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# Thermal and Photochemical Decomposition of Aqueous Bromamine-B†

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Thermal decomposition of aqueous bromamine-B is studied between the temperature range 50–90°C. Photolysis of aqueous bromamine-B is studied with a UV light source ($\lambda = 2537$ Å) and the products have been identified. A suitable photolytic mechanism is suggested based on the observed results.

## INTRODUCTION

Sodium salt of N-bromobenzenesulphonamide or bromamine-B (BAB) has received considerable attention as an oxidimetric reagent.[1–4] A survey of literature reveals that almost no information is available in the literature on the thermal decomposition and photolysis of aqueous bromamine-B solution, except for the photolysis of chloramine-T.[5–7] In the present work, we are reporting our studies on thermal and photochemical stability of aqueous BAB solutions. Thermal stability has been studied over a temperature range of 50–90°C, while photochemical work has been carried out with a UV light source of wavelength 2537 Å. A kinetic study of the photochemical decomposition has also been made.

## EXPERIMENTAL

BAB was prepared[8] from benzenesulphonamide. An approximately decimolar stock solution was prepared and standardized by the iodometirc method. All other reagents were of AR grade. All solutions were prepared in triply distilled water. Thermal decomposition studies were carried out with 0.01 M BAB solutions (25 or 50 mL) in iodine flasks, in a thermostat over a period of 30 min to 4 h.

UV irradiations were carried out with a Philips (Holland) low pressure mercury vapour lamp (15 W) and the wavelength of the light[9] was 2537 Å. The experimental set up has been described elsewhere.[10] Exactly 10 mL of BAB solution were taken in quartz cells and exposed to UV radiation for various intervals of time. The photolytic decomposition was studied for more than two half-lives. The extent of thermal and photochemical decomposition of BAB solutions were determined by iodometic titration of the experimental solution and comparison with a blank solution whereever necessary. The intensity of the

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incident light ($I_0$) falling on the system was determined using the uranyl oxalate actinometer.[9]

A JASCO, Model UVIDEC-610 UV-VIS spectrophotometer with 1.0 cm matched quartz cells was used to record the UV spectra. A direct reading conductivity meter 304 (Systronics) and a digital pH meter, Model LI-120 (Elico) were used for conductance and pH measurements respectively.

FT-IR spectra (KBr disc) were recorded on a BRUKER IFS66v FT-IR spectrometer.

FT-$^1$H and $^{13}$C nmr spectra were recorded on a JEOL GSX 400 MHz NMR spectrometer.

## RESULTS AND DISCUSSION

### Thermal Decomposition

The results of thermal stability of aqueous solution of BAB (0.01 M) over the temperature range 50–90°C for periods varying from 30 min to 4 h are shown in Table 1. It is seen that no decomposition of BAB will take place at 50°C. At 60°C, the solution was stable up to 2h and after 3 h, the percentage decomposition rises to 0.579. Between 70–80°C, the percentage decomposition rises from 0.584 to 1.778. However at 90°C, there is a steady increase in percentage decomposition from 1.778 to 4.735. At temperature above 60°C, free bromine was evolved from the solutions and tests with starch-iodide paper gave positive results. It can therefore be concluded that reactions with BAB should not be carried out at temperatures above 60°C.

TABLE-1
THERMAL DECOMPOSITION OF AQUEOUS BROMAMINE-B (0.01 M) WITH TIME AT DIFFERENT TEMPERATURES

| Time in hrs. | Percent decomposition at | | | | |
|---|---|---|---|---|---|
| | 50°C | 60°C | 70°C | 80°C | 90°C |
| 0.5 | — | — | 0.579 | 1.185 | 1.778 |
| 1.0 | — | — | 0.579 | 1.185 | 2.370 |
| 2.0 | — | — | 0.579 | 1.185 | 2.960 |
| 3.0 | — | 0.579 | 0.579 | 1.185 | 3.552 |
| 4.0 | — | 0.579 | 0.584 | 1.778 | 4.735 |

### Photochemical Decomposition

The photochemical decompostion kinetics of BAB solutions has been studied in the range of 0.01–0.0005 M. The rate constant k increase with dilution from $1.99 \times 10^{-5}$ sec$^{-1}$ to $30.70 \times 10^{-5}$ sec$^{-1}$ in the [BAB] range 0.01–0.0005 M, at $I_0 = 6.0 \times 10^{15}$ quanta/sec and temperature of 25 ± 0.5°C. The results are given in Table-2. A plot of log $V_0/V_t$ against time, where $V_0$ and $V_t$ refer to titre values at

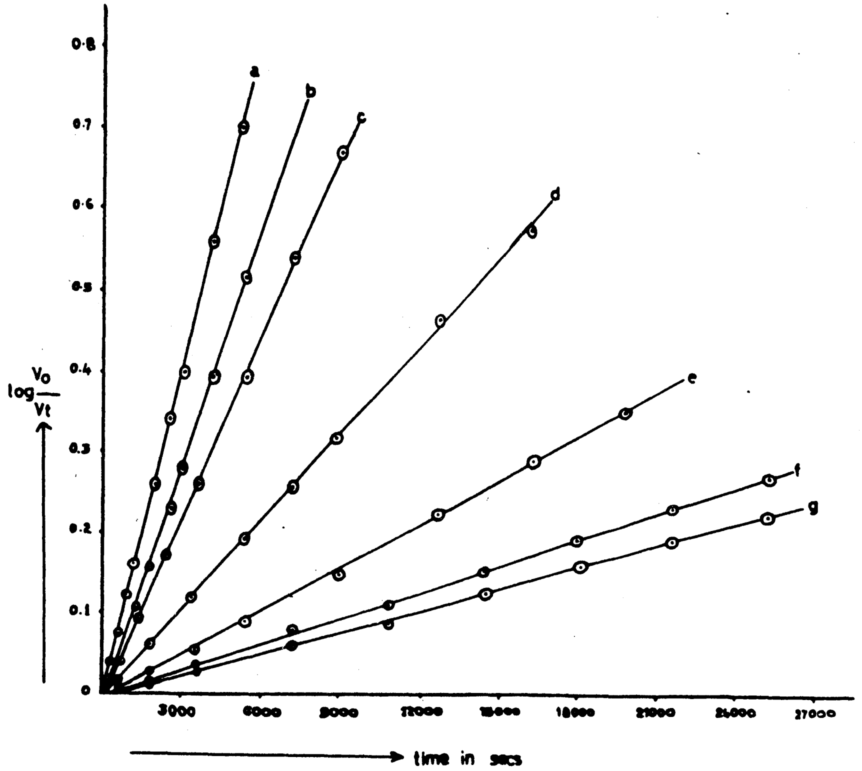


Fig. 1. Plot of log $V_0/V_t$ versus time (secs)
(a to g represents 0.0005 M to 0.01 M [BAB])

zero times and various intervals of time t (secs) respectively and a plot of log k against log [BAB] (negative slope = 0.98) are shown in Figs. 1 and 2, thus indicating first order with respect to [BAB]. The average quantum efficiency ($\phi$) for the disappearance of BAB is 0.18 for 0.01 M, 0.16 for 0.0025 M and 0.14 for 0.0005 M BAB with the intensity of the incident light $I_0$ being $6.0 \times 10^{15}$ quanta/sec at 2537 Å. The quantum efficiency for chloramine-T photolysis[7] was around 0.2 for $I_0 = 6 \times 10^{18}$ quanta/min and $\lambda = 3660$ Å. Experiments between 25 and 35°C show that the temperature coefficient is 1.05 (1.10 for CAT between 30 and 40°C), $k_{35} = 17.808 \times 10^{-5}$ sec$^{-1}$ for 0.001 M BAB. This shows the absence of a thermal reaction in the temperature range of 25–35°C.

Table 3 gives exprimental values of rate constant k for photochemical decomposition of 0.001 M BAB at various incident light intensities $I_0$. The last column gives values of rate R, calculated from the relation R = k [BAB]. A plot of log R against log $I_0$ gives a straight line with a slope of 1.0 and is shown in Fig. 3. A slight decrease in k on photolysis was noticed by the addition of NaBr to BAB solution indicating no side reactions and the results are given in Table 4.

pH measurements showed that solutions of BAB become more acidic upon irradiation (from pH *ca.* 6.0 to *ca.* 3.0) and a slight yellow colouration is noticed

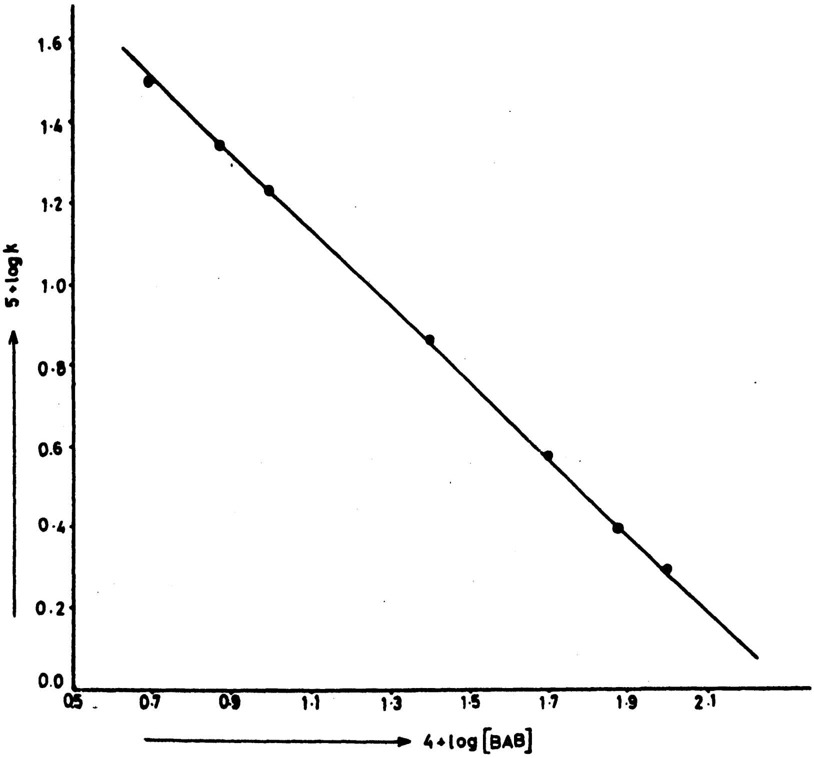


Fig. 2. Plot of 5 + log k versus 4 + log [BAB]

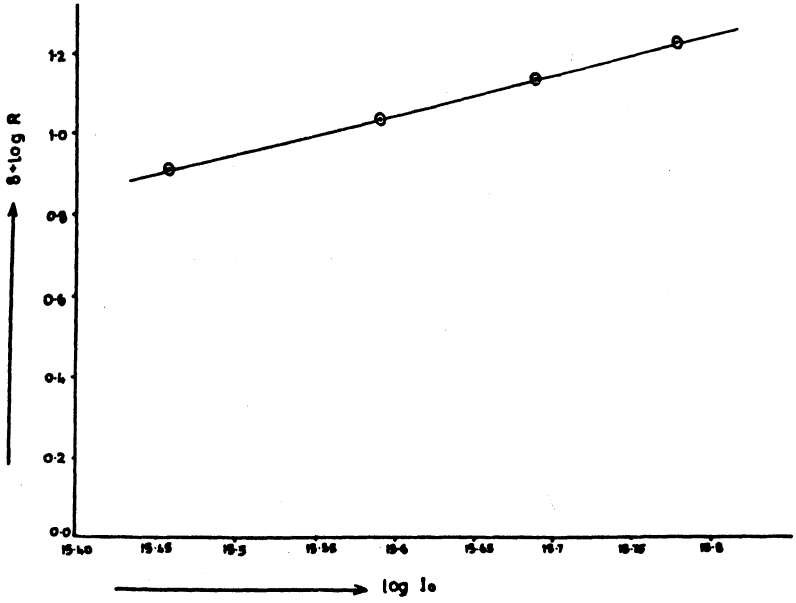


Fig. 3. Plot of 8 + log R versus log $I_0$

after photolysis. The conductivity of the solution slightly increases after photolysis. An attempt was made to identify the photolytic products. No apparent change was noticed in the UV spectrum of the products upon photolysis. Using the TLC technique (chloroform : acetone : benzene = 7 : 1 : 5), only two spots were detected with iodine as the spray reagent indicating the formation of benzensulphonamide and dibromamine-B in the irradiated solution of BAB. Further, the ether extract of the photolysed BAB solution was concentrated and the mixture separated by column chromatography using silica gel as adsorbent and chloroform : acetone (7 : 1 v/v) as eluent. The first fraction was found to contain dibromamine-B (DBB) and benzenesulphonamide (BS) in the second fraction. DBB and BS were further characterised by their IR, $^1H$ and $^{13}C$ NMR spectroscopy. Liberation of free bromine from the photolytic solution was noticed. No complex mixture[11] or resinous products[12] were observed.

TABLE-2
PHOTOCHEMICAL DECOMPOSITION OF AQUEOUS BAB AT DIFFERENT CONCENTRATIONS
($\lambda$ = 2537Å; Temp. = 25 ± 0.5°C; $I_0 = 6.0 \times 10^{15}$ quanta/sec)

| [BAB]mol $dm^{-3}$ | $k \times 10^5$ $sec^{-1}$ |
|---|---|
| 0.01000 | 1.99 |
| 0.00750 | 2.44 |
| 0.00500 | 4.07 |
| 0.00250 | 8.01 |
| 0.00100 | 16.96 |
| 0.00075 | 21.93 |
| 0.00050 | 30.70 |

TABLE-3
EFFECT OF $I_0$ ON THE RATE OF PHOTOCHEMICAL DECOMPOSITION OF AQUEOUS BAB

| [BAB] in mol $dm^{-3}$ | $I_0 \times 10^{-15}$ quanta/sec | $k \times 10^5$ $sec^{-1}$ | $R \times 10^8$ (R=kC) |
|---|---|---|---|
| 0.001 | 2.875 | 8.128 | 8.128 |
| 0.001 | 3.873 | 10.949 | 10.949 |
| 0.001 | 4.902 | 13.858 | 13.858 |
| 0.001 | 6.000 | 16.960 | 16.960 |

TABLE-4
EFFECT OF ADDITION OF NaBr ON THE PHOTOCHEMICAL DECOMPOSITION OF BAB SOLUTION
([BAB] = 0.001 mol $dm^{-1}$; Temp. = 25 ± 0.5°C; $I_0 = 6 \times 10^{15}$ quanta/sec)

| [NaBr] mol $dm^{-3}$ | 0 | 0.05 | 0.20 | 0.35 | 0.50 |
|---|---|---|---|---|---|
| $k \times 10^5$ $sec^{-1}$ | 16.96 | 14.33 | 14.39 | 14.34 | 14.27 |

The photochemical decomposition of BAB solution does not resemble the photochemical reaction mechanisms of either chloramine-T or $OCl^-$ ion. Based on the present work and experimental observations, the rate law for the photolytic decomposition of BAB solutions can be represented by the equaion

$$-\frac{d[BAB]}{dt} = k'\frac{I_0}{[BAB]} \tag{1}$$

where k′ is a constant, $I_0$ is the intensity of the incident light and [BAB] indicates the concentration of BAB solution.

The work of Hardy and Johnston[1] and our work on conductometric studies[13]. indicate the following equilibria with BAB in acid solutions.

$$RNBrNa \rightleftharpoons RNBr^- + Na^+ \tag{2}$$

$$RNBr^- + H^+ \overset{K_a}{\rightleftharpoons} RNHBr \tag{3}$$

$$2RNHBr \overset{K_d}{\rightleftharpoons} RNh_2 + RNBr_2 \tag{4}$$

$$K_d = 5.8 \times 10^{-2} \text{ at } 25°C$$

$$RNHBr + H_2 \overset{K_h}{\rightleftharpoons} RNH_2 + HOBr \tag{5}$$

$$K_h = 4.21 \times 10^{-3} \text{ at } 25°C$$

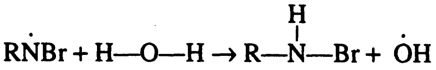
With the above results for the photolysis of BAB solutions and the equilibria of BAB in acid solutions, the following photochemical reaction mechanism has been proposed for the decomposition of BAB solution. The first step is the activation process,

$$RNBr^- + h\nu \rightarrow (RNBr^-)^* \tag{6}$$

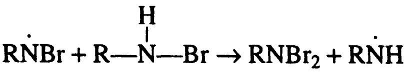
and the second reaction is the formation of $R\dot{N}Br$ as shown below.

$$(RNBr)^* \rightarrow R\dot{N}Br + e^- \tag{7}$$

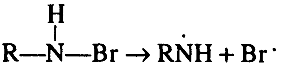
The various propagation reactions could be represented as



$$R\dot{N}Br + H\text{—}O\text{—}H \rightarrow R\text{—}\overset{H}{\overset{|}{N}}\text{—}Br + \dot{O}H \tag{8}$$



$$R\dot{N}Br + R\text{—}\overset{H}{\overset{|}{N}}\text{—}Br \rightarrow RNBr_2 + R\dot{N}H \tag{9}$$



$$R\text{—}\overset{H}{\overset{|}{N}}\text{—}Br \rightarrow R\dot{N}H + Br^{\cdot} \tag{10}$$

$$R\dot{N}H + H\text{—}O\text{—}H \rightarrow RNH_2 + \dot{O}H \tag{11}$$

$$Br^{\cdot} + \dot{O}H \rightarrow HOBr \tag{12}$$

and finally the termination step can be written as

$$Br^{\cdot} + Br^{\cdot} \rightarrow Br_2 \qquad (13)$$

where R is $C_6H_5SO_2$.

The above photochemical reaction mechanism involving various free radicals is well supported by the fractional value of quantum yield (ϕ) observed for the photochemical decomposition, *as not every excited species* $(RNBr^-)^*$ *will take part in the reaction.* As the BAB solution becomes more dilute, there is greater penetration of light through the system and also the deactivation rate $[(RNBr)^* + RNBr^- \rightarrow 2RNBr^-]$ is less and this factor tends to increase the rate with dilution. However, the variation in the quantum yield (ϕ) observed for the photochemical decomposition of BAB in the concentration range of 0.01–0.0005 M is not significant. Probably, by using a high intensity of light ($> 10^{18}$ quanta/sec), valuable information could further be obtained on the photolysis of BAB solution. It may be concluded that the aqueous solution of BAB is not stable thermally at temperatures > 60°C. The rate of disappearance of BAB is proportional to the first power in $I_0$ and inverse first order with respect to [BAB] in the photolysis experiment. The reaction follows a free radical mechanism and the products are $RNH_2$, $RNBr_2$ and $Br_2$.

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