Mechanism of Formation of Triplet States produced by Pulse Radiolysis of Solutions of Naphthalene

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FOLLOWING several recent reports[1-5] of G-values of excited states during the radiolysis of benzene solutions we report here G-values of naphthalene triplet states (N^T) obtained by pulse radiolysis of solutions of naphthalene in deaerated benzene and cyclohexane (Figure). We have employed[6] $\epsilon_{max} = (1\cdot4 \pm 0\cdot3) \times 10^4$ M^{-1} cm.$^{-1}$ for the triplet–triplet absorption of naphthalene.

In contrast to the recently published results of Nosworthy[3] and Land[7] on pulse radiolysis of solutions of anthracene (A) in benzene and cyclohexane respectively, we find a well-defined maximum in the dependence of $G(N^T)$ on naphthalene concentration. This behaviour recalls that observed for luminescence yields from liquid scintillators by Furst and Kallman.[8] Our figure includes a curve based on the equation proposed by these workers, *i.e.*, $G = P[N]/(R + [N])(Q + [N])$ with the selected values $P = 1\cdot68$, $Q = 0\cdot554$, $R = 3\cdot43 \times 10^{-3}$. It appears that the linear relation reported by Nosworthy[3] between $G(A^T)^{-1}$ and $[A]^{-1}$ may fail at higher solute concentrations.

The large $G(N^T)$ for cyclohexane was unexpected, since singlet yields of solutes in non-aromatic solvents [with the notable exceptions of dioxan and 1,2-dimethoxyethane (DME)] are generally lower[9] than in aromatic solvents. On the other hand, the concentration-dependence curves for benzene and cyclohexane and the Furst–Kallman scintillation curves are all similar in shape, suggesting a common mechanism for the production of singlet and triplet states of the solute in both solvents.

An alternative mechanism which has been suggested for the production of A^T is $A^- +$ solvent
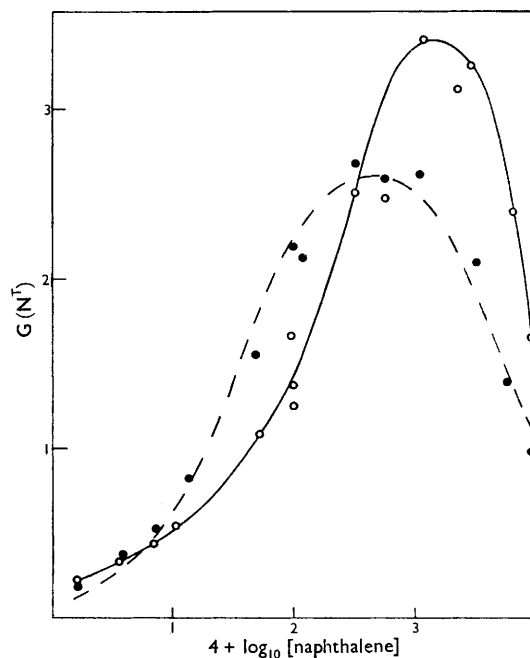
Dependence of G (triplet naphthalene) upon solute concentration for the pulse radiolysis of solutions of naphthalene in benzene (●) and cyclohexane (○). Broken line corresponds to

$$G = 1\cdot68[N]/(0\cdot554 + [N])(3\cdot43 \times 10^{-3} + [N]).$$

cation $\rightarrow A^T +$ solvent, and in support of this it has been found that the presence of second solutes such as N_2O or SF_6 which compete with A for electrons decrease $G(A^T)$ in such solvents as cyclohexane[7] and dioxan.[10] Such a scheme should, however, operate in anthracene– or naphthalene–tetrahydrofuran but much lower values of $G(A^T)$ or $G(N^T)$ are found in these systems.[11]

Our further observation of $G(N^T)$ of >0.4 in naphthalene–dimethoxyethane (14 mM) supports our conclusion; the depressant effect of electron scavengers, which we have also found in this system, may be related to capture of the electron before it returns to a solvent positive ion to form a solvent excited state which then migrates to the solute.

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