calization do not form separated ion pairs in the excited state. The reactions that do occur involve charge exchange ($-OH + Na^+ \rightarrow -ONa + H^+$) and cation attachment ($M + Li^+ \rightarrow MLi^+$). Alpha cyclodextrin has been a good model molecule for these studies. These processes occur for large biomolecules that do not form charge transfer bonds, either because of absence of acidic hydrogens or random orientation of molecular aggregates. Maytansine, a tumor inhibitor that contains sugar moieties and a peptide chain, is an example of a molecule that undergoes this reaction.

Summary. Fission fragments produce tracks in thin films of biological molecules that form a superradiant state because of the high excitation density. Molecular excitation is similar to picosecond laser irradiation, in that nonlinear effects are observed. The added feature is that the acoustic pulse that follows the excitation gives a means of directly identifying products of fast chemical reactions that occur.

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NONHOMOGENOUS CHEMICAL KINETICS IN PULSED PROTON RADIOLUMINESCENCE

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The spatial distribution of absorbed energy influences the yield of chemically active species in a medium exposed to radiation. Diffusive motion of molecules rapidly destroys the initial distribution of primary species in most liquids; consequently, stroboscopic techniques must be used to observe the effects of nonhomogenous chemical kinetics directly. Pulsed radiolysis with electrons has been used extensively to prove the subnanosecond time region. However, the application of this method to other types of radiation, in particular radiations with high linear energy transfer (LET), is limited by the requirement of a large dose per pulse to achieve significant absorption by the chemical species under investigation (1). The use of fluorescence, rather than absorption, to detect the presence of chemical species circumvents this difficulty. By time-resolve emission spectroscopy, the evolution of a small population of excited states can be studied under varied radiation conditions with subnanosecond time

resolution. Through fluorescence quenching, the time evolution of the concentration of nonradiative species can also be investigated.

Samples of 0.04 M benzene in cyclohexane (Nanograde, Mallinckrodt Inc., St. Louis, Mo.) were deaerated by helium purging and placed in an irradiation cell consisting of a cylindrical stainless steel chamber with 2.5 μm Havar foil (Hamilton Technology, Inc., Lancaster, Pa.) for proton beam entrance and a quartz window for light collection. An adequate flow rate was maintained to prevent buildup of stable radiolysis products in the irradiated volume. A scanning spectrometer was used to select a 4-nm band centered about a wavelength of 285 nm. The liquid was irradiated with subnanosecond pulses of protons from a 2 MV accelerator with a 3.33 MHz high voltage radio frequency oscillator for beam chopping. Fluorescence decay was measured by the single photon counting method with a signal derived from the chopper voltage providing zero time reference. Overall time resolution of the system is limited to about 1.5 ns full width at half maximum by response of the photomultiplier. The sample reservoir and irradiation cell were maintained to ± 0.2°C over a temperature range of 15–50°C by means of a thermistor-controlled cooling-heating system.

Fig. 1 compares time-resolved emission from benzene in cyclohexane excited by pulsed proton irradiation at three energies with the fluorescence decay observed with ultraviolet (UV) irradiation. The nonexponential character of the fluorescence decay

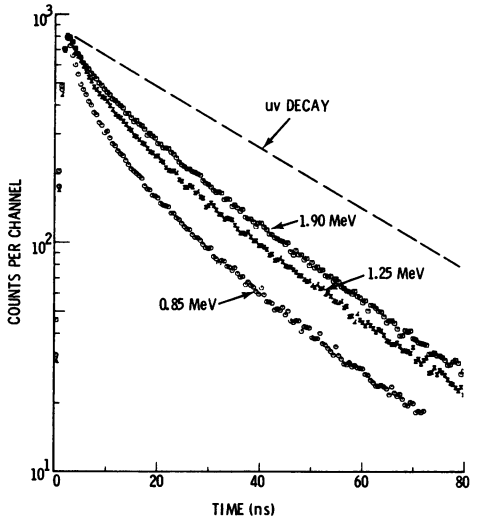

FIGURE 1

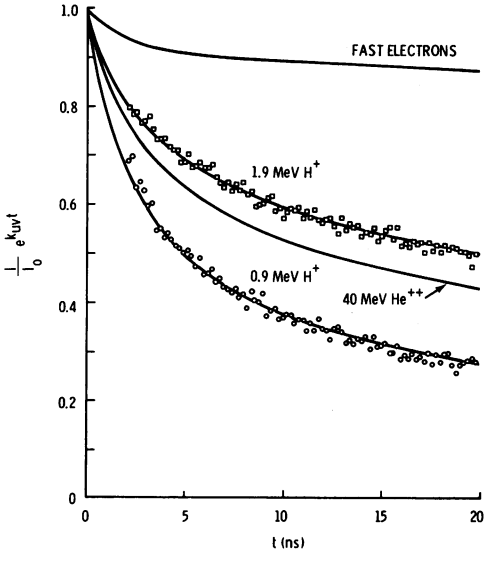

FIGURE 2

FIGURE 1 Fluorescence of benzene in cyclohexane irradiated with protons at several energies. Dashed curve represents exponential decay observed with UV irradiation.

FIGURE 2 Fluorescence predicted by the intratrack quenching model for several types of radiation. Ordinate is the ratio of fluorescence intensity with ionizing and UV irradiation.

with proton irradiation results from a time-dependent concentration of quenching species not present under UV excitation (2). To develop a model for this effect, we assume that excited singlet states of benzene and the radiochemical quenchers are formed in spurs centered about the initial sites of ionization of the liquid. The distribution of chemical species within each spur is assumed to be Gaussian with a variance $\sigma^2(t) = r_0^2 + 2Dt$, where r_0 is the initial spur radius and D is the diffusion coefficient of quenchers and excited states. The model predicts a fluorescence decay of the form

$$-\frac{1}{N_*}\frac{dN_*}{dt} = k_{UV} + k_{spur}(1 + \langle g(\mathbf{r};t)\rangle), \tag{1}$$

where k_{UV} is the quenching rate by solvent perturbations observed with UV irradiation, k_{spur} is the rate of radiochemical quenching in isolated spurs, and

$$g(\mathbf{r};t) = \sum_{\mathbf{r}_j \neq \mathbf{r}} \exp(-(\mathbf{r} - \mathbf{r}_j)^2/4\sigma^2(t)), \tag{2}$$

is the probability that an excited state at position $\mathbf{r}$ will be quenched by radiochemical species from other sites of ionization. We call this the "spur overlap."

Due to the low beam fluence, the probability of chemical reaction between species formed in different proton tracks is small during the time interval over which the fluorescence decay is observed. Hence, we refer to the quenching by radiochemical species as an "intratrack" quenching. As a first approximation, we may neglect the radial dispersion of ionization in the proton track and use the result of Ganguly and Magee (3) to estimate the spur overlap. In this approximation, the predicted fluorescence decay is

$$-\frac{1}{N_*}\frac{dN_*}{dt} = k_{UV} + \frac{k_Q G_Q}{8\sigma^3(t)} + \frac{k_Q G_Q S}{4\sigma^2(t) W}, \tag{3}$$

where k_Q is the second-order quenching rate constant, G_Q is the yield of radiochemical quenchers, S is the stopping power, and W is the energy absorbed per ion. Fig. 2 illustrates the amount of intratrack quenching predicted by Eq. 3 for various types of radiation. Parameters of the model were determined by best fit to the data for 1.9 MeV protons. For fast electrons, the last term in Eq. 3 is small and the fluorescence decay is nearly exponential beyond 5 ns. For proton irradiation from our 2 MV accelerator, the last term in Eq. 3 predominates. Fig. 2 shows that without further adjustment of parameters, the model correctly predicts the fluorescence decay with 0.9 MeV protons.

The fluorescence decay predicted by Eq. 3 for 40 MeV alpha particle irradiation is also shown in Fig. 2. For these energetic heavy ions, transport of energy away from the track core by high-energy secondary electrons should result in a more diffuse pattern of energy deposition than for proton irradiation of the same stopping power. Hence, Eq. 3 may overestimate the intratrack quenching in this case. Calculations are

currently in progress to estimate the effect of the radial distribution of ionization on the fluorescence decay. Monte Carlo techniques are being used to determine the initial spatial distribution of spurs, and the spur overlap is calculated from Eq. 2. The results of these calculations will be compared with measurements of the fluorescence decay with proton and alpha irradiation at the same stopping power. These experiments should provide a crucial test of our intratrack quenching model.

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PICOSECOND PHOTODISSOCIATION AND SUBSEQUENT RECOMBINATION PROCESSES IN CARBOXYHEMOGLOBIN, CARBOXYMYOGLOBIN, AND OXYMYOGLOBIN

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The central problem in the study of hemoglobin is to understand the mechanism of cooperativity among the four subunits of the molecule. This cooperativity is evident in the sigmoidal nature of the oxygen saturation (equilibrium) curve and in the Bohr effect. Paramount in the understanding of cooperativity is the study of the trigger mechanism of ligand release and the tertiary and quaternary protein structural changes subsequent to this. Picosecond time-resolved spectroscopy is a relatively new experimental method capable of critically examining the dynamics of ultrafast molecular events in proteins—processes serving as precursors to other extensive protein structural changes. The application of this method with regard to photodissociation measurements on heme proteins permits one to obtain rate data on such processes in a heretofore inaccessible time region. This information, in turn, allows an analysis of the allosteric mechanism(s) of cooperativity from a totally different experimental perspective.

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