

## Lyoluminescence of Irradiated Carbohydrates. Induced Emission from Diphenylisobenzofuran

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**Summary** Unexpectedly, the emission observed during the dissolution of irradiated carbohydrates in aerated aqueous acetone or an aqueous solution of micelles containing diphenylisobenzofuran is greatly enhanced with respect to the natural lyoluminescence.

LYOLUMINESCENCE (LL), the emission of light occurring during the rapid dissolution of irradiated tissue equivalent materials, such as amino acids and carbohydrates,<sup>1a,b</sup> has attracted attention because of possible applications in comparative dosimetry. In an attempt to characterise the excited species responsible for the emission, originally proposed to be a form of excited molecular oxygen,<sup>2</sup> we have used diphenylisobenzofuran (DPBF). Generally, in photochemistry<sup>3</sup> and biological work,<sup>4</sup> the bleaching of DPBF ( $\lambda_{\max}$  410 nm) is an indication of singlet O<sub>2</sub> (<sup>1</sup> $\Delta_g$ ) involvement. Unexpectedly,<sup>5</sup> we observe an emission which is

enhanced by a factor of  $> 10$  over LL during dissolution of  $\gamma$ -irradiated carbohydrates in aqueous acetone or an aqueous solution of micelles<sup>3</sup> [sodium dodecylsulphate (SDS); 10<sup>-1</sup> mol dm<sup>-3</sup>] containing DPBF (*ca.* 10<sup>-5</sup> mol dm<sup>-3</sup>) where normally if singlet O<sub>2</sub> was directly involved quenching of LL might be expected. No emission as an accompanying phenomenon has been reported during DPBF bleaching by singlet O<sub>2</sub><sup>6</sup> although DPBF does fluoresce with  $\lambda_{\max}$  (emission) *ca.* 480 nm.<sup>7</sup> Using solution filters we have established that the emission peaks at *ca.* 480 nm correspond approximately to the fluorescence maximum of DPBF and, hence, there appears to be an induced emission from this compound *i.e.* chemiluminescence (CL). Whether LL is wholly replaced by this emission or is generated concurrently is extremely difficult to determine spectrally. However, since LL is observed largely at wavelengths  $> 440$  nm<sup>1a,b</sup> direct energy transfer from the excited species responsible

for LL to DPBF [ $\lambda_{\max}$  (excitation) *ca.* 350 nm] appears not to be feasible on energetic grounds.

DPBF-CL exhibits a similar  $O_2$  and dose dependency to LL<sup>5</sup> and is suppressed by radical scavengers, such as hydroquinone. Thus, peroxy radicals ( $RO_2\cdot$ ) generated from radicals trapped in the irradiated solid reacting with  $O_2$  during dissolution are likely candidates for the initial precursors. The exact mechanism by which the CL occurs is difficult to ascertain but may involve a direct reaction of  $RO_2\cdot$  radicals with DPBF, energy transfer from an excited carbonyl produced by disproportionation of  $RO_2\cdot$  radicals,<sup>8</sup> or decomposition of some other intermediate product. As a probe for an excited triplet state precursor we have used anthracene (*ca.*  $10^{-3}$  mol dm<sup>-3</sup>) dispersed in an aqueous solution of micelles in addition to DPBF and find that the DPBF-CL is suppressed in this instance. Anthracene alone in micelles exhibits a luminescence ( $\lambda_{\max}$  *ca.* 390 nm)

with similar characteristics to that of DPBF but with an enhancement of only a factor of 2 over LL.

The original LL is extremely weak and the dose range over which it can be calibrated is limited<sup>1b</sup> even when employing extremely sensitive electronic equipment. The CL which is many times enhanced as for DPBF (or luminol reported previously<sup>9</sup>) may offer a potentially more sensitive system for applications in dosimetry. Furthermore, in this context the utilisation of aqueous solutions containing micelles, as in scintillation work, extends the range of organic fluorescers which can be employed. This medium allows, in addition to efficient dispersion of the fluorescers, rapid dissolution of many types of carbohydrate essential to the detection of the emission, whereas an aqueous organic solvent limits the choice of carbohydrate also.

(Received, 11th October 1978; Com. 1098.)

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