CHROMSYMP. 1992

Study of rapid reaction kinetics by computerized gas chromatography with stroboscopic sampling

E. KÜLLIK* and M. KALJURAND

Institute of Chemistry, Estonian Academy of Sciences, Tallinn, Estonia (U.S.S.R.)

ABSTRACT

The range of application of stroboscopic sampling is extended to two completely different chemical processes: catalysis of the conversion of alcohols to olefins in phosphoric acid (with a time resolution of 1 s and ignition of polypropylenes containing different amounts of flame retardants (with a temperature resolution of 25°C). The required frequency of analysis of the flows whose composition changes with time is considered. It is demonstrated how stroboscopy coupled with computerized chromatography can provide information that is otherwise difficult, expensive or even impossible to obtain.

INTRODUCTION

Depending on the methods used to study reaction kinetics, the chemical reactions may be classified as slow and fast. A characteristic running time for slow reactions exceeds 100 s and is shorter than 10 s for fast reactions[1]. An important parameter in this kind of study is the time resolution of kinetic curves, *i.e.*, the shortest time interval in which an analytical device used in a particular experiment needs in order to process a sampled reaction mixture. For example, using the chromatograph as an analytical device, the time resolution is determined by the sample separation time in the column (its value being usually measured in minutes). To characterize the reaction thoroughly, the reaction mixture must be sampled with a frequency determined from the Nyquist sampling theorem (also known as Kotelnikov's theorem)[2]. It is evident that for fast reaction studies, instruments with a rapid response are needed. In studying complicated macrokinetic reactions, an exact composition in the reaction components at a particular moment in time is also of interest. Chromatography can provide an excellent separation of the reaction components (reagents and products), but at the expense of separation time. Thus, common chromatographic techniques cannot be applied to rapid reaction studies.

Recently, a new technique for providing samples to the chromatograph, stroboscopic sampling, was proposed[3]. This latter enables one to overcome the

restrictions caused by long separation times in rapid reaction studies. The principle of stroboscopic sampling is simple. The process under study is initiated many times and after each initiation a certain time interval pass. The sample is then taken from the reaction vessel and introduced into the chromatograph. By scanning the interval between initiation and sampling from zero to the end of the reaction, it is possible to record concentration curves for reactants and products with an adequate time resolution. The only requirement for effecting stroboscopic sampling is reproducibility of the process under investigation. For most chemical reactions the latter can be realized at the expense of a more or less sophisticated exerimental set-up.

The idea of stroboscopic sampling is fairly old, dating back to the beginning of the century. It has been applied successfully to many optical measurements of rapid phenomena but, to the authors' knowledge, its first application to the case when the signal carrier is mass flow was demonstrated by Kaljurand et al.[3]. Computerization of the experiment is crucial; although several manual kinetic experiments can be considered as "stroboscopic" (see, e.g., ref. 4), human capabilities for generating precise time intervals and complicated sequences of injections (required in stroboscopic sampling) are limited.

Theoretical[5] and preliminary experimental[2,3] investigations of the stroboscopic sampling method appeared to be promising. However, for further validation of the sampling method more thorough studies are needed. In this work, the range of application of stroboscopic sampling was extended to two completely different chemical processes: catalysis of the conversion of alcohols to olefins on phosphoric acid and ignition of polypropylenes containing different amounts of flame retardants. This paper aims to demonstrate how stroboscopy coupled with contemporary computerized chromatography can provide information that is otherwise difficult, expensive or even impossible to obtain.

THEORETICAL

A change in the concentration of the volatile product of a chemical liquid-phase reaction which is carried out by the inert gas passing above the liquid is described by the following equation[6]:

$$C(t) = C_0[\exp(-at) - \exp(-kt)] \tag{1}$$

where $C(t)$ is the concentration at time t, C_0 is a constant and a and k are mass flow and chemical reaction rate constants respectively. Eqn. 1 can be used as the first approximation to describe processes in H_3PO_4 catalysis. We used eqn. 1 to calculate the time resolution necessary for the following stroboscopic experiments. According to the sampling theorem[2], a continuous function can be adequately represented by the set of function values sampled with an interval Δt if $\Delta t < 1/(2f_m)$, where f_m is the maximum frequency in the power spectrum of the function. Omitting straightforward but long Fourier transform calculations, the power spectrum of eqn. 1 can be written as follows:

$$P(f)/P_m = \{[1 + (2\pi f/a)^2] [1 + (2\pi f/k)^2]\}^{-1} \tag{2}$$

where P_m is the maximum value of the power spectrum. As follows from eqn. 2, there is no maximum frequency in the spectrum. At the expense of some small error, $P(f)/P_m$ can be considered as zero when it is less than, say, 10^{-2} and the corresponding frequency set equals f_m. Omitting again simple but time-consuming calculations, we obtain the following for two extreme cases: if $a \approx k$, then $\Delta t < 1/k$, and $a \gg k$, then $\Delta t < (ak)^{-1/2}$. Thus, taking $t = 0.1$ s (a common switching time for mechanical valves), the rate of the processes that can be studied by a given equipment is $k < 10$ s^{-1}. On the other hand, if a more exact value is needed, say $P(f)/P_m < 10^{-4}$, then Δt should be about three times smaller.

EXPERIMENTAL

Equipment

For catalysis studies, the following chromatographic system was used. The reaction column was a 70 mm × 3 mm I.D. glass column filled with a catalyst. The analytical column was a 2 m × 3 mm I.D. metal column filled with Porasil E adsorbent, which is suitable for the separation of light olefins. Two mechanical valves (Valco C6TX) were used in the experiment. One valve performed the injection of the reagent pulses from the reagent stream supply vessel to the reactor and the other injected the products from the end of the reactor column to the top of the analytial column. The chromatograph used in this study was an LHM-80 with a flame ionization detector. The experimental set-up is described in more detail elsewhere[3].

In ignition experiments generation of the continuous reagent flow necessary to effect stroboscopic sampling is not as straightforward as with gaseous or liquid reagents because the polymer sample is a solid. According to contemporary ideas of polymer ignition, a polymer itself does not burn, but its pyrolysis products are responsible for ignition and burning. The last process provides the heat flow necessary for generation of the degradation products[7]. In our experiment, the heat flow to the sample was generated by an external oven whose temperature was set high enough to form a stream of sample degradation products but the ignition of the products was performed in the ignition reactor separated spatially from the oven where the degradation products were formed. The ignition reactor was a quartz tube (30 mm × 3 mm I.D.) and the process was initiated by passing the current impulse through the platinum wire wound around the tube, thus heating rapidly (about 80°C/s) the reagent flow inside the reactor. Sampling from the reactor to the 15 m × 0.5 mm I.D. metal capillary column coated with SE-30 liquid stationary phase (Perkin-Elmer) was performed with a laboratory-made Deans-type pneumatic switch. The pneumatic switch was controlled by a General Valve magnetic valve. By testing the valve we found that it was able to make reproducible injections with a duration as short as 50 ms. However, in this work such a short time resolution was not necessary. The chromatograph was an Intersmat IGC 121C FL with a flame ionization detector. The experimental set-up is described in more detail elsewhere[2].

Chemicals

n-Propanol and *n*-butanol used as reagents in the catalysis study were of "chemically pure" grade. For catalyst preparation, 85% phosphoric acid ("pure" grade) was used, Porasil E (Waters Assoc.) was used as a solid support for the acid. The

H_3PO_4 catalyst was prepared according to a literature procedure[8]. For ignition studies, a propylene–ethylene copolymer containing about 10% of ethylene was used. Four samples contained 0, 10, 20 and 40% of a flame retardant (Masterflam AF 709 by VAMP, Milan, Italy).

Computer and software

All experiments were controlled by an Apple IIe computer through laboratory-made interfaces and software. The built-in software-controlled relays used in Apple IIe game controllers appeared to be a convenient means for "on–off" switching valves and currents. The detector signal was digitized and read to the Apple IIe memory via a laboratory-made analogue-to-digital converter. The Apple IIe started the experiment by switching "on" the reagent sampling valve or current in the ignition reactor. Then, after a predetermined time interval, the computer took the sample from the reactor and switched all currents and valves "off". After recording the detector signal, the computer started a new cycle with different (from a previous cycle) time intervals between the reaction initiation and sampling.

RESULTS AND DISCUSSION

Catalysis on phosphoric acid

A typical set of chromatograms is shown in Fig. 1. By measuring peak areas for
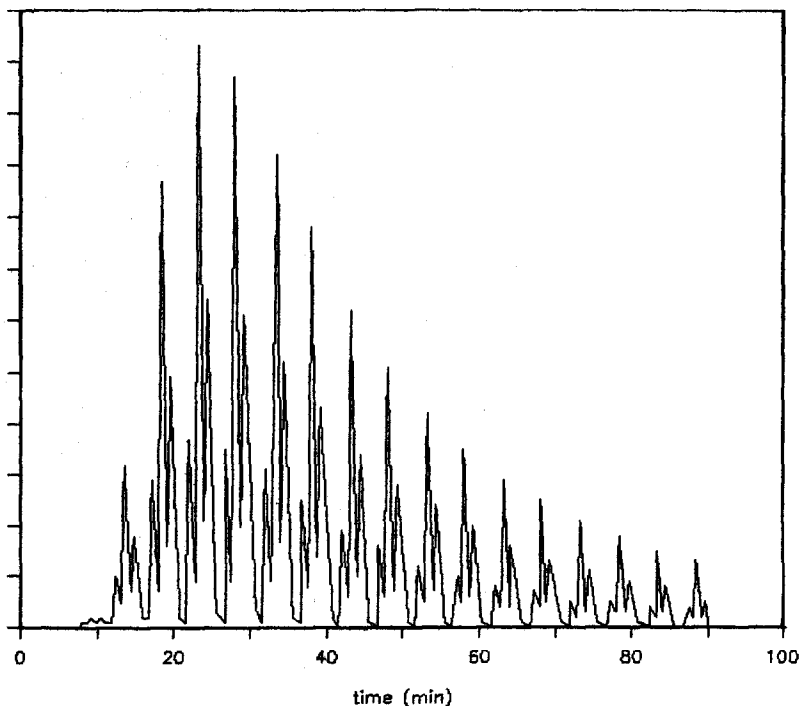

time (min)

Fig. 1. Set of chromatograms of reaction products from *n*-butanol dehydration reaction. Catalyst, Porasil E covered with H_3PO_4. Time resolution, 1 s. Reactor temperature, 283°C. Identification of peaks in triplets (from left to right): 1-butene, *cis,trans*-2-butene and 2-methylpropene. Detector response in arbitrary units.
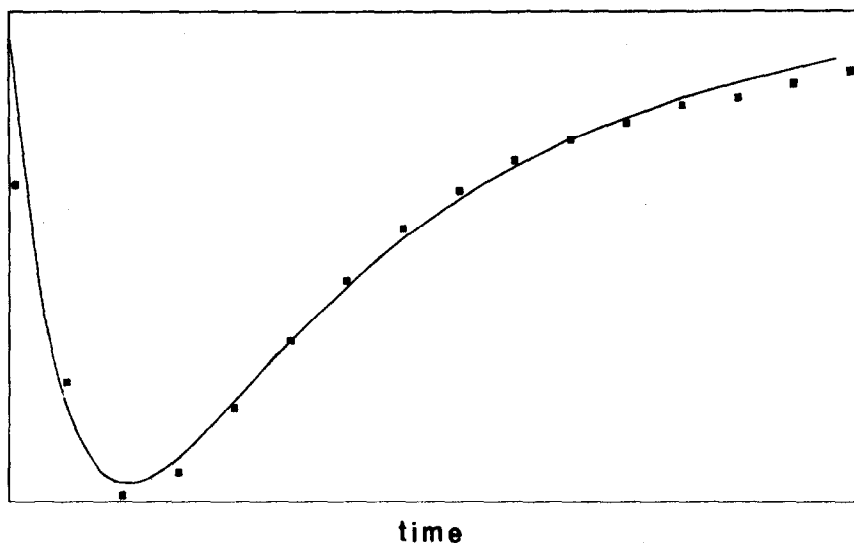
time

Fig. 2. Fitting of *cis*-butene peak areas (from Fig. 1) with the function in eqn. 1. Rate constants: $a = 0.940$ s^{-1} and $k = 0.193$ s^{-1}. Interval between points, 1 s.
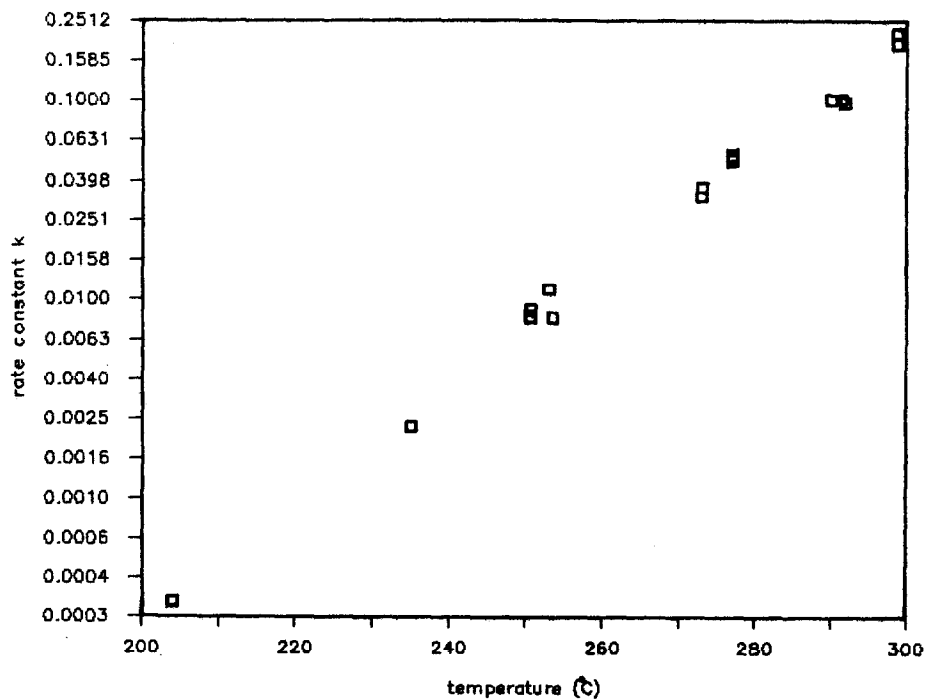

Fig. 3. Rate constant (s^{-1}) of *n*-butanol, k, as a function of temperature (note the logarithmic scale for k). The Arrhenius plot for these data gives the function log $k = 31.01 - 18.74 \cdot 10^3/RT$ with a correlation coefficient of 0.998.

different products it is possible to construct concentration curves for different products and fit the curves to the model in eqn. 1 by the least-squares method. To minimize the difference between the experimental values and the theoretical model, we used both a random search for the best fit and the gradient method. Both procedures are standard in computational mathematics. An example of the best fit obtained is show in Fig. 2. As can be seen, the fit is perfect for the falling part of the curve but problems arise with the rising part of the curve. The error depends strongly on how many experimental points from the beginning of the curve are used for fitting. Hence the model in eqn. 1 is not the best one to describe catalysis in our system and more exact models must be sought. A discussion of the different models that can be used to describe the processes in the reactor is the topic of another paper[9]. However, for the purpose of this paper, the model in eqn. 1 is suitable.

By fitting eqn. 1 to the experimental data we obtain two rate constants, but from the results obtained it is not possible to decide which of the constants is a and which is k. From theory[6], it follows that a depends linearly on the inert carrier gas velocity and is independent of temperature. For k as a chemical reaction rate contstant the opposite applies. Hence by varying the temperature and the carrier gas velocity it is possible to differentiate between rate constants obtained by the least-squares fitting of experimental data. In Fig. 3, the temperature dependence of log k is presented as a function of temperature for butanol reactions. It can be seen that stroboscopic
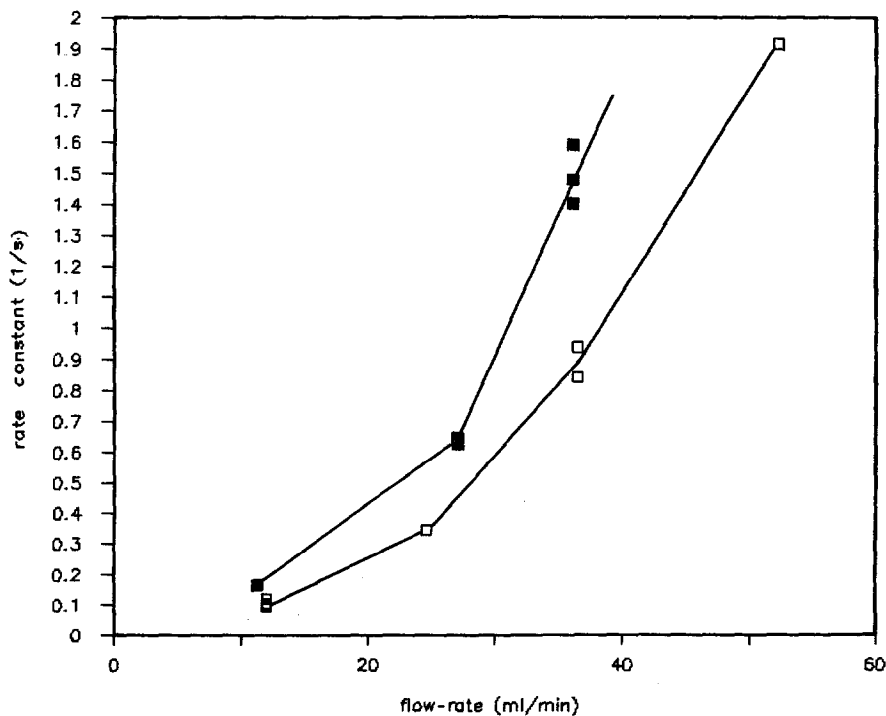

Fig. 4. Mass flow-rate constant, a, as a function of the carrier gas flow-rate through the reactor. Reactor temperature, 283°C. ■, n-Propanol ($k = 0.01$ s^{-1}); □, n-butanol ($k = 0.007$ s^{-1}).

sampling permits the measurement of reaction rate constants of more than three orders of magnitude of k and over a wide temperature range.

In Fig. 4, the dependence of a on the carrier gas velocity is presented. Evidently the function is non-linear, again demonstrating the contradiction with theory, which predicts a linear function. Hence the catalyst used in this work cannot be considered a pure H_3PO_4 liquid catalyst and the support has a strong influence on the reaction course. A complete analysis of the results of this work together with computations of the activation energies, etc., and chemical interpretation of the results will be presented elsewhere[9].

Ignition of polypropylenes

The system performance was tested by oxidation of ethanol. The reproducibility of the overall system was tested by repeating the same experiment many times and recording the product peak height at a certain temperature (450°C). The product peak height reproducibility was 0.3%. The result can be considered acceptable, taking into account that at the ignition temperature the amount of product depends critically on the reaction temperature.

According to the measurement procedure it was possible to record the temperature dependence of the product/reagent concentration curves even under conditions of very rapid self-heating. However, no temperature effects were observed in this experiment. This may be explained by a low concentration of the evolved gases in the carrier stream which, being oxidized, does not provide sufficient heat for the self-heating of the reaction environment. Therefore, in this experiment, the rapid external ballistic heating imitates conditions of self-heating during ignition.

All the samples were analysed in helium and air; 0.1-g samples, when heated at 300°C, provided a continuous and almost constant stream of evolved gases for several hours. Only at the very beginning of the sample heating did the evolution rate oscillate irregularly for the flame retardant-containing samples. Also, it was possible to observe visually extensive foaming of these samples at the experimental temperatures, which may be the reason for the irregular evolution of the degradation products from the polymer samples.

A typical set of chromatograms recorded in air as a function of temperature with a resolution of 25°C or the sample without the flame retardant is shown in Fig. 5. The first peak belongs to the lightest degradation products, probably C_1–C_3 hydrocarbons. It follows from Fig. 5 that the height of the first peak starts to increase after 500°C and the intensity of the other peaks decreases. This is the temperature at which extensive thermal degradation of the evolved products to the lightest compounds begins. The intensity of the first peak passes through a maximum and disappears at 700°C, indicating complete oxidation of the degradation products to water and carbon dioxide. As a flame ionization detector was used, the end products are invisible on the chromatograms. In helium the degradation starts above 540°C and the intensity of the first peak reaches a constant value, as expected.

The effect of the flame retardant is demonstrated in Fig. 6, in which particular temperature points are plotted for samples containing 0 and 40% of the flame retardant as a function of the polymer heating time. It follows from Fig. 6 that the flame retardant influences the heating only at the beginning. A new peak appeared in the chromatogram the intensity of which decreased rapidly and after 1 h the sample behaved like a sample with no flame retardant.
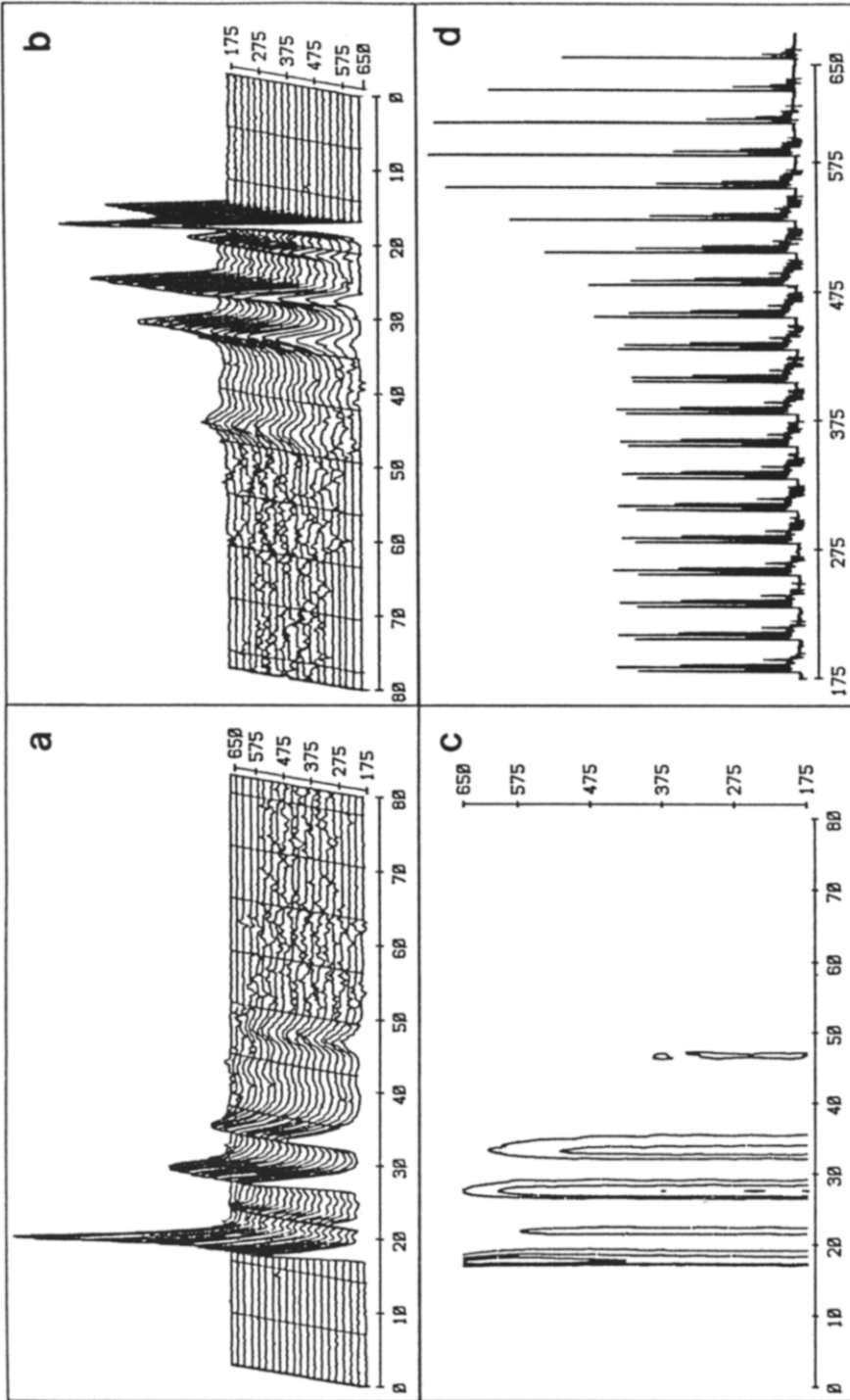
Fig. 5. Different representations of the thermochromatogram of the oxidation reaction of polypropylene degradation products. Polymer heating temperature, 300°C. (a). (b) Stack plots; (c) contour plot; (d) set of reactant chromatograms as they appear on the chart recorder. The time axis (abscissa) represents the chromatographic running time in seconds; the temperature axis (ordinate) represents the oxidation reaction running temperature with a time resolution of 25°C.
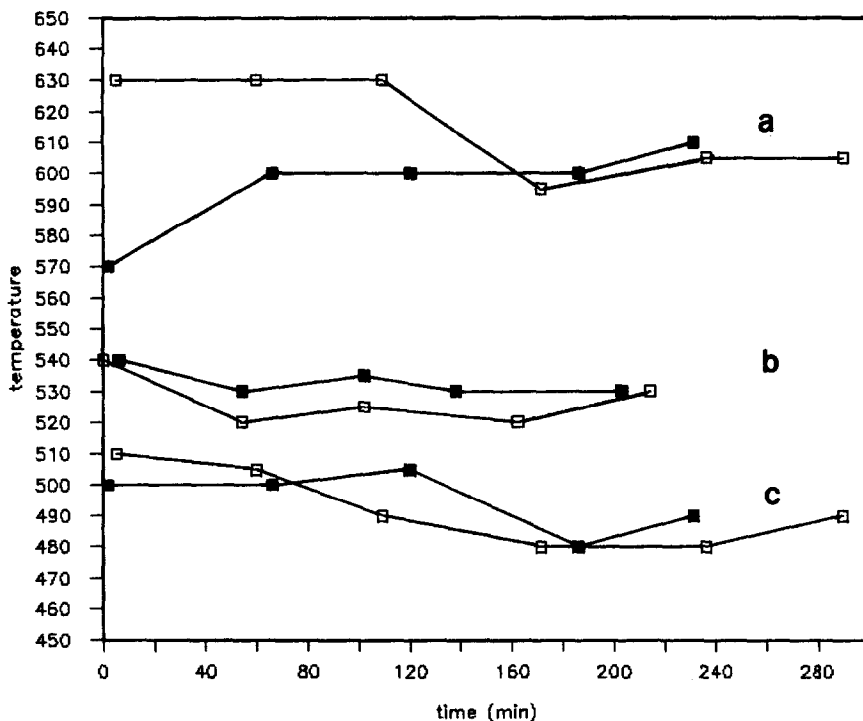
Fig. 6. Particular temperature points on polypropylene ignition thermochromatograms as a function of sample heating time. (a) Temperature of the maximum intensity of the first peak; (b) temperature of the beginning of pyrolysis of the degradation products in helium; (c) temperature of the beginning of pyrolysis of the degradation products in air. $\square$ = 0% flame retardant; $\blacksquare$ = 40% flame retardant. Temperature in °C.

A more detailed analysis of ignition data together with the interpretation of the results from the viewpoint of polymer chemistry will be published in the near future.

So far gas chromatography has been used for the analysis of slow chemical reactions. Recent developments in high-speed chromatography have made possible separations in a few seconds. However, this requires the design of special fast-response chromatographic equipment[10]. As follows from the results of this work, stroboscopic sampling enables common chromatographic equipment to be used.

ACKNOWLEDGEMENTS

REFERENCES

1 E. A. Denisoff, *Kinetics of Homogeneous Chemical Reactions* (in Russian), Vyshaya Schola, Moscow, 1988, p. 19.
2 M. Kaljurand, *Proc. Estonian AS, Chemistry*, 38 (1989) 25.
3 M. Kaljurand, M. Lamberg and E. Küllik, *Proc. Estonian AS, Chemistry*, 37 (1988) 78.
4 A. F. Shushunova and L. Y. Prokhorova, *J. Chromatogr.*, 283 (1984) 365.
5 M. Kaljurand and E. Küllik, *Computerised Multiple Input Chromatography*, Ellis Horwood, Chichester, 1989.
6 A. N. Marinitchev and B. V. Ioffe, *J. Chromatogr.*, 454 (1988) 327.
7 N. Grassie and G. Scott, *Polymer Degradation and Stabilization*, Cambridge University Press, Cambridge, 1984.
8 B. V. Ioffe, N. A. Katsanos, L. A. Kokovina, A. N. Marinitchev and B. V. Stolyarov, *Kinet. Katal.*, 28 (1987) 805.
9 A. N. Bureiko, M. Kaljurand, A. N. Marinichev and B. V. Stolyarov, *Kinet. Katal.*, in press.
10 C. A. Cramers and P. A. Leclerq, *CRC Crit. Rev. Anal. Chem.*, 20 (1988) 117.