The Formation of Excited States on Pulse Radiolysis of Organic Solutions

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VARIOUS mechanisms have been proposed for the high yields of excited triplet state solute molecules formed on pulse radiolysis of dilute solutions of aromatic solutes in organic liquids.[1–5] McCollum and Nevitt[4] concluded that for liquid paraffin solutions all the triplets were produced *via* inter-system crossing from excited singlet precursors. Hunt and Thomas[6] observed that for naphthalene (Naph) in cyclohexane most of the triplet state molecules were formed in less than one nanosec., but a small portion did grow in with a half life of 100 nanosec. Since the yield of these "slow" triplets depended on [Naph] quite differently from the yield of radiation-induced fluorescence they

TABLE

Yields of excited states in argon-saturated naphthalene–cyclohexane solutions

Conc. (m/l.)	$G(^1\text{Naph}^*)_\text{M}$ (±20%)	$G(^1\text{Naph}^*)_\text{C}$	$G(^3\text{Naph}^*)_\text{I.S.}$	Total $G(^3\text{Naph}^*)$ (±5%)
10^{-4}	0·056	—	0·053 ± 20%	0·18
4×10^{-4}	0·15	—	0·12 ± 20%	0·36
8×10^{-4}	0·254	—	0·19 ± 20%	0·50
10^{-3}	0·273	0·273 ± 20%	0·20 ± 20%	0·56
2×10^{-3}	0·374	—	0·27 ± 20%	0·76
5×10^{-3}	0·70	—	0·50 ± 20%	1·12
10^{-2}	—	0·77 ± 30%	0·515 ± 30%	1·2
5×10^{-2}	—	2·0 ± 40%	0·92 ± 40%	2·84
10^{-1}	—	3·1 ± 50%	1·02 ± 50%	3·34

concluded that these "slow" triplets are not formed by intersystem crossing from the excited singlet.

Using μsec pulse techniques, we find that for the naphthalene–cyclohexane aud -benzene solutions the fluorescence spectrum changes significantly above [Naph] = 10 mM due to increased self absorption at short wavelengths and excimer emission[7] at long wavelengths. The yields of fluorescence at 340 $m\mu$ (solely monomer fluorescence) and at 415 $m\mu$ (predominantly excimer fluorescence) are shown as a function of $\log_{10}$[Naph] in the Figure, and the latter is identical to that attributed to the monomer fluorescence by Hunt and Thomas.[6] However the dependence on [Naph] which we observe for the monomer fluorescence is very similar to that reported by Hunt and Thomas for the "slow" triplet yields. Moreover we find that in both solvents the monomer fluorescence yield depends on [Naph] in a very similar way to the total triplet yield and is similarly reduced by an electron scavenger such as N_2O.

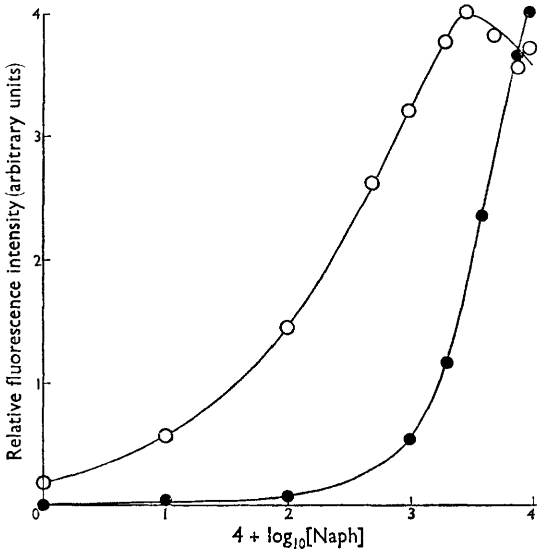

FIGURE. *Concentration dependence of the* 340 $m\mu$ (○) *and* 415 $m\mu$ (●) *radiation-induced fluorescence from naphthalene–cyclohexane solutions.*

Our results suggest either that all triplets are formed by intersystem crossing or that both ^{1}Naph* and ^{3}Naph* have a common precursor. We have therefore measured the yields of ^{1}Naph* produced on pulse radiolysis of dilute (< 5 mM) naphthalene–cyclohexane solutions using McCollum and Nevitt's technique[4] except that the fluorescence was detected photoelectrically instead of photographically. The results of these measurements are shown in the Table, *i.e.* $G(^1\text{Naph}^*)_\text{M}$. The calculated singlet yields [*i.e.* $G(^1\text{naph}^*)_\text{C}$] at [Naph] > 5 mM were obtained using the measured value $G(^1\text{Naph}^*)_\text{M} = 0{\cdot}27$ at [Naph] = 1mM and the concentration dependence of the 340 $m\mu$ fluorescence yield (Figure). The values of ϕ_f, the quantum yield for fluorescence, required for this calculation were obtained[8] using the rate constant $k_3 = (1{\cdot}8 \pm 0{\cdot}6) \times 10^8 \text{M}^{-1}\,\text{sec.}^{-1}$ and the lifetime for ^{1}Naph* at low [Naph] = $(k_1 + k_2)^{-1} = 70$ nanosec. It was assumed that $k_2 = 3k_1$.[9]

$$^1\text{Naph}^* \xrightarrow{k_1} \text{Naph} + h\nu \qquad (1)$$

$$^1\text{Naph}^* \xrightarrow{k_2} {}^3\text{Naph}^* \qquad (2)$$

$$^1\text{Naph}^* + \text{Naph} \xrightarrow{k_3} {}^1\text{Naph.Naph}^* \qquad (3)$$

As can be seen from the Table, we find that excited singlet solute molecules are produced in high yield in agreement with the work of McCollum and Nevitt. The yields of excited triplets formed by intersystem crossing [*i.e.* $G(^3\text{Naph}^*)_\text{I.S.}$] from these singlets were calculated using the values for k_1 k_2, and k_3 given above. The values of $G(^3\text{Naph}^*)_\text{I.S.}$ in the Table show that intersystem crossing from singlets makes a significant contribution to the total $G(^3\text{Naph}^*)$ and it is especially interesting that these values at low concentrations agree reasonably well with the "slow" triplet yields reported by Hunt and Thomas. At higher concentrations however the "slow" triplet yields are much lower. This decrease in the "slow" triplet yields is possibly due to the sharp decrease in the lifetime of the naphthalene singlet at high concentrations. The values of k_1, k_2, and k_3 used above indicate that at concentrations above 0·5 M the excited singlet lifetime is less than 10 nanosec. Triplets formed by intersystem crossing at high concentrations would therefore appear to be "fast" triplets.

The high singlet yields recorded above are also consistent with preliminary results which we have obtained on naphthalene–cyclohexane–xenon solutions. We have observed that 0·2M-xenon, which enhances the rate of intersystem crossing,[10] decreases the fluorescence yield of 0·1 M-naphthalene–cyclohexane solution to approximately zero and increases the triplet yield from 3·3 to 4·2, *i.e.* the total yield of excited molecules (singlet + triplet) at 0·1M is approximately 4·2.

Further work using different solutes in both cyclohexane and benzene as solvents is in progress.

(*Received, January 26th*, 1968; *Com.* 095.)

[1] J. P. Keene, T. J. Kemp, and G. A. Salmon, *Proc. Roy. Soc.*, 1965, *A*, **287**, 494.

[2] E. J. Land, "Pulse Radiolysis", ed. M. Ebert, A. J. Swallow, and J. H. Baxendale, Academic Press, New York, 1965, p. 294.

[3] J. Nosworthy, *Trans. Faraday Soc.*, 1965, **61**, 1138.

[4] J. D. McCollum and T. D. Nevitt, U.S. Tech. Rep., ASD-TDR-63-616, 1963.

[5] R. L. Platzman, *Radiation Res.*, 1965, **2**, 1.

[6] J. W. Hunt and J. K. Thomas, *J. Chem. Phys.*, 1967, **46**, 2954.

[7] I. B. Berlman and A. Weinrab, *Mol. Phys.*, 1962, **5**, 313.

[8] B. Stevens and J. T. Dubois, *Trans. Faraday Soc.*, 1966, **62**, 1525.

[9] C. A. Parker and T. A. Joyce, *Chem. Comm.*, 1966, 234.

[10] A. R. Horrocks, A. Kearvell, K. Tickle, and F. Wilkinson, *Trans. Faraday Soc.*, 1966, **62**, 3393.