Proc. Estonian Acad. Sci. Chem., 1996, **45**, 1/2, 1–8
https://doi.org/10.3176/chem.1996.1/2.01

COMPUTERIZED CHROMATOGRAPHIC MONITORING OF RAPID THERMOOXIDATION REACTIONS

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Presented by T. Tenno

Received 5 February 1996, accepted 3 June 1996

Abstract. A new technique, stroboscopic sampling, was applied for the chromatographic monitoring of rapid thermooxidation reactions. When stroboscopic sampling is used the time resolution of the concentration curves of the reactants and products does not depend on the separation time of the products and reactants in chromatographic column but only on the operating speed of the sampling device. The results of thermooxidation reaction of some aliphatic alcohols within the temperature range of 250–650 °C are reported with temperature resolution of 10 °C.

Key words: computerized chromatography, stroboscopic sampling, thermooxidation.

INTRODUCTION

Two clearly distinctive approaches of computer applications in chemistry can be observed. First, computers are applied for fast calculations. This enables the use in chemistry of mathematical methods known long ago, that could not be implemented because of an enormous amount of calculations (e.g. Fourier transform, multidimensional data analysis, quantum chemical calculations, etc.).

Another approach to the use of computers can be associated with applications where computers control the instruments and perform experiments. There exist experimental procedures that in principle are simple to carry out, but that have still been impossible technically because of the necessity for very quick and very precise control of the experimental setup and several fast measurements. Computerization of the chemical instrumentation enables us to operate at speed, accuracy, and reproducibility unattainable in the case of manual operation, reduces the detection limits of common analytical procedures, and increases their throughputs. Most impressive examples are FTIR and NMR spectroscopy.

Using continuously increasing operation speed and memory capacity of contemporary personal computers, it is possible to design computer based automatic experimental arrangements that crucially differ from the devices designed for human use. In this paper we would like to report the results of an experiment in computerized chromatography, where the time resolution of the chromatographic analysis of time varying processes (e.g. chemical reactions) can be reduced two orders of magnitude using a stroboscopic sampling rule not attainable to a human operator.

The application of conventional chromatography as a method for investigating the kinetics of chemical reactions is restricted to relatively slow processes (with a characteristic run time of more than 10 s). The reason is that the separation of the products and reagents in the chromatographic column requires time and in most favourable cases (short columns, limited number of components) this time of analysis is generally tens of seconds in gas chromatography and tens of minutes in liquid chromatography. Because of the nature of chromatographic separation, the introduction of new concentration values is not possible before the previous separation has been completed. Thus, for the analysis of rapid processes fast scanning methods like MS or FTIR spectroscopy should be used. These methods, however, are much more expensive than the chromatographic technique. Also, the service and handling of the sophisticated instruments require qualified personnel, which is not the case with chromatography.

Recently, a new technique for providing samples to the chromatograph, the stroboscopic sampling, was proposed [1]. This procedure enables one to overcome the restrictions caused by the long separation time in studying rapid reactions. The principle of the stroboscopic sampling is simple: the process under study is initiated many times and when after each initiation a certain time has elapsed, the sample is taken from the reaction vessel and introduced into the chromatograph. By scanning the time 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 a time resolution of 0.1 s. The only requirement for effective stroboscopic sampling is the reproducibility of the process under investigation. For most chemical reactions this can be achieved through more or less sophisticated experimental setup. It follows from the description of the method that the time resolution of monitoring depends only on the operating time of the sampling device but not on the separation time in the chromatographic column.

The idea of stroboscopic sampling is fairly old, dating back to the beginning of this century. It has been successfully applied to many optical measurements of rapid phenomena. Its application to the case when the signal carrier is the mass flow was first demonstrated by Kaljurand et al. [2]. Computerization of the experiment is crucial. Although several manual kinetic experiments can be considered as "stroboscopic", human capabilities to generate precise time intervals and complicated sequences (required in stroboscopic sampling) are limited.

Theoretical and preliminary experimental investigations [1, 2] of stroboscopic sampling method appeared to be promising. However, for further validation of the method thorough studies are needed. In this work the range of the application of stroboscopic sampling was extended to thermooxidation of some aliphatic alcohols. The paper aims to demonstrate how stroboscopy coupled with contemporary computerized chromatography can provide information that is otherwise difficult, expensive, or even impossible to obtain.

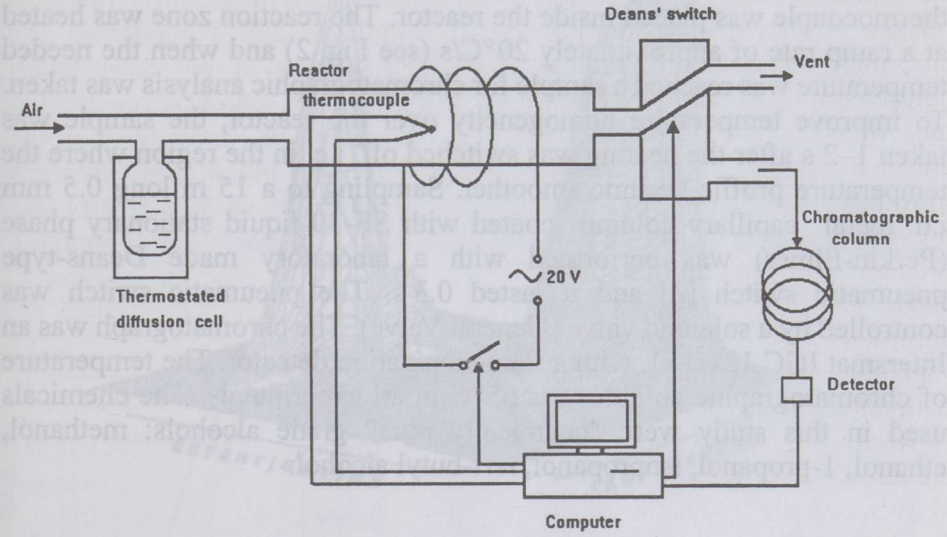

Fig. 1. Experimental setup.

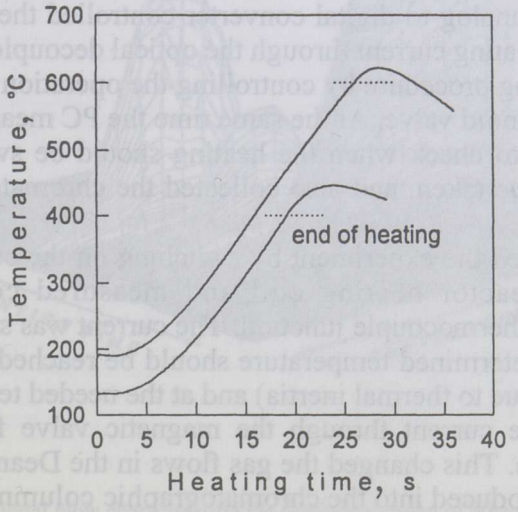

Fig. 2. Typical heating-up curves (temperature of thermocouple in the centre of the reactor). The heating current was turned out at 400 and 600°C respectively.

EXPERIMENTAL

Equipment and chemicals

Our experimental setup is depicted in Fig. 1. The continuous reagent flow necessary to effect stroboscopic sampling was provided by a thermostated test tube with liquid reactant (diffusion cell) located upstream to the reactor on the carrier gas line. Air was used as the carrier gas. The ignition reactor was a quartz tube (30 mm long, 3 mm i.d.) and the process was initiated by passing electric current through the platinum wire wound around the reactor. For monitoring the temperature a PtRh10-Pt thermocouple was placed inside the reactor. The reaction zone was heated at a ramp rate of approximately 20 °C/s (see Fig. 2) and when the needed temperature was reached a sample for chromatographic analysis was taken. To improve temperature homogeneity over the reactor, the sample was taken 1–2 s after the heating was switched off, i.e. in the region where the temperature profile became smoother. Sampling to a 15 m long 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 [3] and it lasted 0.3 s. The pneumatic switch was controlled by a solenoid valve (General Valve). The chromatograph was an Intersmat IGC 121C FL with a flame ionization detector. The temperature of chromatographic column was 65 °C in all experiments. The chemicals used in this study were "chemically pure" grade alcohols: methanol, ethanol, 1-propanol, isopropanol, *tert*-butyl alcohol.

Computer and software

All experiments were controlled by a 486 type PC (66 MHz clock, 8 Mbytes RAM) through Keithley "ADC-16" 16 Hz, 16 bit analog to digital converter. The analog to digital converter controlled the on/off switching of the reactor heating current through the optical decouplers and relays and also the sampling procedure by controlling the operation of Deans' switch through the solenoid valve. At the same time the PC measured the thermocouple voltage to check when the heating should be switched off and a sample should be taken, and also collected the chromatographic detector signal.

The PC started the experiment by switching on the current that passed through the reactor heating coil and measured continuously the temperature of thermocouple junction. The current was switched off 1–2 s before the predetermined temperature should be reached (the temperature rise continued due to thermal inertia) and at the needed temperature the PC switched on the current through the magnetic valve for the period of sampling (0.3 s). This changed the gas flows in the Deans' switch and the sample was introduced into the chromatographic column. After recording a chromatogram of the reactants and products, the computer started a

new cycle. The reactor was heated up to the higher temperature and a sample was taken. So, the temperature interval where the thermo-oxidation occurred (250–650 °C) could be scanned with predefined temperature steps (in our experiments 20 °C).

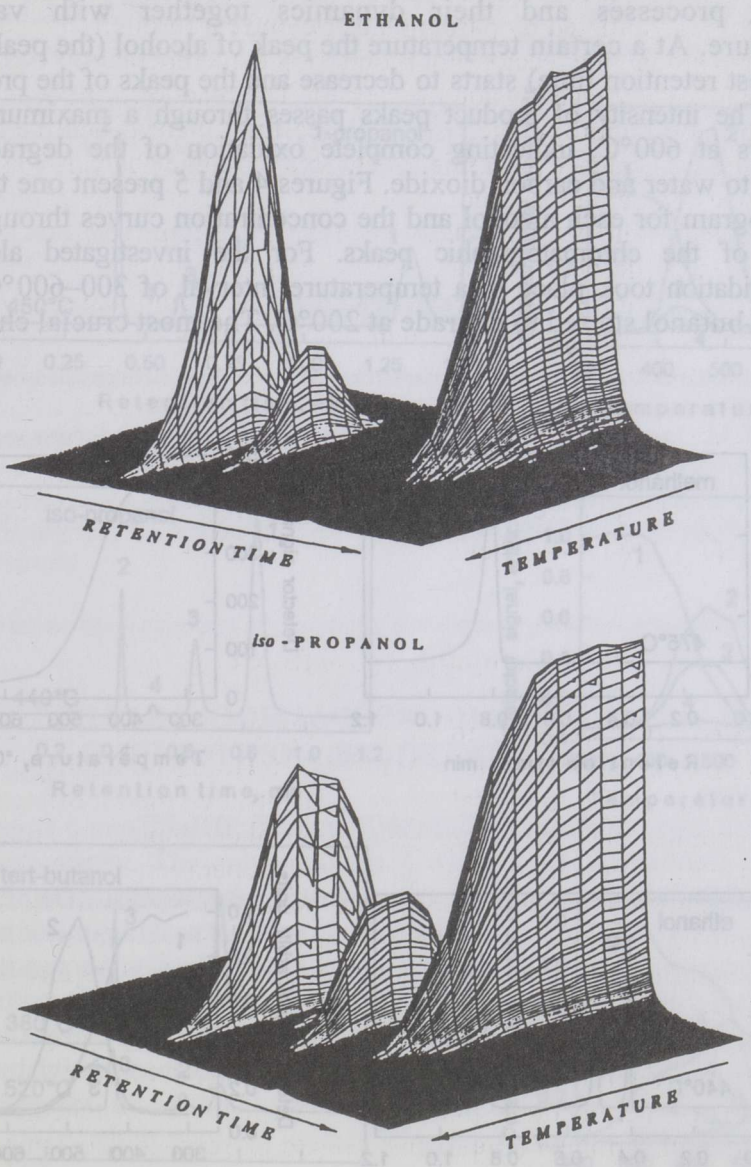

Fig. 3. Three-dimensional plots characterizing the thermooxidation of ethanol and isopropanol.

RESULTS AND DISCUSSION

The reproducibility of the system was tested by repeating the same experiment many times at a certain temperature. The relative standard deviation of the peak height in the series of the same experiments was 2% and this result could be considered as acceptable.

Figure 3 exemplifies the results of thermooxidation kinetics for ethanol and isopropanol. These three-dimensional plots show simultaneously all the occurring processes and their dynamics together with varying temperature. At a certain temperature the peak of alcohol (the peak with the longest retention time) starts to decrease and the peaks of the products appear. The intensity of product peaks passes through a maximum and disappears at 600°C, indicating complete oxidation of the degradation products to water and carbon dioxide. Figures 4 and 5 present one typical chromatogram for each alcohol and the concentration curves through the maxima of the chromatographic peaks. For the investigated alcohols thermooxidation took place in a temperature interval of 300–600°C and only *tert*-butanol started to degrade at 200°C. The most crucial changes

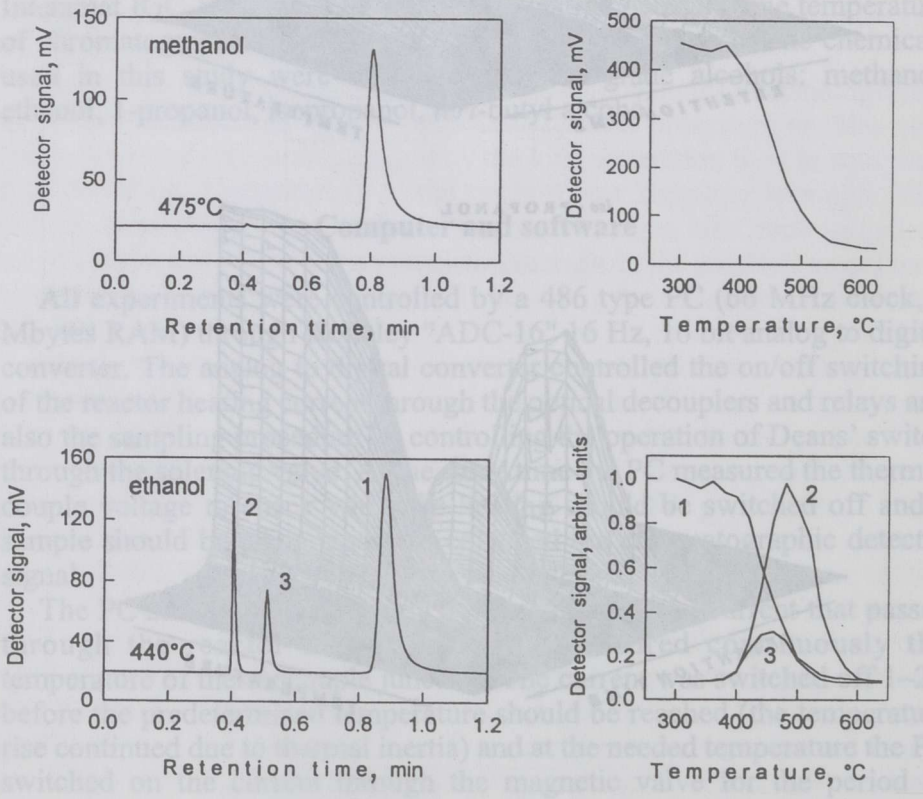

Fig. 4. Typical chromatograms and concentration curves for the thermooxidation of methanol and ethanol.

occurred at 400–500 °C. The detectable products were hydrocarbons (methane, ethane, etc.), though we did not attempt to identify all products. As results show, the methanol thermooxidates directly to CO_2 and H_2O, ethanol forms methane and ethane, which are in turn oxidized at higher temperatures. In the case of *tert*-butanol the methanol's peak splitted at high temperatures (around 500 °C) and we do not know exactly the reasons of this phenomenon. We did not notice any self-heating in the case when the reactant ignited in the reactor. This may be explained by the low

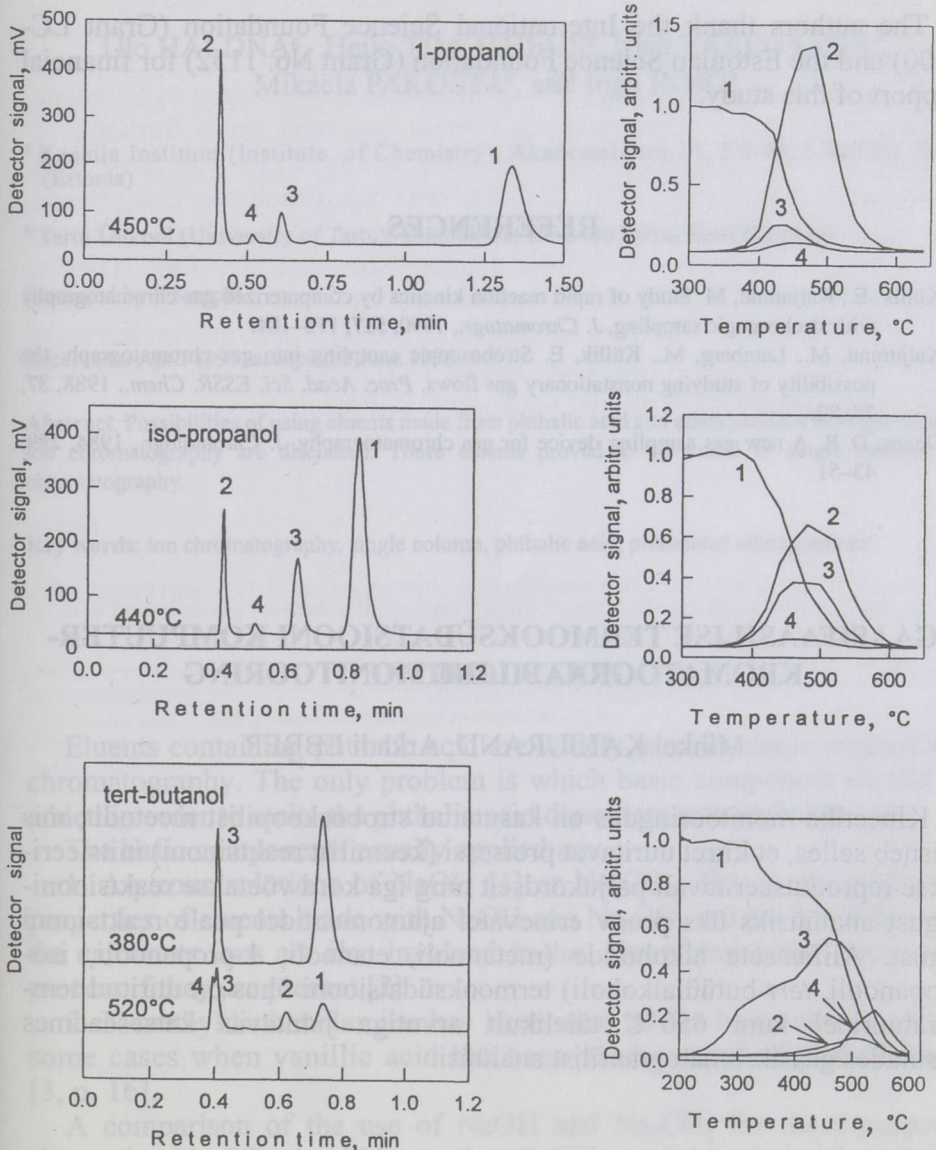

Fig. 5. Typical chromatograms and concentration curves for the thermooxidation of 1-propanol, isopropanol, and *tert*-butanol.

concentration of the reactant in the carrier gas or by an insufficient sensitivity of thermocouple.

To conclude this study we may say that combining computerized chromatography with the stroboscopic sampling technique allows of simultaneous monitoring of the variation of reactant/product concentrations for rapid reactions with a time resolution of 0.1 s.

ACKNOWLEDGEMENTS

The authors thank the International Science Foundation (Grant LC-5000) and the Estonian Science Foundation (Grant No. 1152) for financial support of this study.

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GAASIFAASILISE TERMOOKSÜDATSIOONI KOMPUUTER-KROMATOGRAAFILINE MONITOORING

Mihkel KALJURAND, Arkadi EBBER

Kineetika monitooringuks on kasutatud stroboskoopilist meetodit, mis seisneb selles, et kiiret uuritavat protsessi (keemilist reaktsiooni) initsieeritakse reprodutseeritavalt paljukordselt ning iga kord võetakse reaktsioonisegust analüüsiks üks proov erinevatel ajamomentidel peale reaktsiooni algust. Alifaatsete alkoholide (metanooli, etanooli, 1-propanooli, isopropanooli, *tert*-butüülalkoholi) termooksüdatsiooni õhus on uuritud temperatuuridel kuni 650 °C täielikult arvutiga juhitavas katseseadmes kasutades gaasikromatograafilist analüüsi.