Thermochimica Acta, 62 (1983) 141–147
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

DERIVATOGRAPHIC BEHAVIOUR OF THALLIUM(I) MALONATE

FADHIL JASIM

Department of Chemistry, College of Science, University of Baghdad, Baghdad (Iraq)

(Received 10 August 1982)

ABSTRACT

TG, DTG, and DTA studies of thallium(I) malonate, $CH_2(COOTl)_2$ [= Tl_2(mal)], using the derivatograph, have been carried out under static air and dynamic nitrogen atmospheres in the temperature range ambient to 1050°C. In air or nitrogen the malonate ion decomposes into first, formaldehyde, and second, unstable thallous bicarbonyl oxide which eventually disproportionates into CO and Tl_2O. The latter oxidizes to form Tl_2O_3. The oxidation takes place in two steps. In the presence of nickel powder the steps are combined into a larger one, thereby lowering the oxidation process by 80°C. Two temperature spans are found over which drying and ignition of thallous malonate can be dried and ignited. The kinetic parameters for some decomposition steps in the presence of nickel have been elucidated and found to be 3.307 and 32.535 kcal mole^{-1} for the order of the decomposition reaction and activation energy, respectively.

INTRODUCTION

The isothermal decomposition of copper(II) malonate has been studied at different temperatures [1]. The TG, DTG, DTA, and EGA of bivalent transition metal malonates such as Mn, Fe, Co, Ni, Cu, and Cd malonates have been investigated and a possible reaction mechanism for the decomposition of malonates has been presented [2]. The thermogravimetry of lanthanoid malonate hydrates in static air and in streams of N_2, O_2, and CO_2 was conducted by Nagase et al. [3], and the decomposition process and mechanism proposed. The thermal decomposition temperatures and heats of polymorphic changes of thallium(I) fatty acid salts have been studied derivatographically under air or nitrogen atmospheres [4] and thermodynamic data calculated.

The thermal behaviour of thallium(I) perchlorate under vacuum inert atmospheres has been discussed elsewhere [5]. Vishnu and Srivastava [6] made critical TG and DTG studies of the high temperature volatilization of thallic oxide obtained from different origins and using crucibles made of different materials.

In general, information concerning the thermal decomposition of heavy metal malonates is scanty. To the best of the author's knowledge no hints concerning the thermal degradation of Tl_2(mal) have so far been reported. The present paper deals with the TG, DTG, and DTA behaviour of this metal chelate alone and in the presence of nickel powder.

EXPERIMENTAL

TL_2(mal) was obtained from BDH; nickel powder (purum) was supplied by Fluka AG Buckes SG. All other chemicals, equipment, and techniques were as described previously [7]. The weight of the sample was 200 mg.

RESULTS AND DISCUSSION

Figure 1 shows the TG, DTG, and DTA curves for the thermal decomposition of Tl_2 (mal) under static air atmosphere (solid line) in the temperature range ambient to 1050°C. Quantitative evaluation of the TG and DTG curves indicates first a loss of negligible amounts of volatile impurities and moisture. At 195°C, two consecutive rather steep steps are observed representing the decomposition of thallium(I) malonate. The total loss here is equivalent to the elimination of 39.86 mg, which is equal to the malonate ion originally present in the sample (19.93%). The first small step on the DTG curve exhibits the resolution of two overlapping endothermic reactions where formaldehyde evolves (this is detected by chemical analysis made in separate experiments). The second larger, sharper endotherm which starts at 260°C may be attributed to the decomposition of the presumably formed $Tl_2(CO)_2O$, thallous bicarbonyl oxide, which might be obtained under the absolute anhydrous conditions inside the furnace; its presence has been predicted from evaluation of the TG curve according to the tentative equations

$$CH_2(COOTl)_2 \xrightarrow{\Delta} HCHO + Tl_2(CO)_2O$$

$$Tl_2(CO)_2O \xrightarrow{\Delta} Tl_2O + 2\ CO$$

Although no analytical evidence could be offered for the presence of this bicarbonyl of thallous oxide, TG, DTG and DTA provide a robust testimony for its occurrence.

The comparatively large, sharp exo-peak at 355°C represents the total liberated heat energy due to rapid oxidation of all CO and one-half Tl_2O (gain of 6 mg of oxygen). It is seen from the TG curve that a horizontal plateau continues up to 440°C where a solution of solid Tl_2O_3 and molten Tl_2O has been detected (Table 1). Visual observation of the residue indicates

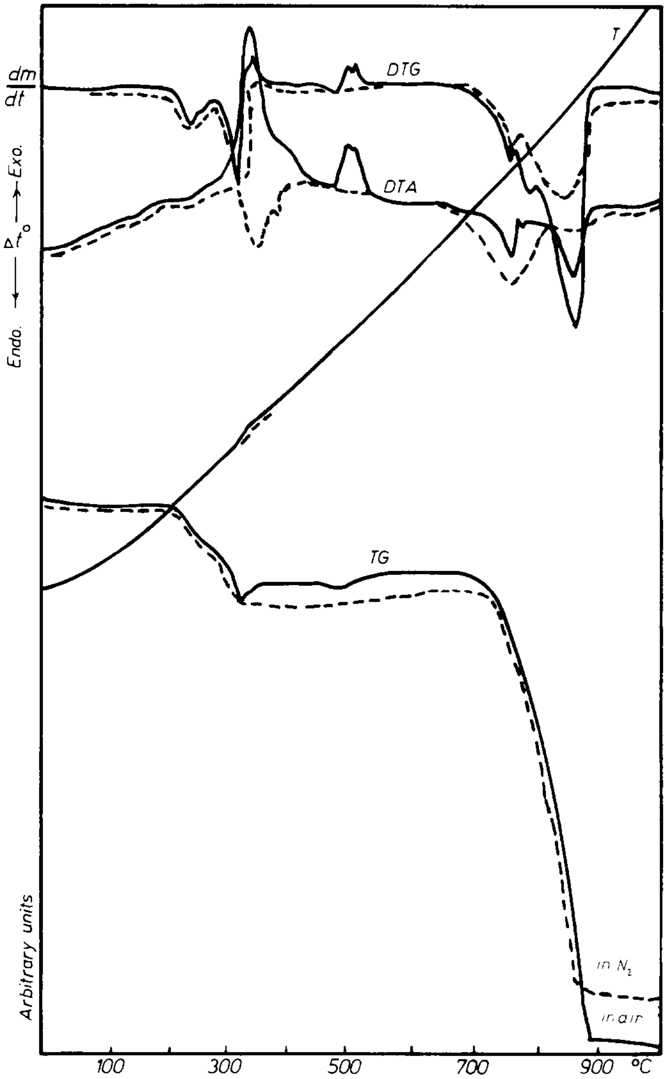

Fig. 1. TG, DTA and DTG curves for the thermal decomposition of thallous malonate.

a black powder containing black lustrous crystals. After 440°C, the second half of Tl_2O is oxidized (gain of another 6 mg) and consequently small exo-peaks are observed on both DTA and DTG curves. The small notches seen on the apexes of the oxidation exotherms indicate that oxidation is a multistep process. The negligible but reproducible loss in weight that precedes the DTG and TG peaks at 440°C may be due to partial volatilization of the Tl_2O melt.

However, on heating a 1 : 1 : : Ni : Tl_2(mal) molar ratio mixture (Fig. 2), the two oxidation steps of thallous oxide are combined in a larger one (gain of exactly 12 mg of oxygen) that extends over a T_i–T_f span of 355–440°C

TABLE 1

d-Spacing and relative intensities of the XRD peaks for thallium(I) malonate samples preheated to 400, 600, and 1020°C in static air atmosphere

	400°C Thallic and thallous oxides			600°C Thallic oxide			1020°C Unknown phases		
d(Å)	3.424	3.292	2.533	3.0354	2.631	1.857	2.263	1.955	1.388
I/I_0	100	90	80	100	40	50	100	35	30

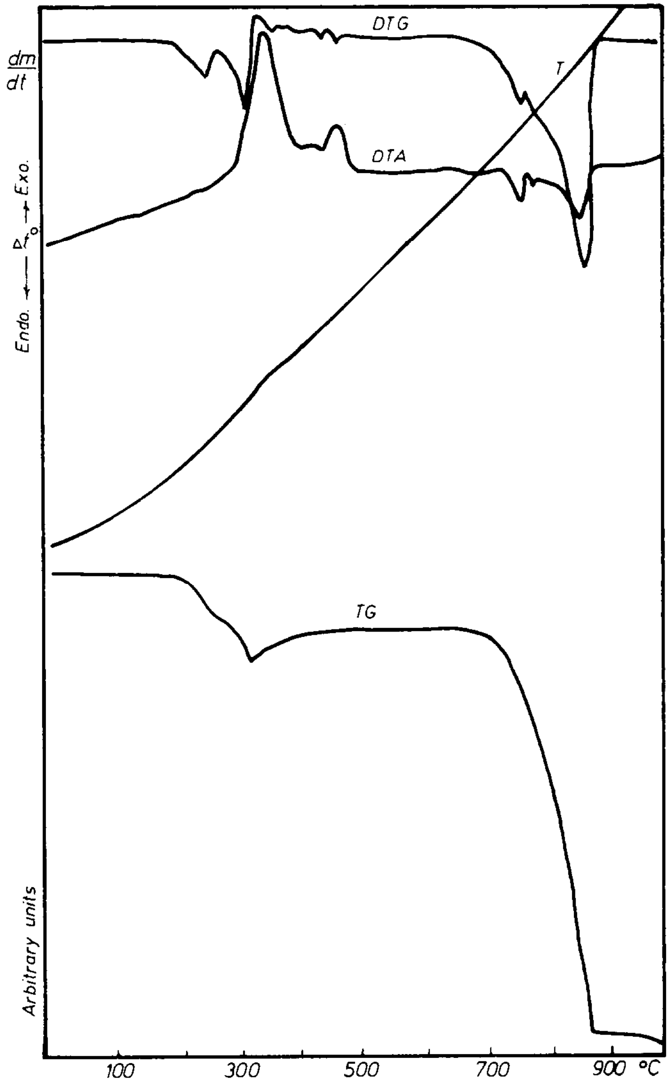

Fig. 2. Effect of nickel metal on the thermal decomposition of thallous malonate.

instead of 355–520° (Fig. 1), which means that nickel powder has lowered the range by 80°C through catalysis, thus behaving as a semiconductor at high temperatures. It is worth noting that the corresponding portion of the DTG curves (Fig. 2) discloses a ripple of tiny reproducible endotherms, suggesting that oxidation to thallic oxide still follows a multistep pathway probably due to differences of free energy values of the intermediate thallous oxide–nickel species formed. Comparing the TG curves of Figs. 1 and 2, it appears that in the presence of nickel powder the plateaus of the TG curves have been more straightened and smoothed.

Since the quantity of nickel remains the same up to the end of the heating program, the horizontal plateau of Tl_2O_3 (Fig. 2) that extends between 480 and 680°C (if this is analytically possible), may be proposed for the ignition of $CH_2(COOTl)_2$ and eventually the gravimetric estimation of thallium(I) and thallium(II) as thallic oxide. Further, the first plateau is perfectly horizontal up to 160°C, therefore it is likely that Tl_2(mal) may be dried anywhere before 160°C; the presence of nickel is necessary although objectionable from an analysis viewpoint. However, in the absence of nickel a narrow plateau (520–600°C) is shown (Fig. 1, solid line) and the same aim as above can be achieved.

From 650°C upwards, DTG and DTA curves exhibit two sharp corresponding endotherms; the small ones represent simultaneous melting and volatilization of thallic oxide which occur between 720–760°C. These are followed by a very tiny endotherm at 750°C representing partial decomposition of Tl_2O_3; then comes a very broad endotherm that continues to 820°C which is perhaps due to a slow equilibrated decomposition of the type

$$Tl_2O_3 \overset{\Delta}{\rightleftharpoons} Tl_2O + O_2$$

Since there is little change in differential temperature here, it is to be concluded that boiling of thallic oxide occurs at about 810°C. Thereafter, the two larger endotherms exhibit the volatilization of thallic oxide, a weight loss process, which finishes at 890°C. A grey powder with black shiny crystals (11.35%) is seen on the bottom and inner walls of the crucible due to the condensate of thallic oxide and the non-stoichiometric oxide of thallium (Table 1). However, in the presence of nickel powder the wide endotherm vanishes which may indicates a sharper boiling and volatilization of thallic oxides.

Experimentation under an inert nitrogen atmosphere (Fig. 1, broken line) has led to the removal of the sharp exotherms (due to oxidation of CO) appearing on the DTG and DTA curves as well as the two steps of the oxidation of Tl_2O; instead, a plateau extending from 365 to 650°C appears. Also, the two small endotherms on the DTA are replaced by a larger, wider endotherm, whereas the next sharp endotherm (Fig. 1, solid line) is excessively flattened (broken line), which means that the rate of volatilization of molecular Tl_2O becomes slower. This is also observed from the broadened endotherm of the DTG curve. Although not reproducible, the amount of residual thallous oxide in the crucible was in the vicinity of 20.9%. XRD analysis of the residual powder (Fig. 1, solid line) preheated to 1020°C reveals, in addition, unknown phases of thallium (Table 1). In order to determine the effect of the crucible's material, some experiments were repeated using conical ceramic instead of platinum crucibles; no important differences were discovered.

The decomposition kinetics of thallous malonate between 180 and 355°C in the presence of nickel is especially marked at $1:1:\mathrm{Ni}:\mathrm{Tl}_2(\mathrm{mal})$. Using the Freeman and Carroll equation [8], calculation of TG and DTG steps (Fig. 2) indicates that the order of the decomposition reaction is 3.307 and the activation energy is 32.535 kcal mole^{-1}. Any attempt to describe the decomposition of thallous malonate alone and over the same temperature range as above has failed, due to difficulty in confining the T_i–T_f range in the absence of nickel. The high value of *n* might be due to the superimposition of many thermal processes.

ACKNOWLEDGEMENTS

The author wishes to express his thanks to Miss Khalida H. Mohammed for performing the X-ray diffraction analysis of sintered samples.

REFERENCES

1 P.S. Bassi and P.C. Kalsi, J. Therm. Anal., 10 (1976) 375.
2 K. Muraishi, K. Nagase and N. Tanaka, Thermochim. Acta, 23 (1978) 125.
3 K. Nagase, K. Muraishi, M. Kikuchi and N. Tanaka, Proc. 6th Int. Conf. Therm. Anal., Vol. 2, Birkhäuser Verlag, 1980, p. 159.
4 T. Meisel, K. Seybold, Z. Halmos, J. Röth and Cs. Melykuti, J. Therm. Anal., 10 (1976) 419.
5 A.S. Giridharan, M.R. Udupa and G. Aravamudan, J. Therm. Anal., 7 (1975) 65.
6 Vishnu Chandra and Vijay Bah dur Srivastava, J. Indian Chem. Soc., 46 (12) (1969) 1112.
7 K.R. Idan and F. Jasim, Thermochim. Acta, 39 (1980) 227.
8 E.S. Freeman and B.J. Carroll, J. Phys. Chem., 62 (1958) 394.