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HEADSPACE ANALYSIS OF RAPID REACTION SYSTEMS BY STROBOSCOPIC SAMPLING

The stroboscopic sampling technique was used to obtain 20 to 30 concentration values of the products of phosphoric acid-catalyzed dehydration of several propyl and butyl alcohols in the temperature interval between 200 and 300 °C. The shortest half-life of the reaction studied was less than 10 sec. Two theoretical functions are proposed for the fitting of the experimental data obtained by the gas chromatographic headspace analysis of the first order reaction with volatile products. A comparison of the three different algorithms showed that the least squares method gives the best fit in computing the parameters of these functions.

Introduction

Up to now a gas chromatographic study of catalytic reactions has been limited by slow processes with the characteristic running time of more than 100 sec. For example, the well-known and important reactions of H⁺ dehydration of alcohols have been studied chromatographically only at low temperatures (lower than 140 °C) where the conversion rate is slow enough to permit the use of the impulse [1] or stop flow method [2]. Recently, the stroboscopic sampling method was proposed for the investigation of reproducible time varied gas and liquid flows [3, 4]. This method enables an approximately three-order decrease in time resolution in the registration of concentration curves as compared to classical chromatographic methods of reaction kinetics studies because in the case of stroboscopic sampling the time resolution does not depend on the separation time of sample (as in the case of impulse or reversed- and stopped-flow chromatography). The stroboscopic sampling method has successfully been used for studying the ignition reaction of ethanol and polypropylene [5, 6]. Also, preliminary studies on the butanol dehydration on phosphoric acid catalyst were promising [4]. In this paper, the kinetics of phosphoric acid-catalyzed dehydration of several propyl and butyl alcohols is studied using stroboscopic sampling.

Another important problem in headspace studies of the reacting systems is the development of a proper physico-chemical model for the process. Consideration of the reaction of liquid catalysis with volatile products leads to the double exponential function for the concentration curve [7] which approximates the experimental data with sufficient precision. However, more exact models should be found and another function for the fitting of experimental results is proposed in this paper.

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Stroboscopic sampling. The principle of stroboscopic sampling is the following: the process under study is initiated many times and a certain time interval passes after each initiation. The sample is then taken out from the reactor vessel and introduced into the chromatograph. By scanning the interval between the initiation and sampling from zero to the end of the reaction, it is possible to record concentration curves for the reactants and products with an adequate time resolution. The only requirement for effecting the stroboscopic sampling is the reproducibility of the process under investigation. For most chemical reactions the latter can be realized in a more or less sophisticated experimental set-up. The idea of stroboscopic sampling is simple and straightforward and can be even realized manually; however, computerization of experiments is crucial because human capabilities for generating precise time intervals and complicated sequences of injections are rather limited.

Continuous gas extraction of reaction mixtures. Let us consider the first order liquid phase reaction with volatile products. The products concentration is monitored by continuous gas extraction of the reaction environment and taking samples periodically out of the extract gas to the chromatograph. In this case, it is shown that the product concentration can be expressed as follows [7]:

$$C(t) = C_0(\exp(-at) - \exp(-kt)), \quad (1)$$

where $C(t)$ is the concentration at the time moment t , C_0 is the constant, k is the reaction rate constant, $a = F/(KV_1)$, F is the extract gas flow rate, V_1 is the volume of the liquid in the reactor, and K is the product equilibrium distribution coefficient. By sampling the extract gas after intervals Δt , a set of detector signal values $h(t_0 + n\Delta t) = h_n$ is obtained, where t_0 is the time moment of the first measurement and n is an integer. From (1) the following difference equation can easily be derived:

$$h_{n+2} + b_1 h_{n+1} + b_0 h_n = 0, \quad (2)$$

where the constants b_0 and b_1 satisfy the following square equation $z^2 + b_1 z + b_0 = 0$ whose two roots are equal to $\exp(-k\Delta t)$ or $\exp(-a\Delta t)$, correspondingly [7]. However, the assignment of the roots to the constants $\exp(-a\Delta t)$ and $\exp(-k\Delta t)$ cannot be made uniquely because of the symmetry of Eq. 1 to a and k . The reaction conditions (flow rate and temperature) must be varied to perform it exactly. Thus, the constants b_0 and b_1 should be found to calculate a and k . This can be done by using the linear regression fitting of Eq. 2 to the experimental data (algorithm I). Another possibility is to solve a set of linear equations (2) to find directly the constants b_0 and b_1 (algorithm II). The derivation is quite straightforward, resulting in

$$\begin{aligned} b_1 &= (c_1 c_{12} - c_2 c_{11}) / (c_{11} c_{22} - c_{12}^2) \\ b_0 &= (c_2 c_{12} - c_1 c_{22}) / (c_{11} c_{22} - c_{12}^2), \end{aligned} \quad (3)$$

where $c_1 = \sum h_{n+2} h_n$; $c_2 = \sum h_{n+2} h_{n+1}$; $c_{11} = \sum h_n^2$; $c_{12} = \sum h_{n+1} h_n$; $c_{22} = \sum h_{n+1}^2$. Algorithms I and II are very similar but the different number of mathematical operations used in different algorithms may lead to significant computational errors and thus the constants calculated do not necessarily coincide.

The constants a and k , too, can be found by the iterative nonlinear least squares fitting of equation (1) to the experimental data using a random or gradient search [8] of the minimum (algorithm III).

Expression (1) can be elaborated by taking into account the retention volume of the product in the reactor, V_g , and a formal parameter s whose

value varies between -1 and $+1$. Instead of Eq. 1 we have the following equation:

$$C(t) = C_0(g_1 \exp(-at) - g_2 \exp(-kt) + g_3 \exp(-t/(V_g/F))), \quad (4)$$

where $g_1 = (1 - asV_g/F)/(1 - aV_g/F)$; $g_2 = (1 - ksV_g/F)/(1 - kV_g/F)$; $g_3 = (1 - ksV_g/F)/(1 - kV_g/F) - (1 - asV_g/F)/(1 - aV_g/F)$. In fact, Eq. 4 is the Burnett-Fowles-Scott formula [9, 10] modified for the reaction systems.

Experimental

Chemicals. 1-Propanol, 1-butanol, and 2-methylpropanol were "chromatographically pure" grade. The catalyst was prepared by covering Porasil-E (80–100 mesh) solid support (Waters Ass.) with a 50% water solution of 85% phosphoric acid (grade "pure"). Details of the catalyst preparation are given in [2].

Equipment. The experimental set-up is presented in Fig. 1. The liquid reagent was in the thermostated vessel and the reagent vapor was stripped out from the vessel through valve 1 (a Valco C6TX six port valve) by the carrier gas stream (He) to the vent. The reaction was initiated in the reactor (15 cm \times 3 mm glass column, packed with catalyst) by filling the loop of valve 1 by the reagent vapor and sampling it to the reactor column. The product's gas stream was carried through valve 2 (a Valco C6TX six port valve) to the vent. The reactor output was also monitored by a TC detector.

The product's gas stream was sampled to the LHM-80 chromatograph (USSR) by valve 2. The sample gas was separated in a metal column (1 m \times 3 mm) filled with Porasil-E and detected by a flame ionization detector.

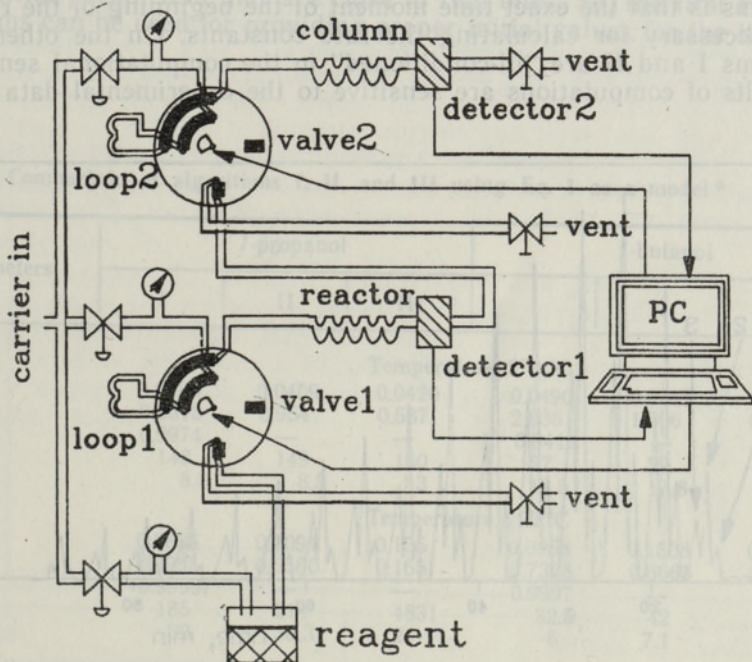


Fig. 1. Experimental set-up for headspace chromatographic analysis of catalytic reaction kinetics.

Procedure. The reaction was initiated by a command from the Apple IIe computer via home-made interfaces. After a certain time interval the computer gave the command to sample the reactor output. When separation was completed in the column, then, according to the stroboscopic sampling logic, the reaction was initiated again and the reactor output was sampled after the interval different from the previous one. Incrementing the interval between initiation and sampling to the time when the product amount became negligible, the concentration curves for all products were registered.

Results and discussion

We suggest the mechanism of alcohols dehydration through the limiting stage of the formation of carbenium ions [11]. This process produces a mixture of olefins which was confirmed by our experiments.

Comparison of different algorithms and models. An example of the chromatogram registered in a typical experiment is presented in Fig. 2. As the redistribution of peak intensities during experiments at different reactor temperatures was not registered, we used the largest product peak intensities for all calculations. In Table 1 a set of a product (*cis*-butene) peak heights data is presented. These data have been used to compare the algorithms. The results are presented in Table 2. A comparison of the mean errors of experimental and computed concentration values in Table 2 shows that algorithms I and II (linear regression) give results with almost the same precision. Algorithm III (the nonlinear least squares method) is significantly superior giving much better precision than algorithms I and II. So, the nonlinear least squares method was used for all final calculations of the rate constants.

Algorithms I and II are noniterational and the result is obtained by a certain finite number of computations. Also, the advantage of these algorithms is that the exact time moment of the beginning of the reaction is not necessary for calculating the rate constants. On the other hand, algorithms I and II are "ill-conditioned" in the computational sense, i. e. the results of computations are sensitive to the experimental data errors.

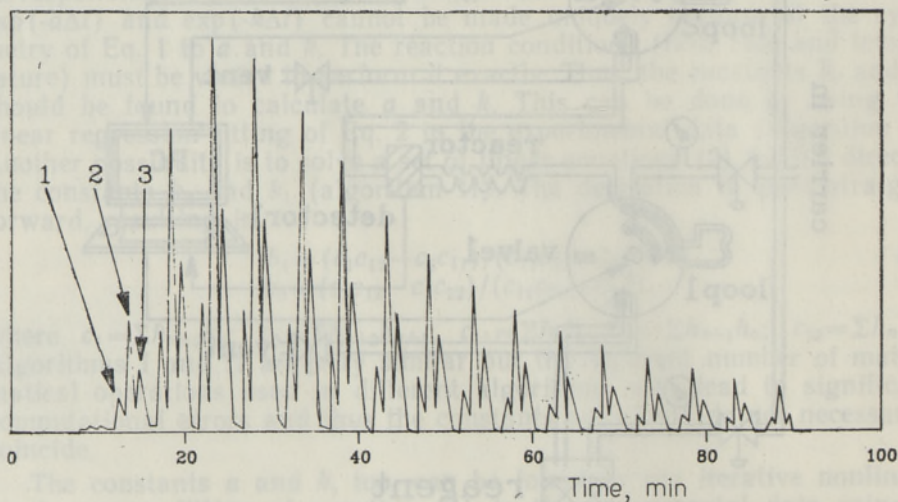


Fig. 2. A set of chromatograms of the dehydration reaction products of *1*-butanol. Time resolution — 1 sec; reactor temperature — 283°C. Identification of peaks in triplets (from left to right): 1 — *1*-butene, 2 — *cis*-butene, and 3 — *trans*-butene.

Table 1

Data on experimental (h_E) and computed* (h_C) product peak heights for the dehydration reaction of *l*-propyl and *l*-butyl alcohol

Time, sec	Temperature 273 °C				Temperature 292 °C			
	<i>l</i> -propanol		<i>l</i> -butanol		<i>l</i> -propanol		<i>l</i> -butanol	
	h_E	h_C	h_E	h_C	h_E	h_C	h_E	h_C
2	87	92	19	20	10	70	2	13
4	124	117	24	23	130	102	25	18
6	121	118	22	21	139	111	26	19
8	111	112	19	19	114	108	17	18
10	102	104	16	17	92	98	14	16
12	94	96	15	15	75	85	11	14
14	87	89	13	14	62	72	9	11
16	80	82	12	12	54	60	8	9
18	74	75	11	11	46	49	7	7
20	70	69	10	10	40	39	7	6
22	65	63	9	9	36	31	6	4
24	61	58	8	8	31	25	5	3
26	55	53	8	7	—	—	—	—

* Computed from Eq. 1 by Algorithm III.

As a result, there is a big error in the determination of rate constants or they cannot be computed at all. The iterative nonlinear least squares algorithm requires much more time than algorithms I and II do, requiring also the knowledge of the moment of the reaction initiation. The convergence of the iteration process can be accelerated by introducing values of the initial parameters that are close to real ones. So, the first two fast algorithms can be used for providing proper initial values for the iteration process.

Table 2

Comparison of algorithms I, II, and III using Eq. 1 as a model*

Parameters	<i>l</i> -propanol			<i>l</i> -butanol		
	I	II	III	I	II	III
	Temperature 273 °C					
k, sec^{-1}	0.0400	0.0409	0.0420	0.0496	0.0585	0.0570
a, sec^{-1}	0.9613	0.954	0.537	2.036	1.306	0.7048
r	0.9974	—	—	0.9412	—	—
C	148	149	160	27	29	31
s	8.3	8.5	3	18.5	17.8	16.8
	Temperature 292 °C					
k, sec^{-1}	0.0885	0.1094	0.155	0.0958	0.1508	0.169
a, sec^{-1}	0.6985	0.6560	0.165	0.7368	0.6665	0.182
r	0.99997	—	—	0.9997	—	—
C	185	214	4831	32.5	42	670
s	32	35.3	21	6	7.1	4

* data from Table 1;

r — correlation coefficient; s — mean standard deviations between experimental and computed peak heights.

An example of fitting the experimental data with functions in Eqs. 1 and 4 using the nonlinear least squares method is presented in Fig. 3. Eq. 4 fits the data much better than Eq. 1 as it should be expected. It is especially evident for the rising part of the concentration curve. Of the two rate constants, this part influences mostly the higher one. It is possible to obtain a perfect fit of data also by Eq. 1 just with the exception of one or two data points at the beginning. This procedure is acceptable when the lowest rate constant (usually k) is needed because the first points influence the smallest value of the rate constant very little and the result is obtained more rapidly using Eq. 1.

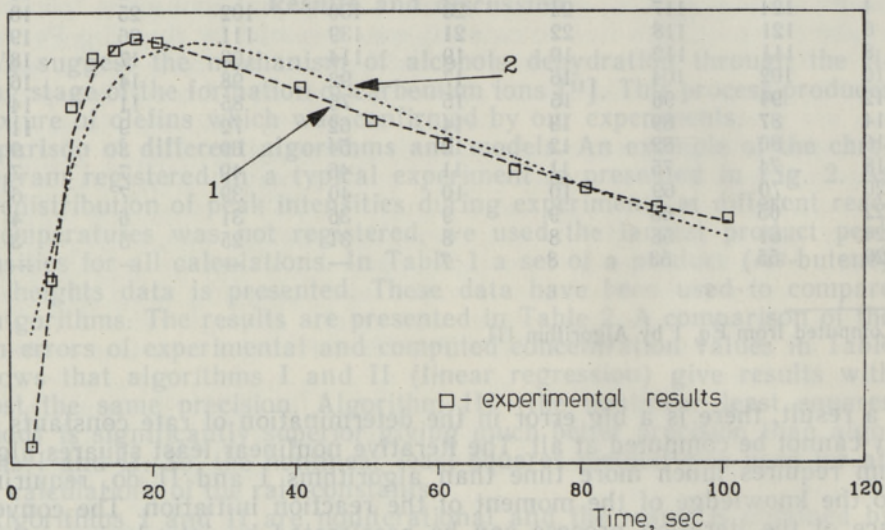


Fig. 3. Fitting the experimental data with different functions. 1 — Eq. 6 with parameters $c_0=15700$, $k=.00738 \text{ sec}^{-1}$; $a=0.3174 \text{ sec}^{-1}$, $V_g=0.3996 \text{ cm}^3$, $s=-0.83$. The average standard deviation of an experimental point error is 2.7%. 2 — Eq. 1 with parameters $c_0=13480$, $k=.00955 \text{ sec}^{-1}$, $a=0.1025 \text{ sec}^{-1}$; standard deviation of an experimental point error is 12.9%. Reactor temperature — 250 °C, and carrier gas flow rate — 12 cm^3/min .

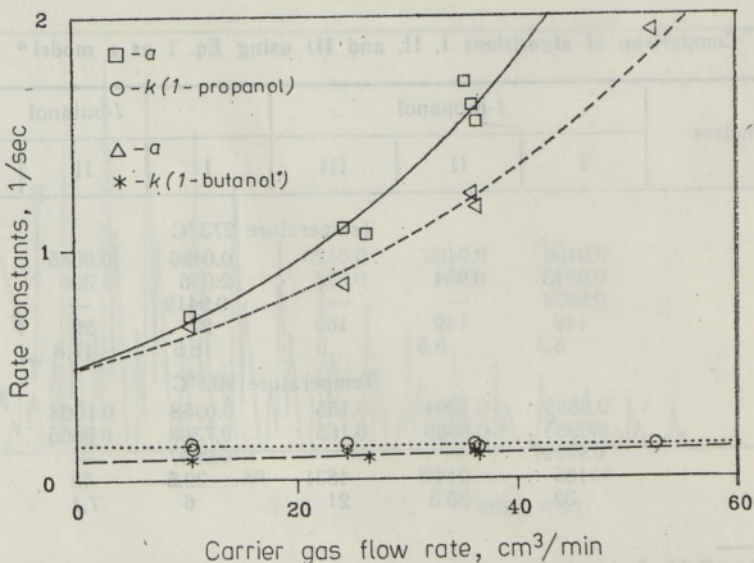


Fig. 4. Dependence of the rate constants on the carrier gas flow rate. Reactor temperature is 283 °C.

Table 3

Reaction rate constants, k (sec^{-1})

Temperature, °C	<i>l</i> -propanol	<i>l</i> -butanol	2-methylpropanol
204	0.0003	0.0005	—
235	0.0023	0.0045	—
250	0.0082	—	0.050
251	0.0089	—	0.055
252	0.0128	—	—
253	0.0112	0.0128	—
	0.0081	0.0143	—
254	0.0253	—	—
273	0.0368	0.0721	—
	0.0332	0.0467	—
	0.0341	—	—
274	0.0537	—	—
277	0.0533	—	0.148
	0.0511	—	0.147
290	0.101	—	0.256
291	—	0.157	—
	0.102	—	0.260
292	0.0975	0.118	—
298	0.2071	—	—
299	0.1936	—	—
	0.217	0.220	—
	—	0.256	—
	0.191	0.284	—
300	0.220	—	—
301	0.228	—	—
	0.209	—	—

As was pointed out in the theoretical part of the paper, the problem of the assignment of the computed rate constants to k and a can be solved by varying the flow rate of the carrier gas through the reactor. The dependence of the rate constants on the carrier gas flow rate is presented in Fig. 4. As can be seen, one of the constants remains unchanged while the other varies nonlinearly with the carrier gas flow rate. So, the first, lower constant can be assigned to k and the second to a . However, the nonlinear dependence of a violates the formula $a = F/(KV_1)$ predicting a linear behavior [7]. Evidently, the process treated in the paper needs further perfection.

The reaction rates for different temperatures are given in Table 3 and the parameters of the Arrhenius equation, $k = A \exp(-E/RT)$, in Table 4. The standard deviations for k are between 3 and 20%, and the standard deviation for E is less than 2 kJ/mol. Here the parameters A , E , R , T denote the frequency factor, activation energy, gas constant, and absolute temperature, respectively.

Table 4

Arrhenius equation ($k = A \exp(-B/T)$) data

Alcohol	A , sec^{-1}	B	$E = B/8.31$, kJ/mol	Correlation coefficient
<i>l</i> -propanol	4.00×10^{13}	18850	157	-0.990
<i>l</i> -butanol	7.05×10^{12}	17750	148	-0.996
2-methylpropanol	2.72×10^8	11720	98	-0.999

The values of the reaction rate constant could be compared with their values measured at lower temperatures: between 91 and 131 °C for 1-butanol and between 81 and 110 °C for 2-methylpropanol measured with a 20% H₃PO₄ catalyst on Chromosorb W support (60–80 mesh) using the stop flow method [2]. The joint Arrhenius equations can be derived for reaction rate data at both low and high temperatures using the linear regression. The resulting equations can be presented as follows:

— for 1-butanol:

$$k = 2 \cdot 10^8 \exp(- (12000 \pm 1000)/T) \quad cc = -0.9935;$$

— for 2-methylpropanol:

$$k = 3 \cdot 10^8 \exp(- (11700 \pm 300)/T) \quad cc = -0.9995,$$

where *cc* is the correlation coefficient. A strong correlation between high and low temperature data demonstrates the reliability of both the data sets.

The ultimate limits of stroboscopic sampling are of interest. The relation for the rate constant value and the necessary time resolution for the concentration curve registration for the function in Eq. 1 is given by the following approximate relation $\Delta t < 1/k$ [6]. The highest rate constant measured in this work was $a = 1.9 \text{ sec}^{-1}$ (see Fig. 3). So, the time resolution $\Delta t = 0.5 \text{ sec}$ was adequate for our reasons. In the case of stroboscopic sampling the time resolution is determined by the valve switching time. For mechanical valves this number is approximately 0.1 sec in conventional experimental set-ups. It follows from this discussion that the upper limit for the values of the rate constant that could be measured using mechanical valves does not exceed 10 sec^{-1} .

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KIIRELT REAGEERIVATE SÜSTEEMIDE ANALÜÜS NENDE AURUFAASI STROBOSKOOPILISE SISESTUSE MEETODIL

Stroboskoopilise sisestuse meetodit kasutati mitmete propüül- ja butüülalkoholi dehüdratatsiooni produktide 20—30 erineva kontsentratsiooni väärtuse saamiseks fosforhappe katalüsaatoriga reageerimisel temperatuurivahemikus 200—300 °C. Lühim pooles-tusaeg, mida mõeldeti, oli väiksem kui 10 s. Eksperimendiandmete kirjeldamiseks kasutati kahte teoreetilist funktsiooni. Omavahel kõrvutati kolme erinevat algoritmi nende funktsioonide parameetrite arvutamiseks. Kõrvutus näitas, et vähemruutude meetod annab katseandmete prima lähenduse.

Андрей БУРЕЙКО, Михель КАЛЮРАНД, Анатолий МАРИНИЧЕВ, Борис СТОЛЯРОВ

АНАЛИЗ ПАРОВОЙ ФАЗЫ БЫСТРОПРОТЕКАЮЩИХ РЕАКЦИОННЫХ СИСТЕМ МЕТОДОМ СТРОБОСКОПИЧЕСКОГО ВВОДА ПРОБЫ

С помощью техники стробоскопического ввода пробы получены 20—30 значений концентраций продуктов реакции дегидратации на фосфорной кислоте. Время наименьшего полупревращения исследуемых реакций было менее 10 с. Предложены две функции для описания результатов эксперимента. Метод наименьших квадратов оказался наилучшим из трех исследованных алгоритмов для вычисления параметров этих функций.

Column	Li	Na	K	Experimental	K	Na+Li	Na+K	K+Na