

## Pulse-Radiolysis of Naphthalene in Methylamine Solution

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**Summary:** A pulse-radiolytic study of a solution of naphthalene in liquid methylamine showed absorption in the UV region with a maximum at 330 nm. The absorption, attributed to naphthalene radical  $C_{10}H_9$ , did not decay via a simple process. Evidence as to the nature of the precursor of the species is discussed.

### Introduction

Pulse radiolysis of some organic electron scavengers in a wide variety of solvents indicated the nature of products observed spectroscopically to be a function of the polarity and reactivity of the solvent.<sup>1</sup> We have observed the generation of the anions of some organic electron scavengers in the irradiated liquid methylamine.<sup>2-4</sup> In the present work we have tried to study spectroscopically the type of products formed in pulse-radiolysis of solutions of naphthalene in liquid methylamine at 298 K.

### Experimental

A mercury-free system was used for the purification and storage of the materials and the preparation of the sample for the radiolytic experiments. Methylamine from Matheson Co. was purified as described earlier.<sup>5</sup> Sulphurhexafluoride from Matheson Co. and naphthalene (extra pure) from Thom Electronics were used as received.

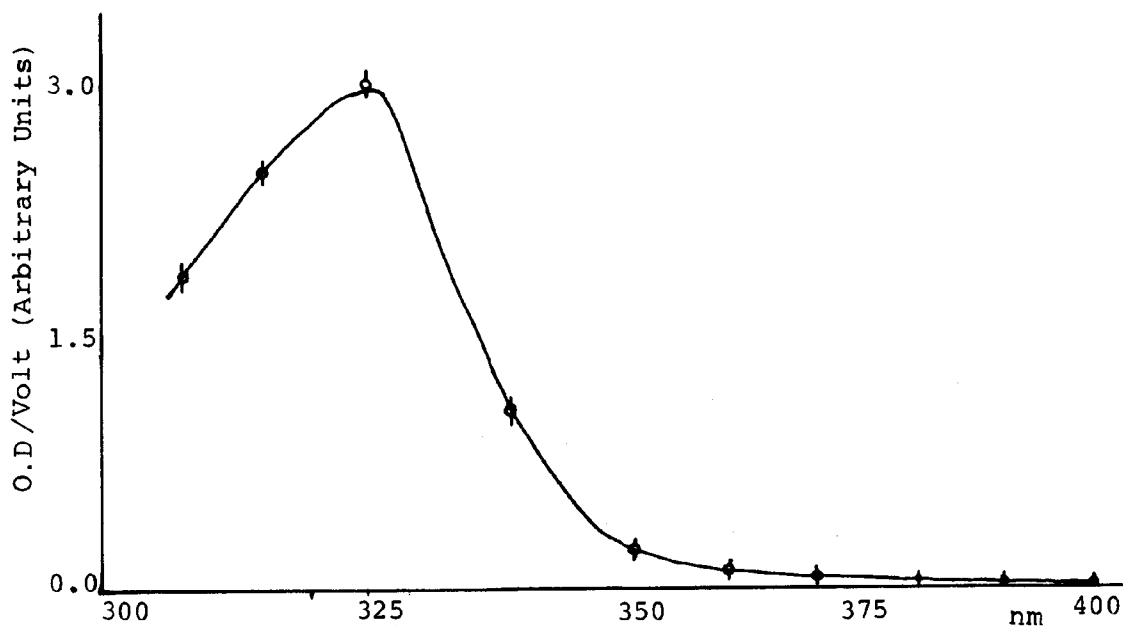
At room temperature the vapour pressure of methylamine is about 3 atm. Hence the flow system usually used in pulse radiolysis of liquid could not be employed in this work. Sealed cells were used. The optical cell was Suprasil quartz cell with a graded seal. An important aspect of the Suprasil cell was that its plane-end windows were sealed inside the cell body. This enabled the cell to withstand the high pressure of methylamine. The cells were cleaned in the same way as adopted for the gas-phase experiments.<sup>5</sup> The filling process was described elsewhere.<sup>6</sup> The volume of liquid methylamine at 298 K in the cell was always 5 ml. To make a solution

in liquid methylamine the required amount of naphthalene was weighed into the dry cell. The cell was kept in liquid nitrogen to avoid any loss of the solute vapour on pumping. When a hard vacuum was achieved, the required amount of methylamine was condensed into the cell at 77 K.  $SF_6$  was condensed into the cell after methylamine. After pumping out any volatile impurities at 77 K, the cell was sealed at the point of constriction.

The pulsed Van de Graaf electron accelerator at the Cookridge High Energy Radiation Centre, Leeds, England was the radiation source. The basic pulse radiolysis system for micro-second pulses has been described elsewhere.<sup>7,8</sup> Light from a xenon lamp (Phillips 150 W CSW) was passed into the irradiation cell through its optical window. The emergent beam was reflected into a monochromator and was then directed onto an EMI 9558 BQ or Hamamatsu (R 446) photomultiplier tube the output of which was fed into a cathode-ray oscilloscope (Tetronix 545B). The dose in each pulse was estimated as described earlier.<sup>6</sup> Oxygenated  $10 \text{ mmole dm}^{-3}$  aqueous potassium ferrocyanide was used as dosimeter.<sup>9</sup>

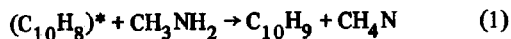
### Results and Discussion

A  $10^{-2} \text{ mole dm}^{-3}$  solution of naphthalene in liquid methylamine was pulsed radiolysed by a  $0.6 \mu\text{s}$  pulse and a dose of about 5 krad per pulse. The absorption was measured in the wavelength range 300 to 800 nm. Absorption was observed only in the UV region with a maximum at 330 nm (Fig. 1). This absorption may be assigned to naphthalene radical  $C_{10}H_9$ . A similar absorp-

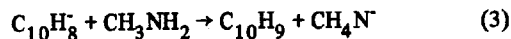


UV spectrum obtained on Irradiating a solution of naphthalene in liquid Methylamine.

tion in triethylamine is assigned to the same species.<sup>1</sup> Keene et al<sup>1</sup> have studied pulse-radiolysis of some organic electron scavengers in a wide variety of solvents. They observed the type of products found spectroscopically to be a function of the polarity and reactivity of the solvent. Our earlier pulse-radiolytic works of solutions of biphenyl,<sup>2</sup> anthracene<sup>3</sup> and trans-stilbene<sup>4</sup> in liquid methylamine gave absorption spectra characteristic of the individual anions. The naphthalene radical may be produced in a hydrogen abstraction reaction by the excited naphthalene molecule (reaction 1).



Or it may be generated as follows:



Or its formation may occur via reaction 4.



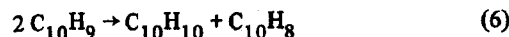
Solvated electrons are formed in the irradiated liquid methylamine<sup>6,10,11,12</sup>. H atoms are produced in the irradiated liquid methylamine.<sup>12</sup> An attempt was made to establish the precursor of  $C_{10}H_9$  by adding a strong

competitor for solvated electrons. Sulphurhexafluoride is a good electron scavenger.<sup>13-16</sup>



$K_4^{13,14} = 1.5 \times 10^{14} \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$  It was found that  $SF_6$  completely removed the peak. This indicated that the formation of  $C_{10}H_9$  radical follows reactions (2) and (3).

The naphthalene radical  $C_{10}H_9$  did not follow a simple decay process. This complication in the kinetics may arise out of the following modes of disappearance by the radical reactions (6,7).



On irradiation polynuclear hydrocarbons like naphthalene and polyphenyls like biphenyl give a polymeric mixture containing materials with higher molecular weight than the original compound.<sup>17</sup> Burr and Scarborough<sup>18</sup> have observed the polymerization of biphenyl radical  $C_{12}H_{11}$  in the irradiated biphenyl. However, the decay of naphthalene radical  $C_{10}H_9$  in triethylamine undergoes a second order process with a rate constant equal to  $(1.13 \pm 0.11) \times 10^6 \text{ } \epsilon_{270 \text{ nm}}^{-1} \text{ s}^{-1}$ .

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