Solid-State Kinetics and Infrared Spectra of Cadmium Soaps

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ABSTRACT

Thermogravimetry has been employed to study the kinetics of
thermal decomposition of cadmium caprate and laurate, and a
probable mechanism of decomposition is proposed. The Free-
man and Carroll method establishes zero-order kinetics. The
energy of activations obtained by the Coats and Redfern method
are consistent with the results of the Freeman and Carroll
method. The infrared absorption spectral characteristics of these
soaps and their respective fatty acids have been reported. The
structures of the soaps are also proposed.

INTRODUCTION

Transition metal soaps have been put to a number of uses in
industry, technology, and allied fields [1-7]. References to their
study in the solid state are sparsely known. Of late, different
scientists have reported IR and diffuse reflectance spectra of a
few transition metal soaps [8-10]. An earlier communication [11]
dealt with the isothermal decomposition of copper(II) soaps and
reported the successful applicability of the Prout Tompkins equation
to such reactions.
The object of the present report is to undertake a systematic study

of the kinetics of the thermal decomposition of cadmium soaps (caprate and laurate) to test the validity of well-known kinetic equations and to examine the thermal stability of these soaps in relation to chain-length compatibility. The IR absorption spectral characteristics of these soaps and their structures have been determined.

EXPERIMENTAL

Materials

Capric and Lauric acids were purified by the method described earlier [12]. Cadmium soaps were prepared by direct metathesis of the corresponding sodium soap in aqueous ethanol with a slight excess of the required amount of cadmium sulfate solution at 50-55°C. The precipitated soaps were washed several times with hot distilled water and then with alcohol to remove the free precipitant and the acid. The cadmium soaps thus obtained were dried in vacuum. The soaps were recrystallized from a hot benzene-methanol mixture (1:1). The soaps obtained were in the hydrated form. All chemicals used were of reagent grade.

The results of elementary analysis were as follows. Cadmium caprate monohydrate (Found: Cd, 23.84; C, 50.41; H, 8.37. Calculated for $CdC_{20}H_{40}O_5$: Cd, 23.77; C, 50.80; H, 8.47%). Cadmium laurate monohydrate (Found: Cd, 21.33; C, 54.30; H, 8.98. Calculated for $CdC_{24}H_{48}O_5$: Cd, 21.25; C, 54.49; H, 9.15%). The TGA was carried out on a TGA instrument made by FCIL, India. The rate of heating was 10°/min. IR absorption spectra of fatty acids and their respective cadmium soaps were determined with a Perkin-Elmer Model 577 grating spectrophotometer in a Nujol mull in the region 4000-400 cm^{-1}.

RESULTS AND DISCUSSION

Thermogravimetry

A plot of the weight loss of the sample w vs time t (Fig. 1) for cadmium caprate and laurate shows that initially the soap decomposes slowly and then rapidly, and finally becomes almost constant. The slight leap in the beginning of the curve may be due to the breaking of the uncoordinated water molecule attached to the soap. The decomposition can be expressed as

$$(RCOO)_2Cd.H_2O \longrightarrow R_2CO + CdO + CO_2 + H_2O$$
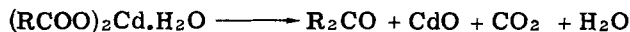
where R represents the alkyl group in the soap anion. The results
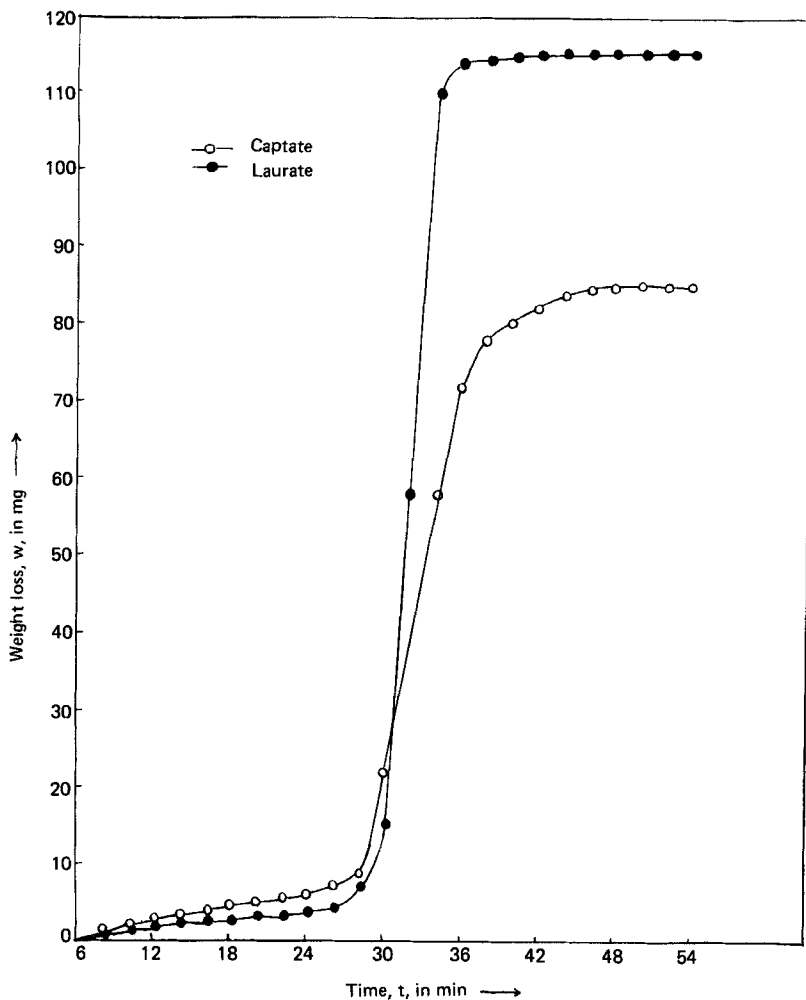
FIG. 1. Thermogravimetric analysis of cadmium soaps.

show that the final residue is cadmium oxide because the weights of
the residues are almost equal to the theoretically calculated weights
of cadmium soaps from their molecular formula.

The Freeman-Carroll method [13] has been applied to these
soaps because the decomposition is continuous and one of the
product is gaseous. The equation is

$$\frac{\Delta \log \dfrac{dw}{dt}}{\Delta \log W_r} = - \frac{E}{2.303R} \frac{\Delta \left[\dfrac{1}{T} \right]}{\Delta \log W_r} + n \tag{1}$$

where E = energy of activation

n = order of reaction

$W_r = (W_0 - W)$, i.e., total loss in weight - loss in weight at time t

$\dfrac{dw}{dt}$ = values of rate of weight loss determined from weight loss
- time curves by drawing tangents at appropriate times.

For convenience, Eq. (1) may be represented as

$$\psi_w = \frac{E}{2.303F} \psi_T + n \tag{2}$$

The plot of ψ_w vs ψ_T yields a straight line passing through origin (Fig. 2), confirming zero-order kinetics (n = 0) for the decomposition of cadmium soaps and is in consonance with the findings of Mehrotra and Kachhwaha [14]. The energies of activation for caprate and laurate are 23.0 and 36.1 kcal/mol, respectively.

Mention may also be made of the fact that during the course of such decomposition the soap molecules are covered by the molecules of the gaseous product. The rate of such a reaction, following zero-order kinetics, may be represented by

$$\frac{dx}{dt} = \frac{K_1 p}{K_2 p + 1} \tag{3}$$

where K_1 and K_2 are constants and p is the pressure of the gaseous product. Rasheed and Bhobe [15] also confirmed zero-order kinetics for zinc stearate and explained that here also the surface is completely covered by the product, and the rate of decomposition becomes constant.

An attempt has been made to make use of the Coats-Redfern [16] derived equation (for n = 0) for the study of solid-state decomposition under dynamic conditions:

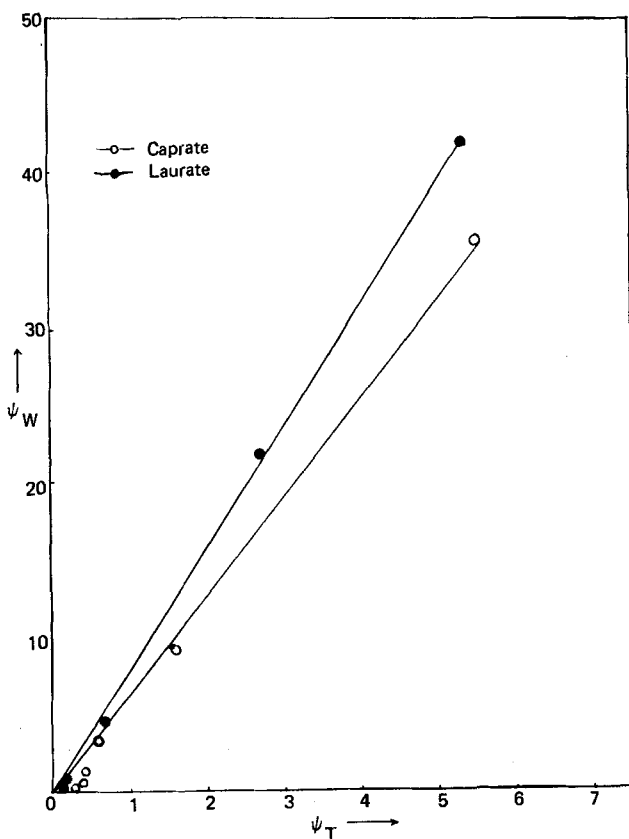$$\log \frac{\alpha}{T^2} = \log \frac{AR}{aE} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.303RT} \tag{4}$$

FIG. 2. ψ_W vs ψ_T plots for cadmium soaps.

where A, a, and α are the preexponential factor, the rate of heating, and the fraction of soap decomposed at time t, respectively. The values of log α/T^2 and T^{-1} for cadmium soaps are given in Table 1. Note that in the Coats and Redfern method the straight-line plots have some points at the beginning and some points at the end that are a bit removed from the straight lines. The energy of activation evaluated from log α/T^2 vs T^{-1} plots for caprate and laurate is 21.2 and 35.4 kcal/mol, respectively. These values are in close agreement with the values obtained from the Freeman-Carroll equation. It is interesting to record that the activation energy increases with an increase in chain length of the carbon atoms in the soap anion.

TABLE 1. Coats-Redfern Parameters

No.	Temperature T (°K)	$\frac{1}{T} \times 10^3$	Cadmium caprate		Cadmium laurate	
			α	$\log \frac{\alpha}{T^2}$	α	$\log \frac{\alpha}{T^2}$
1	573	1.7452	0.0726	-6.6551	0.0457	-6.8559
2	593	1.6863	0.1667	-6.3243	0.0980	-6.4547
3	613	1.6313	0.3632	-6.0947	0.3791	-5.9961
4	633	1.5797	0.5427	-5.8682	0.7189	-5.7461
5	653	1.5313	0.6154	-5.8406	0.7451	-5.7576
6	673	1.4858	0.6624	-5.8349	0.7484	-5.7819
7	693	1.4435	0.6838	-5.8465	0.7484	-5.8073

Infrared Absorption Spectra

In Tables 2 and 3 the frequencies (cm^{-1}) of the IR absorption
maxima of the fatty acids and their respective cadmium soaps are
given with their important assignments.

The absorption spectral characteristics of the aliphatic portion
of acid molecules are mostly unchanged while proceeding from acid
to soap. The absorption band at about 2650 cm^{-1} in soaps is assigned
to the O–H stretching of hydrated water. Due to complexity of hydro-
gen bonding, O–H stretching vibrations in the hydrated soaps are
not completely free. Similar observations have been reported by
Koga and Matuura [17].

Fatty acids are known to exist with a dimeric structure with
hydrogen bonding. The absorption maxima in the spectrum of capric
acid and lauric acid at 1680 and 1700 cm^{-1}, respectively, are due to
the C=O group of these acids which disappears in the soap spectra.
Two new, strong absorption bands appear in the region 1535-1525
and 1460-1450 cm^{-1}. These bands are assigned to the symmetric
and antisymmetric vibrations of the carboxylate ion, respectively.
These observations are in agreement with the frequencies assigned
by Kagarise [18] for phenyl stearic acid. The disappearance of C=O
band in the soap spectra shows that there is resonance in the two
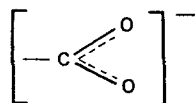C–O bonds of the carboxyl group. This group will have structure

$$\left[-C \underset{O}{\overset{O}{\lessgtr}} \right]^-$$

TABLE 2. Absorption Spectral Characteristics of Capric Acid and Cadmium Caprate[a]

Frequency (cm^{-1})		
Capric acid	Cadmium caprate	Assignment
2660 vs	2660 m	Stretching O–H
1680 vs	-	Stretching C=O
	1525 vs	COO⁻, C–O antisym. stretching
	1460 vs	COO⁻, C–O sym. stretching
1405 vs	-	CH_2 deformation (adjacent to COOH group)
	1375 vs	CH_3 sym. deformation
⎧ 1270	⎧ 1310	
⎨ 1250	⎪ 1270	Progressive bands
⎩ 1220	⎨ 1235	CH_2 twisting and wagging
	⎩ 1165	
1100 S	1110 m	Stretching C–C
930 vs	955 w	OH out-of-plane deformation
720 vs	725 s	Rocking CH_2
660 m	655 w	
605 m	600 w	
530 m	495 w	
470 m	450 w	

[a]Key to abbreviations: vs = very strong, m = medium, s = strong, w = weak.

Mehrotra and Saroha have reported a similar observation for rubidium soaps [19].

A number of progressive bands is observed for both soaps and fatty acids in the 1350-1080 cm^{-1} region. These progressive bands of cadmium soaps are weaker than those of fatty acids. The absorption band in the 955-930 cm^{-1} region may be assigned to the OH out-of-plane deformation.

The absorption spectra of fatty acids and soaps at about 720 cm^{-1} with a strong intensity are observed either as singlets or doublets. These absorptions may be due to the rocking vibration of a chain of the methylene group $-(CH_2)_n-$.

TABLE 3. Absorption Spectral Characteristics of Lauric Acid and Cadmium Laurate

Frequency (cm^{-1})		Assignment
Lauric acid	Cadmium laurate	
2650 w	2660 m	Stretching O–H
1700 s	–	Stretching C=O
	1535 vs	COO⁻, C–O antisym. stretching
1449 m	1450 vs	COO⁻, C–O sym. stretching
1350-1090	1345-1080	Progressive bands
1120 w	1115 m	Stretching C–C
950 s	930 w	OH out-of-plane deformation
720 w	725 m	Rocking CH₂
685 s	700 m	
550 s	620 w	
475 m	590 w	
445 w	500 w	
420 s	470 w	
	435 w	
	410 s	

The absorption maxima of soaps in the 600-400 cm^{-1} region can't be exactly assigned as they are very sensitive to metal. These absorptions are probably due to the modes of lattice water which are also observed in this region. These librational bands are assigned to rocking and wagging modes of lattice water [20].

ACKNOWLEDGMENTS

REFERENCES

[1] A. S. C. Lawrence, J. Inst. Pet. Technol., 31, 303 (1945).

[2] F. Fuben and A. G. Bayer, German Patent 1,172,686 (C1, C07C), (June 25, 1964).

[3] L. W. Kalinowski, French Patent 1,418,876 (C1,C09j; C23C) (November 26, 1965).

[4] Imperial Chemical Industries Ltd., British Patent 1,033,999 (C1,C089), (June 22, 1966).

[5] H. S. Sahid, H. S. Asjad, and Mustaf, J. Sci. Ind. Res. (Pakistan), 10, 197 (1967).

[6] M. Arthur, Canadian Patent 433,433 (March 5, 1946).

[7] B. Jadrnicek and K. Vesely, Collect. Czech. Chem. Commun., 35, 358 (1970).

[8] C. G. Macarovici and G. Schmidt, Rev. Roum. Chim., 9, 693 (1964).

[9] R. Matuura, Nippon Kagaku Zasshi, 86, 560 (1965).

[10] V. P. Mehta, R. C. Govil, and T. N. Nagar, Z. Naturforsch., 25b, 310 (1970).

[11] K. N. Mehrotra, V. P. Mehta, and T. N. Nagar, Ibid., 28b, 90 (1973).

[12] K. N. Mehrotra, V. P. Mehta, and T. N. Nagar, J. Prakt. Chem., 313, 607 (1971).

[13] E. Freeman and B. Carroll, J. Phys. Chem. Ithaca, 62, 394 (1958).

[14] K. N. Mehrotra and R. Kachhwaha, Bull. Inst. Pol., 28, 45 (1978).

[15] A. Rasheed and R. A. Bhobe, J. Indian Chem. Soc., 53, 442 (1976).

[16] A. W. Coats and J. P. Redfern, Nature, 208, 68 (1964).

[17] Y. Koga and R. Matuura, Mem. Fac. Sci., Kyushu Univ., Ser. C, 4, 1 (1961).

[18] R. E. Kagarise, J. Phys. Chem., 59, 271 (1955).

[19] K. N. Mehrotra and S. P. S. Saroha, J. Indian Chem. Soc., 56, 466 (1979).

[20] K. Nakamota, Infrared and Raman Spectra of Inorganic and Coordinated Compounds, 3rd ed., Wiley, New York, 1978, p. 227.