Chemiluminescence in Oriented Systems. Chemiluminescence of Lucigenin in Model-membrane Structures

By JOHN NIKOKAVOURAS,* GEORGE VASSILOPOULOS, and CONSTANTINOS M. PALEOS
(*Department of Chemistry, Nuclear Research Centre 'Demokritos', Aghia Paraskevi, Attikis, Greece*)

Summary The chemiluminescence of lucigenin in didodecyldimethylammonium bilayer aggregates is at least 12 times more efficient than in water, and an emission due to *N*-methylacridone appears in the chemiluminescence spectrum.

IN an earlier report[1] on the chemiluminescence of 10,10′-dimethyl-9,9′-biacridinium dinitrate (lucigenin) in hexadecyltrimethylammonium bromide (CTAB) micellar solutions a significant enhancement of the quantum efficiency was obtained. In addition, the detection of the primary excited product of the light reaction was accomplished because of its appropriate solubilization[2] in the Stern region of the micelles, resulting in considerable hindrance of energy transfer. In extending our work we have undertaken the investigation of the same light reaction in bilayer aggregates,[3] *i.e.* in structures which exhibit higher organization, stability, and rigidity than those of micelles.[4]

It has been discovered that among other amphiphiles a series of dialkyldimethylammonium salts[5] aggregate extensively in water to form bilayer structures (lamellar or vesicles) which resemble biological membranes and may be employed as models[3a] of them.

In this work, lamellar bilayer aggregates were formed by the dissolution of didodecyldimethylammonium bromide (DDAB)[6] in water. The chemiluminescence intensity *vs.* time (*I vs. t*) diagrams were obtained as described earlier.[7] The *I vs. t* diagrams were recorded on the addition of sodium hydroxide (1 ml, 5 M) and hydrogen peroxide (1 ml, 10%) to lucigenin (20 ml, 10^{-4} M) in the presence of DDAB of the appropriate concentration. Each of these experiments was followed by a blank with lucigenin dissolved in water.

The ratio of quantum yields (based on lucigenin employed) in oriented and homogeneous media, *i.e.* $Q_{\text{or}}/Q_{\text{hom}}$, corrected for self-absorption at λ 500 nm, was plotted *vs.* concentration of DDAB in the region 0·1—2 × 10^{-2} M. It should be noted that at high DDAB concentrations (> 1·5 × 10^{-2} M), foaming of the reaction mixture increased its opacity and, therefore, higher correction factors were required, resulting in appreciable scattering of the points on the plot. A least-squares fit of the plot based on 46 experimental points gives rise to equation (1); where $\alpha = 1{\cdot}519$ and $b = 1{\cdot}355$. The

$$Q_{\text{or}}/Q_{\text{hom}} = \alpha \times \exp\,(b[\text{DDAB}]) \qquad (1)$$

increase of quantum yield with concentration of DDAB is considerable (over 12-fold in 1·5 × 10^{-2} M and over 20-fold in 2 × 10^{-2} M DDAB) with no rate increase as is the case with micellar acridan chemiluminescence.[8] It should be noted that in CTAB micellar solution this increase was never greater than 4-fold. The increase in quantum yields with concentration of DDAB may, in the first place, be explained by a modification of the bilayer structure.

The higher organization and stability of bilayer structures as compared with micelles[4] was also reflected in the chemiluminescence spectrum of the reaction. Indeed, the emission of the primary excited product [*N*-methylacridone (NMA)], notorious for eluding detection in homogeneous experiments due to energy transfer (this has been recently attributed to a form of self-absorption[9]) and observed, as already mentioned, in CTAB micellar solutions,[1] is further intensified in bilayer structures as shown in the chemiluminescence spectrum (shoulder in the Figure).

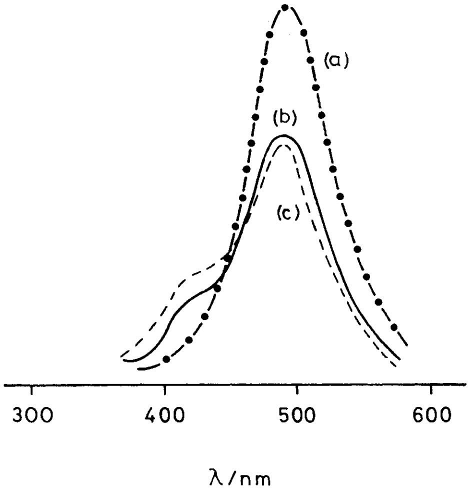

FIGURE. Chemiluminescence spectra in (*a*) aqueous, (*b*) aqueous CTAB (0·1 M), and (*c*) aqueous DDAB (0·01 M) solutions.

The site of solubilization of the excited product has been determined by considering its spectra in solvents of varying polarity. It is located at, or near, the surface of the bilayer. The spectroscopic technique was similar to the one employed in micellar systems.[1,10]

The analogous molecular structures of CTAB and DDAB as well as the qualitative resemblance of their aqueous aggregates, coupled with the observed similarities in their respective absorption and fluorescence spectra favour an analogous mechanism to that proposed for micellar solutions.[1] In the DDAB model-membrane system, however, the decomposition of the intermediate dioxetan[11] at, or near, the surface of the bilayer gives rise to excited NMA, with an excitation efficiency higher than that in homogeneous or even micellar media. In any case, the increased chemiluminescence quantum yields in these oriented aggregates should not be attributed to higher fluorescence efficiencies. Such an effect was not apparent from our fluorescence spectra and previous results.[12]

In conclusion, the rigid and stable bilayer structures of DDAB in water intensify the phenomena observed in micellar systems, further enhancing the quantum efficiency and contributing to the detection of the emission of the primary excited product.

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