

MECHANISM OF CoOOH THERMAL DECOMPOSITION

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ABSTRACT

The mechanism, proposed on the basis of earlier investigations on the kinetics of CoOOH thermal decomposition, explains the complicated type of Arrhenius plot of a process in which the considerable porosity of the solid product is postulated.

INTRODUCTION

Investigating the kinetics of the reaction



we establish¹ that its Arrhenius plot shows a change in the slope at about 285°C with two corresponding activation energy values: up to 285°C, $E_1 = 34.75 \text{ kcal mole}^{-1}$ and above 285°C, $E_2 = 18.91 \text{ kcal mole}^{-1}$. This at present most essential kinetic feature of the process was also confirmed non-isothermally².

As the “contracting disc” model used by us in its initial framework cannot explain this peculiarity, there is call for its further development. Earlier we indicated only cursorily how to proceed. Now, after further investigations, we are in a position to propose a relatively complete and logically grounded hypothesis which satisfactorily explains the Arrhenius dependence of the process.

DISCUSSION

Explanation of the complex Arrhenius dependence

Reaction (1) is a result of two basic physico-chemical processes, differing in their nature, in the solid:

(1) proton transfer between two hydroxyl groups in the solid phase



which is a general symptom of the thermal decomposition of any solid hydroxide³;

(2) electron transfer as a result of the partial change of the valence state from Co^{3+} to Co^{2+}



which is a specific property of CoOOH decomposition, distinguishing it from the decomposition of a large number of metal hydroxides.

It is therefore logical to assume that the electron transfer will in some form be reflected in the kinetics of the investigated process. This provision, as we shall see, will prove to be correct within the framework of a hypothesis. The latter is based on three principal propositions.

(a) No complex form of the Arrhenius dependence is observed during the thermal decomposition of a large number of kinetically investigated metal hydroxides⁴⁻⁹. Consequently, while electron transfer is a specific physico-chemical mark of the CoOOH decomposition, the complex character of its Arrhenius dependence is a specific kinetic mark of that process. There must obviously exist some connection between them. Our next task, therefore, is to detect the physico-chemical character of this connection.

(b) There exists a close connection between CoOOH and Co(OH)₂, both chemically (in ordinary conditions the latter gradually passes into CoOOH) and crystallographically (quite close crystal structures¹⁰).

(c) The activating energy of Co(OH)₂ decomposition (18.75 kcal mole⁻¹⁶) is very close to the value of that magnitude found by us for CoOOH decomposition above 285°C (18.91 kcal mole⁻¹).

The latter two peculiarities show that the thermal decomposition of CoOOH must kinetically be very close to the decomposition of Co(OH)₂.

Let us now examine processes (2) and (3) with a view to the diffusion of their gaseous products through the solid product layer. According to eqn. (1), these occur in a 3:2 ratio in favour of the proton transfer. Moreover, whereas in one proton transfer one water molecule is released, with one electron transfer only a quarter of an oxygen molecule is released, which in view of the above ratio means that there is only one oxygen molecule per six water molecules; and since the water molecule has a radius (1.38×10^{-1} nm) exceeding that of the oxygen molecule ($\sim 1.20 \times 10^{-1}$ nm), this reinforces still more the difference in the conditions of their passage through the solid product layer. This would seem to suggest the following explanation of the complex character of the Arrhenius dependence.

At lower temperatures (below 285°C), owing to the relatively low decomposition rate, a small quantity of gaseous products are released per unit time. Under these conditions the solid product layer, because of its exceedingly great porosity (which for the time being we have to accept a priori as a postulate), represents no obstacle to the passage of the water or the oxygen molecules, regardless of their quite different quantities. Consequently, at present there are no conditions limiting the proton or the electron transfer on the side of diffusion through the solid product layer. We may therefore assume that the two transfers are kinetically equivalent, i.e. they jointly control the decomposition at a 34.75 kcal mole⁻¹ summary value of its activating energy.

At higher temperatures (above 285°C), however, with an increase of the decomposition rate the quantity of gases released per unit time also increases. In our

case this leads to a much faster continuous increase of the quantity of water molecules than of oxygen molecules. Under the new conditions the solid product layer begins to put up a certain relative resistance during its penetration, but only to the water molecules which are much more numerous than the oxygen molecules. As a result, the proton and the electron transfer are no longer kinetically equivalent, and the role of the factor determining the total decomposition rate passes entirely onto the proton transfer as the direct cause of the retardation of the process, as a result of which the value of the activating energy drops to $18.91 \text{ kcal mole}^{-1}$, quite close to that of $\text{Co}(\text{OH})_2$ decomposition ($18.75 \text{ kcal mole}^{-1}$), which is based solely on a proton transfer.

Above 285°C the diffusion processes are still too weak to directly affect the decomposition kinetics established by the applied method, i.e., to exert co-control or separate control on its course, directing its kinetics, respectively, to the transfer diffusion-kinetic or the purely diffusion region. If the diffusion phenomena were to exert such a control on the investigated process with a rise in temperature, directly conditioning thereby the complex character of the Arrhenius dependence, this effect of theirs would obviously manifest itself in a decomposition of the remaining hydroxides as well, which would imply the presence of the same type of Arrhenius dependence in them. But, as we have seen, no such peculiarity is observed.

Consequently, the diffusion processes are here only an indirect cause of the complex Arrhenius dependence. Their effect manifests itself solely on the basis of the specific feature (electron transfer) of the concrete decomposition. Normally, during hydroxide decomposition (proton transfer only) this early effect of diffusion remains hidden to the methods used for kinetic analysis.

As these considerations show, the effect of temperature on the investigated process is more complex: it not only accelerates it but also kinetically differentiates its two elementary physico-chemical acts by the described mechanism. This dual effect of temperature can be successfully albeit formally illustrated by means of a more complex version of the hydrodynamic analogue well known in chemical kinetics, applied here to the effect of temperature. The investigated process is compared in Fig. 1 with water outflow from tank 1 by means of pipes 2 and 3 and collector 4 with

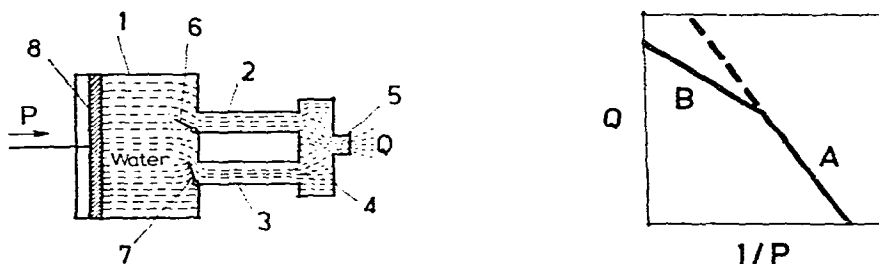


Fig. 1. Hydrodynamic analogue of CoOOH thermal decomposition (longitudinal section viewed from above).

Fig. 2. Dependence of the outflow rate of water (Q) on the reciprocal of the pressure (P).

opening 5. The water's outflow rate Q corresponds to the rate of CoOOH thermal decomposition. The effect of valves 6 and 7, which act in coordination so that the first always lets through six times as much water as the second, reflects the quantitative ratio of the water and oxygen released by reaction (1). Pipes 2 and 3 symbolize the pores in the solid product through which the water and oxygen molecule pass, respectively, in so far as the proton and the electron transfer occur on different places in the CoOOH crystalline lattice and the respective gaseous products cannot mix before leaving the solid phase. The effect of temperature is compared with the value of pressure P exerted on the mobile piston 8.

At low pressures Q is small and the outflow through the pipes occurs without them being entirely filled with water. The dependence of Q on $1/P$, graphically expressed (Fig. 2), corresponds to sector A.

At higher pressures, with Q increasing at a certain moment, pipe 2 is entirely filled with water, while pipe 3 continues to remain only partly filled. From that moment on the flow through 2 faces a certain obstacle (increasing with an increase of P), which is conditioned by the appearance of resistance during the water outflow through the narrow pipe. Now Q will have a smaller value than it would have had if, say, pipe 2 is replaced by a wider pipe, which again will be only partly filled by the flow through it. Consequently, the dependence of Q on $1/P$ at higher pressures will be expressed by sector B (Fig. 2), i.e., the graph obtained is formally analogous to the complex Arrhenius dependence for CoOOH decomposition.

Porosity of the solid product

The shape and size of the system's particles are preserved in the course of reaction (1). This was established in two different ways. First, by studying the powdered material's microscopic pictures ($\times 800$) before and after the process and, second, a careful observation of the solid phase's outer volume showed that it undergoes no change during reaction (1).

The preservation of the shape and size of the system's particles during thermal decomposition is of major importance and has been described in other processes^{9, 11-14}. In view of this peculiarity, the solid product's postulated porosity calls, in our case, for a considerable increase of the surface at the end of the process. The more than five-fold increase of the specific surface (from 9.0 to 49.8 m² g⁻¹) established by BET fully bears out this expectation of the theory.

CONCLUSION

Of course, the proposed hypothesis does not rule out other possible explanations of the complicated Arrhenius dependence. We believe, however, that it offers three major advantages: (1) it takes into account the electron transition, i.e., the at present most typical physico-chemical feature of process (1); (2) it also takes into account the theoretically and practically important property of the thermal decomposition of solids: porosity of the solid product; and (3) it finds a connection

between macrokinetics and the elementary process in the solid, one of the main tasks of any kinetic study¹⁵.

As to the future of our hypothesis, which lends a relative completeness to the first stage of our investigations on the process, we are quite reserved. We therefore consider it now only as a suitable basis for further investigations.

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