Thermal Decomposition of Nickel Squarate Dihydrate, $NiC_4O_4 \cdot 2H_2O$

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Received 29th December, 1980

A kinetic and microscopic study has been made of the thermal decomposition of nickel squarate dihydrate in the solid state. Kinetic characteristics are sensitive to the availability of water vapour and behaviour varies with changes in reactant disposition within the reaction vessel. Reproducible data were obtained by standardization of technique and decomposition rates increased as the reactant mass was reduced. The activation energy for the reaction, found by extrapolation of decomposition rate coefficients to zero mass, was $163 \pm 10 \text{ kJ} \text{ mol}^{-1}$. Kinetic measurements did not, however, permit characterization of the geometry of interface development within individual reactant particles. Microscopic observations provided crucial evidence for the interpretation of rate data. Such evidence revealed that decomposition was accompanied by cracking of the approximately cubic crystallites of reactant and that preferential two-dimensional growth of superficial nuclei preceded penetration of the reaction interface into the separated reactant blocklets.

It is concluded that reaction involved two consecutive steps, dehydration followed by decomposition. A novel mechanism is proposed for the breakdown of the organic anion. It is suggested that nickel bonds to the four-membered unsaturated ring and bonds are then redistributed with the transitory intervention of nickel carbonyl, which rapidly disintegrates at reaction temperature (ca. 500 K) to give the predominant products, metallic nickel and carbon monoxide.

From the extensive studies of the thermal decompositions of nickel salts of organic acids reported in the literature,^{1, 2} it is apparent that changes of anion result in significant variations of kinetic characteristics. Shapes of the fractional reaction (α) against time curves have been ascribed to reactions proceeding preferentially at the surfaces of product particles (metallic nickel and/or nickel carbide). Kinetic obediences of these rate processes have been interpreted as nucleation and growth reactions and support for the proposed models of changing interface geometry has been given by microscopic observations.³ Less progress has, however, been made in characterizing the chemical steps which occur at the active reaction interface. Accordingly, the present study of the decomposition of nickel squarate was undertaken to extend the survey of reactions of nickel salts to include a compound which was not a carboxylate. Moreover, this solid is known to be relatively stable,^{4,5} its properties differ from other squarates containing a divalent cation⁶ and the crystal structure is known.^{7,8}

The isothermal kinetic observations reported here show that the rate of decomposition of nickel squarate depends on the disposition of crystallites within the reaction vessel and we conclude that kinetic behaviour is influenced by the prevailing water-vapour pressure. Due allowance for this effect was necessary in the design of experiments. The present article discusses difficulties inherent in the determination of meaningful kinetic data in such systems and the problems which may arise in using rate measurements in the formulation of mechanisms of solid-state decompositions. Our kinetic and microscopic observations for the pyrolysis of nickel squarate are

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discussed with due regard for these difficulties and a mechanism of reaction, consistent with the experimental evidence, is formulated. Some preliminary observations have already been published.^{9, 10}

EXPERIMENTAL

PREPARATION

Nickel squarate, the nickel salt of squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione, $H_2C_4O_4$) was prepared by the published method,^{7, 11} modified by using nickel acetate instead of nickel chloride to eliminate any possibility that impurity chloride might poison the interface reaction by modifying the catalytic properties of the surface of the metallic product.

A single-salt preparation was used for the major part of the present work. The analysis (Ni: 25.3; C: 22.56 and H: 2.37%) differed from the theoretical composition for NiC₄O₄·2H₂O (Ni: 28.39; C: 23.23 and H: 1.95) but was comparable with compositions reported previously.⁷ Our reactant can be represented approximately as NiC₄O₄·0.090H₂C₄O₄·2.64H₂O: the accommodation of more than two molecules of water per unit formula mass has been discussed.⁷

METHOD

Rates of decomposition were measured from the pressure of gas evolved in a constant-volume vacuum apparatus determined by a McLeod gauge, separated by a 195 K trap from the reactant maintained at constant temperature ± 0.5 K. Samples were outgassed initially for 2 h at 10^{-5} Torr. To obtain reproducible results a strictly standardized experimental routine was maintained using the same glass reactant tube to contain the sample (4 mm internal diameter, 14 mm long sealed at one end and reactant salt retained within it by a loose glass-wool plug). We refer to these decompositions as proceeding under 'standardized reaction conditions'.

RESULTS

PRELIMINARY OBSERVATIONS

Because of irreproducibility observed during preliminary measurements, it was necessary to investigate the influence of prevailing conditions on reaction rates before attempting to obtain quantitative kinetic data.

Examination of partially decomposed salt with the optical microscope indicated irregular onset of reaction. Within partially reacted powder samples some crystallites had apparently decomposed (black), others were unreacted (green) and others again were partially reacted (brown). Also, decomposition of salt packed in a fine tube was first initiated at the outer, open end and progressed inwards.

Vacuum d.t.a. studies¹⁰ showed a dependence of behaviour upon reactant mass. At a small sample mass (8 mg), the later stages of an initial endotherm (peak at 532 K, believed to be dehydration) overlapped with the onset of a large exotherm (peak at 606 K, identified as decomposition), the early stages of which included two subsidiary small maxima. With a larger sample mass (16 mg) the endotherm occurred at *ca*. 555 K and this was followed by unresolved peaks completed by 580 K. Different patterns of behaviour again were found for reactions in air (one large exotherm at 616 K) or in nitrogen (one large endotherm at 592 K).

The simplest explanation of these observations is that dehydration just precedes decomposition but, unless water is withdrawn, may overlap with and inhibit the subsequent salt breakdown. Water retained within and available to the crystallites of the reactant assemblage stabilizes the salt.

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PRODUCTS OF DECOMPOSITION

The only volatile products of decomposition identified by mass-spectrometric analyses were H_2O , CO and CO_2 . From measurements of the pressure of gas evolved in the calibrated volume apparatus, and using 80 and 195 K traps, the stoichiometry of reaction was determined as

$NiC_1O_4 \cdot 0.090H_9C_4O_4 \cdot 2.64H_9O \rightarrow 3.64CO + 0.40CO_2 + Ni.$

CO and Ni are therefore identified as the major products of decomposition with smaller yields of CO_2 . Assuming the water to be evolved unchanged, this does not account for 0.32C, which may remain in the solid residue, 0.18H and -0.08O.

There was no evidence of sublimation of squaric acid or any other decomposition product. Nickel carbonyl could not be identified¹² during careful mass-spectrometric studies in which products were immediately transferred from reactant to the ionization chamber.

KINETICS OF DECOMPOSITION

The *main decomposition* reaction was preceded by a slow process, the *initial reaction*, which represented only a small proportion of the total product.

INITIAL REACTION

Under standardized reaction conditions, initial reactions showed slight variations in characteristics between different samples and the following behaviour pattern emerged from the critical comparative analysis of data from 113 isothermal kinetic experiments. This rate process was zero-order until it was terminated or obscured at *ca.* 1.5% decomposition ($\alpha_i = 0.015$) by the onset of the more rapid and more extensive main reaction: typical α against time plots are given in fig. 1.

No induction period to onset of the initial reaction was apparent, the short intervals preceding reaction, $t_1 = 3.0 \text{ min}$ on average, were required to heat the sample to reaction temperature. Slopes of α against t plots were usually constant, though acceleratory behaviour was just detectable in some experiments. Acceleratory behaviour invariably became apparent on the initiation of the main decomposition. While the initial reaction was usually obscured after $\alpha_i = 0.015 \pm 0.005$, variations between $0.005 < \alpha < 0.040$ were recorded using a 195 K refrigerant trap. Apparent activation energies, calculated both from zero-order rate constants for the initial reaction and from the induction period to onset of the main reaction (t_2) , were $120 \pm 15 \text{ kJ mol}^{-1}$.

Values of α_i were reduced to 0.006 using a cold trap at 80 K and mass-spectrometric analysis confirmed that the relative proportion of carbon dioxide from the initial reaction was greater than that yielded by the main reaction. Induction periods to the main reaction (t_2) were increased on packing the reactant solid in a fine tube and were reduced by dispersing the reactant crystallites on glass wool. Otherwise sample disposition exerted little influence on the kinetics of this reaction.

THE MAIN REACTION

Typical sigmoid α against time plots for the isothermal decomposition of nickel squarate, under standardized conditions in the accumulatory apparatus, are shown in fig. 2. Data fitted the equation

$$[-\log(1-\alpha_{\rm m})]^{\frac{1}{2}} = kt \tag{1}$$

the Avrami-Erofe'ev equation¹ with n = 2, between $0.03 < \alpha_m < 0.95$, where α_m





FIG. 1.—Typical α against time plots for the initial reaction during isothermal decomposition of nickel squarate. This process was usually zero-order, although sometimes acceleratory, and obscured by the onset of the acceleratory phase of the main reaction at $\alpha_i \approx 0.015$.



FIG. 2.—Typical α against time plots for the main decomposition reaction of nickel squarate: 6.0 mg samples heated under standardized reaction conditions. The induction periods (t_2) to onset of the main reaction have been subtracted: 4.5, 16.5, 20, 74 and 120 mins for reactions at 540, 522, 509, 495 and 490 K, respectively.

415 refers to the main reaction only and measurements scaled accordingly $[\alpha_{\rm m} = (\alpha - \alpha_{\rm i})/(1.00 - \alpha_{\rm i})]$. The significance of this kinetic obedience is discussed below. The equation is used here as an empirical expression, permitting the quantitative

INFLUENCE OF REACTANT MASS

comparison of reaction rates, and this obedience is not necessarily intended to imply

the operation of a nucleation and growth mechanism.¹

The influence of reactant mass (between 0.5 and 8.0 mg, measured to within ± 0.1 mg) on kinetics of decomposition was determined at three temperatures, 541, 509 and 490 K. (i) Reactions at 541 ± 1 K generally obeyed eqn (1), although difficulties were experienced in obtaining sufficient data to test this fit adequately using a small reactant mass (≤ 1 mg). The diminution in reaction rate coefficient [k in eqn (1)] with increasing mass of reactant is shown in fig. 3. Values of t_2 were 5 ± 1 min and $\alpha_i = 0.015 \pm 0.005$. (ii) The reactions at 509 ± 2 K were not completely represented by eqn (1) since with the larger reactant masses there were two linear regions, as shown in fig. 4. Again rate coefficients (k) tended to decrease with increase in reactant mass, as shown in fig. 5 [filled circles refer to values for the overall reaction (0.03 < $\alpha_{\rm m}$ < 0.93) or for the first part ($\alpha_{\rm m}$ < 0.5) of the two stage reactions (with $\alpha_m > 0.5$ being represented by open circles)]. The induction periods were $t_2 = 20 \pm 3 \min \text{ and } \alpha_1 = 0.015 \pm 0.005$. (iii) Reactions at 490 ± 1 K did not satisfactorily obey eqn (1); the extent of the initial linear plot diminished with increase in reactant mass (being $0.02 < \alpha_m < 0.5$ at 2 mg or less and $0.02 < \alpha_m < 0.15$ at 8 mg). Thereafter the reaction was more deceleratory than the requirements of eqn (1). Rate coefficients measured for the initial linear stage showed significant irreproducibility $(k = 0.023 \pm 0.013 \text{ min}^{-1})$ but no systematic dependence on reactant mass was found, fig. 6. Induction periods were also variable, $t_2 = 64 - 178 \min \text{ and } \alpha_1 = 0.025 \pm 0.015$.

Fig. 3, 5 and 6 show that the temperature coefficient of reaction rate increases as the reactant mass decreases. Apparent Arrhenius parameters, calculated conventionally using a root mean-square regression analysis, for these, and other data measured at additional temperatures under identical conditions, were: activation



FIG. 3.—Variation of rate coefficient [eqn (1)] with reactant mass for decomposition of nickel squarate under standardized conditions at 541 K.

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FIG. 4.—Plots of $\{-\log(1-\alpha_m)\}^{\frac{1}{2}}$ against time for decomposition of nickel squarate under standardized conditions at 509 ± 2 K using different reactant masses: \bullet , 0.7; ×, 2.0; \bigcirc , 4.0; \blacktriangle , 6.0 and +, 8.0 mg. Contributions of induction period (t_2) and initial reaction (α_i) subtracted out.



FIG. 5.—Variation of rate coefficient [eqn (1)] with reactant mass for decomposition of nickel squarate under standardized conditions at 509 K. Closed circles refer to the overall reaction or the initial stage; where two linear intervals were apparent, the second part shown as open circles.



FIG. 6.—Variation of rate coefficient [early linear region of eqn (1)] with reactant mass for decomposition of nickel squarate under standardized conditions at 490 K.

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energies (E) 94 ± 9 , 131 ± 11 and 153 ± 12 kJ mol⁻¹ and frequency factors $\log_{10} (A/\min^{-1}) = 8.5\pm0.9, 12.5\pm1.1$ and 14.8 ± 1.2 for the reactant masses 6-8, 1-4 and < 1 mg, respectively (standard deviations are given). A compensation¹³ trend is apparent for these reactions proceeding at comparable rates within the same temperature interval. Extrapolation of data to zero mass¹⁴ gives the calculated activation energy for nickel squarate decomposition as 163 ± 10 kJ mol⁻¹. This extrapolation is intended¹⁴ to remove the apparent inhibitory influence of products on decomposition kinetics. Such effects were most significant in reactions at lower temperatures and with larger reactant masses, where obedience to the rate equation was less satisfactory and rate coefficients were less reliable.

INFLUENCE OF REACTANT DISPOSITION

The significant effects of change of disposition of the reactant within the reaction vessel on the decomposition kinetics at 517 K are illustrated in fig. 7. The representative α against time curves are shown for reaction under standardized conditions (\bigcirc), for reactant dispersed on glass wool, both the salt as prepared (\times) and precrushed (+) and for salt crushed and packed in a fine tube (\bigcirc).



FIG. 7.—Influence of reactant disposition on kinetics of decomposition under otherwise standardized conditions at 517 K. α against time plots are given for normal reaction (\oplus), salt dispersed on glass wool in reaction vessel both as prepared (\times) and precrushed (+) and salt crushed and packed in a fine glass tube (\bigcirc).

Reactant packed in a fine tube. Decompositions of salt tightly confined in a glass tube *ca*. 1 mm in diameter, 6 mm in length and sealed at one end did not obey eqn (1) but usually fitted the zero-order equation between $0.05 < \alpha_m < 0.7$ (fig. 7). Reaction could be seen to be initiated below the loose glass-wool plug at the open end of the tube and the green-black reaction zone advanced thereafter progressively

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though the column of reactant. The rate at 517 K was $\times ca$. 0.2 that of reaction of a similar mass of salt in the wider tube used for the standardized experiments. This rate reduction corresponds approximately to the reduction in effective cross-sectional area of the cylindrical reactant mass. Crushing the reactant before packing increased the induction period, t_2 . α_1 values were close to 0.015.

Reactant crushed before decomposition. Crushing the reactant before decomposition under standardized conditions resulted in a just-perceptible reduction in reaction rate ($\times 0.8$ at 500 K) and α against time curves became relatively more deceleratory in the latter stages.

Reactant dispersed on glass wool. Reactant crystallites were dispersed with glass wool, thus allowing more rapid escape of product water and so reducing its availability in the vicinity of the reacting salt. Again these reactions obeyed eqn (1) very satisfactorily but rate coefficients were significantly increased ($\times 1.5$ -2.0 at 510 K) compared with decompositions under standardized conditions.

Precrushing the reactant appreciably changed the kinetics of decomposition of dispersed crystallites (fig. 7). The induction period (t_2) was increased (× *ca.* 2), and the acceleratory phase of reaction was almost eliminated by a rate process that rapidly achieved a maximum rate of reaction, remaining almost constant until $\alpha_m = 0.6$ and strongly decelerated thereafter. The prolonged induction period is attributed to extensive release of water which defers the onset of the main reaction but, once this has been achieved, decomposition is rapid in the already extensively dehydrated salt.

INFLUENCE OF WATER VAPOUR ON REACTION RATE

Reactions at 543 K in the absence of a refrigerant trap yielded 2-3 Torr water vapour and exhibited kinetic characteristics which were indistinguishable from those for a reaction proceeding under standardized conditions. Larger pressures of water vapour, however, inhibited reaction. No reaction had commenced after 180 min at 523 K in 15 Torr water vapour (average t_2 was 12 min) and decomposition was immediately initiated after placing a refrigerant trap on the apparatus. Similarly, no reaction occurred after 60 min at 500 K in the same water-vapour pressure (for which t_2 was 25 min) and a further 12 min induction period followed water condensation.

Decomposition reactions at 508 K were interrupted at values of $\alpha = 0.009$, 0.20 and 0.27, the salt cooled in vacuum, exposed to saturated water vapour for 20 h before evacuation for 3 h at 10^{-5} Torr and reheating to reaction temperature. Induction times for the resumed reactions (6-7 min) were less than those for unreacted salt ($t_2 = 20-30$ min) and corresponded approximately to the warm-up period. Rates of resumed reactions were less than (× 0.5) those for comparable uninterrupted reactions and decreased further (again × *ca*. 0.5) when $\alpha_m > 0.5$. Exposure of partially reacted salt to water vapour does not restore the original induction period but does reduce the reaction rate.

Decomposition of salt at 540 K in 15 Torr water vapour proceeded significantly more slowly than the vacuum reaction. Reactions in water vapour gave no perceptible quantity of sublimate and gaseous product yields were unchanged, confirming that such decompositions were not preceded by hydrolysis.

OTHER PREPARATIONS OF REACTANT

Other preparations of nickel squarate decomposed within the same temperature interval and exhibited generally similar kinetic characteristics to those described above. Data were, however, considered less reliable, since, unlike the present reactant, these salts invariably gave small amounts of sublimate, presumably due to squaric acid in the reactant.

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SURFACE AREA OF THE RESIDUE

A 0.50 g sample of salt was fully decomposed ($\alpha = 1.00$) by slowly heating to 530 K and maintaining it at this temperature for 2 h with evacuation. The surface area was calculated from measurements of the equilibrium nitrogen adsorption isotherm on the residue at 80 K and application of the B.E.T. equation. The surface was found to be 21 m^2 (g nickel metal)⁻¹ which, if the material consisted of equal-sized cubes, corresponds to particles of edge 20-30 nm. This product was pyrophoric, oxidizing with visible ignition when scattered in air.

MICROSCOPIC STUDIES

The sizes and shapes of reactant crystallites and the systematic changes of texture apparent after various known extents of decomposition were determined using a scanning electron microscope, the Cambridge Stereoscan S180.

REACTANT

Crystals were approximately cubic, having dimensions between 4 and 20 μ m, together with a small proportion of smaller particles and fragments. There was occasional twinning and some aggregation of crystallites. The predominant surfaces, the cube faces (100), (010) *etc.*, were generally smooth and cube edges were absent due to the development of appreciably roughened and sometimes cracked surfaces disposed in the (110), (101) *etc.* directions. Typical reactant crystallites are illustrated in plate 1 (8.397).

PARTIALLY DECOMPOSED SALT

In partially decomposed salt, the extent of textural change varied appreciably amongst the identically treated individual crystallites. However, from examination of some 200 representative photomicrographs for reactant, for product ($\alpha = 1.00$) and for ten samples of salt partially decomposed to known extents from $\alpha = 0.042$ to $\alpha \approx 0.8$, the following sequence of systematic changes, occurring during the progress of reaction, was positively characterized.

The first textural feature indicative of the onset of reaction was the appearance of surface wrinkling, plate 2 (10.087). This was soon followed by the development of holes, ca. 0.3 μ m diameter, in cube faces and the irregular production of cracks aligned in directions parallel to cube edges, plate 3 (10.062). During continued reaction the numbers and the sizes of such holes increased (plate 4: 10.037): this is attributed to preferred reaction within each crystallite, since the external surfaces remained smooth.

RESIDUE

On completion of reaction ($\alpha = 1.00$) the residual coherent particles were pseudomorphic with the original reactant crystallites. This residue consisted of finely divided material aggregated into approximately rectangular blocks separated by cracks and pores [plate 5(*a*): 10.136] which were seen to extend to the centre of the crystal in sections exposed on fracture [plate 5(*b*): 9.468].

SURFACE REPLICAS EXAMINED AT HIGHER MAGNIFICATIONS

The above examinations, while giving information concerning the textural changes occurring during crystal decomposition, gave no evidence of the distribution of product at the reaction interface. Accordingly, surface replicas, Au/Pd shadowed, were prepared for examination in a transmission electron microscope (Philips EM400, STEM unit) at higher magnifications. This technique could be used at low α values

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only, since the cellulose acetate/acetone replication material penetrated product cracks so that the salt could not be removed from the replica.

The most useful replicas were obtained for salt decomposed to $\alpha = 0.11$. On some areas [plate 6(*a*)] the texture resembled that found for the prepared salt and in addition there was rectangular surface cracking with evidence of local onset of reaction yielding a finely divided product (particle dimensions were < 50 nm, this is consistent with the state of subdivision of residual metal as estimated from the B.E.T. adsorption of nitrogen isotherm). Rectangular surface cracking with more extensive reaction across crystallite faces is illustrated in plate 6(*b*).

There was no evidence that reaction proceeded by the development of compact nuclei or that decomposition was initiated at identifiable surface features, indeed the indications are that the advance across crystal faces is most irregular. It is probable that reaction similarly develops on faces of cracks penetrating the crystal bulk. We conclude that, after the induction period associated with dehydration, decomposition proceeds to all surfaces by preferred two-dimensional growth and thereafter product formation advances into the bulk of each crystallite fragment, possibly with further cracking and fragmentation of the salt.

DISCUSSION

Inspection of reactant after partial decomposition showed that salt breakdown was initiated inhomogeneously within the reactant mass. Decomposition commenced preferentially in zones from which volatile product escape occurred most readily. It was also found that water vapour could inhibit the onset of reaction. In 15 Torr water vapour no perceptible reaction occurred in intervals of time much greater than the induction periods observed when a refrigerant trap was present. At the highest reaction temperatures (*ca.* 543 K) and small pressures of water vapour (2-3 Torr), however, this inhibitory effect was negligible. These observations lead us to conclude that dehydration precedes decomposition in a two-step salt-breakdown reaction that may be approximately represented by the ideal stoichiometric equations

 $NiC_4O_4 \cdot 2H_2O \rightleftharpoons NiC_4O_4 + 2H_2O$ (dehydration) $NiC_4O_4 \rightarrow Ni + 4CO$ (decomposition).

Build-up of water vapour opposes the first, apparently reversible, step.

Under the reaction conditions studied here these two rate processes usually proceeded concurrently in different parts of the sample, at least to some extent, so that water released from one zone could inhibit the onset of reaction elsewhere, locally and temporarily. This model very satisfactorily accounts for the observed variability of behaviour with reactant disposition. It may be necessary for water-vapour pressure to decrease below a temperature-dependent limiting value before reaction can be initiated. Self-inhibition was apparently most pronounced in zones from which diffusive escape of product water was slowest, for example from amongst closely packed particles and at the lowest reaction temperatures.

A slow initial rate of water loss from the innermost zones of the assemblage of reactant crystallites explains the reduction in reaction rate with increasing sample mass apparent in fig. 4. When more salt is present, the relative proportion sufficiently dehydrated to decompose at any time was reduced and the period required for water to escape by diffusion, following release through displacement of the dehydration equilibrium, was increased. This effect explains the trends shown in fig. 3 and 5; although at 509 K the diminution in rate during the latter stages of decomposition of the larger-mass samples became so pronounced that eqn (1) was no longer obeyed.



PLATE 1.—Reactant crystallites as prepared: nickel squarate.(Plates 1-5 were obtained using the scanning electron microscope. The distance between successive scale dots at the lower edge is recorded below each photograph.)



PLATE 2.-- The first indication of the onset of reaction was surface wrinkling.

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PLATE 3.—During the early stages of reaction, holes appear in the cube faces and cracks develop parallel to the edges.



PLATE 4.—As decomposition proceeds, the holes in the planar crystallite surfaces widen and extend.

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J. Chem. Soc., Faraday Trans. 1, Vol. 78, part 2

Plate 5



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(b)

PLATE 5.—On completion of decomposition ($\alpha = 1.00$) the residual particles are pseudomorphic with the reactant crystallites but penetrated by parallel cracks which, as seen in the fragmented crystal (b), extend to the centre of these particles.

Plate 6



PLATE 6.—Transmission electron micrographs of replicas of surfaces of partially decomposed ($\alpha = 0.11$) nickel squarate. Rectangular surface cracking is found together with onset of irregular surface decomposition.

This kinetic expression did not satisfactorily represent the reaction at 490 K; the brief obedience in the early stages presumably refers to decomposition of the outer layers of the sample and thereafter inhibition became relatively more significant, further deferring reaction in those regions of salt from which water escape was slow. Sensitivity of kinetic behaviour to packing of individual reactant samples also contributes to the scatter of data apparent in fig. 6.

The same considerations account for the pattern of behaviour in fig. 7. Packing salt in the narrow reaction tube reduced the proportion of reactant from which effective water escape was rapid and therefore reaction proceeds inwards slowly. Dispersal of salt on glass wool facilitated water escape from external surfaces, presumably surface distortion at the outer faces of decomposing salt facilitates release, resulting in relatively more rapid reaction compared with the enhanced induction period of the crushed salt. This observation remains an anomalous result but it may be that a combination of the high surface area releasing water vapour and some aggregation of the fine particles at the bottom of the reaction tube effectively opposes the escape of water from the closely aggregated crystallites.

Decomposition after exposure of partially reacted salt to water vapour at ambient temperature did not require a second long induction period, but resumed immediately after salt had been reheated to reaction temperature. The later stages of such rate processes proceeded more slowly, however.

Thus we conclude that zones of established decompositions were not deactivated by exposure to water vapour, but salt which had only undergone partial dehydration probably replaced some of the water lost and so decomposition of this material was effectively deferred. Similar behaviour has been described for nickel formate.¹⁵

This pattern of kinetic behaviour has been described here in detail to emphasize that the observations are fully explained by the two-stage reaction mechanism proposed, in which the important feature is that the onset of decomposition is possible only after at least local dehydration. We consider that this reaction model is a more satisfactory interpretation of *all* our observations than that provided by the more usual¹ mechanistic interpretation of obedience to the Avrami–Erofe'ev eqn (1), which is that reaction is a nucleation and growth process proceeding in the solid state. While there was no indication of melting in the present salt, there was no evidence for the production of large, compact product nuclei either. The changing geometry of reaction interface, as developed in the theory of solid rate kinetics, required here the supplementary consideration that reaction developed inhomogeneously within the zone that constituted the total reactant assemblage. The shape of the reactant mass and the local regions of developing product formation within it exerted some control upon overall kinetic characteristics. Two levels of interface geometry require consideration, therefore: (i) the zones of product formation within the total reactant mass and (ii) the reaction interfaces developed at the surfaces of the individual crystals. Thus, although initially and superficially attractive, the observed obedience to eqn (1) does not provide an acceptable mechanistic model for our observations.

We therefore conclude that the decomposition obeys eqn (1) as a consequence of the occurrence of consecutive reactions initiated inhomogeneously within the reactant crystallite assemblage. The main reaction is initially acceleratory as the prevailing water-vapour pressure is reduced, so permitting salt breakdown of dehydrated crystallites undergoing crack development. Later, the reaction became deceleratory as reactant was consumed and as a consequence of the presence of local aggregates from which water was only slowly withdrawn.

Microscopic evidence indicated that decomposition advanced across surfaces of crystallites disintegrating with crack propagation. Such initial two-dimensional

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growth of nuclei across an expanding reactant surface area, followed by a contracting cube mechanism as decomposition proceeds inwards from particle surfaces, would be expected to fit (approximately) eqn (1). However, this model cannot be accepted here since not all reactant particles decomposed concurrently. Behaviour resembles, in many respects, that exhibited during the decomposition of nickel formate, where dehydration also precedes decomposition and the presence of water inhibits the surface nucleation step.¹⁵

THE DECOMPOSITION REACTION

While it was evident that dehydration preceded decomposition, we cannot be certain that complete elimination of water was required before initiation of salt breakdown became possible. It was clear, however, that the availability of water appreciably stabilized the reactant. It was also evident that the proportion of carbon monoxide in the products was very much greater than that anticipated¹⁶ for the reaction

$$2CO \rightleftharpoons C + CO_2 \tag{2}$$

at this temperature, indicating that no effective metal-surface-catalysed equilibration proceeded on the residual nickel. Deposited carbon may deactivate the catalytic properties of this material.



SCHEME 1.—Schematic representation of decomposition of nickel squarate. The nickel atom or ion shown may be bonded to the metallic nickel which constitutes solid residual product.

A schematic representation of our proposed anion breakdown reaction is given in scheme 1. Following removal of water molecules, a nickel atom or ion interacts with the π electrons of the unsaturated squarate anion to form a ferrocene-type complex

[see also ref. (17)]. This intermediate then rearranges to form nickel carbonyl, which is unstable at reaction temperature, and rapidly decomposes¹⁸ to yield the products. The intervention of the Ni(CO)₄ structure is postulated to account for the relatively high yield of carbon monoxide from this reaction. Moreover, the participation of a (short-range) mobile intermediate explains the coherence¹⁹ of the product particles, sintered in the form of pseudomorphs of the reactant crystallites. The lifetime of such intermediate Ni(CO)₄ must, however, be very short since this compound was sought,¹² but could not be detected, in a careful mass-spectrometric study in which decomposition products were released close to and led directly into the ionization chamber under vacuum conditions. Moreover, there was no indication of metal deposition on the glass walls of reaction vessels. It is therefore suggested that the transitory formation of Ni(CO)₄ occurred at a surface from which it was not readily released, possibly being bonded to the metal product. Such chemisorption would also explain the suppression of the catalytic reaction² at the surfaces of the residual nickel.

We do not associate our calculated activation energy, for the main reaction, with a specific bond-redistribution step, identified thereby as the rate-limiting process in decomposition. Salt breakdown for the present reactant has been shown to occur through two distinct and consecutive reactions and conditions obtaining at the reaction interface are difficult to investigate directly. Several bonds must be reorganized during conversion of the squarate anion to carbon monoxide molecules. Accordingly, we regard the relatively high temperature coefficient recorded for the main reaction as an acceptable value but believe that it would be unrealistic to interpret further the several contributory factors which may control the temperature coefficient of the interface processes and which remain inaccessible to direct study.¹³

OTHER NICKEL SALTS

Apart from the predominant production of carbon monoxide, rather than carbon dioxide, the decomposition characteristics of nickel squarate were generally similar to the behaviour previously reported for several nickel carboxylates.^{1, 2} Reactions proceeded in a similar temperature interval, and shapes of α against time curves and magnitudes of temperature coefficients of reaction rates were comparable.

THE INITIAL REACTION

The initial reaction may be identified as decomposition proceeding by a different and slower mechanism of chemical change than that operating during the main process but which remains possible during salt dehydration. The distinctive character of this process is shown by the relatively lower apparent activation energy $(120 \text{ kJ mol}^{-1})$ (that for the main decomposition is 163 kJ mol^{-1}) and the relatively greater proportion of CO₂ in the volatile products. The constant reaction rate is readily ascribed to decomposition at an effectively constant area of reactant surface, which does not increase until the onset of crack disintegration. Previous work has identified initial limited gas-evolution processes with breakdown of unstable surface species. This model could be applicable, although the occurrence of an alternative and different mechanism of decomposition during dehydration is considered more probable here, since the rate showed no tendency to diminish before being obscured by the onset of the faster and more extensive main decomposition.

MICROSCOPIC OBSERVATIONS

We conclude that an important aspect of the present work is the illustration of the problems inherent in making a meaningful kinetic analysis of a reaction that proceeds to completion in two distinct and consecutive steps but in which a product of the first

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process inhibits onset of the second. Yield against time data here showed systematic variations with reaction conditions, although by strict standardization of technique it became possible to obtain reproducible data. While such kinetic measurements fitted one of the equations which have found wide application³ in studies of solid-state decompositions, it was considered important to support interpretation of this rate data with microscopic observations as more compelling evidence for the characterization of the changing geometry of reaction interface during its development. Our analyses illustrate problems which arise in interpreting yield against time data and the value of supplementing this approach with microscopic investigations of the textural changes which accompany solid-state reactions.

We thank Mr R. Reed for help and advice in obtaining and interpreting the electron micrographs, Dr R. Hamilton and Prof. M. A. McKervey for preparing the nickel squarate reactant and Mr T. Morgan for some kinetic measurements. M.E.B. acknowledges support from the South African CSIR.

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(PAPER 0/1979)