Formation of Solute Excited States and Radicals during Pulse Radiolysis of Naphthalene in Ethereal Solutions

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Yields of solute radicals and triplet and singlet excited states differ markedly for solutions of naphthalene in two ethers, 1,2-dimethoxyethane (DME) and tetrahydrofuran (THF), which have almost the same dielectric constant (7·2 and 7·4 respectively ¹ at 25°C). The concentration dependences reveal that in both solvents the production of radicals and excited states are not inter-related in a simple manner; production of singlet and triplet states do, however, seem to be related.

Considerable attention has been focused on the yield of ionic intermediates in the radiolysis of liquids. The production of the spectrum of e_{aq} in pulse radiolysis of water ² is convincing evidence for an extensive degree of ionization. Lower yields of $e_{solv.}$ are obtained on pulse radiolysis of alcohols ³ and other moderately polar liquids ⁴ and addition to methanol of potent electron scavengers, ⁵ e.g., biphenyl and triphenylcarbinol, which afford optically detectable species $\phi \cdot \frac{1}{2}$ and $\phi_3 C \cdot$ on pulse radiolysis, indicates that $G(e_{solv.}) \simeq 1 \cdot 0$. Pulse radiolysis of solutions of organic electron scavengers in cyclohexane produces only small yields ($G \sim 0.4$) of solute anions ⁶ (or neutral radicals derived therefrom), and, instead, the dominant spectral feature is the triplet-triplet absorption of the solute.⁷ This contrasts (i) with the results of Hamill and his group ⁸ on γ -radiolysis of glassy alkane solutions of similar solutes at 77°K which show extensive formation of solute negative ions, and (ii) with the values of $G(N_2)$ for radiolysis of solutions of nitrous oxide in liquid cyclohexane ⁹ which are presumed to originate for the most part from the reaction, e^- + $N_2O \rightarrow N_2 + O^-$.

It appears then that in the liquid state ionization is taking place with $G \sim 3$ but that in solvents of moderate or low polarity possibilities other than capture by a solute molecule are open to the electron. These include (i) protonation of e^- and (ii) capture by a geminate positive ion, e.g., $\cdot C_6H_{12}^+$, possibly to give an excited solvent molecule. Attempts have been made to relate the yield of electrons which escape geminate recombination to the dielectric constant of the medium.¹⁰ In the present work, yields of solute ionic and excited species have been determined for two ethers of similar dielectric constant to test the validity of such an approach.

EXPERIMENTAL

Naphthalene was of scintillation grade. Both ethers were dried with calcium hydride and then with sodium-potassium alloy (stirred magnetically). They were then fractionally distilled from the alloy under nitrogen.

Pulse radiolysis was performed with 3000 rad pulses of 3 MeV electrons of $0.6 \,\mu$ sec duration delivered from Van der Graff machine supplied by High Voltage Inc. (Amersfoort). The techniques of dosimetry, sample manipulation, degassing and detection of optical transients have been described.¹¹

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Fluorescence emission was measured at 10°C with a Packard model 4322 liquid scintillation spectrometer. An internal tritium source was employed and all solutions were degassed by nitrogen bubbling.

RESULTS

The spectra obtained from $\sim 10^{-2}$ M solutions of naphthalene in DME and THF at the end of the pulse are presented in fig. 1. The nature of the spectra were



FIG. 1.—Pulse radiolysis spectra of $\sim 10^{-2}$ M naphthalene in THF (broken line) and DME (full line).



FIG. 2.—Concentration dependence of $G \varepsilon_{max}$ for naphthalene triplet state for pulse radiolysis of solutions in DME (circles) and THF (triangles).

unchanged when 1M solutions of naphthalene were pulsed. The highly characteristic absorption in the 420 m μ region is that of triplet naphthalene (³N) in agreement with other work in flash photolysis ¹² and pulse radiolysis.⁷ The absorption at

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330 m μ is less characteristic but the spectrophotometric study of γ -irradiated methanolic glasses containing naphthalene and results on the pulse radiolysis of naphthalene in methanol^{3, 13} both make it highly probable that it is due to $\cdot C_{10}H_9$ (denoted hereafter as $\cdot NH$).



FIG. 3.—Concentration dependence of $G\varepsilon_{max}$ for $\cdot C_{10}H_9$ for pulse radiolysis of naphthalene in DME (circles) and THF (triangles).



FIG. 4.—Concentration dependence of (relative) total fluorescence from naphthalene in DME (circles) and THF (triangles).

The concentration dependences of $G\varepsilon_{max}$ for ³N and •NH are presented in fig. 2 and 3, and in fig. 4 are shown the dependences of relative G (fluorescence) upon concentration. The latter includes excimer,¹⁴ in addition to monomer, fluorescence

at high solute concentration and acts only as a qualitative indication of relative singlet yields. $(G({}^{3}N) \text{ may be calculated } {}^{15} \text{ from fig. 2 using } \varepsilon = 1.4 \times 10^{4}$. Assuming $G(e^{-})$ for CH₃OH is 1.0,⁵ ε for .NH is approximately 2×10^{4} from the data of Dainton *et al.*⁷ on pulse radiolysis of naphthalene in methanol.)

Kinetic analysis of every decay was performed; the species at 330 m μ decays with good second-order kinetics with $k_2 = 6.0 \times 10^5 \epsilon$ (DME), $6.7 \times 10^5 \epsilon$ (THF); the triplet decays in an approximately first-order manner with $k_1 = 1.0 \times 10^5 \text{ sec}^{-1}$ (DME), $1.4 \times 10^5 \text{ sec}^{-1}$ (THF).

DISCUSSION

From fig. 1, only two species, i.e., \cdot NH and 3 N, are spectroscopically detectable immediately after the end of the pulse. The concentration dependences reveal that (i) the yield of \cdot NH reaches a plateau in both solvents with a yield in THF approximately twice that in DME; (ii) the triplet yields in both solvents rise monotonically and even at high solute concentration (1 M), when direct excitation of the solute is of great significance in both solvents, the triplet yield in DME is greater than in THF; at low solute concentrations the difference is six-fold; (iii), the difference in triplet yields is mirrored in the relative fluorescence (or solute singlet yield) dependences on solute concentration, which also fail to reach plateau values.

These trends are considered in relation to results obtained with other aliphatic ethers and hydrocarbons. Large yields of solute triplet states have been observed during the pulse radiolysis of naphthalene in dioxan and cyclohexane ¹⁶ and several theories as to their origin have been put forward.^{3, 4, 17, 18}

(a) Solvent-solute ion recombination;

$solv \rightarrow solv^+ + e^-$	(1))
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$$e^{-} + N \rightarrow \cdot N^{-} \tag{2}$$

$$\cdot \operatorname{solv}^+ + \operatorname{solv} \to \cdot \operatorname{solv} + \operatorname{solv} H^+$$
(3)

- solv $H^+ + \cdot N^- \rightarrow \cdot NH + solv$ (4)
 - $\cdot \operatorname{solv}^{+} + \cdot \operatorname{N}^{-} \to {}^{3}\operatorname{N} + \operatorname{solv}$ (5)

$$\operatorname{solv}^{+} + \cdot N^{-} \to {}^{1}N^{*} + \operatorname{solv}.$$
 (6)

(b) Direct excitation by thermalizing electrons :

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$$solv \rightarrow solv + e^{-}$$
 (1)

$$N(\downarrow\uparrow) + e^{-} \rightarrow {}^{3}N(\uparrow\uparrow) + e^{-}.$$
(7)

(c) Transfer of energy from solvent;

$$\operatorname{solv}^+ + e^- \to \operatorname{^1solv}^* + \operatorname{^3solv} \tag{8}$$

$$solv \rightarrow 1 solv + 3 solv$$
 (9)

$$\operatorname{solv}^* + N \to {}^{1}N^* + \operatorname{solv}$$
(10)

$${}^{1}\mathrm{N}^{*} \rightarrow {}^{1}\mathrm{N} + hv \tag{11}$$

$$^{1}N^{*} \rightarrow ^{3}N \tag{12}$$

$$^{1}solv^{*} \rightarrow ^{3}solv$$
 (13)

 $^{3}solv + N \rightarrow solv + ^{3}N.$ (14)

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Steps (8)-(11) are those cited ¹⁹ by those who have performed nanosecond pulsed irradiation of numerous organic scintillator systems; step (10) is regarded as a longrange dipole-dipole interaction.¹⁹ However, Hunt and Thomas ¹⁸ have examined the absorption spectrum of a solution of naphthalene in cyclohexane at the end of a 3-nanosecond pulse and report that most of the solute triplet states are present at the end of the pulse. This observation rules out step (12) as a significant source of triplets because the inter-system crossing time for napthalene, which must be of the same order as the fluorescence decay time, is far too long for such rapid production of triplets to take place. These workers ¹⁸ have also observed an emission at 415 m μ , which they attribute to naphthalene fluorescence, and showed its concentration dependence to be unrelated to that of the triplet yield. This implies that the two excited states are formed in a completely different manner, which is at variance with the present results on DME and THF. The emission at 415 m μ , however, is not that of a naphthalene molecule, which fluoresces at 330 m μ , but of the naphthalene excimer $(\lambda_{max} 393 \pm 3 \ m\mu)^{14}$, ²⁰ which becomes significant only at higher concentrations, and the sharp increase in the fluorescence concentration dependence curve of Hunt and Thomas is a reflection of this for it omits most "monomer" fluorescence.

The present results are considered as evidence against schemes (a) and (b) for the production of triplet states in aliphatic solvents because these are too general and would predict substantial yields of triplets in every aliphatic solvent. The theory that in solvents of low dielectric constant, e.g., cyclohexane, dioxan, the solute ion+solvent ion recombination will occur more readily to give triplets than in those of higher dielectric, e.g., DME and THF, wherein the electrostatic field is reduced and free ions are more likely to persist,¹⁰ is also incompatible with the observed yields of triplets and radicals in these systems.

Significantly, all systems giving rise to substantial yields of triplets also act as scintillators, i.e., give some yield of solute singlets. Examples include naphthalene, anthracene and 2,5-diphenyloxazole in dioxan, cyclohexane, benzene and DME.²¹ The present work draws attention to the qualitative agreement between the concentration dependences of triplets and singlets in DME and THF.

Evidently the appearance of triplets in ethereal solvents is a function of the solvent molecule, which does not behave merely as a continuous dielectric, and is related to its ability to transport singlet excitation in step (10), probably by a non-diffusive process. Hunt and Thomas ¹⁸ have clearly shown that solute singlets are not significant precursors of solute triplets and we propose therefore that triplet excitation (possibly of a collective variety) can migrate through the solvent and be transferred to a solute in processes analogous to those accepted for singlet energy. This ability to transport triplet energy is a function of the molecular structure of the solvent and is displayed by those molecules able to act as scintillator solvents, i.e., by dioxan, cyclohexane and DME but not by THF and diethyl ether.

The remaining question is why are larger yields of radicals or ions obtained for solvents giving low triplet yields, particularly in the present case when the equality of dielectric constant might be supposed ¹⁰ to lead to equal G(free ion)? One answer is that the species formed in steps (8) and (9) can either transfer energy (in the case of DME) or donate an electron to a solute. It has been shown that singlet excited tetramethyl paraphenylenediamine donates an electron to N₂O, SF₆, CO₂, benzyl acetate ²² and naphthalene.²³

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