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Liquid Crystalline Catalysis¹ by Smectic B Solvents Transparent to near-U.V. Radiation

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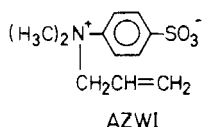
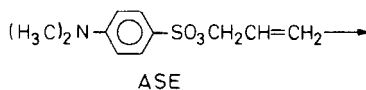
The ASE quaternization reaction has been carried out in the smectic B phase of a new series of liquid crystals, labelled OS, in order to probe the occurrence of liquid crystalline-solvent effects. This reaction was not previously observed in ASE crystals and apparently is not attainable under any other conditions at the temperature and in the time scale of our experiment. The liquid crystalline catalysis is clearly displayed by the ability of OS smectic B solvent to promote the ASE quaternization. The kinetic data support the previously suggested, simple, bimolecular process for the ASE rearrangement in these mesophases. The phase diagrams of OS.44, OS.53 and OS.35 liquid crystals are reported and the B structure of their smectic phases has been demonstrated by X-ray diffraction studies.

INTRODUCTION

The classical style of performing reactions in organic chemistry involves attacks upon a substrate randomly from an isotropic solution. A new area of investigations, paying more attention to the possible influences of solvent organization than to the intrinsic reactivity and steric crowding of particular functions of the reagent, is however growing in importance with time. The amazing biochemical style of performing reactions by enzymes is certainly one of the sources of inspiration for the development of these researches. It has been widely demonstrated that solutes may modify their reactivity within organized solvent assemblies (as liquid crystals¹⁻⁵, vesicles⁷, micelles^{6,8-10}, and membranes¹¹) if they are differentially solubilized in different regions submitted to anisotropic restraints on their orientations and diffusion properties.

Catalytic effects exerted on both monomolecular¹ and bimolecular² reactions by tightly ordered Smectic B (Sm B) solvents have been recently demonstrated by us. A new series of liquid crystals,¹² labelled OS and recently commercialized by E. Merck (Darmstadt), provides the big advantage over ZLI-1409 and ZLI-1544 previously used by us, of being transparent to U.V. radiation. The OS liquid crystals, used as solvents, allow photochemical reactions of solute molecules to be performed in mesomorphic phases and spectrophotometric analysis of thermal reactions to be made without requiring separation of the products from the reaction solutions.

The quaternization reaction of allyl *p*-(dimethylamino)benzenesulfonate (allyl sulfonate ester, ASE) was induced by the Sm B phase of ZLI-1409 only and seems not to be obtainable under any other conditions.² The present X-ray structural analysis demonstrates that the smectic phases of this series are all B in type. The ASE quaternization may hence be used as a probe of the ability of the OS Sm B phases to exert catalytic effects on a process whose energy of activation is mainly determined by the entropy term.



X-RAY DIFFRACTION STUDIES OF OS SERIES

The compounds of the OS series of liquid crystals used in this investigation and their phase transitions are shown in Fig. 1. The transition temperatures were obtained from X-ray powder diffraction experiments and were confirmed by optical microscopy.

The B assignment of the smectic phases of the three compounds is mainly based on the results reported in Fig. 2, which contains the diffraction patterns for the smectic, nematic and isotropic liquid phases of the OS compounds investigated. The Sm B phase is an ordered one with the molecular long axes perpendicular to the smectic layers and hexagonal order within the layers. The intra-layer arrangement of this phase has a periodicity and rigidity similar to that of a two-dimensional solid.

From the low angle Bragg peak observed for the Sm B phase, interlayer distances $d_{001} = 20.8 \pm 0.2 \text{ \AA}$, $d_{001} = 21.0 \pm 0.2 \text{ \AA}$ and $d_{001} = 20.9 \pm 0.2 \text{ \AA}$ were respectively obtained from the OS.44, OS.53 and OS.35 liquid crystals. These values are in satisfactory agreement with the molecular length, $d = 22.5 \pm 0.5 \text{ \AA}$, deduced from the models. The high angle peak corresponds to the 100 hexagonal reflection.¹³ By

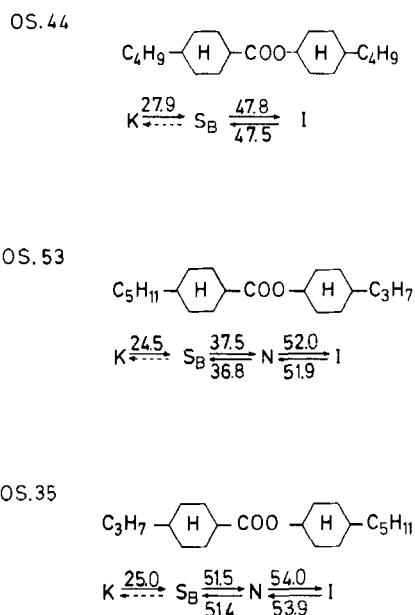


FIGURE 1 The liquid crystals used as catalytic solvents and their phase transitions.

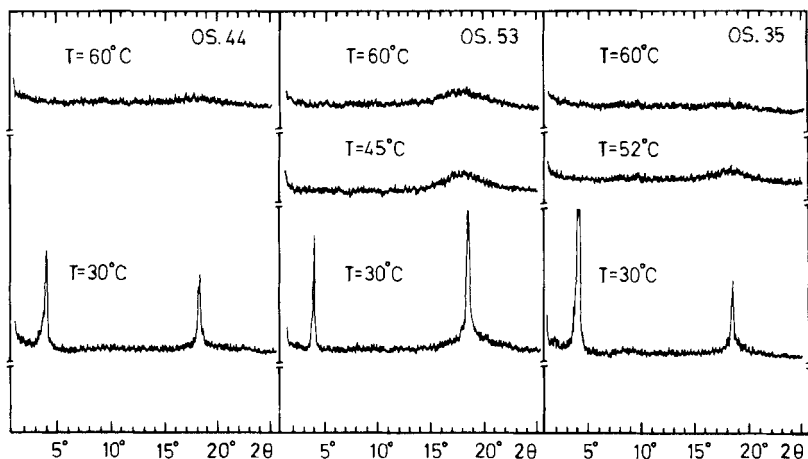


FIGURE 2 The X-ray diffraction patterns for the liquid crystalline and isotropic liquid phases of the OS.44, OS.53 and OS.35 compounds.

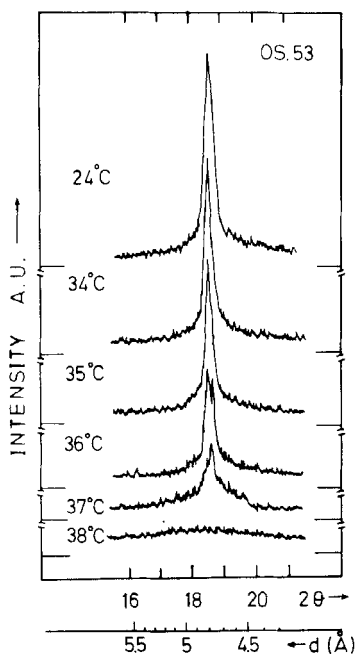


FIGURE 3 High angle region of the diffraction patterns at the Sm B-nematic phase transition of OS.53. The reported d values are calculated by Bragg's law.

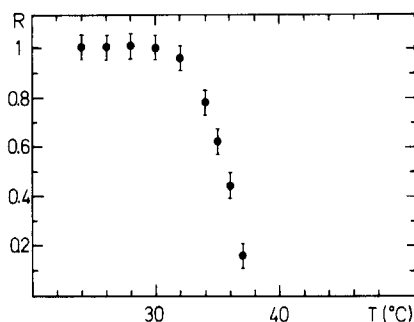


FIGURE 4 Relative integral X-ray diffracted intensity, R , of the (100) Bragg peak as a function of temperature at the Sm B-nematic phase transition of OS.53 ($R = \text{Area}_{7^\circ\text{C}} / \text{Area}_{24^\circ\text{C}}$).

applying Bragg's law, $d_{100} = 4.79 \pm 0.04 \text{ \AA}$, $d_{100} = 4.77 \pm 0.04 \text{ \AA}$ and $d_{100} = 4.77 \pm 0.04 \text{ \AA}$ spacings and hence intermolecular distances of $5.52 \pm 0.05 \text{ \AA}$, $5.51 \pm 0.05 \text{ \AA}$ and $5.51 \pm 0.05 \text{ \AA}$ were obtained for the OS.44, OS.53 and OS.35 compounds respectively. These data are in good agreement with the $d = 5.48 \pm 0.05 \text{ \AA}$ values obtained from the nematic phases of OS.53 and OS.35 by using the modified Bragg equation:¹⁴

$$1.117\lambda = 2d \sin \theta.$$

The low angle peak position does not change appreciably between the nematic and smectic phase, thus confirming that the molecules are perpendicular to the layers. Moreover, a mosaic texture, typical of a Sm B phase, was seen by optical microscopy for the three compounds investigated.

Fig. 3 reports the high angle regions of the diffraction patterns obtained at different temperatures for OS.53 in the range corresponding to the Sm B-nematic phase transition. A progressive reduction of the peak height and a broadening of the peak are observed. The integrated peak area is reported as a function of temperature in Fig. 4. Similar results were obtained for the two other compounds.

KINETICS OF THE ASE QUATERNIZATION REACTION IN OS.35 SOLVENT

The rate of the ASE quaternization reaction was followed at $36 \pm 0.2^\circ\text{C}$ and at $49 \pm 0.2^\circ\text{C}$ by measuring the decrease in absorbance of ASE with time at its $\lambda_{\text{max}} = 284 \text{ nm}$. At 49°C , where the solvent in the

presence of $\geq 10^{-2}\text{M}$ solute is in its isotropic phase, no apparent decrease in concentration of ASE was observed after 14 days. On the other hand at 36°C , where the solvent is in its Sm B phase, the quaternization reaction follows second order kinetics according to the equation:

$$-\frac{d[\text{ASE}]}{dt} = k[\text{ASE}]^2.$$

In fact for an initial concentration, C_0 , of ASE in the range $1 \times 10^{-2}\text{M} \leq C_0 \leq 2.5 \times 10^{-2}\text{M}$, plots of $(1/C - 1/C_0)$ vs. t , where C is the molar concentration of ASE at time t , were strictly linear over at least three half lives. Slopes of these second order plots gave an average rate constant $k = (3.3 \pm 0.2) \times 10^{-5} \text{ dm}^3\text{mol}^{-1}\text{sec}^{-1}$.

A limited range of initial concentrations of ASE was adopted in order safely to avoid rate depressions expected at higher initial concentrations (e.g. $C_0 \geq 6.8 \times 10^{-2}\text{M}$ in a similar smectic solvent²).

The presently determined k may be compared with a previous value $k = (1.1 \pm 0.1) \times 10^{-5} \text{ dm}^3\text{mol}^{-1}\text{sec}^{-1}$ obtained with ZLI-1409 Sm B solvent at 37°C . This more than three-fold increase in rate on passing from the less polar ZLI-1409 to the more polar OS.35 smectic solvent, is as one might predict for a simple $\text{SN2}'$ -like process with a transition state more polar than the starting material.

CONCLUSION

The present results once more display the catalytic ability of Sm B liquid crystals to promote a bimolecular reaction with high entropic demand. The Sm B solvent, by restraining the dynamic properties of the solute reactant molecules, is able to induce molecular collisions with the critical orientation required for the reaction to take place. In particular that was found to be valid for the OS. 44, OS.53 and OS.35 liquid crystal solvents.

In addition, the present kinetic data strongly support the idea that the mechanism of ASE rearrangement in Sm B mesophases follow a simple bimolecular process, as previously suggested.²

EXPERIMENTAL

X-ray diffraction

Goniometric scans were obtained by using a conventional powder diffractometer. Ni-filtered $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) was used.

The divergence of the primary beam impinging on the sample was $\cong 8'$. The generator-sample distance was $\cong 18$ cm and the sample-counter distance $\cong 20$ cm. The sample had thickness of $\cong 1.5$ mm and was sandwiched between two very thin Al sheets fixed to a circular hole in an Al matrix with diameter of $\cong 1$ cm. Heating was obtained by a hot stage containing electrical resistors, whose temperature was controlled to $\pm 0.1^\circ\text{C}$ by a BT 300/301 control system supplied by SMC, Grenoble (France). Pictures were obtained by a Marconi-Elliot toroidal camera using the same radiation emerging from a Rigaku-Denki rotating anode generator. Similar sample holders were employed to those used in the diffractometer. The heating and cooling rates were $1^\circ\text{C}/\text{min}$.

Optical microscopy

Optical observations, with crossed polarizers, were performed by using a polarizing microscope (Leitz Ortolux 2 Pol) equipped with a Mettler FP52 hot-stage. Scan rates of $1^\circ\text{C}/\text{min}$ were used during the heating and of $0.2^\circ\text{C}/\text{min}$ during the cooling.

Kinetic procedure

ASE was dissolved in the OS.35 solvent (0.1 g samples) at $\cong 50^\circ\text{C}$ 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 Sm B phase by immersion in a bath thermostatted at $36 \pm 0.2^\circ\text{C}$. Portions (0.01 g) of the reaction mixture were taken at appropriate intervals and the reaction quenched by dilution with RS-grade ethanol (5 ml). The absorbance of these ethanolic solutions of ASE was determined with a Beckmann DU or a Varian spectrophotometer at $\lambda = 284$ nm.

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