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The use of reduced pressure to expand the capabilities of TGA–FTIR

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Abstract

The benefits of coupling a Fourier transform infrared (FTIR) spectrometer to a thermogravimetric analyzer (TGA) are well known. FTIR spectroscopy provides information about the evolved gases that can lead to a better understanding of the thermal behavior of the sample. The combination of the two techniques can give both qualitative and quantitative information about thermal decomposition and reaction mechanisms.

One of the current limitations of TGA–FTIR is the temperature of the transfer line and the gas cell in the infrared spectrometer. The temperature of the interface to the FTIR cannot be as high as the temperature that can be achieved in the furnace, and this leads to possible trapping of high boiling compounds that are evolved from the sample. In this paper, a system is described for performing TGA–FTIR measurements at reduced pressures, which significantly improves the gas flow characteristics of the system for high boiling compounds. It is shown that reduced pressure also minimizes sample carryover, and reduces or eliminates trapping of material in the transfer line. Data are also presented that show that using the pressure as an experimental parameter can yield additional information about the structure of a sample, and about the thermal decomposition process. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: TGA–FTIR; Infrared spectroscopy; Evolved gas analysis; Reduced pressure

1. Introduction

The potential advantages of interfacing an FTIR to a TGA were originally shown in the early 1980s [1–3]. The coupling of these two techniques provides synergistic information that is not available from either technique alone. As a method of evolved gas analysis (EGA), FTIR is sensitive, fast, and can detect every type of molecule except homonuclear diatomics. Nevertheless, there are certain limitations in the technique that have not been completely overcome. The most important of these is the problem of transfer of high boiling compounds. It was recognized many years ago that high boiling compounds can travel very slowly through the transfer line, causing misleading gas evolution profiles and possible cross contamination of subsequent samples [4]. For TGA coupled with mass spectrometry problems associated with high boiling compounds have been eliminated by the use of a direct coupling technique [5,6] instead of a capillary transfer line. Similar techniques have been attempted with FTIR [7], but have met with limited success because of a number of problems: it is difficult

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to get IR light into such a system, certain optics may become contaminated, and spectra can be a mixture of those from condensed and vapor phase material.

In this work, an alternative approach has been investigated. By using a vacuum tight TGA, it is possible to run experiments at reduced pressures. Using our current equipment, experiments can be conducted at pressures of less than 100 mbar, which can lead to a reduction of boiling point of 100°C or more for some molecules. In addition, it is possible to use the pressure as a parameter in the experiment, since changing the pressure can significantly affect the thermal decomposition behavior of the sample. The additional information obtained in this way can help to elucidate both the structure of the material and the chemistry of the decomposition process.

Three samples will be used to demonstrate the feasibility and the utility of TGA–FTIR at reduced pressures. Salicylic acid has a boiling point of 211°C at 26.3 mbar [8], and therefore serves as an excellent example of a high boiling compound. It can be used to characterize the gas flow characteristics of the experimental apparatus as a function of pressure. Glycerol has a boiling point of 290°C at atmospheric pressure, and 200°C at a pressure of 60 mbar [8]. When heated at atmospheric pressure, however, it partially decomposes. This decomposition occurs not only in the TGA crucible, but also at any colder spots in the system, where the glycerol can be trapped. As will be shown, this can lead to very misleading gas evolution profiles. Finally, PVC that is plasticized with dioctyl phthalate is used as a practical example of the additional information that can be obtained by FTIR, when the pressure is used as a parameter in the experiment.

2. Experimental

Fig. 1 shows a block diagram of the experimental apparatus used for the TGA–FTIR measurements at reduced pressures. The flow rate of the carrier gas, typically nitrogen, is controlled using a Sierra model 810C-DR-2 mass flow controller. The display of the mass flow controller can be read to an accuracy of ± 0.5 ml min^{-1}. The output of the mass flow controller is split into two equal streams that go to the purge gas and protective gas inlets of a Netzsch model TG 209 TGA. In this TGA, the purge and protective gas flows are combined before reaching the furnace, and consequently, the infrared spectra of the evolved gases are independent of the split ratio. The evolved gases are transported via a transfer line to a low volume gas cell, both of which can be heated to a maximum temperature of 250°C, although a lower temperature of 220°C

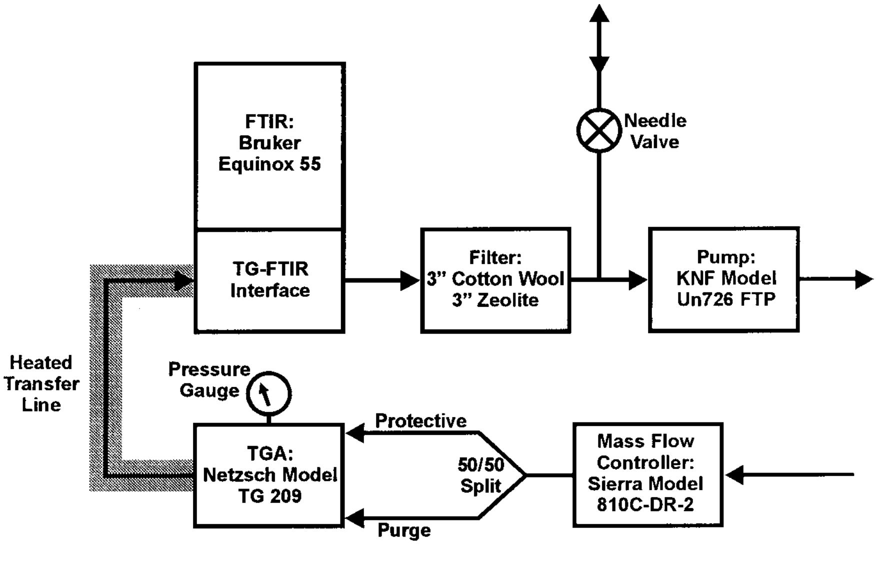

Fig. 1. Block diagram of experimental apparatus used for TGA–FTIR measurements at reduced pressures.

was used for all the experiments reported here. The gas cell is contained in an interface on a Bruker Equinox 55 FTIR spectrometer. The details of the interface have been described previously [9]. After the gas cell, the gases are fed through a filter, which consists of 3 in. of zeolite followed by 3 in. of packed cotton wool, to a KNF model Un 726 FTP diaphragm pump that is designed to handle corrosive gases. The purpose of the filter is to remove any condensable vapors and any particulates that may damage the pump. Immediately prior to the pump is a needle valve that is connected to atmosphere, which is used to control the pressure in the TGA and the gas cell. With this arrangement, the lowest pressure that can be achieved, measured in the TGA, is 60 mbar. The pressure gauge connected to the TGA can be read with an accuracy of ±10 mbar. The model TG 209 TGA, the gas cell, the filter, and the intermediate connections are all vacuum tight so that atmospheric gases cannot leak into the system.

The low volumes of the furnace (2.4 ml), the transfer line (4.7 ml), and the gas cell (8.7 ml) permit low flow rates of 15 ml min^{-1}, which were used for all experiments at reduced pressures. The gas flow rates at reduced pressures are all referenced to standard conditions of 21.1°C and atmospheric pressure. In all cases high purity nitrogen was used as the purge gas. Infrared spectra were collected at 4 cm^{-1} resolution on a continuous basis. For salicylic acid, the TGA was ramped at 15 K min^{-1}, with spectra acquired every 17.5 s. For glycerol, the TGA was ramped at 10 K min^{-1}, with spectra acquired every 17.5 s. For PVC, the TGA was ramped at 10 K min^{-1}, with spectra acquired every 32 s. The system was cleaned between each sample run by heating to 950°C at 50 K min^{-1}, followed by an isotherm for 20 min, with a flow of approximately 30 ml min^{-1} of air. No buoyancy correction was applied to the weight loss data.

The salicylic acid was ACS reagent grade, obtained from Sigma–Aldrich, and was used as received. The glycerol was ultrapure, spectrophotometric grade, obtained from Alfa Aesar, and was used as received. The PVC was standard tubing material obtained from VWR scientific. It was cut into small pieces (<1 mm) to minimize the effects of plasticizer diffusion. Table 1 shows the sample weights used in the experiments reported here.

Table 1
Sample weights used in TGA–FTIR experiments

Sample	Pressure (mbar)/gas flow rate (ml min^{-1})	Weight (mg)
Salicylic acid	1000/35	13.490
Salicylic acid	1000/15	14.002
Salicylic acid	500/15	12.484
Salicylic acid	300/15	13.529
Salicylic acid	200/15	13.673
Salicylic acid	100/15	13.230
Glycerol	1000/15	10.247
Glycerol	60/15	10.440
PVC	1000/15	13.237
PVC	60/15	13.808

3. Results and discussion

To characterize the gas flow characteristics of the system, salicylic acid was heated under nitrogen at different flow rates and pressures. It is well known that when the flow rate of the purge gas is increased, the temporal resolution of the IR response is improved, but at the expense of decreased sensitivity due to greater dilution of the evolved gases. This effect is shown for salicylic acid in Fig. 2. The IR response was obtained by integrating the area under the carbonyl band (1762–1791 cm^{-1}) in the IR spectrum. Apart from a small change in the onset temperature (<2°C), the curves for the rate of weight loss at the two flow rates overlay almost exactly, and the IR response can, therefore, be compared to the rate of weight loss shown in Fig. 3 for a pressure of 1000 mbar. The

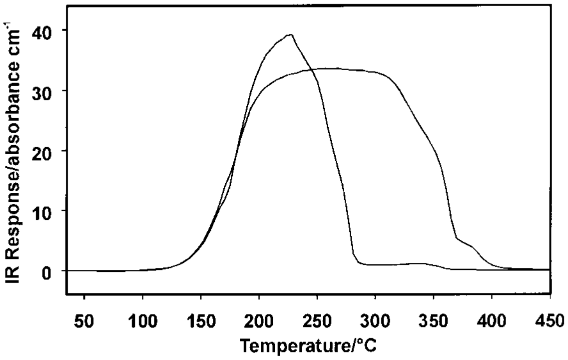

Fig. 2. IR response for salicylic acid at 1000 mbar and flow rates of 35 ml min^{-1} (left) and 15 ml min^{-1} (right) of purge gas. The curves are normalized for sample mass.

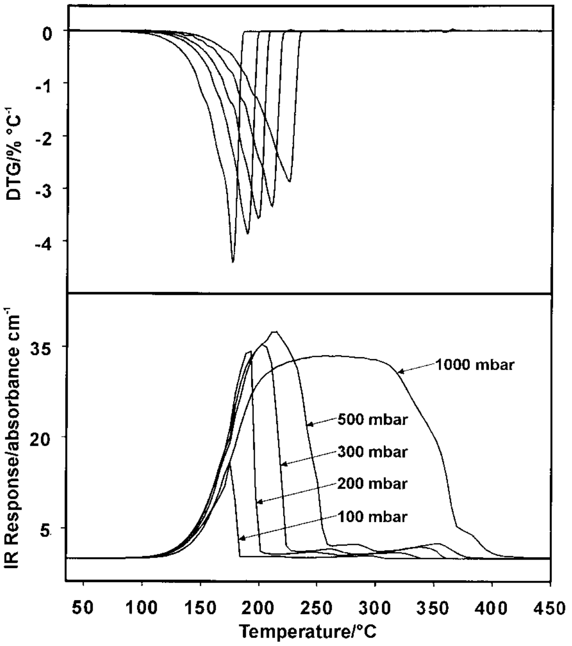

Fig. 3. Rate of weight loss (top) and IR response (bottom) for salicylic acid. For both panels curves are, from left to right, 100, 200, 300, 500, 1000 mbar. All curves are normalized for sample mass.

IR response is proportional to the partial pressure of evolved gas in the gas cell and therefore in an ideal apparatus, at a constant gas flow rate, it would be proportional to the rate of weight loss. In practice, there is considerable peak broadening because of the high boiling point of salicylic acid. At a gas flow rate of 15 ml min^{-1}, there is a large IR response when the furnace temperature has reached 350°C, and some material is detected even at higher temperatures of 400°C. Although the transport of the evolved gas is greatly improved when the gas flow rate is increased to 35 ml min^{-1}, the correspondence between the rate of weight loss and the IR response is still poor. Apart from the general broadening of the response curve relative to the rate of weight loss, it should be noted that peak tailing also exists at temperatures above 280°C. This is due to the trapping of salicylic acid at colder surfaces, such as in the transfer line, and its subsequent gradual sublimation. The gas flow rates could be increased further, with a commensurate improvement in the IR response, but for any TGA there is a limit because excessively high flow rates can cause instability in the balance.

Fig. 3 shows the rate of weight loss and the IR response for the sublimation of salicylic acid at various pressures with a flow of 15 ml min^{-1} nitrogen. The rate of weight loss follows the expected behavior with changing pressure: the maximum rate of weight loss increases as the pressure is reduced, and it occurs at lower temperatures. When the pressure is reduced from 1000 to 500 mbar, the characteristics of the IR response are greatly improved. The IR response at this reduced pressure is similar to that obtained when the gas flow rate was increased to 35 ml min^{-1}. The IR response is further improved when the pressure is dropped to 300 mbar, and at a pressure of 200 mbar there is good correspondence with the rate of weight loss. At this pressure most of the peak tailing has also disappeared. Although both the temporal resolution of the IR response and peak tailing due to trapped material are improved, there is a reduction in sensitivity as the pressure is reduced. Fig. 4 shows the integrated IR response (i.e. the integration of the curves in Fig. 3 over time) as a function of pressure. According to the Beer–Lambert law, the IR absorbance is proportional to the pressure in the gas cell, and there should therefore be a linear relationship between pressure and integrated IR response. This is not the case in practice, however, the slight deviation from linearity being due to partial decomposition of the trapped salicylic acid at high temperatures. This effect is small though, and if it is taken into account then the experimental data show excellent agreement with theory. It should be noted that although the

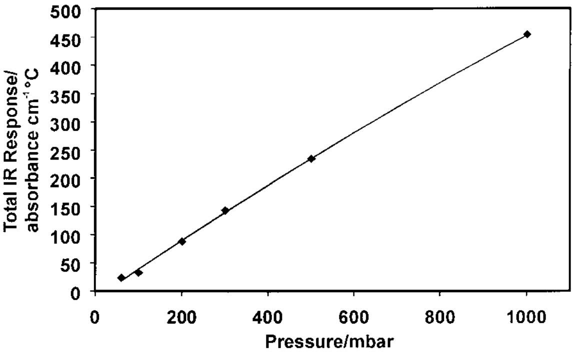

Fig. 4. The integrated IR response for salicylic acid as a function of pressure. The fitted curve is meant only as a guide to the eye.

integrated IR response is lower at reduced pressures, the maximum IR response is slightly better at a pressure of 200 mbar than it is at a pressure of 1000 mbar, because the evolved gas is concentrated into a shorter time. For high boiling compounds, under certain conditions, it is thus possible to obtain an improvement in both sensitivity and temporal resolution by reducing the pressure. The optimum IR response would probably be obtained by using some combination of increased gas flow and reduced pressure, but further work is needed to fully investigate this.

The second example that shows the benefits of TGA–FTIR at reduced pressures is glycerol. It has a high boiling point (290°C) at atmospheric pressure, and partially decomposes when heated. Fig. 5 shows rate of weight loss, the Gram–Schmidt (total IR) response, and the IR response for glycerol (integrated area between 805 and 880 cm^{-1}) as well as two major decomposition products: formaldehyde (integrated area between 1739 and 1747 cm^{-1}) and formic acid (integrated area between 1101 and 1110 cm^{-1}), at a pressure of 1000 mbar. The rate of weight loss shows the behavior expected for a pure material that evaporates without significant decomposition. Nevertheless, the IR data appear to show significant decomposition, even at relatively low temperatures. This is deceptive, however, the IR responses for glycerol and the decomposition products are actually very small at all temperatures because significant quantities of material are being trapped throughout the system. This material continues to evaporate and decompose, and the IR response is therefore spread over a prolonged time period. The constant IR response for the glycerol above 180°C, accompanied by a gradual increase in the concentration of the decomposition products, implies that the material is trapped at several locations. Glycerol trapped in the part of the transfer line close to the FTIR is at constant temperature, and would be expected to gradually move through the system, giving the observed constant response. Glycerol trapped in the part of the transfer line close to the TGA will also gradually evaporate, but this will be accompanied by increased decomposition as the furnace temperature increases. The peak at 330°C in the IR response for the decomposition products indicates that

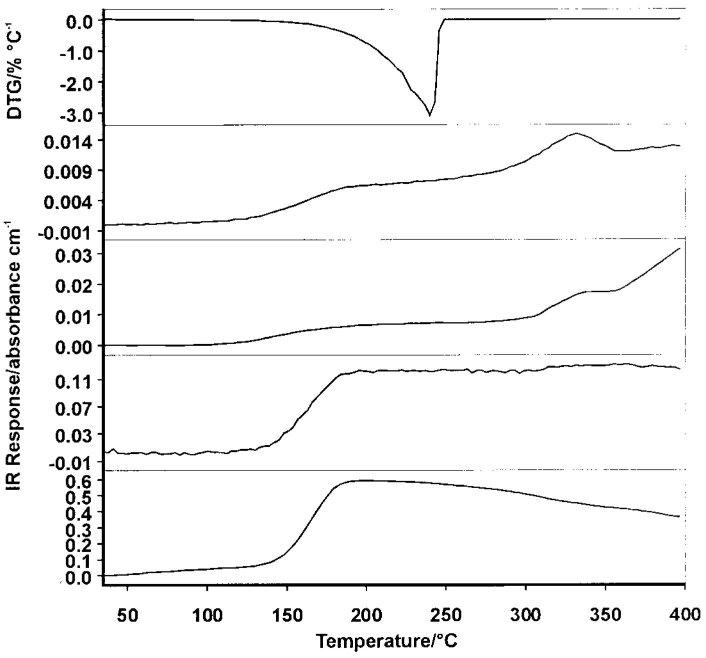

Fig. 5. Rate of weight loss and IR response for glycerol at 1000 mbar. Top to bottom: rate of weight loss, IR response for formic acid, IR response for formaldehyde, IR response for glycerol, Gram–Schmidt response. The maximum rate of weight loss occurs at 240°C.

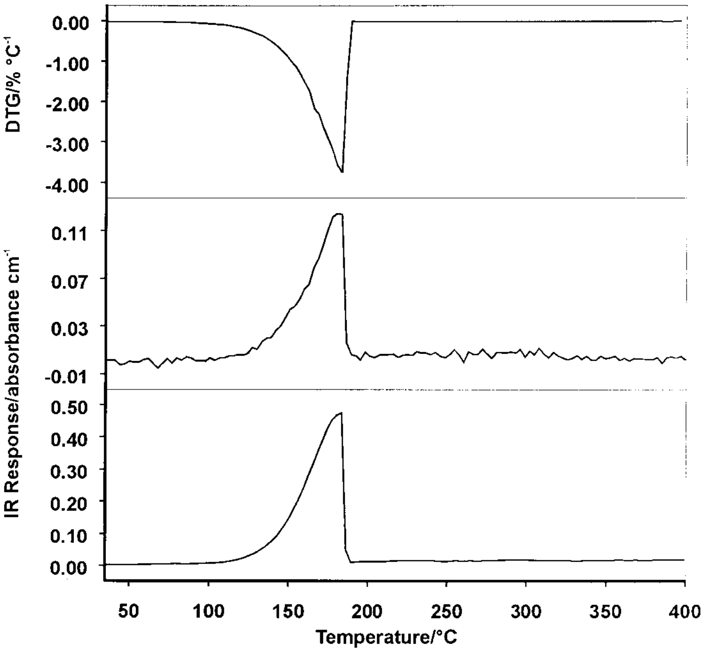

Fig. 6. Rate of weight loss and IR response for glycerol at 60 mbar. Top to bottom: rate of weight loss, IR response for glycerol, Gram–Schmidt response. The maximum rate of weight loss occurs at 182°C.

some glycerol is also trapped at a location that heats up relatively quickly as the furnace temperature is increased. This material is probably in the furnace head, at the point where the transfer line is coupled to the TGA. Although it is easy to understand the behavior of the IR response for pure glycerol, in a complex sample such trapping and subsequent decomposition leads to very misleading gas evolution profiles.

Fig. 6 shows the rate of weight loss, the Gram–Schmidt response, and the IR response for glycerol at a pressure of 60 mbar. At this pressure the boiling point of glycerol is 200°C, which is well below the temperature of the transfer line and IR gas cell. It can be seen that despite the drop in pressure by a factor of 17, the peak sensitivity for glycerol is not significantly reduced, as evidenced by the magnitude of the IR response. There is also now excellent correspondence with the weight loss data, and very little decomposition. It is worth noting that this example also shows the potential for cross contamination of samples. At atmospheric pressure the glycerol trapped in the transfer line takes a very long time to completely move through the system, prohibiting rapid sample turnaround. This problem is completely eliminated at reduced pressures.

Plasticized PVC is used as a final example to show the utility of TGA–FTIR at reduced pressures. It shows that additional information can be obtained about the material composition, and the decomposition process, by using pressure as an experimental parameter. Fig. 7 shows the rate of weight loss, the Gram–Schmidt response, and the IR response for hydrogen chloride (integrated area between 2806 and 2834 cm^{-1}), dioctyl phthalate (integrated area between 1717 and 1775 cm^{-1}), and monobenzyl phthalate (integrated area between 1775 and 1838 cm^{-1}) during the decomposition of plasticized PVC at atmospheric pressure. Fig. 8 shows the IR spectra obtained at the maxima of the Gram–Schmidt response, at 305 and 452°C, along with reference spectra of hydrogen chloride, dioctyl phthalate, and monobenzyl phthalate. The rate of weight loss and the Gram–Schmidt response show that the decomposition occurs in two major steps. In addition, prior to any decomposition of the PVC, there is some volatalization of dioctyl phthalate, but it is too small to be visible

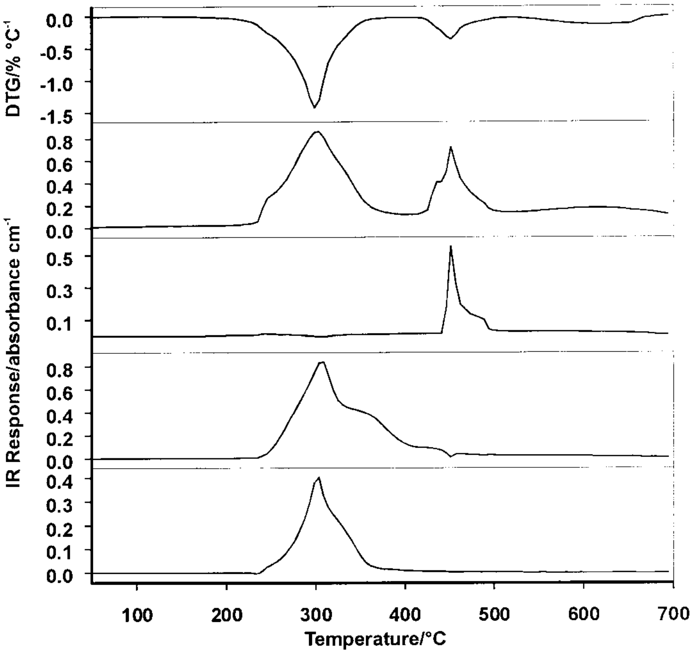

Fig. 7. Rate of weight loss and IR response for PVC at 1000 mbar. Top to bottom: rate of weight loss, Gram–Schmidt response, IR response for dioctyl phthalate, IR response for monobenzyl phthalate, IR response for HCl.

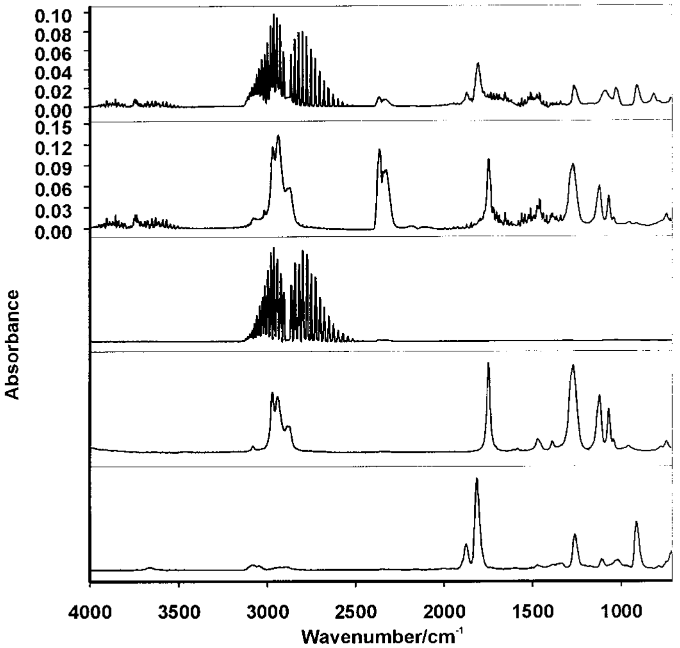

Fig. 8. IR spectra of gases evolved during decomposition of PVC at 1000 mbar. Top to bottom: spectrum at 305°C (initial decomposition stage), spectrum at 452°C (second decomposition stage), reference spectrum of HCl, reference spectrum of dioctyl phthalate, reference spectrum of monobenzyl phthalate.

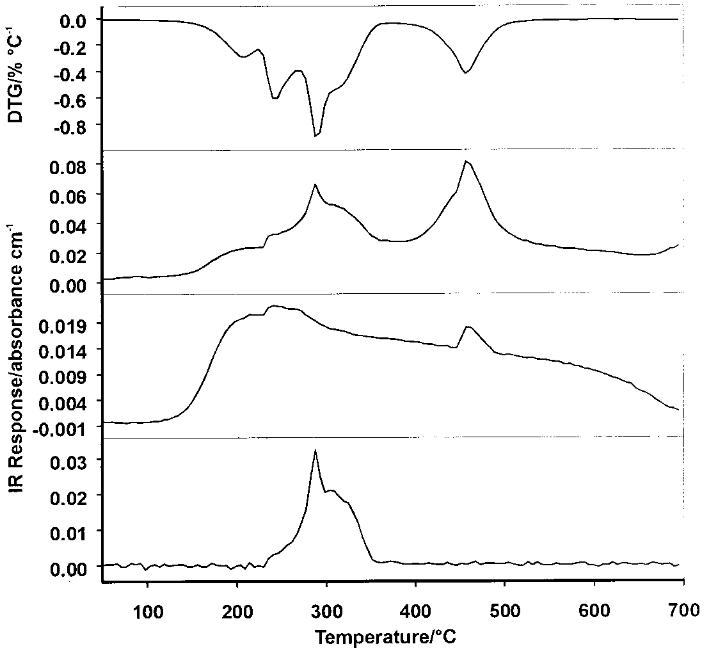

Fig. 9. Rate of weight loss and IR response for PVC at 60 mbar. Top to bottom: rate of weight loss, Gram–Schmidt response, IR response for dioctyl phthalate, IR response for HCl.

in the figures. The second region of weight loss is characterized mainly by the evolution of the dioctyl phthalate plasticizer. Since no HCl is evolved at this stage, it can be concluded that the initial decomposition of the PVC is complete. There is also some carbon dioxide and carbon monoxide evolved during this step, due to residual oxygen trapped in the sample. These gases are very strongly absorbing in the IR, however, and although the peaks are quite large the amount of oxidation is minimal. Of more interest is the first decomposition stage, in which the PVC decomposes and HCl is released. The other major species observed at this stage of the decomposition is monobenzyl phthalate, a compound that is not used as an additive in PVC. Spectral subtraction also indicates the presence of benzene, but other, more dominant, compounds, obscure all its spectral features. It is therefore not visible in the figures.

If the same PVC sample is heated at a pressure of 60 mbar then two major decomposition steps are still observed, as shown in Fig. 9. Fig. 10 shows the IR spectra obtained at the maxima of the Gram–Schmidt response, at 290 and 458°C, along with reference spectra of hydrogen chloride, dioctyl phthalate, and monobenzyl phthalate. As before, in the second decomposition step, the only major compound released is dioctyl phthalate. The rate of weight loss in the first decomposition step has significantly changed though it is now being resolved into three separate transitions, with an additional shoulder. The changes in this decomposition step may merit further investigation, but are not relevant to this discussion. The important observation here is that there is now no evidence of monobenzyl phthalate, the major evolved gases being HCl and dioctyl phthalate. In contrast to the decomposition at 1000 mbar, significant release of dioctyl phthalate now also occurs prior to the PVC decomposition. This is consistent with the results of Mrklić et al. [10], who showed that for PVC foils, the rate controlling step for the loss of dioctyl phthalate from PVC is volatilization from the surface, rather than diffusion. For the small pieces of PVC used in these experiments this should also be true, and reduction of the pressure will greatly speed up this process.

At atmospheric pressure pure dioctyl phthalate has a boiling point of 384°C [11], well above the

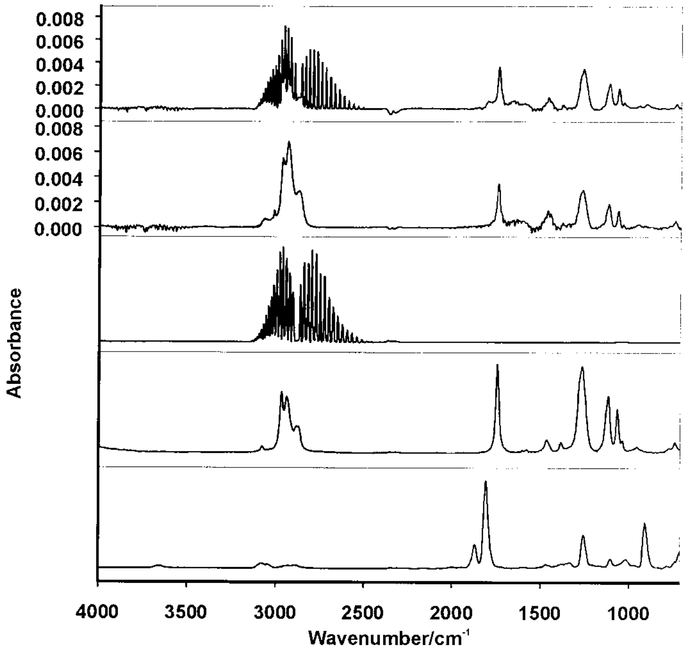

Fig. 10. IR spectra of gases evolved during decomposition of PVC at 60 mbar. Top to bottom: spectrum at 290°C (initial decomposition stage), spectrum at 458°C (second decomposition stage), reference spectrum of HCl, reference spectrum of dioctyl phthalate, reference spectrum of monobenzyl phthalate.

temperature at which the PVC decomposes. Thus, although it is physically released from the polymer, the plasticizer is only evolved slowly from the sample during the first decomposition stage. Since it is still in the sample crucible, it is subject to further decomposition, including attack by chlorine radicals released during the decomposition of the PVC. The reaction chemistry in the crucible is probably complex, and there are a large number of possible reaction products, but only monobenzyl phthalate is seen in large amounts. This is probably due to the fact that this ester has an unusually low boiling point of 105°C at atmospheric pressure, and it, therefore, evaporates as soon as it is formed. When the pressure is reduced to 60 mbar, the boiling point of pure dioctyl phthalate is lowered to about 291°C [12,13], a drop in temperature of more than 90°C. Although this is the boiling point of pure dioctyl phthalate, rather than dioctyl phthalate in PVC, the reduction does give an indication of the significant increase in volatility of dioctyl phthalate at low pressures. This increase in volatility means that most of the plasticizer evaporates before any decomposition or reaction can occur.

4. Conclusions

Reduction of the pressure during a TGA–FTIR experiment can significantly improve the gas flow characteristics for high boiling compounds. As the pressure is reduced there is an improvement in temporal resolution of the IR response that is accompanied by a decrease in the overall sensitivity. The observed relationship between sensitivity and pressure shows excellent agreement with theory. It has also been shown that even though the overall IR sensitivity is reduced, under certain conditions it is possible to improve both the temporal resolution and the peak sensitivity for high boiling compounds.

Reduction of the pressure can also reduce or eliminate trapping and subsequent decomposition of sample in the furnace head and transfer line. This is important if misleading gas evolution profiles are to be avoided. Elimination of sample trapping in the transfer line also minimizes the risk of cross contamination of samples.

The pressure can also be used as a parameter in the experiment. Varying the pressure can provide additional insight into both the material composition and the chemistry of the decomposition process.

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