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TG/FT-IR: an analysis of the conditions affecting the combined TG/spectral response

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Abstract

The results of TG/FT-IR measurements performed on hydrated β -cyclodextrin at different heating rates and with different carrier gas fluxes are reported. It is shown that the shape of the spectral curve (either Gram–Schmidt reconstruction or integrated specific absorbance) and its degree of matching with the DTG curve depend on both the TG heating rate and the carrier gas flow rate. Namely, it is the relative rate of the reaction and of the TG purging that determines the spectral response. The results obtained are wholly accounted for by utilizing a simple “dispersive” definition, as recently proposed by us, for the “relative intensity” of the spectral curve.

Keywords: Cyclodextrin; DTG; FT-IR; Gram–Schmidt; TGA

1. Introduction

Thermogravimetry (TG) measures sample weight as a function of temperature, but gives no information on the chemical basis of the weight change process. The introduction of FT-IR spectrometry as a hyphenated technique with TG allows for the real time collection of spectra of gases evolved during sample heating, so that one can make assignments of the evolved gases to the detected mass losses.

TG/FT-IR has been used successfully to identify the pyrolysis products of a number of polymers, including PTFE, polybutadiene, silicone rubber, polyvinyl acetate and epoxy resins [1].

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In commercially available systems the evolved gases are transferred from the thermobalance to the spectrometer via a heated transfer line by a carrier gas flow. A problem can arise from the partial deposition on cold spots of components, which are then not able fully to reach the IR cell [2]. To overcome this problem, the use of quartz wool filters to keep high molecular mass components completely away from the IR cell has been proposed [3]. Obviously information on these components is then altogether lost. Another way to tackle the problem is to form an aerosol of the high molecular mass components by using helium as carrier gas so that they can fully reach the IR cell [4]. However, in this case the TG atmosphere is restricted to helium. More recently, the problem has been circumvented by the so called on the spot TG/FT-IR technique, in which the IR beam is led to the thermobalance, contrary to the traditional instrumental design [5].

An ideal TG/FT-IR measurement is one in which the spectral curve (Gram–Schmidt reconstruction, GSR) is superimposed on the differential thermogravimetric (DTG) one. In this respect, a serious problem has been encountered in previous work of ours [6]: the influence on the spectral curve exerted by the purging action of the carrier gas. Actually, it has been shown that both the shape of the spectral curve and its match with the DTG curve can be quite different from what might be expected.

The present work reports the results of some TG/FT-IR measurements performed on hydrated β -cyclodextrin to explain the dependence of the spectral response (in the form of both GSR and integrated absorbance) on experimental parameters such as heating rate and carrier gas flow rate.

2. Experimental

TG/FT-IR measurements were performed by using a Nicolet 730 FT-IR spectrometer interfaced to a Du Pont 951 TG analyser controlled by a TA 2000 system. The heated IR gas cell was kept at 240°C by an OMEGA CN310 temperature controller.

β -Cyclodextrin ($C_{42}H_{70}O_{35} \cdot 12H_2O$, from Roquette, France) was recrystallized from aqueous solution at room temperature, ground and then sieved (sieve fraction 38–45 μ m). Samples (≈ 15 mg) of β -cyclodextrin were dehydrated by heating to 200°C (heating rates 5, 10 and 20 K min^{-1}). The line between the TG unit and the heated IR gas cell was swept by a dry nitrogen flux (flow rates 30, 60 and 80 ml min^{-1}). At the end of the experiments the spectral data (8 cm^{-1} resolution, 16 interferograms for each spectral file, DTGS detector, 4000–500 cm^{-1} spectral region) were processed with Nicolet SID proprietary software to generate Gram–Schmidt and integrated absorbance reconstructions (in the present case, water integrated absorbance in the 3900–3500 cm^{-1} region, OH stretching).

Finally, weight and temperature data were transferred to the Nicolet Data Station, so allowing both spectral and thermogravimetric data to be presented as a function of TG temperature (see Figs. 1–4).

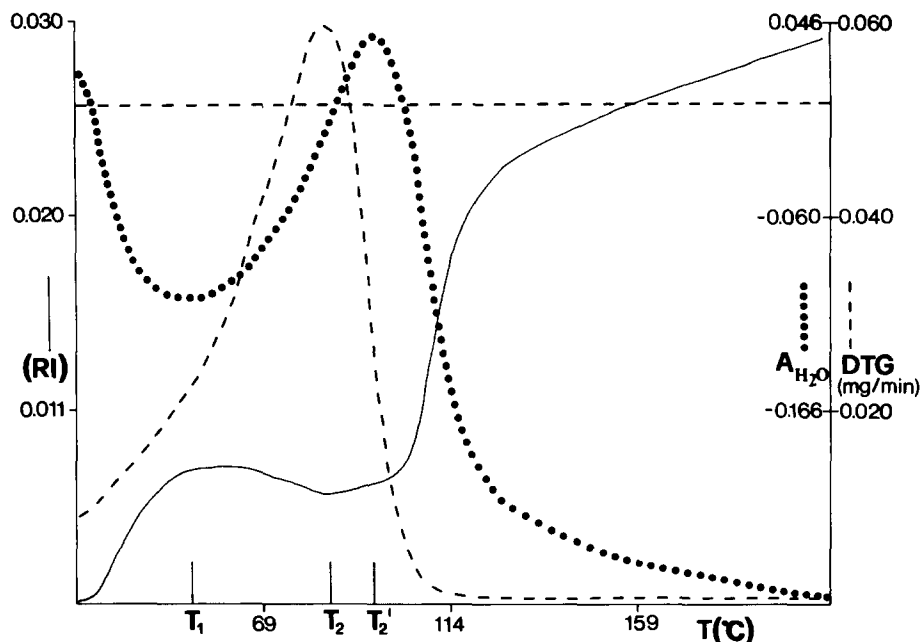


Fig. 1. Dehydration of β -cyclodextrin. Heating rate 5 K min^{-1} , N_2 flow rate 30 ml min^{-1} . Y axes: solid line, GSR; dashed line, DTG; dotted line, $A_{\text{H}_2\text{O}}$. X axis: TG temperature. The horizontal dashed line represents the $A_{\text{H}_2\text{O}}$ zero value.

3. Results and discussion

A typical TG/FT-IR plot reports both the weight change (absolute, percentage or derivative) and the relative intensity, RI of the GSR as a function of temperature. Such a relative intensity in practice measures the differences produced in the successive interferograms by the evolving gases. A dispersive definition of RI has recently been proposed by us [6],

$$\text{RI} = |(I_0 - I_t)/I_0|$$

where I_0 is the IR detector signal (full spectral range) at the start of the run ($t = 0$) and I_t is the IR signal at a time t during the run. If the thermobalance has not been perfectly purged before the run, the I_0 value is evidently affected by the atmospheric moisture (H_2O and CO_2) present in the TG system at the start of the run. Values of I_t are determined by both these atmospheric components still present at time t and the gases evolved by the sample.

In the present case, where the only gas released should be H_2O , I_0 and I_t can be better defined as

$$I_0 = I_{0,\text{CO}_2} + I_{0,\text{H}_2\text{O}}; \quad I_t = I_{t,\text{CO}_2} + I_{t,\text{H}_2\text{O}}$$

where the subscripts CO_2 and H_2O indicate the contribution to the detector intensity of the carbon dioxide (present in the TG environment at the start of the run) and water

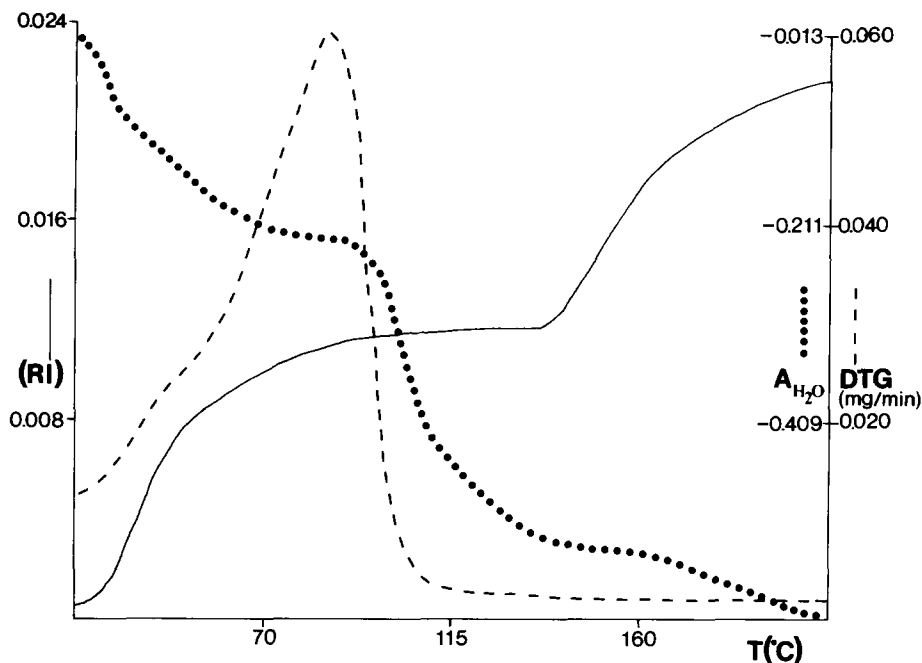


Fig. 2. Dehydration of β -cyclodextrin. Heating rate 5 K min^{-1} , N_2 flow rate 60 ml min^{-1} . Symbols as in Fig. 1.

(both present in the TG atmosphere at the start of the run and released by the sample). As no carbon dioxide is expected to be evolved during the reaction, the CO_2 level in the IR cell should be determined only by the purging action of the carrier gas that sweeps the moisture present in the TG apparatus towards the IR cell. In this case it is given by $I_{t,\text{CO}_2} > I_{0,\text{CO}_2}$, with I_{t,CO_2} progressively increasing as the CO_2 level in the IR cell decreases throughout the run. As regards the water integrated absorbance ($A_{\text{H}_2\text{O}}$, in the range $3900\text{--}3500 \text{ cm}^{-1}$), this can be expressed as $\log [I_{0,\text{H}_2\text{O}}/I_{t,\text{H}_2\text{O}}]$. We will see that, for the same reaction, different situations arise regarding the I_t values. Indeed, different shapes of the spectral curve are observed depending on the selected experimental conditions (heating rate and carrier gas flux). As regards these conditions it should be clear that, as a general rule, a lower carrier gas flow should enhance the IR detector response even if a poorer temporal correlation between TG and spectral data must be expected. Thus, according to the manufacturer's statements, for example, a carrier gas flux of 30 ml min^{-1} should be a good compromise for heating rates of 5 K min^{-1} and less, and the gas flux should range between 80 and 150 ml min^{-1} for heating rates of 15 to 30 K min^{-1} .

3.1. Considering the manufacturer's statements

Fig. 1 represents the results of a TG/FT-IR run performed on β -cyclodextrin (heating rate 5 K min^{-1} ; carrier gas flow rate 30 ml min^{-1}). It should be noted that the

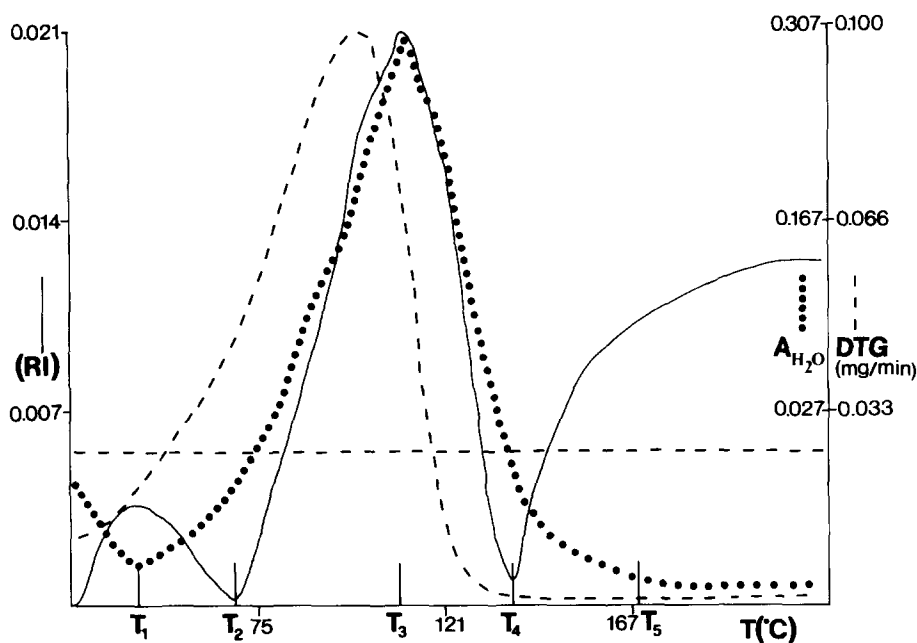


Fig. 3. Dehydration of β -cyclodextrin. Heating rate 10 K min^{-1} , N_2 flow rate 30 ml min^{-1} . Symbols as in Fig. 1. The horizontal dashed line represents the $A_{\text{H}_2\text{O}}$ zero value.

dehydration of β -cyclodextrin occurs at room temperature under a flux of dry nitrogen [7]. The present experimental case is one in which pre-purging of the TG unit cannot be performed.

It can be seen that the expected DTG/GSR matching does not show up at all. To try and explain such a TG/FT-IR plot let us divide it into three sections:

(1) Up to T_1 , the RI increases while $A_{\text{H}_2\text{O}}$ is negative and decreasing. Such a trend reveals that $I_{t,\text{H}_2\text{O}}$ is greater than $I_{0,\text{H}_2\text{O}}$ and increasing. As I_{t,CO_2} is always greater than I_{0,CO_2} and also increases, then both I_t and RI increase. What happens is that the effect of the purging gas prevails over the effect of reaction, although the reaction is under way. Then, at this stage, the water level as seen by the IR detector is decreasing.

(2) Between T_1 and T'_2 , at T_1 , $I_{t,\text{H}_2\text{O}}$ reaches a relative maximum and $A_{\text{H}_2\text{O}}$, in turn, reaches a relative minimum. This means that at T_1 the purging effect (which increases $I_{t,\text{H}_2\text{O}}$) and the reaction effect (which diminishes $I_{t,\text{H}_2\text{O}}$) compensate each other. Beyond T_1 the reaction effect prevails, so that $I_{t,\text{H}_2\text{O}}$ decreases and $A_{\text{H}_2\text{O}}$ increases until T'_2 is reached, which represents the point at which the water level in the IR cell reaches its maximum. As $A_{\text{H}_2\text{O}}$ is now greater than zero, the situation must be $I_{t,\text{H}_2\text{O}} < I_{0,\text{H}_2\text{O}}$. Furthermore, it should be noted that the maximum reaction rate (see the DTG maximum at T_2).

As concerns the RI behaviour we recall that, as $I_t = I_{t,\text{H}_2\text{O}} + I_{t,\text{CO}_2}$ (with $I_{t,\text{H}_2\text{O}}$ decreasing and I_{t,CO_2} increasing), RI can start decreasing only when the $I_{t,\text{H}_2\text{O}}$ decrease

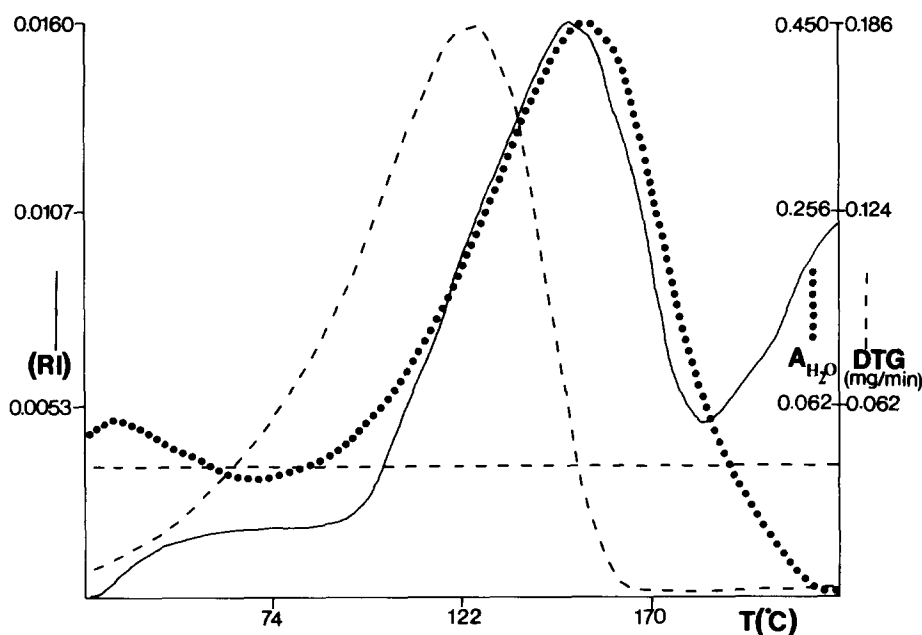


Fig. 4. Dehydration of β -cyclodextrin. Heating rate 20 K min^{-1} , N_2 flow rate 30 ml min^{-1} . Symbols as in Fig. 1. The horizontal dashed line represents the $A_{\text{H}_2\text{O}}$ zero value.

prevails over the I_{t,CO_2} increase. This is why RI begins to decrease well after $A_{\text{H}_2\text{O}}$ starts to increase.

At T_2 the condition $I_{t,\text{H}_2\text{O}} = I_{0,\text{H}_2\text{O}}$ ($A_{\text{H}_2\text{O}} = 0$) is realized, so that

$$I_t = (I_{t,\text{H}_2\text{O}} + I_{t,\text{CO}_2}) > I_0 = (I_{0,\text{H}_2\text{O}} + I_{0,\text{CO}_2})$$

and RI is determined only by the relative values of I_{t,CO_2} and I_{0,CO_2} , which are, in turn, determined by the purging effect. Near T_2 , RI starts, albeit slightly, to increase. This is attributable to a low rate of change of $I_{t,\text{H}_2\text{O}}$ (we are approaching the IR maximum reaction rate where $I_{t,\text{H}_2\text{O}}$ changes from a decreasing to an increasing trend). Therefore I_{t,CO_2} is the factor that determines I_t and, as I_{t,CO_2} increases, I_t and RI also increase.

(3) Beyond T_2 , $I_{t,\text{H}_2\text{O}}$ begins to increase and $A_{\text{H}_2\text{O}}$, in turn, starts to decrease. The RI first keeps slightly increasing, owing to the relatively low rate of increase of $I_{t,\text{H}_2\text{O}}$, until the condition $I_{t,\text{H}_2\text{O}} = I_{0,\text{H}_2\text{O}}$ ($A_{\text{H}_2\text{O}} = 0$) is established again. Beyond this point the reaction rate, as seen by the IR detector, rapidly decreases, so that $I_{t,\text{H}_2\text{O}}$ and, as a consequence, RI rapidly increase.

When the reaction is over, the only effect to be taken into account is the purging effect according to which I_t and RI increase while $A_{\text{H}_2\text{O}}$ decreases. In conclusion, the combined effect of the atmospheric moisture present in the TG system at the start of the run (which initiates the purging effect) and of a low rate of weight loss results in a spectral curve which does not match the DTG one.

3.2. Effect of the carrier gas flow rate

The shape of the spectral curve still looks far from ideal after doubling the carrier gas flow rate (to 60 ml min^{-1}), the heating rate being the same (Fig. 2). At the beginning of the run, again we have $I_{t,\text{H}_2\text{O}} > I_{0,\text{H}_2\text{O}}$ on the same grounds as those that account for Section I of Fig. 1. Then the water vapour released from the sample starts to affect the detector intensity and, since the gas flow rate has been increased but the heating rate and so the weight loss rate have been left unchanged, the water vapour that in unit time enters the IR cell is more diluted by the carrier gas. Therefore the IR detector sees a lower reaction rate than in the preceding case. Correspondingly, the importance of the purging effect exerted by the carrier gas on the moisture present in the TG apparatus is enhanced. This means that the rate of increase of I_{t,CO_2} is higher than that in the case of Fig. 1. As regards the rate of change of $I_{t,\text{H}_2\text{O}}$, it must be remembered that $I_{t,\text{H}_2\text{O}}$ is the net result of two contributions, one increasing (due to the water originally present in the moist atmosphere) and one decreasing (due to the water released during the reaction). As can be deduced from $A_{\text{H}_2\text{O}}$, which is negative and slightly decreasing over the whole DTG peak, $I_{t,\text{H}_2\text{O}}$ is slightly increasing (the purging effect prevails over the reaction effect). As I_{t,CO_2} is increasing, I_t increases as RI does. When the DTG peak is over, it can be seen that, whereas $A_{\text{H}_2\text{O}}$ starts to decrease more rapidly, RI slows down until it becomes almost constant. When this happens the reaction rate seen by the IR detector is decreasing. Then both contributions are increasing. It follows that $I_{t,\text{H}_2\text{O}}$ quickly increases with respect to what happens over the course of the DTG peak. As a consequence, $A_{\text{H}_2\text{O}}$ also quickly decreases. The nearly flat trend of RI in this same period could be due to a sudden decrease of I_{t,CO_2} , which would oppose the increase in $I_{t,\text{H}_2\text{O}}$. This in turn would reflect a release of a minor amount of CO_2 , which has a larger molar absorptivity than H_2O . When the reaction is completed the trends of $A_{\text{H}_2\text{O}}$ and RI are similar to those observed and explained in the final part of Fig. 1.

No significant changes in the shape of the spectral response are noticed when further raising the carrier gas flow rate to 80 ml min^{-1} . It should be noted that the GSR spectral curves of Figs. 1 and 2 are both very far from the ideal one. However, the measurements performed show that the reaction is better seen by the IR detector at the lower gas flow rate, the heating rate being fixed.

3.3. Effect of the heating rate

Fig. 3 illustrates the results obtained at 10 K min^{-1} (gas flow rate 30 ml min^{-1}). At a first glance it is observed that a positive peak is now present in the GSR, even if the GSR and DTG peaks do not overlap as might have been expected. Furthermore, another small GSR peak shows up that has no DTG counterpart. Let us comment on the trends of RI and $A_{\text{H}_2\text{O}}$ represented in Fig. 3.

(1) Up to T_1 , the same comments apply as are reported in the explanation of Fig. 1 up to T_1 . The purging effect again prevails over the reaction effect.

(2) Between T_1 and T_3 , the reaction effect becomes prominent. $I_{t,\text{H}_2\text{O}}$ is now decreasing and soon the condition $I_{t,\text{H}_2\text{O}} = I_{0,\text{H}_2\text{O}}$ is attained. Afterwards, $I_{0,\text{H}_2\text{O}} > I_{t,\text{H}_2\text{O}}$ and $A_{\text{H}_2\text{O}} > 0$. $I_{t,\text{H}_2\text{O}}$ keeps decreasing until it reaches its minimum at T_3 , where the

reaction rate seen by the IR detector reaches its maximum as does $A_{\text{H}_2\text{O}}$. Concerning RI, it can be seen that its trend is a non-monotonic one. Indeed, RI first decreases almost to zero and then increases. Let us remind ourselves that at T_1 the condition $I_t > I_0$ holds. The decreasing trend of RI between T_1 and T_2 can only be explained if, as $I_t = I_{t,\text{H}_2\text{O}}$ (decreasing) + I_{t,CO_2} (increasing), one accepts that the rate of decrease of $I_{t,\text{H}_2\text{O}}$ (related to the reaction effect) is greater than that of the increase of I_{t,CO_2} (related to the purging effect). Since the rate of change of $I_{t,\text{H}_2\text{O}}$ is negative and high, the condition $\text{RI} \approx 0$ is reached in the initial stage of the reaction (compare with the point T_2 of Fig. 1, where RI does not reach zero even though the DTG reaction rate is at its maximum). Beyond T_2 the reaction rate continues to increase, and the condition $I_{t,\text{H}_2\text{O}} < I_{0,\text{H}_2\text{O}}$ is soon realized ($A_{\text{H}_2\text{O}} > 0$). If we recall the definition proposed for RI its increasing trend up to T_3 can be easily explained.

(3) Beyond T_3 , the reaction rate seen by the IR detector progressively decreases until it vanishes. Then $I_{t,\text{H}_2\text{O}}$ increases and $A_{\text{H}_2\text{O}}$ decreases, both of them monotonically. It should be noted that, at T_4 , $A_{\text{H}_2\text{O}}$ and RI are ≈ 0 . The condition of the detector intensity values changes from $I_{t,\text{H}_2\text{O}} < I_{0,\text{H}_2\text{O}}$ to $I_{t,\text{H}_2\text{O}} > I_{0,\text{H}_2\text{O}}$. Then, at T_4 , RI starts to increase again, while $A_{\text{H}_2\text{O}}$ becomes negative but continues to decrease.

Hence we note that, with the carrier gas flow fixed (30 ml min^{-1}), an increased heating rate (from 5 to 10 K min^{-1}) enhances the detector response. Actually, over the reaction, the weight loss rate and then that of variation of the gas composition entering the IR cell is higher than at 5 K min^{-1} . Hence the effect of the gas released by the sample soon prevails over that of TG purging by the carrier gas in determining the detector response. The result is the appearance of a positive spectral peak.

The TG/FT-IR plot of a run performed at 20 K min^{-1} (30 ml min^{-1}) is reported in Fig. 4.

Initially $A_{\text{H}_2\text{O}}$ is positive and increasing. This means that $I_{t,\text{H}_2\text{O}} < I_{0,\text{H}_2\text{O}}$ with $I_{t,\text{H}_2\text{O}}$ decreasing, so that RI in turn increases. Afterwards $A_{\text{H}_2\text{O}}$ remains close to zero and RI stays fairly constant. This is due to the reaction rate, which is higher at 20 K min^{-1} , so that it can be said that the purging effect and the reaction effect are already at about the same level in the very early stages of the reaction. When the reaction effect prevails over the purging one, $I_{t,\text{H}_2\text{O}}$ monotonically decreases until the reaction rate seen by the IR detector attains its maximum: RI and $A_{\text{H}_2\text{O}}$ increase up to a maximum value.

After this point the reaction rate begins to decrease, $I_{t,\text{H}_2\text{O}}$ increases and $A_{\text{H}_2\text{O}}$ decreases monotonically down to negative values. The RI also decreases until $I_{t,\text{H}_2\text{O}}$ is slightly less than $I_{0,\text{H}_2\text{O}}$ (still $A_{\text{H}_2\text{O}} > 0$). Beyond this point, RI increases. However, since it can be seen that RI does not reach zero and $I_{t,\text{H}_2\text{O}}$ is still increasing ($A_{\text{H}_2\text{O}}$ decreases), such an inverted trend could be explained by a release of CO_2 by the sample that would make I_{t,CO_2} decrease to such an extent that I_t and, as a consequence, RI actually increase.

4. Conclusions

From the TG/FT-IR results obtained for the β -cyclodextrin dehydration process, it can be seen that the shape of the spectral reconstruction curves depends on both the

carrier gas flow rate and the TG heating rate. In fact, it has been shown that it is a combination of these two experimental variables that determines the kind of instrumental response which can, in any case, be accounted for by the proposed dispersive definition of relative intensity [6].

Once a carrier gas flow rate that maximizes the IR detector response for the system under study has been established (30 ml min^{-1} in the present case), the heating rate can be set to such a value as to obtain positive spectral peak(s).

It has been shown that the GSR positive peak does not necessarily superimpose on the DTG one (see Figs. 3 and 4) and, in some instances, even no peak (see Figs. 1 and 2) or a false GSR peak may appear (see Fig. 3). This stems from the fact that the spectral response is determined not only by the gas(es) evolved by the reaction occurring in the TG system but also by the gaseous components present at the start of the run in the TG atmosphere and brought into the IR cell by the purging action of the carrier gas. Then, depending on the relative rates of weight loss (related to heating rate) and of purging by the carrier gas (related to gas flow rate), different situations can arise as concerns both the appearance of the spectral curve (GSR) and its degree of matching with the DTG curve.

Hence a suitable combination of heating rate and carrier gas flux represents a critical condition to be attained mainly when dealing with reactions (such as β -cyclodextrin dehydration) taking place already at room temperature and evolving gases (H_2O and CO_2) present in the atmosphere.

In such cases the choice of heating rate and carrier gas flow rate cannot be made according to the instructions provided with the instrument as a rule of thumb but rather constitutes a trial and error problem.

Finally, it has to be noted that the unexpected release of atmospheric gaseous components by the sample (CO_2 in the present instance) can in fact be made evident by analysing the shape of the spectral curve in the light of the dispersive definition of relative intensity.

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