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Oxidation of 9-Benzyl-*N*-methylacridinium A Highly Efficient Chemiluminescent Reaction

Short Communication

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9-Benzyl-*N*-methylacridinium iodide reacts with potassium persulphate in *N*,*N*-dimethylformamide to give *N*-methylacridone and light with a quantum yield of over 8×10^{-2} Einstein · mol^{-1}. Chemiluminescence also results on mere illumination of a 9-benzyl-*N*-methylacridinium salt solution.

(Keywords: 9-Benzyl-N-methylacridinium, persulphate; Chemiluminescence)

Oxydation von 9-Benzyl-N-methylacridinium — Eine hochwirksame Chemilumineszenz-Reaktion (Kurze Mitteilung)

9-Benzyl-*N*-methylacridiniumjodid reagiert mit Kaliumpersulfat in *N*,*N*-Dimethylformamid zu *N*-Methylacridon und Licht mit einer Quantenausbeute von über 8×10^{-2} Einstein · mol^{-1}. Chemilumineszenz tritt auch bei bloßer Belichtung einer Lösung von 9-Benzyl-*N*-methyl-acridiniumsalz auf.

The basic structure of the title compound has been employed in chemiluminescence experiments in an effort to correlate the strong chemiluminescence of biological systems with the decomposition of 1,2-dioxetanes and dioxetanones[1,2]. Thus, low temperature photooxidation of 9-benzylidene-*N*-methylacridan or cyclisation of 9-hydroperoxy-9-bromobenzyl-*N*-methylacridan results in an unstable intermediate, presumably the corresponding dioxetane, the decomposition of which is efficiently chemiluminescent. Similar results are obtained from photosensitised oxygenation[3] and ozone oxidation[4,5] of 10,10'-dimethyl-9,9-biacridylidene, the excited product always being *N*-methylacridone (*NMA*).

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We now wish to report the strongly chemiluminescent reaction of 9-benzyl-*N*-methylacridium (*BMA*) salts with persulphate in aprotic solvents such as *DMF*, *DMSO* and acetonitrile.

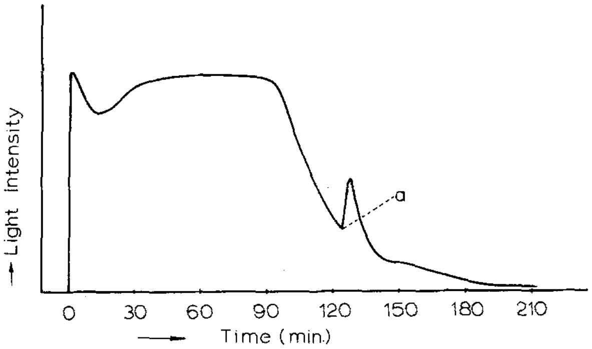

Fig. 1. Intensity-time diagram of the *BMA* (20 ml, 10^{-5} *M*, in *DMF*) light reaction on addition of a potassium persulphate saturated *DMF* solution (1 ml). Further addition of 1 ml persulphate at point (a)

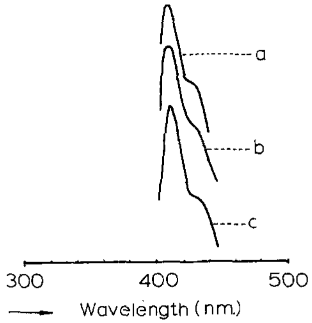

Fig. 2. *a* Fluorescence spectrum of *NMA* under the conditions of the light reaction. *b* Fluorescence spectrum of the mixture at the light reaction. *c* Chemiluminescence spectrum of the light reaction

Reactions of chromatographically pure *BMA* iodide synthesized according to *Decker* and *Hock*[6] were carried out in the chemiluminescene-measurements set-up earlier described[7] by squirting (more than once if necessary) 1 ml saturated solutions of potassium perchlorate into 20 ml, $10^{-5}M$ solutions of *BMA* iodide. The integrals of the light intensity-time diagrams thus obtained were then compared with the known integral at the Luminol Standard[8,9] light reaction under the same conditions and geometry and the chemiluminescence quantum yields were calculated.

The chemiluminescence observed was most efficient in *DMF* solution; the intensity-time diagram is shown in Fig. 1. The reaction quantum yield was found equal to 3.3×10^{-2} Einstein · mol^{-1} based on *BMA* employed. Correction due to self-absorption of the solution at the chemiluminescence maximum at 415 nm raises this yield to over 3.7×10^{-2} Einstein · mol^{-1}.

The reaction's excited product is *NMA* as can be seen in Fig. 2, where the chemiluminescence spectrum is compared with the fluorescence spectra of the spent reaction mixture and the fluorescence spectrum of *NMA* under the conditions of *BMA* chemiluminescence (Aminco-Bowman spectrophotofluorometer, spectra uncorrected).

Although it is too early to propose a mechanism for the light reaction, the following facts should be noted: (a) Reaction of persulphates in *DMSO*, *DMF* etc gives rise to free radicals[10,11]. (b) Inconclusive results were obtained when 1 ml of free radical scavenger (allyl alcohol) was added to the reaction mixture; a dramatic decrease in light intensity was observed in *DMSO*, yet, in *DMF* solutions it resulted in an unexpected increase of the light sum (over 100%) raising the quantum yield to over 8×10^{-2} Einstein · mol^{-1}. (c) Oxygen is necessary for the light reaction; passage of nitrogen through the reaction mixture almost zeroed the light intensity. (d) Iodide ions are involved in the reaction sequence. (e) Autoxidation leading to peroxyintermediates should be considered; mere illumination (365 nm) of a *BMA* solution resulted in substantial chemiluminescence most prolonged in acetonitrile.

Finally it should be emphasized that this reaction's quantum yield as high as 8×10^{-2} (almost eight times higher than that of the classical Luminol light reaction) classifies it among the most efficient nonbiological chemiluminescent reactions.

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