

Decay of Biphenyl<sup>-1</sup> and Pyrene<sup>-1</sup> in Liquid Methylamine at 298K

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**Summary:** A pulse-radiolytic study shows that the anion of biphenyl decayed in liquid methylamine via a first order process. The absorptions at 410 and 640 nm both decayed with the same rate – constant.  $k$  is  $(2.4 \pm 0.3) \times 10^5 \text{ s}^{-1}$  in the concentration range  $1.16 \times 10^{-3} - 5 \times 10^{-2} \text{ mol dm}^{-3}$  of biphenyl. However, in a  $5 \times 10^{-4} \text{ mol dm}^{-3}$  solution of biphenyl  $k$  is  $(1.1 \pm 0.06) \times 10^5 \text{ s}^{-1}$ . The anion of pyrene showed an absorption spectrum with a maximum at 490 nm. It decayed by a second order process having  $2k = (3.5 \pm 0.4) \times 10^5 \epsilon_{490} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . When a solution of pyrene containing  $10^{-3} \text{ mol dm}^{-3}$  methylamine hydrochloride was irradiated, the order of the decay remained unchanged, but  $2k$  was reduced to  $(1.3 \pm 0.2) \times 10^5 \epsilon_{490} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

## Introduction

Decay kinetics of the anion of biphenyl has been studied in polar media like methanol, ethanol and isopropanol<sup>1</sup>. It was therefore thought to study the decay of the anion of biphenyl in liquid methylamine. The decay of the pyrene anion has also been studied.

## Experimental

Methylamine and sulphurhexafluoride from Matheson Co. were purified as described elsewhere<sup>2</sup>. Biphenyl (puriss) from Koch Light was used as received. Pyrene was zone refined. The pulse-radiolytic cell was capable of with standing a high pressure of methylamine at 298K<sup>3</sup>. The pulsed Van de Graaf electron accelerator at the Cookeridge High Energy Radiation Centre, Leeds, was the radiation source. The basic pulse radiolysis system for microsecond pulses has been described elsewhere<sup>4,5</sup>.

## Results

A  $10^{-2} \text{ mol dm}^{-3}$  solution of biphenyl in methylamine was pulse-radiolysed with a dose of about 1.5 krad in a  $0.2 \mu\text{s}$  pulse and the absorption in the wavelength range 270-690 nm measured. The spectrum revealed a strong UV band with a maximum at 410 nm and a broad visible band with peaks at 600 and 640 nm. This is the characteristic spectrum of the anion of biphenyl<sup>6</sup>. The absorption was eliminated when a  $10^{-2} \text{ mol dm}^{-3}$  solution of biphenyl was pulse radiolysed in the presence of an efficient electron scavenger,  $\text{SF}_6$ . The absorption was attributed to the anion of biphenyl. The absorption was not affected by radiation products or depletion of the solute (Table 1). The best straight line from a plot of  $\log D$  versus time was obtained by a weighted least mean squares procedure (Fig. 1).  $D$  is optical density at a time  $t$ . The values of rate – constant in different concentrations of biphenyl is shown in Table 2. As indicated in Table 2,  $k$  is  $(1.1 \pm 0.06) \times 10^5 \text{ s}^{-1}$  in a  $5 \times 10^{-4} \text{ mol dm}^{-3}$  solution of biphenyl and is  $(2.4 \pm 0.3) \times 10^5 \text{ s}^{-1}$  in the concentration range  $1.16 \times 10^{-3} - 5 \times 10^{-2} \text{ mol}$

Table 1. Effect of Successive pulses on Optical Density in Solutions of Biphenyl at 640 nm.

[Biphenyl]/mol dm <sup>-3</sup>	No. of Pulses	Optical Density/ Arbitrary Units
5 x 10 <sup>-4</sup>	1	1.00
	2	0.98
5 x 10 <sup>-3</sup>	1	1.00
	2	0.98
	3	1.02
2 x 10 <sup>-2</sup>	1	1.00
	2	0.98
	3	0.97
	4	1.00

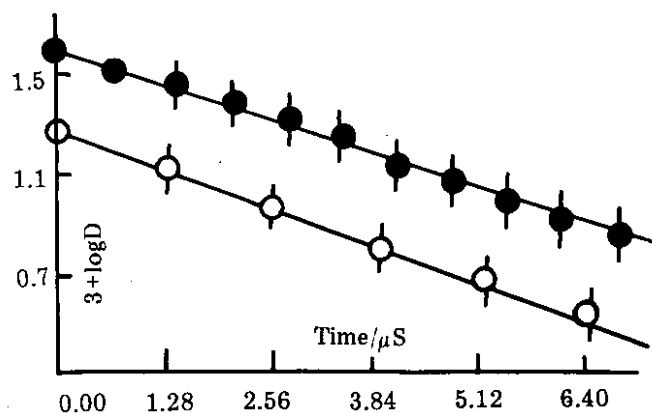


Table 2. Rate-constants for the Decay of the Anion of Biphenyl at 298K.

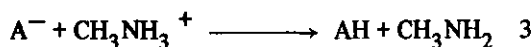
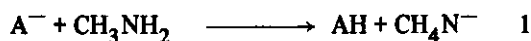
[Biphenyl]/mol dm <sup>-3</sup>	λ/nm	<sub>1</sub> k/10 <sup>5</sup> s <sup>-1</sup>	Dose/krads
5 × 10 <sup>-4</sup>	640	1.1	1.2
	410	1.1	1.0
		1.2	0.5
1.16 × 10 <sup>-3</sup>	640	2.3	1.2
	410	2.7	1.2
		2.7	0.5
5 × 10 <sup>-3</sup>	640	2.1	1.3
	410	2.5	1.1
5 × 10 <sup>-2</sup>	630	2.5	1.6
		2.4	0.4

dm<sup>-3</sup>. This difference is above the limits of experimental errors. The absorptions of 410 and 640 nm both decayed via first order reactions with the same rate-constant. This is consistent with both the absorptions being attributed to the same species.

The pulse irradiation of a 5 × 10<sup>-2</sup> mol dm<sup>-3</sup> solution of pyrene in methylamine was done in the range 350 – 550 nm using a 0.2 μs pulse. The absorption spectrum following a dose of about 1.3 krads per pulse had a maximum at 490 nm. This is the characteristic spectrum of the anion of pyrene<sup>7</sup>. The absorption at 490 nm was eliminated by SF<sub>6</sub>. In this case also the absorption was not affected by radiation products or depletion of the solute (Table 3). A plot of 1/D versus time gives a straight line, indicating that the anion of pyrene decayed by a second order process (Fig. 2).  ${}_2k = (3.5 \pm 0.4) \times 10^5 \epsilon_{490} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . When a solution of pyrene containing 10<sup>-3</sup> mol dm<sup>-3</sup> methylamine hydrochloride was irradiated, the order of the reaction causing removal of the anion was again 2, but  ${}_2k$  was reduced to  $(1.3 \pm 0.2) \times 10^5 \epsilon_{490} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

### Discussion

The first order decay process of the anion of biphenyl (A<sup>-</sup>) may involve one or more of the following reactions 1,2 and 3:



The reaction 3 would be a pseudo first order process provided [CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>] is very high compared with [A<sup>-</sup>]. This is unlikely since the equilibrium constant for self-

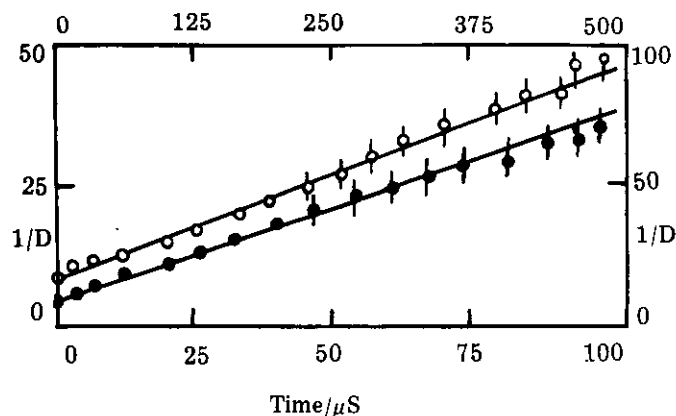
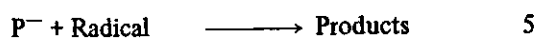
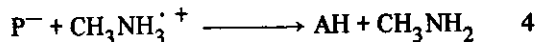


Table 3. Effect of Successive Pulses on Optical Density in Solution of Pyrene at 490 nm.

[Pyrene]/mol dm <sup>-3</sup>	No. of Pulses	Optical Density/ Arbitrary Units
5 × 10 <sup>-2</sup>	1	1.00
	2	0.99
	3	1.01
2 × 10 <sup>-2</sup>	1	1.00
	2	1.00
	3	1.00
	4	1.00
	5	1.00
	6	1.00

dissociation of methylamine is expected to be small. In case A<sup>-</sup> decays via reaction 2 the rate constant of pseudo-first order process increases with [A]. This is not observed in the present work in the concentration range 1.16 × 10<sup>-3</sup> – 5 × 10<sup>-2</sup> mol dm<sup>-3</sup>, although there is a decrease in the rate-constant in a 5 × 10<sup>-4</sup> mol dm<sup>3</sup> solution. The anion of biphenyl decayed in liquid methylamine via a first order process (reaction 1). In methanol, ethanol and iso-propanol the anion of biphenyl decayed by a first order process by reacting with the solvent molecules<sup>1</sup> (Table 4).

The second order decay of the pyrene anion (P<sup>-</sup>) in methylamine may be via reactions 4 and 5.



CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> ions are the main ions in methylamine<sup>8</sup>. The order of the decay of the pyrene anion remained unchanged when a solution of pyrene was irradiated in the presence of methylamine hydrochloride. This implies

Table 4. Rate-constant for the Decay of the Anion of Biphenyl in different media.

Solvent	Rate Constant for Decay
	${}_1k/10^5 \text{ s}^{-1}$
Methylamine	<sup>a,b</sup> 2.4 ± 0.3
Methanol	<sup>c</sup> 17 ± 3
Ethanol	<sup>c</sup> 4.4 ± 0.4
iso-Propanol	<sup>c</sup> 0.72 ± 0.14

<sup>a</sup>Values from this work. <sup>b</sup> ${}_1k = (1.1 \pm 0.06) \times 10^5 \text{ s}^{-1}$  obtained in a solution of  $5 \times 10^{-4} \text{ mol dm}^{-3}$  of biphenyl is not included here because this low value is beyond the experimental uncertainty. <sup>c</sup>Values are taken from reference 1.

that the anion of pyrene did not decay via reaction 4. Moreover,  $\text{CH}_3\text{NH}_2 \cdot \text{HCl}$  reduced the rate-constant to 36% of the original value. It is difficult to account for this reduction.

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