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Mendeleev Commun., 1993, **3(5)**, 203–204

Mendeleev Communications

Photoionization and Photochemiluminescence of Luminol in Aqueous Solution

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UV photolysis of luminol (5-amino-2,3-dihydrophthalazine-1,4-dione) in aqueous solution *via* one-photon photoionization gives the luminol radical and an hydrated electron, which reacts with the dissolved oxygen to form the superoxide radical; recombination of the luminol radical with superoxide leads to chemiluminescence.

The chemiluminescence (CL) of luminol (5-amino-2,3-dihydrophthalazine-1,4-dione) initiated, for example, by potent oxidants or photoinitiated by sensitizers such as thiazine and xanthene dyes is well known and important for various analytical applications.[1,2] It is of interest to find new routes for initiating CL. We have shown that UV absorption by luminol in sensitizer-free aqueous solution also causes CL (*i.e.* photo-CL).[3] A mercury lamp photolysis of concentrated solutions of luminol in DMFA was earlier reported,[4] but CL was not measured in that work. Using laser flash photolysis we have proved that the one-photon photoionization of luminol is an initiation step of the photo-CL. These results are presented below.

The recrystallized luminol (LH_2) (Koch-Light Lab.) was used in this study. The other chemicals were of reagent grade and used without further purification. Spectral and kinetic measurements were carried out using a conventional spectrophotometer, spectrofluorometer (in the mode of measuring phosphorescence) and laser flash photolysis. During the flash photolysis sample solutions were excited by the second harmonic (347 nm) of a Q-switched ruby laser.

Under photoexcitation of aqueous air-saturated solutions of LH^- ($pK_{a1} = 15.2$, $pK_{a2} = 6.4$[5]) CL is observed. The spectrum of this photo-CL is similar to that for all luminol chemiluminescence.[1] The excitation spectrum of photo-CL matches the

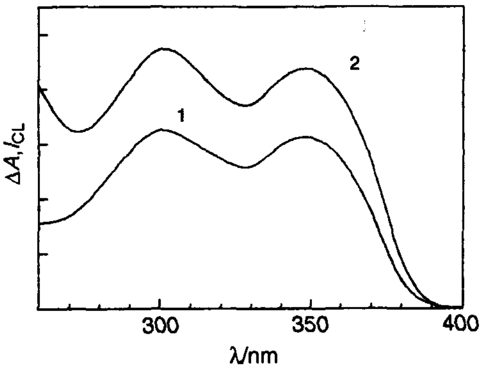

Fig. 1 Absorption spectrum of luminol (1) and excitation spectrum of the photochemiluminescence (2), arbitrary units. Aqueous solution, pH 12.

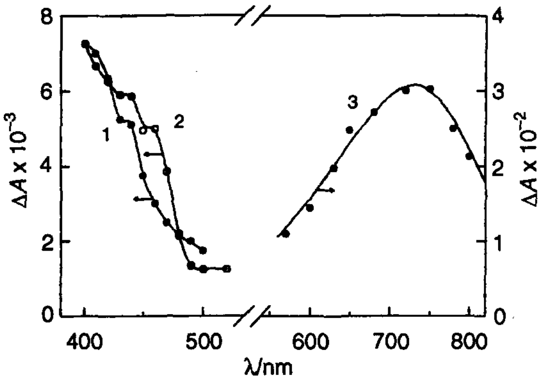

Fig. 2 Transient absorption spectra after 100 ns obtained on flash photolysis (347 nm) of 10^{-4} mol dm^{-3} luminol in aqueous solution: pH 7.5 (1·3); pH 12 (2); 0.01 mol dm^{-3} KNO_3 (1·2).

luminol absorption spectrum in the near UV region (Fig. 1). Fig. 2 shows the initial transient spectra obtained after flash exciting a deoxygenated solution of luminol at different pH. The broad absorption around 720 nm decays on the 1 μs time scale, disappearing after addition of 0.01 mol dm^{-3} KNO_3, or oxygen saturation, and was assigned to the hydrated electron, e^-_{aq}.[6] The absorption at 400–500 nm hardly changes after addition of the acceptors of e^-_{aq}, but depends on pH. Its decay curve shows relatively fast (tens of microseconds) and slow (hundreds of microseconds) regions. The initial spectra of this transient absorption at pH 7.5 and pH 12.3 (Fig. 2) correspond to the absorption spectra of neutral ($LH^{\cdot}$) and deprotonated ($L^{-\cdot}$) luminol radicals, respectively, obtained by pulse radiolysis.[7] Thus, the transient absorption at 400–500 nm was assigned to the luminol radical. Despite a p*K* value of 7.7 for the protolytic equilibrium[8] between $LH^{\cdot}$ and $L^{-\cdot}$, the initial spectrum at pH 7.5 corresponds to 'pure' $LH^{\cdot}$, because deprotonation to the equilibrium state occurs within a few microseconds. This process is kinetically resolved especially at ~ 460 nm, where the difference in the spectra of $LH^{\cdot}$ and $L^{-\cdot}$ is more prominent. Increasing pH accelerates deprotonation of $LH^{\cdot}$. At pH ~12 deprotonation proceeds faster than the time resolution of the laser flash photolysis apparatus (~30 ns), and the spectrum of L^- is observed immediately after the flash. These results give clear evidence for the photoionization of luminol, reaction (1).

$$\mathrm{LH^- \xrightarrow{h\nu} LH^{\cdot} + e^-_{aq};\ LH \rightleftharpoons L^-} \qquad (1)$$

Linear dependence of the absorption of e^-_{aq} *versus* excitation energy indicates a one-photon mechanism for the photoionization (Fig. 3). The quantum yield of the luminol photoionization measured by comparison (under identical experimental conditions) with that of aqueous chlorpromazine[9] is $(1.4 \pm 0.3) \times 10^{-2}$. Note that the one-photon mechanism provides a generation of radical species even for UV light of low intensity.

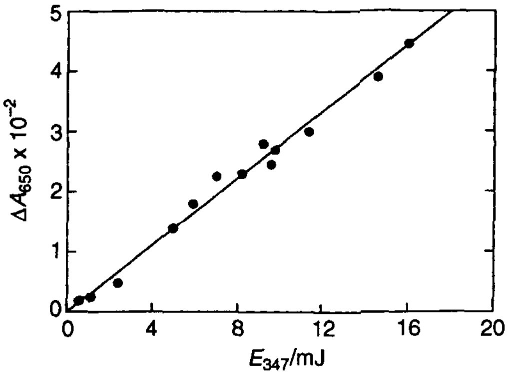

Fig. 3 Dependence of transient absorption at 650 nm (*cf.* Fig. 2) *vs.* excitation energy.

The photo-CL quantum yield, *i.e.* the ratio of quanta emitted to quanta absorbed by luminol, was estimated by comparison with that of the sensitized luminol CL, where the light is absorbed by a sensitizer.[2] This is equal to ~ 5×10^{-5} for 10^{-5} mol dm^{-3} luminol in an air-saturated solution at pH 12, illuminated at 350 nm.

In an air-saturated solution e^-_{aq} rapidly reacts with the dissolved oxygen (rate constant 2.1×10^{10} mol^{-1} dm^3 s^{-1})[6] giving superoxide radical, $O_2^{-\cdot}$ It is firmly established that one of the pathways of luminol CL is a reaction between the luminol radical and $O_2^{-\cdot}$ according to reactions (2)–(4).[10]

$$\mathrm{L^{-\cdot} + O_2^{-\cdot} + H^+ \rightarrow LOOH^- \rightleftharpoons LHOOH} \qquad (2)$$

$$\mathrm{LOOH^- \rightarrow CL} \qquad (3)$$

$$\mathrm{LHOOH \rightarrow dark} \qquad (4)$$

We believe that the superoxide channel is crucial for the luminol photo-CL, as for the sensitized CL.[2] It is consistent with the observation that the maximum intensity of photo-CL is proportional, upon continuous photoexcitation, to both the photoexcitation intensity and the luminol concentration (at low optical density).

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Received: Moscow, 24th March 1993
Cambridge, 1st June 1993; Com. 3/01836I