Proc. Estonian Acad. Sci. Chem., 1990, **39**, N 4, 218–226 https://doi.org/10.3176/chem.1990.4.05

УДК 543.544.8:541.127

Mihkel KALJURAND

INVESTIGATION OF RAPID REACTION KINETICS BY COMPUTERIZED GAS CHROMATOGRAPHY WITH STROBOSCOPIC SAMPLING

(Presented by J. Kann)

Introduction

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

Recently a new technique of sampling to the chromatograph — stroboscopic sampling — has been proposed. This technique enables to overcome the restrictions caused by long separation times necessary for rapid reaction studies. The principle of stroboscopic sampling is simple and straightforward. The process under study is initiated many times and after each initiation a certain time interval passes. The sample is then taken from the reaction vessel and introduced to the chromatograph. It is possible to record concentration curves for reactants and products with an adequate time resolution by scanning the interval between initiation and sampling from zero to the end of the reaction. The only requirement for realizing stroboscopic sampling is reproducibility of the process under investigation. For most chemical reactions the latter can be realized by using a more or less sophisticated experimental set-up.

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

Theoretical [⁵] and preliminary experimental $[^{2}, ^{3}]$ investigation of the stroboscopic sampling method seemed to be promising. However, for a further approval of the sampling method more thorough studies are needed. In this paper the range of the application of stroboscopic sampling is extended to two completely different chemical processes: catalysis of alcohols on phosphoric acid to olefins, and ignition of polypropylenes containing different amounts of flame retardants. This paper aims at demonstrating how stroboscopy coupled with modern 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 entrained by the inert gas passing above the liquid is described by the following formula [⁶]:

$$C(t) = C_0 (e^{-at} - e^{-kt});$$
(1)

where C(t) is the concentration at the time t, C_0 is a constant, a and k are mass flow and chemical reaction rate constants. Eq. 1 can be used as the first approximation to describe processes in H₃PO₄ catalysis. We used Eq. 1 to estimate 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 the 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 Eq. 1 can be written as follows

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

where P_m is the maximum value of power spectrum. As follows from Eq. 2, there is no maximum frequency in the spectrum described by Eq. 2. 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 for two extreme cases: if a=k, then $\Delta t < 1/k$, and if $a\gg k$, then $\Delta t < (ak)^{-1/2}$. Thus, taking $\Delta t=0.1$ sec (a common switching time for mechanical valves), the rate of the processes that can be studied by the given equipment is $k=10 \text{ sec}^{-1}$. On the other hand, if a more exact estimation is needed, say, $P(f)/P_m < 10^{-4}$, then Δt should be about three times lower.

Experimental

Equipment. For catalysis studies, a two-dimensional chromatography was used. The reaction column was a $70 \text{ mm} \times 3 \text{ mm}$ glass column filled with a catalyst. The analytical column was a $200 \text{ mm} \times 3 \text{ mm}$ metal column filled with Porasil E adsorbent suitable for 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 reaction column and the other injected the products from the end of the reactor column to the top of the analytical one. The chromatograph used in this study was LHM-80 with a flame-ionization detector. The experimental set-up is described in more detail in [³].

In ignition experiments, generation of the continuous reagent flow necessary to realize stroboscopic sampling is not as straightforward as in the case of gaseous or liquid reagents because the polymer sample is a solid. According to contemporary ideas of polymers ignition a polymer itself does not burn, but its pyrolysis products are responsible for ignition and burning. The burning process provides the heat flow necessary for the 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 $(30 \text{ mm} \times 3 \text{ mm})$ and the process was initiated by passing the current impulse through the platinum wire wound around the tube, thus heating rapidly (about $80 \,^{\circ}C/sec$) the reagent flow inside the reactor. Sampling from the reactor to the 15 m×0.5 mm metal capillary column coated with SE-30 liquid phase (Perkin-Elmer) was performed by a self-made Deans-type pneumatic switch. The pneumatic switch was controlled by a General Valve Corporation magnetic valve. By testing the valve we found that the latter was able to make reproducible injections whose duration is as short as 50 msec. However, in the present work, so short a time resolution was not necessary. The chromatograph was an Intersmat IGC 121C FL with a flameionization detector. The experimental set-up is described in more detail in [2].

Chemicals. N-propanol and n-butanol used as reagents in catalysis study were "chemically pure" grade. For catalyst preparation, 85% phosphoric acid was used (grade "pure"). Porasil E (Waters Assoc., Inc.) was used as a solid support to acid. The H_3PO_4 catalyst was prepared according to the procedure described in [8]. For ignition studies, a poly-(propylene-co-ethylene) copolymer containing about 10% of ethylene was used. Four samples contained 0%, 10%, 20% and 40% of a flame retardant, recpectively.

Computer and software. All experiments were controlled by an Apple IIe computer through self-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 self-made analog-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 phosphorus acid. A typical set of chromatograms is shown in Fig. 1. By measuring peak areas for different products it is possible to construct concentration curves for different products and fit the curves to model (1) applying the least squares method. To minimize the difference between the experimental values and a theoretical model, we used both a random search of the best fit and the gradient method. Both the procedures are standard in computational mathematics. An example of the best fit obtained is shown in Fig. 2. As seen in this Figure, the fit is perfect in the falling part of the curve, but problems arise in the rising part of the curve. The fit error depends strongly on how many experimental points from the beginning of the curve are used for fitting. So, model (1) is not the best one to describe catalysis in our system and more exact models must be searched for. A discussion of different models which can be used to describe the processes in the reactor is the topic of another paper [⁹]. However, model (1) is suitable for the purpose of the present paper.



Fig. 1. Set of chromatograms of reaction products from *n*-butanol dehydration reaction. Catalyst is Porasil E covered with H_3PO_4 . Time resolution is 1 sec. Identification of peaks in triplets (from left to right): 1-butene, cis-, trans-butene, and isobutene. Reac's temperature was 283 °C.



Fig. 2. Fitting cis-butene peak areas (from Fig. 1) with function in Eq. 1. Rate constants are a=0.940 sec⁻¹ and k=0.193 sec⁻¹. Interval between points is 1 sec; y-axis is reversed.



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



Fig. 4. Mass flow rate constant, a, as a function of the carrier gas flow rate through reactor. Reactor temperature T=283 °C. Filled squares — n-propanol (k=0.01 sec⁻¹); open squares — n-butanol (k=0.007 sec⁻¹).

By fitting Eq. 1 to the experimental data we obtain two rate constants. However, from the results obtained it is not possible to decide which of the constants is a and which is k. From the theory [6] it follows that adepends linearly on the inert carrier gas velocity and is independent of temperature. For k as a chemical reaction rate constant the case is the opposite. So, varying the temperature and the carrier 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 temperature function for different reactions of alcohols. As follows from Fig. 3, stroboscopic sampling enables measurement of reaction rate constants of more than three orders of the k value and in a wide temperature range.

In Fig. 4, the dependence of a on the carrier gas velocity is presented. Evidently, the function is nonlinear demonstrating again the contradiction with the theory that predicts a linear function. So, the catalyst used in this work cannot be considered a pure H₃PO₄ liquid catalyst and the support has a strong influence on the reaction course. A complete analysis of the results of the present work together with computations of the activation energies, etc., and chemical interpretation of the results will be presented in a separate paper [⁹].

Ignition of polypropylenes. The system performance was tested by ethanol oxidation. 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 (T=450 °C). The product peak height reproducibility was 0.3%. The result should be considered acceptable, taking into account that at the ignition temperature the product amount 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 the conditions of very rapid self-heating. However, no temperature effects were observed in this experiment. This may be explained by a low concentration level of the evolved gases in the carrier stream which, being oxidized, does not provide enough heat for the self-heating of the reaction environment. So, in this experiment, the rapid external ballistical heating imitates conditions of self-heating during ignition.

All the samples were analyzed in helium and air 0.1 g samples which provided, when heated at 300 °C, a continuous and almost constant stream of evolved gases for several hours. Only in the very beginning of the sample heating the evolution rate oscillates chaotically for the flame retardant containing samples. Also, it was visually possible to follow an extensive foaming of these samples at the experimental temperatures which may be the reason for a chaotic 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 is shown in Fig. 5. The first peak on the chromatograms belongs to the lightest degradation products; probably hydrocarbon from methane to propane. It follows from Fig. 5 that the height of the first peak starts to increase after T=500 °C. The intensity of the other peaks decreases. This is the temperature at which an extensive thermal degradation of the evolved products to the lightest ones begins. The intensity of the first peak passes the maximum and disappears at 700 °C indicating a complete oxidation of the degradation products to H₂O and CO₂. As the FID detector was used in the chromatograph, 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 it should do.



Fig. 5. Thermochromatogram of the polypropylene degradation products. Polymer heating temperature was $300 \, ^{\circ}\text{C}$, a and b are stack plots, c is a contour plot, and d is a set of reactant chromatograms as they appear on the chart recorder. The time axis (x) represents the chromatographic running time in sec. The temperature axis (y) represents the oxidation reaction running temperature with the time resolution of $25 \, ^{\circ}\text{C}$.



Fig. 6. Particular temperature points on polypropylene ignition thermochromatograms as a function of sample heating points on porproduct grants at 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 (open squares — 0% FR, filled squares — 40% FR).

The effect of the flame retardant is demonstrated in Fig. 6 where 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. 5 that the flame retardant influences the heating in its beginning only. On the chromatograms, a new peak appeared whose intensity decreases rapidly and in an hour the sample behaves like a sample with no flame retardant.

A more detailed analysis of ignition data together with an interpretation of the results from the viewpoint of polymer chemistry is to be published in [10].

Acknowledgements. The author would like to thank A. Bureiko for performing H_3PO_4 catalysis measurements, Dr. B. V. Stolyarov and Dr. A. N. Marinitchev from Leningrad University for fruitful discussions and providing the catalyst, and Dr. M. Elomaa from Helsinki University for providing the polypropylene samples and for discussions on polymer ignition problems.

REFERENCES

Денисов Е. Д. Кинетика гомогенных химических реакций. М., 1988, 19.

- Денисов Е. Д. Кинетика томогенных лимических реакцин. И., 1966, 15.
 Кальюранд М. Анализ нестационарных потоков вещества: возможности компью-терной хроматографин // Изв. АН ЭССР. Хим., 1989, 38, № 1, 25—33.
 Kaljurand, M., Lamberg, M., Küllik, E. Stroboscopic sampling into gas chromato-graph: the possibility of studying nonstationary gas flows // Proc. Acad. Sci. ESSR. Chem., 1988, 37, N 2, 78—82.

3 Eesti TA Toimetised. K 4 1990

- 4. Shushunova, A. F., Prokhorova, L. Y. Kinetic investigation of the thermal decomposition of organic peroxides by pulse chromatography // J. Chromatogr., 1984, 283, 365-370.
- 5. Kaljurand, M., Küllik, E. Computerised Multiple Input Chromatography. Chichester,
- Ellis Horwood Ltd., 1989. Marinitchev, A. N., Ioffe, B. V. Theoretical aspects of the application of head-space analysis to the investigation of reaction kinetics in solutions // J. Chromatogr., 1988, 454, 327-334,
- Grassie, N., Scott, G. Polymer Degradation and Stabilization, Cambridge, Cambridge 7. Univ. Press, 1984.
- Опу. Ртевз, 1984.
 Иоффе Б. В., Катсанос Н. А., Коковина Л. А., Мариничев А. Н., Столяров Б. В. Изучение кинетики жидкофазных химических реакций методом газовой хрома-тографии с обращением потока // Кинетика и катализ, 1987, 28, № 4, 805—810.
 Бурейко А. Н., Кальюранд М. Р., Мариничев А. Н., Столяров Б. В. Изучение ки-нетики дегидратации спиртов методом стробоскопического ввода пробы // Ки-
- нетика и катализ (in press). 10. Elomaa, M., Kaljurand, M. Rapid oxidation kinetics of thermo-oxidative degradation products of polypropylene by gas chromatography with stroboscopic sampling // J. Chromatogr. Sci., in press.

Estonian Academy of Sciences. Institute of Chemistry

Received Feb. 26, 1990

Mihkel KALJURAND

KIIRETE REAKTSIOONIDE KINEETIKA UURIMINE STROBOSKOOPILISE SISESTUSEGA ARVUTIKROMATOGRAAFIA ABIL

On näidatud stroboskoopilise sisestuse võimalusi kiirete keemiliste reaktsioonide gaasikromatograafilisel uurimisel. Meetodit on rakendatud kahe protsessi puhul: alkoho-lide katalüüsil fosforhappega ja polüpropüleeni süttimisel. Stroboskoopiline sisestus võimaldab mõõta katalüütilise reaktsiooni kiiruskonstante laias temperatuurivahemikus ning detailselt uurida polüpropüleeni süttimise kineetikat. Reaktsioonile avaldab mõju proovis sisalduv antipüreen ainult polümeeri soojendamise alguses.

Михкель КАЛЬЮРАНД

ПРИМЕНЕНИЕ КОМПЬЮТЕРНОЙ ХРОМАТОГРАФИИ СО СТРОБОСКОПИЧЕСКИМ ВВОДОМ ПРОБЫ ДЛЯ ИЗУЧЕНИЯ БЫСТРОПРОТЕКАЮЩИХ РЕАКЦИЙ

Продемонстрированы возможности стробоскопического ввода пробы для изучения быстропротекающих реакций. Исследовано два процесса: катализ спиртов на фосфорной кислоте и воспламенение полипропиленов. Показано, что стробоскопический ввод пробы позволяет измерять константы скорости реакции в широком интервале температур, а также детально изучать кинетику воспламенения полипропилена. Введение в полипропилен антипирена влияет на скорость реакции только в начале нагревания полимера.