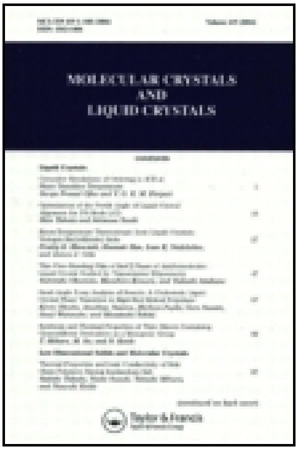

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REACTIVITY AND CONFORMATIONAL CONTROL UTILIZING LIQUID CRYSTALLINE SOLVENT MEDIA

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Abstract By examining reaction kinetics through the phase transitions of thermotropic and lyotropic liquid crystalline media, several cases of marked reactivity control have been discovered. In lyotropic surfactant media, a number of reactions show marked discontinuities in reaction rates through the transitions from rod-like to disc-like phases. In thermotropic media, we have taken advantage of the phenomenon of reentrance to afford a phase sequence with decreasing temperature in which one proceeds from less ordered (nematic) to ordered (smectic) to less ordered again (reentrant nematic). The thermal isomerization of an indigo dye in such a medium indeed shows anti-Arrhenius behavior as a consequence of this phase sequence. We have also found that the atropisomerization of 1,1'-binaphthyl increases in rate through the nematic-smectic and smectic-solid transitions, presumably as a consequence of decreasing the barrier from transition state to product in the more ordered phases. Finally, we have demonstrated that achiral solutes which normally show degeneracy of their enantiomeric twist states can behave as though they have a unique twist sense in a chiral liquid crystal environment. Such effects occur for both polymeric solutes and for substituted oligophenyls. The overall message is: liquid crystals can be utilized as media to achieve control of both reactivity and conformation for a wide variety of organic reactions.

INTRODUCTION

It is the purpose of this paper to point out the use of liquid crystals as solvent media. Just as the crystal environment is useful in controlling reactions and can produce profound changes in reactivity and orientation as compared to the liquid state, liquid crystals have anisotropic features and an abundance of phase transitions that can also be used for reactivity and conformational control. This topic is in fact a very old theme in liquid crystal research, having first been explored by Svedberg in 1916.[1]

LYOTROPIC MEDIA

Lyotropic liquid crystals are essentially extended micellar phases that have many of the features which make micelles and vesicles so interesting for reactions and solubilization. Because they are concentrated detergent-like solutions, they solubilize 100 fold more organic material than do conventional micellar media.

There exists a wide variation in the structure of lyotropic liquid crystals, analogous to the rich polymorphism of thermotropic liquid crystals. It is therefore possible to vary the nature of the aggregate profoundly and examine the influence of aggregate structure on reactivity. A particular class of lyotropics are those with either nematic or cholesteric ordering which have appropriate viscoelastic properties to respond to external torques such as magnetic or electric fields, surface alignment, etc. We have found that for both bimolecular and unimolecular reactions there are profound effects on reaction kinetics through the phase transitions from rod-like to disc-like to spherical (ordinary micellar) aggregates.

Prior to our recent work, four studies had been made in lamellar phases of cationic detergents. Ahmed and Friberg[2] studied the hydrolysis of p-nitrophenyl laurate in the lyophase water-cetyltrimethylammonium bromide (CTAB)-hexanol, and reported a pronounced increase in reaction rate. Bacon et al[3] studied hydrolysis of 4-substituted benzylidene-t-butyl- aniline N-oxides in dodecylammonium chloride-H_2O and reported a pronounced decrease in reaction rate in the lamellar phase. Studies of oxidation of benzaldehyde in the liquid crystalline phase of an alkylbetaine-benzaldehyde-water indicated that the oxidation rate decreased in the lyophase.[4] A study of the hydrolysis of procaine hydrochloride, procaine methyl chloride and procaine ethyl chloride in a polyoxyethylene-(6)tridecanol-water system in the lamellar phase indicated rate decreases.[5] The authors argued that the substrates are located within the extended micelle where they are presumably protected from hydrolytic bond cleavage. In general, then, these studies are consistent with the ideas regarding reactions in ordinary and reversed micellar media. Localizing one reactant within a micelle will frequently protect it from the hydrophilic environment, but if it is buried in the core of a reversed micelle containing an aqueous phase, reactivity will be enhanced.[6]

The plan of our initial work in this area was to focus on those nematic lyotropic phases which show rod-disc-sphere transitions as a function of temperature and/or concentration of surfactant. These transitions can be observed both optically and thermodynamically in a liquid crystal and are well-defined critical phenomena. Two aspects of the behavior of the lyotropic phase on reactivity could then be expected: (1) the increase in solubilization of organic substrate, and (2) the influence of the micellar medium, its extent of aggregation, the size and shape of the micelle, which change at the critical point, on the rates and products of reaction.

We have studied the kinetics of four different reactions in three different solvent media, and we will summarize the results of these studies below.

(1) Bromination of trans-stilbene in sodium decylsulfate-decanol-water.[7]

Sodium decylsulfate(SDS)-decanol-water is a particularly convenient solvent system for study because there is a small region of its ternary phase diagram in which, as a sensitive function of concentration or temperature, transitions occur between three phases: N_L, N_C and I. These symbols represent, respectively, an aggregate having a bilayer structure, a cylindrical structure, and an isotropic, less aggregated, phase of spherical micelles.

It was the strategy of our study to investigate the kinetics of a bimolecular reaction through these phase transitions in order to ascertain the effects of environment on the reactivity. The reaction chosen was the bromination of trans-stilbene, since there already existed a careful study of this system in aqueous micelles and vesicles.[8] We showed that the N_C phase provides an environment in which the rate of reaction drops significantly as compared to the N_L phase, and that this decrease occurs when one enters N_C by either raising the temperature at fixed concentration or raising the sodium decylsulfate concentration at fixed temperature. This work represented the first example of the clear influence of micellar size and shape on reactivity.

(2) The o-iodosobenzoic acid (IBA) catalyzed hydrolysis of p-nitrophenyl laurate (NPL) in myrystyltrimethylammonium bromide (MTAB)-water-decanol -ammonium bromide.[9]

Ester hydrolysis is a frequently studied model reaction, and a great body of literature exists with p-nitrophenyl as the leaving group because of its easy spectroscopic detection. In this cationic detergent system, N_L and N_C phases exist depending on the amount or presence of ammonium bromide and decanol in the MTAB-water mixture. Measurements of the rate constant for this system indicate a substantial rate differential between rod- and disc-like phases.

(3) Unimolecular rearrangement of a spiropyran in potassium laurate (KL)-decanol-water.[10]

Spiropyrans are known to isomerize more or less reversibly with light (photochromism) or heat (thermochromism).[11] Presumably such species are primarily within the extended micelles of KL or are strongly interacting with their surface. The interesting question is whether unimolecular reactions in a micellar medium involve strong enough interactions between medium and substrate to show a rate effect that depends on the size and shape of micelle. Rate changes at the phase transitions were indeed observed.

(4) o-Iodosobenzoic acid catalyzed hydrolysis of phosphinate esters in nematic lyophases.[12]

Recent publications by Durst et al[13] on thiophosphonate and phosphinate ester hydrolysis, and Moss et al[14] on phosphate ester hydrolysis in micellar media were the starting point for our investigation of the utility of lyophases as media for phosphorous ester hydrolysis. Two substrates were selected for our initial studies: 4-nitrophenyl ethyl (phenyl) phosphinate (PNPEP) and 4-nitrophenyl isopropyl (phenyl) phosphinate (PNPIP).

A similar approach to that adopted in the ester hydrolysis studies was chosen. Reactions were conducted in the dilute micellar phase of MTAB/H_2O, as well as the N_C, N_L and I phases, some of which include decanol and ammonium bromide in the phase. A dramatic result was obtained: there is a greater than three order of magnitude difference in the rate constants in the N_L and N_C phase.

The fact that N_L aggregates serve as a protective environment whereas N_C aggregates allow the reaction to occur rapidly is an important example of reactivity control that merits full explanation. We have infrared evidence that the ester is solubilized well within the hydrocarbon core of N_L aggregates, but in N_C and I aggregates the solute is near the aqueous interface where catalyst is presumably located.

Although we achieved rapid hydrolysis of phosphinate ester in the N_C phase, the rate constant was about a factor of 40 lower than the corresponding dilute micellar phase. It occurred to us[15] that at the high surfactant concentration, the catalyst/aggregate ratio was much smaller than in the dilute micellar solution. Accordingly, we designed experiments in which phosphinate ester hydrolyses were conducted at constant catalyst/aggregate ratio. Under these conditions, the rates of reaction in concentrated surfactants are essentially the same as those in dilute micellar medium (actually, slightly faster in concentrated surfactants).

Thus, the nematic lyophase of MTAB/H_2O is a highly appropriate medium for conducting reactions of phosphorous esters. Such a phase solubilizes 100 fold greater concentrations than conventional micellar phases. At identical catalyst to aggregate ratios, the rates of reaction are as fast as micellar reactions in spite of the enormously higher viscosity. It is anticipated that similar utility as reaction media can be found with other surfactant liquid crystals and other substrates.

THERMOTROPIC MEDIA

Since a review of reactions in thermotropic phases has recently appeared,[16] we will describe here two recent studies undertaken by our group. Firstly it occurred to us that the phenomenon of reentrance[17] affords a phase sequence with decreasing temperature in which one proceeds from less ordered to ordered and then **to less ordered again.** Our expectation was that a reaction run in such a media might show a decrease in rate as one enters the smectic phase, but would increase in rate as one reenters the nematic phase. Such anti-Arrhenius behavior would be extremely interesting to find, and is very rare in chemical systems.

We studied[18] the effect of the nematic - smectic A - reentrant nematic phase transitions on the kinetic of the thermal isomerization of cis-N,N'-diacetylindigo (cis-DAI). A liquid crystal mixture of 4-nheptyl-4'-cyanobiphenyl (7CB), 4-n-octyloxy-4'-cyanobiphenyl (8OCB), and 4-n-pentyl-4'-cyanoterphenyl (5CT) in the ratio of 73:18:9 by weight, shows a nematic phase between 65.6-26.9°C, a smectic A between 26.1-10.1°C and a reentrant nematic phase below 10.1°C. This particular liquid crystal mixture has the advantages that the reentrant nematic phase is stable, does not supercool, and shows reversible enantiotropic transitions.

The Arrhenius plot of the rate constants shows the anticipated discontinuities at the phase transitions. The rate constants for the nematic and reentrant nematic phases fit a straight line. However, entrance and departure from the smectic phase show an abrupt decrease and increase in the rate respectively.

Further evidence for this behavior was found by determining the instantaneous rate constants of a single sample at different temperatures. After determining the changes in concentration during 0.1 to 0.3 half-lives, the solution was rapidly heated (or cooled) utilizing a circulating bath prestabilized to the desired temperature. From the slope of a plot of the changes in concentration with time, two sets of rate constants (k(inst)) were determined for heating and cooling.

Activation energies determined in the reentrant nematic and in the smectic phase are the same ($\approx$15 kcal mol^{-1}) within experimental error, and also similar to that obtained in benzene.[19-22] However, because of the small temperature range, these values are inherently inaccurate. The rate constants in the liquid crystalline phases are approximately 10 times faster than those in benzene, a solvent with a considerably lower viscosity. Ganapathy et al[19] have found that in a cholesteric mixture, DAI has a similar activation parameter to that in benzene and the isomerization reaction is not affected by the viscosity of the solvent. The mixed cyano-substituted oligophenyl would be expected to have a much greater dielectric constant than benzene, and this probably is responsible for the higher reactivity observed.

In a second example, we have found that the atropisomerization of 1,1'-binaphthyl increases in rate through the nematic-smectic and smectic-solid phase transitions. This substrate has two optically active forms and one can resolve them by heating-cooling-recrystallization cycles as proposed by Wilson and Pincock.[23] R-(-)-1,1'binaphthyl (BN) in a liquid crystal mixture of 7CB, 8OCB and 5CT in the proportions 83:8:9 shows a twisted-nematic and an induced smectic-A phase with a nematic-smectic transition temperature at 19°C. Atropisomerization of BN (1% wt.) in the nematic-smectic and solid phases of this solvent shows an increase in rate with increasing order of the phase! Similar observations have been reported by Naciri et al[24] for the nematic-solid transition in MBBA, who argued that the effect may be a consequence of decreasing the barrier from transition state to product in the more ordered phases. Another possibility is that the substrate is rejected into "puddles" of lower ordered phases where the reaction really occurs, an explanation which has been evoked to explain the phenomenon of reaction acceleration in frozen solutions.[25] Thus far we have not been able to distinguish between these mechanistic possibilities.

CONFORMATIONAL CONTROL IN CHIRAL LIQUID CRYSTAL MEDIA

We have demonstrated that achiral solutes which normally show degeneracy of their enantiomeric twist states can behave as though they have a unique twist sense in a chiral liquid crystal environment. Such effects occur for both polymeric solutes and for substituted oligophenyls. In the most dramatic example, the addition of ~ 0.2 mole % of 4-4'-bis(2-butyloctyloxy)-4-quaterphenyl (QP) to a cholesteric solvent causes a 22% reduction of the pitch, an effect much larger than that of a typical chiral solute.[26] What was explored in this work is the possibility that a non-optically active oligophenyl will adopt a preferred twist conformation in a cholesteric medium. The cholesteric solvent employed consisted of N-(4-methoxybenzylidene)-4-butylaniline (MBBA) doped with 0.4 weight % of cholesteryl propionate (CP) The pitch of this cholesteric solvent at 20°C is ~ 110 μm as measured in the "fingerprint texture". The achiral solutes employed were QP, p-terphenyl (TP), 4-n-pentyl-4"-cyano-p-terphenyl (T15), 4-n-nonyloxy-4'-cyanobiphenyl (M27), 4-cyano-1-[trans-4-n-pentylcyclohexyl]-benzene (S1114), bicyclohexyl (BC), and 4-n-pentyl-4'-cyanobicyclohexane (S1185). For comparison purposes, the chiral solute 4-[(S)-(-)-2-methylbutyloxy]-4'-cyanobiphenyl (C15) was also studied. The most profound shortening of the pitch was observed for QP, which has an apparent helical twisting power (HTP) greater than that of the optically active solute C15! Terphenyls, biphenyls, and phenylcyclohexanes produced small decreases in pitch and have HTP's of the same order of magnitude. Both BC and S1185 do not perturb the pitch significantly. Since all work was performed in the limit of very low concentration, these pitch fluctuations cannot be expected to be caused by any other factor than a preferred conformational effect.

In a polymeric example, an optically inactive poly(alkylisocyanate) dissolved in a chiral liquid crystal environment also markedly affected the pitch of the matrix.[27] In both right and left handed cholesteric solvents, the polymer adopted the same conformation as the solvent causing a shortening of the pitch in both cases. An optically active polyisocyanate used as a reference caused pitch shortening in a left handed cholesteric and pitch lengthening in a right handed cholesteric, as was expected. These observations clearly imply that a wide structural range of dynamically racemic materials may be subject to and in turn affect the chiral properties of liquid crystals.

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