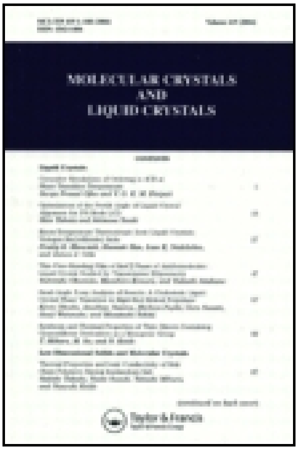

Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

Fluorescence Decay of Liquid Scintillator Systems After High-Energy Excitation

Peter K. Ludwig [a]

[a] Department of Chemistry and the Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana, 46556

Version of record first published: 21 Mar 2007.

To cite this article: Peter K. Ludwig (1968): Fluorescence Decay of Liquid Scintillator Systems After High-Energy Excitation, Molecular Crystals, 4:1-4, 147-156

To link to this article: http://dx.doi.org/10.1080/15421406808082906

Molecular Crystals, 1968. Vol. 4, pp. 147–156
© Copyright 1968 Gordon and Breach Science Publishers
Printed in Germany

Fluorescence Decay of Liquid Scintillator Systems After High-Energy Excitation.

PETER K. LUDWIG

Department of Chemistry and the Radiation Laboratory,† University of Notre Dame, Notre Dame, Indiana 46556

Received August 9, 1966

1. Introduction

The development of fast electro-optical instrumentation over the last ten years[1–9] has not only extended dynamic luminescence studies into the range of a few nanoseconds but also made such studies possible with low light intensities. Measurement of luminescence-decay curves over several decades of intensity variation are now feasible.

One result of the increased sensitivity of experimental techniques is the observation that many liquid scintillator systems exhibit a non-exponential fluorescence decay after UV or high-energy excitation. It has been shown that in the case of UV-excitation the observed deviations from exponentiality can be understood by considering the formation of excited dimers; i.e., excimers.[10, 11] It appears that excimer formation is a quite common phenomenon with planar aromatic scintillator molecules.[12, 13] For UV excitation the dynamic behavior of fluorescence of liquid scintillator systems seems therefore sufficiently understood.

A superficial inspection of liquid scintillator fluorescence after excitation by high-energy irradiation appears to indicate that the dynamic fluorescence behavior does not essentially differ from that of fluorescence excited by UV. This statement is particularly true in cases where the scintillator has a long decay-time ($>10^{-8}$ seconds) and has a strong tendency to form excimers. However, the fluorescence decay curves for fast liquid scintillators, which have no, or little, tendency for excimer formation, also show non-exponential decay characteristics when excited by high-energy radiation, although the same system after UV excitation

---

† The Radiation Laboratory is operated by the University of Notre Dame under contract with the U.S. Atomic Energy Commission. This is AEC Document No. C00-38-505.

displays exponential decay. The non-exponentiality, therefore, does not seem related to dimer formation. Figures 1 and 2 (discussed in Section 2) show the fluorescence decay curves for 30 kv X-ray and UV excited PPO and p-terphenyl in cyclohexane.

Similar differences of UV and high-energy excited liquid scintillator systems have been reported by Laustriat and Voltz.[14] Their systems consisted of aromatic solvents like benzene or toluene with small amounts of scintillator which presumably had no tendency for excimer formation.

2. Experimental Part

The fluorescence decay curves for PPO and pTP in cyclohexane presented in Fig. 1 and Fig. 2 were obtained by two different techniques.

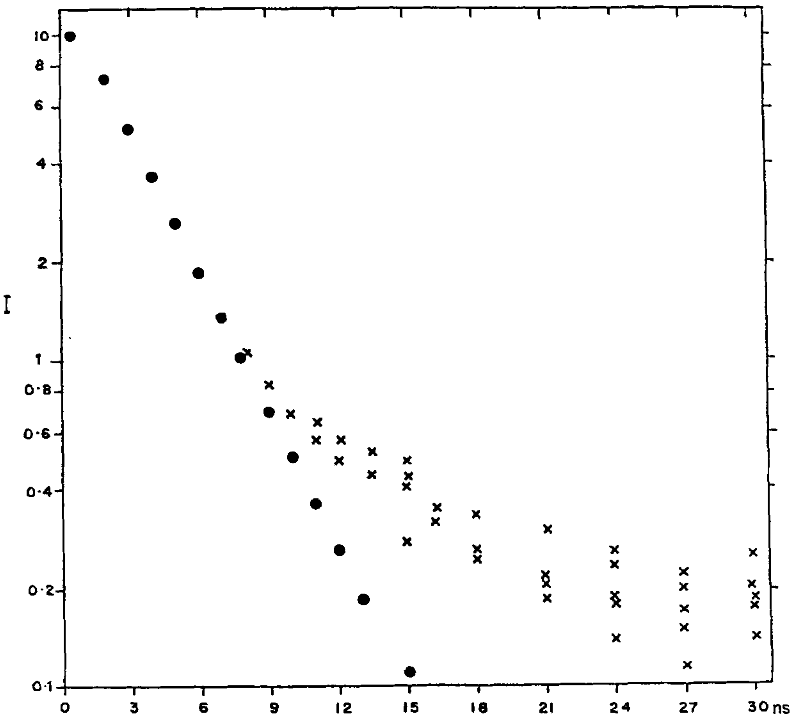

Figure 1: Luminescence decay curve for 0.3 g/l PPO in cyclohexane (degassed). ● ● ● ● ● UV excitation; × × × × 30 kV X-ray excitation. (All curves are normalized to the same initial intensity. The initial decay for both forms of excitation is the same and represented by the dotted curve. Intensity is expressed in arbitrary units.)

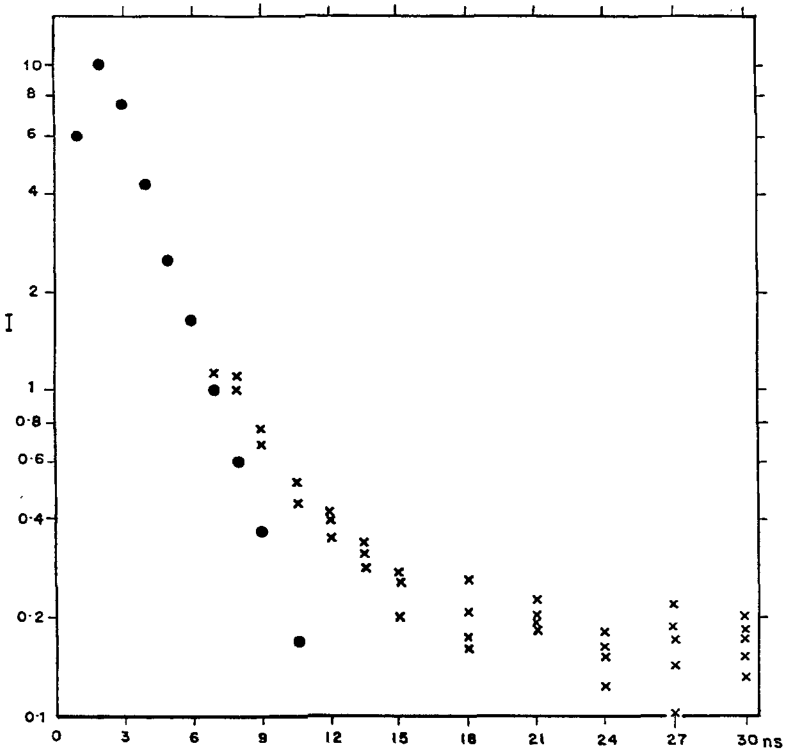

Figure 2: Luminescence decay curve for 0.3 g/l p-terphenyl in cyclohexane (degassed). ● ● ● ● UV excitation; × × × × × 30 kV X-ray excitation. (All curves are normalized to the same initial intensity. The initial decay for both forms of excitation is the same and represented by the dotted curve. Intensity is expressed in arbitrary units.)

In the case of high-energy excitation the optical sampling technique of Dreeskamp and Burton[3] was employed while the decay curves for UV excitation were obtained utilizing a monophoton technique.[15] The sources were, respectively a 30 kV X-ray tube[16] and a pulsed hydrogen lamp.[17] The duration of the excitation pulses was about 1 ns with a decay of about 0.8 ns.

The scintillator materials were zone refined prior to use. The cyclohexane used in the systems described here was gas-chromatographically purified.

All solutions were deaerated by flushing with nitrogen saturated with solvent at the vapor pressure of the solution for about 10–15 minutes.

3. Discussion of Experimental Data

In spite of the presently limited amount of experimental data on liquid organic scintillators some generalizations can be made about their luminescence decay.

The luminescence decay of binary liquid organic scintillator systems containing either an aromatic or an aliphatic solvent exhibits a long component after high-energy excitation. This component cannot be attributed to dimer formation under the given experimental conditions.

Aromatic and aliphatic solvent systems display a distinct difference. The decay of the fast luminescence component in an aromatic solvent system depends on the scintillator concentration; it is independent of such concentration in the case of a non-aromatic solvent (cyclohexane,[4] dioxane†).

4. Discussion of Possible Mechanisms

Laustriat and coworkers interpreted the long luminescence component on the basis of a triplet-triplet annihilation mechanism. They assumed that the interaction of high-energy radiation with the system leads by internal conversion processes to the formation of solvent triplet states of significantly long lifetimes. These excited states can interact to give the excited singlet state which transfers its energy to the scintillator. This mechanism is supposed to account for the slow luminescence. The initial fast part is assumed to result from direct formation of excited singlet solvent molecules and subsequent energy transfer to acceptor molecules, just as has been generally accepted for several years.

The assumption of energy transfer from an excited solvent molecule to explain the fast luminescence component and the proposed triplet annihilation mechanism to explain the long luminescence component can, however, hardly apply to binary scintillator systems containing aliphatic solvents or more specifically, cyclohexane. Although comparatively long-lived excited states of aromatic solvents such as benzene or toluene are well known no such state has been convincingly established for cyclohexane.[18, 19] A different mechanism for the fluorescence of scintillator-cyclohexane systems may therefore be profitably considered.

---

† The result for dioxane was obtained by S. Rodemeyer in this Laboratory.

Even for an aromatic solvent like benzene it is questionable whether a triplet-triplet annihilation mechanism can account for the slow luminescence component after high-energy excitation. There exists evidence that the triplet state of liquid benzene under such conditions has a lifetime of less than 10^{-8} seconds.[20, 21, 22] Such a short lifetime is not consistent with the slow component in the luminescence decay of benzene-scintillator systems.

5. Consideration of Radiation Chemical Data

Numerous investigations of the radiation chemistry of cyclohexane systems may provide an answer to the problem. In several studies of this kind it was shown that ionic reactions in this solvent play an important role.[23–26] This evidence for ionic reactions is circumstantial and based on chemical reactions of cyclohexane systems under high-energy irradiation. In addition, however, rather direct evidence for ions is obtained from electroconductivity measurements.[27–30] Such measurements indicate also that mean lifetimes of about 10^{-7} seconds are possible for a non-negligible fraction of the ions produced in cyclohexane by high-energy radiation.

The possibility of comparatively long-lived ionic species in high-energy irradiated solvent systems has been considered also on theoretical grounds. It is generally accepted today that energy deposition of high-energy radiation, for instance alpha, gamma or beta radiation, occurs in localized regions along the path of the energetic particle.[31–34] In such localized regions, such as spurs, blobs and short tracks, high densities of reactive species, such as radicals, excited states, electrons, and ions, exist.

From theory it is concluded that ionic reactions at least in water would be extremely fast, that is, of the order of 10^{-12} seconds. It was also realized, however, that such rapid relaxation of energetic electrons in low dielectric-constant systems is difficult to understand theoretically.[35, 36] Specifically the problem is the following: while energy loss of energetic electrons in a liquid organic solvent is quite probable for energies above a few ev and thus is expected to occur over distances of a few angstroms it is difficult to rationalize the dissipation of the electron energy in the range between thermal and molecular vibrational levels. The probability loss of energy by the electron in that region seems to be small. On the other hand, an electron in that energy range still has sufficient energy to travel significant distances away from the parent ion before thermalization. Also, there exist very energetic primary electrons which, forming their own track, can escape the electrostatic field of the parent ion (∂-rays). The expected charge separation is therefore capable of accounting for much longer recombination times.

Presently, little theoretical work is available to provide reliable information on ion lifetimes. The problem is further complicated by the fact that ion-ion, or ion-electron recombination will not be purely a diffusion-controlled process; the electrostatic field must also be considered. This field effect would lead to faster specific rates than are to be expected for diffusion-controlled processes.

Experimental evidence and theoretical considerations, therefore, suggest the importance of ionic processes in high-energy irradiated cyclohexane systems. Although no quantitative statement is here made, it is suggested that the long luminescence component in X-ray excited cyclohexane-scintillator systems is the result of ionic processes.

6. Proposed Mechanism

Consider a solvent S,[37] scintillator X and products P. For the system cyclohexane-fast scintillator the following processes are considered to be relevant for the luminescence.

Ionization of cyclohexane

$$S \rightarrow S^+ + e^- \tag{1}$$

Recombination and product formation

$$S^+ + e^- \rightarrow P \tag{2}$$

Scavenging of electrons by scintillator

$$e^- + X \rightarrow X^- \tag{3}$$

Charge transfer to scintillator

$$S^+ + X \rightarrow S + X^+ \tag{4}$$

Neutralization reactions leading to excited states of scintillator

$$X^- + X^+ \rightarrow X_2^* \quad \text{or} \quad X + X^* \tag{5}$$

$$X^- + X^+ \rightarrow X^* + S' \tag{6}$$

Fluorescence from excited scintillator

$$X^* \rightarrow X + h\nu \tag{7}$$

Other processes like internal quenching of excited scintillator have been omitted from this scheme in order not to obscure the important ionic reactions. Furthermore, a quantitative treatment of the elementary reactions with the hope of development of a theoretical luminescence decay law is not possible at the present time. The difficulty of a quantitative treatment of the problem lies in the fact that the system to be considered is inhomogeneous; i.e., concentrations of reactants are simply non-uniform. As the result of diffusion processes local concentrations vary with time but in the cases of ions and electrons the diffusional processes are further complicated by the effect of local electric fields. Neither diffusion coefficients, nor "initial" dimensions of the excited regions, nor distributions of reactants are known.

Despite the discouraging quantitative aspect of the problem it seems nonetheless possible qualitatively to explain the overall experimental observations.

7. Fast Decay Component

As mentioned in Section 3 the fast component is independent of scintillator concentration in cyclohexane as long as self-quenching can be neglected. This situation is different from that in aromatic solvent systems; in such systems, at low scintillator concentrations the increase of apparent decay time reflects the life time of the solvent rather than that of the scintillator.[3] If one applies the energy transfer mechanism generally used for aromatic solvent systems to cyclohexane scintillator systems one obtains transfer constants, k_t, of the order of 10^{11} to 10^{12} $M^{-1}\,sec^{-1}$. The formalism of homogeneous reaction kinetics does not apply to the much more complicated situation under consideration.[19] Because diffusional processes cannot account for such rate constants, rather special assumptions must be made regarding the excited states of the solvent.[19] Further, as already indicated, no experimental evidence for excited states of cyclohexane has yet been found.

Use of an ionic reaction scheme eliminates the problems introduced by the assumptions of excited cyclohexane. The observed luminescence decay rates can be understood as the result of the spatial distribution of the reactants.

The unexcited scintillator distribution may be considered uniform throughout this system. On the other hand, the charged species are localized in spurs, blobs, or short tracks. The initial sizes of such regions are not exactly known. For water, initial spur radii of about 20 Å have been assumed.[31] For systems with low dielectric constants the value is expected to be considerably larger.[27,30] At any given time the concentration of charged species within the spur may be described by some distribution function the form of which is not known. In order to form an excited scintillator molecule within a time shorter than the time resolution capability of the instrumentation it is necessary that the charged particles and scintillator molecules (according to the reaction scheme given) are sufficiently close together. Under such conditions interionic reactions, like (6), would appear to be favored. If scintillator emission were instantaneous, the fluorescence decay curve would reflect the distribution function for the mutual distances between the reactants. In real cases, however, in which rates of the recombination reactions are usually much faster than the emission process 7 (or the time resolution of the instrument used), such an effect would not be observable.

This description, although over-simplified, serves nonetheless to demonstrate the basic fact that the fast component of light emission does not depend on scintillator concentration. Lowering the scintillator concentration decreases the total light yield but does not affect the fast component of the decay curve.

8. Long Fluorescence Component

The observed slow component of luminescence after high-energy excitation of cyclohexane systems must next be considered. In the case of systems made up from aromatic solvents this tail has been attributed to triplet-triplet annihilation of the solvent molecules. The phenomenon in cyclohexane systems can hardly be explained on the same basis. Again it appears to be more plausible to account for this observation by ionic processes such as discussed in Section 6. If one extends the ideas of Section 7 to reactions (5) and (6), but with particular consideration of the case where the reactants are sufficiently separated, it follows that formation of excited scintillator molecules, rather than the emission process, will be rate determining.

For instance, to account in this way for luminescence 30 ns after excitation of the cyclohexane p-terphenyl system by process (5) or (6), one must assume an average separation of the reactants of at least 100 Å neglecting electric field effects. Separation of the reactants by such distances is well within the range to be expected theoretically.[5] Actually, much larger charge separations exist (note ∂-rays) though, presumably with decreasing frequency.

9. Other Evidence

In some recent work, shortly to be published, Huque and this author, have shown that a negative-ion former is particularly informative when used as a quencher for it clearly distinguishes between effects that can be attributed to ions and those which are ascribable to excited species.

10. Conclusion

Luminescence decay curves in cyclohexane scintillator systems excited by high-energy radiation are interpretable in terms of ionic reactions. A mechanism involving excited solvent molecules does not seem plausible. The behavior in scintillator systems with aromatic solvents may well follow the same scheme. However, in such case the existence of "long-lived" excited solvent molecules may make the energy-transfer process rate controlling and obscure the ionic reactions.

REFERENCES

1. Swank, R. K. and Buck, W. L., *IRE Trans. Nucl. Sci.*, NS-5, 183 (1958).
2. Dreeskamp, H. and Burton, M., *Phys. Rev. Letters*, **2**, 45 (1959).
3. Burton, M. and Dreeskamp, H., *Z. Elektrochem.*, **64**, 165 (1960).
4. Burton, M. and Yguerabide, J., *Nucl. Electron.*, I, 71 (1962).
5. Dresskamp, H., Ghosh, A. K. and Burton, M., *Rev. Sci. Instr.*, **32**, 304 (1961).
6. Berlman, I.B., *J. Chem. Phys.*, **34**, 1083 (1961).
7. Steingraber, O. J. and Berlman, I. B., *Rev. Sci. Instr.*, **34**, 524 (1963).
8. Bollinger, L. M. and Thomas, G. E., *Rev. Sci. Instr.*, **32**, 9 and 1044 (1961).
9. Koechlin, Y., *Thesis*, University of Paris, 1961.
10. Yguerabide, J. and Burton, M., *J. Chem. Phys.*, **37**, 1757 (1962).
11. Birks, J. B., Dyson, D. J. and Munro, I. H., *Proc. Roy. Soc.*, **A275**, 575 (1963).
12. Förster, T. and Kasper, K., *Z. Elektrochem.*, **59**, 977 (1955).
13. Stevens, B., Ban, M. I. and Walker, M. S., Annual Tech. Rep., U.S. Dept. of Army Contr. No. DA-91-591-EUG-2745.
14. Laustriat, G., *Intern. Conf. on Scintillators*, Argonne Natl. Lab., June 1966.
15. Amata, C. D., Great Lakes Regional Meeting, Am. Chem. Soc., Chicago, 16–17 June 1966.
16. Dunlee Corp., 1023 Pusheck Road, Bellwood, Illinois.
17. D'Alessio, J. T. and Ludwig, P. K., *IEEE Trans. Nucl. Sci.*, NS-12, 351 (1965).
18. Lipsky, S., Remarks at the International Symposium on Organic Scintillators, Argonne Natl. Lab., 20 June 1966; S. Feinleib and S. Lipsky, J. Chem. Phys., paper submitted for publication.

19. Burton, M., *J. Mol. Crystals*, to be published International Symposium on Organic Scintillators, Argonne Natl. Lab., June 1966.
20. Hentz, R. R., Peterson, D. B., Srivastava, S. B., Barzynski, H. F. and Burton, M., *J. Chem. Phys.*, **70**, 2362 (1966).
21. Dubois, J., Intern. Conf. Luminescence, Munich, September 1965.
22. Cundall, R. B., *Trans. Faraday Soc.*, **61**, 1968 (1965).
23. Dyne, P. J., *Can. J. Chem.*, **43**, 1080 (1965).
24. Gallivan, J. B. and Hamill, W. H., *Trans. Faraday Soc.*, **61**, 1 (1965).
25. Scholes, G. and Sime, M., *Nature*, 202, 895 (1964).
26. Sherman, W. V., *J. Chem. Soc.*, 599 (1966).
27. Hummel, A. and Allen, A. O., *Disc. Faraday Soc.*, **36**, 95 (1963).
28. Freeman, G. R., *J. Chem. Phys.*, **39**, 988 (1963).
29. Freeman, G. R., *J. Chem., Phys.*, **43**, 93 (1965).
30. Hummel, A., Allen, A. O. and Watson, F. H., *J. Chem. Phys.*, **44**, 3426 (1966); ibid. **44**, 3431 (1966).
31. Magee, J. L., *J. Am. Chem. Soc.*, **73**, 3270 (1951).
32. Samuel, A. H. and Magee, J. L., *J. Chem. Phys.*, **21**, 1080 (1953).
33. Mozumder, A. and Magee, J. L., *Radiation Res.*, **28**, 255 (1966).
34. Magee, J. L., Funabashi, K. and Mozumder, A., 6th Japan Conf. on Radio Isotopes, 1966.
35. Mozumder, A., to be published.
36. Platzman, R. L., *Radiation Res.*, **2**, 1 (1955).
37. Burton and his coworkers note that greater generality and equal plausibility apply if *S* represents the entire system. In such case some modification of the details of representation of the mechanism is desirable. Cf. Ref. 20; Milton Burton, Proc. of 4th Japan Conf. on Radioisotopes, October 1961, published by the Japan Atomic Industrial Forum, p. 423–433, (in English).