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Y. K. Yarovoy [a] & V. M. Sava [b]

[a] Department of Chemistry, Temple University, Philadelphia, PA, 19122

[b] Physico-Chemical Institute, National Academy of Sciences, Odessa, 270080, Ukraine

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Spontaneous Chemiluminescence During Oxidation of Cholesteryl Esters in Cholesteric and Isotropic Phases

Y.K. YAROVOY[a*] and V.M. SAVA[b]

[a]*Department of Chemistry, Temple University, Philadelphia, PA 19122 and* [b]*Physico-Chemical Institute, National Academy of Sciences, Odessa, 270080, Ukraine*

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Chemiluminescence during free radical oxidation of cholesteryl esters has been studied in isotropic and cholesteric liquid crystalline phases. A dramatic enhancement of the chemiluminescent intensity was observed in the cholesteric phase. The emitter of chemiluminescence in this reaction is an electron excited ketone that forms during recombination of cholesteryl ester peroxyl radicals. It was shown that an enhancement of the intensity is due to an increase in both quantum yield of the excited state and emission yield of the emitter as the phase order increases. These phenomena are attributed to interplay between the orientational order of the medium and the anisometry of the reacting species. An increase in quantum yield of the excited state of the emitter is explained in terms of the increased rigidity of the transient tetraoxide complex during recombination of peroxyl radicals of cholesteryl esters in an anisotropic environment.

INTRODUCTION

Effects of liquid crystalline solvents on the dynamics and kinetics of a variety of photophysical and chemical processes is an area of continuous interest [1–6]. The ability of mesophases to alter solute reactivity by imparting constraints on reaction transition states due to shape/size considerations has been clearly demonstrated with unimolecular reactions whose product distribution depends on conformational factors: liquid crystals favor reactions whose transition states are most compatible with the ordered solvent matrix [2b,7]. A number of photophysical processes, such as fluorescence emission yield and quenching [4,8], excimer and exciplex formation [4,7,9], were also found to be influenced by liquid crystalline ordering. There have been reported examples of bimolecular reactions

* Correspondence Author.

[10–13], where the change in mutual orientation of reactants caused by the liquid crystalline solvent results in a pronounced change in the reaction rate.

In spite of intensive research in this field, one interesting process, namely, chemiluminescence, has not as yet received appropriate attention. The phenomenon of chemiluminescence involves both chemical and photophysical transformations, and in some cases it offers an advantage in the exploration of the influence of an anisotropic environment on molecular conversions. Furthermore, such a study would directly address the key question of chemiluminescence – the effect of the medium on quantum yield of the emitter excited state.

The use and analysis of liquid crystalline solutions for photochemical and photophysical studies is complicated by such factors as different solubilization sites of solute reactants within the mesophase, and the possibility of a phase separation. One might avoid the problems of uneven distribution of reactants and phase separation by studying reactions occurring between molecules (as well as their excited forms or radicals) of the liquid crystalline solvent itself. If such reactions are chemiluminescent, one can also investigate the emission yield and its quenching in different phases without using an external excitation source.

An example of such a reaction is the free radical oxidation of mesogenic cholesteryl esters. Small amounts of an initiator of free radicals diluted in the media usually do not noticeably perturb the mesophase order. Peroxyl radicals of cholesteryl esters which lead the oxidation chain and produce an emitter of chemiluminescence, electron excited ketones [14], -- have the same size and shape as solvent molecules (with average molecular weight about 500). These factors might facilitate an analytical treatment of the phase-induced changes in the kinetics of such processes.

In previous studies we already reported a sharp increase in chemiluminescence intensity in the liquid crystalline phase [15]. There was also observed an increase in the recombination rate of free radicals and a decrease in the efficiency of radical initiation, which correlated with the orientational order of the solvent [16]. In this paper we present a detailed study of the influence of the cholesteric phase on quantum characteristics of chemiluminescence of cholesteryl esters during their oxidation.

EXPERIMENTAL SECTION

Materials

Commercially available (from Aldrich) cholesteryl esters – cholesteryl pelargonate (CP), cholesteryl valerate (CV), cholesteryl myristate (CM), and cholesteryl

oleate (CO) were recrystallized from diethyl ether-ethanol solutions (2:5) two times prior to use. The nematic liquid crystal n-pentylcyanobiphenyl (5CB) (EM Chemical, Co.) was used without purification. This compound was employed as a solvent for diluting the cholesteric compositions. A composition of CP:CV:CM (45:45:10), exhibiting a cholesteric mesophase on cooling in the temperature range from 87° C to room temperature, was employed for the kinetic studies. At 60°C (the temperature at which the chemiluminescence was recorded) the wavelength of maximum light reflection (λ_{max}) for this composition is 395nm; on cooling, λ_{max} increases to 470nm as the temperature decreases to 30°C. When this composition is diluted with 5CB in a ratio of 1:1, the resulting mixture has a clearing point at 52°C: the wavelength of maximum light reflection increases from 610nm at 50°C to 640nm at 35°C. A free radical initiator - lauroyl peroxide (LP) (Aldrich) was recrystallized from benzene and then ethanol. A chemiluminescent sensitizer -- tristhenoyltrifluoroacetonate europium 1,10-phenanthroline $(TTA)_3Eu(Phen)$ was synthesized according to the method described in reference [17]. Rhodamine B was purchased from Aldrich and used as received.

Methods and Instrumentation

The temperatures of the phase transitions of individual liquid crystals, their mixtures and compositions doped with chlorobenzene were determined from optical observations using a Nikon polarizing microscope equipped with a Mettler FP 82 hot stage. These measurements were supported by differential scanning calorimetry using a TA Instruments Model DSC 2920.

The quantum yield of the emission of fluorescence of the sensitizer $(TTA)_3Eu(Phen)$ η_s was determined in liquid crystalline solvents using a luminometer SDL-1 (LOMO, St.Petersburg). Cuvettes of varying length light paths were employed to exclude effects of the light scattering in cholesteric and nematic phases. Rhodamine B was used as a fluorescent standard whose quantum emission yield (0.69) is practically invariant to solvents. Samples were excited at 365 and 510 nm.

Chemiluminescence intensity was recorded on the chemiluminometer based on the single photon counting technology. The instrument was designed and developed in the Physico-Chemical Institute, Academy of Science of Ukraine (Odessa) [18]. In this design (Fig. 1), the light collection efficiency is maximized by placing a sample very close to the cathode of the thermally insulated photomultiplier. A spontaneous photoemission of the detector is reduced (to less than 100 counts per second in the dark) by cooling to −20°C. The sample compartment was thermostated using Peltier elements to an accuracy of ± 0.5 °C. The photon counting was integrated at intervals of one second. The instrument was

calibrated to read absolute values of the emitted light by using a radioactive standard solution consisting of tritiated hexadecane in toluene with diphenyloxazole and p-phenyl-bis(5phenyloxazole) as scintillators, according to the method described by Hastings and Weber [19]. The absolute precision of the measurements was ± 5×10^2 Photon/s·cm^2. A reaction vessel was a custom made vial in the shape of an overturned mushroom with a flat bottom of 12.6 cm^2 and a 14/20 $ neck. The vial was made to fit precisely into the sample compartment of the chemiluminometer.

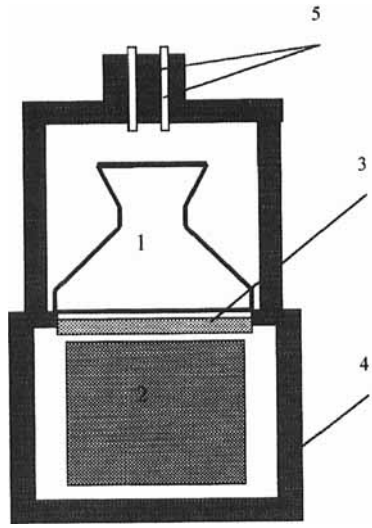

FIGURE 1 Schematic drawing of photon counter and vial housing for measuring superweak luminescence. 1-vial; 2-photon counter; 3- transparent thermal insulator; 4-housing with provision for temperature control; 5-cover with inlet and outlet

The high sensitivity of the instrument allowed recording chemiluminescence of very small amounts of cholesteryl esters – usually 50–200 mg. In order to ensure that small amounts of viscous samples form a uniform layer on the bottom of the vial, the samples were introduced as solutions in diethyl ether. Then the ether was quickly evaporated by vacuuming the vial in situ using the outlet in the cover of the sample compartment.

The steady-state chemiluminescence of cholesteric compositions was recorded as a function of time at different temperatures. In the non-steady-state experiments the vial containing 50–80 mg of the cholesteric composition was evacuated, purged with argon and reevacuated. This cycle was repeated three times. After equilibrating to a preset temperature the background intensity of the chemi-

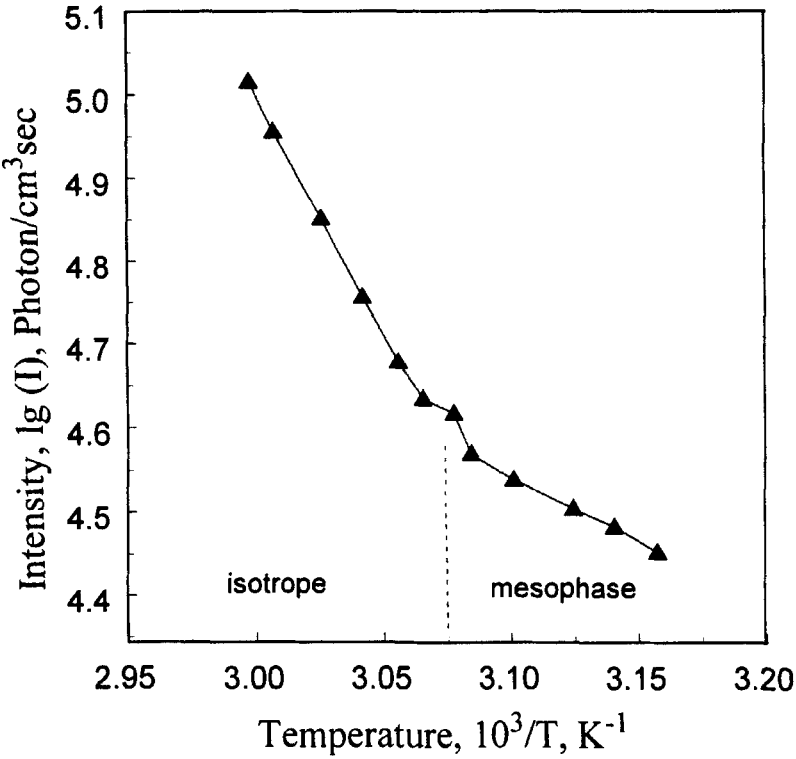

FIGURE 2 Temperature dependence of the intensity of chemiluminescence of a mixture of CO:CP (90:10). Dashed line indicates the temperature of the phase transition

luminescence was recorded. Then, oxygen was let into the reaction vessel and the rise in intensity was monitored as a function of time.

In a series of experiments with a stepwise increase of thickness of the sample layer (the mass of the sample in the vial), it was shown that the diffusion of oxygen into a thin (< 100 μm) layer of cholesteric compositions is not a limiting factor in the reaction of conversion of alkyl radicals $\mathbf{R}^{\bullet}$ to peroxyl radicals $\mathbf{ROO}^{\bullet}$.

RESULTS AND DISCUSSION

The phase transition between cholesteric and isotropic phases of a cholesteric liquid crystal can be induced by (i) increasing the temperature, (ii) changing the composition of the liquid crystalline system, or (iii) introducing a small amount of organic solvent such as chlorobenzene. Chlorobenzene is a stable solvent

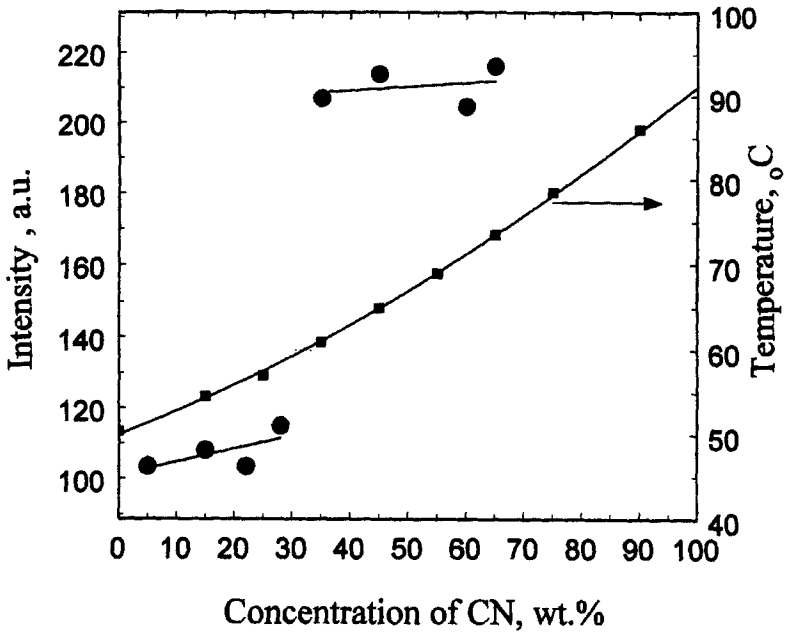

FIGURE 3 Dependence of the chemiluminescence intensity (•) at 60°C and the temperature of cholesteric-isotropic transition on the composition of the binary mixture CO:CP

commonly used as an inert reaction medium for kinetic studies of liquid-phase free radical oxidation of hydrocarbons and other organic compounds [22, 24]. Therefore, the addition of chlorobenzene, apart from a slight effect of dilution, does not affect the kinetics of reactions (I), (II) and (VI) [20].

As illustrated in Fig.2 a strong temperature dependence of chemiluminescence may mask the effect of the phase when the phase transition is induced by the temperature change. Yet the intensity in the mesophase appears to be higher than the values of **I** obtained by an extrapolation from the isotropic phase, and the activation energy (as evidenced by the slope) is quite different. The induction of the phase transition at a constant temperature by methods (ii) and (iii) provides more direct evidence of the phase effect. As shown in Fig.3 (solid circles), the intensity of chemiluminescence measured at 60°C increases approximately two times when a slight change in the composition (an increase in CP/CO ratio) induces a transition to the cholesteric from the isotropic phase. Further increase in the ratio of CP/CO does not affect the intensity, which confirms that the observed sharp increase in **I** is due mainly to the phase transition. When small amounts of chlorobenzene were added to another cholesteric composition

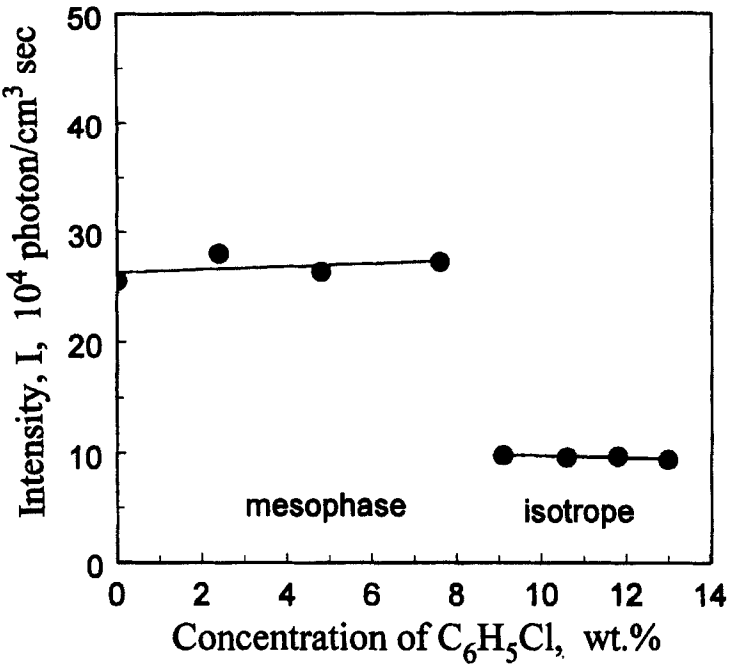

FIGURE 4 Chemiluminescence intensity I of the oxidized cholesteric mixture – CP:CV:CM (45:45:10) as a function of concentration of added chlorobenzene. Temperature 60 °C

CP:CV:CM at 60 °C, the intensity of chemiluminescence was not affected until the concentration of chlorobenzene reached approximately 8.0 wt.%. At concentrations above this threshold value the intensity drops more than two times as the composition becomes isotropic (Fig.4). Thus these data unambiguously indicate a drastic effect of the cholesteric phase on the intensity of chemiluminescence.

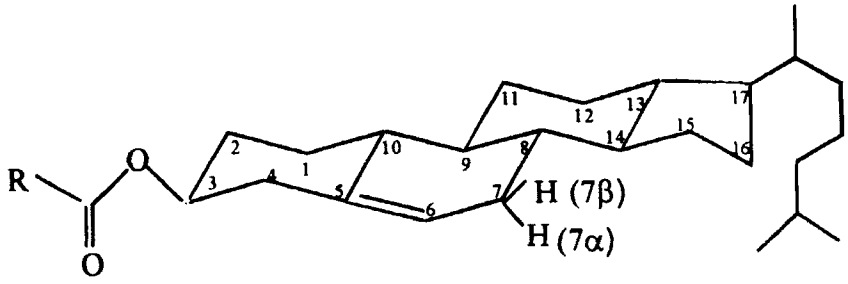

FIGURE 5 The structure of a cholesteryl ester molecule

When discussing emission (and/or absorption) of light at wavelengths within the region of selective (Bragg's) reflection in cholesteric liquid crystals, one may also consider the possible effects of interaction of light with the periodic cholesteric structure (pitch) [21]. In our experiments incremental changes in the composition or progressive addition of chlorobenzene caused apparent shortening of the pitch of cholesteric mixtures (a blue shift in color was observed); however, no essential changes in the intensity of emitted light was recorded within the cholesteric phase (Figures 3 and 4). Furthermore, no principal difference in chemiluminescence behavior was observed through the phase transition in two compositions with different pitches: CP:CV:CM with $\lambda_{max} = 395$nm and CP:CV:CM/ 5CB (1:1) with $\lambda_{max} = 610$nm. Therefore, one may reasonably conclude that the main factor affecting the intensity of chemiluminescence is the molecular orientational ordering rather than the supramolecular spiral structure of the cholesteric phase. In order to explain this phenomenon a mechanism of the chemiluminescent reaction should be examined.

Oxidation of cholesterol and its fatty acid esters by molecular oxygen may lead to several dozens of oxidation products [22]. However, when cholesteryl esters are autoxidized in a melt or a solution of aprotic solvents (such as benzene, chlorobenzene, etc.) at moderate temperatures (60 – 120 °C), the main oxidizing site is the 7th carbon atom in the steroidal fragment (Fig.5) and the oxidation process yields epimeric 7α- and 7β- products: 3β-alkanoyloxy-cholest-5-ene-7-hydroperoxide,3β-alkanoyloxy-cholest -5-ene-7-ol, and 3β-alkanoyl-oxycholest-5-ene-7-one [14,23]. Under these conditions the reaction follows a well known scheme for free radical chain oxidation of hydrocarbons [20] and can be described in early stages of oxidation by a sequence of three elementary reactions: initiation (I), chain propagation (II) and chain termination (VI) (Scheme 1):

$$\text{Initiator} \xrightarrow[O_2, RH]{k_i} ROO^{\bullet} \qquad \text{(I)}$$

$$ROO^{\bullet} + RH \xrightarrow[+O_2]{k_2} ROOH + ROO^{\bullet} \qquad \text{(II)}$$

$$ROO^{\bullet} + ROO^{\bullet} \xrightarrow{k_6} ROH + O_2 + \eta^{*}R{=}O + (1-\eta^{*})R{=}O \qquad \text{(VI)}$$

Chemiluminescence is excited in the process of peroxyl radical disproportionation (reaction VI), which produces 3β-alkanoyloxy-cholest-5-ene-7-ol, oxygen and 3β-alkanoyloxycholest-5-ene-7-one (R=O) in the triplet state [24–27]. Intensity of chemiluminescence **I** (in photon/s) is proportional to the rate of reaction (VI), and in a steady-state condition (when the rate of radical initiation equals the rate of radical termination) is given by the following equation:

$$I = 0.5\eta^*\eta\, k_6[ROO^\bullet]^2 = 0.5\eta^*\eta_e W_i \quad (1)$$

where η^* is the quantum yield of excited states of ketone R=O*, η_e is the emission yield of excited ketone, k_6 is the rate constant of the peroxyl radical disproportionation, [ROO$^\bullet$] is the steady-state concentration of peroxyl radicals, W_i is the rate of free radical initiation. The rate of free radical initiation $W_i = k_i$ [In], where k_i is the constant of initiation, and [In] is the concentration of the initiator.

According to equation (1), changes in the intensity of chemiluminescence may be caused by changes in three variables: the rate of initiation, emission yield of excited ketones, and excitation yield of excited states. Previously [15b,16] we reported that the rate of radical initiation decreases by 10–20% (depending on the initiator and the medium) in the liquid crystalline phase with respect to the isotropic phase. For example, the initiation rate due to thermal decomposition of lauroyl peroxide (the initiator used in this study) decreases from 4.9×10^{-8} mol/l·s in the cholesteric phase to 4.2×10^{-8} mol/l·s in the isotropic phase of the mixture CP:CV:CM (45:45:10) (concentration of LP = 0.9×10^{-2} mole/l, temperature 60°C). Thus the reason for the more than 100% increase in the intensity of chemiluminescence in the mesophase should be an increase of quantum characteristics of this process; namely, excitation and emission yields of the emitter.

In determining these parameters we followed a method described in detail by Belyakov et.al.[19b,27] for the liquid phase oxidation of organic substances. In this method, an effective sensitizer (activator) S of luminescence is added into the system. The luminescence of the sensitizer is excited by the energy transfer from the primary emitter (excited ketone) and the same process determines the quenching of ketones. If the quantum emission yield η_s of the sensitizer is known, the concentration dependence of chemiluminescence on the sensitizer [S] allows the determination of the quantum emission yield η_e of the primary emitter according to the following equation:

$$\frac{1}{I/I_0 - 1} = \frac{1}{\eta_s/\eta_e - 1} + \frac{1}{\eta_s/\eta_e - 1} \times \frac{1}{\tau \cdot K_{se}} \times \frac{1}{[S]} \quad (2)$$

where I_0 and I – are the initial and the current intensities of the chemiluminescence; η_s and η_e – are the quantum yields of sensitizer radiation and emission of the chemiluminescence emitter respectively; [S]- is the concentration of the sensitizer; τ – is the life time of the excited state of the emitter; K_{se} – is the rate constant of the energy transfer from the emitter to the sensitizer. The chemical excitation yield η^* can be then calculated from equation (1) when the initiation rate W_i and the emission yield η_e are known.

Fig.6 gives two plots (for the cholesteric and isotropic phases) of the intensity of chemiluminescence as a function of concentration of the sensitizer in coordinates of equation (2). One can see a distinct difference in the slope and the inter-

cept of these plots, indicating changes in all quantum parameters as the system undergoes a transition from the cholesteric to isotropic phase. Analysis of the data according to equation (2) yields only the ratio of η_s to η_e. In order to determine η_e, the sensitizer emission yield η_s was determined independently in both phases using a luminometer SDL-1.

The values of the quantum parameters for two cholesteric systems -- a mixture CP:CV:CM (45:45:10) and the same mixture diluted with a nematic liquid crystal 5CB, are given in Table I. 5CB is a chemically stable liquid crystal which is not readily oxidized under conditions of cholesteryl ester oxidation and, consequently, its introduction into the CP:CV:CM mixture does not affect the kinetics of reactions in Scheme I.

TABLE I Qauntum parameters of the chemiluminescence of cholesteric compositions during their oxidation. CP:CV:CM, T=60°C; (CP:CV:CM):5CB, T=50°C

Composition	*Quantum yield*							
	$10^2\,\eta_s$		$10^5\,\eta_e$		$10^3\,\eta^*$		$\tau K_{se}\times 10^{-5}$	
	mes	*is*	*mes*	*is*	*mes*	*is*	*mes*	*is*
CP:CV:CM (45:45:10)	4.30	2.05	1.05	0.42	2.10	1.50	6.30	4.20
(CP:CV:CM):5CB (50:50)	6.35	2.60	0.67	0.24	2.00	1.60	–	–

Table I shows that all quantum parameters of the systems change through the phase transition. It should be noted here that the nature of quantum emission yield and quantum chemical excitation yield is quite different; the former reflects photophysical processes of radiationless decay and energy transfer, the latter, formation of the electronically excited state of a molecule in the course of a chemical reaction, and therefore, these parameters should be discussed separately.

An increase in the quantum emission yield of a chemiluminescent emitter η_e (and a sensitizer η_s) is consistent with the known fact of the growth of the emission yield of luminescent dopants in both thermotropic [28, 29] and lyotropic [30] liquid crystalline phases. For example, a sharp increase in luminescence intensities was observed upon transition from the isotropic to smectic phase of dodecylcyanobiphenyl [29a]. An increase in fluorescence intensities in the cholesteric phase is reported for a system comprised of cholesteryl nonanoate and 0.2 % pyrene [29b]. In another study, the emission quantum yield of a thiacyanine dye was observed to increase twice in a lyotropic liquid crystal with respect to a micellar solution. Parallel with the augmentation of the quantum yield is the increase in the lifetime of the excited state [30]. Since typical lifetimes of the excited state of emitting molecules (of order of 10^{-9}s) are long enough to allow

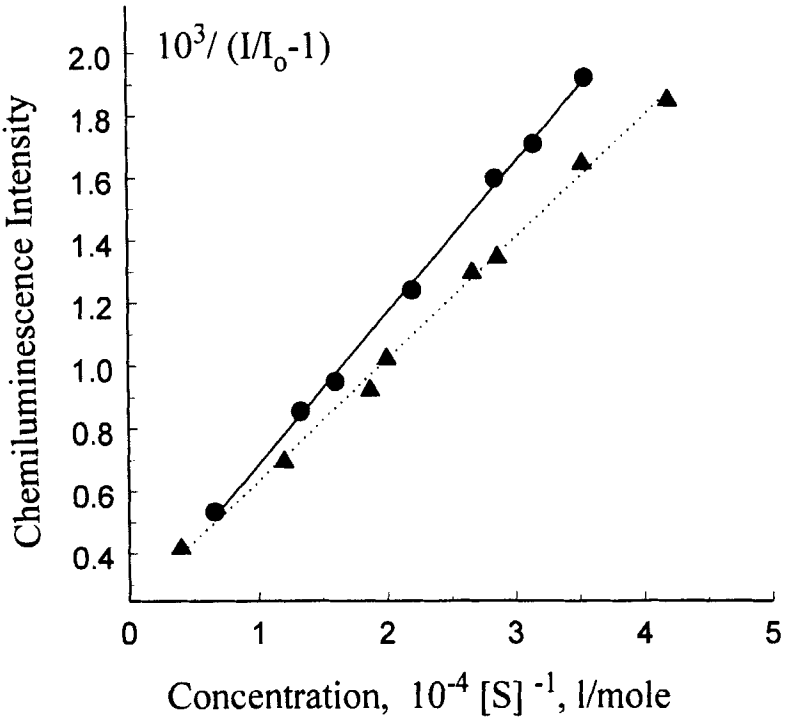

FIGURE 6 Chemiluminescence intensity as a function of concentration of the sensitizer $(TTA)_3$ Eu(Phen) in the mixture – CP:CV:CM (45:45:10); • – mesophase, △ – isotropic phase. Temperature – 60°C

interaction with surrounding molecules, the inhibition of radiationless decay and increased quantum yield in more ordered media has been rationalized in terms of rigidization of the emitter by the local environment encountered in liquid crystals.

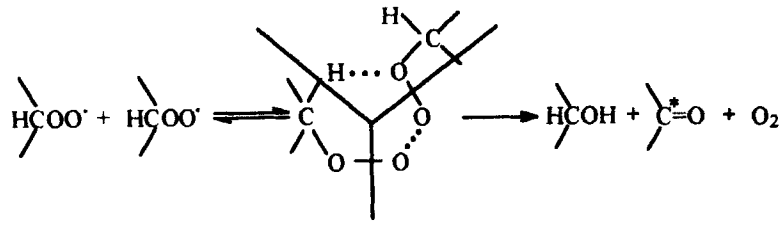

FIGURE 7 The structure of the transient tetraoxide complex formed during the disproportionation of secondary peroxyl radicals according to Russel mechanism

An increase in the chemical excitation yield in the liquid crystalline media has not been previously reported. We propose the following rationalization of this phenomenon. Assume a Russel mechanism [31] for recombination of secondary peroxyl radicals (reaction VI). According to this mechanism the recombination proceeds through the concerted breakdown of the transient six-membered tetraoxide (Fig. 7) complex resulting in the formation of the ultimate products: alcohol, oxygen and ketone. The chemiluminescence emitter of this reaction is a ketone in a triplet excited state. The excitation yield of ketone in this case is considered to correlate with the rigidity of the transitional tetraoxide complex [24,27]. As was discussed earlier in the text, the reactive center of an oxidized cholesteryl ester (CE) is the carbon atom in the 7^{th} position in the steroid fragment. According to X-ray spectroscopic data [32] a molecule of CE has a shape of a slightly flattened rod with the ratio of diameter to length about 1:3. The active center, 7^{th} carbon atom, is located approximately in the middle of the rod. Space modeling of 7-peroxyl radicals of CE shows that the proton and two oxygens of the peroxyl group H-C-O-O tend to arrange in a plane perpendicular to the long axis of a CE molecule. Therefore, when two coupling radicals are oriented in a parallel fashion, the transient tetraoxide complex acquires a flat configuration that increases its rigidity due to $\pi - \pi$ conjugation in the tetraoxide ring plane (Fig.8). Taking into consideration that the mesophase favors parallel orientation of rod-like CE molecules, it is reasonable to suggest that the number of more rigid tetraoxide transient complexes increases in the cholesteric phase, thus increasing the excitation yield of the product. The proposed explanation is in agreement with the well recognized notion that the individual encounters between reagents and the separation of products from the transition state for a reaction are intrinsically anisotropic because certain angles of approach and of separation between reactants and products are preferred, as are certain planes of rotation of the reagent and product molecules.

CONCLUSIONS

Spontaneous and activated chemiluminescence during free radical oxidation of cholesteryl esters has been studied though the phase transition from the cholesteric to isotropic phase. A dramatic increase in the intensity was observed in the cholesteric phase. Analysis of the kinetics of the oxidation showed that an increase in chemiluminescence intensity is due to an increase in chemical excitation yield and emission yield of the emitter (electronically excited ketone). The effect is ascribed to the ability of the ordered solvent to discriminate between

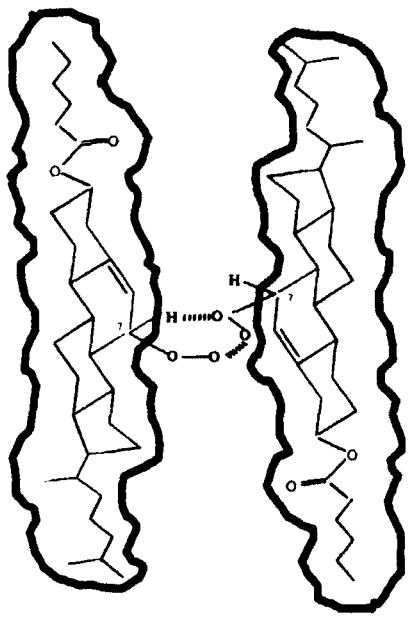

FIGURE 8 Schematic representation of coupling peroxyl radicals of cholesteryl esters in the cholesteric phase

parallel and perpendicular transition states on the basis of their size-shape compatibility with the ordered solvent matrix.

References

1. R.G. Weiss, In *Photochemistry in Organized and Constraint Media*; V. Ramamurthy, Ed.; VCH Publishers, Inc.: New-York, (1991); Chapter 14.
2. (a) W.J. Leigh, in *Liquid Crystals – Applications and Uses*; B. Bahadur, Ed.; World Interscience: Bangalore, (1990); Vol. II, Chapter 27; (b) W.J. Leigh and D.S. Mitchell, *J. Am. Chem. Soc.*, **114**, 5005 (1992).
3. V.A. Batyuk, T.I. Shabatina, T.N. Boronina, and G.B. Sergeev, *Kinetics of Chemical Reactions in Liquid Crystals*, Ser. *Kinetika i Kataliz*, VINITI: Moscow, (1990).
4. T. Wolff, *Adv. Colloid Interface Sci.*, **59**, 31 (1995).
5. (a) B. Samori and L. Fiocco, *J. Am. Chem. Soc.*, **104**, 2634 (1982);
   (b) B. Samori, P.D. Maria, P. Mariani, F. Rustichelli and P. Zani, *Tetrahedron*, **43**, 1409 (1987).
6. (a) Y.K. Yarovoy and M. M. Labes, *Mol. Cryst. Liq. Cryst.*, **292**, 163 (1997);
   (b) Y. Yarovoy, X. Luo, A. Nunez, and M. M. Labes, *Mol. Cryst. Liq. Cryst.*, **289**, 1 (1996).
7. (a) R.G. Weiss, *Tetrahedron*, **44**, 3413 (1988);
   (b) J. Naciri, G.P. Spada, G. Gottarelli and R.G. Weiss, *J. Am. Chem. Soc.*, **109**, 4352 (1987).
8. (a) V.C. Anderson, B.B. Craig, and R.G. Weiss, *J. Phys. Chem.*, **86**, 4642 (1982);
   (b) V.C. Anderson, B.B. Craig and R.G. Weiss, *Mol. Cryst. Liq. Cryst.*, **97**, 351 (1983).
9. M.F. Sonnenschein and R.G. Weiss, In *Photochemistry on Solid Surfaces*; M. Ando and T. Matsuura, Eds.; Elsvier: Amsterdam, (1989), p 526.

10. (a) G.B. Sergeev, V.A. Batyuk and T.I. Shabatina, *Kinet. Katal.*, **24**, 538 (1983);
(b) V.A. Batyuk, T.I. Shabatina and G.B. Sergeev, *Mol. Cryst Liq. Cryst.*, **166**, 105 (1989);
(c) V.A. Batyuk, T.N. Boronina, G.E. Chudinov and G.B. Sergeev, *Liq. Cryst.*, **4**, 181 (1989).
11. (a) P.D Maria, P. Mariani, F. Rustichelli and B. Samori, *Mol. Cryst. Liq. Cryst.*, **116**, 115 (1984);
(b) P.D. Maria, A. Lodi, B. Samori, F. Rustichelli and G. Torquati, *J. Am. Chem. Soc.*, **105**, 653 (1983);
(c) B. Samori and L. Fiocco, *J. Am. Chem. Soc.*, **104**, 2632 (1982);
(d) S. Melone, V. Mosini, R. Nicoletti, B. Samori and G. Torquati, *Mol. Cryst Liq. Cryst.*, **98**, 399 (1983);
(e) B. Samori, P.D. Maria, P. Mariani, F. Rustichelli and P. Zani, *Tetrahedron*, **43**, 1409 (1987);
(f) P.D. Maria, B. Samori, A. Tampieri and P. Zani, *Bull. Chem. Soc. Jpn.*, **61**, 1772 (1988);
(g) G. Albertini, P. Mariani, F. Rustichelli and B. Samori, *Mol. Cryst. Liq. Cryst.*, **163**, 163 (1988).
12. T. Yamaguchi, T. Yoshida, T. Nagamatsu, T. Kunieda, T. Honda and M. Hirobe, *Tetrahedron Lett.*, **32**, 1729 (1991).
13. (a) W.J. Leigh, *Can. J. Chem.*, **63**, 2736 (1985);
(b) W.J. Leigh and D.S. Mitchell, *J. Am. Chem. Soc.*, **110**, 1311 (1988).
14. (a) R.L. Vardanyan, G.E. Dingchan, B.B. Khanukaev and A.S. Vartanyan, *Kinet. Kataliz*, 19, 72 (1978);
(b) R.L. Vardanyan. O.A. Dzhanghiryan and G.V. Parsyan, *Armyanskiy Khim. Zhurnal*, **36**, 735 (1983).
15. (a) Y.K. Yarovoy and V.M. Sava, In *Third All Union Meeting on Chemiluminescence, Abstracts*; Riga, Lithuania, (1990), p 4;
(b) Y.K. Yarovoy, *Ph. D. Thesis*, Moscow State University Moscow, (1991);
(c) Y.K. Yarovoy, T.I. Shabatina, V.A. Batyuk and G.B. Sergeev, In *Summer European Liquid Crystal Conference, Abstracts*; Vilnius, (1991), G 42.
16. (a) Y.K. Yarovoy, T.I. Shabatina, V.A. Batyuk and G.B.Sergeev, *Mol. Cryst. Liq. Cryst.*, **191**, 283 (1990);
(b) T.I. Shabatina, Y.K. Yarovoy, V.A. Batyuk and G.B. Sergeev, *J. Mater. Chem.*, **4(5)**, 761 (1994).
17. H. Bauer, I. Blanc and D. Ross, *J. Am. Chem. Soc.*, **86**, 5131 (1964).
18. V.M. Sava and Y.L. Zherbin, *Patent USSR No.851114*, (1981); V.M Sava and Y.L. Zherbin, *Patent USSR* No. *1042448*, (1983).
19. (a) J.W. Hastings and G. Weber, *J. Optical Soc. Am.*, **53**, 1410 (1963);
(b) V.A. Belyakov, R.F. Vasilyev and G.F. Fedorova, *Khimia Vysokikh Energiy*, **12**, 247 (1978).
20. (a) *Chain Reactions in Liquid-Phase Hydrocarbon Oxidation*; N.M. Emanuel, E.T Denisov and Z.K. Maizus, Nauka: Moscow, (1965);
(b) *Oxidation of Ethylbenzene (Model Reaction)*; N.M. Emanuel and D. Gal, Nauka: Moscow, (1984).
21. (a) I.P.Il'chishin, E.A. Tikhonov, V.F. Tishchenko, and M.T.Shpak, *Pis'ma Zh. Eksp. Teor. Fiz.*, **32(1)**, 27 (1980);
(b) I.P.Il'chishin, A.G.Kleopov, E.A.Tikhonov, and M.T.Shpak, Izv.Akd. Nauk SSSR, Ser.Fiz., 45(8), 1376 (1981);
(c) *Optics of Cholesteric Liquid Crystals*, V.A.Belyakov and A.S.Sonin, Nauka: Moskow, p.206, (1982).
22. *Cholesterol Autoxidation*; L.L. Smith, Plenum Press: NY, London, (1985).
23. Y.K. Yarovoy, V.A Batyuk, A.I Galatina and M.Y. Piotrovskaya, *Zhurnal Obschey Khimii (Russian Journal of General Chemistry)*, **59**, 1973 (1989).
24. R.F. Vasiliev, *Optica and Spectrosk.*, **18**, 236 (1965).
25. *Experimental Methods of Chemical Kinetics*; N.M. Emanuel and G.B. Sergeev, Eds.; Vysshaya shkola: Moscow, (1980).
26. *Chemiluminescent Methods of Slow Chemical Processes Study*; V.H. Shlapintokh, O.N. Karpukhin and L.M. Postnikov, Nauka: Moscow, (1966).
27. (a) V.A Belyakov, R.F. Vasilyev and G.F. Fedorova, *Sov. Phys. Optics and Spectroscopy*. **24**, 419 (1968);
(b) V.A. Belyakov, R.F. Vasilyev and G.F. Fedorova, *Izvestia Acad.Nauk SSSR Ser Fizika.*, **32**,

1325 (1968);
(c) V.A Belyakov, R.F. Vasilyev and G.F. Fedorova, *Izvestia Acad.Nauk SSSR Ser. Fizika*. **42**, 613 (1978).
28. (a) X. Tomkiewicz and A. Weinreb, *Chem. Phys. Lett.*, **3**, 229 (1969);
(b) C. Baur, A. Stieb and G. Mier, *J. Appl. Phys.*, **44**, 1905 (1973);
(c) A.A. Minko and V.S. Rachkevich, *Optika i Spektroskopia*. **64**, 673 (1988).
29. (a) R. Subramanian and L.K. Patterson, *Chem. Phys. Lett.*, **93**, 578 (1982);
(b) T.V. Novak, R.A. Mackay and E.J. Poziomek, *Mol. Cryst. Liq. Cryst.*, **20**, 213 (1973).
30. V. Ramesh, S. Mathew, and M.M Labes, *Mol. Cryst. Liq. Cryst. Letters*, **6(2)**, 35 (1988).
31. G.A. Russel, *J. Am. Chem.* **Soc.**, **79**, 3871 (1957).
32. *Struktura Zhidkikh Kristallov (Structure of Liquid Crystals)*; Z.Y. Gotra, N.V. Kulik and Z.M. Mikityuk, Naukova dumka: Kiev, (1989).