

Theory of light emission from γ -ray-irradiated organic substances when dissolved

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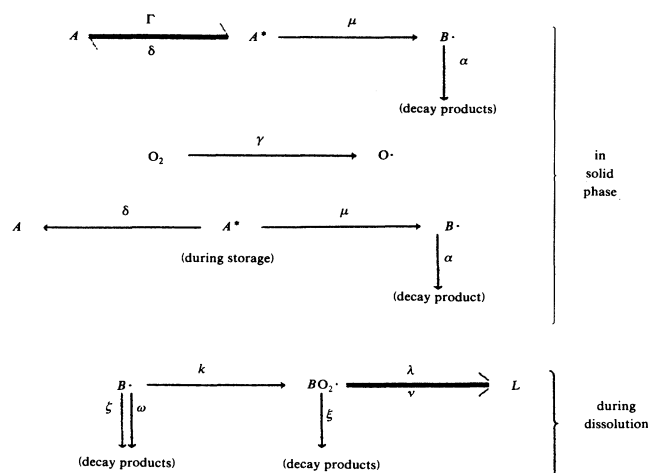
(Received 7 August 1992)

A theoretical model to explain general properties of lyoluminescence, a process which emits light when certain substances irradiated with ionizing radiations are dissolved in a suitable solvent, has been developed. The model has been developed utilizing the existing schemes and postulates of lyoluminescence. The model fits well with experimental results.

Lyoluminescence (LL) is a process by which certain substances on exposure to ionizing radiations emit light when dissolved in a suitable solvent. LL was discovered about 100 years ago by Wiedemann and Schmidt.¹ Although LL was found to be useful in radiation dosimetry and much work has been done in this field,² no consistent and coherent theoretical model exists for the quantitative predictions of LL. Starting with basic interactions we, in this present work, developed a kinetic model considering all possible physico-chemical processes, utilizing existing major concepts and postulates of the phenomenon. It is to be noted in this connection that the application of a similar kinetic model in radiation-effect studies in materials has proven effective in producing good results.³ The model thus developed is capable of a quantitative prediction of the general behavior of LL. We present in this article the mechanism of LL from organic substances upon γ -ray irradiation.

On γ -ray irradiation, energetic electrons deposit energy in the sample and free radicals are formed on breakage of chemical bonds of the sample. Although the exact process of the light emission has not yet been positively identified, it has been known⁴ that free radicals thus formed play a key role in LL. Of all possible schemes to explain LL, the Russell-Vassil'ev (RV) scheme^{5,6} seems to be capable of explaining many of the features of LL. According to the RV scheme, alkyl radicals are produced in the sample during irradiation which are then oxidized to form peroxy radicals on dissolution. These then combine to form excited carbonyls (triplet) which during transition to ground state emit light in the wavelength range 397–510 nm. Deexcitation is, however, one of the several mechanisms by which the peroxy radicals take part in the emission of light, the details of which are discussed by Ettinger and Puite.⁷ According to Ettinger and Puite, the oxygen present in the sample is responsible for oxidation of the alkyl radicals.

It is obvious, therefore, that in LL the entire process takes place in two distinct stages: one in the solid phase of the sample during irradiation and storage and the other in the liquid phase during dissolution. The entire process can be represented by a rate kinetic model schematically represented below:



Here A^* is the excited molecule of the sample (A) produced with a frequency Γ on irradiation, which then may break with a frequency μ to form alkyl radicals ($B\cdot$) or may quench back with a frequency δ ($B\cdot$ may also decay at a rate α). Also during irradiation, oxygen present in the sample is dissociated at a frequency γ to form reactive nascent oxygen ($O\cdot$), which is lost in subsequent reactions. One may note that both Γ and γ are proportional to the irradiation dose rate. The solid sample after irradiation for a time T is usually stored for some time (say τ) before dissolution. The rate kinetic equations representing the reactions proceeding during the solid phase represented above can be written as

$$[\dot{A}^*] = \Gamma[A] - (\delta + \mu)[A^*], \quad (1)$$

$$[\dot{B}\cdot] = \mu[A^*] - \alpha[B\cdot], \quad (2)$$

$$[\dot{O}\cdot] = -\gamma[O_2], \quad (3)$$

$$[\dot{A}^*] = -(\mu + \delta)[A^*], \quad (4)$$

$$[\dot{B}\cdot] = \mu[A^*] - \alpha[B\cdot]. \quad (5)$$

The last two equations are derived from the reactions that take place during storage of the sample after irradiation as shown above.

Even at the highest dosage commonly used for irradiation, a negligible fraction of the parent molecule would be affected by the irradiation and hence $[A]$ has been approximated to be a constant. The solution of Eq. (1) is given by

$$[A^*] = \frac{\Gamma[A]}{(\delta + \mu)} [1 - e^{-(\delta + \mu)t}], \quad (6)$$

the solution of Eq. (2) becomes

$$[B\cdot] = \frac{\mu\Gamma[A]}{(\delta + \mu)\alpha} [1 - e^{-\alpha T}] - \frac{\mu\Gamma[A]}{(\delta + \mu)(\delta + \mu - \alpha)} [e^{-\alpha T} - e^{-(\delta + \mu)T}], \quad (7)$$

and the solution of Eq. (3) is given by

$$[O_2] = [O_2]_0 e^{-\gamma T}, \quad (8)$$

where $[O_2]_0$ is the oxygen concentration initially present in the sample. It is to be noted in this connection that the unit of time has been conveniently chosen in the units of dose received (Gy). Solutions of Eqs. (4) and (5) are pretty trivial and using Eqs. (6) and (7) in the solutions of Eqs. (4) and (5), we get

$$[B\cdot] = \frac{\mu\Gamma[A]e^{-\alpha T}}{\alpha(\delta + \mu - \alpha)} [1 - e^{-\alpha T}] - \frac{\mu\Gamma[A]e^{-(\mu + \delta)T}}{(\delta + \mu - \alpha)(\mu + \delta)} [1 - e^{-(\mu + \delta)T}]. \quad (9)$$

Therefore, $[B\cdot]$ is the alkyl radical concentration just prior to dissolution.

During dissolution, as shown in the reaction schematics, alkyl radicals ($B\cdot$) thus formed combine with the oxygen forming peroxy radicals ($BO_2\cdot$) at a rate $k[O_2]$ which subsequently recombine forming the excited carbonyls in the triplet state which emit light (L) during transition to the ground state or through other photochemical reactions. Here, λ, ν are two- and three-body photochemical reaction frequencies, respectively; ξ and ω are the two- and three-body loss rates of the alkyl radicals ($B\cdot$), respectively, and ξ is the loss rate for the peroxy radicals ($BO_2\cdot$). The relevant rate kinetic equations for the above processes can be written and the solutions can be obtained similarly. The details of derivation were presented elsewhere;⁸ we shall present here the final result.

The concentration of peroxy radicals thus formed is given by

$$[BO_2\cdot] = \frac{k[O_2]_0 e^{-\gamma T}}{\xi} \frac{(\sigma/\omega)[B\cdot]_r e^{-\sigma t}}{[B\cdot]_r (1 - e^{-\sigma t}) + (\sigma/\omega)}, \quad (10)$$

where $\sigma = \xi + k[O_2]$ (assuming peroxy radicals are formed in equilibrium).

According to the scheme described above the total light yield (L) will be

$$L = \lambda \int_0^\infty [BO_2\cdot] dt + \nu \int_0^\infty [BO_2\cdot]^2 dt. \quad (11)$$

Substituting the value of $[BO_2\cdot]$ from Eq. (9) in the above equation, we get

$$L = \frac{\lambda k [O_2]_0 e^{-\gamma T}}{\omega \xi} \ln \left[1 + \frac{[B\cdot]_r}{(\sigma/\omega)} \right] + \frac{\sigma \nu k^2 [O_2]_0^2 e^{-2\gamma T}}{\omega^2 \xi^2} \left[\frac{[B\cdot]_r}{(\sigma/\omega)} - \ln \left[1 + \frac{[B\cdot]_r}{(\sigma/\omega)} \right] \right]. \quad (12)$$

This is the equation for total light yield.

The model was then tested with experiments carried out with lactose (lactose monohydrate obtained from BDH Chemicals). Two types of measurements are relevant to test the validity of this model, namely the measurement of total light yield (L) and the concentration of alkyl radicals $[B\cdot]$. The total light yield was measured using conventional lyoluminescence reader² which essentially consists of a glass cell coupled on top of a photomultiplier in which the irradiated sample was allowed to dissolve in a suitable solvent. The total light yield was measured with conventional electronics, while the concentration of alkyl radicals $[B\cdot]$ was obtained from ESR experiments.⁹ Direct comparison of $[B\cdot]$ and L as obtained from experiments with Eqs. (9) and (12), respectively, is difficult as values of all the parameters are not known. In view of this, we resort to fitting these equations with experimental observations. This type of fitting is not uncommon in physics, rather the parameters obtained from such fitting give useful information on the mechanism as is shown below.

ESR data providing absolute concentrations of alkyl radicals are available for a few samples, of which complete data up to saturation are available for lactose only. Hence we choose lactose in our fitting procedure with Eq. (9). The fitting of Eq. (9) with ESR measurements for lactose is presented in Fig. 1. The values of the parameters obtained from the fitting are as follows: $\mu\Gamma[A] = 6.3 \times 10^9 \text{ Gy}^{-2} \text{ g}^{-1}$, $\alpha = 2.78 \times 10^{-5} \text{ Gy}^{-1}$, $(\mu + \delta) = 1.28 \times 10^{-3} \text{ Gy}^{-1}$, and $\tau = 195.6 \text{ Gy}$. Although we could not obtain values of all the individual parameters, we still gain knowledge of the shelf life (α^{-1}) of alkyl radicals, lifetime $[(\mu + \delta)^{-1}]$ of excited states A^* ,

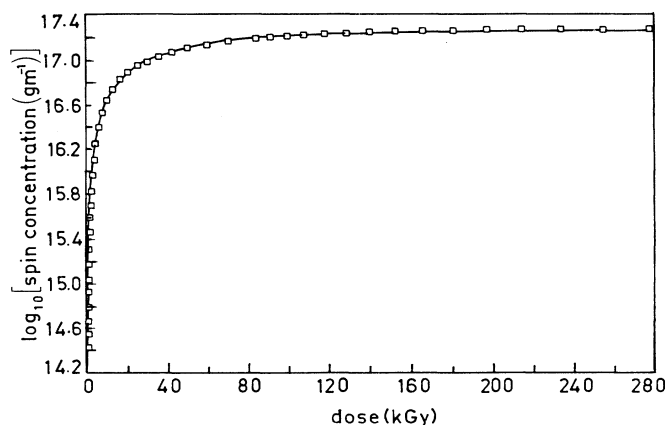


FIG. 1. Comparison of experimental results of lactose obtained from ESR spectroscopy with fitted values of Eq. (9). (Dose rate: 20 Gy/min.)

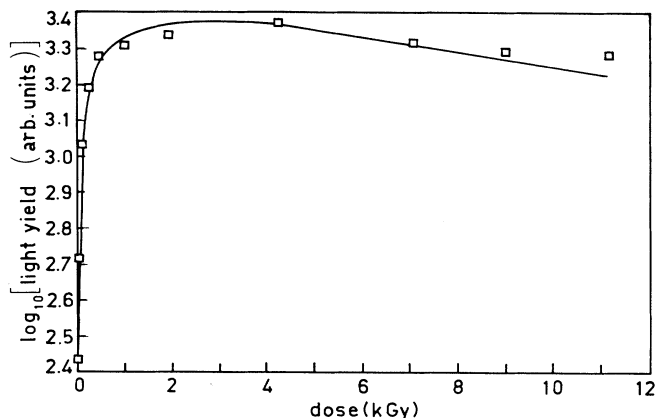


FIG. 2. Comparison of experimental results of lactose obtained from lyoluminescence studies with fitted values of Eq. (12). (Dose rate: 12 Gy/min.)

and the storage time (τ). In this experiment, lactose was irradiated with a dose rate 20 Gy/min and hence we obtain the shelf lives of alkyl radicals (α^{-1}) to be about 30 h and storage time (τ) to be about 10 min. Although the storage time, etc., was not specified in the experiment so as to verify, we know that shelf lives of alkyl radicals are usually long (several days) and the storage time (time between stoppage of irradiation and dissolution) obtained is

not unrealistic.

Using the interpolated values of the radical concentration $[B\cdot]$ obtained from the fit of ESR data, LL data were chisquare-fitted with Eq. (12). The fitting of the data is shown in Fig. 2. Values of the parameters thus obtained from such fitting are $\lambda k[O_2]/\xi\omega = 1.695 \times 10^{-9}$ Gy; $\sigma\nu k^2[O_2]_0^2/\xi^2\omega^2 = 1.136 \times 10^6$ in arbitrary units; $\sigma/\omega = 1.30 \times 10^{13} \text{ g}^{-1}$ and $\gamma = 6.729 \times 10^{-5} \text{ Gy}^{-1}$.

The first two parameters represent amplitudes of two-body and three-body light yielding processes, respectively, the third one represents threshold radical concentrations for the saturation of light emissive processes, and γ was defined before.

The good agreement of the results of two independent experiments with Eqs. (9) and (12) as observed from the figures indicates that the kinetic model presented in this paper provides a possible mechanism of LL. The paper also verifies the postulates of Ettinger and Puite⁷ of the oxidation reaction utilizing the oxygen present in the sample, otherwise γ would have been zero. Nonzero values of γ is responsible for the drop in the light yield after saturation as observed in the LL curve (see Fig. 2). It is to be noted in this connection that this drop in light yield after saturation had until now remained unexplained. This model is also found to provide good agreement with experimental results carried out with sucrose and mannose, which was presented in Ref. 8, and with measured light yield of heat-treated samples, which will be published soon.

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