BNWL-SA 4314
CONF-720530--8

FLUORESCENCE EXCITATION AND QUENCHING IN ORGANIC
LIQUIDS UNDER ULTRA-VIOLET AND IONIZING RADIATION*

M. L. West

Battelle
Pacific Northwest Laboratories
Richland, Washington

May, 1972

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Single photon counting techniques have been used to study the fluorescence response and time dependence of dilute solutions of benzene in cyclohexane excited by proton and ultra-violet (u.v.) radiation. Luminescence emitted after proton excitation decays non-exponentially whereas the same solutions under u.v. excitation show exponential decay. We have attempted to show that these results are consistent with a diffusional quenching model whereby excited benzene molecules created along a localized proton track are quenched as they diffuse from initial reaction sites.

The experimental technique⁽¹⁾ has been previously described and is illustrated in Fig. 1. Proton pulses of less than 0.5 nsec are available from a Van de Graaff accelerator using a 3.330 MHz high voltage oscillator for chopping. A commercially available deuterium flash lamp is used for u.v. excitation measurements. Emitted photons from the excited sample are collected with quartz optics, passed through a scanning spectrometer and focused on a cooled photomultiplier tube. For u.v. excitation, a second detector observes the exciting light source, and for proton excitation, a second signal is derived from the r.f. chopper. Single photon pulses

*This paper is based on work performed under United States Atomic Energy Contract AT(45-1)-1830.

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

selected within the gated period of a time to pulse height converter are counted as a function of their delay after the zero time pulse and displayed in a multichannel analyzer that is programmed by a small on-line digital computer.

Emission spectra (Fig. 2) are identical under the two modes of excitation and correspond to monomer emission from the first excited singlet state of benzene. Decay of this singlet emission is shown in Fig. 3. The exponential decay under u.v. excitation is properly described by a single time independent decay rate K_{UV} . Fluorescence decay under proton excitation is non-exponential and has been parameterized by a time dependent decay rate $K(t)$, defined as the logarithmic derivative of intensity with respect to time. The lower curves in Fig. 3 illustrate this time dependence over several orders of magnitude of fluorescence decay. Decay curves were obtained for the temperature range 5 - 50°C and in all cases the decay from proton excitation was non-exponential.

An interpretation of these differences in decay must come from a consideration of the special characteristics of excitations induced by ionizing radiation. These excitations do not take place uniformly throughout the medium but occur in localized volumes where the density of radicals and other transient species can be exceedingly high. Track structure models developed to explain LET effects of ionizing radiation have grouped these localized volumes into spurs, for the case of low LET radiation, and tracks for more densely ionizing radiation. Intermediate entities include blobs and short tracks. Based on these models, a 1-2 MeV proton can be

MASTER

approximated by a cylindrical track. In such tracks one has to consider the possibility of radical-radical and radical-excited state interactions as well as the effects of diffusion from these highly localized volumes.

Existing models based on the inhomogeneous distribution of radicals were developed primarily to explain molecular and radical yields resulting from radical-radical and radical-scavenger interactions. Here we consider excited state-radical interactions and the resulting effects on fluorescence decay. These simultaneous effects of quenching and diffusion are mathematically described by the coupled equations,

$$\frac{\partial S^*(r,t)}{\partial t} = D \nabla^2 S^*(r,t) - K_{UV} S^*(r,t) - K_{RS} C_R(r,t) S^*(r,t) \quad (1)$$

$$\frac{\partial C_R(r,t)}{\partial t} = D \nabla^2 C_R(r,t) - K_{RR} C_R(r,t)^2 - K_{SR} S^*(r,t) \quad (2)$$

Quantities $S^*(r,t)$ and $C_R(r,t)$ are the space-time distributions of excited states and radicals, respectively; D is the diffusion coefficient; K_{UV} is a sum of the fluorescence emission and unimolecular quenching rates $[k_f + k_q]$ and equals the reciprocal of excited state lifetime for u.v. excitation; K_{RS} is the rate of excited state-radical interaction; K_{RR} is the rate of radical-scavenger interaction; ∇^2 is the Laplacian operator.

Boundary conditions appropriate for solutions of these equations have been considered for existing models of diffusion kinetics. The track is parameterized in terms of an initial radius r_0 and initial excited state and radical densities per unit track length. Excited state and radical densities are assumed to obey

$$S^*(r,t) = S(t) \phi(r,t) \quad (3)$$

$$C_R(r,t) = C_R(t) \phi(r,t) \quad (4)$$

where $S(t)$ and $C_R(t)$ are the total number of excited states and radicals at time t , respectively, and $\phi(r,t)$ is the probability density of finding an excited state or radical at (r,t) . This is the prescribed diffusion hypothesis of Samuel and Magee. (2)

Solution of equation (1) for quenching by a single type radical where that radical is assumed to disappear by radical-radical combination is

$$S^*(t) = S_0 e^{-K_{UV}t} e^{-K_{RS} \int_0^t R(t) dt} \quad (5)$$

where

$$R(t) = \frac{C_R(t)}{2\pi L(2r_0^2 + 4Dt)} \quad (6)$$

$$C_R(t) = \frac{C_0}{\frac{K_{RR}C_0}{8\pi DL} \ln \frac{r_0^2 + 2Dt}{r_0^2}} \quad (7)$$

and C_0/L is the number of initial radicals per unit track length.

A one radical model seems appropriate, as one does not expect great differences in the quenching rates of different radicals with excited molecules. This is also consistent with the view that quenching by radicals is a diffusion controlled process and that every encounter leads to deactivation of the excited molecule. Radical-radical reaction rates for aromatic hydrocarbons typically lie within 10^9 - 10^{10} lit/mole-sec with an upper limit of $1-2 \times 10^{10}$ lit/mole-sec.

Values of the excited state density $S^*(t)$ have been obtained by numerical integration of equation (5) for $K_{RR} = .5 \times 10^{10}$ lit/mole-sec (Fig. 4) and $K_{RR} = 1 \times 10^{10}$ lit/mole-sec. (Fig. 5). The fluorescence lifetime $\tau = 1/K_{UV}$ was taken as 3×10^8 sec. which corresponds to that of benzene in cyclohexane at

22 °C. The radical-excited state quenching rate was varied from a value of 0 lit/mole-sec. which gives exponential decay, to 10^{11} lit/mole-sec., which exceeds the upper limits of realistic values and causes noticeable non-exponential decay. This non-exponential decay for intermediate values of K_{RS} is perhaps better illustrated by plotting the logarithmic derivative of S^*/S as was done for the experimental data shown previously for proton excitation. From equation 5 we obtain the expression

$$\frac{d}{dt} \ln (S^*/S_0) = -K_{UV} - K_{RS}R(t) \quad (8)$$

Figures 6 and 7 display this logarithmic derivative of excited state density.

A comparison of these curves with our experimental decay curves for proton excitation shows that for K_{RR} in the range $0.5 - 1 \times 10^{10}$ lit/mole-sec, the radical-excited state quenching rate lies between $1-5 \times 10^{10}$ lit/mole-sec. This is consistent with values of $1-2 \times 10^{10}$ lit/mole-sec predicted for diffusion controlled reactions in cyclohexane where quenching occurs for every collision.

In Fig. 8 we have compared the predicted decay of spurs and tracks for rate constants, $K_{UV} = 3.3 \times 10^7 \text{ sec}^{-1}$, $K_{RR} = 10^{10}$ lit/mole-sec and $K_{RS} = 3 \times 10^{10}$ lit/mole-sec, to decay from u.v. excitation. For spur type distributions, representing low LET radiation, non-exponential decay is only observed for the first few nanoseconds and would likely be undetected in experiments of poor experimental resolution. For track type distributions, the non-exponential decay is apparent for the first 30-40 nanoseconds.

Although precise fits have not been made to the experimental fluorescence decay curves obtained for proton excitation, we have demonstrated that this model is consistent with the observed non-exponential decay. More stringent tests will come from investigations of liquid systems whose rate constants and track parameters have been tentatively fixed from radiation chemistry experiments on radical and molecular yields.

References

1. L. L. Nichols and W. E. Wilson, Appl. Opt., 7, 167 (1968).
2. A. H. Samuel and J. L. Magee, J. Chem. Phys. 21, 1080 (1953).

DELAY COINCIDENCE COUNTING SYSTEM

Figure 1

OPTICAL EMISSION SPECTRUM
OF BENZENE (.02 M) IN CYCLOHEXANE

Figure 2

Figure 3

Fig. 4

Fig. 5

Fig 6

Fig. 7

Fig. 8

COMPLIMENTARY COPY
FROM
TECHNICAL INFORMATION OPERATION
DO NOT RETURN