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Effect of Vitamins C and P on the Chemiluminescence of Lucigenin in Model Membrane Structures

Short Communication

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The chemiluminescence quantum yields of the lucigenin light reaction in didodecyldimethylammonium bromide lamelar aggregates are affected by the presence of vitamins C and P. A dramatic lowering of the chemiluminescence quantum yield is observed in the presence of sodium *L*-ascorbate, the reaction is virtually unaffected by nicotinamide and the quantum yields are raised by almost a factor of 2 in the presence of sodium nicotinate at high concentrations.

(Keywords: Chemiluminescence; Membranes; Photochemistry; Vitamins)

Wirkung der Vitamine C und P auf die Chemilumineszenz von Lucigenin in Modell-Membranstrukturen (Kurze Mitteilung)

Die Chemilumineszenz-Quantenausbeuten der Lucigenin-Lichtreaktion in lamellaren Didodecyldimethylammoniumbromid-Aggregaten werden bei Gegenwart von Vitamin C und P beeinflußt. Es wird in Gegenwart von Natrium-*L*-ascorbat eine dramatische Erniedrigung der Quantenausbeuten beobachtet, die Reaktion ist praktisch unbeeinflußt von Nicotinamid und bei Gegenwart von Natrium-nicotinat in hohen Konzentrationen wird die Quantenausbeute nahezu um einen Faktor 2 erhöht.

The reaction of 10,10′-dimethyl-9,9′-biacridinium nitrate (lucigenin) with hydrogen peroxide in alkaline solutions is a classical chemiluminescent system with a maximum quantum yield of over 10^{-2} Einstein mol^{-1}. Working with this reaction we have shown[1] that chemiluminescence in micellar media, (a) reveals the primary emission in cases where energy transfer to other species masks the emission of the primary excited product in the chemiluminescence spectrum and (b) the less

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polar microenvironment of the Stern region in which the excitation step takes place, increases the quantum yield of the light reaction. Replacement of micelles by a more stable membrane-mimetic agent [didodecyldimethylammonium bromide (*DDAB*) lamelar aggregates, serving as a simple model of biological membranes] results in a dramatic enhancement of the above effects[2]. At least one chemical factor increasing the rigidity and stability of biological membranes (cholesterol), also affects the chemiluminescence of lucigenin in *DDAB* lamelar aggregates giving rise to further enhancement[3] of the above (a) and (b).

We now wish to report the effect of vitamins C and P on the chemiluminescence quantum yields and spectroscopy of the lucigenin light reaction in *DDAB* lamelar aggregates.

The light reactions were carried out in an Aminco "Chem-glow" photometer modified to run continuously, on addition of NaOH (30 μl, 1.7 *N*) and H_2O_2 (30 μl, 3.3%) to a centrifuged 250 μl aqueous solution 10^{-2} *M* in *DDAB* and 10^{-5} *M* in lucigenin, in the presence of varying concentrations of sodium *L*-ascorbate, nicotinamide, and sodium nicotinate.

In Fig. 1*b* the quantum yields corrected for self-absorption and expressed as present *Q* (*Q* = 100 at sodium *L*-ascorbate zero concentration) are plotted as a function of sodium *L*-ascorbate concentration; each point in Fig. 1 is the result of two measurements, one in the presence and one in the absence of sodium *L*-ascorbate. It should be noted here, that although NaOH and H_2O_2 are in excess, (a) sodium *L*-ascorbate competes with lucigenin for H_2O_2 and (b) vitamin C induces chemiluminescence of lucigenin even in the absence of H_2O_2, if only to a lesser extent[4]. In order to take into account these effects, the above experiments were repeated in the absence of *DDAB* (homogeneous system) and the results are shown in Fig. 1*a*. It is clear that for a given sodium *L*-ascorbate concentration, the quantum yield of the light reaction in the oriented system is lower than in the homogeneous system, an observation in contrast to our previous results[1–3] but attributable again to structure modification of the membrane-mimetic agent, caused in this case by vitamin C. The drop in quantum yields in both the homogeneous and the oriented system as the sodium *L*-ascorbate concentration increases is not connected with the effect under study and is apparently due to influence of the reducing sodium *L*-ascorbate on the critical reduction-oxidation steps of the lucigenin light reaction.

In agreement with the effect of sodium *L*-acorbate on the quantum yields, the emission of *N*-methylacridone, the primary emitter, in the chemiluminescence spectrum was less clearly defined in the presence of

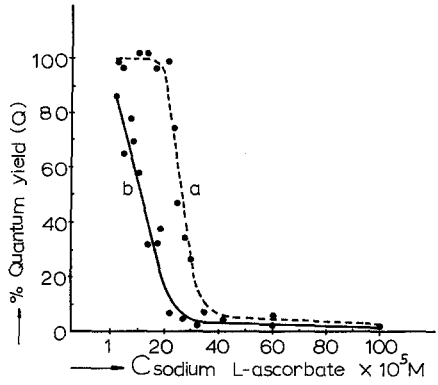

Fig. 1. Chemiluminescence percent quantum yields as a function of sodium *L*-ascorbate concentration *a* in the absence of *DDAB*, *b* in the presence of *DDAB* ($c_{DDAB}\,10^{-2}\,M$; $c_{\text{Lucigenin}}\,10^{-5}\,M$; $c_{H_2O_2}\,9\cdot10^{-2}\,M$; $c_{\text{NaOH}}\,16\cdot10^{-2}\,M$)

sodium *L*-ascorbate and certainly far less clearly defined than in the presence of cholesterol[3].

The study of the effect of vitamin P (P-factor) on the chemiluminescence of lucigenin in *DDAB* lamelar aggregates was less problematic but less rewarding as well. Nicotinamide had very little effect on the quantum yields at concentrations up to $5\cdot10^{-1}\,M$. Sodium nicotinate, on the other hand, was more efficient in affecting quantum yields, but high nicotinate concentrations were required for this effect to become apparent; a slight increase was observed at sodium nicotinate concentrations of 1 and $2\cdot10^{-1}\,M$, which was raised to a twofold increase at a concentration of $5\cdot10^{-1}\,M$.

In conclusion vitamins C and P influence in opposite directions the chemiluminescence of lucigenin in *DDAB* lamelar aggregates, owing, as we believe, to structure modifications of the membrane mimetic agent.

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