

EVOLUTION OF THE DIHALIDE ION Br_2^- IN AQUEOUS SOLUTIONS

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Summary

Aqueous solutions of NaBr were prepared and placed in a 25 cm long quartz cell. After a photolyzing flash a transient absorption due to Br_2^- , centred at $\sim 3500 \text{ \AA}$ and $\sim 1500 \text{ \AA}$ wide was observed in agreement with Grossweiner and Matheson. The kinetics of Br_2^- decay was studied at concentrations ranging from 10^{-5} to $10^{-1} M$. The decay was found to be at all concentrations a second order process and to become slower from 10^{-5} to $10^{-3} M$ and faster from 10^{-3} to $10^{-1} M$. The kinetics of the decay was explained as due to three simultaneous bimolecular reactions; the rate constants for these reactions were determined. Additional proofs for the postulated mechanism, in which the species Br_2 and Br_3^- participate, were derived from absorption measurements of the end-products and other flash photolysis experiments which were performed at temperatures higher than 300 K.

Introduction

Alkali halide solutions have been the object of flash photolysis [1 - 6] and pulse radiolysis studies [7 - 14]. Dihalide ion formation by flash photolysis of alkali halide aqueous solution was observed by Grossweiner and Matheson [1]; these workers noted the presence of transient absorption bands in the 3500 \AA region when photolyzing alkali halide aqueous solutions and attributed it to the presence of I_2^- , Br_2^- and Cl_2^- dihalide ions. Subsequently [2] the same workers, investigating in detail the evolution of the species I_2^- obtained from the flash photolysis of KI in aqueous solution, discovered a concentration dependence of this process in the range of concentrations from 5×10^{-4} to $10^{-2} M$ and established that the disappearance of I_2^- is a second order process which becomes faster at lower concentrations. The purpose of the present work is the study of the mechanism of the decay kinetics of the transient species Br_2^- in aqueous solution.

Experimental

The absorption spectra measurements were performed on a Cary Model 14 dual beam absorption spectrophotometer.

The flash photolysis experiments were performed with an apparatus which could be operated in two different modes: (a) the flash photolysis spectroscopic mode, and (b) the kinetic spectrophotometric mode. With both (a) and (b) the solutions were kept in a cylindrical quartz vessel of 1 in. diameter and 10 in. length. The diameter of the cross-section probed was 2 mm. The vessel was placed at the center of a cylindrical silver plated and rodiated metal cavity, 13 cm in diameter. Alongside the cell, two linear xenon flash tubes provided the photolyzing flash; these flash tubes were powered by a 20 μ F capacitor charged at 9 kV. The geometrical length of the flash was 10 in.

In mode (a) above the spectral lamp was a Suntron 6C (Xenon Corp.) flash tube powered by a 2 μ F capacitor charged at 8 kV: the lamp was triggered a set time after the photolyzing flash. The transient absorption was observed by means of a Jarrell Ash 3 meter Wadsworth type spectrograph and recorded on a Kodak spectroscopic film. In mode (b) the probing beam was obtained by means of a continuous 75 W high pressure xenon lamp Model K-1 (Xenon Corp.) and the transient absorption signal was observed through an Ebert type Jarrell Ash 1/4 m monochromator and an EMI 9662B photomultiplier. The signal from the photomultiplier was presented on a Tektronix Model 564B scope and photographed. The slits of the monochromator had both a width of 150 μ m resulting in a resolution of ~ 25 Å. The linearity of the photomultiplier was verified by the use of neutral density filters.

Great precautions were taken to examine the flash light intensity inside the sample cell; a non-uniform intensity gradient across the cell results in a non-uniform concentration of the transient species Br_2^- . In order to investigate this effect we performed the following calculation based on an argument suggested by Grossweiner and Matheson [2]. The following assumptions are made: (1) the intensity of the photolyzing flash is practically constant in the region in which Br^- absorbs, *i.e.* 2000 to 2200 Å [15]; (2) the quantum yield for the production of Br_2^- is independent of wavelength.

The following function is introduced:

$$f(x) = -\frac{1}{I_0} \frac{dI}{dx} = 2.303 [\text{Br}^-] \int_{2000 \text{ \AA}}^{\infty} \epsilon(\lambda) \exp\{-2.303 [\text{Br}^-] \epsilon(\lambda)x\} d\lambda$$

- where $\epsilon(\lambda)$ = extinction coefficient of Br^- ,
 $[\text{Br}^-]$ = concentration of Br^-
 I_0 = light intensity of the photolyzing flash at the surface of the reaction cell, and
 I = light intensity of the photolyzing flash at a distance x cm away from the wall of the reaction cell.

$f(x)$ is the fraction of light absorbed by Br^- in the region between x and $x + dx$, x being the distance from the cell's wall. The following approximate formula, based on our absorption measurements, was used for $\epsilon(\lambda)$:

$$\epsilon(\lambda) = -60 \times 10^8 \lambda + 131,000 \text{ for } 2000 \times 10^{-8} \leq \lambda \leq 2150 \times 10^{-8}$$

$$\epsilon(\lambda) = 2000 \exp[-28 \times 10^5 (\lambda - 2150 \times 10^{-8})] \text{ for } \lambda \geq 2150 \times 10^{-8}$$

where λ is expressed in cm.

The reaction cell has a diameter of 2.54 cm; one particular point of the cell can be reached by light coming from two opposite sides of the cell's surface and, therefore, the meaningful function is $f(x) + f(2.54 - x)$ which in Fig. 1 is plotted against $1.27 - x$ for six different Br^- concentrations. Figure 1 represents, apart from a scale factor, and within the limits of the assumptions made, the distribution of the concentration of Br_2^- across the cell; notice that the point $1.27 - x = 0$ corresponds to the center of the cell. It is clear from Fig. 1 that for all concentrations the light absorbed across the cell was uniform in a cross-section about the center of 2 mm radius. These findings were confirmed experimentally: (a) the peak concentration of Br_2^- following the photolyzing flash varied strongly for solutions with high Br^- concentration when the diameter of an iris inserted in the optical path was varied from, say, 5 to 10 mm, (b) with the iris' radius set at 1 mm the peak concentration of Br_2^- for $[\text{Br}^-] = 1, 10^{-1}$ and $10^{-2} M$ did not change as expected from Fig. 1, and (c) upon reducing the radius of the iris from 1 to 0.5 mm or increasing it to 2 mm, the peak concentration of Br_2^- did not vary for any concentration of Br^- .

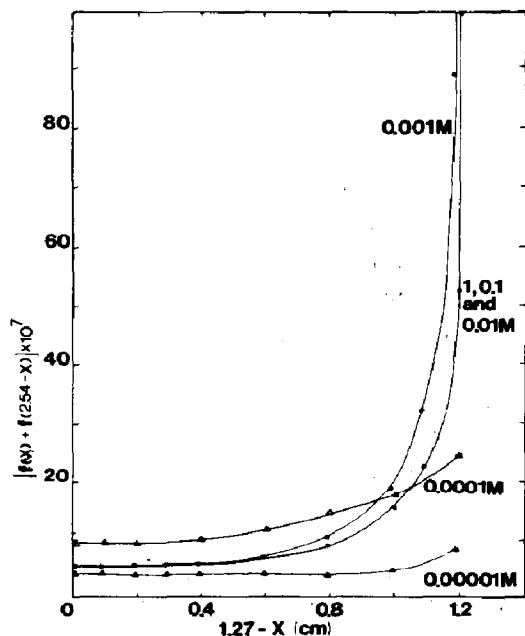


Fig. 1. $f(x) + f(2.54 - x)$ against $1.27 - x$.

Results

Absorption spectra

The absorption spectrum of a 10^{-4} M aqueous NaBr solution was measured; the optical density plot presents a band with an edge at ~ 2200 Å and a peak at ~ 1970 Å. The values of the extinction coefficient $\epsilon(\lambda)$ can be approximated by the formula given in the previous section; at ~ 1970 Å $\epsilon \approx 11,400$ l mol $^{-1}$ cm $^{-1}$.

In order to identify the stable product species, an aqueous solution of 10^{-4} M NaBr was subjected to twenty flashes of photolyzing light; to obtain these flashes two 10 μ F capacitors were charged at 8 kV resulting in 640 J pulses. The absorption spectrum of such solution after irradiation is given in Fig. 2, together with the spectrum of a non-irradiated 10^{-3} M solution which is reported for comparison; the presence of an additional band at ~ 2700 Å in the irradiated solution has to be noted.

The spectrum of Br_3^- was also measured; Br_3^- can be produced by adding bromine to an acidic aqueous bromide solution [7]. When such a solution was examined two absorption bands appeared, one with $\lambda < 2450$ Å attributed to Br^- and another centered at ~ 2700 Å which is attributed to Br_3^- . This latter band resembled in both location and shape the band at ~ 2700 Å in Fig. 2.

Photolysis data

We examined an aqueous solution of 10^{-1} M NaBr by using the apparatus in the flash photolysis spectroscopic mode. The film revealed the presence of a diffuse absorption band centered at ~ 3500 Å; the delay between the photolyzing flash and the spectral flash was initially set at 50 μ s. Setting the delay at increasingly longer times the absorption band was seen to fade out, preserving its diffuse shape and to disappear entirely. As the band centered at ~ 3500 Å faded out another band appeared with a high wavelength edge at ~ 3000 Å.

Aqueous solutions of NaBr with concentrations 10^{-5} , 1.25×10^{-5} , 2×10^{-5} , 5×10^{-5} , 10^{-4} , 2×10^{-4} , 10^{-3} , 10^{-2} and 10^{-1} M were examined with the flash photolysis apparatus in the kinetic mode. Figure 3 shows a typical picture taken by the oscilloscope camera after flashing a 10^{-3} M NaBr aqueous solution; the energy of the photolyzing flash was 810 J as for all the measurements and the monochromator setting was 3500 Å. The picture is actually a four exposure photograph in which the upper straight line represents the base line in absence of any light; the deflection from this base line was obtained by monitoring just the scattered light from the photolyzing flash and represents the shape of the flash pulse; the lowest (noisy) straight line represents the deflection of the scope due to the continuous probing light of the K-1 lamp when no photolyzing flash was present; the decaying trace is the photomultiplier signal in the presence of the probing light right after the photolyzing flash was triggered.

Figure 3 can be used to illustrate how the information on the disap-

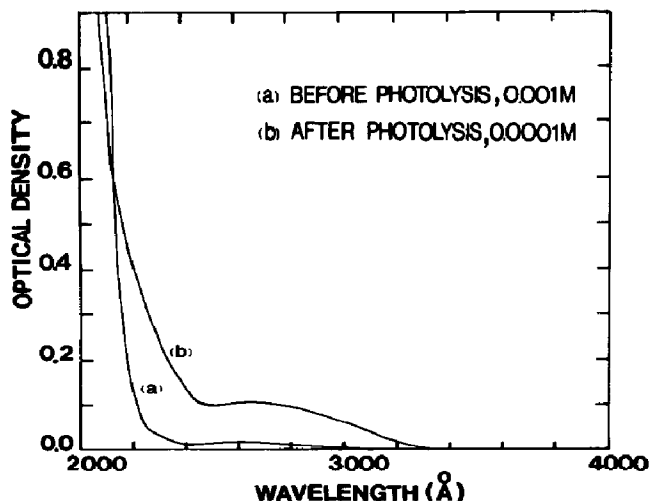


Fig. 2. Absorption spectra of NaBr aqueous solutions.

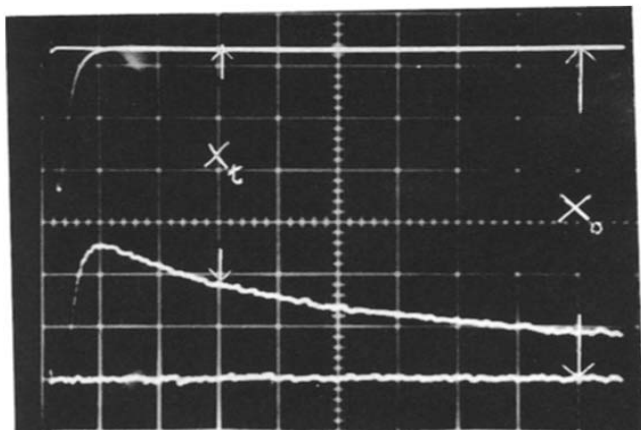


Fig. 3. Typical decay pattern of the Br_2^- transient absorption. ($100 \mu\text{s}/\text{div}$, $0.2 \text{ V}/\text{div}$; $[\text{Br}^-] = 10^{-3} \text{ M}$).

pearance of Br_2^- was obtained. The deflection X_0 is proportional to the intensity of the probing light at the cell input and the deflection X_t is proportional to the intensity of the light at the cell output at the time t after the photolyzing flash. According to Beer's law these two quantities are related by the equation:

$$X_t = X_0 10^{-\epsilon_2(\lambda) [\text{Br}_2^-]_t L}$$

where $\epsilon_2(\lambda)$ = extinction coefficient of Br_2^- ,
 $[\text{Br}_2^-]_t$ = concentration of Br_2^- at time t after the photolyzing flash,
 and L = length of the cell.

From this relation the optical density of Br_2^- at a time t after the photolyzing flash, called $D_2(t)$ can be derived:

$$D_2(t) = \log_{10} \frac{X_0}{X_t} = \epsilon_2(\lambda) [\text{Br}_2^-]_t L$$

Knowing $\epsilon_2(\lambda)$ for the particular wavelength used and the length of the cell (25 cm), it is possible to derive the concentration of Br_2^- at a particular time t .

A series of measurements were performed with the following provisions: (a) for each concentration the disappearance of Br_2^- was examined by setting the monochromator first at 3500 and then at 3800 Å, and (b) for each concentration and each wavelength three pictures were taken. This resulted in six pictures for each concentration containing essentially the same information.

The optical density $D_2(t)$ when plotted against time on a semilog plot for first-order decay did not yield a straight line regardless of concentration, excluding a first-order process. For second-order decay $D_2(t)^{-1}$ was plotted *versus* time and Fig. 4 presents some of these plots; $D_2(t)^{-1}$ is reported in correspondence to the peak absorption (3500 Å) and at the other wavelength used (3800 Å). The points reported in Fig. 4 refer to one particular picture for each concentration.

The slopes of the D_2^{-1} *versus* t lines are reported in Table 1. Figure 5 reports the same slopes in correspondence to $\lambda = 3500$ and 3800 Å; each point represents the average from the data obtained from three pictures. We note here that the points on the 3800 Å curve can be brought in coincidence with the corresponding points on the 3500 Å curve by scaling them down by a factor of ~ 0.85 .

Finally, we explored the regions of the spectrum other than the one occupied by the species Br_2^- and detected the presence of a transient absorption with peak at ~ 2700 Å. Figure 6 illustrates the kinetic response of this absorption at its peak (2700 Å). These data were obtained for 1 M NaBr; concentrations of 10^{-1} and 10^{-2} M gave similar patterns. No significant photolysis signal was obtained for concentrations 10^{-3} M or smaller.

In order to gain some additional information on the mechanism by which the transient species Br_2^- disappears, flash photolysis measurements were made on NaBr solutions above room temperature. A special double-walled quartz (commercial grade) cell was used; it consists of an inner cylinder of 2.54 cm diameter and 25 cm length and an outer cylinder of 6.54 cm diameter and 22 cm length; water was circulated between the inner and outer cylinder and the NaBr solution was kept inside the inner cylinder. A "Constant Temperature Bath and Circulator" Model K-2 by Lauda Corp. was inserted in the water circuit; this instrument allows a range of temperatures of the circulating water from room temperature to 100 °C.

A 10^{-1} M aqueous NaBr solution was put in the inner cell and measurements were made in the kinetic mode with the monochromator set at 3500 Å. The temperature of the solution was measured by inserting a thermometer into the inner cell; the temperatures selected for the study were 23, 39 and 57 °C. For these measurements the flash tubes were energized by two 10 μF capacitors, charged at 10 kV resulting in flash energy of 1000 J. The inverse of the optical density, when plotted against

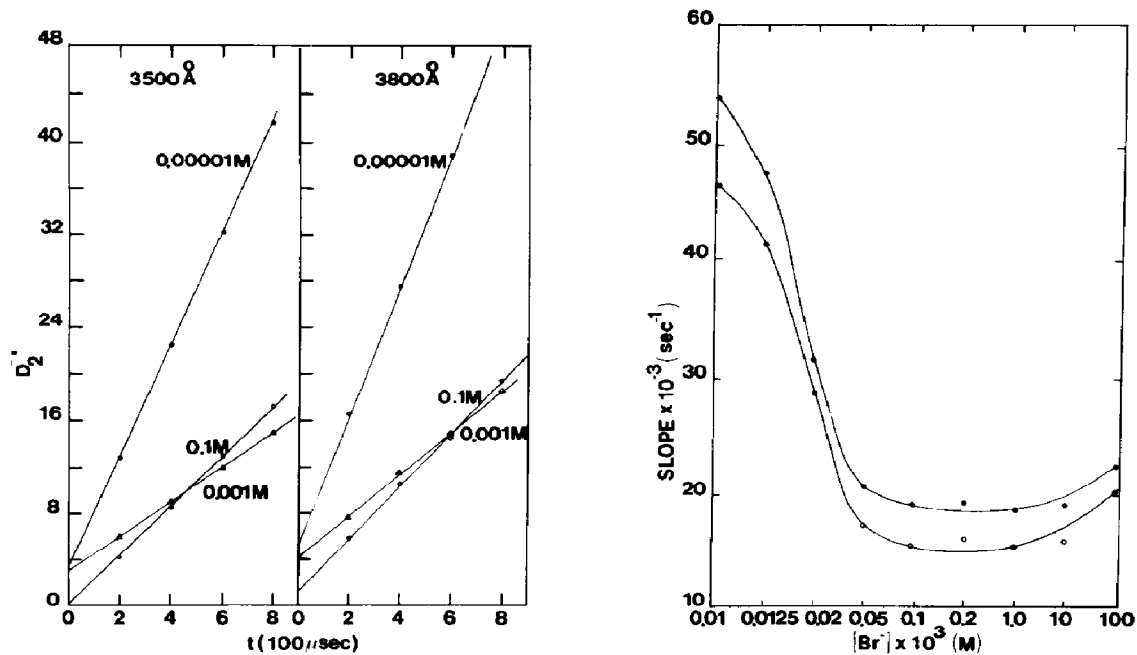


Fig. 4. Disappearance of Br_2^- as a second-order process.

Fig. 5. Slopes of $[D_2^{-1}, t]$ lines versus Br^- concentration.

TABLE 1

Slope of $[D_2^{-1}, t]$ line

$[Br^-]$ (M)	Slope at 3500 Å (s^{-1})	Slope at 3800 Å (s^{-1})	Ratio
0.00001	46600	54100	0.861
0.0000125	41200	47600	0.866
0.00002	28600	31700	0.902
0.00005	17200	20600	0.835
0.0001	15400	19100	0.806
0.0002	16300	19300	0.845
0.001	15300	18500	0.827
0.01	16100	19000	0.847
0.1	20000	22500	0.889

time yielded a straight line at all temperatures consistent with a second-order decay. The slopes of D_2^{-1} (inverse of the optical density of Br_2^-), versus t lines were plotted against $1/T$ on a semilog paper for possible detection of an Arrhenius type of temperature dependence, but did not yield a straight line, as it is shown in Fig. 7.

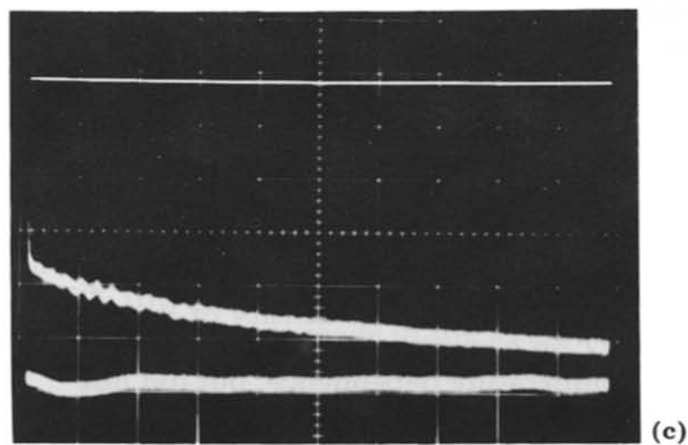
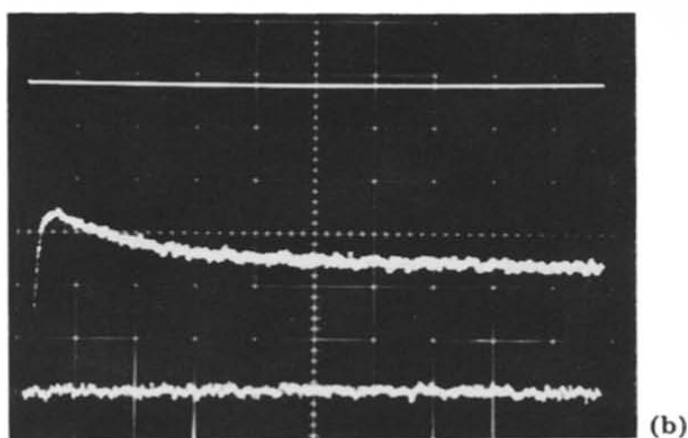
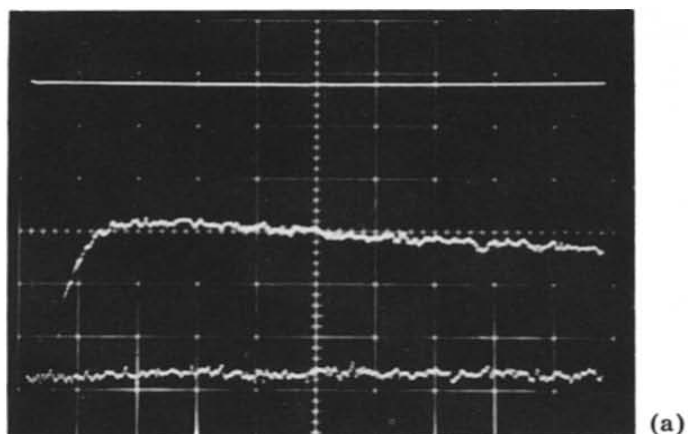


Fig. 6. Transient absorption pattern at 2700 \AA of a 1 M NaBr aqueous solution (0.2 V/div); (a) 100 \mu s/div ; (b) 500 \mu s/div ; and (c) 50 ms/div .

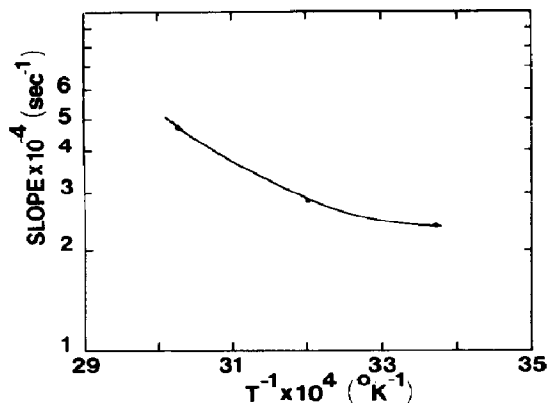


Fig. 7. Slopes of $[D_2^{-1}, t]$ lines versus $1/T$ (T = temperature).

Discussion

The experimental data available deal with the following: (a) absorption spectra of the reactants, (b) absorption spectra of the products, (c) kinetic data in both photographic and photoelectric forms of the transient species, and (d) kinetic data in both photographic and photoelectric forms of the products.

The tasks before us are the following: (1) interpretation of the individual piece of experimental evidence, and (2) interconnection of all the data and setting up an overall model.

The first task consists essentially in a process of identification of stable and transient species; the second task consists in the establishment of a mechanism for the disappearance of the transient species brought about by the flash photolysis.

Absorption spectra

The absorption spectrum of the species Br^- in aqueous solution was found to be in agreement in both shape and extinction coefficient with those obtained by Rabinowitch [17] and Marcus [18].

Another relevant spectrum is the one of Br_3^- . It was found that the characteristic band of Br_3^- located at $\sim 2700 \text{ \AA}$ [3] could be obtained by using either an aqueous acidic KBr solution with bromine added to it or a NaBr aqueous solution after flash irradiation (Fig. 2). We base on this experimental fact the conclusion that Br_3^- is definitely among the products following the flash photolysis of NaBr.

Basic considerations derived from the flash photolysis data

The following considerations can be made:

(1). The absorption spectra clearly identify the species Br^- and Br_3^- . The extinction coefficient of Br_3^- at the peak of the absorption band, which occurs at $\sim 2700 \text{ \AA}$, is $36,000 \text{ l mol}^{-1} \text{ cm}^{-1}$. The extinction coefficient of Br_2 is expected to be two orders of magnitude smaller at the peak

of its absorption band (4000 Å); it is then clear that the absence of the Br₂ absorption spectrum from the irradiated NaBr solution may be due to the fact that this species is a weak absorber; for this reason its presence as a product of the Br₂⁻ disappearance cannot be excluded, but has to be demonstrated on the basis of other evidence. On the other hand, the presence of Br₃⁻ as a product of the reaction by which Br₂⁻ disappears is shown directly in both spectroscopic and kinetic measurements.

(2). The spectroscopic data present the experimental evidence for the presence of a transient species which has been identified as Br₂⁻ [1 - 3]. The fact that for increased delays between these two flashes the Br₂⁻ absorption band centered at ~ 3500 Å fades out preserving its shape confirms that this entire band is associated with the same species. We noted that as the Br₂⁻ band disappears, the Br₃⁻ band with a high wavelength edge at ~ 3000 Å appears.

(3). The kinetic data on the Br₂⁻ disappearance clearly show that it takes place *via* a second-order process (Fig. 4). Some experimental evidence excludes that this process is elementary: (a) the rate constant for the Br₂⁻ disappearance depends on the concentration of Br⁻ (Fig. 5), and (b) the rate constant of the Br₂⁻ disappearance process, when plotted against the inverse of temperature, fails to show an Arrhenius type of dependence (Fig. 7).

(4) Since the process by which Br₂⁻ disappears is not elementary but it is found to be exactly of a second order, we can conclude it must consist of more than one simultaneous elementary processes.

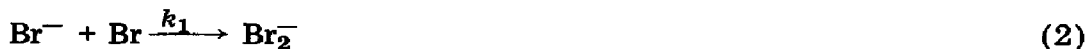
Having made these preliminary conclusions, we can now proceed to interpret the mechanism by which Br₂⁻ disappears.

Mechanism of the Br₂⁻ disappearance

Light absorption in the ultra-violet by the halide ions in aqueous solution produces solvated halogen atoms and aqueous electrons. In the flash photolysis of aqueous halide solutions the primary photochemical reaction is initiated by a strong pulse of light (photolyzing flash); this reaction can be expressed as:



where e_{aq} is the aqueous electron. The formation of the transient species Br₂⁻ follows right after the primary process according to the reaction:



Based on the experimental evidence furnished by both spectroscopic and kinetic data, we have already concluded that the Br₂⁻ decay has to be of second order and non-elementary with Br₃⁻ as a detectable product. Furthermore, we noted that the rate constant depends on the concentration of Br⁻ as in Fig. 5. In other words, we know that the time evolution of the concentration of Br₂⁻ (in symbol [Br₂⁻]) obeys the following differential equation in compliance with a second-order reaction:

$$-\frac{d[\text{Br}_2^-]}{dt} = \beta[\text{Br}_2^-]^2 \quad (3)$$

where β is the rate constant (dependent on $[\text{Br}^-]$). The solution of eqn. (3) can be written as:

$$\frac{1}{[\text{Br}_2^-]_t} - \frac{1}{[\text{Br}_2^-]_0} = \beta t \quad (4)$$

where $[\text{Br}_2^-]_t$ is the concentration of Br_2^- at time t and $[\text{Br}_2^-]_0$ is the concentration of Br_2^- at a time $t = 0$ which is arbitrarily set after the end of the photolyzing flash.

In practice it is convenient to rewrite eqn. (4) in terms of the optical density of Br_2^- , i.e. $D_2 = \epsilon_2 L [\text{Br}_2^-]$:

$$\frac{1}{D_2(t)} - \frac{1}{D_2(0)} = \frac{\beta}{\epsilon_2(\lambda)L} t \quad (5)$$

where $\epsilon_2(\lambda)$ = extinction coefficient of Br_2^- .

From the above expression we know that the slope of the $[D_2^{-1}, t]$ line is equal to $\beta/\epsilon_2(\lambda)L$ and thus Fig. 5 gives the β dependence on $[\text{Br}^-]$ apart from a factor $1/\epsilon_2(\lambda)L$.

Since the disappearance process is non-elementary, there must be at least two elementary reactions taking place simultaneously while this process goes on. But, no matter how many reactions are involved, the time evolution of $[\text{Br}_2^-]$ must satisfy eqn. (3) to be in agreement with the experimental results. We are now going to propose several possible mechanisms of the Br_2^- disappearance and to examine each case in detail on the basis of the experimental results.

Case 1

The first elementary reaction we are going to propose is the second-order reaction:



This reaction is second order and produces the species Br_3^- which was found experimentally to be a product of the Br_2^- disappearance. We may assume that reaction (6) takes place simultaneously with the formation of Br_2^- (reaction 2). If this is the case then the time evolution of $[\text{Br}_2^-]$ and $[\text{Br}]$ must follow the equations:

$$-\frac{d[\text{Br}_2^-]}{dt} = 2k_2[\text{Br}_2^-]^2 - k_1[\text{Br}][\text{Br}^-] \quad (7)$$

$$-\frac{d[\text{Br}]}{dt} = k_1[\text{Br}][\text{Br}^-] \quad (8)$$

Obviously eqn. (7) does not fall into the same form of eqn. (3). If we add eqn. (7) to eqn. (8) we get:

$$-\frac{d}{dt} ([\text{Br}_2^-] + [\text{Br}]) = 2k_2 [\text{Br}_2^-]^2 \quad (9)$$

For this equation to agree with (3), $[\text{Br}]$ has to be proportional to $[\text{Br}_2^-]$, *i.e.*

$$[\text{Br}] = R[\text{Br}_2^-] \quad (10)$$

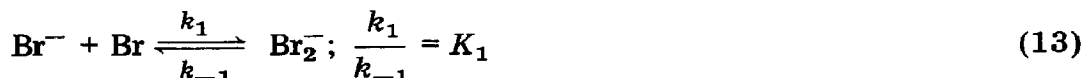
where R is a constant. From eqn. (9) we then obtain:

$$-\frac{d}{dt} [\text{Br}_2^-] = \frac{2k_2}{1+R} [\text{Br}_2^-]^2 \quad (11)$$

The condition (10) can be fulfilled if we assume that the reverse reaction of reaction (2):



simultaneously participates in the process and that equilibrium between Br , Br^- and Br_2^- has been reached by the time the measurements on the disappearance of Br_2^- are made:



The equilibrium constant can also be expressed as:

$$K_1 = \frac{[\text{Br}_2^-]}{[\text{Br}][\text{Br}^-]} \quad (14)$$

Since under the experimental conditions $[\text{Br}^-]$ does not vary much during the process, the condition stated in (10) may be considered to be true and

$$R \approx \frac{1}{K_1[\text{Br}^-]} \quad (15)$$

Finally, since we have included reaction (12) into our consideration, eqns. (7) and (8) must be rewritten as:

$$-\frac{d[\text{Br}_2^-]}{dt} = 2k_2[\text{Br}_2^-]^2 - k_1[\text{Br}][\text{Br}^-] + k_{-1}[\text{Br}_2^-] \quad (16)$$

and

$$-\frac{d[\text{Br}]}{dt} = k_1[\text{Br}][\text{Br}^-] - k_{-1}[\text{Br}_2^-] \quad (17)$$

By adding eqn. (16) to (17), once again we get eqn. (11). If we compare eqn. (11) with eqn. (3) we obtain that:

$$\beta = \frac{2k_2}{1+R} \quad (18)$$

As we further analyse eqn. (18), we see that the rate constant β should only decrease with decreasing $[\text{Br}^-]$. This property does not agree with the kind

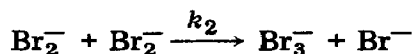
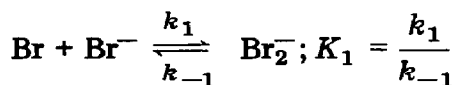
of dependence on $[\text{Br}^-]$ reported in Fig. 5. Thus the above mechanism cannot properly explain the disappearance of Br_2^- .

Case 2

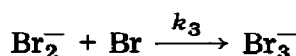
The next mechanism we are going to propose includes the introduction of another elementary reaction which may participate in the disappearance of Br_2^- and yield the product Br_3^- . This reaction is:



Now the mechanism would proceed according to the following:



and



In this case, as for the previous one, we find that the reaction with the rate constant k_{-1} has to be introduced in order to satisfy the condition of a second-order process. The following equations now describe the time evolution of $[\text{Br}_2^-]$ and $[\text{Br}]$, respectively:

$$-\frac{d[\text{Br}_2^-]}{dt} = 2k_2[\text{Br}_2^-]^2 - k_1[\text{Br}][\text{Br}^-] + k_{-1}[\text{Br}_2^-] + k_3[\text{Br}_2^-][\text{Br}] \quad (20)$$

and

$$-\frac{d[\text{Br}]}{dt} = k_1[\text{Br}][\text{Br}^-] - k_{-1}[\text{Br}_2^-] + k_3[\text{Br}_2^-][\text{Br}] \quad (21)$$

Adding the two equations above, and using eqn. (10) we obtain:

$$-\frac{d[\text{Br}_2^-]}{dt} = \frac{2k_2 + 2k_3R}{1 + R} [\text{Br}_2^-]^2 \quad (22)$$

Again we have a second-order process with the rate constant depending on the concentration of Br^- :

$$\beta = \frac{2(k_2 + k_3R)}{1 + R} \quad (23)$$

From Fig. 5 we know that the rate constant β has a minimum when plotted against $[\text{Br}^-]$, but eqn. (23) does not generate a minimum for any value of R . In fact, consider the derivative:

$$\frac{d\beta}{dR} = \frac{2(k_3 - k_2)}{(1 + R)^2} \quad (24)$$

If $k_3 = k_2$, β is the same for all values of R ; if $k_3 > k_2$, β increases with increasing R , i.e. decreasing $[\text{Br}^-]$; if $k_3 < k_2$, β decreases with increasing R .

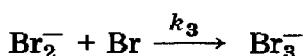
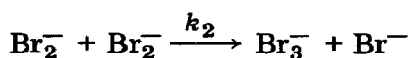
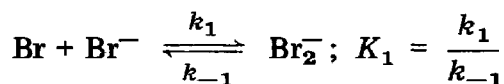
Again we see that the mechanism we have proposed here fails to agree with the experimental results.

Case 3

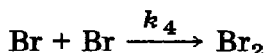
At this stage it is clear that the mechanism of the Br_2^- disappearance may be more complicated than the ones considered in cases 1 and 2 above. This leads us to consider, in analogy with the mechanism proposed by Grossweiner and Matheson [2] for the disappearance of I_2^- , the introduction of the reaction:



The presence of the Br_2 as a product is not in disagreement with the experimental results; Br_2 may not have been detected on account of its small extinction coefficient. The mechanism is now represented by the following equations:



and



In this case too the reaction with the rate constant k_{-1} has to be present. The time evolution of $[\text{Br}_2^-]$ and $[\text{Br}]$ is described by the following two equations:

$$-\frac{d[\text{Br}_2^-]}{dt} = 2k_2[\text{Br}_2^-] - k_1[\text{Br}][\text{Br}^-] + k_{-1}[\text{Br}_2^-] + k_3[\text{Br}_2^-][\text{Br}] \quad (26)$$

and

$$-\frac{d[\text{Br}]}{dt} = 2k_4[\text{Br}]^2 + k_1[\text{Br}][\text{Br}^-] - k_{-1}[\text{Br}_2^-] + k_3[\text{Br}][\text{Br}_2^-] \quad (27)$$

By adding the two previous equations, and taking eqn. (10) into account we obtain:

$$-\frac{d[\text{Br}_2^-]}{dt} = \frac{2(k_2 + k_3R + k_4R^2)}{1 + R} [\text{Br}_2^-]^2 \quad (28)$$

which is a second order equation with a rate constant given by:

$$\beta = \frac{2(k_2 + k_3R + k_4R^2)}{1 + R} \quad (29)$$

For this mechanism to be in agreement with the experimental results, β has to show a minimum when plotted against R . We take note of the fact that:

$$\frac{d\beta}{dR} = \frac{2(k_3 - k_2) + 4k_4R + 2k_4R^2}{(1 + R)^2} \quad (30)$$

Setting this expression equal to zero, we obtain the value:

$$R_0 = -1 \pm \sqrt{1 - \frac{k_3 - k_2}{k_4}} \quad (31)$$

The only meaningful solution is the one with the + sign; moreover, in this case, for R_0 to be positive as it should, $(k_3 - k_2)/k_4$ must be negative, *i.e.* it must be $k_2 > k_3$. Taking the second derivative of β with respect to R , we find:

$$\frac{d^2\beta}{dR^2} = \frac{4(k_4 - k_3 + k_2)}{(1 + R)^3} \quad (32)$$

Since R is taken to be positive, the condition $k_2 > k_3$ assures $d^2\beta/dR^2$ to be positive, *i.e.* the point $R = R_0$ is a minimum in the β versus R curve.

Finally, we examine other characteristic dependences of β on R : (a) for $R \rightarrow 0$, $\beta \rightarrow 2k_2$; (b) the slope of the β versus R curve at $R = 0$ is given by $2(k_3 - k_2)$; (c) the slope of the β versus R curve for very large R ($R \gg 1$) is given by $2k_4$. In principle the value of β for $R = 0$ could give k_2 , the slope at $R = 0$ could give k_3 once k_2 is known, and the slope for $R \gg 1$ could give k_4 . However, we must not forget that $R = 1/[K_1[\text{Br}^-]]$ with K_1 also to be determined. We have really four unknowns: K_1 , k_2 , k_3 and k_4 . We know experimentally the value of $[\text{Br}^-]$ for which β presents a minimum; this knowledge, together with eqn. (31) can in principle give us K_1 , once k_2 , k_3 and k_4 are known.

Fitting the proposed mechanism into the kinetic data

In order to fit the proposed mechanism into the kinetic data the slope of the $[D_2^{-1}, t]$ line is plotted in Fig. 8 against the inverse of the concentration of Br^- . These values correspond to the wavelength $\lambda = 3500 \text{ \AA}$; since the ratio between the slope at 3800 \AA and the slope at 3500 \AA is practically constant, no new information can be derived from the consideration of the slopes at 3800 \AA .

In Fig. 8, the theoretical points were found by adjusting the four parameters K_1 , k_2 , k_3 and k_4 for the best possible fit. It was found that such fit could be obtained by assigning the following values to those parameters: $K_1 = 3.3 \times 10^3 \text{ l/mol}$; $k_2 = 1.6 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$; $k_3 = 1.37 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$; and $k_4 = 1.2 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$. The theoretical and experimental values are also reported in Table 2.

These values can be compared with the values for similar parameters in the case of the disappearance of I_2^- [2]: $K_1 = 1.2 \times 10^4 \text{ l/mol}$, $k_2 = 3.9 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$, $k_3 = 7.7 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ and $k_4 = 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$.

It can be noted from Fig. 8 that the fit is good in the range of concentration from 10^{-2} to 10^{-5} M ; the discrepancy occurring at 10^{-1} M may indicate a deviation at this high concentration from the proposed mechanism.

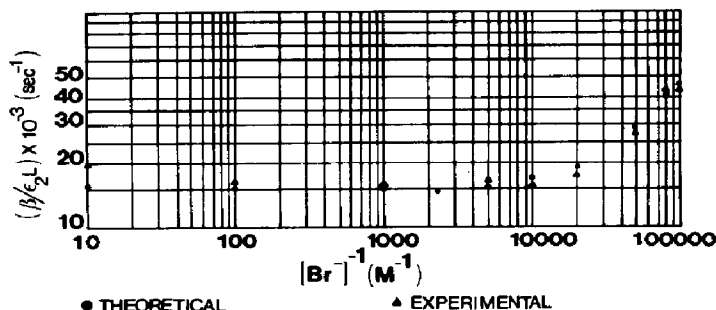


Fig. 8. Experimental and theoretical values of $\beta/\epsilon_2 L$ versus $[\text{Br}^-]^{-1}$.

TABLE 2

Theoretical and experimental values of $\beta/\epsilon_2 L$ at 3500 Å

[Br ⁻] (M)	$\beta/\epsilon_2 L$ (s ⁻¹)	
	Experimental	Theoretical
0.00001	46600	47142
0.0000125	41200	40206
0.00002	28600	29840
0.00005	17200	19651
0.0001	15400	16510
0.0002	16300	15244
0.001	15300	15018
0.01	16100	15324
0.1	20000	15394

Products following the Br_2^- disappearance

We want now to deal with the products whose appearance accompanies the Br_2^- decay. At this point we can say: (1) Br_3^- is a product of the Br_2^- disappearance; we ascertained this fact spectroscopically; (2) Br_2 is also a product accompanying the Br_2^- decay as indicated in the discussion of the mechanism of the Br_2^- disappearance; (3) the presence of both species does not affect spectrally the evolution of Br_2^- in the sense that the photolysis signal observed for the Br_2^- species reflects solely the presence of the Br_2^- ions; this is due to the lack of overlapping between the Br_3^- and the Br_2^- absorption bands, and the weak extinction coefficient of Br_2 .

For this last reason, the evolution of Br_3^- can be followed by looking, as we did, in the region of the spectrum that pertains to this species. An outcome of this investigation is Fig. 6 that relates to Br_3^- . It is interesting to compare this Figure with Fig. 3 which gives a typical pattern for the disappearance of Br_2^- . The scattered light in both Figures affects the first 50 μs or so; after this initial period Br_2^- is seen to decay (and we have already studied this process). Br_3^- instead increases in concentration and reaches a maximum at $\sim 200 \mu\text{s}$ after the photolyzing pulse (Fig. 6(a)), it then decays for about

1.5 ms (Fig. 6(b)) and continues, after this time, to decay at a slower rate (Fig. 6(c)); we are confronted here with the presence of two superimposed decay processes: the one more prominent between 200 μ s and 1.5 ms that we shall call "fast" and the one more prominent after 1.5 ms that we shall call "slow".

It will be assumed that as the species Br_2^- disappears the following equilibrium tends to be established among the species Br^- , Br_2 and Br_3^-

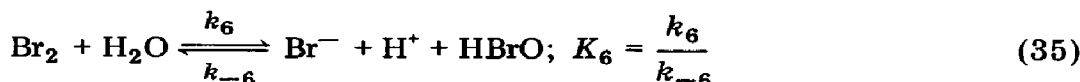


where K_5 has the known value 16.0 l/mol [19].

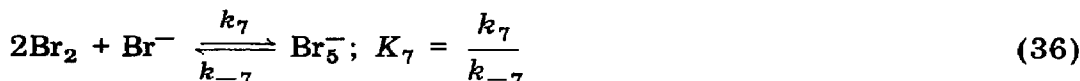
Taking the above equations into account, the evolution of the Br_3^- species follows the equation:

$$\frac{d[\text{Br}_3^-]}{dt} = k_2[\text{Br}_2^-] + k_3[\text{Br}_2^-][\text{Br}] + k_5[\text{Br}^-][\text{Br}_2] - k_{-5}[\text{Br}_3^-] \approx (k_2 + k_3R)[\text{Br}_2^-]^2 + k_5[\text{Br}^-][\text{Br}_2] - k_{-5}[\text{Br}_3^-] \quad (34)$$

For the time evolution of Br_2 we have also to consider the following equilibria [19]:



and



In order to appraise qualitatively the time evolution of Br_3^- and Br_2 , we shall make the simplifying assumption that the rates of the reactions leading to the equilibria (35) and (36) are much smaller than the rates of the reactions leading to the equilibrium (33). As a result of the above assumption:

$$\frac{d[\text{Br}_3^-]}{dt} \approx (k_2 + k_3R)[\text{Br}_2^-]^2 + k_5[\text{Br}^-][\text{Br}_2] - k_{-5}[\text{Br}_3^-] \quad (37)$$

and

$$\frac{d[\text{Br}_2]}{dt} \approx k_4R^2[\text{Br}_2^-]^2 - k_5[\text{Br}^-][\text{Br}_2] + k_{-5}[\text{Br}_3^-] \quad (38)$$

It is helpful to list the values of the following parameters:

$[\text{Br}^-]$ (M)	$R = 1/K_1[\text{Br}^-]$	$(k_2 + k_3R) \times 10^{-9}$ ($M^{-1} \text{ s}^{-1}$)	k_4R^2 ($M^{-1} \text{ s}^{-1}$)
1.0	3×10^{-4}	1.600	1.08×10
10^{-1}	3×10^{-3}	1.604	1.08×10^3

(continued overleaf)

(Continued from previous page)

$[\text{Br}^-]$ (M)	$R = 1/K_1 [\text{Br}^-]$	$k_2 + k_3 R \times 10^{-9}$ ($M^{-1} \text{ s}^{-1}$)	$k_4 R^2$ ($M^{-1} \text{ s}^{-1}$)
10^{-2}	3×10^{-2}	1.640	1.08×10^5
10^{-3}	3×10^{-1}	2.011	1.08×10^7
10^{-4}	3	5.710	1.08×10^9
10^{-5}	3×10	42.700	1.08×10^{11}

It is quite clear then from eqns. (37) and (38) that the rate of formation of Br_3^- at the time right after the photolyzing pulse is much greater than the rate of formation of the species Br_2 in the same time period if the concentration of Br^- is relatively high ($[\text{Br}^-] > 10^{-3} M$). In this case the Br_2^- disappearance causes a very fast build up of the Br_3^- concentration.

Assuming $[\text{Br}^-] > 10^{-3} M$, we can explain the time evolution of Br_3^- as follows: (1) immediately after the end of the photolyzing flash:

$$\frac{d[\text{Br}_3^-]}{dt} \approx (k_2 + k_3 R)[\text{Br}_2^-]^2$$

i.e. the slope of the $[\text{Br}_3^-]$ versus time curve is positive but decreases as time goes by; (2) the rapid increase in $[\text{Br}_3^-]$ enhances the importance of the term $-k_{-5}[\text{Br}_3^-]$ in eqn. (37); the slope of $[\text{Br}_3^-]$ versus time becomes negative. This occurrence takes place experimentally at $\sim 200 \mu\text{s}$ after the photolyzing pulse; (3) following this, the term $k_5[\text{Br}^-][\text{Br}_2]$ starts building up and makes the slope of $d[\text{Br}_3^-]/dt$ less negative; (4) $[\text{Br}_2^-]$ decreases to negligible values after a time $\sim 1.5 \text{ ms}$. At this time the term in eqn. (37) which is proportional to $[\text{Br}_2^-]$ can be omitted and:

$$\frac{d[\text{Br}_3^-]}{dt} = k_5[\text{Br}^-][\text{Br}_2] - k_{-5}[\text{Br}_3^-]$$

The net effect of the $[\text{Br}_3^-]$ decrease and of the $[\text{Br}_2]$ increase gives a change of the slope $d[\text{Br}_3^-]/dt$ to a less negative value; (5) from eqn. (38), we expect $[\text{Br}_2]$ to be always increasing with time, at a slower rate in the first $200 \mu\text{s}$, at an increased rate after that time up to 1.5 ms , and again at a slower rate after this time. Unfortunately, because of the low extinction coefficient of Br_2 , no kinetic data on this species are available, and the above conclusion about Br_2 cannot be confirmed experimentally.

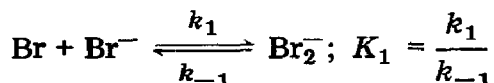
The experimental kinetic data on the Br_3^- evolution in Fig. 6 were obtained for a concentration of $1 M$ NaBr; the concentrations 10^{-1} and $10^{-2} M$ gave similar patterns in agreement with the above explanation. For a concentration of $10^{-3} M$ NaBr or smaller, the equilibrium constant K_5 of eqn. (33) indicates that smaller equilibrium concentrations of Br_3^- would result; experimentally no significant photolysis signal could be obtained.

Conclusions

The object of the present investigation was mainly the study of the evolution of the transient species Br_2^- in aqueous solution. This species is created following the primary process which consists of the absorption of a photon and consequent transfer of an electron to the solvent. Following the primary process, the atomic species Br readily combines with the Br^- ion in solution to yield the species Br_2^- .

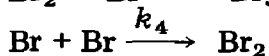
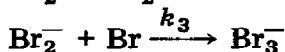
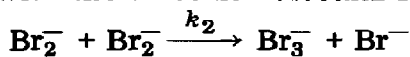
The results of the present investigation can be summarized as follows:

(1). Immediately following the primary process, the following equilibrium is established:



(2). The disappearance of Br_2^- follows by a second-order process. The dependence of the rate constant on the concentration of Br^- and the deviation from an Arrhenius type of dependence on temperature indicate that this process is the outcome of more than one elementary process.

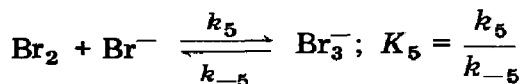
(3). The kinetic data on Br_2^- are consistent with the equilibrium above and with the three bimolecular reactions:



(4). The equilibrium constant K_1 and reaction constants k_2 , k_3 and k_4 were obtained by the use of kinetic spectrophotometry on solutions with various Br^- concentrations: $K_1 = 3.3 \times 10^3$ l/mol; $k_2 = 1.6 \times 10^9$ l mol⁻¹ s⁻¹; $k_3 = 1.37 \times 10^9$ l mol⁻¹ s⁻¹; $k_4 = 1.2 \times 10^8$ l mol⁻¹ s⁻¹.

(5). The species Br_3^- and Br_2 appear as products of the Br_2^- disappearance. Direct spectroscopic evidence is available for Br_3^- and indirect evidence for the presence of Br_2 is furnished by the kinetic data.

(6). The detailed spectroscopic study of the species Br_3^- uncovered a mechanism for the Br_3^- evolution, consistent with the equilibrium



Alkali halide solutions have been the subject of several studies including the present one. An approach similar to ours, including static and kinetic absorption measurements in a wide range of temperatures and concentrations could be used to extend the available knowledge of such systems as I^- and Cl^- . Various solvents could be used to clarify further the process of electron transfer from anions in solution. An attempt could also be made to generate photochemically the hydrated electrons in air-free solutions of Br^- . The extended knowledge of the details of the chemical reactions could lead to a better understanding of the elementary molecular transformations.

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