

DEHYDRATION OF SOME INORGANIC COMPOUNDS BY CW CO₂ LASER IRRADIATION AND THERMAL HEATING. A COMPARATIVE STUDY

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(Received 23 September 1987)

ABSTRACT

A comparison was performed between the laser and the thermal (“classical”) heating dehydration of H_3BO_3 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{LiOH} \cdot \text{H}_2\text{O}$. Different reaction routes and different intermediate and final products were evidenced in a direct correlation with laser absorptivity by the reaction products.

INTRODUCTION

Initiation and control of chemical reactions under the action of IR laser radiation has recently received much experimental and theoretical attention, mainly in relation to the possibility of achieving selective influence on the reaction course by means of vibrational excitation (see for example, refs. 1–4).

Laser controlled chemical reactions allow the production of high purity substances, through the advantages of (i) a strong localized heating, (ii) the accurate space and time control of the irradiation process, (iii) the lack of wall effects, and (iv) the increased spectral absorption.

However, further detailed investigations are still necessary in order to clarify the similarities and differences between the laser conducted and the “classical” chemical reactions, and in order to decide in each case, based on this information, the advisability of implementing laser conducted technologies in the laboratory or in industrial processes. With this in mind, we have performed and report herewith some careful investigations of the laser

versus thermal ("classical") dehydration of H_3BO_3 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{LiOH} \cdot \text{H}_2\text{O}$.

EXPERIMENTAL

We undertook the decomposition of H_3BO_3 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{LiOH} \cdot \text{H}_2\text{O}$ by irradiation with a power-stabilized CW CO_2 laser source which was operated on the P20 ($\nu \approx 944 \text{ cm}^{-1}$) line at an output power of $P \approx 25 \text{ W}$. All substances used in experiments were of analytical purity grade, and uniform exposure to laser radiation of the powder-form substances was achieved by ensuring (i) smooth recirculation of the material in the reaction cell, and (ii) homogeneous heating [5]. The obtained reaction products were chemically-analysed by means of the complexometric method.

To perform a comparison with the thermal ("classical") decomposition process, small samples of the three substances under investigation were submitted to controlled heating up to $\approx 1273 \text{ K}$ in a derivatograph MOM Q-1500 D (Paulik type) with a heating rate of $\approx 10 \text{ K min}^{-1}$. Differential thermoanalysis (DTA) curves were recorded with an accuracy of $\approx 1 \text{ mV}$. Thermogravimetry (TG) curves were also recorded. Air atmosphere, platinum crucibles and Al_2O_3 reference were used.

RESULTS

Laser irradiation

The decomposition of the three compounds proceeds in this case according to the reactions specified in the second column of Table 2. Some typical results concerning the time-evolution of the concentration of the final reaction products are given in Figs. 1 and 2 and in Table 1.

Based upon these data kinetic constants of the three reactions were evaluated. The results are also given in the second column of Table 2.

Thermal heating in the derivatograph

Typical DTA and TG curves recorded by the thermal decomposition of the three products are given in Figs. 3-5

The information on the derivatograms was analysed with the aid of the equation [6]

$$\ln[F(1 - \alpha)] = -\frac{E}{RT} + \ln \frac{A}{b} + L \quad (1)$$

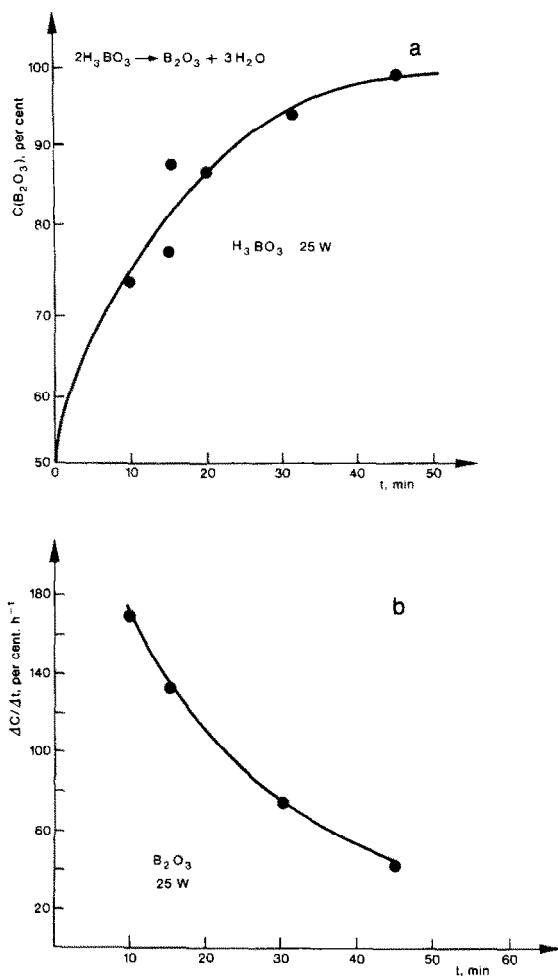


Fig. 1. Plots of changes with time of the concentration C (a) and of the concentration variation rate, $\Delta C/\Delta t$ (b) of B_2O_3 by laser decomposition of H_3BO_3 .

where

$$F(1 - \alpha) = \int_0^\alpha \frac{dx}{f(1 - x)} \quad (2)$$

stands for the conversion integral. We used

$$f(1 - \alpha) = (1 - \alpha)^n \quad (3)$$

which is known as the reaction order model. In these equations α is the conversion degree ($d\alpha/dt$ stands for the reaction rate), T is the absolute temperature, E the activation energy in kcal mol^{-1} , A is the preexponential factor with dimensions of s^{-1} , b is the heating rate of the apparatus,

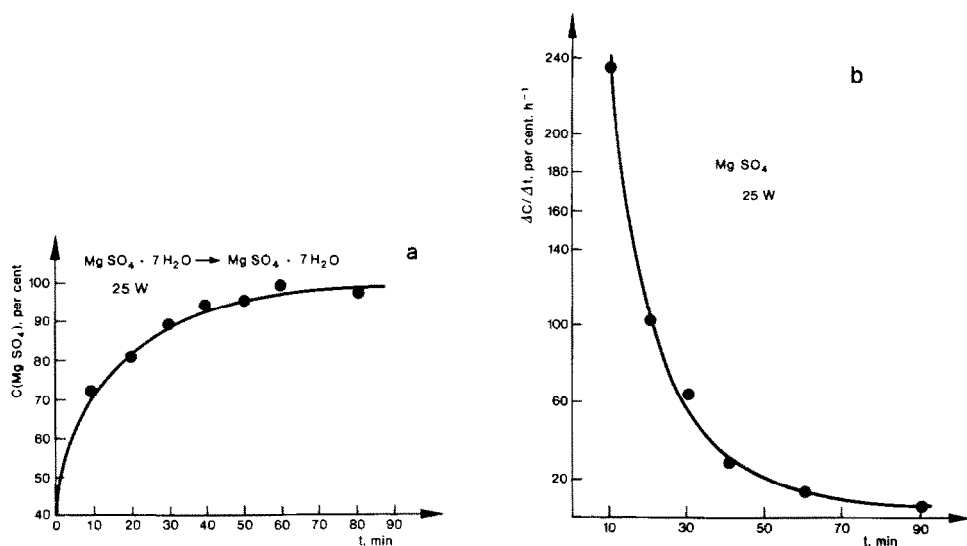


Fig. 2. Plots of changes with time of the concentration, C (a) and of the concentration variation rate, $\Delta C/\Delta t$ (b) of MgSO_4 by laser decomposition of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

$R = 1987 \text{ kcal mol}^{-1}$ and L is a correction factor. The inferred values of the parameters n , A , E are given in the second column of Table 2 along with the reaction routes in this case and the values of the correlation coefficient τ . Also, in the first column of Table 2 the value of the parameter $k = A e^{-E/RT}$ is specified.

TABLE 1

Concentration data of the reactants in the cases of laser decomposition of H_3BO_3 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{LiOH} \cdot \text{H}_2\text{O}$

	H_3BO_3						
$100 - C$ (%)	76	57	41	29	20	13	8
$-\frac{\Delta C}{\Delta t}$ (% min^{-1})	4.8	3.8	3.2	2.4	1.8	1.4	1
	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$						
$100 - C$ (%)	56	36	23	15	11	8	
$-\frac{\Delta C}{\Delta t}$ (% min^{-1})	4.4	2.0	1.3	0.8	0.4	0.3	
	$\text{LiOH} \cdot \text{H}_2\text{O}$						
$100 - C$ (%)	44		25		15		9
$-\frac{\Delta C}{\Delta t}$ (% min^{-1})	5.6		1.9		1		0.6

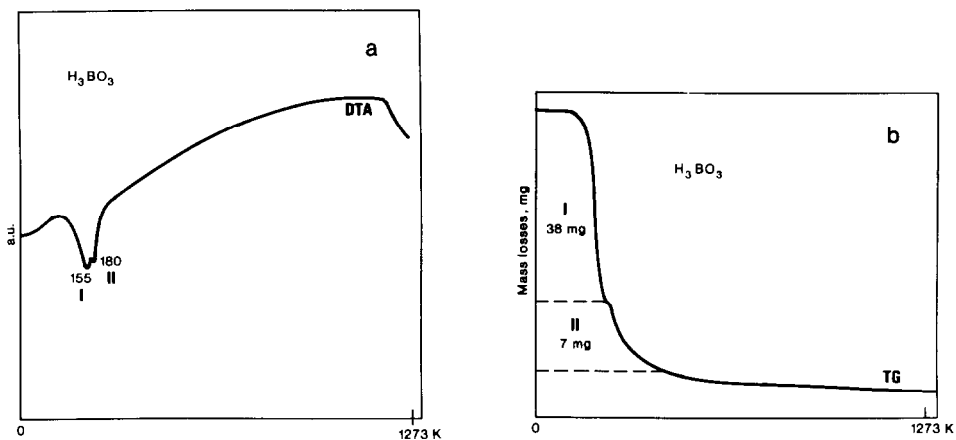


Fig. 3. The differential thermoanalytical (DTA) (a) and thermogravimetical (TG) (b) curves of H_3BO_3 decomposition.

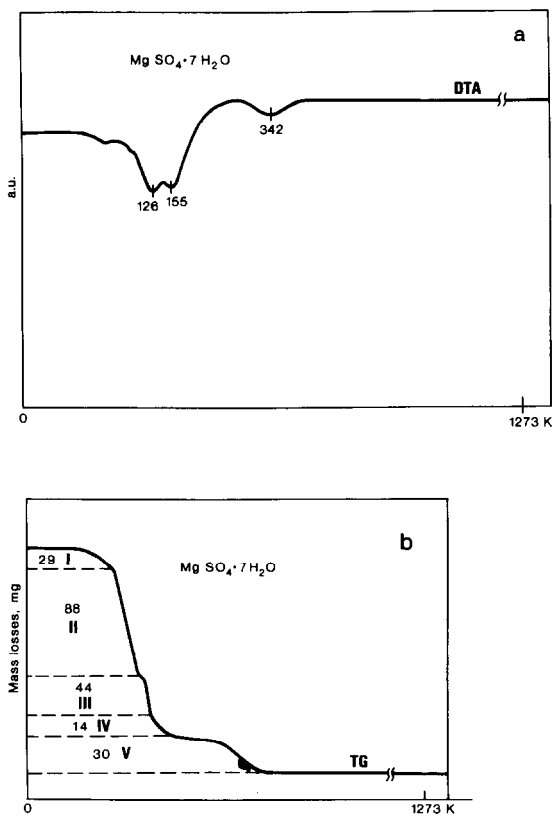


Fig. 4. The differential thermoanalytical (DTA) (a) and thermogravimetical (TG) (b) curves of $MgSO_4 \cdot 7H_2O$ decomposition.

TABLE 2

Comparative reaction routes and kinetics data on laser versus thermal ("classical") decomposition of H_3BO_3 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{LiOH} \cdot \text{H}_2\text{O}$

Substance	Laser irradiation	Thermal heating in the derivatograph
H_3BO_3	$2\text{H}_3\text{BO}_3 \rightarrow \text{B}_2\text{O}_3 + 3\text{H}_2\text{O}$ $n = 3/2$ $\ln k = 2.1 \text{ min}^{-1}$ $\tau = 0.999$	(i) $4\text{H}_3\text{BO}_3 \rightarrow \text{H}_2\text{B}_4\text{O}_7 + 5\text{H}_2\text{O}$ $n = 1$ $E = 20 \text{ kcal mol}^{-1}$ $A = 10^{10} \text{ s}^{-1}$ $\tau = 0.999$
		(ii) $\text{H}_2\text{B}_4\text{O}_7 \rightarrow 2\text{B}_2\text{O}_3 + \text{H}_2\text{O}$ $n = 3$ $E = 24.6 \text{ kcal mol}^{-1}$ $A = 10^{10} \text{ s}^{-1}$ $\tau = 0.986$
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ $\rightarrow \text{MgSO}_4 + 7\text{H}_2\text{O}$ $n = 0.7$ $\ln k = 3 \text{ min}^{-1}$ $\tau = 0.994$	(i) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ $\rightarrow \text{MgSO}_4 \cdot 6\text{H}_2\text{O} + \text{H}_2\text{O}$ $n = 1$ $E = 13 \text{ kcal mol}^{-1}$ $A = 10^5 \text{ s}^{-1}$ $\tau = 0.992$
		(ii) $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ $\rightarrow \text{MgSO}_4 \cdot 3\text{H}_2\text{O} + 3\text{H}_2\text{O}$ $n = 1$ $E = 38.5 \text{ kcal mol}^{-1}$ $A = 10^{19} \text{ s}^{-1}$ $\tau = 0.996$
		(iii) $\text{MgSO}_4 \cdot 3\text{H}_2\text{O}$ $\rightarrow \text{MgSO}_4 \cdot 1.5\text{H}_2\text{O} + 1.5\text{H}_2\text{O}$ $\rightarrow \text{MgSO}_4 \cdot \text{H}_2\text{O} + 0.5\text{H}_2\text{O}$ $n = 1$ $E = 40 \text{ kcal mol}^{-1}$ $A = 10^{19} \text{ s}^{-1}$ $\tau = 0.985$
		(iv) $\text{MgSO}_4 \cdot \text{H}_2\text{O} \rightarrow \text{MgSO}_4 + \text{H}_2\text{O}$ $n = 1$ $E = 44 \text{ kcal mol}^{-1}$ $A = 10^{14} \text{ s}^{-1}$ $\tau = 0.998$
$\text{LiOH} \cdot \text{H}_2\text{O}$	$\text{LiOH} \cdot \text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}_2\text{O}$ $n = 0.7$ $\ln k = 2.6 \text{ min}^{-1}$ $\tau = 0.9885$	(i) $\text{LiOH} \cdot \text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}_2\text{O}$ $n = 1$ $E = 15 \text{ kcal mol}^{-1}$ $A = 10^7 \text{ s}^{-1}$ $\tau = 0.980$
		(ii) $2\text{LiOH} \rightarrow \text{Li}_2\text{O} + \text{H}_2\text{O}$ $n = 1$ $E = 24 \text{ kcal mol}^{-1}$ $A = 10^3 \text{ s}^{-1}$ $\tau = 0.990$

DISCUSSION

We first note that the reaction orders for all thermal decompositions are $n = 1$: there is no laser reaction of this order.

Using thermal decomposition with a $\approx 10 \text{ K min}^{-1}$ rate all the three investigated substances undergo dehydration in two or even more steps, whereas laser dehydration is in every case characterized by a unique step. This is probably a very rapid development of the intermediate stages with kinetics superposed by a unique, stable and slow process, which is in our opinion the diffusion of the evolved gas. This assumption is further confirmed by the inferred order of the decomposition reactions of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{LiOH} \cdot \text{H}_2\text{O}$ under the action of laser radiation, which is precisely $n = 0.7$ (i.e. very close to $n = 2/3$, as predicted by the contracting sphere model [7]).

Other important features revealed by this comparative study are that the three substances are not only following different reaction routes in laser irradiation and pure thermal heating, and also that the final products can be different in the two cases. We observe indeed that by both laser and thermal decomposition of H_3BO_3 and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ one obtains B_2O_3 and MgSO_4 respectively, whereas in the case of laser and thermal decomposition of $\text{LiOH} \cdot \text{H}_2\text{O}$ different final products are obtained, i.e. LiOH by laser irradiation and Li_2O by thermal heating.

These behaviours depend upon the absorptivity at $\lambda \approx 10.4 \mu\text{m}$ of the substances forming during laser irradiation. Thus, according to ref. 2, during the laser thermochemical reactions a positive feedback is established between the chemical and the thermal degrees of freedom of the system. More precisely, from the chemical point of view, the laser conducted process is

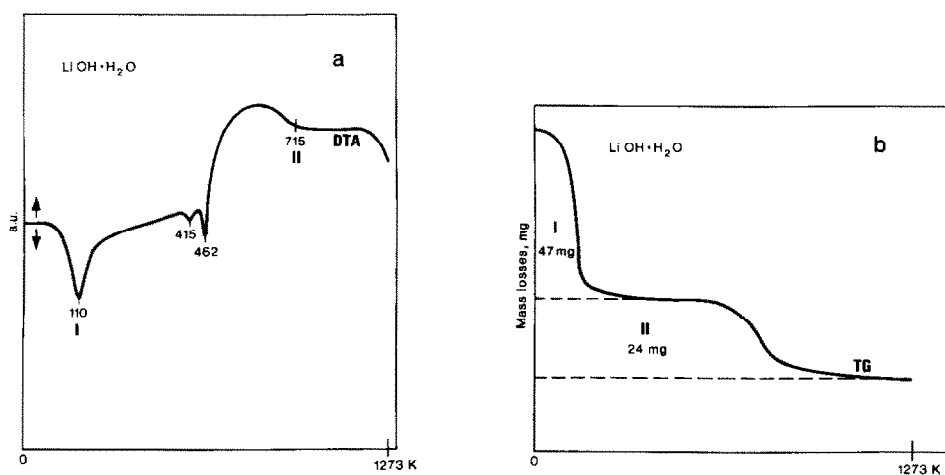


Fig. 5. The differential thermoanalytical (DTA) (a) and thermogravimetical (TG) (b) of $\text{LiOH} \cdot \text{H}_2\text{O}$.

considered to proceed in a reactions chain as follows

substance + $h\nu \rightarrow$ substance \rightarrow product(s)

product(s) + $h\nu \rightarrow$ product(s)^{*} \rightarrow other product(s)

(i) Whenever the reaction product(s) absorb(s) laser radiation better than the initial substance, a positive feedback is established and the reaction accelerates due to the fast rise of temperature. This is precisely the case of laser dehydration of H_3BO_3 and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. Indeed, according to our determinations, B_2O_3 and MgSO_4 absorptivities at $\lambda \approx 10.4 \mu\text{m}$ are 25 and 20% respectively, larger than the corresponding absorptivities of the respective starting substances.

(ii) In the opposite case, when the reaction product(s) absorb(s) the laser radiation poorly, the reaction rate slows down, the process is stabilized, and at the limit stops. In our case, this was observed in the laser dehydration of $\text{LiOH} \cdot \text{H}_2\text{O}$. Indeed the $\lambda \approx 10.4 \mu\text{m}$ radiation absorptivity of LiOH is approximately one sixth of the absorptivity of $\text{LiOH} \cdot \text{H}_2\text{O}$.

CONCLUSIONS

Laser and thermal ("classical") dehydration of H_3BO_3 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{LiOH} \cdot \text{H}_2\text{O}$ proceeded according to different routes resulting, in one case ($\text{LiOH} \cdot \text{H}_2\text{O}$), in different reaction products. Also the kinetics of the reaction appeared to be different in the two cases: "classical" thermal decomposition type by thermal heating and a typical diffusional one by laser irradiation [8,9]. These path ways were found to be in a direct relation with the absorptivity of laser radiation of the intermediate/final reaction products.

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