Band Broadening in Solid Phase Reactors Packed with Catalyst for Reactions in Continuous-Flow Systems

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The band broadening in a catalytic bed reactor, in which pulses of reactant are introduced into a stream of liquid flowing through the bed of solid catalyst, is discussed. The chemical reaction concerned and the separation of the product(s) from the pulse of reactant cause band broadening, which is dependent on the reaction rate and on the difference in the retention of product(s) and reactant. A quantitative relationship has been derived for the case of first-order kinetics. The decomposition of diacetone alcohol on alumina and the catalytic hydrolysis of 1-naphthyl *N*-methylcarbamate on a basic ion exchanger have been studied as model systems; the results are in agreement with the mathematical model. The validity of this model can probably be extended to other solid phase reactors and reactions adhering to first-order and pseudo-first-order kinetics.

Postcolumn reaction detectors have recently gained more widespread acceptance in liquid chromatography due to their ability to widen the range of application of conventional detection modes such as UV–visible, fluorescence, or electrochemical detection and due to their enhanced selectivity and sensitivity for trace analysis in complex matrices. Recent reviews (*1*, *2*) have shown that three basic designs are available: mainly tubular nonsegmented reactors for fast reactions, packed bed reactors for intermediate kinetics, and tubular segmented-flow reactors for slow reactions.

The usefulness of packed bed reactors can be particularly pronounced, when the packing material of the bed directly participates in the reaction. Such solid phase derivatization reactions can either proceed with the packing acting as a reagent or as a catalyst.

The occurrence of chemical reactions going on during the chromatographic separation process was until recently considered an undesirable phenomenon. The first practical use of such solid phase reactions was made in kinetic studies in GC and an excellent review on this subject has been written by Langer and Patton (*3*). The advantages of solid-state reactions in LC, wherein the reagent is present as solid, supported on an inert medium or chemically bonded to a suitable support, have been recently also recognized and reviewed by Krull and Lankmayr (*4*). In a very recent paper Krull et al. (*5*) have discussed more concretely the polymeric reduction of carbonyl compounds following separation by LC.

Of even higher actuality is the use of the reactor bed material as catalyst, where the solid support is not consumed and can therefore be used repeatedly over a prolonged period of time, provided that no catalyst poisoning takes place. The concept of heterogeneous catalysis in solid phase reactors, i.e., for catalytic hydrolysis or redox reactions, is quite new. Vratny et al. (*6*) have reported on the use of an ion-exchanger catalyst for the hydrolysis of disaccharides prior to their detection. Another line in this direction is the use of chemically bonded enzymes for on-line heterogeneous enzymatic reactions as reviewed recently by Bowers (*7*).

One of the important aspects to be considered in the use of solid phase reaction detectors is band broadening. For conventional bed reactors we assume that ideally the reagents and products are not retained on the inert packing material, consisting for example of glass beads or polymer material. The band broadening on such a bed reactor depends on parameters such as packing geometry, average particle size, tortuosity, linear flow velocity, and diffusion coefficients. Band broadening is then a combination of axial molecular diffusion and convective mixing and has been discussed extensively by Deelder et al. (*8*).

Band broadening on solid phase reaction detectors depends, in addition to the above mentioned phenomena, also on the reaction itself. A certain retention of the analytes to be derivatized has to be effective in order for an efficient reaction to take place. This holds also for the concept of heterogeneous catalysis. Unfortunately in the few existing publications, very little attention has been focused on this phenomenon of "reaction band broadening".

The possible complexity of band broadening phenomena can be demonstrated by the chromatogram in Figure 1 which was obtained recently in our group in a pilot study on the example of a catalytic parallel dehydration and retroaldolization of 2-(1-hydroxycyclohexyl)cyclohexanone on alumina. A group of broad and overlapping peaks of peculiar shape was obtained for this complex reaction and it is evident that such broadening and peculiar peak shapes result from differences in the retention of product(s) and reactant. This type of "reaction band broadening" due to the simultaneous separation and reaction processes taking place has been reported and discussed earlier by other authors (*3*).

In this study it is our aim to recognize and understand the main factors responsible for the additional (reaction) band broadening in solid phase reactions and to show the feasibility of heterogeneous catalysis in postcolumn reaction detectors. For this purpose two model reactions of the relatively simple case of an irreversible first-order reaction have been chosen: (1) the retroaldolization of diacetone alcohol on alumina and (2) the hydrolysis of 1-naphthyl *N*-methylcarbamate (Sevin, Carbaryl) on anion exchangers. A relationship is proposed between the "reaction band broadening" expressed as variance σ_r^2 and the rate constant and capacity factors of reactant and product. Finally the validity of such a model is tested experimentally.

THEORY

A mathematical model was developed by Langer and Patton (*3*) for the description of an irreversible first-order reaction taking place in a chromatographic column. The model is derived for a general case: the reaction can take place in the stationary and/or in the mobile phase. Since we are examining heterogeneous catalyzed reactions, the reaction in the mobile phase will be omitted in the next discussion.

The model is valid, if the following conditions are fulfilled: (1) The reaction proceeds isothermally and adsorption and reaction heats are negligible. (2) The conditions of linear

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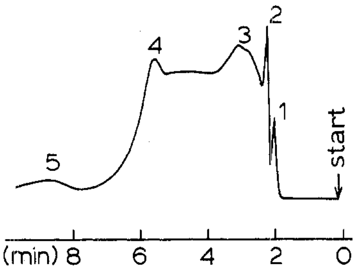


Figure 1. Reaction chromatogram of 2-(1-hydroxycyclohexyl)cyclohexanone on alumina: reaction temperature, 57 °C; mobile phase, pure hexane; UV detection at 280 nm; column, 250 × 4.2 mm; flow rate, 1.0 mL/min; (1) nonretained compound (toluene); (4) reactant; (2, 3, and 5) reaction products.

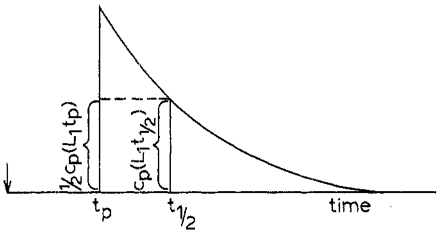


Figure 2. The output concentration of product as a function of time.

chromatography are fulfilled. (3) The linear velocity of the mobile phase is constant. (4) The bed of catalyst is homogeneous and the catalyst activity and adsorption properties are constant in each part of the bed. (5) The reaction rate is independent of mass transfer phenomena.

Under these conditions, the mass balance of reactant R and product P can be expressed in the form of partial differential equations. Solving these equations for a square-wave input pulse, Langer and Patton (*3*) have found that for a column with length L the output concentration of the product, $c_P(L,t)$, can be expressed by

$$c_P(L,t) = n_P c_0[\exp(k_{app}t_{in}) - 1]\ \exp[-k_{app}(t - t_P)] \qquad (1)$$

In equation 1, n_P is the number of product molecules formed from one molecule of reactant, t_P for maximum output concentration of product (see also Figure 2), c_0 is the initial concentration of reactant in the square-wave input pulse having width t_{in}, and k_{app} is a constant defined as

$$k_{app} = k_r \frac{t_{s,R}}{t_{s,R} - t_{s,P}} \qquad (2)$$

where $t_{s,R}$ and $t_{s,P}$ are the times spent by R and P in the stationary phase ($t_R > t_P$ being chosen as an example) and k_r is the rate constant of the first-order reaction.

In chromatographic practice, the width of a peak is usually measured at half of its height. For the present model, the width is given by the distance on the t axis between points t_P and $t_{1/2}$ as is shown in Figure 2. The maximal output concentration of P, at the time t_P, is

$$c_P(L,t_P) = n_P c_0[\exp(k_{app}t_{in}) - 1] \qquad (3)$$

Besides, at half the peak height (see Figure 2)

$$c_P(L,t_{1/2}) = \frac{1}{2}c_P(L,t_P) \qquad (4)$$

Solving eq 1, 3, and 4, a relationship between the width of the product peak, $(t_{1/2} - t_P)$, and the apparent rate constant k_{app} is obtained

$$(t_{1/2} - t_P) = \ln 2(1/k_{app}) \qquad (5)$$

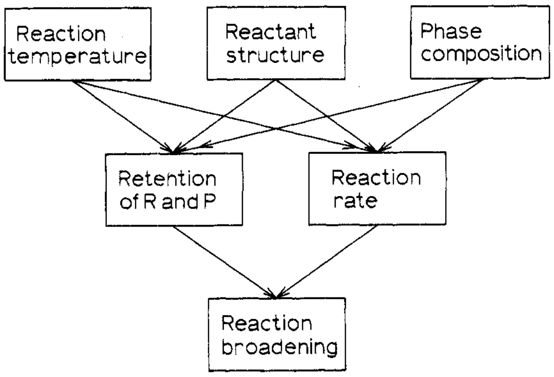


Figure 3. The influence of experimental parameters on reaction broadening.

The mathematical model of Langer and Patton, which was derived under the above conditions, describes an ideal chromatographic reactor free of any band broadening except for reaction broadening σ_r. In the case of a real reactor, however, the other broadening mechanisms operating in addition to reaction broadening and expressed as the variance σ_n^2 (σ_n = nonreaction broadening) are mutually independent and the observed total variance, σ_t^2, is given as the sum of contributions σ_n^2 and σ_r^2

$$\sigma_t^2 = \sigma_n^2 + \sigma_r^2 \qquad (6)$$

Let us assume, that nonreaction broadening has the same value for product and reactant. Then, the reaction broadening σ_r can be separated from the nonreaction one by measuring the variance of the product peak for the separate injections of product and reactant

$$\sigma_r^2 = (\sigma_t^2)_{prod} - (\sigma_n^2)_{prod} \qquad (7)$$

A similar approach was used by Jurchak (*9*) in a GC study of acetaldoxime isomerization.

For a Gaussian peak, the width at half its height is given at $2(2 \ln 2\sigma_t)^{1/2}$. By analogy, replacing $(t_{1/2} - t_P)$ in eq 5 by variance σ_r^2, one obtains a relationship between σ_r and k_{app}. When $t_{s,R}$ and $t_{s,P}$ are transformed into capacity factors k_P' and k_R', one has a simple relation between σ_r, k_r, k_P', and k_R'

$$\sigma_r = \frac{\sqrt{\ln 2}}{8}(1/k_{app}) = \frac{\sqrt{\ln 2}}{8}\,\frac{(1 - k_P'/k_R')}{k_r} \qquad (8)$$

The expression has the required property of vanishing for the following conditions: $k_P' = k_R'$ and $k_r = \infty$. If the capacity factors are equal, no reaction broadening is observed. If the rate constant k_r approaches infinity, the pulse of the reactant is immediately converted into the pulse of the product at the start of the catalyst bed and passes through the rest of the bed without any reaction broadening. For the rest, it is interesting to note that for first-order kinetics, the reaction band broadening is independent of the mobile phase flow rate.

Consideration of Real Reaction Systems. Several experimental parameters can be considered in real reaction systems. These parameters and their influence on the dependent variables are shown in Figure 3. Of these, the reactant structure is usually given, since we have to analyze for a particular analyte or group of analytes. The phase composition in the reactor is dictated by the mobile phase needed for the separation process, but some variation is possible by selecting different separation mechanisms. Another phase parameter is the choice of catalyst and the quality of a given catalyst bed, i.e., active sites available, surface area, pores, particle size, passivation, etc. Nevertheless, variation possibilities for these parameters are quite limited in practice. The reaction temperature remains therefore the parameter which can be most easily changed. According to the law of Arrhenius an increase of reaction temperature increases k_r and hence diminishes (see eq 8) the reaction band broadening, σ_r. The upper limit of the temperature is usually given by the thermal stability of the catalyst and/or the reactant and product(s) or by the boiling point of the mobile phase in the reactor. The latter can be increased by using high back pressures across the reactor bed.

Prior to an experimental verification of eq 8 it is necessary to examine whether the conditions postulated for our model (points 1–5 above) are fulfilled in a real reaction system. For points 1–3 this can easily be acknowledged if we assume a noncompressible mobile phase and dilute samples. For point 4 we have to realize that nonhomogeneity of a catalyst bed can arise from gradual poisoning of catalyst particles. Strongly adsorbed impurities from the mobile phase or injected samples can partially deteriorate the bed. An axial temperature gradient caused by insufficient preheating of the mobile phase at the reactor inlet can have a similar effect and hence violate condition of point 4.

As to point 5 the following can be said: the major part of the catalyst surface is the inner surface of the walls of the pores; the contribution of the outer surface of the catalyst particles is hence negligible. Thus, the rate of mass transport to the active sites, which are distributed on the catalyst surface, is determined by the diffusion through the stagnant film surrounding the particles and by the subsequent diffusion into the pores.

The effect of both mass-transfer types on the reaction rate depends on the diameter d_p of the catalyst particles. As a general rule the smaller catalyst particles enable a more rapid mass transfer. Thus, the use of sufficiently small particles in the packed bed reactors will not only considerably diminish the total band broadening, σ_t, but will also improve the mass transfer and, thus, increase the reaction rate. Under conditions of sufficiently rapid mass transfer, the observed reaction rate is hence determined only by chemical processes.

The experimental test for the influence of transport phenomena on the reaction rate involves kinetic measurements using fractions of catalyst with different d_p (*10*). A simple criterion presented by Weisz and Prater (*11*) can be used in the case of first-order kinetics. In the absence of pore resistance and for spherical particles of diameter d_p, the following relationship holds:

$$\frac{(-r)_{\mathrm{obsd}} d_p^2}{36 D_{\mathrm{eff}} c_R} < 1 \qquad (9)$$

where $(-r)_{\mathrm{obsd}}$ is the observed reaction rate, c_R the reactant concentration, and D_{eff} an effective diffusion coefficient depending on the structure of the porous solid. The ratio of D_{eff} and the diffusion coefficient for the reactant in the mobile phase is between 0.05 and 0.2 for many porous solids (*12*). Diffusion coefficients, which can be calculated by means of the Wilke–Chang equation (*13*), are about 10^{-5} cm^2/s for many medium and small size solutes and common mobile phases. Thus, D_{eff} in eq 9 is about 5×10^{-7} cm^2/s. Using the definition of the reaction rate for first-order kinetics, $(-r)_{\mathrm{obsd}} = k_r c_R$, and eq 8, one obtains the following criterion (for $k_P' \ll k_R'$):

$$\sigma_r/d_p^2 > 1.3 \times 10^{-3} \qquad (10)$$

for σ_r in seconds and d_p in micrometers. From this we can conclude that a reaction rate is influenced by the pore resistance if σ_r is smaller than 0.13 s for d_p = 10 μm or smaller than 6.5 s for d_p = 70 μm, respectively.

The film resistance can be tested experimentally by changing the hydrodynamic conditions in a catalyst bed (*10*). In our case, if—in accordance with eq 8—σ_r is independent of the flow rate, film resistance of any kind (mass or heat transfer) can be neglected.

EXPERIMENTAL SECTION

Decomposition of Diacetone Alcohol. Diacetone alcohol, which was prepared by the condensation of acetone over $Ba(OH)_2$ and rectified under vacuum, contained only traces of acetone. *n*-Heptane and 2-propanol used as mobile phase were of analytical grade (Baker, Deventer, The Netherlands).

A stainless-steel column (200 × 4.6 mm i.d.) was packed with LiChrosorb Alox-T (Merck, Darmstadt, GFR) with particle size 10 μm. A slurry of 3.5 g of alumina in 30 mL of methanol was sonicated for 1 min and then immediately pumped into the column with a slurry packing apparatus equipped with a Haskel MCP-110 pneumatic amplifier pump (Haskel, Burbank, CA). The column was flushed with 50 mL of acetone and then with 50 mL of mobile phase to remove the packing solvent. By use of *n*-heptane with 1% of 2-propanol as a mobile phase and toluene as test solute, the column had about 3500 plates at a flow rate of 1.0 mL/min and 20 °C.

The apparatus consisted of a reciprocating Altex 110 A pump and a pulse dampener (Kontron, Zürich, Switzerland), a Valco (3000 psi) sampling valve with 20 μL loop and a UV-visible LC-55 (Perkin-Elmer, Norwalk, CT) spectrophotometer operated at 280 nm. The reactor was immersed in a thermostated bath (Tamson, Zoetermeer, The Netherlands), the temperature of which was maintained with a precision of ±0.5 °C. Ethylene glycol was used as a heating medium.

The sampling valve and the reactor were connected by a 20 cm long piece of stainless-steel capillary (0.25 mm i.d.) immersed in the thermostat bath; the capillary served as a mobile phase preheater. A cooling capillary coil (50 × 0.25 mm i.d.) connected the output of the reactor with the detector cell. A short column was downstream of the cell as a flow resistance to keep the content of the reactor in a liquid form.

For each temperature or mobile phase composition, the reactor was conditioned for 1 h. Then the solutions of diacetone alcohol and acetone dissolved in the mobile phase (5×10^{-3} mol/L) were injected several times at constant flow rate and band broadening was calculated according to eq 7.

Hydrolysis of 1-Naphthyl *N*-Methylcarbamate. Demineralized distilled water and analytical-grade methanol (Baker) were used for the preparation of the mobile phase. The *o*-phthalaldehyde (OPA) reagent (*14*) used for the detection of liberated amine was prepared from 100 mL of 0.05 M aqueous borate buffer (pH 9.1), 0.1 mL of mercaptoethanol (Merck), and 0.1 g of OPA (Merck). The carbamate solution was prepared from a technical formulation; 0.1 g of Carbaryl was suspended under sonication in 5 mL of pure methanol and the insoluble additives were filtered off with a Millipore 0.5-μm filter. The solution was slowly evaporated and the solid residue of carbamate weighed. Then pure methanol was added to prepare a solution of approximately 1 mg/mL, which was diluted with mobile phase to the required concentrations.

The pump, pulse dampener, and the sampling valve were the same as in the previous part of the work. The detection system consisted of a reactor, a low volume mixing T-piece and 40 cm of PTFE capillary (0.3 mm i.d.) coiled to a diameter of approximately 8 mm. The OPA reagent was added via a syringe pump LD 13 A (Labotron Messtechnik GmbH, Gelting, F.R.G.) with a flow rate of 30 μL/min. A fluorimetric detector (Type 204 A, Perkin-Elmer) was connected with a linear recorder (BD 8, Kipp and Zonen, Delft, The Netherlands). The detector was operated at λ_{ex} = 340 nm and λ_{em} = 455 nm. The catalytic reactor was adapted from a HPLC column (60 × 4.6 mm i.d.) equipped with Swagelok couplings and 2-μm stainless-steel frits. The reactor was heated by means of a glass heating mantle, which was closed by rubber stoppers and attached to a glycol heating bath (Tamson, Zoetermeer, The Netherlands). Two different anion-exchanger resins having tetraalkylamonium groups in acetate form were used: Amberlite Resin GC-400 (Rohm and Haas, Philadelphia, PA) with particle size about 200 mesh (d_p = 70 μm) and Aminex A-28 (Bio-Rad, Richmond, CA) with particle size 9 ± 2 μm. The first material was graded by elutritiation to remove fine and coarse particles. Both resins were stable up to 120 °C. The materials were swollen 24 h before packing in water–methanol (50%), which was also used as a packing liquid. The empty reactor was attached to a slurry reservoir (column 30 × 0.4 cm i.d.) and, after pouring the slurry in, immediately packed at a flow rate of 5 mL/min. Similar results were obtained with Aminex A-28 when an upward packing procedure with a magnetically stirred slurry reservoir was used. After the packing, the reactor was heated at 110–120 °C and flow rate 1 mL/min (water–methanol, 1:1) for 6 h before

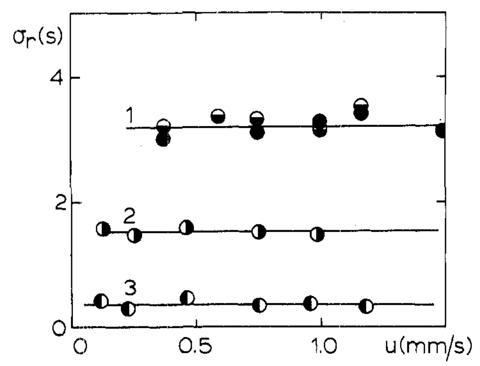
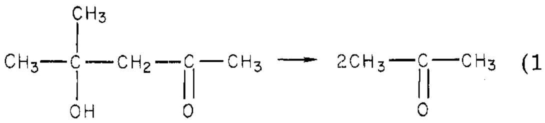


Figure 4. The dependence of the reaction band broadening, σ_r, for 1-naphthyl *N*-methylcarbamate on flow rates and various reaction conditions: Amberlite GC-400, 1, t_{react} = 57 °C (30 and 70% MeOH); Aminex A-28, 50% MeOH (2, t_{react} = 59 °C; 3, t_{react} = 83 °C).

measurement to remove unstable tetraalkylammonium groups.

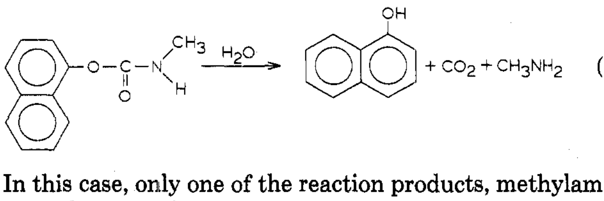
RESULTS AND DISCUSSION

The Model Reactions. As has been mentioned above, the mathematical model is based on first-order kinetics. Both examined reactions proceed under relatively mild conditions. The only observed product of the diacetone alcohol decomposition on alumina in the temperature range of 60–120 °C is acetone (*14*)


$$CH_3-C(CH_3)(OH)-CH_2-C(=O)-CH_3 \longrightarrow 2CH_3-C(=O)-CH_3 \quad (11)$$

If various alumina catalysts and nonpolar solvents such as *n*-heptane, toluene, or decaline are used, the reaction obeys zero-order kinetics. However, it was observed that the addition of a small amount of 2-propanol not only decreases the reaction rate but also changes the reaction order, *n*, from 0 to 1 (*14*). Thus, the advantage of choosing this particular model system lies in the possibility of influencing the reaction order via the change of mobile phase composition.

The requirement for first-order kinetics is also fulfilled for the base-catalyzed hydrolysis of 1-naphthyl *N*-methylcarbamate (*15*)



(12)

In this case, only one of the reaction products, methylamine, was selectively detected via a fluorogenic reaction with OPA reagent (*16*).

Dependence of σ_r on Flow Velocity. The variance, σ_r^2, calculated by means of eq 7 has been plotted against the linear velocity of the mobile phase for both reactions (see Figures 4–6).

For the carbamate hydrolysis, which was true first-order kinetics, band broadening, σ_r is seen (eq 8) to be independent of the flow velocity (Figure 4).

For the diacetone alcohol decomposition reaction it comes as no surprise that we find a flow-velocity dependence of σ_r (Figure 5). This model reaction can assume between first-order and zero-order kinetics depending on the mobile phase composition, as mentioned earlier (*14*). As can be seen from Figure 5, with 10% 2-propanol in *n*-heptane, one is getting close to first-order kinetics and the flow-rate dependence of σ_r becomes rather small. When the reaction order, *n*, differs more from unity, i.e., at lower concentrations of 2-propanol, σ_r changes strongly with velocity (see Figure 5).

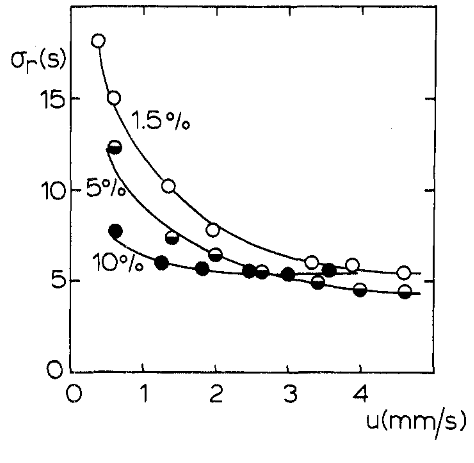


Figure 5. The dependence of the reaction band broadening, σ_r, for the diacetone alcohol decomposition on mobile phase compositions (1.5–10% 2-propanol in *n*-heptane), t_{react} = 115 °C.

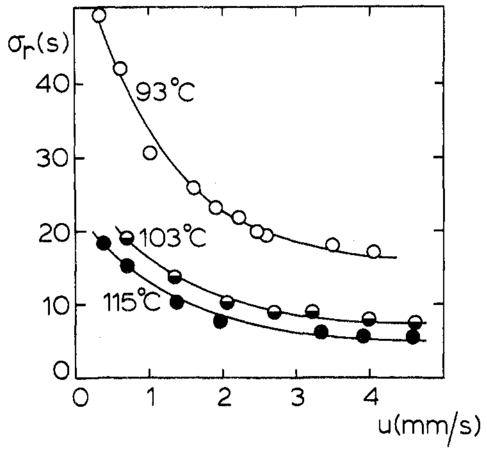


Figure 6. The dependence of the reaction band broadening, σ_r, for the diacetone alcohol decomposition on temperatures; mobile phase, 1.5% 2-propanol in *n*-heptane.

Dependence of σ_r on Mobile Phase Composition. For the diacetone alcohol model dependence on mobile phase composition has been discussed in the previous section and is only indirectly effective via the change in reaction order.

For the carbamate hydrolysis it is interesting to observe that the reaction band broadening is not much affected by the composition of the mobile phase (Figure 4, curve 1). An explanation for this is that the reaction product, methylamine, is nearly unretained on an ion exchanger whereas the reactant, 1-naphthyl *N*-methylcarbamate, is strongly retained as confirmed by UV detection. Consequently the term $(1 - k_P'/k_R')$ in eq 8 reaches unity and remains unchanged throughout the range of mobile phase compositions examined.

Dependence of σ_r on Reaction Temperature. In accordance with eq 8 and the law of Arrhenius one can expect a significant decrease of the reaction band broadening, σ_r, with increasing temperature. This tendency was actually observed for both model reactions, as can be seen in Figures 4 and 7 for the carbamate hydrolysis and in Figure 6 for the diacetone alcohol decomposition. Actually, providing the term $(1 - \ln k_P'/k_R')$ does not noticeably change with reaction temperature over the temperature range studied, σ_r should be directly proportional to $1/k_r$. An Arrhenius plot of $\ln (1/\sigma_r)$ vs. $1/T$ displaying such a result is shown in Figure 8.

Comparison of Catalysts. A simple comparison of the performance of the catalysts used for the carbamate hydrolysis, Aminex A-28 and Amberlite GC-400, can be done via Figure 7. Similar results are obtained with both ion exchangers, with the larger reaction band broadening in the

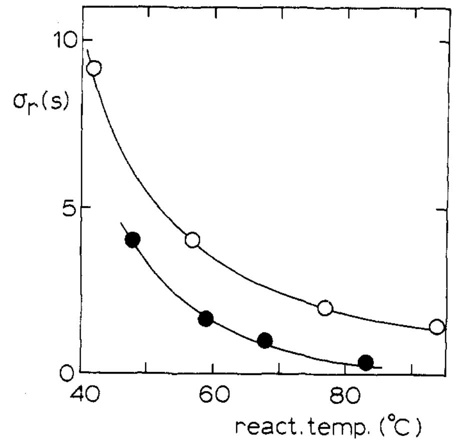


Figure 7. The dependence of the reaction band broadening, σ_r, on the reaction temperature for the 1-naphthyl *N*-methylcarbamate hydrolysis: ○, Amberlite GC-400; ●, Aminex A-28.

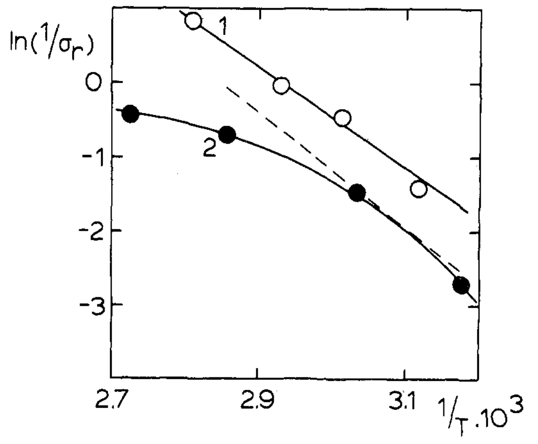


Figure 8. Arrhenius plot of ln $(1/\sigma_r)$ vs. $1/T$ for the 1-naphthyl *N*-methylcarbamate hydrolysis. Conditions: 50% MeOH; 1, Aminex A-28; 2, Amberlite GC-400.

case of Amberlite GC-400 being attributable to the relatively large particle size (70 vs. 9 μm).

A further comparison is made in Figure 8, where Arrhenius plots are depicted for both ion exchangers. The difference between the dashed extrapolated straight-line curve and the experimental curve 2 for Amberlite GC-400 indicates a relative increase of σ_r as a result of pore resistance. This assumption is supported by the rough estimations made on the basis of eq 10 where it was concluded that for $\sigma_r < 6.5$ s for a catalyst of $d_p = 70$ μm, a slowdown of the reaction by pore resistance can take place. This conclusion was based on calculations for various inorganic porous solids. It may well be expected that the effective diffusion coefficients, D_{eff}, for swollen ion exchanger particles will be even smaller than those for the inorganic materials, thereby making the occurrence of pore-resistance effects even more likely.

The linear Arrhenius plot obtained for Aminex A-28 (Figure 8, curve 1), on the other hand, confirms that the carbamate hydrolysis reaction on these smaller 9-μm particles is not influenced by mass transport; hence, as expected, pore resistance is absent. An apparent activation energy of about 15 kcal/mol was calculated from this plot. This value comes surprisingly close to the activation energy of 16.4 kcal/mol, which was reported for the hydrolysis of 1-naphtyl *N*-methylcarbamate in a homogeneous reaction system using base catalysis (*15*).

Finally it can be concluded that the independence of σ_r from the flow rate (Figure 4) indicates the independence of σ_r—and, thus, k_r—of the film resistance for both materials tested.

In conclusion, the comparison of the two ion exchangers on the basis of the Arrhenius plot shows the possible negative influence of the pore resistance phenomenon on σ_r, when solids of larger particle size are used. The use of small particles, therefore, is not only recommended to minimize the normal band broadening effects, σ_n, but also to reduce the reaction band broadening, σ_r, and, hence, σ_t of the system.

CONCLUSION

A simple relationship has been proposed in this paper between the reaction band broadening σ_r and the rate constant k_r and capacity factors k_R' and k_P' of reactant and product, respectively, for reactions following first-order kinetics. This relationship is in good agreement with experimental data obtained with two model systems. It has also been shown, that the reaction broadening caused by the ongoing chemical reaction and the simultaneous separation of product(s) and reactant(s) in the catalytic bed can easily be distinguished from the other band broadening mechanisms. The present study has shown that bed reactors packed with small catalyst particles and operated at the highest possible temperature have a favorable effect on reaction band broadening as well as normal band broadening of the products formed. For the rest, although the model systems are based on catalytic reactions it can be assumed that the relationship proposed and the conclusion drawn are valid for all solid phase reactions which adhere to first-order or pseudo-first-order kinetics, which is probably the case for the majority of the currently known solid phase reactor principles.

The usefulness of this type of reactor as postcolumn reaction detector in liquid chromatography is currently further explored in our laboratories.

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