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Thermal studies of organozinc films.
Part 11

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Abstract

The thermal stability of organozinc films was studied by thermogravimetric analysis (TGA) between 25 and 550°C min^{-1}. The decomposition temperatures were obtained from the maximum of the first derivatives of the TG curve. The kinetic parameters of the thermal decomposition were determined by the Arrhenius equation. All the films degraded in one step with a very small weight loss. Films prepared with toluene and THF exhibit higher weight losses, 23.77% and 12.48%, respectively, and zinc-2-propanol film is the most stable (1.11% weight loss).

The variation in thermal stability is discussed in relation to the various solvents used and comparisons are made with the results reported for Pd, Ge and In organo films. For organozinc films, the stability decreases for the solvents used in the order: dimethyl sulphoxide (DMSO), isobutyl methyl ketone, 2-butanone, ethanol, 2-propanol, acetone, dimethylformamide (DMF), tetrahydrofuran (THF).

The activation energies of the thermal degradation are comparable with those for organo-Pd films. The order of reaction for the thermal decomposition of organozinc films was found to be −0.5 for most of them, with films prepared from ethanol and toluene having zero reaction order. The pre-exponential factor, the reaction order and the activation energy of the decomposition for organozinc films have been determined for most of the solvents.

INTRODUCTION

The deposition and formation of regular layers of a certain material on a solid of different composition is usually achieved to modify or improve its properties, e.g. the electrical, magnetic and optical properties [1–4].

For some applications (catalysts, ceramics and in the paint industry), powders consisting of uniform spherical particles are highly desirable because their optical characteristics can be better controlled.

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In this work, the preparation and thermal properties of organozinc films are described. From their thermograms, it is possible to obtain information about the stability of these films. We have used chemical liquid deposition (CLD) [5,6] with non-aqueous living colloidal metals [7,8].

When metal atoms are allowed to deposit with organic solvents at low temperature, atom agglomeration takes place [5–8]. Colloidal-sized metal particles are formed by the migration and clustering of metal atoms. By removing the solvent from these sols, particle growth can occur by combination to larger and larger particles or films [5–8], or by flocculation due to weak cluster–cluster interactions [9]. These colloidal solutions can serve as precursors for metal films.

A study of the properties of ZnO particles dispersed in ethanolic solutions was recently reported [10]. Spherical ZnO particles were obtained after drying; these particles are morphologically very similar to our Zn–benzene and Zn–toluene powders.

Another colloid ZnS organosolv in DMF produced a transparent colourless solution [11]. In contrast, our Zn–DMF colloid is black and stable at room temperature.

Finally, a comparison with other organometallic films [12] is made. The Zn films were prepared with the organic solvents acetone, 2-butanone, isobutyl methylketone, dimethylformamide (DMF), tetrahydrofurane (THF), dimethyl sulfoxide (DMSO), ethanol, 2-propanol, benzene, toluene, and their subsequent evaporation.

EXPERIMENTAL

Colloid synthesis

The colloids were prepared by co-condensation of the solvents with the metals at 77 K using a metal atom reactor [13,6]. The following solvents were used following freeze–thaw degasification: acetone, 2-butanone, isobutyl methylketone, DMF, THF, DMSO, ethanol, 2-propanol, toluene and benzene. The approximate concentration could be calculated from the weight of metal evaporated and solvent added by assuming that all the metal evaporated is on the colloid (around 10^{-3} M).

Metal films

The metal-like films were prepared by evaporating the solvent on a glass cover under vacuum (10^{-3} Torr) for 2–3 h. Then the films were pumped out for another 24 h. The dried films were analysed; their metal content ranged from 64 to 80%. No melting point was observed.

Thermogravimetry

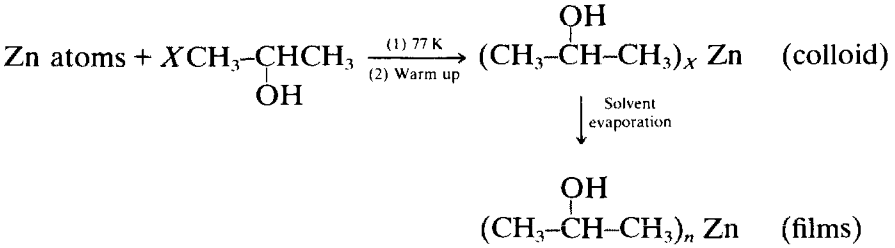
A Perkin-Elmer Model TGS-2 thermogravimetric system, with a microprocessor-driven temperature control unit and a TA data station, was used. The weights of the samples were recorded accurately and were generally in the range of 4–10 mg.

The sample pan was placed in the balance system and the temperature was raised from 25 to 550°C at a heating rate of 10°C min^{-1}. The weight of the sample pan was recorded continuously as a function of the temperature.

RESULTS AND DISCUSSION

The syntheses and properties of metal films have been reported by us [6, 14].

Zinc films are easily prepared by evaporation of the respective solvents under vacuum [14]. The organozinc films exhibit a high metal content (approx. 80%) and low levels of carbon and hydrogen.



$$\text{Zn atoms} + X\,\mathrm{CH_3{-}\underset{\displaystyle OH}{C}HCH_3} \xrightarrow[\text{(2) Warm up}]{\text{(1) 77 K}} (\mathrm{CH_3{-}\overset{\displaystyle OH}{C}H{-}CH_3})_X\,\mathrm{Zn} \quad \text{(colloid)}$$

$$\downarrow \text{Solvent evaporation}$$

$$(\mathrm{CH_3{-}\overset{\displaystyle OH}{C}H{-}CH_3})_n\,\mathrm{Zn} \quad \text{(films)}$$

$n = 2, 4$

These films are easily oxidized in the presence of oxygen, but they are stable in inert atmosphere. The formation of films from colloids with non-aqueous solvents (ketones and alcohols) by just letting them dry is more interesting. Colloid formation can occur either by amalgamation to larger particles or films [5, 8], or by formation of cluster interactions [15]. The films obtained cannot be redissolved in organic solvents. Interestingly, these films were also metallic in appearance, with a small amount of residual organic material.

The decomposition reaction is irreversible so that the rate-dependent parameters, such as the activation energy and the order of reaction may be calculated from a single experimental curve [16]. From the Arrhenius equation, we can obtain information about the specific rate constant k and the activation energy E.

The thermal decomposition kinetics of the thermogravimetric weight loss can be expressed in terms of the kinetic equation $-\mathrm{d}\alpha/\mathrm{d}t = k(1-\alpha)^n$, where α is the fraction of the sample weight reacted at time t, n is the reaction order and k is the specific rate constant. The reaction rate $d\alpha/dt$ was calculated using a differential technique with a heating rate v [17].

Using the eqn. (1) with $v = 10°\text{C min}^{-1}$, and expressed in K, we obtain

$$\beta = \ln\left[\frac{(d\alpha/dT)}{6(1-\alpha)^n}\right] = \ln A - \frac{E}{RT} \tag{1}$$

A computer linear multiple regression program was used to calculate the kinetic parameters E and A from a linear least-squares fit of the data in a semilog plot of β against $1/T$ (see Fig. 1). A straight line should be obtained, and E and A can be calculated from the slope and intercept, respectively. This method is very similar to that reported by Ma et al. [18]. The coefficients of linear correlation range from 0.9915 to 0.9988.

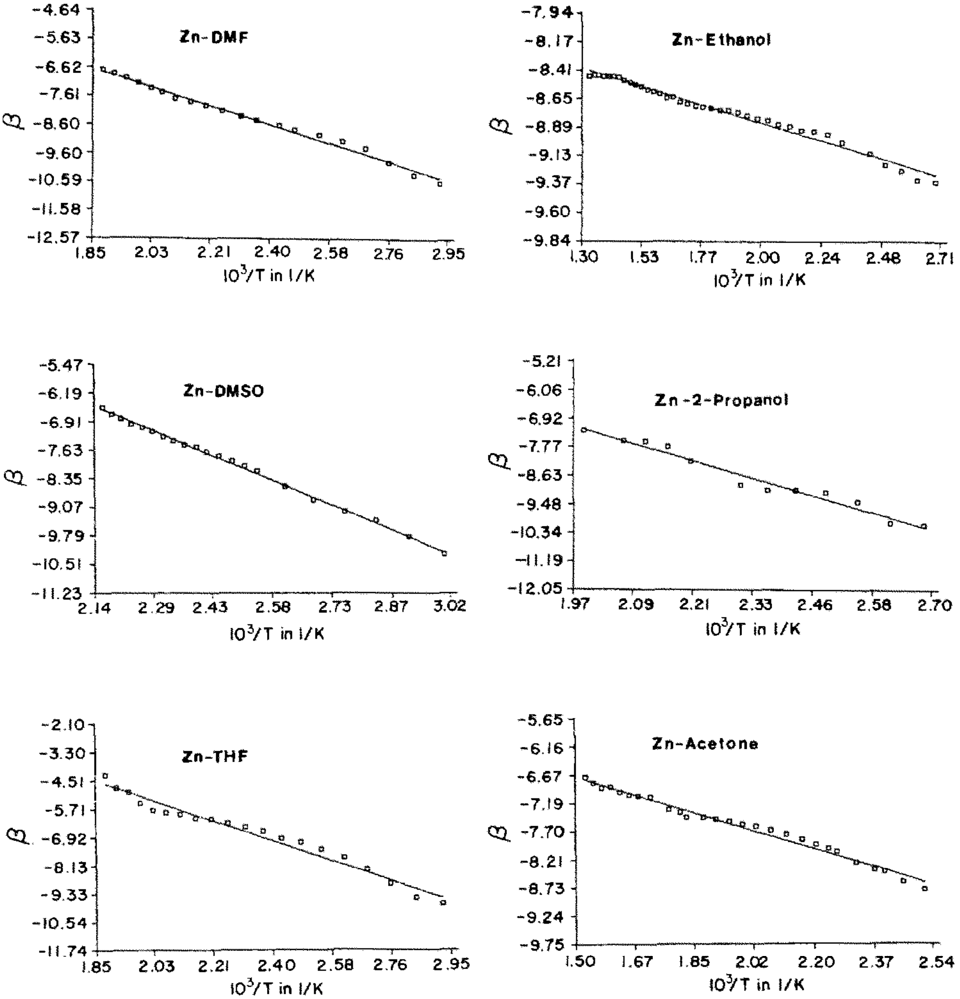


Fig. 1. Arrhenius plot for the thermal decomposition of some organozinc films according to eqn. (1).

TABLE 1

Correlation between weight loss (%) and temperature for organozinc films

Temp./°C	Film 1	Film 2	Film 3	Film 4	Film 5	Film 6	Film 7	Film 8	Film 9	Film 10
50	–	–	–	–	–	0.31	–	–	0.30	–
100	0.40	–	–	1.22	3.81	2.86	0.98	0.12	2.09	0.81
150	0.86	0.18	0.25	3.04	8.04	7.83	1.60	0.35	3.62	1.69
200	1.36	0.78	1.17	5.11	9.19	9.89	2.00	0.98	4.62	4.37
250	1.64	1.48	1.29	6.14	9.96	11.80	2.50	1.09	5.55	15.52
300	1.75	2.08	3.20	6.54	10.58	13.00	2.89	1.11	6.40	23.19
350	1.84	3.43	4.02	6.54	11.06	14.17	3.47	1.11	7.28	23.25
400	1.81	5.38	5.28	6.84	11.69	15.82	41.16	1.11	8.10	23.67
450	1.88	6.70	6.27	7.35	12.33	17.65	4.70	1.11	8.82	23.68
500	1.90	7.23	7.29	8.16	12.40	18.84	4.95	1.11	8.82	23.77
550	1.90	7.52	8.00	8.30	12.48	19.96	4.99	1.11	8.82	23.77

Key: 1, Zn–acetone; 2, Zn–2-butanone; 3, Zn–isobutyl methyl ketone; 4, Zn–DMF; 5, Zn–THF; 6, Zn–DMSO; 7, Zn–ethanol; 8, Zn–2-propanol; 9, Zn–benzene; 10, Zn–toluene.

The weight losses with temperature (Table 1) of these organozinc films show that they are very stable, as with less than 10% weight loss, except, Zn–THF, Zn–DMSO and Zn–toluene which show between 12.48% and 23.77% weight loss.

The activation energy values of the films containing carbonyl or related groups are very similar, ranging from 16.10 for acetone to 39.60 kJ mol^{-1} for THF (Table 2). The highest values are obtained with toluene and benzene, with 40.30 and 51.60 kJ mol^{-1}, respectively. These values are probably higher due to the formation of very thin powders instead of films.

Furthermore, 2-propanol gives a very similar value to that obtained with acetone, probably due to the inductive effect of the methyl group and the

TABLE 2

Kinetic parameters for organozinc films

Films	n	E_a/(kJ mol^{-1})	Z/(s^{-1})	Temp. range/°C
Zn–acetone	−0.5	16.10	2.3×10^{-2}	125–380
Zn–2-butanone	−0.5	26.70	2.5×10^{-2}	172–508
Zn–isobutyl methyl ketone	−0.5	23.60	1.9×10^{-2}	170–548
Zn–DMF	0	36.60	1.0	70–400
Zn–THF	−1.0	39.60	83.7	70–260
Zn–DMSO	−0.5	36.10	16.2	60–190
Zn–ethanol	0	5.50	5.0×10^{-2}	100–480
Zn–2-propanol	−0.5	35.50	3.8	100–230
Zn–benzene [a]	−0.5	51.60	1.1×10^{4}	45–450
Zn–toluene [a]	0	40.30	2.1	160–280

[a] These are not films; they look like metal powders.

almost identical size of the molecules. However, Zn–ethanol, being a small molecule, shows a behaviour similar to that of Pd–ethanol [12]. This is due to the higher oxidation potential of Zn, and as a consequence, the film exhibits the lowest activation energy.

These E_a values are lower than those obtained from Pd, Ge and In films due to the higher oxidation potential of Zn. Most of the films exhibited a reaction order of -0.5 for the decomposition reaction, probably due to the very high stability of the films and the complex elimination of some of the solvent incorporated. The thermostability of these metal films depends on the solvent incorporated.

Finally, it should be noted that these films are easily oxidized and the TG sample must be prepared and handled with care. This is the first report for the preparation and thermal decomposition of these films so no comparative data are available.

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REFERENCES

1 G.D. Parfitt and J. Ramsbotham, J. Oil Colour Chem. Assoc., 54 (1971) 356.
2 R.M. Cornell, A.M. Posner and J.P. Quirk, J. Chem. Technol. Biotechnol., 30 (1980) 187.
3 A.J. Frank, I. Willner, Z. Goren and Y. Degoni, J. Am. Chem. Soc., 109 (1987) 3568.
4 C. Morrison and J. Kiwi, J. Chem. Soc. Faraday Trans. 1, 85 (1989) 1043.
5 G. Cárdenas-Triviño, M. Alvial J. and K.J. Klabunde, Bol. Soc. Chil. Quím., 35 (1990) 277.
6 G. Cárdenas-Triviño and K.J. Klabunde, Bol. Soc. Chil. Quím., 33 (1988) 163.
7 G. Cárdenas-Triviño, K.J. Klabunde and E.B. Dale, Langmuir, 3 (1987) 986.
8 S.T. Lin, M.T. Franklin and K.J. Klabunde, Langmuir, 2 (1986) 259.
9 K.J. Klabunde, G. Cárdenas T. and M.T. Franklin, US Patent 4,877,647, 1989.
10 E. Matijevic, M. Ocaña and W. Peter Hsu, Langmuir, 7 (1991) 291.
11 T. Yamamoto, K. Osakata, A. Taniguchi and E. Kubota, Chem. Mater., 4 (1992) 562.
12 G. Cárdenas T. and L.H. Tagle D., Thermochim. Acta, 184 (1991) 131.
13 G. Cárdenas T. and P.B. Shevlin, Bol. Soc. Chil. Quím., 32 (1987) 111.
14 G. Cárdenas T. and R. Oliva C., Bol. Soc. Chil. Quím., 38 (1993) 49.
15 E.B. Zuckerman, K.J. Klabunde, B.J. Olivier and C.M. Sorensen, Chem. Mater., 1 (1989) 12.
16 E.S. Freeman and B. Carroll, J. Phys. Chem., 621 (1958) 394.
17 W.Y. Wen and J.W. Lin, J. Appl. Polym. Sci., 22 (1978) 2285.
18 S. Ma, G. Huang and J.O. Hill, Thermochim. Acta, 184 (1991) 131.