

Application of a rate kinetic model of lyoluminescence on heat-treated samples

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A rate kinetic model to explain the general behavior of lyoluminescence has been recently proposed. The present work demonstrates another example of the validity of the model in explaining the observed effect of lyoluminescence from heat-treated samples. The samples after irradiation with γ rays were kept molten at their melting points for different periods of time before dissolution. The light yield on dissolution was found to decrease with samples kept molten for longer periods of time. It has been shown that the observed effect can be explained when changes in the rate of reaction mechanism and diffusion of oxygen due to heating are incorporated in the model.

I. INTRODUCTION

Lyoluminescence (LL) is a mechanism by which some substances irradiated with ionizing radiations emit light when dissolved in a suitable solvent. Although LL was discovered about one hundred years ago,³ no consistent theory for quantitative prediction of the light yield exists. Recently, we proposed a rate kinetic model^{1,2} based on all possible physicochemical processes which is capable of explaining many of the features of LL. One of the papers¹ presents in brief the rate kinetic model and its comparison with experimental results obtained from lactose, while the other² presents the rate kinetic model in detail and comparison of the model with measured results from other saccharides—namely, mannose and sucrose. We demonstrate in this paper another example of the validity of the model in explaining the observed behavior of heat-treated samples when dissolved in a suitable solvent. This paper deals with heating of saccharides (mannose and sucrose) irradiated with γ rays at their melting points. The samples were kept in the molten state for different periods of time. The samples thus treated were then dissolved in pure water and the light output was detected using a LL reader developed in our laboratory.⁴ The model gives a good fit with the observed results when the effects of heating on various parameters and on the reaction mechanism are included. We present in Sec. II the experimental details, while in Sec. III we present the extension of the rate kinetic model^{1,2} to explain the observed behavior for heat-treated samples. In Sec. IV we present a comparison of experimental results with our extended model and the conclusion is presented in Sec. V.

II. EXPERIMENTAL METHODS

In the present experiment, a monosachharide (mannose, obtained from Sigma Chemicals), and a disachharide (sucrose, obtained from BDH Chemicals), were irradiated using the irradiation facility available at Saha Institute of Nuclear Physics, Calcutta. Samples

were irradiated for several hours at a dose rate of 2 Gy/sec. The samples thus irradiated were taken in stoppered glass vials and melted in a nitrogen environment in a temperature-controlled oil bath. The melting of the samples was checked visually. Fully melted samples were kept in the neighborhood of the melting temperatures for different periods of time before allowing them to resolidify at room temperature. We have also noted that irradiated samples melt at temperatures slightly lower than the melting point, which was also observed by Bartlett, Brown, and Durrani,⁵ and explained on the basis of changes in the solid matrix after irradiation. Both electron spin resonance (ESR) spectra and light yield from unirradiated and irradiated samples were measured. ESR spectra was taken using a Varian E-112 spectrometer (X band, 100-kHz modulation frequency) available at the Regional Sophisticated Instrumentation Centre located at Bose Institute, Calcutta. Light yield was measured using a solvent-injection-type dissolution apparatus described elsewhere.⁴ This consists of a dissolution chamber placed on top of a photomultiplier tube. Integrated total light output was recorded using conventional electronics.

III. EXTENDED RATE KINETIC MODEL

According to the rate kinetic model proposed by us, on γ irradiation, alkyl radicals are formed in the sample on breakage of chemical bonds. The model uses the Russel-Vassil'ev (RV) reaction scheme^{6,7} and the postulates of Ettinger and Puite⁸ used in explaining LL. According to the RV scheme, alkyl radicals thus produced are oxidized to form peroxy radicals on dissolution. These then combine to form excited carbonyls in their triplet state, which during transition to their ground state emit light in the wavelength range 397–510 nm. There might be other mechanisms by which peroxy radicals take part in the emission of light. We refer the readers to the schematic diagram of the possible reaction mechanisms described in our earlier paper.¹ According to this scheme, the total light yield (L) from an irradiated sample can be given by the equation

$$L = L_1 e^{-\gamma T} \ln \left[1 + \frac{[B^*]}{L_3} \right] + L_2 e^{-2\gamma T} \left[\frac{[B^*]}{L_3} - \ln \left[1 + \frac{[B^*]}{L_3} \right] \right], \quad (1)$$

where $[B^*]$ is the concentration of alkyl radicals immediately before the melting of the sample and $L_1 = \lambda k [O_2] / \omega \xi$, $L_2 = \sigma \nu k^2 [O_2]^2 / \omega^2 \xi^2$, and $L_3 = \sigma / \omega$. Here λ , μ , σ , ζ , ξ , and ω have the same meanings as in Ref. 1.

On heating we expect, in general, a change in the concentration of alkyl radicals by enhanced reaction losses and a change in the concentration of oxygen present in the sample due to diffusion losses. These two effects will play an important role in the variation of the light yield in the LL process. Hence, in order to explain the change due to heating, we have to incorporate the diffusion loss of absorbed oxygen and the reaction loss of radicals from the heated sample.

In considering the reaction loss of radicals in the heated sample, the enhancements of the reaction frequency due to rise in temperature and due to the increase in diffusivity are not considered separately but a net resulting enhancement in reaction frequency is considered. Also, since the two-body reaction rates are larger than many-body reaction rates, we consider in this work only the two-body processes. Therefore, the reaction rate α in the reaction mechanism for a solid phase untreated sample will now be different, say η . The reaction may be described as



when η is the bimolecular loss frequency of B in the heated sample.

At any particular temperature, the free-radical popula-

$$[O_2](x, y, z, t) = \int \int \int \frac{dx' dy' dz'}{(4\pi Dt)^{3/2}} [O_2](x', y', z', 0) \exp - \frac{(x-x')^2 + (y-y')^2 + (z-z')^2}{4Dt}, \quad (4)$$

where t is the melting time of the sample. The convolution integral with the initial number density $[O_2](x', y', z', 0)$ is evaluated considering that the diffusion loss occurs only through the top free surface of the sample in the test tube (z' being along the axis of the test tube). To eliminate the effect of diffusion from the sides and the bottom of the test tube (which we assume here to be flat) we integrate out the x' and y' coordinates (from $-\infty$ to $+\infty$) and evaluate the z' integral from $z' = -h$ to $z' = h$, h being the height of the sample in the tube (this eliminates the transverse diffusion gradient everywhere and also eliminates the axial diffusion gradient at $z' = 0$). Thus we get

$$[O_2](x, y, z, t) = \left[\frac{p[O_2]}{2} \right] \left\{ \operatorname{erf} \left[\frac{h-z}{\sqrt{4Dt}} \right] + \operatorname{erf} \left[\frac{h+z}{\sqrt{4Dt}} \right] \right\}. \quad (5)$$

tion remaining in an irradiated sample at time t can best be described by the first-order decay equation

$$[\dot{B}^*] = -\eta[B^*],$$

or

$$[B^*_t] = [B^*]_0 e^{-\eta t},$$

where t is the time for which the irradiated sample is kept at its melting point, $[B^*]_t$ is the free-radical population at annealing time t , and $[B^*]_0$ is the population just prior to annealing (i.e., at time $t = 0$). This is actually the radical concentration of the sample after both irradiation for time T and storage for a period τ .

The other effect which influences the light yield of heat-treated samples is the diffusion loss of the oxygen absorbed in the sample. This diffusion loss is slightly complicated by the fact that not only does loss occur over a range of temperature (at the time of melting) and over different phases (during melting), but the absorption of oxygen is also temperature dependent. This diffusion loss may be considered to occur in two stages—one during heating and melting of the solid sample, and the other during which the sample is maintained molten over a variable period of time (heat-treatment time). During heating and before reaching the melting point some oxygen is lost from the sample. Defining p as the survival factor, the amount of oxygen left in the sample can be written as $p[O_2]_0$. The diffusion loss of oxygen from the sample, when the sample is held at its melting point for a variable period of time, can be written as

$$\left[\frac{\partial}{\partial t} - D \nabla^2 \right] [O_2] = 0, \quad (3)$$

where D is the diffusion constant of O_2 in the molten sample. This gives

The volume-averaged oxygen concentration is thus obtained as

$$[O_2] = p[O_2]_0 \left\{ \operatorname{erf} \left[\sqrt{h^2/Dt} \right] - \left[\sqrt{Dt/\pi h^2} \right] \times \left[1 - e^{-h^2/Dt} \right] \right\} = p[O_2]_0 f(t). \quad (6)$$

It is to be noted here that the error function used in $f(t)$ was computed using the series representation

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \left\{ \sum_{j=0}^{\infty} (-1)^j \frac{x^{2j+1}}{(2j+1)j!} \right\} \quad (7)$$

which is valid for small x (for $x > 3.1$, $\operatorname{erf}(x) \cong 1.0$ has been used for ease of calculation).

Therefore the equation for total light yield [Eq. (1)] for samples without heat treatment is modified as follows when the effect of heat treatment is included:

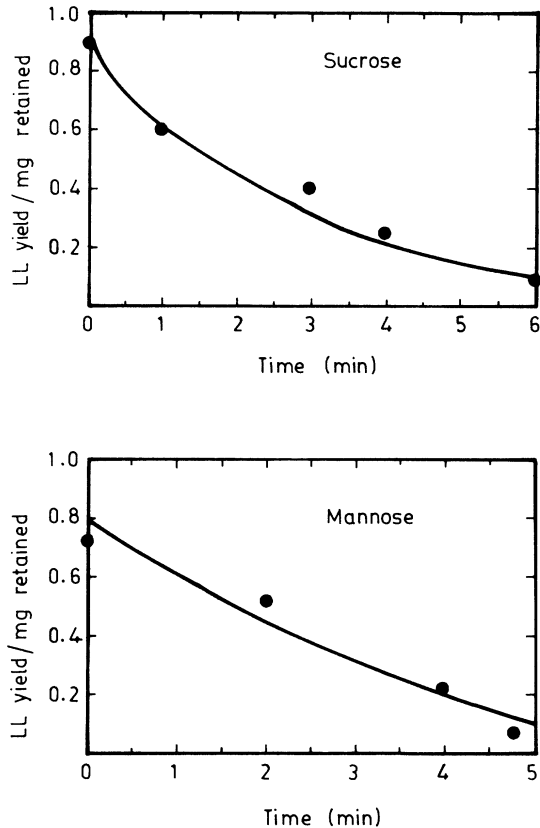


FIG. 1. Theoretical fit to the results of fraction of light yield retained per mg of sucrose and mannose after heat treatment.

$$\begin{aligned}
 L = & L_1 p f(t) e^{-\gamma T} \ln \left[1 + \frac{[B^*]}{L_3} e^{-\eta t} \right] \\
 & + L_2 p^2 f^2(t) e^{-2\gamma T} \\
 & \times \left[\frac{[B^*]}{L_3} e^{-\eta t} - \ln \left[1 + \frac{[B^*]}{L_3} e^{-\eta t} \right] \right]. \quad (8)
 \end{aligned}$$

IV. COMPARISON OF EXTENDED MODEL WITH EXPERIMENTAL RESULTS

In this section, attempts have been made to predict the time-dependent decay of the LL yield in γ -irradiated organic samples following heat treatment at the melting point, using Eq. (8), and to compare this with measured results. The integrated light yields (L) from samples irradiated at a particular dose and kept molten at a temperature close to the melting point for different times were measured. As stated earlier, the radical concentration corresponding to the particular dose can be obtained from the ESR dose response curve. ESR data for man-

TABLE I. Values of the parameters obtained by fitting the data of heat-treated mannose and sucrose with Eq. (8). The irradiation dosages of mannose and sucrose are 7200 and 928 Gy, respectively.

Sample	p	η (Gy ⁻¹)	t_0 (min)
Mannose	0.779	1.55	35
Sucrose	0.794	0.44	520

nose^{5,9} and sucrose⁵ available only in the linear region (not up to the saturation dose) have been fitted to an equation of the form

$$\ln[B^*] = \ln a + b \ln T, \quad (9)$$

where $[B^*]$ is the concentration of alkyl radicals, a and b are constants, and T is the irradiation time measured in units of dose received. Values of different parameters such as $\nu k[O_2]/\xi\lambda$, $\sigma\nu/\lambda^2$, γ , and σ/ω are obtained using our model and are already presented in our earlier paper.² These values will be utilized in Eq. (8) in fitting the experimental results of heat-treated samples. Using the values of these parameters and interpolated values of radical concentrations, the experimental data related to decay curves of mannose and sucrose have been compared with Eq. (8) using χ^2 fitting. The fitted curves are presented in Fig. 1 along with the experimental results. The fitting gives some valuable information, such as the radical recombination reaction frequency η during melting. It also provides the value of two other parameters (p and t_0) related to diffusion of oxygen inside the sample due to annealing. Values of these parameters are presented in Table I. It is worth mentioning that the diffusion constant D of oxygen through the sample during melting can be found from the values of $t_0 (=h^2/D)$, if the sample height h is known.

V. CONCLUSION

Results from heat-treated samples are found to be in agreement with the results predicted using the rate kinetic model of LL. The agreement demonstrates the ability of our model^{1,2} to predict the LL dose response as well as the radical recombination kinetics as measured by the LL technique. The present study also indicates that oxygen diffuses very slowly through the sample, as is evidenced from the large value of t_0 . So it is obvious that the LL yield decreases with time mainly due to the radical reaction loss. From the value of p , we also see that about 20% of oxygen is lost from the sample during melting.

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