Photosensitized Chemiluminescence of Luminol, 6-Aminophthalazine-1,4(2*H*,3*H*)-dione

By KONSTANTIN KUSCHNIR and THEODORE KUWANA*

(*Department of Chemistry, Case Western Reserve University, Cleveland, Ohio* 44106)

LUMINOL [6-aminophthalazine-1,4(2*H*,3*H*)-dione] emits[1] a bright chemiluminescence in aqueous alkaline solutions containing hydrogen peroxide, ferricyanide, and oxygen or in DMSO containing oxygen and t-butoxide. Chemiluminescence can also be generated when luminol is electro-oxidized[2] in either alkaline aqueous or DMSO–O_2 solutions. The products of the reactions in 70% DMSO have been identified as aminophthalate ion and nitrogen.[3] From the close coincidence of the fluorescent spectrum (λ_{max} 424 nm.) of this ion and the chemiluminescence spectrum, it has been considered as the emitter. An endoperoxide[4,5] has been proposed as the precursor to the ion, from energetic considerations. Analogous reactions involving endoperoxides are known: these peroxides decompose with emission of light.[6] The carboxy-groups in the aminophthalate ion each contain an oxygen derived from the same oxygen molecule.[3] More recently, theoretical considerations[7] have supported this structure.

A possible route to this endoperoxide is the reaction of excited singlet oxygen[8] with the mono- or di-negative anion of luminol. Fluorescein or eosin-y (sensitizers)[9] was introduced into alkaline luminol solutions which had been enriched with either oxygen or argon, and irradiated at wavelengths coinciding with the fluorescent excitation wavelength of the sensitizer. Light emission occurred at λ_{max} 424 nm. which is shorter than the irradiation wavelength. The irradiation wavelength was chosen as that which produced the maximum fluorescence of the sensitizer in the absence of luminol. Maximum chemiluminescent intensity in the presence of luminol was found to coincide with this irradiation wavelength (Table).

The observed chemiluminescent intensity is 10—20 times greater in the presence of eosin-y than in the presence of fluorescein under identical solution conditions and with identical irradiation intensity. This is in reverse order of the fluorescent quantum yields: 0·85—0·92 for fluorescein and 0·19 for eoxin-y.[10] These results may reflect the population level of the triplet sensitizer (triplet levels: fluorescein 51—54 kcal.; eosin 43—46 kcal.) which produces the excited oxygen singlet.

Our preliminary results indicate that the luminescent intensity depends on the concentrations of luminol, sensitizer, and oxygen. We have also attempted to generate $^1O_2$ by electrodeless discharge[12] and to introduce it into alkaline luminol at low pressures. Chemiluminescence at λ_{max} 424 nm. resulted. This experiment is not conclusive because of the presence of low levels of O_3 which can produce chemiluminescence.

Similarly, singlet oxygen generated from the reaction mixture described by Ogryzlo[13] was transferred into alkaline luminol solutions by low pressure-pumping. Chemiluminescence was observed but removal of chlorine from the gas stream is difficult, and whether singlet oxygen was responsible for the emission could not be definitely ascertained. The introduction of chlorine directly into alkaline luminol with or without H_2O_2 produces strong chemiluminescence. A red emission[13,14] characteristic of $(^1\Delta O_2)_2$ was observed from these reaction mixtures.

Fluorescein (M)	Fluorescence[a] λ_{max} (nm.)		Chemiluminescence[b] λ_{max} (nm.) luminol	
$1{\cdot}0 \times 10^{-6}$	493	514	[c]	[c,d]
$1{\cdot}0 \times 10^{-5}$	493	515	493	424
$1{\cdot}0 \times 10^{-4}$	508	523	508	422
$1{\cdot}0 \times 10^{-3}$	524	530	524	416

Eosin-y (M)	Fluorescence[a] λ_{max} (nm.)		Chemiluminescence[b] λ_{max} (nm.) luminol	
$0{\cdot}5 \times 10^{-6}$	518	536	517	422
$0{\cdot}5 \times 10^{-5}$	518	537	518	424
$0{\cdot}5 \times 10^{-4}$	537	547	537	424
$0{\cdot}5 \times 10^{-3}$	554	566	554	418

[a] No luminol present; [b] luminol 10^{-2}M, pH 13; [c] no chemiluminescence observed; [d] λ-shift may be due to overlapping adsorption by sensitizer with increased concentration.

The half-life of luminescent emission of alkaline luminol sensitized with eosin-y is *ca.* 5 msec., which is the same magnitude as that observed for the chemiluminescence generated electrochemically.[2]

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