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Note

THERMAL DECOMPOSITION OF ZINC(II) SALICYLATE DIHYDRATE

P.S. BASSI, P.C. KALSI and C.M. KHAJURIA

Department of Chemistry, University of Jammu, Jammu-180001 (India)

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Recently, the thermal decompositions of metal carboxylates have aroused considerable interest [1—5]. Because of the wide use of the salicylates biologically, both as medicinal agents and as antiseptics, a systematic study of the thermal decomposition of salicylates has been started. The present paper describes the thermal decomposition of zinc salicylate dihydrate. A survey of the literature shows that thermal decomposition of zinc salicylate dihydrate has not been studied so far. The rate of the reaction has been followed gravimetrically while the decomposition products have been analysed by chemical analysis, IR spectra and X-ray diffraction studies. Derivatographic studies of zinc salicylate dihydrate have also been recorded at $10^{\circ}C\ min^{-1}$.

EXPERIMENTAL

$Zn(C_6H_4 \cdot OH \cdot COO)_2 \cdot 2\ H_2O$ was prepared [6] by mixing equal volumes of 2 M sodium salicylate and 1 M zinc chloride at room temperature. The fine crystalline precipitates of dihydrate, which separate after a few seconds, were filtered off under vacuum, washed with water and air-dried. The composition of the compound was established by precipitating Zn as $Zn(NH_4)PO_4 \cdot 6\ H_2O$ [7], IR spectra and the microanalysis of carbon and hydrogen. The carbon and hydrogen were found to be C = 45.0% and H = 4.0% (expected, C = 44.7% and H = 3.7%).

For the isothermal dehydration and decomposition studies, about 0.2 g of the sample was taken and the reaction studied by the method described earlier [8]. The dehydration was studied at 343, 353 and 363 K, while the decomposition was studied at 493, 503 and 513 K.

The dehydration and decomposition was also studied by fixing the particle size (80—120 mesh sieves). It was noticed that particle size has no effect on the nature of the kinetic curves.

The simultaneous DTG—DTA—TG curves of zinc salicylate dihydrate were recorded by means of a Paulik—Paulik—Erdey MOM derivatograph (Hungary).

Decomposition of zinc salicylate dihydrate was also carried out by taking the sample in a tube placed in a beaker containing paraffin liquid heated constantly at 513 K by means of heating coils. The temperature of the paraffin bath was kept constant throughout the reaction. The solid organic decompo-

sition products which condensed were collected and analysed. The main decomposition products were found to be salicylic acid and phenol.

Infrared spectral studies were carried out on the Specord spectrophotometer in Nujul Mulls in the range 4000—650 cm^{-1}. Infrared spectra of some of the samples were also recorded on the Perkin-Elmer Model 621 using KBr pellets in the range 4000—200 cm^{-1}.

X-ray diffraction powder pattern was employed to detect the products of decomposition using CuK_α radiations.

RESULTS AND DISCUSSION

Isothermal dehydration

Plots of α, the fractional decomposition vs. time t for the isothermal dehydration of zinc salicylate dihydrate are shown in Fig. 1. At 343 K, the reaction was complete after 40 min and the loss in weight corresponds to the formation of anhydrous zinc salicylate. The identity of the product was confirmed by chemical analysis and IR spectra. It is clear from Fig. 1 that there is a linear relationship between α, the fractional decomposition, and time t at various temperatures at least up to $\alpha = 0.95$. The energy of activation was found to be 61.0 ± 5 kJ $mole^{-1}$ from the Arrhenius plot. This behaviour cannot be ascribed to induction and the indications are that the reaction centres [9,10] are already present in larger quantities. The fast linear reaction at 363 K and the absence of a sigmoid curve initially, can all be regarded as evidences in favour of the presence of reaction centres.

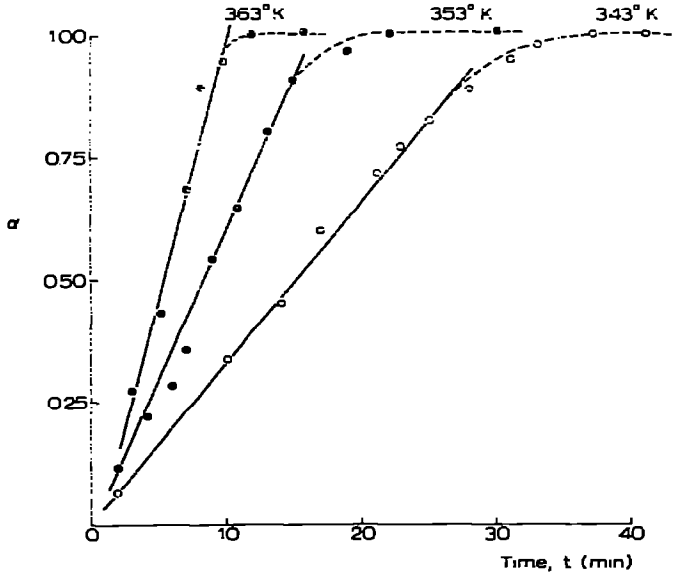


Fig. 1. Plots of α vs. t at different temperatures for the isothermal dehydration of $Zn(C_6H_4 \cdot OH \cdot COO)_2 \cdot 2\,H_2O$.

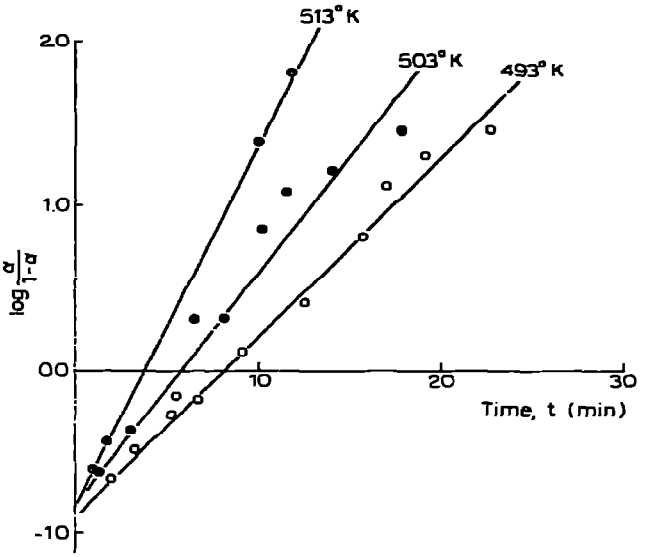


Fig. 2. Test of the Prout—Tompkin equation for the isothermal decomposition of $Zn(C_6H_4 \cdot OH \cdot COO)_2 \cdot 2\,H_2O$.

Isothermal decomposition

Isothermal decomposition of zinc salicylate dihydrate was studied at 493, 503 and 513 K. At 493 K, the reaction was complete after 50 min and the loss in weight corresponds to the formation of $Zn(C_6H_4 \cdot OOC \cdot O)$. The identity of this product was established by chemical analysis and IR spectra. The kinetic data were analysed with the help of different kinetic models proposed for such reactions, but the isothermal decomposition curves were best fitted by the Prout—Tompkins equation [11]. Plots of $\log \alpha/1-\alpha$ vs. time t are shown in Fig. 2. The values of α, up to which this equation is

TABLE 1

X-ray diffraction data of the final decomposition product of zinc salicylate dihydrate

Final product		ASTM data file	
d(Å)(obs. values) [a]	Intensities	d(Å)	Intensities
2.81	55	2.82	76
2.63	95	2.60	56
2.48	50 br [b]	2.47	100
1.58	100	1.62	40
1.49	5	1.47	35
1.37	3	1.37	28
1.34	25	1.35	14
1.21	2	1.22	5
1.07	25	1.09	10

[a] Only data for characteristic diffraction lines of ZnO are given.
[b] br = broad.

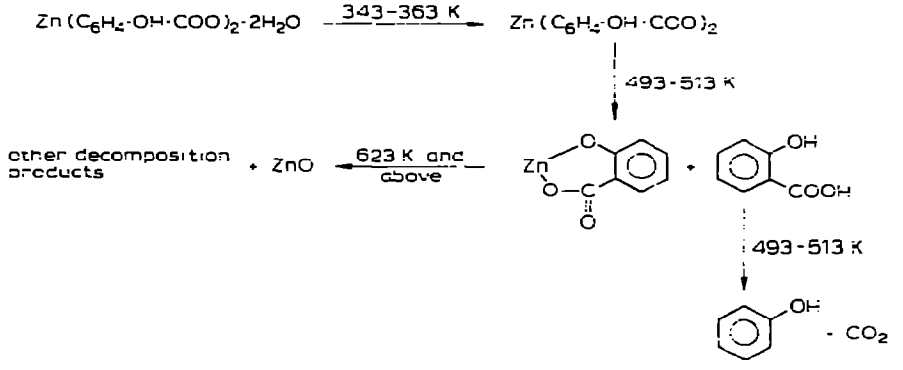
applicable is 0.20—0.96. This is not applicable in initial stages because of the dehydration of the dihydrate to the anhydrous product. The activation energy for the isothermal decomposition comes out to be 79.8 ± 5 kJ $mole^{-1}$ from the Arrhenius plot.

The decomposition was also studied at 623 K and the loss in weight corresponds to the formation of zinc oxide (calculated loss = 0.1540 g; found = 0.1538 g). The product at this temperature was subjected to X-ray examination and the diffraction lines that appeared (Table 1) were identical to those of ZnO reported in the literature [12,13].

Analysis of other decomposition products

The solid organic decomposition products were analysed and were found to be salicylic acid and phenol. Their identities were established by standard organic tests, melting point determination and IR spectra.

The following mechanism is proposed for the decomposition of zinc salicylate dihydrate on the basis of various studies



Derivatographic studies

The simultaneous DTG—DTA—TG curves of the sample were recorded with 200 mg sensitivity and at the heating rate of 10°C min^{-1} in static air atmosphere in a circular platinum crucible. The weight of the sample taken was 200 mg and was loosely kept in the crucible. The curves are shown in Fig. 3.

Three peaks at 383, 545 and 753 K were obtained in the DTG curve. The corresponding DTA curve shows two endothermic peaks at 393 and 553 K and one exothermic peak at 833 K. The TG curve shows three arrests conforming to the formation of anhydrous salt (calculated loss = 0.0192 g; expected = 0.020 g), $Zn(C_6H_4 \cdot OOC \cdot O)$ (calculated loss = 0.090 g; expected = 0.092 g) and zinc oxide (calculated loss = 0.152 g; expected = 0.156 g) at the temperatures 353—413, 493—623 and 663—893 K, respectively.

The DTA curve of the sample in static air atmosphere was also taken using a DTA apparatus fabricated at IIT Bombay. The Al_2O_3 (calcinated at 1200°C) was used as the reference material. The particle size of the sample taken was below 240 mesh sieves. The weight of the sample taken in the

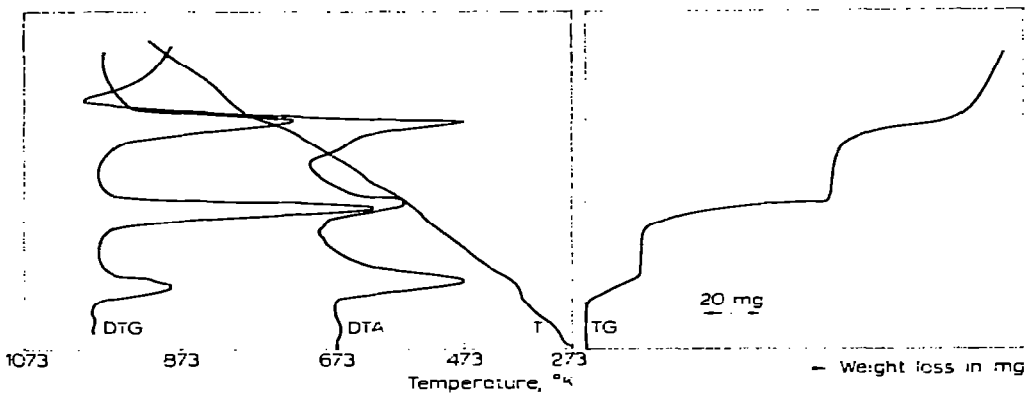


Fig. 3. Derivatogram for $Zn(C_6H_4 \cdot OH \cdot COO)_2 \cdot 2\ H_2O$ at a heating rate of 10°C min^{-1}.

platinum crucible was 0.16678 g and was tightly packed. At 8°C min^{-1}, there were two endothermic peaks at 366 and 493 K and a broad exothermic peak in the region 626—738 K.

Mathemaiical analysis of the TG curve

The TG curve was studied in detail. The kinetic parameters, i.e. order of reaction n, and the activation energy E, were calculated from the TG curve. The order of reaction n was obtained using the equation given by Horwitz and Metzger [14]. The order of reaction for the dehydration step and for decomposition was found to be unity. After determining n, an integral method was employed in the evaluation of kinetic parameters for dehydration and decomposition. For this purpose, the Coats—Redfern relation [15] was employed in the suitable form when $n = 1$. The activation energies for the dehydration comes out to be 62 ± 5 kJ $mole^{-1}$ and for the decomposition step is 85 ± 5 kJ $mole^{-1}$. These values are in good agreement with the values obtained under isothermal conditions.

Infrared spectral studies

The IR spectra of zinc salicylate dihydrate, its dehydration and decomposition products at various temperatures reveal that the sample, when heated at 363 K, retains all the principal bands of zinc salicylate dihydrate except the frequencies at 1190 cm^{-1} (w) and 3400—2930 cm^{-1} (s, br) due to the presence of water; thus indicating the elimination of water at this temperature. The IR spectra of the product at 513 K, the temperature at which anhydrous zinc salicylate decomposes to form an intermediate, shows the further absence of bands at 810 cm^{-1} (m) and 1340 cm^{-1} (m) and the appearance of a strong new frequency at ~1420 cm^{-1}. The missing IR frequency indicates the absence of an —OH group (phenolic) while the additional stretching frequency can only be assigned to the formation of a new M—O—C bond in the intermediate compound.

Thus the mechanisms of non-isothermal and isothermal dehydration and

decomposition as proposed above and supported by chemical and physico-chemical studies agree with each other.

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