Monatshefte für Chemie 109, 831—838 (1978)

Monatshefte für Chemie

Ozonization of 10,10′-Dimethyl-9,9′-biacridylidene in the Presence of Tetracyanoethylene. An Efficient Chemiluminescent Reaction

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(Received 19 November 1977. Accepted 27 November 1977)

10,10′-Dimethyl-9,9′-biacridylidene in aqueous pyridine reacts with ozone yielding *N*-methylacridone and light with a quantum efficiency in the order of $1.7 \cdot 10^{-2}$ Einstein mol^{-1}. In the presence of tetracyanoethylene, the primary excited product is again *N*-methylacridone, but the quantum efficiency is raised to $2.8 \cdot 10^{-2}$ Einstein mol^{-1}. The chemiluminescence and fluorescence spectra are reported and the reaction mechanism is discussed.

Ozonisierung von 10,10′-Dimethyl-9,9′-biacridylen in Gegenwart von Tetracyanoethylen. Eine wirkungsvolle Chemilumineszenz-Reaktion

10,10′-Dimethyl-9,9′-biacridylen reagiert in wäßr. Pyridin mit Ozon zu *N*-Methylacridon, wobei Licht in einer Quantenausbeute von $1{,}7 \cdot 10^{-2}$ Einstein mol^{-1} abgegeben wird. In der Gegenwart von Tetracyanoethylen ist das primär angeregte Produkt wieder *N*-Methylacridon, die Quantenausbeute wird jedoch auf $2{,}8 \cdot 10^{-2}$ Einstein mol^{-1} angehoben. Die Chemilumineszenz- und Fluoreszenzspektren werden angegeben und der Reaktionsmechanismus wird diskutiert.

Introduction

The reaction of Lucigenin (10,10′-dimethyl-9,9′-biacridinium nitrate) with hydrogen peroxide in alkaline media is one of the classical and most efficient chemiluminescent reactions known. It has been established that the primary emitter is *N*-methylacridone[1–3] (*NMA*), probably produced *via* exoenergetic decomposition of an intermediate dioxetane[3–5] (**5**); in this reaction sequence, 10,10′-dimethyl-9,9′-biacridylidene (*DBA*) (**1**) is considered to be a first step and a key intermediate. Reaction of *DBA*, under conditions similar to those of the Lucigenin chemiluminescence, results in light emission which is again characteristic of the excited *NMA* product. Furthermore, reactions of *DBA* with singlet oxygen[4], experiments specifically designed to give rise to dioxetane (**5**), were shown to be chemilumines-

0026-9247/78/0109/0831/$ 01.60

cent, while low temperature photosensitised oxygenation[6] of *DBA* further establishes the involvement of **5** in the process leading to light emission from excited *NMA*.

Although no quantum yields were reported, reaction of *DBA* with ozone in a variety of solvents has been shown[7] to be a light emitting process, possibly involving dioxetane **5**, the primary emitter being again *NMA*. In yet another report[8], low temperature ozonization of *DBA* in pinacolone produces a thermally unstable intermediate whose decomposition is chemiluminescent, the emission being that of the *NMA* fluorescence. After a very elaborate isolation process, a thermally unstable white solid is obtained which is chemiluminescent with a quantum yield of over 10^{-2} Einstein mol^{-1}.

Since ozone cleavage of a double bond undoubtedly proceeds *via* an initial ozonide, which has been shown to be a stronger oxidising agent than ozone[9] and since tetracyanoethylene *TCE* has been shown to abstract an oxygen atom[10] giving tetracyanoethylene epoxide and eventually the two carbonyl compounds arising from the reduced initial ozonide, it was thought that ozonization of *DBA* (**1**), in the presence of *TCE* would facilitate the process leading to excited *NMA*, thus improving the reaction's chemiluminescence quantum yield.

Experimental

Production of Ozone

A self-constructed *Siemens*-type ozonizer[11] was employed giving an ozone-air mixture 0.26% *v/v* at a flow rate of 340 ml min^{-1}.

10,10′-Dimethyl-9,9′-biacrylidene (DBA) (**1**)

Acridine was converted to *N*-methylacridinium sulphate[12], which on reaction with alkaline potassium ferricyanide gave *N*-methylacridone[13]; reduction of *N*-methylacridone with Zn and *Ac*OH[14] gave very impure and difficultly purified *DBA*; reduction with Zn and HCl in *Et*OH gave better yields of pure *DBA*. This was repeatedly recrystallized from pyridine till chromatographically pure and was characterized by elemental analysis and infrared spectroscopy.

Chemiluminescence Intensity—Time Diagrams

Ozonized air was bubbled through the reaction mixture in a glass vessel positioned in front of an EMI 9514 B photomultiplier tube, operating at 900 V and connected with a Varian F-80 recorder. The reaction vessel—photomultiplier system was housed in a self-constructed dark chamber with suitable inlets for gaseous and/or liquid reagents. The measurements were carried out on 25 ml samples of *DBA* solutions in aqueous pyridine; the *DBA* concentration was $2 \cdot 10^{-5} M$; the pyridine: water ratio was varied to establish the optimum conditions regarding the solvent. The *TCE* (Aldrich-Europe, freshly sublimed) concentration range was then swept to obtain the optimum *TCE* concentration for maximum quantum efficiency. In another instance the appropriate amount of water was squirted in a solution of *DBA* in pure pyridine while air was bubbled through the mixture.

Chemiluminescence Quantum Yields

The intensity—time curves recorded in the course of the reaction, such as those shown in Fig. 1, were integrated with the aid of a very accurate planimeter and the areas thus obtained were compared with the area recorded during the standard[15,16] luminol light reaction, under the same optical geometry. Correction of the light-sums obtained due to the S-11 photocathode's spectral response were unnecessary as the chemiluminescence of both luminol and our reaction falls in the same spectral region. A rough correction of the light sums recorded regarding the solution's self-absorption was, however, imperative; correction factors were obtained in this case, taking into account the radius of the reaction vessel and the mean transmittance of the solutions employed before and after the light reaction at a wavelength of 425 nm. The correction factors thus established were 2.5 and 3.3 for the reactions in the absence and in the presence of *TCE*, resp., under conditions of optimum efficiency.

Spectra

Excitation and fluorescence spectra were recorded on an Aminco-Bowman spectrophotofluorometer calibrated with a quartz "pen-ray" lamp and are uncorrected. Percent transmittance was determined with the aid of a Cary 14 spectrophotometer, while infrared spectra were run on a Perkin-Elmer 521 spectrophotometer. Chemiluminescence spectra were recorded on the Aminco-Bowman instrument, employing fast scanning rates and wide slits, with the excitation source off, at reasonably flat sections of the intensity-time diagrams and were verified by a series of intensity-time diagrams, with the emission monochromator set at intervals of 10 nm.

Results and Discussion

The reaction of *DBA* with ozone was studied in aqueous pyridine. Pyridine is a reasonably good solvent for *DBA* whose very low solubility in most solvents renders its study problematic. The light reaction was, however, found to be more efficient in pyridine-water mixtures, the efficiency increasing on increasing the percentage of water present, an effect apparently limited only by the insolubility of *DBA* in water. By varying the pyridine:water proportion, the optimum conditions for a high quantum efficiency were established at a pyridine:water ratio of about 80:20.

A note of caution should be made at this point, regarding the addition of water to a solution of *DBA* in pyridine, which results in substantial light emission and *DBA* consumption even though the water employed was triply distilled; this effect certainly justifies further investigation. In any case, the solutions should be employed immediately after preparation. Spontaneous luminescence[1] of *DBA* was also observed in our experiments but its intensity was negligible compared to the intensities obtained from our light reactions.

On passage of ozonized air through a *DBA* solution in aqueou pyridine, light is emitted, the intensity-time diagram of which is shown in Fig. 1 *a*. In the presence of *TCE* the above light reaction gives rise to the intensity-time diagram shown in Fig. 1 *b*. On integration of the intensity-time diagrams, correction for self-absorption effects and comparison with the luminol standard, the reaction's chemiluminescence quantum yields (based on *DBA* employed) were determined to be $1.7 \cdot 10^{-2}$ in the former and $2.8 \cdot 10^{-2}$ Einstein mol^{-1} in the latter case. As hoped, the presence of *TCE* in the reaction mixture results in both a faster and a more efficient light reaction. The concentration of *TCE* required for the above optimum quantum yield was found equal to $1.5 \cdot 10^{-4} M$, almost 8 times higher than the concentration of *DBA*. Although an olefin: ozone ratio of 1:1 would be a requirement more in agreement with the literature[9,10], it should be taken into account that our reaction takes place at room temperature, in which case *TCE* itself reacts with ozone; such a reaction, however, was found to be completely dark, at least under the conditions of sensitivity employed in our experiments.

The excited product of the *DBA* ozonization light reaction in the presence of *TCE* is *NMA* as shown in Fig. 2, where the fluorescence spectrum of *NMA* (a), is compared with the fluorescence spectrum of the spent reaction mixture (b) and the reaction's chemiluminescence spectrum (c). The fluoresence spectrum of *NMA* was obtained in aqueous pyridine (80:20) to match the conditions of the light reaction. Fig. 2 *b* shows the transition from the *DBA* to the *NMA* fluorescence as the light reaction in the presence of *TCE* proceeds. After 100 minutes of ozonization the reaction mixture exhibits mainly the fluorescence of *NMA*. Fig. 2 *c* shows the chemiluminescence spectra as the reaction in the presence of *TCE* proceeds. Here, again, as the concentration of *DBA* is diminished and the probability of excitation energy transfer back to unreacted *DBA* is minimized, the emission spectrum of *NMA* appears. The apparent inversion of peak intensities in the *NMA* emission is due to a dramatic increase of absorption of the reaction mixture in this spectral region.

Comparison of the three spectra, i.e., the fluorescence spectrum of the suspected emitter, the fluorescence spectrum of the spent reaction mixture and the chemiluminescence spectrum of the reaction, is a common practice when trying to establish the involvement of a suspected excited product in a chemiluminescent reaction and is based on the fact that light-emission due to an electronic transsition comes always from the lowest electronically excited state, irrespectively of the mode of excitation, be it absorption of light,

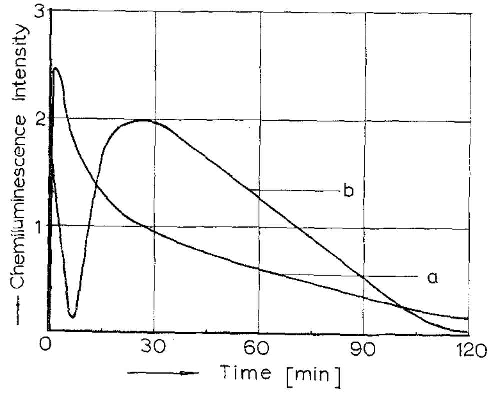


Fig. 1. Light Intensity-Time diagrams during ozonization of *DBA* solutions in aqueous pyridine (a) in the absence and (b) in the presence of *TCE*

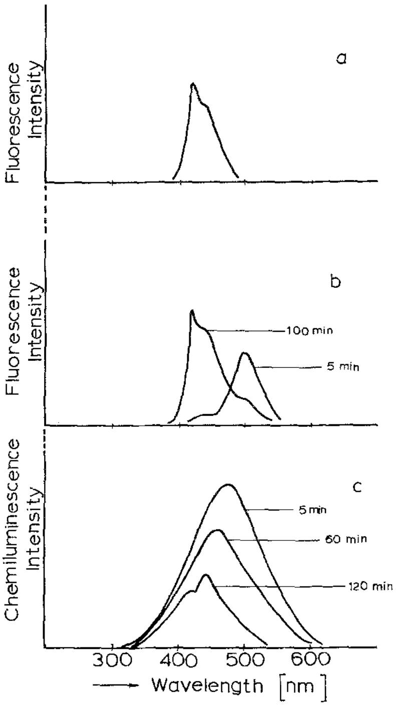
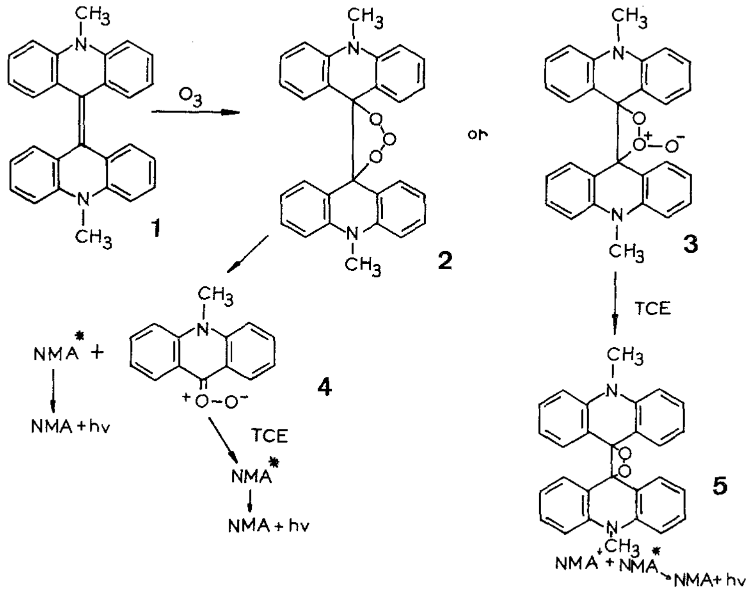


Fig. 2. (a) Fluorescence spectrum of *NMA* in aqueous pyridine; excitation λ_{max} 380 nm. (b) Fluorescence spectra of a solution of *DBA* and *TCE* in aqueous pyridine after ozonization for 5 min and 100 min; excitation λ_{max} 380 nm. (c) Chemiluminescence spectra of a solution of *DBA* and *TCE* in aqueous pyridine on ozonization for 5, 60 and 120 min

chemiexcitation or any other form of energy enrichment. The chemiluminescence spectrum of a reaction should, therefore, be identical with the fluorescence spectrum of the excited product, although in practice, the low quality of the chemiluminescence spectra due to the wide slits and fast scanning rates unavoidably employed, should be taken into account.

Scheme 1



Having thus established the identity of the reaction's primary excited product, a reaction mechanism is proposed explaining the increased quantum efficiency of the reaction in the presence of *TCE* (Scheme 1).

Of the five primary olefin-ozone adducts visualized in the *Criegee*[9] mechanism of ozonolysis, a 1,2,3-trioxolane such as **2** is most favored, although, despite evidence for the contrary, an oxy-1,2-dioxetane such as **3** is not improbable. Formation of a peroxy-epoxide should be ruled out since the strict requirement of increased steric hindrance[9, 17] is not met in *DBA*. Similarly, an olefin-ozone σ-complex[9] should be ruled out for the same reasons, while an olefin-ozone π-complex[9] such as those detected by *Bailey*[18] at very low temperatures should be also ruled out because, even if its decomposition to the initial reactants, as proposed, was exoenergetic enough to result in light emission of the observed wavelength, *DBA* should not be consumed and certainly *NMA* would not be the primary emitter.

The primary ozonide in our reaction is therefore, most probably, 1,2,3-trioxolane **2** whose intermediate decomposition gives rise to *NMA* (a part of it electronically excited) plus carbonyl oxide[9] **4**. De-excitation of *NMA* results in emission of light, while *TCE* strips[17] the terminal oxygen of the carbonyl oxide producing more *NMA* (a percentage of which is again electronically excited); de-excitation of *NMA* gives then rise to an additional light emission.

Alternatively, a less probable, yet more attractive oxy-1,2-dioxetane **3** is initially formed, whose terminal oxygen atom is removed[9, 17] by *TCE* yielding 1,2-dioxetane **5**; concerted cleavage of **5** results in two *NMA* molecules, a percentage of one being electronically excited. As decomposition of 1,2-dioxetanes to the corresponding carbonyl moieties is a strongly chemiluminescent reaction[19] (a number of "classical" strongly chemiluminescent reactions are thought to involve the decomposition of a 1,2-dioxetane), facilitation of its formation by the presence of *TCE* should certainly give rise to exceptionally high quantum yields.

Both routes, therefore, are consistent with the increased quantum efficiency of the light reaction in the presence of *TCE* and it should be noted that a quantum yield (based on *DBA* employed) as high as $2.8 \cdot 10^{-2}$ Einstein mol^{-1} classifies this reaction among the most efficient non-biological light reactions known.

Acknowledgement

The authors wish to thank Mrs. *E. Sekeri-Papazoglou* for her assistance in the above described experiments.

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