Journal of Chromatography, 520 (1990) 109–119
Elsevier Science Publishers B.V., Amsterdam

CHROMSYMP. 1906

Chromatograms of second-order reactions on chromatographic columns

R. THEDE, E. BELOW, D. HABERLAND and H. PSCHEIDL*
Department of Chemistry, University of Greifswald, Soldtmannstr. 23, DDR-2200 Greifswald (G.D.R.)

ABSTRACT

The application of the EICR model to several second-order reactions in a gas chromatographic reactor is demonstrated. Reaction gas chromatograms were obtained and rate constants were evaluated. With the rigid EICR assumptions, which, however, are more realistic than the ICR assumptions, at least the estimation of second-order rate constants becomes possible in a fairly simply way, requiring only a knowledge of retention times, half-width values, pulse areas and inlet amounts of the reactants.

INTRODUCTION

Reaction gas chromatographic processes have been investigated since the early 1960s by a number of workers [1–3] Nearly all of these have dealt with first-order reactions, because in this instance an analytical solution of the model equations is possible.

Reaction gas chromatography requires no special apparatus except a normal gas chromatograph. Packed columns are to be preferred to capillary columns because of the lower pressure drop. The evaporated reactant is passed through the column by a carrier gas and produces one or more products at any part of the separation column. Hence the chromatographic reactor is characterized by the simultaneous occurrence of chemical reaction and separation processes, which produce typical reaction chromatograms, as shown in Fig. 1 for irreversible reactions.

Although the shape of irreversible *n*th-order reaction chromatograms can be generalized to a certain extent, there are marked differences between first-order and non-first-order reactions occurring on gas chromatographic columns: (i) for non-first-order reactions the conversion depends on the reactant pulse shape, whereas for first-order reactions it does not; (ii) non-first-order reactions often require more than one reactant, which can cause problems in the experimental set-up of these reactions; and (iii) no part of the reaction chromatograms bears a simple relationship to the rate constant in a non-first-order reaction; with first-order reactions there is a possibility to evaluate rate constants from the decay of the product pulse to the reactant pulse [4].

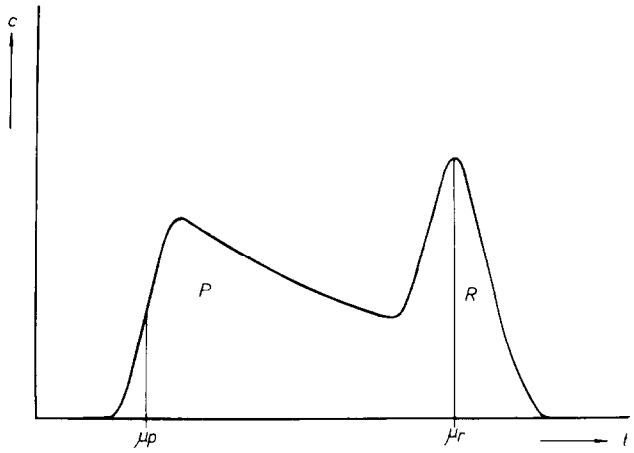

Fig. 1. Typical reaction gas chromatogram of an irreversible reaction [10].

MATHEMATICAL MODELLING

The problems in the mathematical treatment are due to the non-linearity of the system of partial differential equations that models the chromatographic reactor. Assuming isothermal conditions, linearity of the sorption isotherm and a constant phase volume ratio, the model eqn. 1a should be sufficient [5] for the description of a gas–liquid chromatographic reactor in which a self-condensation reaction of the type 2R→P proceeds.

$$D \cdot \frac{\partial^2 c}{\partial x^2} - u \cdot \frac{\partial c}{\partial x} - 2k_g c^2 - k_f(qc-a) = \frac{\partial c}{\partial t}$$
$$- 2k_1 a^2 \cdot \frac{v_g}{v_l} + k_f(qc-a) = \frac{\partial a}{\partial t} \tag{1a}$$

A second-order reaction of the type $R_A + R_B \rightarrow P$ is described by the model equation

$$D_A \cdot \frac{\partial^2 c_A}{\partial x^2} - u \cdot \frac{\partial c_A}{\partial x} - k_g c_A c_B - k_{fA}(q_A c_A - a_A) = \frac{\partial c_A}{\partial t}$$
$$- k_1 a_A a_B \cdot \frac{v_g}{v_l} + k_{fA}(q_A a_A - a_A) = \frac{\partial a_A}{\partial t} \tag{1b}$$

If the flow-rates are high enough, diffusion can always be neglected, and the order of the differential equation systems is decreased to one.

These first-order differential equation systems are integrated over the time coordinate with infinitive limits, which converts concentration into concentration–

time areas and first derivatives with respect to time to zero. In the self-condensation reaction the following is obtained:

$$-u \cdot \frac{\mathrm{d}m}{\mathrm{d}x} - 2k_g \int_0^\infty c^2 \mathrm{d}t - k_f (qm - m') = 0$$

$$-2k_1 \cdot \frac{v_g}{v_l} \int_0^\infty a^2 \mathrm{d}t + k_f (qm - m') = 0 \tag{2}$$

If the chemical reaction in the liquid phase is not limited by the mass transfer, the following simplification is possible:

$$k_g \int_0^\infty c^2 \mathrm{d}t + k_1 \cdot \frac{v_g}{v_l} \int_0^\infty a^2 \mathrm{d}t \approx k_a \int_0^\infty c^2 \mathrm{d}t \tag{2a}$$

Further, the concentrations in the non-linear terms can be written by the use of their distribution density:

$$c = m\, \Psi(x,t) \tag{2b}$$

The addition of eqn. 2 and the introduction of the simplifications in eqns. 2a and 2b yields

$$-u \cdot \frac{\mathrm{d}m}{\mathrm{d}x} - 2k_a m^2 \int_0^\infty \Psi^2 \mathrm{d}t = 0 \tag{3a}$$

$$k_a = k_g + k_1 K q$$

Analogous operations with Eqn. 1b lead to a formulation for second-order reactions with two reactants:

$$-u \cdot \frac{\mathrm{d}m_A}{\mathrm{d}x} - 2k_a m_A m_B \int_0^\infty \Psi_A \Psi_B \, \mathrm{d}t = 0 \tag{3b}$$

$$k_a = k_g + k_1 K_A q_B$$

Now the separation of the variables and a partial solution of eqns. 3a and 3b is carried out (in eqn. 3b the term m_B can be substituted by $m_B = m_{BO} + m_A - m_{AO}$ because of the stoichiometry of the reaction):

$$\frac{m_0}{m} = 1 + \frac{2k_a m_0}{u} \int_0^L \int_0^\infty \Psi^2 \, \mathrm{d}t \, \mathrm{d}x \tag{4a}$$

(for one reactant) and

$$\ln\left(\frac{m_{0A}}{m_A}\right) + \ln\left(\frac{m_{0B}/m_{0A} + m_A/m_{0A} - 1}{m_{0B}/m_{0A}}\right) =$$

$$\frac{-k_a\,(m_{0A} - m_{0B})}{u} \int_0^L \int_0^\infty \Psi_A \Psi_B \, \mathrm{d}t \, \mathrm{d}x \tag{4b}$$

(for two reactants). A complete analytical solution can be found if it is possible to approximate the distribution densities in eqns. 4a and 4b by a suitable function, which must depend on time and on the length coordinate. Therefore, experimental investigations were carried out with reactions which, although complex, are totally second order.

EXPERIMENTAL

For the investigation of several second-order reactions, a GCHF 18.3 gas chromatograph (Academy of Sciences of the G.D.R., Chromatron Production Department, Berlin, G.D.R.) was used, equipped with a flame-ionization detector. A Hewlett-Packard (Avondale, PA, U.S.A.) Model 3380 A plotting integrator was used for the determination of retention times and pulse areas.

RESULTS AND DISCUSSION

Aldol condensation of n-propanal

The aldol condensation of *n*-propanal to form 2-methyl-2-pentenal was used for the investigation of second-order reactions of the type $2R \rightarrow P$ [6].

Investigation of *n*-propanal with diglycerol as stationary phase yields normal elution chromatograms without substantial tailing. By heating diglycerol to about 100°C one can dissolve potassium hydroxide in it and use the solutions obtained for the preparation of a chromatographic reactor in which the base-catalysed aldol condensation of *n*-aldehydes can occur. Propanal was preferred because sampling is easier than with acetaldehyde and the product can be better maintained than with butanal.

The reaction was carried out on several columns with Gas-Chrom Q (60–80 mesh) as carrier and diglycerol–potassium hydroxide solution (0.36–1.15 *M* in amounts of 15% on the carrier material) as the stationary phase. Typical reaction gas chromatograms are shown in Figs. 2 and 3, reflecting the dependence of the conversion on the flow-rate and the inlet amount of *n*-propanal, respectively. Whereas the increase in conversion with decrease in flow-rate is due to the prolongation of the reaction, the increase in the conversion with increase in the inlet amounts of the reactant corresponds to the dependence of second-order reactions on the concentrations at the beginning of the reaction. Elsewhere [7] it has been demonstrated that the dependence of the conversion on the inlet amount can be used to determine the reaction order; a reaction order of two was obtained for the on-column aldol condensation reported here.

The dependence of the conversion on the inlet amount of the reactant can be used for studying the alteration of the reactant pulse with increasing distortion by the second-order reaction. It can be seen from Fig. 2 that the shape does not change dramatically. Also, investigation of the dependence of the half-width value of the reactant pulse yielded no substantial additional broadening in the conversion range up to 70% (see Table I) (note that the values measured include the influence of the product pulse, giving higher values). No significant influence of the reaction on the retention time of the reactant was found.

From these results the following conclusions seem to be possible: in the range from small to medium conversions the pulse shape is predominately produced by

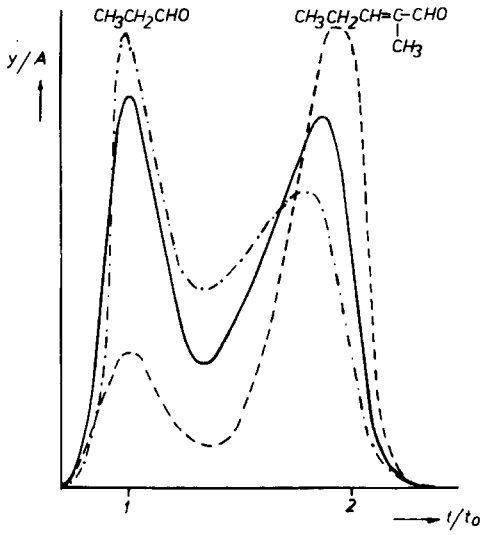

Fig. 2. Reaction gas chromatograms of the aldol condensation of *n*-propanal with various flow-rates.

chromatographic effects in reaction gas chromatography with second-order reactions; consequently, the retention time and standard deviation do not differ considerably from their values in normal chromatography. The generalization of these results leads to a model of an extended ideal chromatographic reactor (EICR) [6].

In the case of an ideal chromatographic reactor (ICR) [2], the following assumptions were made additionally to those mentioned above: there is a equilibrium between the mobile and the stationary phase; and there is no pulse spreading within the column. Especially the last assumption is too rigid for the investigation of second-order reactions and not necessary for calculations on first-order reactions, because the conversion in first-order reactions does not depend on pulse spreading (with near-equilibrium conditions of course).

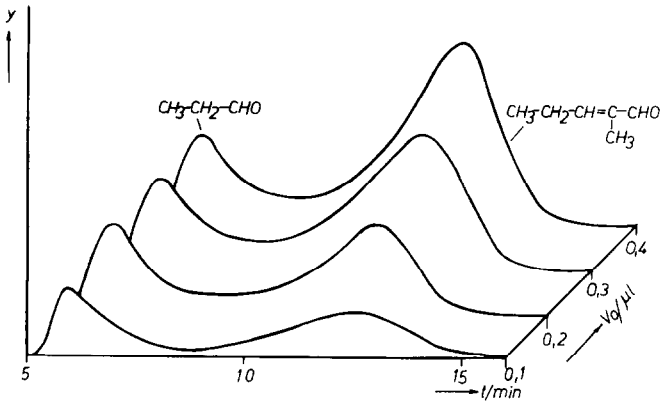

Fig. 3. Reaction gas chromatograms of the aldol condensation of *n*-propanal with various inlet amounts.

TABLE I

DEPENDENCE OF THE HALF-WIDTH VALUE OF THE PROPANAL PULSE ON THE CONVERSION IN ALDOL CONDENSATION

Conditions: 80°C, 15% diglycerole–KOH on Gas-Chrom Q.

Conversion (%)	Half-width (min)
0	0.70
40	0.71
67	0.72
75	0.74
80	0.75

The EICR model rejects these assumptions, substituting them by the following: in order to obtain analytical expressions of eqns. 4a and 4b, which are parts of the model, a normal distribution is assumed for the pulse shape as the normally used first approximation for chromatographic peaks; and the retention time and variance (second power of the standard deviation) become linear functions of the column length at constant flow-rates, which corresponds to the limitation that the EICR model can only be applied in the range from small to medium conversions.

The most profound idealization is the assumption of a normal distribution for the reactant pulse in any case, but this actually makes the analytical treatment of the model equations possible, leading to very simple analytical equations, as will now be seen; for more details, see ref. 8.

The distribution density in eqn. 4a can now be expressed with the following equations, using the results of ideal linear chromatography [9]:

$$\Psi \overset{!}{=} \frac{1}{\sqrt{2\pi\sigma(x)}} \cdot \exp\left\{-\frac{[t - \mu(x)]^2}{2\sigma(x)^2}\right\} \tag{5}$$

$$\mu(x) = \frac{x}{l}\,\mu(l)$$

$$\sigma(x)^2 = \frac{x}{l}\,\sigma(l)^2$$

Now the integration of the distribution density in eqn. 4a can be carried out, yielding after minor rearrangement [6,10]

$$m = \frac{m_0}{\dfrac{2\,k_a m_0 t_0}{\sqrt{\pi}\;\sigma\;(l)} + 1} \tag{6}$$

In commercial gas chromatographs there is usually no possibility of obtaining the pulse area at the column inlet. Therefore, it is necessary to calculate it, *e.g.*, with the help of an internal standard:

$$\frac{A_S}{f_S A_R} = \frac{2k_a}{\sqrt{\pi}}\left[\frac{m_0 t_0}{\sigma(l)}\right] \tag{7}$$

Where A_S = peak area of standard; f_S = sensitivity factor of standard. The remaining inlet pulse area must be given in terms of concentration–time–area and can be calculated from the inlet amount and the flow-rate:

$$m_0 = n_0/\dot{v} \tag{8}$$

A plot of the left-hand side of eqn. 7 *vs.* the product $m_0 t_0/\sigma(l)$ should yield a straight line, from the slope of which the reaction rate can be calculated.

In the aldol condensation the apparent rate constant amounted to 908 l/mol · min (correlation coefficient 0.97) at 80°C. Because there is no reaction occurring in the gas phase, the liquid-phase rate constant could be easily obtained with eqn. 3a and amounted to 36 l/mol · min. The recalculation of the kinetic results of Jiminez and Broche [12] with respect to the on-column conditions yields rate constants that are about one order of magnitude higher, but they investigated the reaction in aqueous solutions.

Acylation of aminobenzene

As mentioned above, second-order reactions can require two reactants. In our opinion, the best way to bring about such reactions under chromatographic conditions is to sample the more volatile reactant at a certain time after the less volatile reactant. Then the more volatile will overtake the less volatile reactant, and during the time they are mixed within the column the reaction can occur.

Introducing the EICR conditons (eqn. 5) into eqn. 4b and replacing the ratio m_A/m_{A0} by the inert standard ratio, an analytical equation for a reaction of type A + B→P could be derived, which is valid if the separation is complete at the outlet *and* at the inlet of the column:

$$\ln\left(\frac{A'_{A0}}{A'_A}\right) + \ln\left(\frac{m_{0B}/m_{0A} + A'_A/A'_{A0} - 1}{m_{0B}/m_{0A}}\right) = \frac{-k_a t_0}{|\mu_A(l) - \mu_B(l)|}(m_{0A} - m_{0B}) \tag{9}$$

With this method we examined the acetylation of aniline with acetic anhydride to form acetanilide and acetic acid. To ensure that no reaction occurred between the acetylating agent and the stationary phase, Apiezon L was employed [15% on Chromosorb W AW DMCS (60–80 mesh)], although not the best suited for this separation (Fig. 4). A glass injection system and glass columns were used, but tailing could not been avoided. Conversions of up to 50% were achieved.

For the evaluation of the rate constant, the ratio of the reactant pulse area to the area of the internal standard was measured first without any reaction occurring and

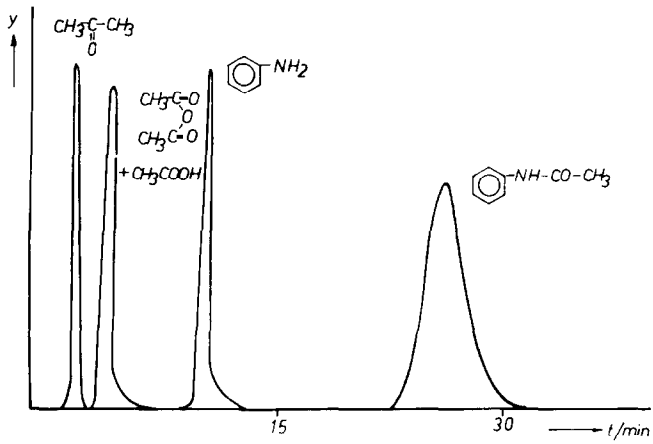

Fig. 4. Reaction gas chromatogram of the acylation of aminobenzene [17].

then with a reaction occurring. With varying inlet amounts of the reactant a series of conversion data were obtained. A plot of the left-hand side of eqn. 9 *vs.* the product $(m_{0A} - m_{0B})t_0/|\mu_A(l) - \mu_B(l)|$ yielded a straight line with a correlation coefficient of 0.99. From the slope the apparent rate constant (k_a = 11 600 l/mol · min) could be evaluated. The corresponding reaction rate in the stationary phase was obtained from eqn. 3b and amounted to 950 l/mol · min. The recalculation of the on-column data to those provided by Hipkin and Satckel [12] yielded a correspondence of the rate constants within an order of magnitude, although they worked with mixtures of dioxane and water as solvent.

Friedel–Crafts alkylation of benzene with ethyl bromide

With second-order reactions it may happen that sufficient conversion cannot be obtained under the existing conditions. Increasing the inlet amounts of the reactant sometimes leads to adequate results. With increasing amounts of the reactant substance, however, there is a risk leaving the range of linearity of the sorption isotherm, which always leads to great problems in the interpretation of the results. It is then preferable to stop the carrier gas flow for a well defined time interval (stopped-flow method) [13]. If two reactants are involved, first the reactants are sampled as in the pulse-overlay method, and when the mass centres of the pulses are congruent the carrier gas is stopped (pulse-overlay–stopped-flow method).

The mathematical modelling is different from the cases discussed above. It is based on the fact that at the moment of stopping the carrier gas the distribution of the reactant concentration is "frozen" along the length coordinate. During the stop period the column works as a batch reactor with distributed concentrations. However, only the sum conversion of the column can be obtained after the stop at the column outlet. Approximating the distribution density of the reactant concentration by eqn. 5 a set of analytical equations were derived [6,14]:

$$\frac{A'_A}{A'_{A0}} \overset{!}{=} \frac{m_A\ (k_a)}{m_{A0}} \tag{10a}$$

$$m_A\ (k_a) = \int_0^1 c_A\ \mathrm{d}\left(\frac{x}{l}\right) \tag{10b}$$

$$c_A = c_{A0} \cdot \frac{R - C}{R - C \exp\left[c_{A0}\ (C - R) k_a^+\ t_D\right]}$$

with:

$$C = \frac{c_{B0}}{c_{A0}}$$

$$R = \frac{1+q_A}{1+q_B}$$

$$c_{i0} = m_{i0}\ \Psi_i(x,\ t_s)$$

$$k_a^+ = \frac{k_a}{1+q_A}$$

For the determination of the rate constant, the ratio of reactant to internal standard area must be measured first without any reaction occuring (A'_{A0}), and then with a reaction occurring (A'_A), *i.e.*, with pulse overlay and stopping of the carrier gas flow. Now the rate constant can be established by numerical fitting according to eqn. 10a, as follows.

The concentration–time area m_A (k_a) is calculated by the numerical integration of the theoretical rest concentration c_A over the total column length, assuming a certain starting value of k_a. A systematic variation of k_a according to the principles of optimization leads to a value at which eqn. 10a is satisfied or nearly satisfied. Note that eqn. 10 is valid for non-considerable conversions during the flow period and neglect of diffusion. Because there is no flow, the latter could cause problems. There is, however, the possibility of a decrease in temperature after stopping the carrier gas, which could concentrate almost the whole substance in the stationary phase, in which diffusion is much lower than in the mobile (gaseous) phase.

We examined the Friedel–Crafts alkylation of benzene with ethyl bromide using this method (Fig. 5). The catalyst was $AlCl_3$, which was dissolved in Kel-F Oil No. 3 [15] as stationary phase. Because of the low temperature (20°C) the product did not leave the column. Hexane was employed as an internal standard. Conversions of up to 30% could be obtained with reaction durations of up to 120 min. A series of rate contants were determined with varied duration of the stop, which proved to be constant at 32 mol/l · min.

From eqn. 3b, the rate constant in the stationary phase was calculated and amounted to $6.6 \cdot 10^{-4}$ l/mol · s. Jungk *et al.* [16] investigated this reaction with Al_2Br_6 as catalyst in 1,2,4-trichlorobenzene at 20°C and found a third-order rate constant of 0.233 l^2/mol^2 · s. The corresponding rate constant for on-column conditions was evaluated by dividing the stationary phase rate constant by the concentration of Al_2Cl_6 (0.02 mol/l), and amounted to 0.033 l^2/mol^2 · s.

Rate constants obtained by reaction gas chromatography often have no exact correspondence in the literature because of the different nature of the stationary phase compared with solvents which are normally used in kinetic investigations. However, the data presented here demonstrate that the rate constants obtained are of reasonable

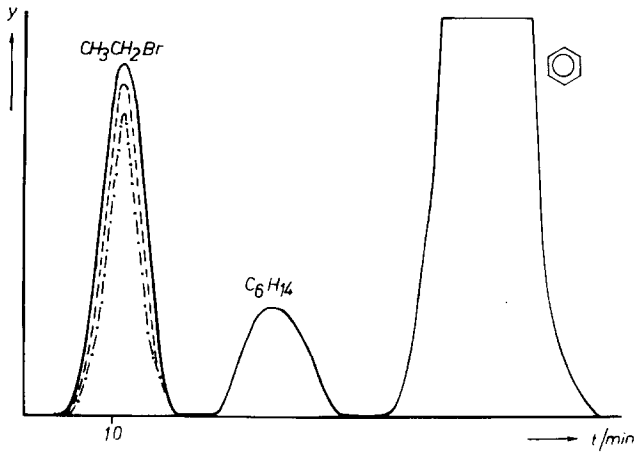

Fig. 5. Reaction gas chromatogram of the Friedel–Crafts alkylation of benzene with ethyl bromide.

magnitudes. The analytical equations provided here must be consisted as first approximations, with which basic data can easily be derived for further investigations.

SYMBOLS

A	pulse area
A'	ratio of pulse area to area of internal standard
a	effective concentration in the stationary phase ($a = c_l\ v_g/v_l$)
c	concentration in the gaseous phase
D	diffusion coefficient
K	partition coefficient
k_g, k_l	chemical rate constants for the gaseous (g) or liquid (l) phase
k_a	apparent rate constant, defined by eqn. 4
l	length of column
m	0 moment [pulse ($c-t$) area; m' in the liquid phase]
n	reaction order
q	retention capacity ($q = Kv_l/v_g$)
t	time
t_0	dead time
t_S	time of stop
t_D	duration of stop
u	linear flow-rate
v	volume
$\bar{v}$	volume flow-rate
x	length coordinate
y	signal of detector
μ	first absolute moment (retention time)
σ	standard deviation of the pulse

REFERENCES

1 G. A. Gaziev, V. Y. Filinovski and N. I. Yanovskii, *Kinet. Katal.*, 4 (1963) 688.
2 S. H. Langer and J. E. Patton, in J. H. Purnelly (Editor), *New Developments in Gas Chromatography*, Wiley, New York, 1973, pp. 294*ff*.
3 H. Pscheidl, K. Bethke and D. Haberland, *Z. Chem.*, 18 (1978) 393.
4 J. E. Patton, H. Kung and S. H. Langer, *J. Chromatogr.*, 122 (1976) 487.
5 J. A. Jönsson, *Chromatography: Theory and Basic Principles*, Marcel Dekker, New York, 1985.
6 R. Thede, H. Pscheidl and D. Haberland, *Z. Phys. Chem. (Leipzig)*, 271 (1990) 471.
7 R. Thede, H. Pscheidl and D. Haberland, *Z. Chem.*, 28 (1988) 148.
8 R. Thede, E. Möller, H. Pscheidl and D. Haberland, *Z. Phys. Chem. (Leipzig)*, in press.
9 K. Yamaoka, T. Nakagama, *J. Chromatogr.*, 117 (1976) 1.
10 R. Thede, *Thesis*, University of Greifswald, Greifswald, 1986.
11 J. Jiminez and A. Broche, *Bull. Soc. Chim. Fr.*, (1961) 1499.
12 J. Hipkin and D. P. N. Satckel, *J. Chem. Soc. B*, (1966) 348.
13 C. S. G. Phillips, A. J. Hart-Davies, R. G. L. Saul and J. Wormald, *J. Gas Chromatogr.*, 5 (1967) 424.
14 E. Below, *Thesis*, University of Greifswald, Greifswald, 1988.
15 H. Pscheidl, E. Oberdörfer, E. Möller and D. Haberland, *J. Chromatogr.*, 365 (1986) 383.
16 H. Jungk, C. R. Smooth and H. C. Brown, *J. Am. Chem. Soc.*, 78 (1956) 2185.
17 F. Nohmie, *Thesis*, University of Greifswald, Greifswald, 1989.