

CONCENTRATION EFFECTS IN THE CHEMILUMINESCENCE OF LUMINOL

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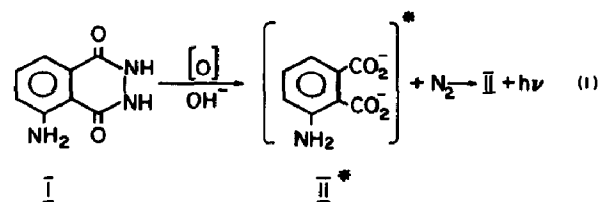
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Summary

A 10^{-2} M basic solution of luminol undergoes an oxidation reaction accompanied by a chemiluminescence emission with $\lambda_{\max} = 480$ nm. By comparing the chemiluminescence spectra with the relevant fluorescence spectra at luminol concentrations of 10^{-2} and 10^{-3} M it can be concluded that the emitting species is the 3-aminophthalate ion. This observation is in agreement with the accepted mechanism for chemiluminescence.

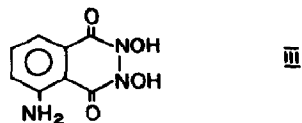
1. Introduction

The chemiluminescence (CL) accompanying the oxidation reaction of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione (I)) has been extensively studied. The mechanism adopted for the reaction [1 - 6] states that the emitting species is the 3-aminophthalate (3-AP) ion (II) formed from the oxidation of I:



The evidence given in support of scheme (1) is based on the equivalence between the CL spectrum and the emission spectrum of 3-AP [7]. In aqueous solutions λ_{\max} of both the CL and the emission spectra are at 425 nm and in aprotic solutions such as dimethyl sulphoxide they are 480 nm [8]. It was claimed by Nikokavouros and Vassilopoulos [9] that the CL is in the UV spectral region and that the observed emission is from an excited luminol molecule formed by subsequent absorption of the UV CL emission. Thus the equivalence between the CL and the fluorescence spectrum is attributed to the formation of an excited luminol molecule. In addition, analysis of the

reaction products [10] revealed the presence of many species including 3-AP. One of the products, which has the proposed structure III,



undergoes an efficient oxidation reaction leading to CL spectra with λ_{\max} at 475 nm. Under the same experimental conditions (H_2O_2 and $\text{K}_3\text{Fe}(\text{CN})_6$ concentrations) the CL spectrum of luminol has λ_{\max} at 480 nm. It is the purpose of this paper to give some evidence for concentration effects which do not require the formation of either species III [10] or the assumption of CL emission of 3-AP in the UV followed by luminol fluorescence [9].

2. Experimental

The CL spectra were measured using a 0.5 m Bausch and Lomb monochromator equipped with an IP 28 photomultiplier connected to a Keithley 610 B electrometer. The spectra were recorded by following the CL decay and measuring the peak CL intensity every 10 nm. Fluorescence spectra were obtained by using a nitrogen laser excitation (Moletron UV 400) and a similar monochromator. The photomultiplier output was fed into a Moletron LP 20 photometer. Absorption spectra were taken on a Cary 14 spectrophotometer. Luminol (Eastman AR) was used without further purification.

3. Results and discussion

The first series of measurements was taken at the concentration range employed in most of the studies of luminol CL [6]. 10^{-3} M solutions of luminol at various NaOH concentrations, 3% H_2O_2 and 0.05 M $\text{K}_3\text{Fe}(\text{CN})_6$ were used. The following measurements were taken: (a) CL spectra; (b) fluorescence spectra of luminol prior to oxidation; (c) fluorescence spectra of 3-AP after the reaction was completed and of several luminol and 3-AP mixtures during the course of the reaction; (d) absorption spectra of luminol and 3-AP.

Basically, what we have found agrees with the reported studies [6]. Curve a of Fig. 1 shows the CL spectrum and Fig. 2 shows the fluorescence spectra of 10^{-3} M luminol at various stages of the reaction. It is clearly seen that the CL spectrum matches the fluorescence spectrum of 3-AP (Fig. 2, curve d) and not that of luminol. Since we have used a UV excitation (337.1 nm of the nitrogen laser) we can rule out the possibility that the observed CL spectrum is the consequence of re-excitation of luminol by a primary UV CL emission as suggested by Nikokavouros and Vassilopoulos [9]. The results support the accepted mechanism represented in scheme (1).

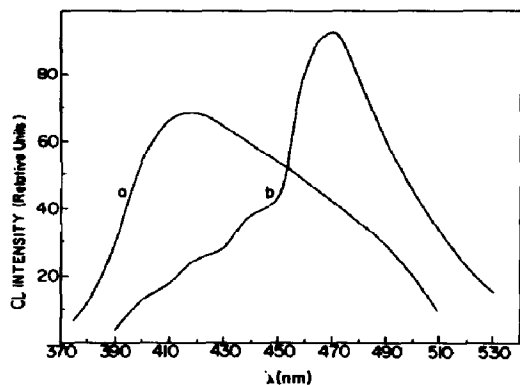


Fig. 1. Chemiluminescence spectra of luminol solutions: curve a, 10^{-3} M; curve b, 10^{-2} M. Corrected spectra all with 0.05 NaOH, 0.1% H_2O_2 and 10^{-3} M $K_3Fe(CN)_6$.

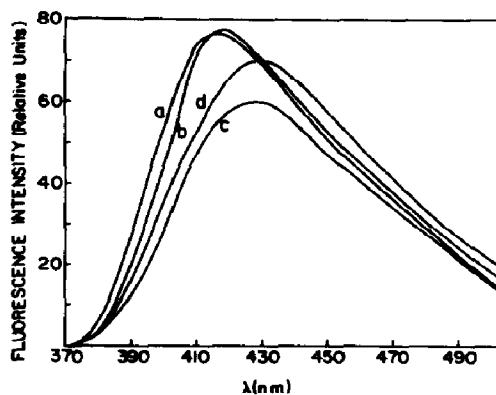


Fig. 2. Nitrogen laser excited fluorescence spectra: curve a, 10^{-3} M luminol solution; curve b, after 10% reaction; curve c, after 50% reaction; curve d, after complete reaction (3-AP fluorescence spectrum). Corrected spectra.

The second series of measurements were taken with 10^{-2} M solutions of luminol but without changing the concentrations of NaOH, H_2O_2 and $K_3Fe(CN)_6$. The CL spectrum is shown in curve b of Fig. 1. The fluorescence spectra of luminol, the luminol-3-AP mixture and 3-AP are depicted in curves a, b, c and d respectively of Fig. 3. Again we observe that the CL spectrum matches the fluorescence spectrum of 3-AP. Although both spectra are red shifted they are the same; this proves that scheme 1 is basically a correct description of the CL reaction. Moreover, a comparison of the fluorescence spectra of luminol at low and high concentrations (curves a of Figs. 2 and 3) shows no indication of the concentration effect in pure luminol. The evolution of the 480 nm band in the course of the reaction suggests that this emission band should be associated with the 3-AP species. The red shift with increase of concentration can be explained, for example, by assuming excimer

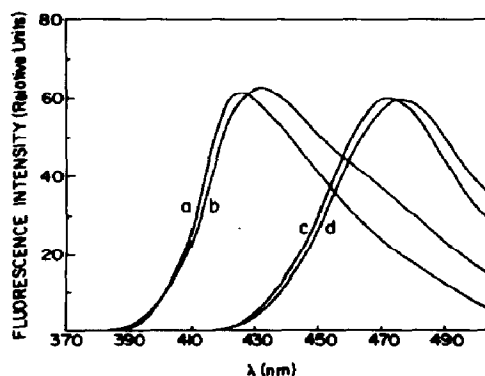


Fig. 3. Nitrogen laser excited fluorescence spectra: curve a, 10^{-2} M luminol solution; curve b, after 10% reaction; curve c, after 50% reaction; curve d, after complete reaction (3-AP fluorescence spectrum). Corrected spectra.

formation of 3-AP at high concentrations. This is supported by the observation that the fluorescence of pure 3-AP as a function of concentration follows the same pattern as shown in Fig. 3. Measurement of the absorption spectra of all the samples shows that no changes with concentration occur which rules out the possibility that this red shift is due to complex formation in the ground state. In addition, the positions of the absorption bands of luminol and of 3-AP prove that inner filter effects can be ignored.

It can thus be summarized that the present study supports the mechanism of CL which involves formation of an excited 3-AP molecule and that this is the emitting species in the CL reaction of luminol at all concentrations (scheme (1)). In addition, a novel concentration effect in the CL reaction was observed, the nature of which requires additional study.

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