CHEMILUMINESCENCE IN ORIENTED SYSTEMS: CHEMILUMINESCENCE OF 10,10′-DIMETHYL-9,9′-BIACRIDINIUM NITRATE IN MICELLAR MEDIA†

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(Received August 17, 1981)

Summary

A comparative study was made of the chemiluminescence of 10,10′-dimethyl-9,9′-biacridinium nitrate during its reactions with alkali and hydrogen peroxide in micellar and isotropic media. In the former medium the quantum efficiency increased markedly, but most importantly it was possible to detect for the first time light emission from the primary excited product which has always been prohibited in this reaction owing to unrestricted energy transfer in isotropic media.

1. Introduction

The structure of micelles [1, 2] and their effects on certain chemical reactions [2 - 4] have been studied very extensively recently since they are subjects of considerable scientific interest. Micelles are conveniently and reproducibly formed and have the remarkable property of solubilizing [1, 2, 5] or otherwise properly orienting suitable molecules. Depending on the solubilization site of the substrate(s), varying environmental effects are produced on the solubilizates and therefore micellar media are suitable for the investigation of catalytic [2 - 4], photophysical [6, 7], photochemical [8, 9] and primarily biological processes [2]. Specifically micelles have served as models for biological processes. Conversely, it is also possible to use physicochemical evidence to deduce the structural and dynamic properties of micelles.

In view of the above possibilities it seems reasonable to investigate chemiluminescence reactions in micellar media. In this first report the classical 10,10′-dimethyl-9,9′-biacridinium nitrate (lucigenin) light reaction was chosen for investigation in the micellar solutions formed by the dissolution

†Part of this work was presented at the Second International Symposium on Bioluminescence and Chemiluminescence, San Diego, CA, U.S.A., August 26 - 28, 1980.

0047-2670/82/0000-0000/$02.75

of cetyltrimethylammonium bromide (CTAB) in water. The main purpose of this work was to determine the solubilization site of the reactants and/or the intermediates and also to determine whether the microenvironment of the micelle affects the quantum efficiency and the chemiluminescence spectroscopy compared with those obtained in the homogeneous experiment.

2. Experimental details

CTAB was purified by recrystallization from a 4:1 (by volume) acetone: ethanol mixture and was dried in vacuum over phosphorus pentoxide. Lucigenin (K & K) was used without further purification.

2.1. Chemiluminescence intensity–time diagrams

The intensity–time (I–t) diagrams were recorded on addition of 1 ml of 5 N sodium hydroxide and 1 ml of 10% hydrogen peroxide to 20 ml of 2×10^{-4} M lucigenin in the appropriate aqueous CTAB solution. Each of these experiments was followed by a blank, *i.e.* an experiment performed in the absence of CTAB (homogeneous experiment).

The reaction vessel was positioned in front of an EMI 9514B photomultiplier operating at 1000 V and connected to a Bruker B-R70D recorder and a Time TS100A integrator; both the reaction vessel and the photomultiplier were housed in a specially constructed dark chamber with suitable inlets for gaseous and/or liquid reagents [10]. The integrals of the I–t diagrams thus obtained were then compared with a luminol standard [11, 12] under the same optical geometry, and after the appropriate corrections the quantum yields were calculated on the basis of the lucigenin employed.

2.2. Spectra

The excitation and fluorescence spectra were recorded on an Aminco–Bowman spectrophotofluorimeter calibrated with a quartz pen-ray lamp and were not corrected. Chemiluminescence spectra were recorded at reasonably flat sections of the I–t diagrams on the same instrument employing fast scanning rates and wide slits with the excitation source off.

Absorption spectra were obtained with a Cary 14 spectrophotometer.

3. Results and discussion

An examination of the lucigenin light reaction in conjunction with the proposed models for micellar structure and chemical reactivity offers a strong incentive for performing this classical chemiluminescent reaction in micellar media. Thus, in reactions occurring inside micelles advantage is taken of the fact that the reactant(s) are solubilized in sites of a specific polarity to isolate or bring together these or other species and to induce a

preferred orientation. However, before proceeding with the investigation of this reaction it is appropriate to discuss some problems associated with the effects of added solutes on micellar structure [3]. The effects on rates are less obvious than the effects on micellar structure since there is no certainty that micellar changes will be reflected by changes in the rates of reactions at a micellar surface [3]. This subject will not be further discussed at this point.

As has been extensively reported [3], various solutes or solvents modify and sometimes even disrupt micellar structure. We were therefore very concerned with the nature and quantities of the chemicals participating in micellar reactions and primarily with those that may destroy micelles. Of the chemicals employed in our experiments, sodium hydroxide used at relatively high concentrations could possibly affect the CTAB structure. However, it has been found that hydroxides do not bind to CTAB while the bromide binding decreases slightly as the sodium hydroxide content is increased [13 - 16]. Since not all of these investigations were supported by quantitative data, it cannot be concluded with certainty that CTAB is not affected. More recent work by Chaimovich *et al.* [17], however, provides definite results on the binding of hydroxides to CTAB with a selectivity coefficient for KOH with respect to bromine of 0.08 ± 0.02 which again shows that hydroxides compete inefficiently with bromides for sites at the micellar surface. It should be noted at this point that even with this selectivity coefficient a considerable percentage of the bromides will be replaced by hydroxides in the experiments with the dilute micellar solution, and therefore the micellar structure will be modified but will not be disrupted. Furthermore, as will become evident later in the discussion of the mechanism of the reaction, micellar structure modification is not critical for this type of experiment, and what primarily interests us is the preservation of CTA^+ cation aggregation for the possible solubilization of the compounds involved in the light reaction. The site of solubilization and its effects on the reaction are also subjects of extreme importance for this investigation. Returning to micellar modification, we have in reality tried to induce such changes by increasing the concentration of the surfactant or by the addition of other counter-ions. Analogous problems are encountered with other micellar reactions, as for example in hydrolysis reactions in CTAB in the presence of hydroxides [2, 5, 18] which only make sense on the assumption that although the micellar structure is modified by the hydroxides the aggregation of the surfactants is preserved.

In addition, the number of micelles existing in the solution as well as their shape and size depend among other factors on the concentration of the surfactant [19]. Therefore in our experiments for determining the influence of the above factors on this reaction, micellar solutions containing various amounts of CTAB were used. For the relatively low CTAB concentrations a spherical micellar model is assumed which is transformed to a rod-shaped [3] micelle at the high concentration employed in the final experiment (Table 1).

TABLE 1

Q_{mic}/Q_{hom} as a function of the cetyltrimethylammonium bromide concentration and the lucigenin-to-micelle ratio

CTAB[a] (M)	Q_{mic}/Q_{hom}	*Lucigenin*[b]*/micelle*[c]
5×10^{-4}	0.73	—
2.5×10^{-3}	1.5	8.00
5×10^{-3}	2.0	4.00
7.5×10^{-3}	2.7	2.60
1×10^{-2}	3.1	2.00
1.75×10^{-2}	3.0	1.14
2.5×10^{-2}	3.7	0.80
5×10^{-2}	3.3	0.40
1×10^{-1}	4.0	0.20

[a]The CMC of CTAB is 9×10^{-4} [22].
[b]The lucigenin concentration is always 2×10^{-4} M.
[c]This is the average number of lucigenin molecules per micelle calculated assuming a CTAB aggregation number of 100 [23].

However, the micellar shape modification does not have much effect on the rate of micellar reactions [20, 21] or very probably on other properties. Thus in a typical series of experiments given in Table 1 the ratio Q_{mic}/Q_{hom} of the quantum yield obtained under micellar conditions to that obtained under homogeneous conditions is tabulated as a function of the CTAB concentration and as a function of the ratio of lucigenin to micelle. The same results are presented diagrammatically in Fig. 1. It is seen from these data that the quantum efficiency increases when the CTAB concentration rises above a certain value which is approximately equal to the critical micelle concentration (CMC) of the pure surfactant. However, a considerably higher quantum efficiency than that of the homogeneous experiment is

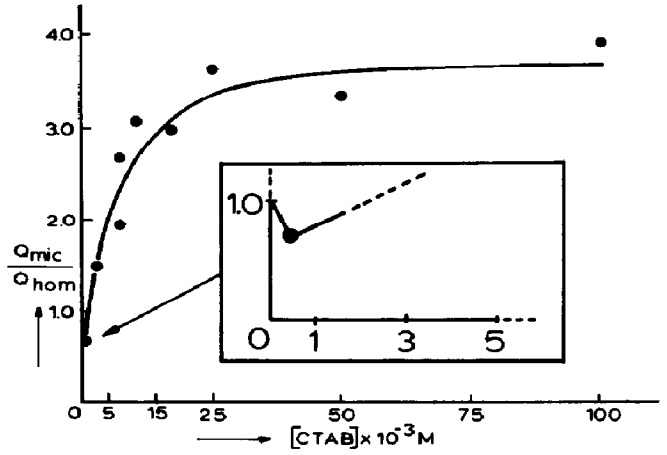

Fig. 1. Variation of Q_{mic}/Q_{hom} as a function of the CTAB concentration.

associated with the presence of a large number of micelles in solution. In addition, the quantum efficiency does not seem to be much affected by the shape and size of the micelles. It is also observed that at CTAB concentrations below the CMC the quantum efficiency is even lower than that of the homogeneous experiment. This favours the previous assumption that the increased quantum efficiency depends on the presence of micelles in solution and not on the involvement of CTAB in the reaction as a common chemical reactant. Finally, it was found that the high chemiluminescence efficiency of the micellar experiments results from a longer emission duration rather than from a high chemiluminescence intensity.

For the rationalization of these results the dioxetane mechanism [24 - 27] has to be considered with the micellar model recently reported by Menger [1]. At relatively low concentrations the micelles are spherical with a rather disorganized structure in which the Stern region (previously characterized and called the Stern layer) includes both the polar heads of the surfactant and a significant fraction of the mobile alkyl chain. In this area there is considerable contact between the alkyl chain and the water rather than shielding of the non-polar nucleus by an ion double layer. Thus deep "grooves" of varying polarity are formed inside which molecules or intermediates of different polarity and bulkiness can solubilize. A typical example is that water molecules may reach even beyond the sixth carbon atom of the long chain of the surfactant. According to this model the core occupies only 15% - 20% of the micelle and has a dielectric constant similar to that of pure hydrocarbons.

In view of the above discussion there is great flexibility in accommodating the various species involved in this reaction inside the CTAB micelles. Lucigenin is repelled from the micellar interface owing to its charge; it therefore seems that a non-ionic intermediate formed by the reaction of lucigenin with the alkali migrates to the Stern region. Similarly, in analogous experiments in 0.01 M sodium dodecyl sulphate the ratio Q_{mic}/Q_{hom} was found to be 2.3, *i.e.* close to the value obtained in the corresponding CTAB micellar experiment. Thus the negatively charged micellar surface does not significantly alter the quantum efficiency, a fact favouring the assumption that a non-ionic species is apparently involved which solubilizes in the Stern region. Hydrogen peroxide also migrating to the Stern region may react simultaneously with the non-ionic species to form a dioxetane intermediate which decomposes via an exoenergetic route producing the primary emitter, *i.e.* *N*-methylacridone (NMA) [24, 28].

The solubilization site of NMA can be determined spectroscopically [3]. The absorption spectrum of NMA in 0.01 M CTAB solution (Fig. 2) differs from those obtained in hexane (it would have an almost similar spectrum if it was solubilized in the micellar core) and in water but resembles that obtained in ethanol. Since it is known [4] that the micellar surface, or rather the Stern region, is significantly less polar than water but somewhat more polar than ethanol, we conclude that NMA would have to be solubilized in an area with a polarity comparable with that of ethanol, *i.e.* in the Stern region.

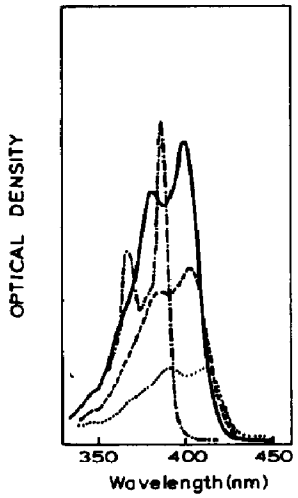

Fig. 2. UV spectra of NMA in various media: ——, ethanol; - - - -, CTAB; — · — · —, hexane; ·····, water.

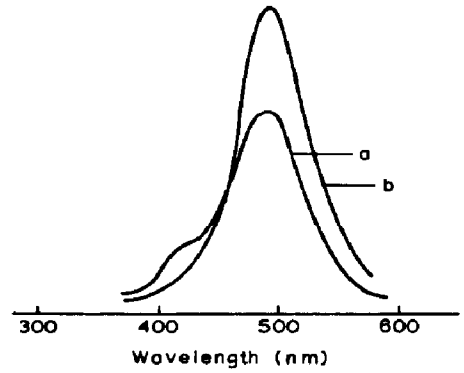

Fig. 3. Chemiluminescence spectra of the lucigenin light reaction in aqueous 0.1 M CTAB (curve a) and an aqueous solution (curve b).

Furthermore, the detection of the primary emission of NMA in the micellar medium was achieved from the very beginning of the light reaction in its chemiluminescence spectrum (the shoulder in Fig. 3). This was possible because of its solubilization in the Stern region of the micelle. The spectral differentiation was pronounced at low lucigenin-to-micelle ratios; the fluorescence spectra obtained during the light reaction were affected in the same manner but even more strongly. The chemiluminescence spectrum may be explained by the fact that NMA, being the primary emitter, is formed and solubilized inside the micelle where there are apparently some restrictions in energy transfer; consequently the chemiluminescence spectrum resembles that of the NMA fluorescence more closely. In contrast, in the homogeneous experiment energy transfer to other species results in a chemiluminescence spectrum which does not match the NMA fluorescence spectrum.

The higher chemiluminescence efficiency is therefore attributed to higher excitation efficiency of the dioxetane decomposition in the less polar environment of the Stern region. In any case it did not result from an increased fluorescence efficiency. Such an effect was not apparent from our fluorescence spectra or from earlier results [29].

We also checked the effect of salts on the quantum efficiency of micellar 0.01 M CTAB experiments by adding sodium chloride. An increase of about 30% in the quantum efficiency was observed which may be attributed to the occurrence of less quenching because of the displacement of bromides by chlorides. However, it seems that Cl^- is inefficient in displacing Br^- from CTAB micelles; this has also been determined by other workers [16, 30] in related studies.

Furthermore, the change in the slope of the curve shown in Fig. 1 for the reaction under investigation and possibly of similar curves for other chemiluminescence reactions could form the basis for the determination of the CMC under the specific reaction conditions prevailing in each experiment.

The failure to detect excimer chemiluminescence at high lucigenin-to-micelle ratios can be attributed to the unsuitability of the primary emitter.

In conclusion, as well as enhancing quantum efficiency the micellar medium employed in these experiments allows detection of light emission from the primary excited product in a case in which this emission is well known to be masked by energy transfer.

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