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NEMATIC SOLVENT EFFECTS IN THE ISOMERIZATION OF 2,4,6-TRIMETHOXY-s-TRIAZINE

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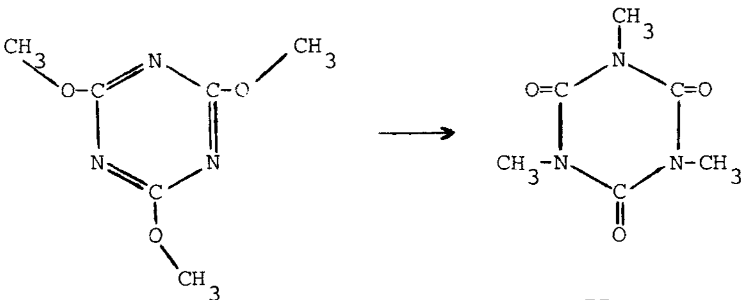
ABSTRACT: Thermal isomerization of 2,4,6-trimethoxy-s-triazine in nematic solvent proceeds faster and with a smaller loss in entropy of activation than in the isotropic phase.

INTRODUCTION

Liquid crystalline solvents share many properties of the usual liquid solvent; the major difference is the anisotropy of the liquid crystalline state. The nematogenic solvent, di(p-methoxyphenyl) trans cyclohexane-1,4-dicarboxylate (DMCD) demonstrates distinctly different characteristics in the nematic and the isotropic states.[1] As a solvent, di(p-methoxyphenyl) trans cyclohexane-1,4-dicarboxylate alters the rate of many reactions. For example, it influences the polymerization of a linear molecule like phenylacetylene.[2] Again, it has little or no influence on the Claisen rearrangement.[3] In this report, we wish to point out a comparison of the thermodynamic parameters in the thermal isomerization reaction in the nematic and isotropic phases of DMCD. The reaction we are studying is



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The thermal isomerization of 2,4,6-trimethoxy-s-triazine, I, to 1,3,5-trimethyl-2,4,6-trioxohexahydro-s-triazine, II, is a second-order reaction in the absence of a solvent[4] and also in nitrobenzene catalyzed with quaternary ammonium halides.[5] In the latter study the rate of isomerization was followed by nmr, at a temperature above 150°; the product is essentially all the N,N,N-trimethyl derivative, II. The isomerization of I, proceeds through intermediate steps of O,O,N- and O,N,N-trimethyl derivatives and these intermediates were identified from infrared,[4] nmr and from mass spectra.[4] Rate studies followed by nmr[5] show the O,N,N-trimethyl intermediate isomerizes many times faster than I, as expected because of the loss of aromatic character in the s-triazine ring of I. The isomerization of I to II, is accompanied by the loss in energy of 6 kcal/M based on the heats of formation of isomers I and II.[6] The thermal isomerization of I to II follows second-order kinetics in the different solvents used in this study. The reactions were heated above 150° and results in 60% conversion.

EXPERIMENTAL SECTION

Materials--I, was prepared from cyanuric chloride and methanolic sodium hydroxide.[7] Improved yields are obtained from cyanuric chloride recrystallized from benzene. The product, 80% yield, melted at 133.5° (DTA).

Di(p-methoxyphenyl)trans-cyclohexane-1,4-dicarboxylate. This nematic solvent was prepared from trans-cyclohexane-1,4-dicarboxylic acid and p-methoxyphenol by the acid chloride route in toluene as the solvent. The crystal-nematic transition temperature is 142° and the nematic-isotropic transition, 245°. These temperatures were determined by Differential Thermal Analysis.

Cholestanyl p-Methylbenzoate. This compound was added to the DMCD to disorient the nematic organization and lower the temperature of the solvent. It was prepared from distilled p-methylbenzoyl chloride following the procedure reported by Wiegand.[8]

Kinetics. Solutions of I, containing 0.649 M were prepared in ampoules under nitrogen in the different solvents at room temperature. These ampoules were placed in an auxillary bath heated at 147° ± 0.5°, and shaken intermittently for ten minutes to assure homogeneity.

The ampoules were then placed in the constant temperature bath controlled to ± 0.04°, and the time recorded. These samples were removed at selected times, cooled, opened and the contents dissolved in chloroform. The composition of each solution was determined from nmr spectra. Trimethyl cyanurate (I) shows a singlet at 4.0 ppm for the methyl protons, while in the isomerized product (II) the absorption shifts to 3.3 ppm relative to T.M.S. The relative error found in this method of analysis is within 5% based upon the analysis of synthetic mixtures of trimethyl cyanurate (I), and the isomerized product (II). The data were taken on an A-60 nmr spectrometer which was equipped with a Model V-6058A Spin Decoupler. The isotropic phase of DMCD was prepared by adding 21.37 mol% of cholestanyl p-methylbenzoate to the DMCD. Solutions of I, were prepared as outlined above.

RESULTS AND DISCUSSION

In comparison with isotropic liquids, the oriented reactant molecules in nematic solvents have lost a degree of freedom. This suggests that reactions in nematic solvents lead to a smaller loss in the entropy of activation than in isotropic solvents. This feature tends to increase the rate of reaction in the nematic phase in comparison with the isotropic state of the same solvent.[9]

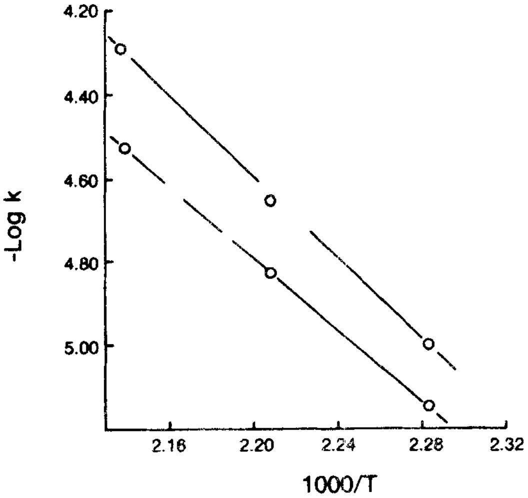

FIGURE 1. Rate of Isomerization in Nematic and Isotropic Phase

In Figure 1, are the log k vs 1/T plots for the isomerization reaction in the nematic and isotropic phases of DMCD. From the slope of the lines the energy of activation for the reactions in various phases can be obtained. Thermodynamic parameters for the reaction in the nematic and isotropic phases were calculated from the energies of activation (Table 1).

Table 1

Activation Parameters for the Isomerization

Solvent	$\Delta H^{\ddagger}$ [a]	$\Delta S^{\ddagger}$ [a]	$\Delta G^{\ddagger}$
	kJ mol^{-1}	J $mol^{-1}K^{-1}$	kJ mol^{-1}
nematic	89.0	-140.9	153.0
isotropic	79.5	-165.2	154.4

[a] Calculated at 180°C.

The entropy of activation for the isomerization reaction in the nematic phase is more positive than in the isotropic liquid. The rate constants in the nematic phase are modestly larger (Fig. 1) suggesting reactant I, has its molecules oriented in this mesophase.

We have also found the rate of isomerization of I in nitrobenzene is about twice as fast as in the nematic phase of DMCD; with biphenyl as the solvent the rate constant is smaller. This difference in rate appears to be due to the large differential in dielectric constants of nitrobenzene and biphenyl.

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