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THE KINETICS AND MECHANISMS OF THERMAL DEGRADATION OF SOME DIVALENT METAL SALTS OF MONO(HYDROXYETHYL) PHTHALATE

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ABSTRACT

The thermal decomposition of lead and manganese salts of mono(hydroxyethyl) phthalate was studied by thermogravimetry and differential scanning calorimetry. The kinetic parameters for the various stages of decomposition of these salts were calculated by different methods and mechanisms are proposed to explain the results.

INTRODUCTION

The kinetics of the thermal degradation of substances are usually studied by measuring rates of change in physical properties, such as weight, over a series of constant temperatures. The rate of change of weight with temperature of a substance can be determined from thermogravimetry. From the thermogram, the kinetic parameters for the various reaction stages can be determined by both differential and integral methods. Differential methods are more sensitive for detecting changes in mechanism and may tend to magnify experimental scatter. Further, the calculated activation energy may be too high if the order of the reaction n is less than 1 and too low if n is greater than 1. Generally the most accurate data are calculated from the medium-steep parts of the TGA curve. Although the integral methods are simpler and quicker than differential methods, they require the use of successive approximations for maximum accuracy. Integral methods based on experiments with a constant heating rate tend to yield kinetic parameters that are mutually agreeable. These methods should be used only after the order of the reaction is clearly established.

Sestak [1] and Sharp and Wentworth [2] made a comparison of the kinetic results calculated by different methods. We have calculated the kinetic parameters for the decomposition of lead and manganese salts of mono(hydroxyethyl) phthalate, $M(HEP)_2$, where $M = Pb^{2+}$ or Mn^{2+}, by different integral methods. The mechanisms of decomposition of these salts are also discussed. The integral methods used are those of Coats and Redfern [3], Doyle [4] and Murray and White [5].

EXPERIMENTAL

Materials

The metal salts of mono(hydroxyethyl) phthalate, $M(HEP)_2$, where $M = Mn^{2+}$ or Pb^{2+}, were prepared as reported previously [6]. The purity of these salts was established from spectral and thermal analysis studies.

Apparatus and procedure

Thermogravimetric analysis (TGA) was carried out in a Perkin-Elmer TGS-2 instrument at a heating rate of 10°C min^{-1} in an atmosphere of nitrogen. Differential scanning calorimetric analysis (DSC) was carried out in a Perkin-Elmer-DSC-1B instrument in an atmosphere of nitrogen at a heating rate of 10°C min^{-1}.

Most kinetic treatments are based on the relationships

$$\frac{\mathrm{d}c}{\mathrm{d}t} = k\mathrm{f}(c) \tag{1}$$

where c = conversion, t = time, k = a temperature dependent rate constant and $\mathrm{f}(c)$ = a temperature independent function of c. The constant k is generally assumed to have the Arrhenius form

$$k = A\,\mathrm{e}^{-E/RT} \tag{2}$$

where A = pre-exponential factor, E = activation energy, R = gas constant, and T = absolute temperature. In homogeneous kinetics, conversion is defined in terms of concentration, and the conversion function would be assumed to have the form

$$\mathrm{f}(c) = (1 - c)^n \tag{3}$$

where n = order of reaction. By combining eqns. (1)—(3) and including the rate of temperature rise, the following integral form of the equation can be written

$$\int_0^c \frac{\mathrm{d}c}{(1-c)^n} = \frac{A}{\beta} \int_{T_0}^{T} \mathrm{e}^{-E/RT}\,\mathrm{d}T \tag{4}$$

where T_0 = absolute temperature. Integration of the terms on the left-hand side gives

$$\int_0^c \frac{\mathrm{d}c}{(1-c)^n} = \frac{(1-c)^{1-n} - 1}{1-n} \text{ for } n \neq 1 \tag{5}$$

$$= \ln(1 - c) \text{ for } n = 1 \tag{6}$$

For the right-hand side of eqn. (4) various authors used different approximations for the calculation of kinetic parameters:

Coats and Redfern

$$\int_{T_0}^{T} e^{-E/RT}\,dT = \left(\frac{RT^2}{E}\right)\left[1-\frac{2RT}{E}\right]e^{-E/RT}$$

Plots

$$\log\left[\frac{-\ln(1-c)}{T^2}\right] \text{ vs. } \frac{1}{T} \text{ for } n = 1$$

and

$$\log\left[\frac{(1-c)^{1-n}-1}{T^2(1-n)}\right] \text{vs. } \frac{1}{T} \text{ for } n \neq 1$$

Doyle

$$\int_{T_0}^{T} e^{-E/RT}\,dT = -2.315 - 0.4567\,\frac{E}{RT} \quad \text{for } 20 \geqslant \frac{E}{RT} \geqslant 60$$

Plots

$$\log[\ln(1-c)] \text{ vs. } \frac{1}{T} \text{ for } n = 1$$

$$\log\left[\frac{(1-c)^{1-n}-1}{1-n}\right] \text{ vs. } \frac{1}{T} \text{ for } n \neq 1$$

Murray and White

$$\int_{T_0}^{T} e^{-E/RT}\,dT = \left(\frac{RT^2}{E}\right) e^{-E/RT}$$

Plots

$$\ln[\ln(1-c)] - 2\ln T \text{ vs. } \frac{1}{T} \text{ for } n = 1$$

$$\ln\left[\frac{(1-c)^{1-n}-1}{1-n}\right] - 2\ln T \text{ vs. } \frac{1}{T} \text{ for } n \neq 1$$

The activation energies are calculated from the equations graphically after introducing the appropriate approximations assuming the correct order of the reaction, which is established by differential methods wherever necessary.

RESULTS AND DISCUSSION

Figures 1 and 2 show the TGA—DSC curves of $Mn(HEP)_2$ and $Pb(HEP)_2$. The activation energies calculated for various degradation steps in the TGA

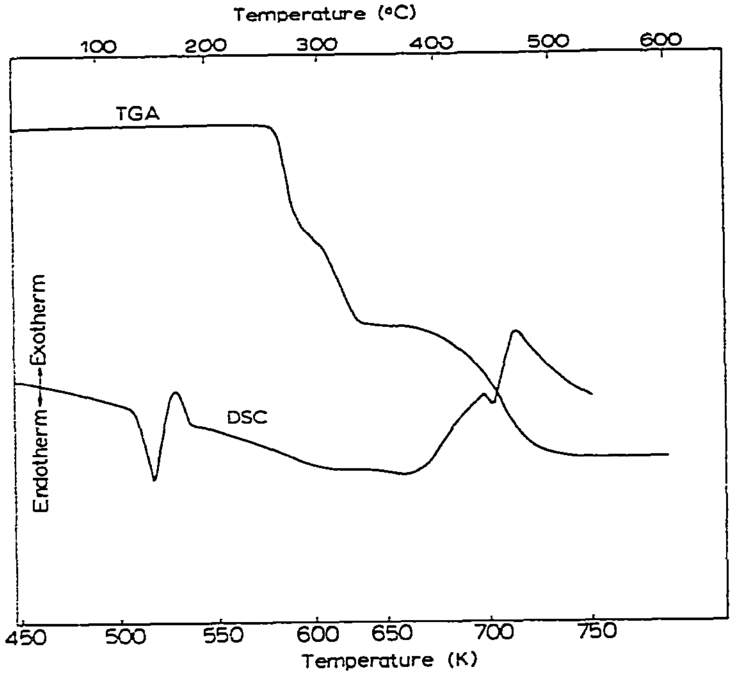


Fig. 1. TGA (°C) and DSC (K) curves of $Mn(HEP)_2$.

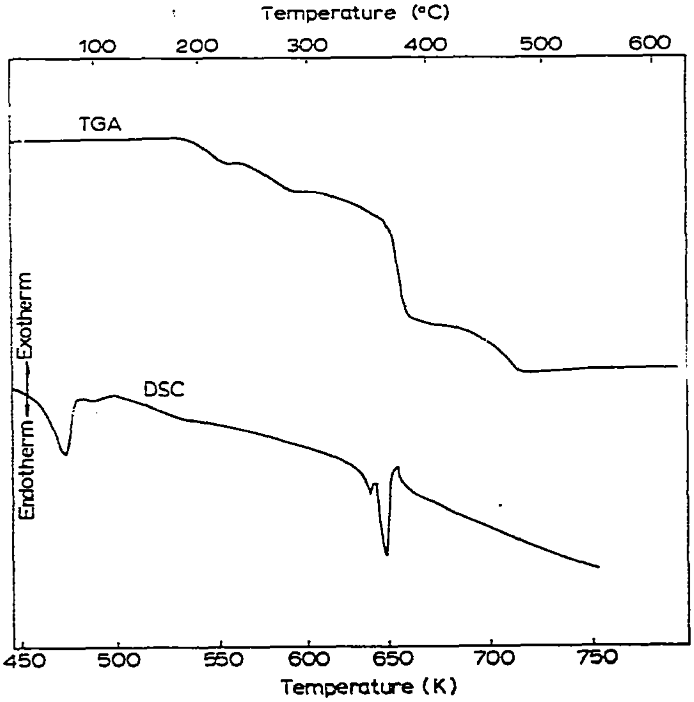
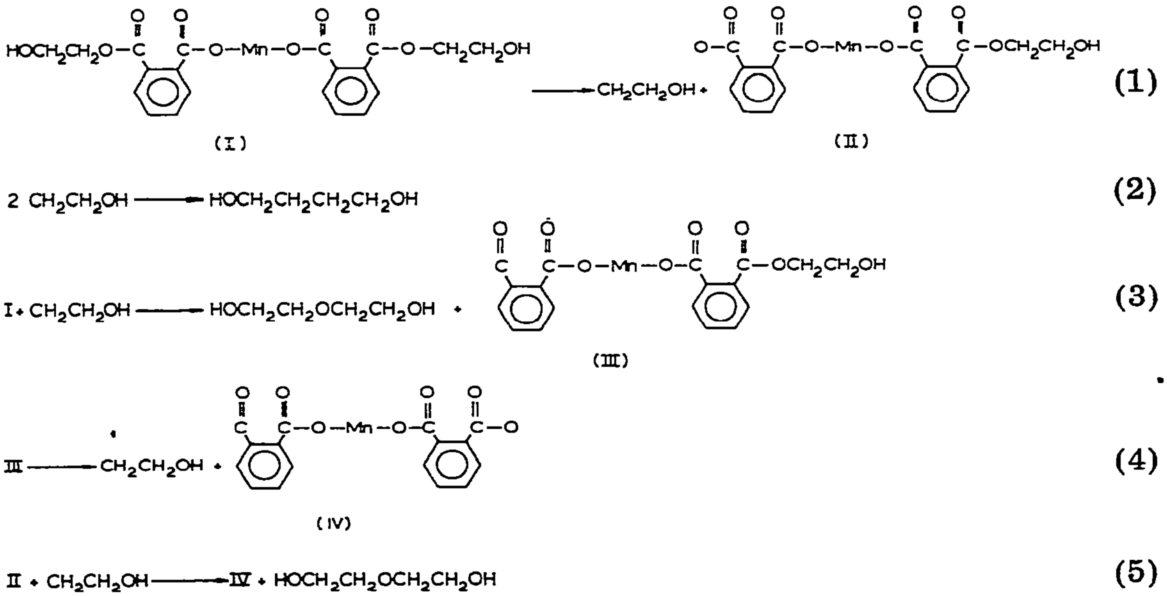


Fig. 2. TGA (°C) and DSC (K) curves of $Pb(HEP)_2$.

curves of Pb(HEP)$_2$ and Mn(HEP)$_2$ show that the modes of decomposition of these two salts are completely different even though they have similar structures. Assuming the correct orders for the decomposition of a particular group, corresponding to a weight loss in the TGA curve, the energies of activation were calculated by integral methods. The decompositions of Mn(HEP)$_n$ (stage I) and Pb(HEP)$_2$ (stage II) deviate from the first order mechanism, as was evidenced by a curvature in the plot of $\ln(1 - c)$ vs. $1/T$. So, the reaction orders for these two stages were calculated to be 1.5 and 1.3, respectively, by the methods of Freeman et al. [7,8].

In the case of Mn(HEP)$_2$, the TGA—DSC curves and the calculated orders of reactions showed that the decomposition of the salt takes place in three stages. The first stage involves steps (1)—(5).

Stage I



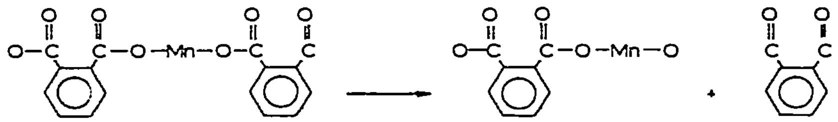
$$2\ CH_2CH_2OH \longrightarrow HOCH_2CH_2CH_2CH_2OH \qquad (2)$$

$$II + CH_2CH_2OH \longrightarrow IV + HOCH_2CH_2OCH_2CH_2OH \qquad (5)$$

Step 1 denotes the slow decomposition of I to give CH_2CH_2OH radicals, which interact with I in a rate determining step to give III and $HOCH_2CH_2O$-CH_2CH_2OH. The radical III decomposes fast to give CH_2CH_2OH and IV. Coupled with the bimolecular termination of CH_2CH_2OH (step 2), reactions (1)—(4) constitute the chain decomposition of stage I. Radical II also reacts with the intermediate CH_2CH_2OH radicals to yield IV. This mechanism for stage I explains the order (1.5) and the high activation energy (150 kcal mole^{-1}) for the simultaneous decomposition of CH_2CH_2OH and OCH_2CH_2OH groups from the salt. The weight loss (first stage) at 251—279°C and an endotherm followed by an exotherm in the same temperature range corresponds to the above decomposition mechanism.

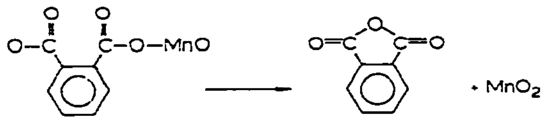
The second (step 6) and third (step 7) stages of the decomposition involve simple first order kinetics, indicating the step-wise decomposition of two groups, one after the other.

Stage II



(6)

Stage III



(7)

The activation energies calculated for the second and third stages are 52 and 48 kcal $mole^{-1}$ respectively. The weight loss (TGA), endotherms and exotherm (DSC) in the temperature range studied correspond to the decomposition of the groups in the above way. The kinetic data calculated by the integral methods for all the above stages of decomposition are presented graphically in Fig. 3 and are given in Table 1.

Although the structure of $Pb(HEP)_2$ is similar to that of $Mn(HEP)_2$, the thermogram, DSC curve and the calculated kinetic parameters show that the mode of decomposition for this salt is entirely different to that of

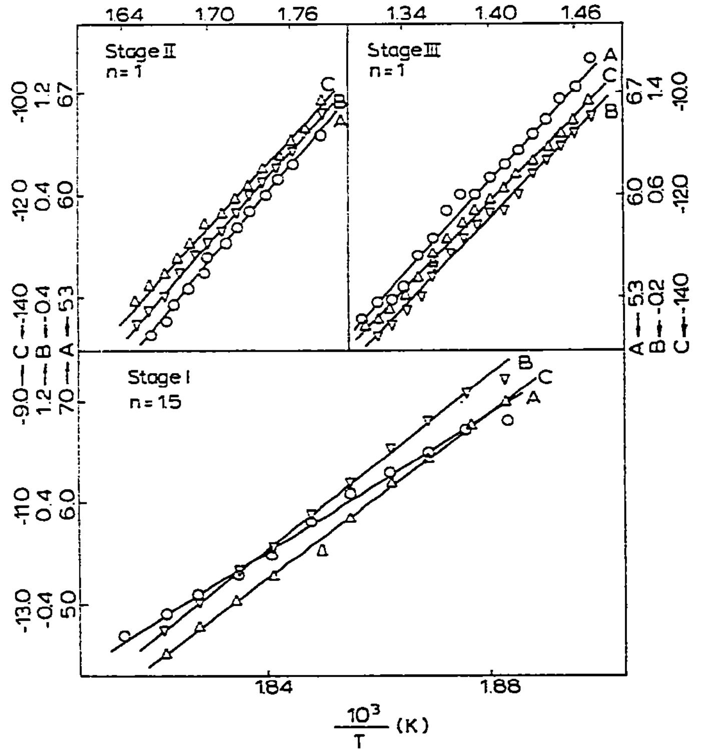


Fig. 3. Kinetic analysis of the thermogram of $Mn(HEP)_2$. A, Coats and Redfern's method (⊙); B , Doyle's method (▽); and C, Murray and White's method (△).

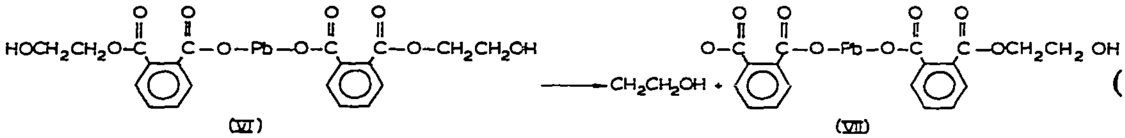
TABLE 1

Kinetic parameters from the TGA curve of $Mn(HEP)_2$ by integral methods

Step no.	Temperature range (°C)	Stage	Order of the reaction n	E (kcal mole^{-1})		
				Coats and Redfern	Doyle	Murray and White
1	251—279	I	1.5	149	145	159
2	279—328	II	1	52	51	54
3	328—498	III	1	46	46	51

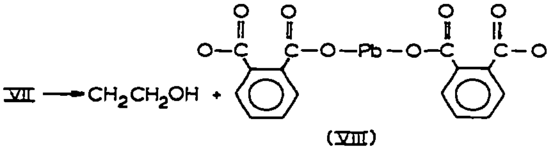
$Mn(HEP)_2$. The thermogram showed that the decomposition of the manganese salt takes place in four different stages. The mechanism of decomposition of $Mn(HEP)_2$ can be written as follows.

Stage I



(8)

Stage II

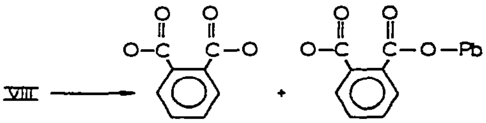


(9)

$$CH_2CH_2OH + \text{VII} \longrightarrow HOCH_2CH_2CH_2CH_2OH + \text{VIII} \quad (10)$$

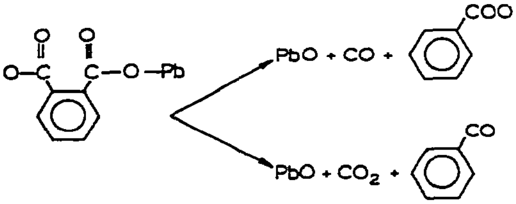
$$2\ CH_2CH_2OH \longrightarrow HOCH_2CH_2CH_2CH_2OH \quad (11)$$

Stage III



(12)

Stage IV



(13)

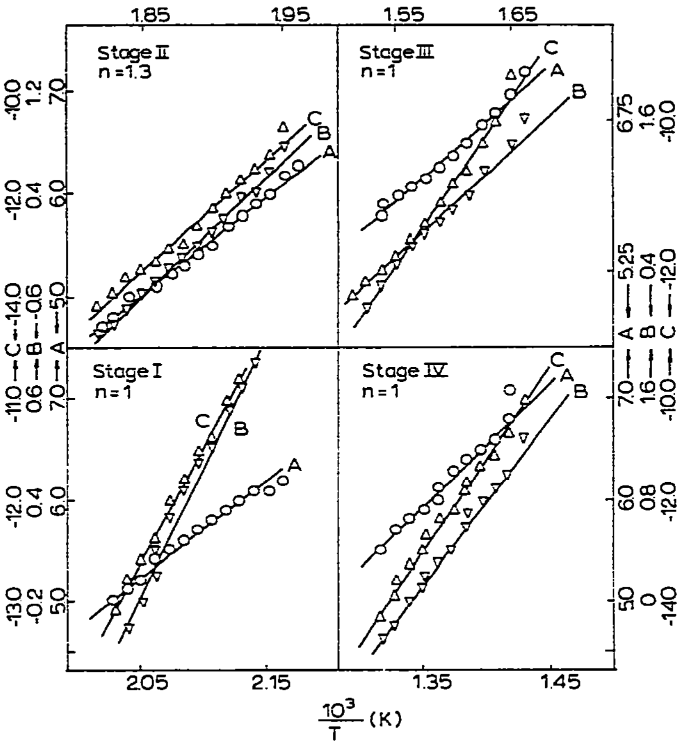


Fig. 4. Kinetic analysis of the thermogram of Pb(HEP)$_2$. A, Coats and Redfern's method (⊙); B, Doyle's method (▽); and C, Murray and White's method (△).

The first (step 8) and the third (step 12) stages involve simple first order decompositions. The 1.3 order for the second stage of reaction can be explained from eqns. (9)—(11). The fourth stage (step 13) takes place stepwise, as indicated in the TGA curve corresponding to the elimination of both CO and CO$_2$ followed by PhCO and PhCOO in a subsequent step. Since the weight loss curve is not well defined for a small temperature interval (378—384° C) corresponding to the loss of CO and CO$_2$, it was not possible to calculate the associated kinetic parameters. The discontinuities in the TGA and DSC curves support the above mechanism. The kinetic data cal-

TABLE 2

Kinetic parameters from the TGA curve of Pb(HEP)$_2$ by integral methods

Step no.	Temperature range (°C)	Stage	Order of the reaction n	E (kcal mole^{-1})		
				Coats and Redfern	Doyle	Murray and White
1	193—230	I	1	49	52	58
2	230—290	II	1.3	45	46	49
3	290—378	III	1	50	49	55
4	384—498	IV	1	71	71	75

culated by the integral methods are presented graphically in Fig. 4 and are given in Table 2.

Of the three integral methods used for the calculation of activation energies, the results obtained from the methods of Coats and Redfern and Doyle are in close agreement, whereas that obtained from Murray and White is slightly high. However, in general, the agreement of the results is quite good.

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REFERENCES

1 J. Sestak, Talanta, 13 (1966) 567.
2 J.H. Sharp and S.A. Wentworth, Anal. Chem., 41 (1969) 2060.
3 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
4 C.D. Doyle, J. Appl. Polym. Sci., 6 (1962) 639.
5 P. Murray and J. White, Trans. Br. Ceram. Soc., 54 (1955) 151.
6 B. Durairaj and K. Venkata Rao, Polym. Bull., 1 (1979) 723.
7 E.S. Freeman and B. Caroll, J. Phys. Chem., 62 (1958) 394.
8 E.S. Freeman and D.A. Anderson, J. Polym. Sci., 54 (1961) 253.