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Liquid Crystalline Catalysis. Kinetics of the Rearrangement of Allyl *p*-(Dimethylamino)benzenesulfonate in a Smectic B-Solvent

Paolo De Maria,* Bruno Samorì,† Anna Tampieri,† and Paolo Zani†
Dipartimento di Chimica Organica, Via Archirafi 20, 90123 Palermo, Italy
†Dipartimento di Chimica Organica, Viale Risorgimento 4, 40136 Bologna, Italy
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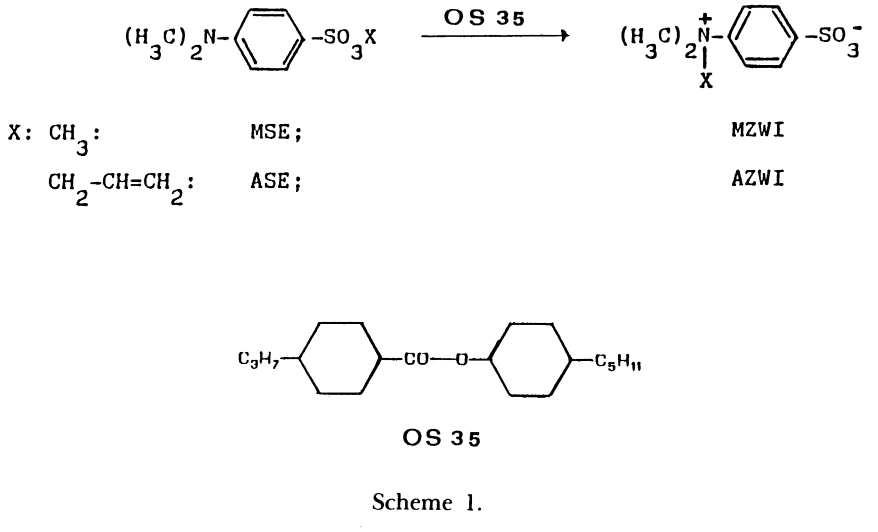
Allyl *p*-(dimethylamino)benzenesulfonate (ASE) was found to promptly rearrange to the corresponding quaternary zwitterion (AZWI) in a smectic, liquid crystalline solvent (OS 35) 4-pentylcyclohexyl 4-propylcyclohexanecarboxylate. On the contrary, this reaction does not occur in isotropic solvents. In the present study we investigate the effect of temperature and of reactant concentration on the reaction rate. A plot of log k vs. $1/T$ shows a strog upward curvature. In addition, the rate constant, k, strongly depends on ASE concentration: relevant rate depression occurs beyond a threshold value of solute concentration, which in turns depends on temperature. These results are interpreted in terms of reaction mechanism and solute-solvent interaction. From these results we can conclude that smectic B phase has a strong catalytic effect on this particular kind of nucleophilic displacement. Furthermore, catalysis does not depend on solute expulsion from the bulk of the phase; finaly, the detailed mechanism of the catalytic effect may depend on the different location of the solute in distinct solubilization sites existing within the smectic mesophase.

In view of the interest in the field of reactivity within anisotropic media,[1a—e] we have recently exploited the use of smectic (Sm) mesophases in order to prove catalytical effects that the internal organization of these mesomorphic solvents can exert on properly chosen model reactions. Particularly we have reported that smectic B (SmB) solvents (ZLI 1409;[2a,b] ZLI 1544;[2a] ZLI 1756;[2c] OS 44;[2b] OS 53;[2d] OS 35;[2d]) can induce relevant rate variations on the quaternization reaction of *p*-(dimethylamino)benzenesulfonic esters (Scheme 1). The rearrangement of pure solid methyl *p*-(dimethylamino)benzenesulfonate (MSE) to the corresponding quaternary ammonium zwitterion (Scheme 1) was previously described as an example of reaction promoted by appropriate intermolecular orientations in the solid phase.[3] On the contrary allyl *p*-(dimethylamino)benzenesulfonate (ASE) does not rearrange in its crystalline state because of a different kind of molecular orientation within the crystal lattice.[4]

When both esters (MSE and ASE) are dissolved in SmB mesophases a very clean quaternization reaction (Scheme 1) is promoted at a rate higher than that in the melts. On the other hand MSE and ASE do not react at any detectable rate when dissolved in common organic (isotropic) solvents or even in the nematic (N) phases of the investigated liquid crystals. This is the first instance in which Sm solvents are shown to promote a rearrangement which requires a precise orientational control to take place.

Now we report here a more complete kinetic treatment showing the peculiar effects of solute concentration and temperature on the rate of ASE quaternization which are not explainable in the framework of reactivity in common (isotropic) solvents but require a detailed knowledge of the phase equilibria within the SmB liquid crystalline solvent.



Scheme 1.

Results

We have published preliminary results[2] from which it stems that the quaternization reactions of ASE and MSE (Scheme 1) are simple second order processes and that the mechanisms, most likely, are dimeric, $\mathrm{S_N}2'$ type pathways. However these are limited results as those concerning MSE were obtained in a liquid-crystalline solvent (ZLI 1409) which is not transparent in the spectral region where reactant and product do absorb. The opacity of the solvent to UV light prevented us from following the reaction course directly. The results concerning ASE were obtained at a single temperature and within a narrow range of solute concentrations. From our previous work it emerged that most kinetic features remained to be clarified. A study of the change of the observed rate constant, *k*, with temperature was still to be done in order to provide useful information on the activation parameters, and, therefore, on the mechanistic details of the assistance assured by the liquid crystalline solvent to the reaction. In fact, interesting temperature effects have been recently observed by Weiss and collaborators in reactions performed within liquid crystalline phases.[5]

Temperature Effect. Kinetic measurements on ASE conversion to AZWI were carried out in the temperature interval $44>T>28$ °C in the SmB phase of the OS-35 liquid crystalline solvent. Provided that the concentration of ASE was less than that of the threshold value (see below), *k* is strictly second order at each individual temperature. The values of *k* at the different temperatures and the investigated concentration ranges where *k* turned out to be strictly second order are reported in Table 1. An Arrhenius-type plot of log *k* vs. $1/T$ (Fig. 1) shows a strong upward curvature. Apparently log *k* tends to infinity when *T* approaches the transition (SmB→N) temperature of 49 °C. However because of the superimposed concentrations effect (see following section) the temperature interval $44<T<49$ °C is not experimentally accessible to our kinetic technique. For example, even at 44 °C *k* is rigorously independent of ASE concentration only when $[\mathrm{ASE}]<10^{-2}\ \mathrm{mol\cdot dm^{-3}}$.

Concentration Effect. The observed second order rate constant, *k*, is by no means independent of total solute concentration at "high" initial ASE concentration. It sharply decreases beyond a definite value of concentration, which, in turn, depends on temper-

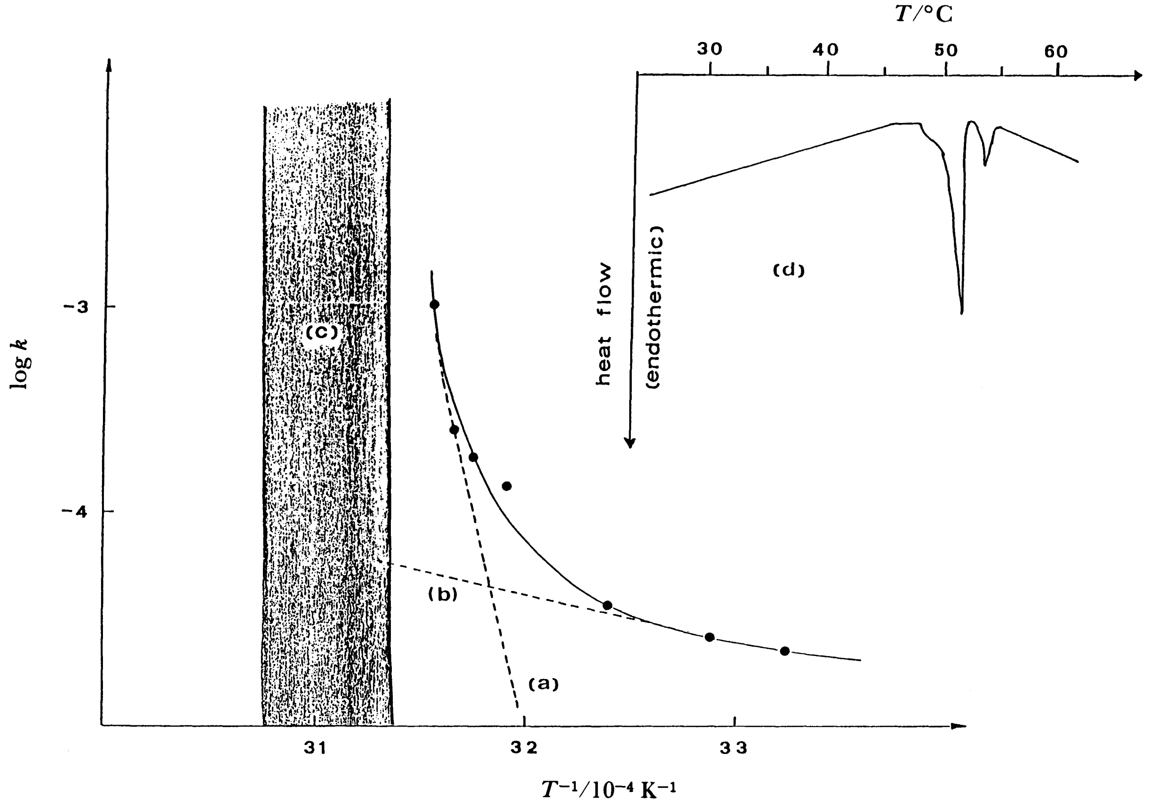


Fig. 1. Arrhenius-type plot for the ASE quaternization in OS 35 SmB phase at ASE concentrations lower than those of the temperature-dependent threshold values (see text and Fig. 2). Lines (a) and (b) are hypothetical straight lines extrapolated from the higher- and lower-temperature data, respectively. The shaded area (c) represents the temperature interval corresponding to the width of the Differential Scan Calorimetry (DSC) peak in (d). Profile (d) is the DSC trace showing the Smectic→Nematic and Nematic→Isotropic transition for the reacting solution at ASE concentration equal to $1.05\times10^{-2}\ \mathrm{mol\cdot dm^{-3}}$.

ature. The dependence of k on concentration, at one temperature (40 °C), is graphically depicted in Fig. 2. We have evidence that the concentration value at which rate depression starts (threshold concentration), dramatically decreases with increasing temperature. For example, while k is practically coincident with the values determined in more dilute solutions at 36 °C and initial [ASE] 10^{-1} mol·dm^{-3}, at 44 °C and initial [ASE] $2\cdot10^{-2}$ mol·dm^{-3} k is some 20 times lower than the values determined in dilute solutions (Table 1). More dramatically, at 47 °C, where the solvent is still in its smectic phase, disappearance of ASE was not detected after 11 days even at initial [ASE] as low as 5×10^{-4} mol·dm^{-3}

Discussion

The "real" catalytic effect of OS 35 SmB mesophase on the ASE quaternization is clearly displayed by the following data. Whereas 15% conversion to AZWI is achieved in one day at 44 °C in the melt phase, 67% conversion can be obtained in SmB diluted solutions under the same conditions of temperature and time. Moreover we found total conversion of ASE after five days in OS 35 at 44 °C and only after 26 days in the pure melt. From the kinetic data at different temperatures (Fig. 1) it can be seen that the second-order rate constant increases with temperature far more than predicted by a "normal" Arrhenius behavior. To explain this anomalous curvature the most likely reason is that the assistance provided by the SmB solvent is varying with temperature and that this effect is being superimposed upon the "normal" Arrhenius behavior.

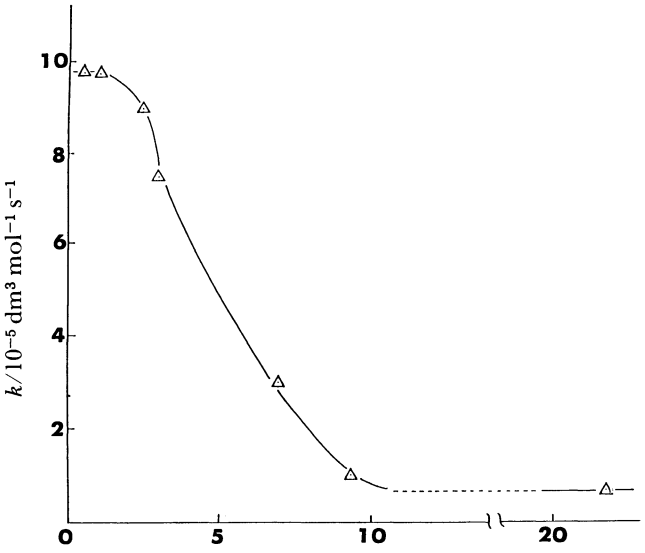


Fig. 2. Dependence of the kinetic constant on the solute concentration at 40 °C. The threshold value of ASE concentration at which rate depression starts and the second-order constant becomes dependent on total solute concentration is clearly displayed.

The rate breakdown observed with increasing "total" solute concentration also deserves some comments. The sigmoidal shape (Fig. 2) can be explained by a very sudden loss of solvent cooperative effects on the reaction. This discontinuity resembles those observed for thermodynamic parameters in phase transitions.[6] In addition this is further clearcut evidence that the liquid crystalline catalysis cannot be ascribed only to solute bulk aggregation out of the solution. Optical microscopy shows[7] that such solute aggregation occurs only at the highest [ASE] concentrations where the reaction rate becomes very low. Turning again to the temperature effect, one can recall that in general cases the simplest explanation of a curved Arrhenius plot (as in Fig. 1) is the existance of two competitive reaction mechanisms[8] each with its own A and E_a values (sketched by lines (a) and (b) in Fig. 1) and dominating in two different temperature intervals. Therefore a breakdown from linearity occurs at intermediate temperatures when both mechanisms are operating. However this often happens over a temperature interval much wider than the present one. Furthermore two independent mechanisms are hardly conceivable for ASE quaternization. On the contrary our results can be better explained considering that our reaction was not a single-step process due to the occurrence of the reaction in more than one catalytic site provided by

Table 1. Temperature Effect on the Second-Order Rate Constant k in the Quaternization Reaction of ASE in OS 35 SmB-Solvent

Temperature/°C	k/dm^3 mol^{-1} s^{-1}	[ASE]/mol dm^{-3}(intervals)[a]	
28	2.5×10^{-5}	9.8×10^{-3}	2.45×10^{-2}
31	2.7×10^{-5}	9.8×10^{-3}	2.45×10^{-2}
36	3.3×10^{-5}	9.8×10^{-3}	1.00×10^{-1}
40	9.8×10^{-5}	9.8×10^{-3}	1.00×10^{-2}
42	13.0×10^{-5}	4.9×10^{-3}	9.8×10^{-3}
43	15.0×10^{-5}	4.9×10^{-3}	9.8×10^{-3}
44	45.0×10^{-5}	4.9×10^{-3}	9.8×10^{-3}

a) Investigated concentration intervals of ASE where k is strictly second order. At higher values, depending upon temperature, k decreases with [ASE] as discussed in concentration effect.

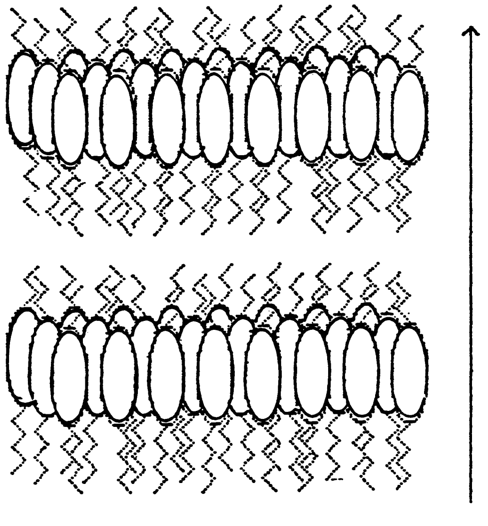


Fig. 3. Layered structure of Sm liquid crystalline media. The rigid-core- and alkyl-chain-sublayers are sketched by ellipsoids and tails respectively.

the solvent. In fact we recently presented evidence[7] arising from linear dichroism (LD) that ASE molecules are located in two different sites within the SmB phase of OS 35.

OS 35 molecules have a fairly rigid core and flexible alkyl chains. This molecular shape leads to a layered structure for the SmB, in which alternating sequencies of sublayers are determined by the alignment in planes of the centers of gravity of adjacent cores or of adjacent tails (Fig. 3). The rigid cores and the more flexible aliphatic tails may therefore provide two distinct solubilization sites for ASE. The LD technique revealed that one site, (characterized by an ASE absorption maximum at 263 nm in the LD spectrum) is more ordered and differently populated than the other (LD maximum at 277 nm). This more ordered site is likely provided by the core. In addition it appears from the same LD data that the partition of ASE between these two sites strongly depends upon temperature. These results may be interpreted in kinetic terms as a sort of pre-equilibrium type situation in which the nature and relative population of the two sites are strongly temperature dependent. Within this framework the concave shape of Fig. 1 should be explained as a positive deviation at lower temperature from the Arrhenius line (a). Similar but far less pronounced effects played by cooperative solvent assistance were recently found even in isotropic solvents such as 2-buthoxyethanol-water and *t*-butyl alcohol-water neutral ester hydrolysis.[9a,b] These effects also led to curvatures in the Arrhenius plots and were attributed to the assistance by aggregates (called "moving units") whose formation depends in a nonlinear manner upon temperature and molar fraction of the solvents.

Experimental

ASE was prepared as previously described.[2b,3] After 2 recrystallizations from petroleum ether (bp 40—60 °C) a material of mp 39—40 °C was obtained. OS 35 was kindly supplied by E. Merck (Darmstädt).

Kinetic Measurements. The general procedure employed can be summarized as follows: ASE was dissolved in the OS 35 solvent (0.1 g. samples) at 50 °C by quick injections of volumes of a diethyl ether solution of known concentration. After complete evaporation of the ether, the homogeneous solution of ASE was rapidly cooled down into its SmB phase by immersion in a bath thermostatted at the desired temperature. Portions (ca. 0.01 g) of the reaction mixture were taken at appropriate intervals and the reaction quenched by dilution with RS-grade ethanol (5 cm^3). The absorbance of these ethanolic solutions of ASE was determined with a Beckmann DU or a Varian spectrophotometer at λ=284 nm. The kinetics were followed[2d] over at least three half lives and were second order according to the equation $-\mathrm{d}[\mathrm{ASE}]/\mathrm{d}t=k[\mathrm{ASE}]^2$

Least-squares-slopes of these second order plots gave average rate constants, k, accurate to ±8% at worst.

DSC Measurements. DSC measurements were carried out on a Perkin Elmer Calorimeter Model DSC-2. scan rate was 1 °C min^{-1}. Aluminium containers of 20×10^{-6} dm^3 capacity were used.

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