# Precursors to the Chemiluminescence of Luminol, 6-Aminophthalazine-1,4(2*H*,3*H*)-dione

By J. H. BAXENDALE

(*Chemistry Department, The University, Manchester* M13 9PL)

*Summary* Chemiluminescence produced by the pulse radiolysis of luminol solutions occurs as the result of a bimolecular reaction of an intermediate, suggested to be a peroxy radical, which is the third product in a series of consecutive reactions beginning with the oxidation of luminol by OH radicals.

LUMINOL [6-aminophthalazine-1,4(2*H*,3*H*)-dione] in alkaline solution produces chemiluminescence in a variety of oxidising conditions involving usually hydrogen peroxide and/or oxygen. The many previous studies on the system have usually entailed measurements of luminescent intensity in conjunction with kinetic observations on the oxidising system.[1-3] It seems well established that the final emitting species is the excited 3-amino-phthalate ion,[3] but the mechanism of its formation from luminol is obscure.

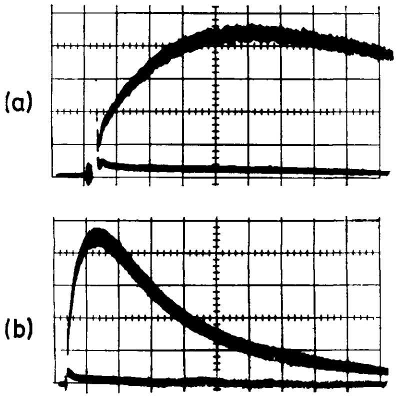


FIGURE. 1 *Build up* (*a*) *and decay* (*b*) *of the emission at* 425 *nm produced in* 100μM *luminol solution containing oxygen at* pH 9·5 *following a* 1μs *pulse of* 10 *MeV electrons.*

We report that the same chemiluminescence can be excited in alkaline luminol solutions by pulse radiolysis, the only requirement being the presence of oxygen. In this system it is also possible to follow short lived transient species produced from the luminol by absorption measurements and to correlate these with the emission kinetics We have made the following observations: (i) The build-up and decay of the luminescence following a 1 μs electron pulse occur over tens and hundreds of microseconds respectively depending on conditions, (Figure 1). These times are much longer than the lifetime of the excited amino-phthalate ion which we find to be $< 5$ ns and hence must be determined by chemical reaction rates. (ii) The reaction is initiated by OH radicals produced by the electron pulse as evidenced by an increase in luminescence when $N_2O$ is present (which gives OH from $e_{aq}$) and a decrease when methanol is present (which will compete with luminol for OH). (iii) Transient species are produced which absorb between 220—1100 nm and kinetic measurements in the range 400—700 nm show that the initial product R· of the reaction of OH with luminol ($k = 1 \times 10^{10} \text{M}^{-1} \text{s}^{-1}$, Figure 2a) reacts rapidly with oxygen ($k = 1 \times 10^{9} \text{M}^{-1} \text{s}^{-1}$, Figure 2b). The latter gives a species X which undergoes a pH dependent change to Y over some tens of microseconds (Figure 2b) and then Y decays over hundreds of microseconds (Figure 2c).

The latter process is found to be second order in Y ($k = 3 \times 10^{8} \text{M}^{-1} \text{s}^{-1}$) and in view of the time scale involved seems likely to be the one responsible for the emission. This agrees with our general observation that the decay of the emission intensity ($I$) is faster at higher pulse doses, and that the kinetics of the decays are quantitatively consistent with the emission step being:

$$\text{Y} + \text{Y} \longrightarrow (\text{Z})^* \longrightarrow \text{Z} + h\nu$$
$$k = 3 \times 10^{8} \text{M}^{-1} \text{s}^{-1}$$

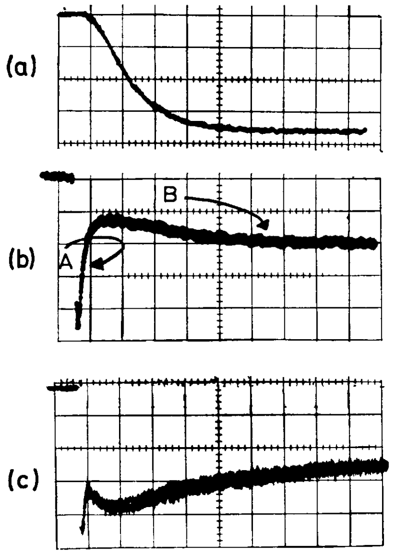
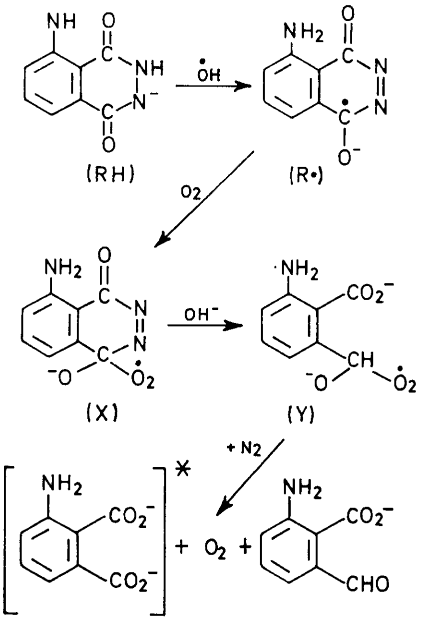


FIGURE. 2. *Oscilloscope traces showing successive absorption changes at* 550 *nm in a luminol solution at* $p$H 10 *following a* 1 $\mu$s *electron pulse* (*a*) $\dot{O}H + RH \rightarrow R^{\bullet} + H_2O$, *formation of* $R^{\bullet}$ (1 $\mu$s *per division*). (*b*) *A;* $S^{\bullet} + O_2 \rightarrow X$ *followed by B;* $X \rightarrow Y$ (5$\mu$s *per division*). (*c*) *Above changes followed by* $2Y \rightarrow$ *products* + *light* (100$\mu$s *per division*).

Such a reaction would require a linear relationship between $I^{-\frac{1}{2}}$ and t as we have observed. These observations are consistent with the mechanism shown in the Scheme.



SCHEME

A similar scheme may be applicable when the luminescence is produced by the various additives which have been used since all are likely sources of oxidising free radicals. The suggested emission *via* reaction of peroxy radicals would bring the luminol system into line with current ideas on luminescence in other systems.[4]

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[1] F. McCapra, *Quart. Rev.*, 1966, **20**, 485.
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[3] J. Lee and H. H. Seliger, *Photochem. and Photobiol.*, 1970, **11**, 247.
[4] V. A. Belyakov and R. F. Vassil'ev, *Photochem. and Photobiol.*, 1970, **11**, 179.