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REACTION KINETICS DETERMINED BY PITCH CHANGES IN LIQUID CRYSTALS

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Abstract A rapid, convenient method of continuously following the kinetics of a reaction conducted in a liquid crystalline phase is described. Conceptually any reaction consuming, producing or changing the concentration of a chiral species produces a shift in the wavelength of maximum reflection of a cholesteric solvent, and the reaction consequence can be directly seen by an observer when this wavelength is in the visible region. Examples are presented involving the formation of a Schiff base from an aldehyde and an amine, and for amine exchange reactions of Schiff bases, both conducted in a "red" cholesteric solvent. The technique may afford an approach to cumulative thermal dosimetry.

Considerable interest exists in studying reaction rates and products in liquid crystalline systems to examine the possibilities of orientational effects or rate effects due to the anisotropic properties of the medium, as well as any implication to reactions in biologically significant ordered mesophases.[1-7] It occurred to us that a convenient and rapid kinetic method of following a reaction in a cholesteric liquid crystal was to take advantage of its unique optical properties -- the reflection band for which $\lambda_{max} = \bar{n}p$ where $\bar{n}$ is the average refractive index and p is the pitch of the cholesteric array.[8] These bands are perturbed by the presence of a chiral solute,[9-11] and any reaction producing, consuming or changing the concentration of chiral species can be expected to produce a wavelength shift in the cholesteric. If these effects occur in the visible region, one directly visualizes the kinetics of the reaction. Such a visualization can be used to provide a dosimeter indicative of a given thermal profile, i.e. by interfacing the appropriate reaction kinetics and temperature dependence with the appropriate cholesteric solvent, useful cumulative thermal dosimeters can be designed.

For small concentration changes ΔC of an optically active component, the induced change of pitch Δp is given by $\Delta(1/p) = \alpha\ \Delta C$, where α is the "helical twisting power".[10] In general, if concentration changes are produced by the following chemical reaction:

$$\nu_1 A_1 + \nu_2 A_2 + \ldots + \nu_\ell A_\ell \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \nu_{\ell+1} + \ldots + \nu_m A_m$$

the overall pitch change for species n at time t is given by:

$$\Delta(1/p)_t = \alpha_n^o \Delta[A_n]_t;\ \alpha_n^o \nu_n = \left[\sum_{\text{products}} \alpha_j \nu_j - \sum_{\text{reactants}} \alpha_i \nu_i\right].$$

The form of the rate equation for both first and second order reactions can easily be expressed in terms of $\Delta(1/p)$, α and the appropriate rate constants. As typical cases (Table I), we studied the formation of a Schiff base from an aldehyde and an amine, and amine exchange reactions of Schiff bases. When $k_f \gg k_r$ or when the reaction is far from equilibrium, and $[A_1]_0 = [A_2]_0 = a$, the rate equation has the form:

$$\frac{a^2}{\Delta(1/p)_t} = \frac{1}{k_f \alpha t} + \frac{a}{\alpha} \qquad (1)$$

For a racemization reaction,[12] such as that between (-)EBPEA and (+)α-phenethylamine, $k_f/k_r = K_{eq} \cong 1$, and the appropriate form of the rate equation becomes:

$$\ell n\left(1 - \frac{\Delta(1/p)_t}{\Delta(1/p)_{eq}}\right) = -\ 2\ k_f a t$$

Typical data are given in Fig. (1) for the kinetics of formation of a Schiff base. The solvent employed is a relatively temperature independent red cholesteric mixture consisting of 40 weight % of a ternary mixture of cholesteryl oleyl carbonate, cholesteryl chloride, and cholesteryl nonanoate in weight ratios of 2:1.1:0.9, and 60 weight % of "Nematic Phase V", itself a eutectic mixture of p-methoxyazoxybenzenes which are p' substituted with ethyl and n-butyl groups (E. Merck & Co.). The reactants were separately dissolved in solvent, mixed on a glass slide, covered, thermostated on a small thermoelectric cold stage (Bailey Instrument Co.) and mounted in a Cary 14 spectrophotometer to measure changes in wavelength of minimum transmission.

Table I. Reaction Parameters for Formation and Exchange Reactions of Schiff Bases in a Cholesteric Solvent

Reaction[a]	$(\alpha^o/\bar{n})_{20^oC} \times 10^{-4} cm^{-1} mole^{-1}$	$k_{f_{20^oC}}$ $mole^{-1} min^{-1}$	E* Kcal $mole^{-1}$	$K_{eq_{20^oC}}$[b]
EBA + (-)PEA $\rightleftharpoons$ (-)EBPEA + H_2O	1.9 ± 0.1	0.14 ± 0.01	8.0	8.5
EBA + (-)BPEA $\rightleftharpoons$ (-)EBBPEA + H_2O	2.6 ± 0.1	0.08 ± 0.01	6.1	6.5
(+)EBPEA + (-)PEA $\rightleftharpoons$ (-)EBPEA + (+)PEA	3.0 ± 0.2	0.22 ± 0.01	9.3	1.0
(-)EBBPEA + (+)PEA $\rightleftharpoons$ (+)EBPEA + (-)BPEA	-3.8 ± 0.15	0.19 ± 0.03	11.0	1.1
EBBA + (-)PEA $\rightleftharpoons$ EBPEA + NH_2-  -Bu	1.9 ± 0.1	0.06 ± 0.01	11.0	5.0

(a) EBA, p-ethoxybenzaldehyde; PEA, α-phenethylamine; EBPEA, N-(p-ethoxybenzylidene)-α-phenethylamine; BPEA, p-bromo-α-phenethylamine; EBBPEA, N-(p-ethoxybenzylidene)-p-bromo-α-phenethylamine; EBBA, N-(p-ethoxybenzylidene)-p-n-butylaniline.

(b) Calculated from the relationship $K_{eq} = \left[\frac{\Delta(1/p)_{eq}}{a\alpha - \Delta(1/p)_{eq}}\right]^2$

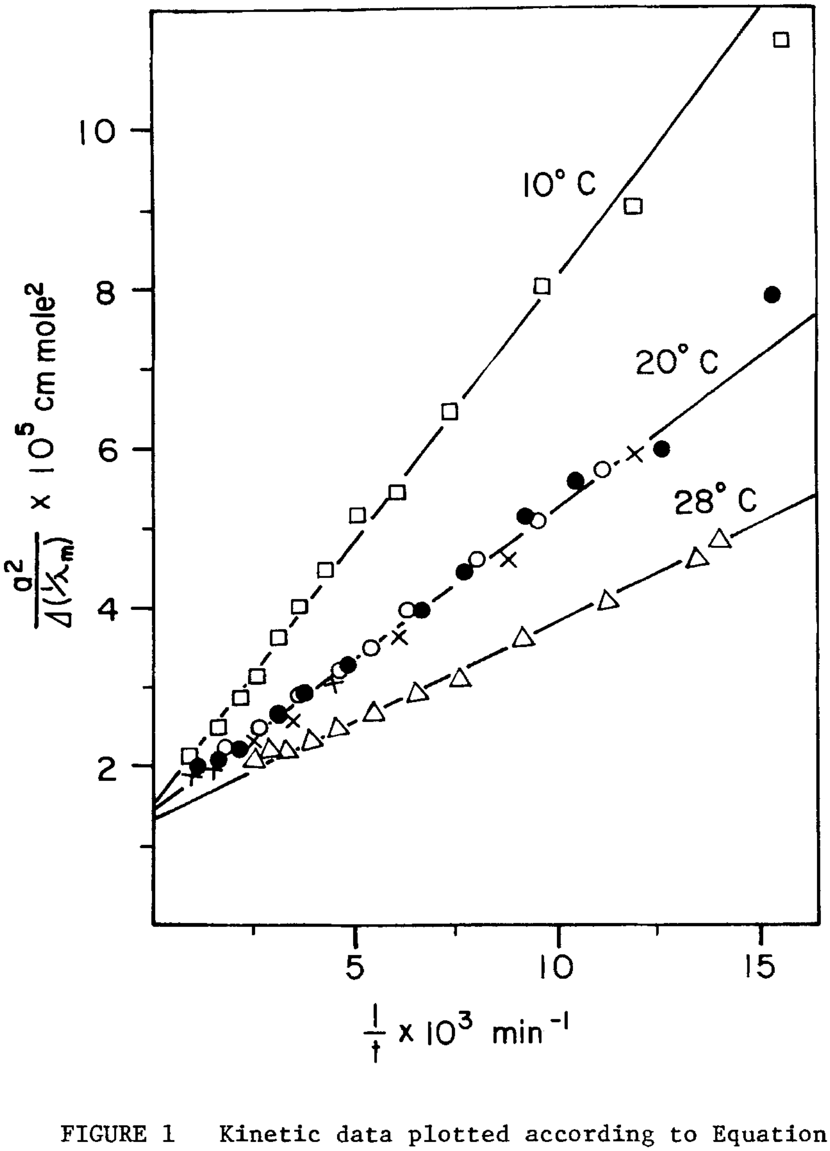

FIGURE 1 Kinetic data plotted according to Equation (1) for the reaction between 0.27M EBA and (-)PEA. At 20°C, the three different symbols indicate three independent determinations of the rate constant.

In addition to the rate constants, the kinetic data allow an estimate of the helical twisting power, α, of the individual species; $\alpha_{EBPEA} \sim 1.5 \times 10^4 cm^{-1} mole^{-1}$ and $\alpha_{EBBPEA} \sim 2.2 \times 10^4 cm^{-1} mole^{-1}$. These values are in good agreement with those determined directly.

With the exception of the reaction between EBBA and PEA, both the amine exchange and Schiff base formation reactions give good second order kinetic plots. In both cases the mechanisms probably involve attack of amine on either protonated aldehyde or Schiff base, and it is only at constant proton concentration that a simple second order rate equation should be expected. The EBBA-PEA amine exchange shows strong negative deviations of $a^2/\Delta(1/p)$ at long reaction times, possibly because of a decrease in pH as the reaction proceeds. Alternatively, since the cholesteric-isotropic transition temperature decreases as the reaction proceeds, the rate may be increasing as a consequence of a premonitory change in the order parameter of the liquid crystal as one approaches the phase transition. Since it is possible to study reaction rates by the present technique through the phase transition, more information should be afforded on this question from the experiments in progress.

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12. K_{eq} may not be exactly 1 due to the optically active solvent environment.[7]