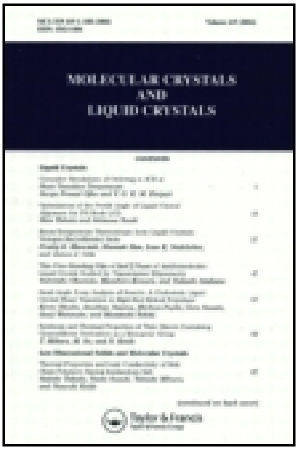

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REACTIVITY OF ORGANIC COMPOUNDS IN FROZEN AQUEOUS DISPERSED SYSTEMS

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Abstract The hydrolysis of p-nitrophenylacetate in aqueous solutions of inorganic salts, gelatin and silica gel suspensions at temperatures under 273 K is used as a model to ascertain the relation between the kinetic regularities of chemical reactions in frozen aqueous disperse systems and their phase state as well as conditions under which the samples are formed.

INTRODUCTION

The reactivity of organic compounds in aqueous systems at sub-zero temperatures can be realized only if molecular mobility occurs. Reaction sites in frozen solutions of low- and high-molecular weight substances, as well as suspensions, are usually represented by inclusions of a nonfreezing mother liquor, liquid films at the interphase boundaries and also by solution filling pores in the solid particles and in the ice. Under these conditions the reaction usually obeys the same mechanism that is typical of that occurring in the liquid phase at normal temperatures. Thus the hydrolysis of esters is distinguished by the major principles of acid-base catalysis.

The kinetic features of reactions in frozen aqueous disperse systems formed by freezing of solutions of low- and high-molecular weight substances, as well as suspensions, have been studied with the hydrolysis of p-nitrophenylacetate (p-NPA) taken as a model.
The phenomenon of reaction acceleration due to the concentration of dissolved reagents in a nonfreezing liquid phase is a distinct kinetic manifestation of the heterophase nature of frozen solutions. Competition between the concentration effect and the oppositly directed influence of temperature on the rate constant (the Arrhenius law) gives rise to bell-shaped curves for the dependency of the observed reaction rates on temperature.[1,2] In the absence of phase diagrams for the reactive multicomponent frozen mixtures, the concentration effects have been approximately calculated with the use of cryoscopic con-

stants.[2] Because of the nonideality of the solutions, the limited solubility of many, especially organic, compounds in water and partial inclusion of the reagents into the ice, these calculations frequently do not allow us to describe adequately the concentration conditions in frozen solutions. The kinetic consequences of partial crystallization of nonaqueous components of frozen solutions have been studied elsewhere.[3-5] The reasons for the kinetic factors observed can be conventionally divided into two groups: first, changes of the physico-chemical properties of the medium and, second, decreasing quantities of the reactive dissolved substances in the reaction zone.

Crystallization of water, crystalline hydrates of salts and water-salt eutectics of freezing buffer solutions e.g. phosphate[6], results in the shift of the pH in nonfreezing liquid, which, in turn, affects the shape and position of the experimentally observed dependence of the reaction rates on the initial pH value.[3]

As the temperature, and therefore volume, of the nonfreezing liquid are decreased, the concentration of one or a few reagents may attain a limit. In these cases no further growth of the reagent concentration is possible and they begin to crystallize. The result is that the concentration of the reagents in the solution becomes quasi-steady, being controlled by the reaction-dissolution rate balance.[4] If the consumption of the reagent in the reaction is completely compensated by dissolution of the precipitate, then the concentration in the reaction zone corresponds to the solubility value and does not depend on that in the solution prior to freezing. In this case the observed kinetic order of the reaction with respect to the reagent undergoing crystallization is equal to zero. A decrease in the observed kinetic order of hydrolysis with respect to p-NPA, whose crystallization took place in the course of cooling, was observed in studies of the reaction rate temperature dependence and at a fixed temperature with increasing initial p-NPA concentration.[7] Note that the lower temperature and smaller volume of the nonfreezing reaction medium, the lower the initial p-NPA concentration at which transition to the zero kinetic order is observed.

The equilibrium phase state of the samples can be attained during freezing over a time comparable to that of the observation of the reaction. That is why the transition of p-NPA hydrolysis to zero order in frozen solutions in the presence of a catalyst (hydroxylamine) took place after 30-45 min from the instant the samples were frozen.[4]

The kinetic features of chemical reactions in a nonfreezing liquid phase of solutions being frozen and cooled down to temperatures above the eutectic points (T_e) have been discussed elsewhere.[1] Later studies have indicated that T_e is not a low-temperature boundary for the reaction[8] as even at these temperatures a significant portion of the molecules retain mobility comparable with that in solutions.[9,10]

Kinetic studies of p-NPA hydrolysis in frozen aqueous salt solutions at temperatures below T_e indicate that a sharp decrease in the reaction medium volume occurring in a narrow temperature interval is accompanied by the slowing-down of the process due to the freezing - out of the reaction mixture components.[8] In quaternary mixtures containing hydroxylamine as the catalyst, such as H_2O - KF - p-NPA - NH_2OH and H_2O - NaF - p-NPA - NH_2OH [5], a deceleration of the reaction at $T < T_e$ is preceded by its acceleration at $T \approx T_e$ due to the increasing in concentrations of p-NPA and hydroxylamine in the reaction zone during the water-salt eutectic crystallization.

The direct relationship between the possibility plus the kinetic features of the reactions in frozen systems, on the one hand, and the phase state of the system, on the other, allows us to suggest that the influence on the structure of the samples by modification of their crystallization conditions must be followed by definite changes in reaction kinetics. Crystallization in an ultrasonic field permits us to produce denser polycrystalline samples with smaller intercrystalline inclusions.[11] Therefore the concentration of the impurities (in our case the reagents) localized in the intercrystalline inclusions of mother liquor[12] is higher in the ultrasound-irradiated samples than in the control ones. As a result of this, the rate of p-NPA hydrolysis in the samples frozen in an ultrasonic field is higher than that in nonirradiated ones and the transition to the zero kinetic order with respect to the reaction substrate occurs at lower initial concentrations as compared with those of control samples.[13]

As mentioned above, the possibility of reactions in frozen multicomponent systems is directly associated with the presence of nonfreezing liquid and it is its amount that determines the total volume of the reaction zone. It has been shown that for a number of water-salt mixtures at a constant p-NPA concentration and at temperatures both above and below T_e there exists a region of salt concentration where its growth leads to an increase in the observed initial rate of hydrolysis.[4] Due to the fact that the salt content is responsible for the weight amounts of the phases coexisting at the experimental temperature rather than their composition, the acceleration effect of the salt additives is attributed to a growing amount of the reactive dissolved p-NPA resulting from an increase of the reaction zone volume. The rate grows till the volume of the nonfreezing liquid becomes sufficient for maintaining the whole of the substrate in the dissolved state.

In heterogeneous disperse systems the bound water at the interphase boundaries retains high molecular mobility at temperatures under 273 K.[14] No studies of the possibility of chemical reactions in volume occupied by nonfreezing water in such systems and the kinetics of these processes have been made.

The nonfreezing water films have been found at very low temperatures near the surface of silica gel and in its pores.[15] These liquid inclusions act as reaction sites where the reagents capable of crystallizing in the absence of additions can be maintained in a reactive state at sub-zero temperatures.[16-18] A correlation between the accelerating effect of silica gel additives on p-NPA hydrolysis in frozen Na_2HPO_4, NaF and $Na_2B_4O_7$ solutions, and NMR data indicating an increased fraction of a mobile phase in the samples has been disclosed.[17]

An important property of frozen silica gel suspensions is that a nonfreezing liquid retains constant volume between 270 and 258 K.[17] Therefore, in the presence of silica gel in this temperature region, stabilization of the concentration conditions takes place and as a result the temperature dependence of the observed p-NPA hydrolysis initial rate obeys the Arrhenius law.[17]

The freezing-melting cycles of aqueous hydrophilic dispersions are in many cases accompanied by hysteresis phenomena.[19] This implies that, in temperature regions specified for a system, the volume of a nonfreezing liquid in samples approaching the experimental temperature "from above", will be greater than that when the same temperature is set by heating. The nonequilibrium state of frozen dispersions is manifested by the fact that, in samples first overcooled and then heated to the experimental temperature (243 K), the concentration of dissolved reagents will be higher and therefore the the reaction rate is twice that when the same temperature is reached "from above".[17]

For cryobiology it would be interesting to look at protein reactions in frozen solutions. Among the most important factors, whose effect on the rate of protein reactions may vary as a result of freezing and the associated redistribution of the components between the coexisting phases, one can mention the state of the macromolecules in solution. A sharp change in the concentration conditions, and other physicochemical properties of the medium during the course of freezing, may give rise to conformational changes of the macromolecules, their aggregation, salting-out, gelation, etc. In this case kinetic measurments may serve as a test for structural changes of protein solutions upon cooling and freezing.

Frozen solutions of gelatin contain nonfreezing water.[19] This renders them convenient for studies of protein reactions in the frozen state. It has been shown that gelatin displays catalytic activity with respect to the hydrolysis of p-NPA.[20] The nature of the catalytic activity is associated, in our mind, with the presence in the polypeptide chain of amino acid residues in possession of nucleophylic properties.[21]

At normal temperatures the increase of ionic strength by the addition of NaCI or K_2HPO_4 to the solutions of gelatin causes its precipitation and the associated marked reaction deceleration. On freezing to 268 K, the rate drop is observed at an appreciably lower salt concentration and is seemingly due to the same reason. This fact suggests that in frozen electrolyte-containing protein solutions the two components are localized in the same nonfreezing regions. The co-localization of the low- and high-molecular weight reagents leads, as in the cases mentioned above, to the appearance of a bell-shaped temperature dependence of the observed initial reaction rate as well as to the lowering of the experimentally found kinetic order of hydrolysis with respect to p-NPA as its initial concentration is increased.

In the case of partial p-NPA crystallization (zero order reaction) the temperature dependence of the hydrolysis rate in a frozen water - gelatin - p-NPA - K_2HPO_4 system becomes more complicated. The extremum disappears and the reaction rate decreases with lowering temperature, the graph showing changes in the various sections by differing appreciably in slopes toward the temperature axis. As follows from the NMR data, in the region 273-248 K, the nonfreezing water content of the samples decreases smoothly so that the breaks in the graph cannot be related to the abrupt concentration jumps resulting from sharp changes in the reaction volume. At the present time one can put forward only conservative considerations concerning the reasons responsible for the observed disturbance of the reaction rate temperature dependence. It is probable that as the fractions of water which are more loosely bound to the protein gradually freeze-out in the gelatin-water-salt system, in narrow temperature regions there takes place structural transitions with the associated changes in the physico-chemical properties of the reaction medium and/or accessibility of the catalytically active sites. At the same time, changes in protein hydration, as compared with the total nonfreezing water content of the sample, may be small. In this context, establishment of the relation between the structural changes of polymer-containing frozen aqueous systems and their reactivity or catalytic activity may be promising for future low-temperature studies.

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