

Kinetics and selectivity of chemical processes in fluid solutions

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Abstract: The motives for carrying out chemical processes in supercritical fluid solutions are outlined. Variation of pressure and temperature within extended ranges allows to optimize reaction conditions with respect to chemical kinetics, transport properties and phase behaviour. Free-radical polymerization in the fluid phase provides the additional advantage of continuously tuning the properties of the polymeric material by changing reaction pressure and temperature. Examples of novel fluid phase reactions are presented together with kinetic studies of free-radical polymerization up to kbar pressures.

INTRODUCTION

The interest in studying the properties of supercritical fluid states and particularly in carrying out chemical reactions in fluid solutions is rapidly growing (1,2). At supercritical temperature density can be continuously varied between gaseous and liquidlike states which is associated with large changes in physical properties. Variation of pressure P and temperature T in the supercritical state thus corresponds to having access to a multitude of solvent materials with gradually changing thermophysical, dielectric and transport properties. As a consequence, chemical reactivity may be significantly influenced by changing P and T , in particular under conditions of strong diffusion control. In fundamental studies the dependence of unimolecular processes on molecular surroundings has been systematically investigated and rate expressions which combine standard unimolecular rate theory with Kramers-Smoluchowski theory have been derived (3): Arguments for carrying out chemical processes in supercritical fluid phase are: (a) Reaction in an extended P and T range provides the opportunity to find process conditions which are optimal with respect to kinetics and selectivity; (b) Solvent properties may be easily adjusted to the special requirements of the process, e.g. homogeneity may be achieved for the reaction mixture and inhomogeneity, as required for product recovery, may be reached simply by decompression; and (c) Heat and mass transfer processes can be very efficient under supercritical conditions.

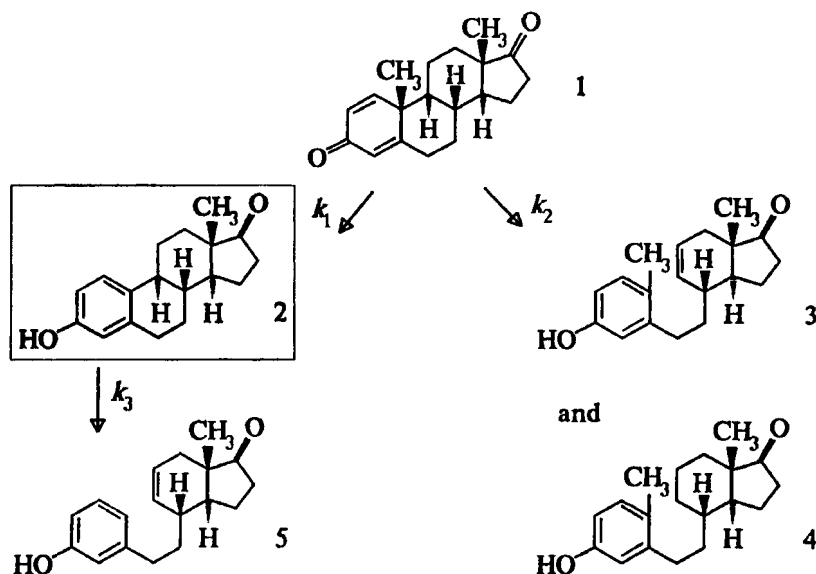
Performing free-radical homo- and copolymerizations in fluid phase is particularly interesting because polymer properties are determined by the kinetics of the polymerization process. Thus by continuously varying reaction conditions in supercritical fluid phase an almost unlimited number of different polymers can be produced. As polymer properties together with polymer concentration and with P and T also influence polymerization phase behaviour, there is an enormous flexibility in performing fluid phase polymerizations. The archetype for such reactions is high-pressure ethylene polymerization. Because of the large technical interest in this process, the detailed study of kinetic parameters in a wide region of states

remains an important task. These investigations have recently been extended to acrylate monomers (4) which, among others, are used as comonomers in ethylene copolymerizations.

The current interest in fluid phase reactions centers around combining several of the above-mentioned aspects: chemical reactivity, selectivity, diffusion-control, heat transfer, mass transfer, and phase behaviour, in such a way as to yield optimum performance for the entire chemical process. To outline several of the individual aspects, examples of (i) a novel fluid phase synthesis of estrone, of (ii) free-radical polymerization kinetics of acrylics and methacrylics, and of (iii) polymer modification reactions in supercritical fluid phase will be presented in the subsequent text.

ESTRONE SYNTHESIS IN SUPERCRITICAL FLUID PHASE

Estrone 2 (see Scheme 1) is technically produced by a gas phase pyrolysis of 1,4-androstadiene-3,17-dione (ADD) 1. According to the patent literature, the reaction is run at temperatures between 400 and 850 °C, preferably between 500 and 650 °C (5). At such high temperatures, tar and soot are also formed which seriously restricts continuous estrone production over extended periods of time.



Scheme 1 Kinetic scheme for the fluid phase decomposition (aromatization) of ADD (1) in fluid tetralin (only major products are given)

By carrying out the reaction in a supercritical fluid phase, e.g. of tetralin (tetrahydronaphthalene) which also provides hydrogen that is required within the ADD-to-estrone reaction, tar and soot formation may be avoided as their precursor species, due to the excellent solvent properties of the supercritical fluid, are easily and continuously removed from the reactor. Further arguments for reaction in a compressed supercritical fluid emerge from an inspection of the kinetics (6). The essential kinetic features are depicted in Scheme 1 which shows that parallel to estrone 2 production also undesired ring-opened species 3 and 4 are formed and, within a consecutive-type reaction, estrone may decompose to another undesired product 5. Kinetic analysis of rate coefficients k_1 and k_2 (see Scheme 1) in fluid tetralin over an extended temperature range shows (Fig. 1), that only above 550 °C selectivity of estrone production, as given by $k_1/(k_1 + k_2)$, reaches values of 80 per cent (and further increases toward

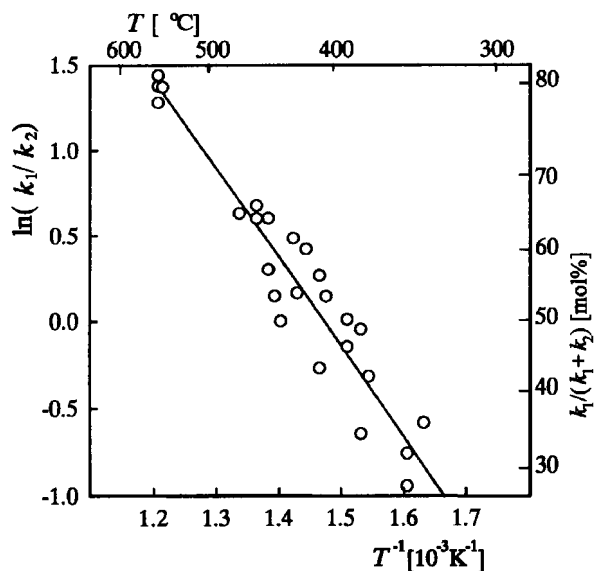


Fig. 1 Arrhenius plot of estrone selectivity in the fluid phase decomposition of ADD (1) in tetralin at pressures around 100 bar

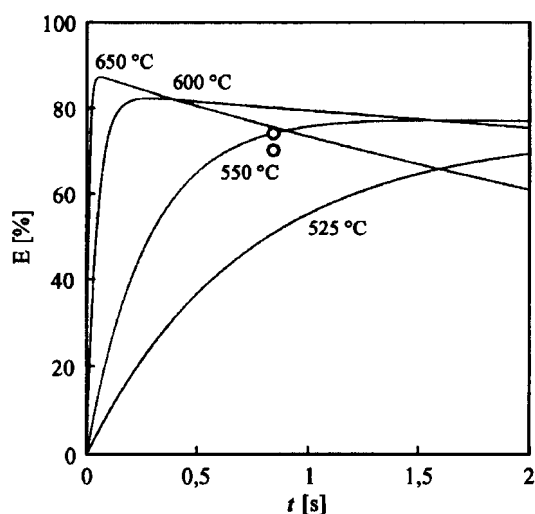


Fig. 2 Estrone yield E in the fluid phase decomposition of ADD (1) as a function of reaction time t ($P=100$ bar)

still higher temperature). Thus there is a requirement of very quickly passing through the temperature range below $550\text{ }^{\circ}\text{C}$ where decomposition of 1 into the undesired products 3 and 4 is fast with k_2 exceeding k_1 at temperatures below $400\text{ }^{\circ}\text{C}$. This requirement is easily met by conducting the 1 to 2 aromatization in supercritical fluid phase where heat transfer is excellent. By reaction in fluid tetralin at $550\text{ }^{\circ}\text{C}$ (T_c (tetralin) = $446\text{ }^{\circ}\text{C}$) estrone yields above 70 per cent have already been obtained. Two data points are presented in Figure 2. The curves of estrone yield vs. residence time t in a tubular reactor are calculated from kinetic data measured for the rate coefficients k_1 , k_2 , and k_3 (6). The data refer to a pressure of 100 bar. The very low residence times required for selective reaction at high temperature are not easily adjusted. (The decrease in estrone yield toward larger times at high T is due to estrone decomposition, see Scheme 1). On the other hand, reaction at lower temperature leads to unsatisfactory yields. There seems to be an optimum temperature range between 550 and $600\text{ }^{\circ}\text{C}$. The advantages of performing the aromatization in fluid phase essentially refer to reaction engineering aspects, such as favourable solvent properties, excellent heat transfer and smaller reactor size (due to the largely enhanced density as compared to a gas phase process at around ambient pressure). It should be noted that tetralin acts as a reactant, as heat transfer agent, and as (tunable) fluid phase material which ensures solubility and also allows easy product recovery by decompression and/or cooling.

FREE-RADICAL POLYMERIZATIONS AND POLYMER MODIFICATION REACTIONS

The high-pressure ethylene polymerization together with ethylene-acrylate and ethylene-(meth)acrylic acid copolymerizations are important technical processes, carried out at pressures and temperatures up to 3500 bar and $350\text{ }^{\circ}\text{C}$, respectively. As was shown above for the action of tetralin in fluid phase aromatization, ethylene in fluid phase polymerizations serves several purposes: It acts as the (main) reactant and is the tunable solvent which ensures both solubility during polymerization and easy product recovery after passing the reactor. As poly-

mer properties are determined by the actual kinetic situation during the time interval when a particular polymer molecule grows, typically of less than one second duration, the knowledge of rate coefficients within an extended P and T range is required for the modeling and optimization of fluid phase polymerization processes. The rate coefficients of propagation, k_p , and of termination, k_t , have been quantitatively measured for several monomers, by methods which use excimer lasers for initiation in conjunction with on-line vibrational spectroscopic analysis for the detection of monomer, partly with a time resolution of a few microseconds (4,7 - 10). Termination rate, k_t , is particularly sensitive toward monomer conversion (or polymer content) and changes by almost three orders of magnitude are found in ethylene bulk polymerization at monomer conversions up to 75 per cent (8,11). The variation of k_t with conversion may be very different even for monomers which appear to be rather similar. This situation is illustrated (Fig. 3) by the conversion dependence of relative termination rates k_t/k_t^0 in bulk free-radical polymerization of butyl acrylate (4) and of butyl methacrylate (12) where k_t^0 refers to the limiting situation of zero conversion in the very initial period of polymerization. The differences in k_t of BA and BMA are due to the relevant mechanisms of diffusion-controlled termination (11): translational diffusion, segmental diffusion, and reaction diffusion, contributing at quite different extents to overall termination in both monomers. Major distinctions arise from segmental diffusion being rather restricted in BMA and from k_p being low in BMA which reduces free-radical termination via reaction diffusion (11, 12).

Studies of copolymerization kinetics are even more complicated, in particular as the number of kinetic parameters is considerably enhanced and as problems may arise in selecting an adequate scheme for deriving individual rate coefficients. Reactivity ratios r which are defined as the ratio of homo- to cross-propagation for a given free-radical chain end are less difficult to be obtained. Fig. 4 shows Arrhenius plots for the two (binary) reactivity ratios r_E and r_{BA} of the fluid phase copolymerization of ethylene and butyl acrylate at 2000 bar (13). Knowledge of r_E and r_{BA} allows to directly relate the monomer content of the polymerizing mixture to copolymer composition. By copolymerization or, if necessary, by terpolymerization in an extended fluid range an enormous variety of polymeric materials can be made.

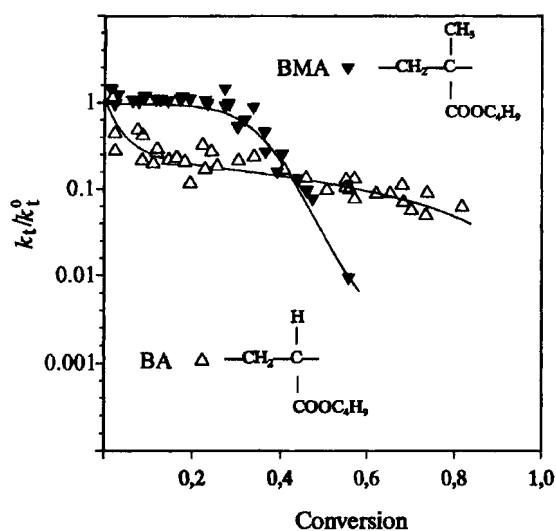


Fig. 3 Conversion dependence of k_t/k_t^0 for the bulk homopolymerizations of BMA, at 30 °C/ 1000 bar, and BA, at 25 °C/ 2000 bar

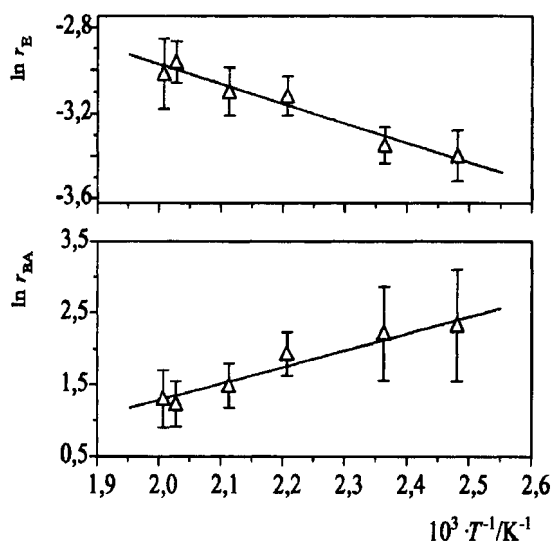
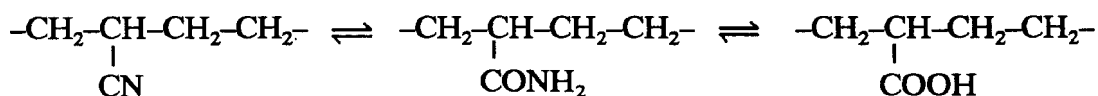


Fig. 4 Arrhenius plots of the reactivity ratios r_E and r_{BA} in ethylene-butyl acrylate copolymerization at 2000 bar

As an alternative to copolymerization, similar copolymeric materials may be produced via polymer modification reactions in supercritical fluid phases. Thus ester functionalities of an ethylene-butyl acrylate copolymer, by reaction in supercritical fluid ammonia, have been converted into nitrile functionalities (via the intermediate formation of amide functionalities (14)). In these reactions NH_3 acts as reactant, dehydration agent, and as the tunable solvent. Similar reactions may be performed with water as the reactant and as the tunable fluid solvent. Scheme 2 shows a reaction sequence in which nitrile groups of an ethylene-acrylonitrile copolymer, via amide groups, are transformed into carboxyl functionalities (15).



Scheme 2 Polymer modification reactions in fluid water

The variation with reaction time of the content of functional groups in the polymer modification reaction of a fully hydrogenated butadiene-acrylonitrile copolymer (35.7 mol % acrylonitrile) in fluid water at 250 °C and 1500 bar is shown in Fig. 5. The nitrile groups under these conditions are completely converted into either carboxyl groups, to about 70 per cent, or amide groups, to about 30 per cent. These percentages can be varied by changing P and T . Higher and even complete conversion of functional groups into carboxyl moieties may be reached by multiple reaction or by the addition of another component which suitably shifts the equilibrium. The product which corresponds to an ethylene-acrylic acid copolymer is also accessible by polymer modification reaction of ethylene-acrylate copolymers in fluid water (16). Thus the same functional group may be introduced by reaction in fluid water of different kinds of polymers, containing acrylate, amide and nitrile groups. Beyond these applications in polymer modification, reactions in fluid water appear to be of a general, widespread interest. The promising aspects of using supercritical water in extraction processes and in particular in the treatment and destruction of waste are outlined by Brunner (17).

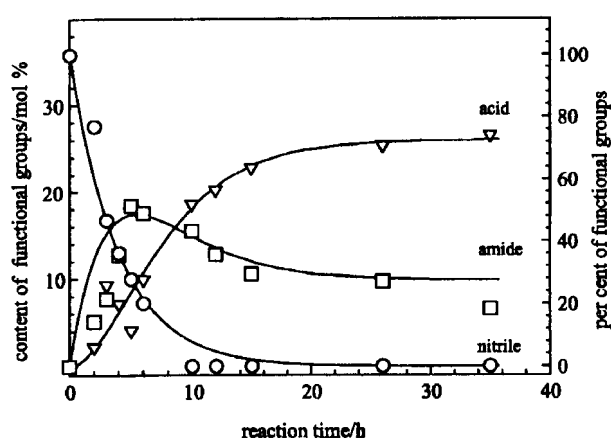


Fig. 5 Dependence of nitrile, amide and acid content on reaction time for the polymer modification reactions of fully hydrogenated butadiene-acrylonitrile copolymer (35.8 mol % acrylonitrile) in fluid water at 250 °C and 1500 bar.

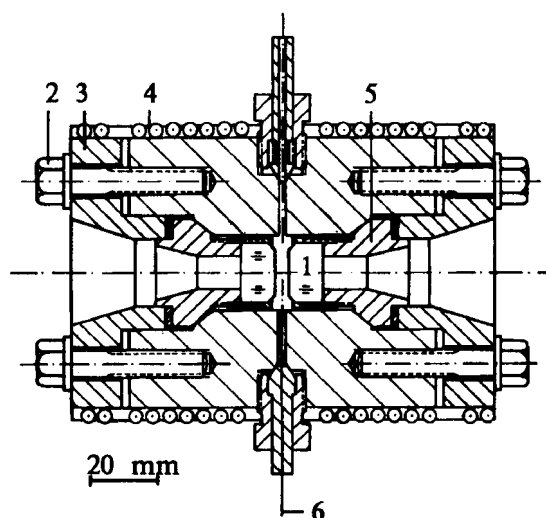


Fig. 6 Optical high-pressure cell
1 windows, 2 bolt, 3 flange,
4 heating, 5 plug,
6 sheathed thermocouple.

It should be noted that the dielectric constant of fluid water may be significantly changed even at supercritical temperature ($T_c = 374^\circ\text{C}$) where values up to 30 can be reached (18). Water thus provides an excellent example for using the potential of continuous density variation in the supercritical state to create an almost unlimited number of solvent situations simply by changing pressure and temperature of one material. The resulting flexibility may lead to difficulties in selecting optimum reaction conditions if this procedure is exclusively based on experiments and too many data are required. Thus measurements need to be accompanied by theoretical work to model chemical reactivity, transport properties and phase behaviour. Among the on-line techniques for the quantitative analysis of fluid systems at pressures up to several kbar and at temperatures up to several hundred $^\circ\text{C}$ infrared and near-infrared spectroscopy are particularly valuable. Various optical cells that can be used under conditions of simultaneous high pressure and high temperature have been developed and used (19) with the basic design tracing back to work in *E. U. Franck's* group at the University of Karlsruhe. As an example, an optical high-pressure cell for operation up to 3500 bar and 350 $^\circ\text{C}$ is shown in Fig. 6. The windows are mounted on stainless steel plugs and sealed according to the Poulter principle which is a modification of Bridgman's unsupported area principle. Each plug is pressed against the cylindrical cell body by a flange which is secured by several, mostly six or eight, bolts. The optical path length is given by the distance between the windows. Through holes which are drilled perpendicular to the axis of the cell, sample material is introduced and a sheathed thermocouple is inserted. The autoclave is heated electrically from outside.

For absorption experiments from 2000 to 50 000 cm^{-1} sapphire is unrivalled as a window material but a few other materials can also be used. Details about the design of the cell in Fig. 6 and of more complicated devices, partly equipped with internal cells, are given in Ref. (19) where also examples of applying quantitative on-line absorption spectroscopy toward the study of chemical reactions and chemical equilibria in fluid phases are presented.

CONCLUSIONS

Varying pressure and temperature in the supercritical fluid state allows to continuously tune solvent properties of a substance. Concentrations are significantly changed as are transport properties and phase behaviour. Pressures of a few kbar are sufficient to also influence rate coefficients. The availability of an extended P and T range thus allows to optimize reaction conditions. Free-radical polymerization in fluid phases is of particular importance as, in addition to reaction rates, the properties of the polymeric product may be varied within wide ranges. Investigations into reactions in and with supercritical water appear to be very rewarding because solvent properties, such as dielectric constant, can be varied to a large extent even above T_c .

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