International Journal of Mass Spectrometry 287 (2009) 128–133

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Isoconversion effective activation energies derived from repetitive injection fast gas chromatography/mass spectrometry

Robert L. White

Department of Chemistry & Biochemistry, University of Oklahoma, 620 Parrington Oval, Norman, OK 73019, United States

ARTICLE INFO

Article history:
Received 5 July 2008
Received in revised form 6 November 2008
Accepted 1 December 2008
Available online 9 December 2008

Keywords:
GC/MS
Activation energy
Thermal analysis
Evolved gas analysis

ABSTRACT

Evolved gas analysis by using fast temperature programmed gas chromatography/mass spectrometry is described. A small volume gas chromatograph oven is used to permit rapid heating and cooling of a capillary gas chromatography column, resulting in short analysis cycle times. This capability permits automated sampling and analysis of a purge gas effluent stream generated during thermal analysis of a solid sample. Species-specific mass spectral information extracted from successively acquired chromatograms can be used to generate concentration profiles for volatile products produced during sample heating. These species-specific profiles can be used for calculation of isoconversion effective activation energies that are useful for characterizing the thermal reaction processes.

1. Introduction

Thermal analysis involves heating samples and measuring changes in their properties as a function of temperature. The basic premise of thermal analysis is that the material composition dictates the temperature-dependent properties of the sample. Conventional thermal analysis methods include: thermogravimetric analysis, thermomechanical analysis, differential thermal analysis, and differential scanning calorimetry. These methods are used to monitor temperature-dependent changes in solid-state bulk properties and do not provide information regarding specific chemical species. When multiple measurements with different sample heating rates are employed for thermal analyses of the same material, thermodynamic parameters that are characteristic of the chemical reactions responsible for temperature-dependent sample changes can be calculated. These thermodynamic parameters and how they change as a function of sample temperature can provide insight into the nature of underlying thermal reactions and molecular transformation mechanisms.

Bulk property information derived from thermal analysis techniques in which decomposition volatiles are removed from heated samples by an inert purge gas can be augmented by evolved gas analysis, which can be used to identify and quantify volatile products. Mass spectrometry [1] and infrared spectrophotometry [2] both provide structural information regarding volatiles generated during thermal analyses and are commonly employed as evolved gas analyzers. Species-specific evolution profiles can be obtained by evolved gas analysis when analyzer signals can be correlated with the concentrations of individual substances entrained in purge gas effluent. Unfortunately, the structural information afforded by mass spectrometry and infrared spectrophotometry evolved gas analyzers often consist of overlapping contributions from multiple mixture components, making species-specific detection difficult or impossible. To facilitate species-specific analysis when evolved gases contain many components, gas chromatography can be employed to separate mixture components prior to structure-specific detection. In fact, several gas chromatography/mass spectrometry (GC/MS) evolved gas analysis methods have been developed. The stepwise pyrolysis GC/MS technique involves subjecting a solid sample to sequentially higher temperatures [3–5]. Evolved gases produced while heating the sample to each successively higher temperature are analyzed by GC/MS to yield species-specific temperature profiles for volatile mixture component concentrations. Because thermal analysis is paused while evolved gas mixtures are analyzed, chromatographic separations requiring long times and involving multiple GC oven temperature ramps can be employed. Another GC/MS evolved gas analysis technique involves the use of repetitive isothermal separations to analyze gases at equal time intervals while samples are heated at a constant rate [6–11]. By sampling at time intervals of 1 min or less, these methods can provide accurate species-specific concentration profiles that can be used for thermodynamic parameter calculations. However, the use of this method is restricted to situations when evolved gas constituents can be

E-mail address: rlwhite@ou.edu.

1387-3806/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2008.12.002

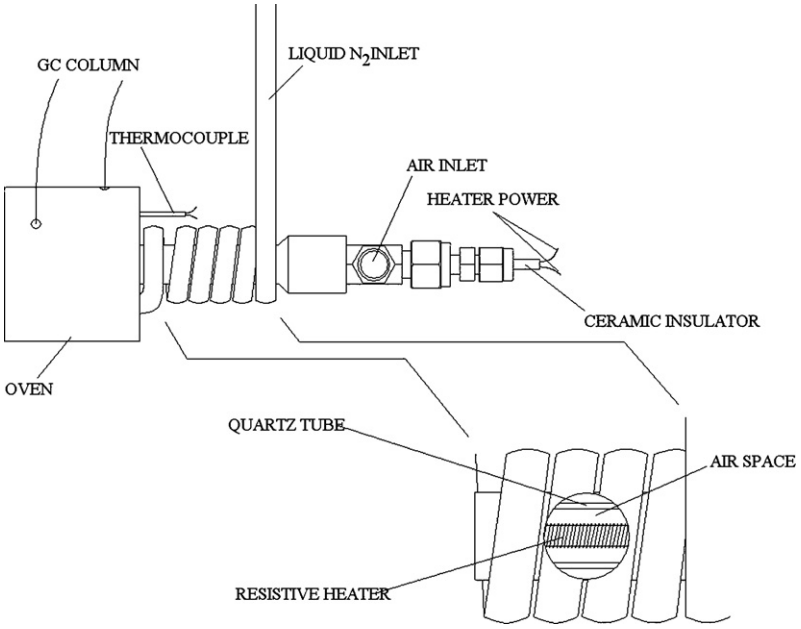

Fig. 1. Schematic drawing of the repetitive injection gas chromatography oven.

effectively separated by isothermal gas chromatography. A third approach to GC/MS evolved gas analysis involves the use of fast temperature programmed gas chromatography to separate mixture components. Compared to isothermal GC/MS, generating volatile product concentration versus temperature profiles by non-isothermal repetitive injection GC/MS is more difficult because separations require longer measurement times (e.g., several minutes). However, non-isothermal GC/MS must be used when mixture components have significantly different chromatographic retention properties. When non-isothermal GC/MS is necessary, a rapid means of cooling the chromatographic column back to the starting temperature after each GC column temperature ramp is needed to minimize analysis cycle times. This is typically done by introducing liquid nitrogen to the chromatographic oven. Thus, evolved gas sampling cycle times for non-isothermal GC/MS include the chromatographic separation time and the time required for cooling. It is demonstrated here that species-specific concentration profiles for evolved gas constituents can be obtained with sufficient accuracy to permit thermodynamic parameter calculations when fast gas chromatography/mass spectrometry is combined with thermal analyses that employ slow sample heating rates. The repetitive injection temperature programmed GC/MS analyses described here were facilitated by the use of a new small volume gas chromatography oven that can be rapidly heated and cooled [12].

2. Experimental

Fast GC/MS analyses were conducted by using a specially designed oven that was capable of efficiently heating and cooling a capillary gas chromatography column rapidly. A schematic drawing of this apparatus is shown in Fig. 1. The 2 in. diameter cylindrical oven is 1.5 in. deep and holds a capillary column coiled to a diameter of about 1.5 in. Three connections to this small oven allow for introduction of heated air, liquid nitrogen coolant, and the placement of a thermocouple for column temperature measurement. By heating an air flow that passes over a resistive wire heater, the capillary column was heated during temperature ramp chromatographic separations. The capillary column was rapidly cooled by allowing liquid nitrogen to enter the oven. The column could be reproducibly heated at a rate of up to 10 °C/s and could be cooled at about the same rate with liquid nitrogen. For the repetitive injection chromatogram measurements described here, about 40 mL of liquid nitrogen was required to cool the column from its maximum temperature back to the starting ramp temperature.

The gas chromatographic oven shown in Fig. 1 was placed inside of an 8 in. × 6 in. × 3 in. aluminum box along with an automated gas sampling valve (model 6C6UWT, VICI Valco Instruments) and a variable flow splitter valve (model MCVT-1, SGE Analytical Science). By using pieces of 1/4 in. thick insulation, this box was divided into three thermally isolated sections. The center section contained the gas chromatograph oven. The injection compartment containing the 6-port sampling valve was placed on the left side of the oven and the effluent splitter valve that was used to control the amount of column exit gas entering the mass spectrometer was located to the right side of the GC oven. Separate heaters and temperature controllers (model CN76000, Omega Engineering, Inc.) allowed the injection and detector valve sections to be maintained at constant high temperatures (>200 °C) while the gas chromatograph oven temperature was varied from low to high temperature during temperature programmed gas chromatographic separations. The aluminum enclosure, containing the injection valve, GC oven, and splitter valve, was attached to the GC inlet of a Hewlett Packard 5973 quadrupole mass spectrometer. GC/MS oven temperatures were measured and adjusted by using a model CN3251 (Omega Engineering Inc.) temperature controller, which simultaneously controlled heating and cooling. The flow of liquid nitrogen coolant to the GC oven was turned on and off based on signals from the CN3251 temperature controller with the use of an ASCO model 8263G205LT (Teragon Research) solenoid valve. Repetitive injections were made by using a DVSP-2 digital valve sequence programmer (VICI Valco Instruments) attached to an ETMA micro-electric actuator (VICI Valco Instruments). Injections were made as a result of a signal sent from the CN3251 temperature controller to the digital valve sequence programmer. The start of each temperature programmed heating ramp was initiated by a computer that was interfaced to the CN3251 controller. This computer also recorded temperature measurements at 1 s intervals in order to store GC oven temperature profiles.

Samples employed for thermal analyses were comprised of polystyrene mixed with HY zeolite. Polystyrene (MW = 2700) was

obtained from Aldrich Chemical Company and used without further purification. NaY zeolite ($SiO_2/Al_2O_3 = 5.3$) was obtained from Universal Oil Products (UOP). Sodium ions were removed from the catalyst by ion exchange with 1.0 M ammonium nitrate. The resulting ammonium zeolite was then calcined at 550 °C for 3 h to produce HY. Samples contained 5% polymer by weight. Polymer/zeolite samples were heated in flowing helium (25 mL/min) inside of an apparatus designed to be used for variable temperature infrared studies. The details of this sample chamber are described elsewhere [13]. The sample chamber purge outlet was connected to the heated injection valve by using a 1/16 in. i.d. stainless steel transfer line which was maintained at 200 °C by using a heating tape. Solid sample sizes employed for studies described here were approximately 5 mg. GC/MS sample injection volumes were determined by the size of the sample loop attached to the injection valve, which had an internal volume of 100 μL. The mass spectrometer was operated with an ion source pressure of 1×10^{-5} Torr at 12 scans/s over a mass range from m/z 50 to 150. Chromatographic separations were made by using a 4 m long 0.25 mm i.d. HP5-MS fused silica capillary column with a 0.25 μm stationary phase thickness and a helium flow rate of 2.5 mL/min. The chromatographic column temperature program used for separations began with a ramp from 20 to 100 °C at a rate of 1.3 °C/s followed by a 2 °C/s ramp to 170 °C. The column was then cooled back to 20 °C in about 20 s to prepare for the next injection. Previous studies have shown that chromatographic peak retention time relative standard deviations increase with increasing column heating rate but are at most 0.6% when a 2 °C/s heating rate is employed [12]. This corresponds to maximum retention time variations of 0.003–0.009 min for substances eluting between 30 and 90 s.

3. Results and discussion

The advantages of employing repetitive injection temperature programmed GC/MS for monitoring evolved gas streams were demonstrated by using the technique for analysis of the decomposition products formed when a mixture of polystyrene and HY zeolite was heated. When polyolefins are heated in the presence of solid acids, a variety of hydrocarbon products are produced. These products exhibit characteristic concentration versus temperature profiles. Fig. 2 shows the results obtained by using repetitive injection GC/MS for the analysis of the evolved gas produced when a

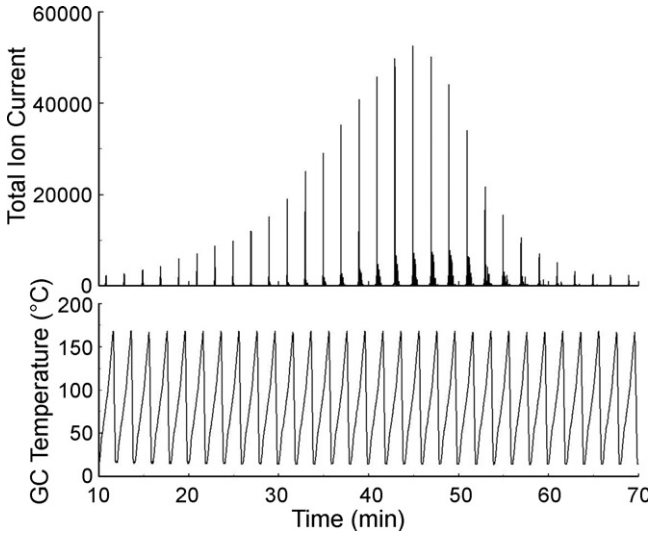

Fig. 2. Repetitive injection chromatograms (top) and gas chromatograph oven temperature profile (bottom) measured during thermal analysis of a polystyrene/HY sample.

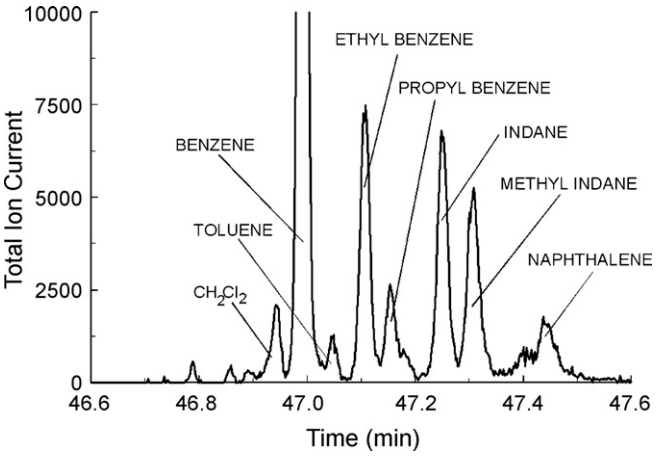

Fig. 3. A portion of a single repetitive injection chromatogram.

sample containing polystyrene and HY zeolite was heated from 220 to 340 °C at a rate of 2 °C/min. The upper portion of Fig. 2 shows the repetitive injection GC/MS chromatograms obtained within this sample temperature range. Although GC/MS chromatograms were measured for 100 min while the sample was heated from 200 to 400 °C, only the 30 chromatograms obtained during the time when most volatile products evolved from the sample are shown. The lower portion of Fig. 2 shows the GC oven temperature measured at 1 s intervals throughout the data collection period. GC/MS chromatograms were obtained at 2 min intervals, corresponding to sample temperature increments of 4 °C. The shapes of the individual chromatograms change with time, indicating that volatile mixture component compositions varied with time (i.e., sample temperature). Fig. 3 shows an expansion of one of the chromatographic separations extracted from those in Fig. 2. This chromatogram resulted from injecting evolved gases at the 46 min mark into the thermal analysis. The nearly baseline separated peaks eluted in a time span of less than 1 min. Methylene chloride, which was the first eluting peak, was a residual background component left over from a previous sample holder cleaning. Repetitive injection GC/MS chromatograms indicated that the concentration of methylene chloride remained relatively constant throughout the thermal analysis, confirming that it was a background constituent. The other peaks labeled in Fig. 3 represent polystyrene decomposition products [14]. By employing a 4 °C evolved gas sampling interval, smooth concentration versus temperature profiles were obtained for each separated component. Repetitive injection temperature programmed GC/MS analyses using the same conditions were repeated with sample heating rates of 0.5 and 1 °C/min in order to generate the species-specific concentration profiles that were needed for thermodynamic parameter calculations.

Effective activation energies (E_a) were calculated from species-specific concentration versus temperature profiles by using a modification of the isoconversion method developed by Ozawa [15]. The isoconversion method is based on the assumption that the state of a system at an arbitrary conversion (C) is independent of heating rate. The method assumes that a constant process is responsible for the physical change, but does not require a specific reaction model (i.e., it is model-free) [16]. Based on the Arrhenius equation, the kinetics of solid sample reactions can be described by [17]:

$$\frac{d(C)}{dt} = k(T)f(C) = A \exp\left(-\frac{E_a}{RT}\right) f(C) \quad (1)$$

where $f(C)$ is the reaction model in terms of conversion, $k(T)$ is the rate constant, T is the absolute temperature, t is time, R is the gas constant, A is the frequency (pre-exponential) factor, and E_a is the activation energy. Vyazovkin [17] has pointed out that if a measured

physical value is proportional to the extent of conversion, numerical differentiation can be used to estimate Arrhenius parameters by using Eq. (1). However, numerical differentiation considerably lowers the signal-to-noise ratio of experimental data. Integration of Eq. (1) provides another basis for evaluating Arrhenius parameters from experimentally derived data.

$$g(C) \equiv \int_0^C \left[\frac{1}{f(C)}\right] d(C) = A \int_0^t \exp\left[-\frac{Ea}{RT(t)}\right] dt \quad (2)$$

In Eq. (2), $g(C)$ is the integral form of the reaction model and $T(t)$ is a function that represents the variation of temperature during a given measurement. If a constant heating rate is applied, then $T(t) = T_o + Ht$, where T_o is the initial temperature and H is the heating rate (dT/dt). Substitution into Eq. (2) leads to Eq. (3), which has no analytical solution [17].

$$g(C) = \frac{A}{H} \int_0^T \exp\left[-\frac{E_a}{RT}\right] dT = \left(\frac{A}{H}\right) I(E_a, T) \quad (3)$$

From the assumption in the isoconversion method that the integral reaction model $g(C)$ depends on conversion but not the heating rate, $g(C)$ is fixed for a given conversion. The $I(E_a,T)$ integral in (3) can be replaced by Doyle's approximation [18] when $E_a/RT \geq 20$ (Eq. (4)). A linear relationship between $\ln(H)$ and $1/T$ for a given conversion can then be obtained by Eq. (5), or in general by Eq. (6).

$$I(E_a, T) \approx \left(\frac{E_a}{R}\right) \exp\left(-\frac{5.331 - 1.052E_a}{RT}\right) \quad (4)$$

$$\ln(H) = -\frac{1.052E_a}{RT} + \ln\left[\left(\frac{AE_a}{g(C)R}\right) - 5.331\right] \quad (5)$$

$$\ln(H) = -\frac{1.052E_a}{RT} + B \quad (6)$$

Guidelines for the interpretation of isoconversion E_a versus conversion plots have been given by Vyazovkin et al. [19]. When a single process is responsible for a temperature-dependent change, calculated E_a values are constant with respect to conversion [20]. However, when contributions from multiple processes change with conversion, E_a values change. An increase in the effective E_a value with respect to conversion results from increased contribution from a parallel reaction process that has a higher activation energy. Effective E_a values decrease with conversion when there is a change in the rate limiting step or a decreased contribution from a process with a high E_a.

By taking advantage of the rapid analysis cycle time afforded by repetitive injection temperature programmed GC/MS, detailed species-specific concentration profiles representing the temperature dependence of volatile mixture compositions were obtained. Species-specific concentration profiles can be generated by plotting total ion current chromatographic peak areas as a function of the sample temperature at the time of GC injection. Profiles with better signal-to-noise can be obtained by using extracted ion chromatograms rather than total ion current. Although the same fragment ion may be found in mass spectra for more than one component, the ion signal corresponding to a specific substance can be selected based on a retention time range. For example, Fig. 4 shows the m/z 91 extracted ion chromatogram derived from the total ion chromatogram in Fig. 3. The m/z 91 ion is present in the mass spectra for toluene, ethyl benzene, propyl benzene, indane, and methyl indane, which are the mixture components responsible for the 5 peaks shown in Fig. 4. By restricting the m/z 91 ion signal peak integration to between 47.08 and 47.15 min, the portion of the m/z 91 ion signal derived from ethyl benzene can be selected and a species-specific concentration profile can be generated. In a similar manner, species-specific concentration profiles were generated for benzene (m/z 78), toluene (m/z 92), ethyl benzene (m/z 91), propyl benzene (m/z 105), indane (m/z 117), methyl indane (m/z 117), and naphthalene (m/z 128). With the exception of toluene, the ions selected were for the base peaks in the mass spectra for these substances. The toluene m/z 92 ion was slightly lower in intensity than the m/z 91 base peak, but the m/z 92 ion was preferred for generating toluene concentration profiles because it had a much lower intensity than m/z 91 in the adjacent eluting ethyl benzene spectrum.

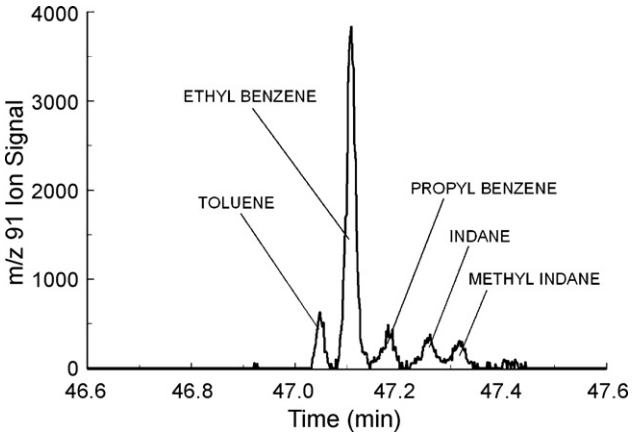

Fig. 4. The m/z 91 extracted ion chromatogram derived from the total ion current chromatogram in Fig. 3.

The temperature ranges over which volatiles evolve and the shapes of species-specific concentration profiles provide insight into the reaction processes that are responsible for sample transformations. Eqs. (5) and (6) can be used to compute "effective" thermodynamic parameters that are characteristic of these reaction processes when multiple heating rates are employed to study the same sample. To employ repetitive injection GC/MS measurements for calculations of species-specific isoconversion effective activation energies, data from 3 different sample heating rates were obtained. Because optimization of the 5% polystyrene/HY sample evolved gas chromatographic separation yielded a total analysis cycle time of 2 min, heating rates for the three data sets employed for isoconversion effective activation energy calculations were chosen to be: 2, 1, and 0.5 °C/min. This required measuring 50, 100, and 200 repetitive injection chromatograms while heating samples, resulting in 4, 2, and 1 °C increments at which evolved gases were sampled, respectively. Species-specific concentration profiles were integrated and normalized to yield conversion plots. For the

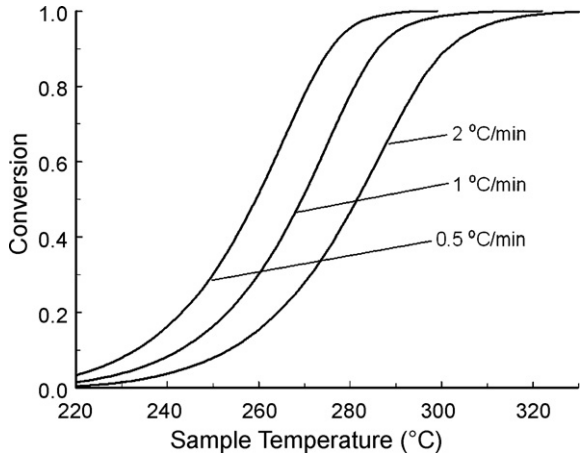

Fig. 5. Conversion versus sample temperature profiles for benzene evolution obtained at different thermal analysis heating rates.

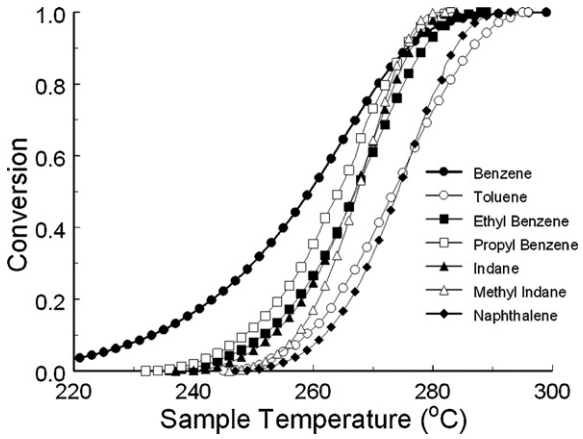

Fig. 6. Conversion versus sample temperature profiles for the volatile products formed by heating poly(styrene) in the presence of HY catalyst.

graphs shown here, conversion is defined as the fraction of the total area under the concentration versus temperature profile reached at selected temperatures.

Benzene conversion profiles obtained by repetitive injection GC/MS analysis while heating the polystyrene/HY sample are shown in Fig. 5. The profile at the highest temperature (right plot) corresponded to a 2 °C/min sample heating rate. The other two profiles corresponded to the 1 and 0.5 °C/min sample heating rates. The conversion curve shift toward lower temperatures with slower heating rates is typical of linearly heated samples. Fig. 6 shows conversion versus sample temperature profiles for all seven volatile products obtained by using the 0.5 °C/min heating rate. The symbols used to distinguish between volatile products were placed at every other data point. Benzene was the first volatile product to be detected and naphthalene was the last. This is consistent with a proposed catalytic reaction mechanism that requires a substantial amount of benzene loss from polymer chains before naphthalene can be formed [14]. It is interesting that the toluene profile is close to the naphthalene profile, indicating that it is primarily formed late in the polymer cracking process. Conversion profiles for the other volatile products were between the benzene and naphthalene profiles and had significant overlaps, suggesting that these products may be formed by similar reaction mechanisms.

Species-specific isoconversion effective activation energy versus conversion plots are shown in Fig. 7. Activation energy errors were estimated to be about ±5 kJ/mol, which was based on the average linear regression slope error calculated when experimental data

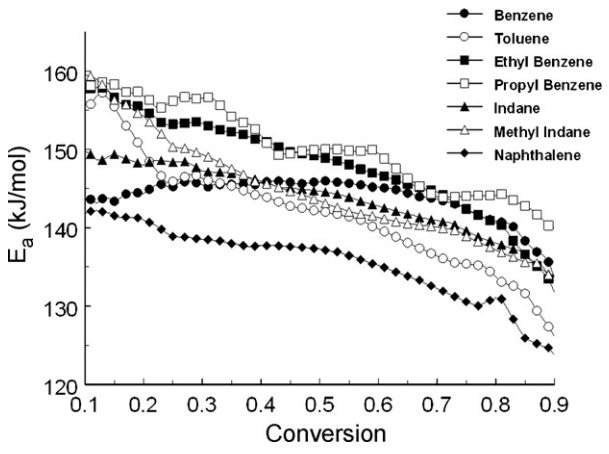

Fig. 7. Effective activation energy versus conversion plots for the volatile products formed by heating poly(styrene) in the presence of HY catalyst.

was fitted to Eq. (6). Each plot in Fig. 7 denotes the change in effective activation energy as a function of conversion for the formation of the specified volatile product. Effective activation energies represent the total energy expended to form volatile products. This energy includes chemical reaction activation energies as well as contributions from transport mechanisms involved in the movement of the volatile product from the solid surface to the gas phase. The effective activation energy range of the seven volatile products is consistent with previously reported volatilization activation energies derived from thermogravimetric measurements when the same polystyrene sample was cracked by silica alumina and HZSM-5 catalysts [14]. Except for benzene and toluene, activation energies decreased slightly with increasing conversion, indicating that reaction mechanisms did not change abruptly throughout the thermal transformation. The benzene activation energy increased slightly until about 0.5 conversion, after which the activation energy began to decrease, suggesting that benzene was produced by multiple reaction pathways. The toluene activation energy decreased by about 10 kJ/mol between 0.1 and 0.25 conversion and then continued to decrease at a slower rate, suggesting that there was a change in the rate limiting step for the reaction process leading to the formation of this volatile product. The naphthalene plot lies below the others, suggesting that the process responsible for the formation of naphthalene had the lowest activation energy. This would seem to be inconsistent with the fact that naphthalene was the last volatile product to appear in GC/MS chromatograms (Fig. 6). However, the low activation energy for naphthalene formation may be consistent with the previously proposed reaction scheme in which initial loss of benzene from the polymer backbone results in the formation of significant unsaturation in the remaining polymer residue [14]. Cyclization of conjugated double bonds in this residue can subsequently form naphthalene. The activation energy for this cyclization reaction is apparently slightly lower than the other reaction pathways. Thus, the reason that naphthalene is formed last in the thermal transformation is because the conjugated double bond system is not initially present in the polymer and must be formed by other reaction mechanisms before naphthalene can be produced.

4. Conclusions

Although repetitive injection temperature programmed GC/MS can be employed for calculating effective activation energies for thermal processes, the experimental procedure is currently time intensive. The amount of time required for data acquisition increases significantly as the sample heating rate is decreased, requiring 100, 200, and 400 min, respectively, for the 2, 1, and 0.5 °C heating rate experiments described here. Accurate concentration profiles are needed for activation energy calculations, so it is unlikely that using a sample temperature interval much larger than 4 °C will yield acceptable results. Instead, future endeavors should focus on reducing the chromatographic separation time so that faster sample heating rates can be employed. The fast gas chromatography apparatus described here is capable of heating at 10 °C/s, therefore the minimum separation time for a particular thermal analysis measurement will be dictated by the evolved gas composition and the characteristics of the capillary column employed for the separation. However, by employing extracted ion chromatograms and integrating peak areas over narrow retention time ranges, it should be possible to generate species-specific concentration profiles even when significant chromatographic peak overlap occurs, provided that adjacent eluting component mass spectra contain at least one mutually exclusive ion.

References

[1] S. Materazzi, Appl. Spectrosc. Rev. 33 (1998) 189.

[2] S. Materazzi, Appl. Spectrosc. Rev. 32 (1997) 385.
[3] L.H. Perng, J. Appl. Polym. Sci. 79 (2001) 1151.
[4] L.H. Perng, Polym. Degrad. Stabil. 69 (2000) 323.
[5] J.F. Lin, C.F. Ho, S.K. Huang, Polym. Degrad. Stabil. 67 (2000) 137.
[6] M. Elomaa, M. Kaljurand, M. Koel, M. Kudrjashova, Thermochim. Acta 336 (1999) 73.
[7] M. Koel, M. Kudrjasova, K. Tonsuaadu, M. Peld, M. Veiderma, Thermochim. Acta 322 (1998) 25.
[8] M. Koel, M. Kaljurand, C.H. Lochmuller, Anal. Chem. 69 (1997) 4586.
[9] W.H. McClennen, R.M. Buchanan, N.S. Arnold, J.P. Dworzanski, H.L. Meuzelaar, Anal. Chem. 65 (1993) 2819.
[10] E.C. Sikabwe, D.L. Negelein, R. Lin, R.L. White, Anal. Chem. 69 (1997) 2606.
[11] D.L. Negelein, E. Bonnet, R.L. White, J. Chromatogr. Sci. 37 (1999) 263.
[12] R.L. White, Chromatographia, in press, doi:10.1365/s10337-008-0850-9.
[13] D.R. White, R.L. White, Appl. Spectrosc. 62 (2008) 116.
[14] R. Lin, R.L. White, J. Appl. Polym. Sci. 63 (1997) 1287.
[15] T. Ozawa, Thermochim. Acta 203 (1992) 159.
[16] S. Vyazovkin, W. Linert, J. Solid State Chem. 114 (1995) 392.
[17] S. Vyazovkin, J. Comput. Chem. 18 (1997) 393.
[18] C.D. Doyle, J. Appl. Polym. Sci. 6 (1962) 639.
[19] S. Vyazovkin, V. Goryachko, V. Bogdanova, V. Guslev, Thermochim. Acta 215 (1993) 325.
[20] S. Vyazovkin, Int. J. Chem. Kinet. 28 (1996) 95.