Electric Field Dependence of Thermal and Mass Diffusion of Methyl Red Doped in MBBA Studied by Transient Grating Method

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Received November 7, 1995

Properties of rod-shaped molecules forming liquid crystalline phases are greatly affected by electric field due to relatively large polarizabilities. A lot of theoretical and experimental studies have been carried out to investigate deformations of liquid crystal structures occurring above a critical electric field, so called Freederickzsz effect. Detailed understanding of the electric field effect on the dynamics of liquid crystalline molecules is important in both basic scientific and practical views since liquid crystal devices are operated under electric field. Thermal diffusivity and diffusion coefficient are relevant parameters in studies of liquid crystalline molecules. When two coherent laser pulses are overlapped spatially and temporally, spatial modulation of refractive index formed by the interference of electric field can diffract a probe beam like a transmission grating. As the interference pattern disappears rapidly through various relaxation mechanisms, it is called transient grating (TG). The fringe spacing, \( d \) depends on the wavelength of the excitation laser, \( \lambda \) and the crossing angle of the excitation beams, \( \theta \) by the relation, \( d = (\lambda/2) \sin (\theta/2) \). Since the fringe spacing is in the range of \( 10^6 \) to \( 10^9 \) \( \mu \)m, TG method can be used to study many dynamic phenomena in microscopic scale including the dynamics of liquid crystalline molecules.

We report preliminary results of the electric field effect on the TG decay for methyl red (MR) doped in N-(4-methoxybenzylidene)-4-butylaniline (MBBA). The reagents from Aldrich are used without further purification. MBBA forms nematic phase between 22 and 42 \( ^\circ \)C. The full description of the setup for TG experiment will be given in a forthcoming paper. Briefly, the second harmonic (532 nm) of Q-switched Nd:Yag laser, operated at 0.2-1 Hz, is used as the excitation pulse and the decay of TG is probed by 5 mW cw He-Ne laser. For the studies of liquid crystal molecules which have no absorption in the visible region, dye molecules are usually doped for the application of optical methods. The sample cell made of sandwiched ITO glass has a thickness of 200 \( \mu \)m when a teflon tape is used as a spacer. The optical density of MR is about one when the concentration of the sample is about \( 10^{-4} \) M. Cell temperature is maintained by keeping the cell in a water circulating copper block.

Figure 1 shows the TG decay at 45 \( ^\circ \)C when the electric field is not applied. As the sample temperature is higher than transition temperature (nematic to isotropic) of MBBA, anisotropy of the matrix is not considered here. Biexponential decay of largely different time constants is observed and time constants of fast and slow components are 7.1 \( \mu \)sec and 6.6 msec, respectively. Photophysics and photochemistry of MR, which have been investigated in various media, suggest that main relaxation mechanisms of TG induced by nsec laser pulses are thermal relaxation and mass diffusion of photoactivated MR. Non-radiative decay of MR and intermolecular energy transfer to give local heating along the fringe pattern are very fast compared with the width of the employed laser pulse (\( \sim 10 \) nsec). The fast component of the decay is due to relaxation of temperature gradient of the MBBA matrix. As the time constant for the isomerization of the photoexcited cis-MR into trans form in MBBA is very

![Graph](image-url)
Figure 2. Electric field dependence of the decay time constants. The experimental conditions are the same as in Figure 1 except the electric field. (a) Decay time constants of fast component. Note the time scale. (b) Decay time constants of slow component.

Figure 3. Electric field dependence of (a) thermal diffusivity and (b) diffusion constant of MR. These transport numbers are determined from the decay times of Figure 2.

long compared with mass diffusion, the slow component is attributed to mass diffusion of photoactivated MR.

When the diffusion processes are dominant processes of the relaxation of TG, the decay time constant of TG signal, τ is related to corresponding diffusion constant, D as \( \tau^{-1} = D \lambda_q^2 \). Here, \( \lambda_q \) is the wavevector corresponding to \( 2\pi/d \). The fast component of TG decay is connected with thermal diffusivity, \( D_T \), which is expressed with thermal conductivity (\( \lambda_T \)), density (\( \rho \)) and heat capacity (\( C_v \)). \( D_T = \lambda_T / (\rho C_v) \). The slow component due to mass diffusion is described with diffusion coefficient. Decay time constants from the data of Figure 1 give thermal diffusivity of \( 6.1 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1} \) and diffusion constant of \( 6.8 \times 10^{-7} \text{ cm}^2 \text{ sec}^{-1} \), which agree with the reported values. The reported thermal diffusivity for MBBA\(^9\) is \( 8.4 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1} \) and the diffusion constant of MBBA\(^{10}\) is \( 5.0 \times 10^{-7} \text{ cm}^2 \text{ sec}^{-1} \). The determined physical quantities for MR doped in MBBA and pure MBBA are assumed to be identical above. Of course, above values should be confirmed from the dependence of the decay time on the fringe spacing.

Liquid crystalline molecules are highly susceptible to external field even in the isotropic phase because of short range order.\(^{11}\) Figure 2 shows the electric field dependence of decay time constants and the diffusion constants calculated from the decay time constants are plotted in Figure 3. The electric field is applied in the direction of the excitation pulse, which is perpendicular to the grating wavevector. The other experimental conditions are the same as in Figure 1. Meanwhile thermal diffusion is independent of the electric field, mass diffusion becomes faster under larger electric field. The response to the electric field looks like a step function with a threshold electric field of around \( 5 \times 10^5 \text{ V/m} \). Intermolecular energy transfer attributed to thermal diffusion mainly occurs via phonon-like motions of large amplitudes in condensed phases.\(^{12}\) The low frequency motions do not change much the polarization of the medium so that the fast component due to thermal diffusion is not affected by the external electric field.

The electric field effect on mass diffusion is somewhat surprising. Since the electric field is applied in the direction perpendicular to the grating wavevector, the diffusion across the fringe pattern is expected to be independent of the applied field. Effects of electric or magnetic field on the properties of the liquid crystalline molecules are usually linear to the field strength over the critical field strength.\(^{11,12}\) The effect of the electric field on mass diffusion results from the electric properties of MR and the matrix (MBBA), and relative direction of the electric field and the grating wavevector. The photoexcited cis-MR has relatively large dipole moment and molecular motions of polar molecules - especially rotational diffusion - are greatly affected by the electric field. However, the effect of the electric field perpendicular to the diffusion direction is considered to be limited. The polar matrix molecules also align along the electric field to develop the polarization in the field direction and diffusion of polar molecules is regarded to be more effective in more polar medium. Although motions of polar molecules are activated under the electric field or in largely polarized medium, the electric effects are limited for the diffusion along the direction perpendicular to the anisotropy.

Acknowledgment. This work is supported by Basic Science Research Program of Ministry of Education (BSRI-95-6401), and Korea Science and Engineering Foundation.
A Stereoselective Synthesis of syn-β-Amino Alcohols via Iodocyclization

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Received November 13, 1996

In recent years the stereoselective synthesis of β-amino alcohols is an increasingly important area in organic synthesis. They are indispensable peptide isosteres for the development of HIV protease, renin and ACE inhibitors. Besides their utility as such therapeutic agents, β-amino alcohols have been employed as chiral auxiliaries, and they are also expected to serve as chiral building blocks for the construction of glycosidase inhibitors.

Several approaches to optically active β-amino alcohols have been explored such as the addition reaction of organometallics to α-amino aldehydes, the reduction of α-amino ketones, nitroalcohol reaction, the hydroboration of enamines and the ring opening of epoxy alcohols with amine. Alternatively we sought to exploit a practical asymmetric synthetic route to them, based on the electrophile promoted cyclization of allylic or homoallylic alcohols which comprise a nucleophilic nitrogen tethered through the aliphatic oxygen. Although Cardillo et al. pioneered this strategy, we elected to reinvestigate the cyclization reaction in a more systematic manner to attain a facile procedure to β-amino alcohols with superior stereoreinduction. This paper describes our stereocontrolled pathway to syn-β-amino alcohols via iodocyclization of homoallylic trichloroacetimidates derived from 3-buten-1,2-diols.

Allylic and homoallylic substrates 1–6 were prepared from 1,2-isopropylidenebutane-1,2,4-triol, which was converted into iodide, eliminated and deprotonated in sequence to furnish 3-buten-1,2-diol 1 in 71% overall yield (Scheme 1). Diol 1 reacted with TBDPSCI, pivaloyl chloride and TESCI to produce TBDPS ether 2 (90%), pivalate 3 (57%) and TBS ether 4 (81%), respectively. The hydroxyl group of 4 was protected with ethyl vinyl ether and pivaloyl chloride, and then desilylated to yield ethoxyethyl ether 5 (82%) and pivalate 6 (86%), respectively. While 2-methyl-3-buten-1-ol 7 is commercially available, 2-isopropyl-3-buten-1-ol 8 was obtained from diethyl malonate over 6 steps in 40% overall yield.

After treatment of allylic alcohols 2 and 3 with trichloroacetonitrile in the presence of DBU in acetonitrile at 0 °C, the resulting trichloroacetimidates were cyclized in situ using iodine and potassium carbonate at room temperature. The results are summarized in Table 1. While a 1:1 mixture of oxazolines 9 and dihydro-1,3-oxazines 10 was formed from TBDPS ether 2, only oxazolines 11 could be isolated from pivalate 3. Although stereochemical outcomes were not so excellent, it was noted that the identical aziridine could be generated from trans-9, trans-10 and trans-11 (side infra).

In addition better stereoselectivity was observed from 2 in favor of trans-isomers. Homoallylic alcohols 1, 5–8, containing a chiral substituent at the allylic position, were functionalized into trichloroacetimides, of which in situ iodination was performed with iodine and sodium bicarbonate at 0 °C. The experimental data are shown in Table 2. A relatively low stereoselectivity was resulted from 7 (entry 1). Although satisfactory stereoin-