdot}1 < \alpha < 0{\cdot}85$) with an activation energy of $45{\cdot}0 \pm 1{\cdot}0$ kcal./mole (α is the fractional decomposition). The activation energies for the formation of benzene and of benzoic acid were very close to the same value. Other products identified were carbon monoxide, phenol, biphenyl, nickel metal, nickel carbide, and nickel oxide. A rection mechanism is proposed to account for these results.

A similar study of the thermal decomposition of the nickel salt of cyclohexanecarboxylic acid gave irreproducible kinetic results, and from the data obtained it is concluded that cyclohexanecarboxylic acid was the main initial product and that subsequent catalytic breakdown of this acid yielded a range of secondary products.

In a previous Paper [1] a study of the rates of formation of aromatic hydrocarbons on heating small amounts of a number of organic compounds with a large excess of nickel oxide was reported. Some of the results were explained by a mechanism in which it was suggested that nickel benzoate was a reaction intermediate, after reaction of the organic compound

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[1] A. K. Galwey, *J. Catalysis*, 1965, **4**, 34.

with the oxide surface. No previous study of the thermal decomposition of nickel benzoate could be found, and little detailed work on its chemical properties has been published. The present study was undertaken to investigate the kinetics of the thermal decomposition of the salt in the absence of added oxide. Rates of formation of those products found in greatest yield are reported, but detailed chemical separations designed to identify and determine quantitatively every possible product were not undertaken. A comparative study of a similar salt, in which the aromatic nucleus was saturated, the nickel salt of cyclohexanecarboxylic acid, was attempted, and results are discussed.

EXPERIMENTAL AND RESULTS

Nickel Benzoate.—Reactant. Analysis of the reactant [B.D.H. Laboratory Reagent grade; " approx. $(PhCO_2)_2Ni$ "] used throughout the study gave Ni 16·55% (dimethylglyoxime determination in triplicate), and C 48·1% and H 4·5% (both by combustion analysis), which may be compared with Ni 16·55%, C, 47·4%, and H 4·55% calculated for $(PhCO_2)_2Ni,3H_2O$. Pfeiffer and Müllenheim [2] reported that nickel benzoate forms a trihydrate. *X*-Ray examination showed the reactant to be crystalline.

The thermal decomposition reaction. Experimental methods are described in appropriate sections below.

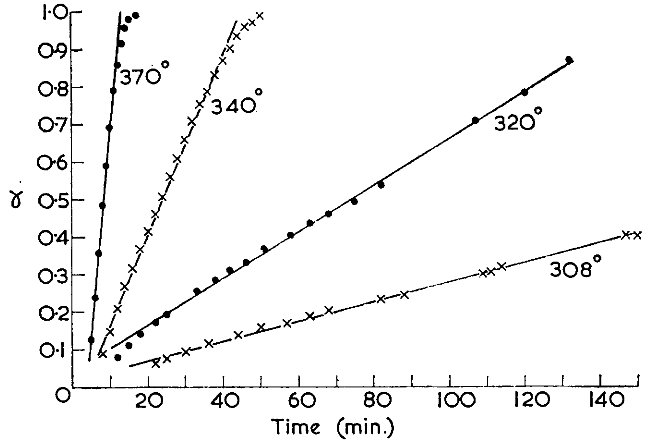

FIGURE 1. Plot of fractional decomposition (α) against time for the formation of carbon dioxide during the thermal decomposition of nickel benzoate at different temperatures

Carbon dioxide. The sample was initially evacuated for *ca.* 2 hr. at *ca.* 10^{-6} mm. before being heated to constant reaction temperature. The kinetics of formation of gaseous products were studied from measurements of the pressure of gas evolved in the constant-volume apparatus at suitable time intervals using a McLeod gauge separated from the reaction vessel by a −80° trap.

Gas-chromatographic analyses of the gaseous products showed that carbon dioxide was formed in the highest yield. No trace of ethane or propane was detected with the radioactive ionisation detector which is more sensitive to these hydrocarbons than to carbon dioxide.[3] The yield of carbon dioxide from decomposition of 1 mole of nickel benzoate [assumed to be $(PhCO_2)_2Ni,3H_2O$ only] varied from 0·65 mole at 315° to 0·77 mole at 370°. A small yield of carbon monoxide, 0·030 mole/mole of salt decomposed, was also detected.

Typical plots of fractional decomposition (α) against time for the evolution of gaseous products (−80° trap) from reactions at a number of temperatures are shown in Figure 1. Measurements were tested to see if the reactions were first-order and if they obeyed the Prout–Tompkins kinetic equation,[4] but the fit to these was considerably less satisfactory than to the zero-order equation which was obeyed within the approximate range $0{\cdot}1 < \alpha < 0{\cdot}85$. An Arrhenius plot, from zero-order rate constants, gave the activation energy of carbon dioxide formation

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[2] P. Pfeiffer and S. V. Müllenheim, *J. prakt. Chem.*, 1933, **137**, 9.

[3] A. K. Galwey, *Talanta*, 1962, **10**, 1043.

[4] P. W. M. Jacobs and F. C. Tompkins, " Chemistry of the Solid State," Butterworths, London, 1955, ch. 7.

as 45·0 ± 1·0 kcal. mole^{-1}. A zero-order rate constant for reaction using a $-195°$ trap was on the same Arrhenius line.

The rates of decomposition of nickel benzoate samples, to which finely divided nickel metal had been added, were, within experimental error, equal to those found for decomposition of the pure salt at the same temperature. Benzoic acid, alone or mixed with an equal weight of nickel oxide, when subjected to the normal reaction procedure at 400° gave $<2\%$ of the yield of carbon dioxide found from decomposition of that weight of salt which contained the same weight of acid.

Benzene. The experimental method used for the quantitative study of the formation of small volumes of hydrocarbon products has been described previously.[1,5] Volatile products from the reaction occurring at the heated end of an evacuated sealed tube were condensed at the other end of the tube which was chilled to $-195°$. The condensed products were subsequently analysed by gas chromatography. Benzene was identified from retention distance measurements on two different columns, silicone oil and dinonyl phthalate, each supported on Celite. Measurements showed that decomposition of 1 mole of salt yielded 0·020 mole of benzene. No other C_5- or C_6-hydrocarbon or naphthalene was detected, but qualitative measurements over the silicone oil column at 100° indicated that biphenyl was also a product.

Measurements of fractional decomposition (α) with time for the benzene formation reaction at 206—329° gave zero-order rate constants which fell on, or on an extrapolation of, the Arrhenius line for rate constants from the carbon dioxide formation reaction. The mean energy of activation, using data for the formation of both products, was 44·0 ± 1·0 kcal. mole^{-1}.

Phenol. The yield of phenol, measured by gravimetric determination as the tribromo-derivative in water extracts of the sublimate, from reactions at 400° was 0·41 mole phenol/mole of salt decomposed. Sublimates were collected in the apparatus used to study benzene formation since it was believed that in carbon dioxide formation studies phenol distilled to the cold trap and was not retained in the sublimate.

Benzoic acid. During studies of the kinetics of carbon dioxide evolution a white sublimate was formed immediately outside the heated zone. *X*-Ray and infrared measurements showed this to be benzoic acid, and the latter measurements showed that no significant amount of other possible products (*i.e.*, benzoic anhydride, phenol, etc.) was present. Measurements of the rate of benzoic acid formation were made by interruption of the reaction at known intervals and titration of the sublimate with 0·1N-sodium hydroxide. Rapid neutralisation of the alkali confirmed that the sublimate consisted almost entirely of acid with little, if any, anhydride. This technique did not give accurate kinetic data, but the following results were obtained. (i) Decomposition of 1 mole of salt yielded 0·97 mole of benzoic acid. (ii) α–Time plots for the formation of benzoic acid were somewhat deceleratory; approximate first-order rate constants gave an activation energy of 47 ± 5 kcal. mole^{-1}. (iii) The initial slope of the benzoic acid α–time plot was greater than that for the carbon dioxide formation reaction at the same temperature. A plot of values of α for benzoic acid formation against simultaneously determined values for carbon dioxide formation is shown on Figure 2. Results obtained from reactions at 230—370° were all close to the single line.

Non-volatile products. The appearance of the reactant showed that melting always occurred before 10% of the carbon dioxide had been evolved. Gravimetric measurements showed that 23·3% of the reactant remained as solid on completion of the decomposition.

X-Ray studies showed that after 2 min. heating at 347°, in a vacuum, no detectable change in the crystal structure of the reactant had occurred. After 6 min. at 352° ($\alpha = 0{\cdot}1$) a diffuse pattern similar to that of nickel carbide was found; line-broadening suggested small crystallite size. After 15 min. at 346° or 355° ($\alpha \sim 0{\cdot}4$) the *X*-ray pattern was closely similar to that of nickel carbide, indicating this to be the main solid product; small amounts of oxide were present also. After 180 min. at 341° ($\alpha = 1{\cdot}0$) the diffraction pattern of the residue showed nickel carbide to be the main product with trace amounts of metal and oxide. 90 min. at 352° ($\alpha = 1{\cdot}0$) yielded nickel metal with traces of oxide, but carbide was absent.[6] The residue, from the reaction with $\alpha > 0{\cdot}1$, gave no diffraction pattern characteristic of the original reactant, but considerable low-angle scattering suggested the presence of an almost amorphous phase in the solidified melt.

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[5] A. K. Galwey, Proceedings of Third International Congress of Catalysis, North Holland Publishing Co., Amsterdam, 1965, p. 791.

[6] L. J. E. Hofer, E. M. Cohn, and W. C. Peebles, *J. Phys. Chem.*, 1950, **54**, 1161.

Decomposition in the presence of hydrogen. A number of measurements of the rate of formation of benzene and of carbon dioxide from the thermal decomposition reaction in the presence of 30 mm. gaseous hydrogen were made using a mass spectrometer to follow the reaction. Closely comparable zero-order kinetic behaviour for the formation of both products was observed. There was no evidence of cyclohexane formation.[7]

The Nickel Salt of Cyclohexanecarboxylic Acid.—Reactant. Slightly more than 2 mol. of cyclohexanecarboxylic acid (Eastman Kodak; Pract. grade) was warmed with that weight of " nickel carbonate " (B.D.H. Laboratory Reagent grade; " low in Co and Fe ") which contained 1 atom of nickel, until the slow gas evolution was complete. Further warming of the viscous mixture finally yielded an emerald green solid which *X*-ray examination showed to contain a crystalline phase. Analysis of the single preparation of salt gave C 47·95%, H 7·15%, and, assuming the ignition residue to be NiO, Ni 18·3%, compared with C 50·8%, H, 7·3%, and Ni 17·75% calculated for $(C_6H_{11}CO_2)_2Ni,H_2O$.

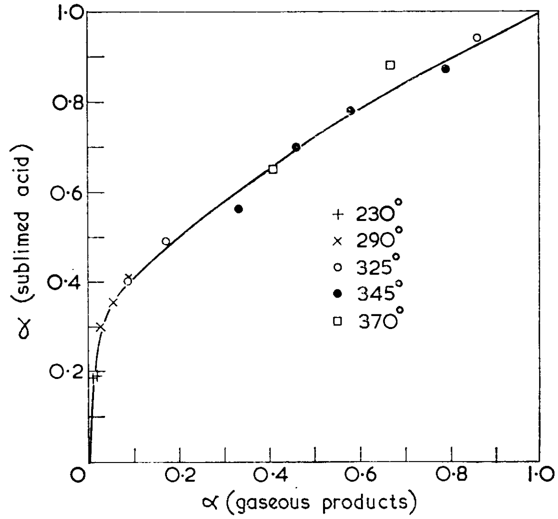

FIGURE 2. Plot of α for the carbon dioxide formation reaction against simultaneously determined values of α for the benzoic acid formation reaction at different temperatures

Kinetic measurements of the thermal decomposition were attempted by the methods described above, but here data were, in general, irreproducible. The results obtained are summarised below.

Gaseous products. The salt decomposed when heated above ~220° in a vacuum, to yield gaseous products. The rate of reaction depended on the state of sub-division of the reactant and on whether distilled product acid was present on the cool walls of the reaction vessel immediately beyond the heated zone. Three sets of kinetic experiments on reaction at 250—400° were attempted using (i) −80° trap, (ii) −195° trap, or (iii) a −195° trap immediately outside the heated zone to reduce diffusion of distilled product acid back to the reactant surface. Reactions were irreproducible and complex, plots of volume of product gas against time for typical experiments under reaction conditions (iii) are shown in Figure 3.

Hydrocarbon formation. C_6-Hydrocarbons only were studied. Decomposition of 100·0 mg. of reactant yielded 1·0 mg. of benzene and smaller amounts of cyclohexane (0·01 mg.) and cyclohexene (0·002 mg.). Results were insufficiently reproducible to enable kinetic studies to be made. Cyclohexene was the most abundant hydrocarbon product in the very early stages of reaction.

Water. At <200° the salt lost 7·5% of its weight while negligible yields of acid and of gaseous products were found. It is believed that this represents loss of 1 mol. of water of crystallisation from the reactant.

Volatile acid. Decomposition of 100·0 mg. of salt yielded 56·0 mg. of acid as a mixture with the anhydride, the proportion being temperature-dependent. Again kinetic measurements were irreproducible.

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[7] O. Beeck and A. W. Ritchie, *Discuss. Faraday Soc.*, 1950, **8**, 159.

Solid products. 22·2% of the reactant remained as solid residue. *X*-Ray studies showed nickel metal to be the main component but nickel oxide and, below 350°,[6] nickel carbide were were also formed in appreciable yield.

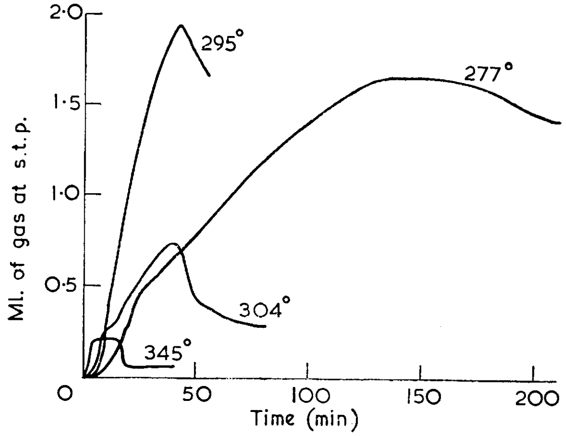

Figure 3. Pressure–time plots for the formation of gaseous products during the thermal decomposition of the nickel salt of cyclohexanecarboxylic acid at different temperatures using a liquid-nitrogen refrigerant trap

Discussion

Nickel Benzoate.—Reaction products. Yields of products given above may be summarised:

$$\mathrm{PhCO_2)_2Ni,3H_2O} \longrightarrow \mathrm{0{\cdot}97PhCO_2H + 0{\cdot}41C_6H_5OH + 0{\cdot}020C_6H_6 + 0{\cdot}70CO_2 + 0{\cdot}030CO} + x\mathrm{C + Ni} + \mathrm{(NiO + H_2O)}$$

where the products in brackets were not quantiatively measured. *X*-Ray studies showed the residue to consist largely of carbide and, if the oxide in this was neglected, the value of x was 1·97. Neglecting water of crystallisation, the above equation does not account for $C_{1\cdot93}H_{1\cdot60}O_{0\cdot22}$. The products represented by this fraction of the reactant were not retained in the residue, and the only component identified was biphenyl. Extensive cracking of the hydrocarbon nuclei in the presence of the finely divided carbide did not occur, since C_2—C_7-hydrocarbons, other than benzene, were not found.

Kinetics of reaction. Identification of reaction intermediates was not possible for this salt where decomposition occurred in an opaque melt which solidified to a largely amorphous solid. The scheme outlined below, however, accounts for the main features of the results.

On average, each " molecule " of reactant yielded one molecule of acid product, some 30% of which (Figure 2) was given by an initial fast reaction while the remainder was formed at a rate similar to that of carbon dioxide formation. We suggest, therefore, that this initial fast reaction resulted from hydrolysis of the salt by reaction with the water of hydration. When unreacted constituent water had been volatilised, benzoic acid was subsequently formed as the result of the same rate-determining step as that which yielded carbon dioxide.

Measurements of the carbon dioxide formation reaction did not fit kinetic equations characteristic of simple homogeneous reactions, and it did not involve an autocatalytic process since the rate was not appreciably influenced by the addition of powdered nickel metal. It is therefore necessary to consider complex reaction mechanisms. It is known [8] that the rate of formation of products from the second of two successive first-order reactions is close to zero order over a considerable range of α. The carbon dioxide formation reaction, the most accurately measured set of kinetic data in the present study, may therefore be explained by a mechanism of this type which may be represented:

$$\mathrm{(PhCO_2)_2Ni,3H_2O} \longrightarrow \mathrm{X} \longrightarrow \mathrm{PhCO_2H + CO_2 + Ni\cdot + C_6H_5\cdot + H_2O}$$

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[8] S. Glasstone, " Physical Chemistry " Macmillan, London, 1951, 2nd edn., Fig. 246, p. 1077.

The concentration of X initially increased and later decreased as reaction proceeded. The nature of X was not established but it may have been a lower hydrate or the anhydrous salt. A similar scheme accounts for the formation of phenol from that fraction of the salt which had been hydrolysed during the initial benzoic acid formation reaction

$$PhCO_2NiOH,nH_2O \longrightarrow Y \longrightarrow PhOH + Ni\cdot + CO_2 + H_2O$$

Secondary or side-reactions may form further products and cause the observed inequality of yields of carbon dioxide and benzoic acid. Reaction of carbon dioxide with nickel carbide yielded [9] carbon monoxide and nickel oxide above ~300°.

The above scheme accounts for the observation that the energies of activation for formation of carbon dioxide, benzene, and benzoic acid were all close to the same value if it is assumed that very nearly the same amount of energy was necessary to form the transition complex from reactants X and Y. Furthermore, the value was close to those found for the formation of the same products in the thermal decomposition of nickel phthalate [10] and for the decomposition of nickel mellitate.[11] This suggested that the structures of the transition complexes in all these decomposition reactions were very similar, and it is tentatively suggested that reaction involved initial rupture of the bond between the nickel atom and the carboxyl group.

Product nickel atoms and phenyl radicals, mentioned in the above equations, reacted to yield benzene, nickel carbide, and other products. There was no evidence that appreciable cracking occurred, but some breakdown of aromatic nuclei must have occurred to yield nickel carbide. It is suggested that the product phenyl radicals were initially adsorbed on crystallites of solid product and disproportionation yielded benzene and dimerisation yielded biphenyl. Possibly terphenyl and other polynuclear hydrocarbons may have been formed but these were not identified. The formation of polynuclear hydrocarbons is consistent with the calculated C/H ratio for that fraction of the reactant not quantitatively determined in the products. The disproportionation reactions of the phenyl radicals also yielded dehydrogenated hydrocarbons which may be strongly adsorbed on the crystallites and polymerise to yield species which were not volatilised from the reactant at decomposition temperature. This was the carbon retained in the residue.

The formation of nickel carbide from this reaction in the melt contrasts with the formation of a nickel–carbon finely divided mixture from the decomposition of nickel phthalate [10] which did not melt before decomposition. This difference in the solid products was unexpected, since most of the other products of reaction were very similar, and it is attributed to differences in the stereochemistry of reactions occurring in the different environments. It seems reasonable to suppose that radicals from reaction in the melt may approach the metal surface in a variety of orientations some of which may result in further reactions. This contrasts with reaction occurring in the vitreous solid [10] where stereochemical constraint may preclude the possibility of certain subsequent reactions of the radical adsorbed at the surface of the solid.

The results of the present study are entirely consistent with the conclusion, reached previously,[1] that nickel benzoate may be formed as an intermediate in reactions yielding benzene when certain organic compounds are heated in the presence of excess of nickel oxide. Approximate first-order rate constants for benzene formation in the present study gave log k at 625°K as $-1{\cdot}35$ (same units as previously [1]). This was close to the value for reaction of benzoic acid on nickel metal ($-1{\cdot}00$) but greater than the value found for reaction on nickel oxide ($-4{\cdot}10$). The activation energy was, however, the same, within experimental error, for all three reactions. It is concluded, therefore, that the excess of oxide modified the reaction by spreading the reactant as a thin layer of melt over the oxide surface so that the effective concentration of the reactant, and thus the rate of reaction, was reduced relative to that occurring in the melt formed from pure salt. The oxide may

[9] A. K. Galwey, *J. Catalysis*, 1963, **2**, 176.
[10] A. K. Galwey, *J. Catalysis*, in the press.
[11] A. K. Galwey, unpublished results.

remove hydrogen and water (if present) from the reactant species in the melt but did not completely inhibit the benzene-forming disproportionation reaction.

The Nickel Salt of Cyclohexanecarboxylic Acid.—Analytical results showed that the reactant contained less than the stoicheiometric proportion of acid. Since *X*-ray studies indicated this substance to contain substantial amounts of a crystalline phase absent from the materials used in its preparation, it was concluded that the reactant contained a high proportion of the required salt.

Kinetic results for the decomposition reaction were so irreproducible that the mechanism could not be established. The following results were, however, apparent. (i) The salt did not melt prior to decomposition. (ii) On decomposition, the salt distilled acid from the reaction zone; no experimental conditions could be found which prevented diffusion of distilled acid back to the reactant. The rate of evolution of gaseous products was little influenced by temperature but was dependent on reactant particle size and on the presence or absence of acid at the edge of the heated zone. It was concluded, therefore, that reaction consisted of distillation of acid from the reactant, subsequently followed by catalytic cracking at the solid surface of the residue. The products of cracking probably included methane, carbon monoxide, carbon dioxide, and possibly hydrogen since secondary reactions, probably diffusion-controlled, resulted in a decrease in pressure of products when a $-195°$ trap was used (Figure 3). (iii) Benzene was the predominant hydrocarbon product; it is known that cyclohexane is dehydrogenated on nickel at these temperatures.[7] Cyclohexene, detected in trace amounts, may be a primary product but it would be expected to disproportionate readily on nickel under reaction conditions. (iv) The marked dissimilarity of reaction of the two salts studied shows that the saturated ring was not dehydrogenated before the decomposition reaction. Similarly, it seems unlikely, in the decomposition of nickel benzoate in the presence of hydrogen, that any hydrogenation of the ring occurred before decomposition. It is concluded, therefore, that decomposition of the two salts occurs by quite different reaction mechanisms.

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