781. *The Thermal Decomposition of Basic Ferric Salts of Benzoic Acid and of Phthalic Acid*

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When heated *in vacuo*, basic ferric benzoate melted and decomposed to yield benzoic acid, benzene, carbon dioxide, ferrosoferric oxide, probably water, and smaller amounts of other products, which have not been identified. Kinetic measurements showed that the energy of activation of the reaction yielding the three volatile products mentioned was 40 ± 2 kcal./mole.

Basic ferric phthalate did not melt during decomposition, but yielded phthalic anhydride and ferrosoferric oxide as the main products. The energy of activation of the formation of acid anhydride was 42 ± 3 kcal./mole. The yields of carbon dioxide and of benzene were too small to enable the kinetics of the formation of these compounds to be adequately studied.

Reaction mechanisms to account for the results are suggested.

A RECENT trend in the investigation of mechanisms of heterogeneous catalytic reactions has been the study of the reactivity of adsorbed species which may be formed at the surface of the solid. For example, in a recent study [1] of the mechanisms of the thermal decomposition of formic acid vapour and of the water-gas reaction catalysed by magnesia, the decomposition of one possible intermediate, magnesium formate, was examined. This approach was used to establish by which of several reaction-paths the chemical change occurred. Kinetic studies of the thermal decomposition of transition-metal salts of simple organic acids, *e.g.*, formic,[2] oxalic,[2] and aliphatic acids [3] have been undertaken. However, few studies of the thermal reactions undergone by salts of aromatic acids have been reported, and the present Paper forms part of a study in this field. The object of the work was to investigate the kinetics of the decomposition reaction, and to identify the products

[1] J. J. F. Scholten, P. Mars, P. G. Menon, and R. van Hardeveld, Third International Congress on Catalysis, Paper I.57, North-Holland Publishing Co., Amsterdam, 1964.

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

[3] J. Leicester and M. J. Redman, *J. Appl. Chem.*, 1964, **12**, 357.

formed as result of the reactions occurring at elevated temperature between the organic radicals in the presence of metallic iron and/or iron oxides.

EXPERIMENTAL

Materials.—Basic ferric benzoate. B.D.H. " basic ferric benzoate " was used and was analysed by combustion and precipitation of the metal hydroxide and ignition (Found: C, 54·25; H, 4·1; Fe, 14·95. Calc. for $C_{14}H_{11}FeO_5$: C, 53·35, H, 3·5; Fe, 17·7%).

Basic ferric phthalate. This salt was prepared by a method based on the observations of Bobtelsky and Bar-Gadda.[4] B.D.H. " Laboratory Reagent Grade " phthalic acid (35 g.) was dissolved in 1 litre of a 1 : 1 mixture of ethanol and water with the minimum amount of AnalaR ammonium hydroxide required to complete solution. AnalaR ferric chloride (54 g.) in 1 litre of the same solvent, was added dropwise with thorough mixing. The pale brown precipitate was filtered, washed, finally dried for 2 hr. at 150°, and analysed as above (Found: C, 39·5; H, 2·55; Fe, 21·7. Calc for $C_8H_5FeO_5,\frac{1}{2}H_2O$: C, 39·05; H, 2·45; Fe, 22·7%). The *X*-ray diffraction pattern of this salt showed a single diffuse line and three diffuse haloes, indicating that no well defined crystalline phase was present.

Methods.—The formation of carbon dioxide was studied by measurements with a McLeod gauge of the pressure of gas developed at known times in a constant-volume apparatus. A weighed quantity of the sample was introduced into a small tube, and evacuated for 2 hr. at $\sim 10^{-6}$ mm. before being isolated from the pump and heated to reaction temperature. A carbon dioxide–acetone trap was placed between the reaction vessel and the McLeod gauge; the sublimation of the acid was studied in the same apparatus; reactions were interrupted at appropriate intervals and the amount of sublimed acid on the wall of the reaction vessel determined with standard alkali.

The formation of hydrocarbon was studied by a method which has been described in detail elsewhere.[5]

X-Ray-diffraction patterns obtained for the solid reaction products (Fe-filtered Co K_α-radiation) were identified by comparison with patterns obtained from authentic compounds.

RESULTS AND DISCUSSION

Thermal Decomposition of Basic Ferric Benzoate.—Solid product. Melting of the reactant occurred early in the decomposition. When the reaction was complete (300—400°) 100·0 mg. of salt yielded 33·7 mg. of solid residue; *X*-ray studies of this residue showed that ferrosoferric oxide was the only detectable crystalline product. No crystalline phase was detected in the non-volatile material from interrupted reactions.

Sublimate from the heated zone. The infrared spectrum of a solution of the sublimate was virtually identical with that of a similar solution of benzoic acid. No benzoic anhydride, phenol, or other expected product was detected. Complete decomposition of 100·0 mg. of the salt (300—400°) yielded 39·6 mg. of benzoic acid, and this was independent of the mass of reactant (14—40 mg.).

A plot of α, the fractional decomposition, for the formation of benzoic acid, against simultaneously measured corresponding values of α for the formation of carbon dioxide (Figure 1) shows that the formation of acid is initially relatively rapid, and is followed by a period where both reactions proceed at comparable rates. These results also show that the *relative* rate of formation of both products is independent of temperature, since all the results approach a single line. First-order plots for the formation of benzoic acid at 282—340°, after completion of the initial fast reaction, give the energy of activation as 40·2 ± 2 kcal./mole.

Benzene. Measurements (230—350°) made during the initial stages of the reaction, where the formation of benzene obeys the zero-order kinetic equation give the energy of activation as 41 ± 2 kcal./mole. Complete decomposition of 100·0 mg. of the salt at 420° yields 1·4 mg. of benzene.

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[4] M. Bobtelsky and I. Bar-Gadda, *Analyt. Chim. Acta*, **1953**, **9**, 446.

[5] A. K. Galwey, Third International Congress on Catalysis, Paper I.50, North-Holland Publishing Co., Amsterdam, **1964**.

Other organic products. Trace amounts of chlorobenzene ($\sim 1 \times 10^{-3}$ mg. 100 mg. of salt decomposed) were detected by gas chromatography; this product results from traces of chloride impurity in the salt. The sublimate from the decomposition reaction gave a phenolic odour, but the quantity of phenol present was too small to be detected by precipitation as tribromophenol from an aqueous extract.

Carbon dioxide. The gaseous reaction products from decompositions at 300—420° were almost completely condensed at −195°, showing carbon dioxide to be the only important gaseous product. Decomposition of 100·0 mg. of the salt yielded between 5·5 and 6·5 mg. of carbon dioxide, and the scatter of results could not be correlated with variations in the mass of reactant or the temperature of reaction. Pressure–time measurements showed this reaction to be deceleratory throughout (Figure 2). The results approximately obey both the first- and second-order equations over the ranges $0{\cdot}05 < \alpha < 0{\cdot}6$ and $0{\cdot}15 < \alpha < 0{\cdot}8$; the energies of activation were 37 ± 4 and 39·7 ± 1·5 kcal./mole, respectively.

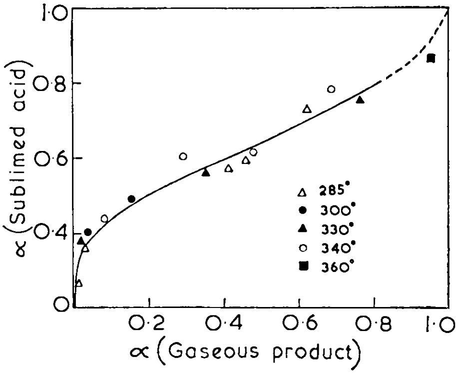

FIGURE 1. Plot of α (fractional decomposition) for the sublimed acid reaction against α for the formation of carbon dioxide in the thermal decomposition of basic ferric benzoate at various temperatures

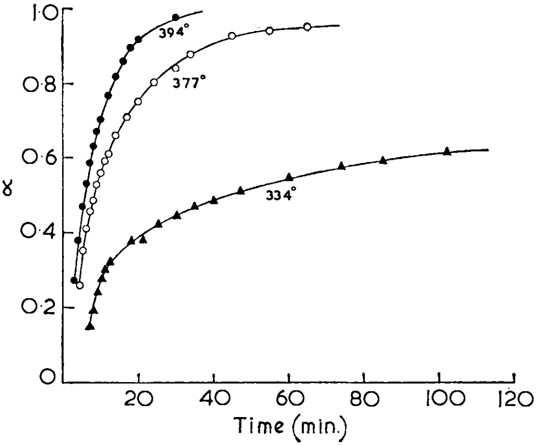

FIGURE 2. Plot of α against time for the formation of carbon dioxide during the thermal decomposition of basic ferric benzoate at various temperatures

Water. Gas-chromatographic studies showed that water was a significant product. Measurements of loss of weight on completion of the initial fast acid-formation reaction showed that 6% of the reactant was not accounted for by the formation of acid or carbon dioxide, and is believed to represent the initial evolution of water.

Thermal Decomposition of Basic Ferric Phthalate.—Solid products. The appearance of the residue showed that melting did not occur during thermal decomposition at 250—400°. Complete decomposition at 320—400° of 100·0 mg. of the salt, yielded 35·0 mg. of residue. Combustion analysis showed that the residue contained 9·3% carbon, and measurements of surface area, from nitrogen adsorption at −195° and use of the B.E.T. equation gave a surface area of 110 ± 10 m.^{2} g.$^{-1}$. *X*-Ray diffraction showed that this solid contained ferrosoferric oxide and small amounts of a second, unidentified, crystalline phase. Ferrosoferric oxide was also detected in the residue from interrupted reactions.

Sublimate from the heated zone. Infrared spectra of solutions of the solid sublimate were identical with similar solution spectra of phthalic anhydride. Titration of solutions of the sublimate showed that complete decomposition of 100·0 mg. of the salt, at 260—350°, yielded 47·3 mg. of phthalic anhydride. Kinetic studies of this reaction showed that initially some 20% of the yield sublimed rapidly. The subsequent slower deceleratory reaction approximately fitted the first-order kinetic equation at 240—340°, giving an energy of activation of 42 ± 3 kcal./mole. A comparable plot to that of Figure 1 for the results of this reaction gave considerable scatter, and no significant trends could be recognised.

Benzene and other organic products. The decomposition of 100 mg. of the salt at 430° yielded 2×10^{-4} mg. of benzene; this was too small for satisfactory kinetic studies to be made. Chlorobenzene ($\sim 2 \times 10^{-3}$ mg.) was also formed, probably from chloride impurity in the reactant. The odour suggested that phenol was present in the sublimate, but the quantity was too small to be detected by precipitation as the tribromo-derivative.

Carbon dioxide. Results showed that complete decomposition of 100·0 mg. of the salt at 280—340° yielded 3·0 mg. of carbon dioxide. Kinetic measurements (300—400°) showed that this reaction approximately obeyed the second-order equation in two regions, $0 < \alpha < 0{\cdot}4$ and $0{\cdot}4 < \alpha < 0{\cdot}7$. Rate constants from these plots gave the very approximate Arrhenius energy of activation of 20 ± 5 kcal./mole. Reaction above 350° yielded a small amount of carbon monoxide.

Water. Some 10—11% loss in weight of reactant on completion of the initial rapid distillation of acid was not accounted for by the weight of anhydride sublimed, and it was concluded that this represented initial evolution of water.

Sublimation of Acid.—A number of experiments were made in which acid was distilled under the conditions used for kinetic studies and in the presence of the solid products from a completed decomposition of a basic ferric salt. The results showed that the volume of gaseous products formed during distillation of benzoic acid was small ($< \sim 5\%$) compared with the yield from the decomposition of the salt containing the same weight of acid. In similar experiments, phthalic acid or anhydride gave about 20% of the gas yielded by the decomposition of the salt; these results were somewhat irreproducible. Sublimation of the latter two substances in the absence of the solid reaction products from the decomposed salt also resulted in appreciable decomposition.

Thermal Decomposition of Basic Ferric Benzoate.—The analytical results indicated that the reactant contained more than the stoicheiometric proportion of benzoic acid. Preparation of reactant of the exact composition was not attempted, since (i) the salt was hydrolysed by water, (ii) several basic ferric benzoates have been reported,[6] and (iii) a significant proportion of the total acid in the product was initially sublimed (~12% of the reactant). It is believed that reaction probably occurred in a melt which contained the solid products and a mixture of the following species: $Fe(OH)_3$; $Ph{\cdot}CO_2Fe(OH)_2$; $(Ph{\cdot}CO_2)_2FeOH$; possibly $(Ph{\cdot}CO_2)_3Fe$; ions formed on dissociation, and possibly also small amounts of water and benzoic acid.

The quantitative determinations of the products reported above account for 86·7% of the weight of reactant (including 6% believed to be water); further water was probably formed during the reaction. When an approximate allowance was made for the carbon contained in the residue, it was found that the 13% (by wt.) of reactant not detected in the products consisted of carbon and hydrogen in approximately equal atomic proportions, and smaller amounts of oxygen.

The initial rapid evolution of benzoic acid is attributed to distillation during establishment of equilibrium within the melt. It was not found possible to characterise the species formed as reaction intermediates in the opaque melt, but the scheme outlined below explains the main results. Kinetic data and experiments in which ferrosoferric oxide was added to the reactant before it was heated afforded no evidence that the reaction was autocatalytic. The kinetic measurements showed that the energies of activation for the formation of benzoic acid, benzene, and carbon dioxide were all close to 40 kcal./mole; values for carbon dioxide indicated that the order of the reaction was somewhat greater

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[6] R. F. Weinland and A. Herz, *Ber.*, 1912, **45**, 2662.

than unity. It was therefore concluded that these products resulted from rapid reactions after a single rate-determining step, which may be represented as

$$(Ph{\cdot}CO_2)_2{\cdot}Fe{\cdot}OH \longrightarrow Ph{\cdot}CO_2H + (PhCO_2{\cdot}Fe{:}O)$$

The benzoic acid was rapidly volatilised and the uncharacterised intermediate (bracketed) decomposed to yield the other products found. It is concluded from the kinetic data that, after decomposition of the unstable intermediate, particles of solid product may be nucleated relatively rapidly, and that radicals resulting from this reaction may be adsorbed at the surface of the group of iron atoms. Part of the oxygen present in these radicals is desorbed as carbon dioxide, part is incorporated in the product oxide, and some may be converted into water. Adsorbed phenyl radicals underwent disproportionation, yielding benzene and carbon, which was retained on the solid product. Polymerisation of phenyl radicals, to yield biphenyl, terphenyl, and other condensed polymers, accounts for that fraction of the reactant not identified in the products, but for which the analytical results indicated $C : H \sim 1 : 1$. Small amounts of phenol may be formed by reaction between adsorbed phenyl radicals and hydroxyl radicals (or ions) at the surface of the solid. Similarly, traces of chloride in the reactant may be expected to react with adsorbed phenyl radicals to form chlorobenzene.

Thermal Decomposition of Basic Ferric Phthalate.—The composition of this salt was close to that of the basic hemihydrate. An *X*-ray examination of the reactant showed that no crystalline phase was present; hence, decomposition may be regarded as occurring in an almost completely amorphous material.

The reaction products account for about 96% of the weight of reactant, which includes the somewhat approximate estimate of the initial yield of water. Analytical results showed that the unidentified 4% consisted largely of carbon, with smaller amounts of hydrogen and oxygen.

The initial fast formation of acid anhydride is attributed to some hydrolysis of the reactant, to yield acid, which is subsequently dehydrated rapidly. The main reaction yielded the same product by a rate-process with an energy of activation of 42 ± 3 kcal./mole. However, part of the phthalic anhydride was decomposed at the solid surface, yielding ferrosoferric oxide as the solid residue. Decomposition also occurred in the gaseous phase, as was shown by experiments in which the acid was sublimed under the reaction conditions. Carbon dioxide may thus be formed by two mechanisms, which is consistent with the observation that the measurements did not fit a simple kinetic law.

The concentration of surface hydrogen during reactions yielding phenylene radicals was so low that the formation of benzene by hydrogen-transfer was a relatively improbable process, a fact that would account for the low yield of benzene. By a similar mechanism to that mentioned in the preceding section, phenol and chlorobenzene may be formed from reactions between the adsorbed phenyl radicals present in low concentrations (resulting from hydrogen-transfer processes) and adsorbed hydroxyl groups, or the chloride impurity.

Conclusions.—The reactions of both salts yielded similar products, but the relative yields were significantly different. From the heated salts there sublimed a proportion of the acid product, and this is believed to result from hydrolysis during the heating to reaction temperature. The energies of activation for the subsequent formation of the products from both salts are close to 41 kcal./mole, which suggests that the same rate-determining step may occur in the decomposition of each substance. It is suggested that the initial reaction is rupture of the bond between the carboxyl group and the ferric ion. This is consistent with the results [7] of a study of the thermal decomposition of a basic ferric salt of mellitic acid, where the energies of activation of the decomposition reactions were 40 and 43 kcal./mole, and where the same initial step in the decomposition reaction has been postulated.

[7] A. K. Galwey, unpublished work.

The secondary processes occurring in the decomposition of the two present salts differ. The results for the reactions of basic ferric benzoate are interpreted as indicating the formation of a molecule of acid and an unstable intermediate, which decomposes in the melt to give appreciable quantities of benzene and carbon dioxide. This contrasts with the conclusions reached for basic ferric phthalate, where relatively small yields of secondary products are formed by reaction in the gaseous phase, or on the surface of particles of product. There is evidence that both salts yield small amounts of further organic products, but these have not been characterised.

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