

EVOLUTION OF Cl_2^- IN AQUEOUS NaCl SOLUTIONS

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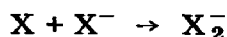
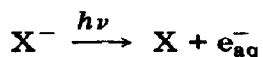
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Summary

Following an intense excitation by a photolysing flash, a transient absorption band centered at about 3400 Å and approximately 1000 Å wide was observed in aqueous NaCl solutions ranging in concentration from 5×10^{-4} to 2 M. This band was attributed to the presence of Cl_2^- ions. The disappearance of Cl_2^- was found to be a second order process with a rate constant which was dependent on the NaCl concentration. At ambient temperature the kinetics was satisfactorily explained as being due to three simultaneous bimolecular reactions the rate constants of which were obtained. Furthermore, the decay of Cl_2^- was observed to follow the same mechanism at elevated temperatures. All three bimolecular reactions were found to have Arrhenius-type temperature dependences.

1. Introduction

Alkali halide solutions have been the object of flash photolysis [1 - 7] and pulse radiolysis [8 - 13] studies. Transient absorption bands centered in the 3500 Å region have been identified as being due to dihalide ions. The formation of dihalide ions (X_2^-) in aqueous alkali halide solutions using the flash photolysis technique is believed to be



The evolution of the species I_2^- in aqueous KI solutions has been studied in detail by Grossweiner and Matheson [2]. The disappearance of I_2^- has been found to be a second order process which becomes faster with decreasing I^- concentration. Wong and Di Bartolo [7] have studied the decay characteristics of Br_2^- in aqueous NaBr solutions and have established

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that the disappearance of Br_2^- also follows a second order decay with a rate constant which is dependent on the Br^- concentration. In the following we report on a study of the decay mechanism of the species Cl_2^- in aqueous NaCl solutions.

2. Experimental

The flash photolysis apparatus used in this work has been described in detail elsewhere [7]. It consists of a cylindrical suprasil sample cell (outer diameter, 2.5 cm; length, 25 cm) with fused-on optically flat end windows. Lying on either side of the cell are two linear high energy flash tubes that provide the necessary photolysing energy. The cell and the flash tubes are enclosed in a silver- and rhodium-plated cavity. In the spectroscopic mode the transient absorption spectrum is obtained by the action of an analysing flash set at a certain time after the photolysing flash; the aim of this measurement is to locate the transient absorption band. In the kinetic mode a continuous xenon lamp is used to monitor the decay of the transient species. Precautionary measures were taken in this mode to ensure a uniform intensity gradient across the cell. This is done to avoid the formation of a non-uniform concentration of the transient species across the cell which may yield distorted signals. Such an effect was checked experimentally by inserting an adjustable iris diaphragm in front of the reaction cell containing a 2 M NaCl solution. Following a photolysing flash the shape of the disappearance pattern was observed to be reproducible for iris diameter settings ranging from 2 to 5 mm. The signal appeared to be distorted with diameters larger than 5 mm. Therefore the diameter of the iris was set at 5 mm throughout the entire investigation. The linearity of the photomultiplier was verified by using a set of neutral density filters. When experiments were performed at elevated temperatures, forced hot air was sent towards the cavity containing the sample cell and the photolysing flash tubes. By regulating the flow rate and the input voltage of the heating element properly, the temperature of the solution could be controlled to within 1 °C of the desired temperature. The temperature of the solution inside the cell was found to be constant to within ± 1 °C.

A Cary 14 spectrophotometer was used for conventional absorption measurements.

3. Results and discussion

3.1. Absorption spectra

The absorption spectra of a 10^{-4} M aqueous NaCl solution were measured at several temperatures. An absorption band with an edge near 2100 Å was observed and was attributed to Cl^- ions. The extinction coefficients of Cl^- (at about 1900 Å) were determined to be 4700, 7800 and 11 300 $\text{l mol}^{-1} \text{cm}^{-1}$ at 20, 40 and 60 °C respectively.

The absorption spectrum of an irradiated 0.1 M NaCl solution was also obtained in an attempt to identify any long-lived product species of the Cl_2^- decay. Such irradiation consisted of 30 photolysing flashes of energy 640 J; however, within the sensitivity limit of the instrument, the absorption spectra failed to reveal any new band.

3.2. Flash photolysis data

3.2.1. Spectroscopic mode

A 0.1 M aqueous NaCl solution was irradiated by an 810 J photolysing flash; the delay time between the photolysing flash and the spectral flash was set at 50 μs . The transient absorption spectrum revealed the presence of a very weak and structureless band, centered at about 3400 Å and approximately 1000 Å wide. These spectroscopic data give experimental evidence of the presence of the transient species which has been identified as Cl_2^- [2]. With increasing time delay between the photolysing and spectral flashes the transient band fades out with preservation of its shape; this confirms that the entire transient band is associated with the same species Cl_2^- . In the region 2500 - 4000 Å no new absorption band was observed after the disappearance of Cl_2^- . This indicates that the product species due to the decay of Cl_2^- either do not exist in this spectral region or cannot be detected because of their very low optical density.

3.2.2. Kinetic mode

The evolution of the species Cl_2^- at room temperature was investigated in the kinetic mode in 0.0005, 0.001, 0.002, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1 and 2 M NaCl solutions. A series of measurements were performed using 810 J photolysing flashes and with the wavelength of the monochromator set at 3400 Å.

A typical disappearance pattern of Cl_2^- in a 0.005 M aqueous NaCl solution at ambient temperature is shown in Fig. 1(a). The upper and lower straight lines represent total absorption (no light) and total transmission of the probing continuous xenon light respectively. The curve represents the probing light intensity at the cell output (as a function of time) as the transient species Cl_2^- decays. The concentration of Cl_2^- can then be derived from this figure according to Beer's law:

$$\log (X_0/X_t) = \epsilon [\text{Cl}_2^-]_t L$$

where ϵ is the molar extinction coefficient of Cl_2^- , $[\text{Cl}_2^-]_t$ is the concentration of Cl_2^- at time t and L is the length of the optical path. At 3400 Å, ϵ has been reported by Anbar and Thomas [9] to be approximately $1.2 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. The term $\epsilon [\text{Cl}_2^-]_t L$ is defined as the optical density D_t of Cl_2^- at time t . A plot of D_t^{-1} versus t always yielded a straight line (see Fig. 2), indicating that Cl_2^- decays following a second order reaction:

$$-\frac{d[\text{Cl}_2^-]}{dt} = \beta [\text{Cl}_2^-]^2 \quad (1)$$

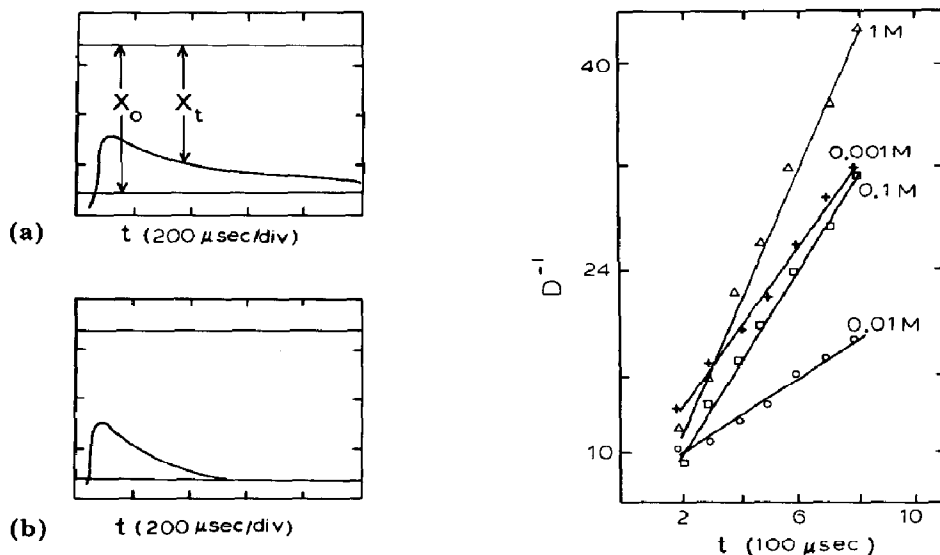


Fig. 1. Typical disappearances of the Cl_2^- ion in 0.005 M aqueous NaCl solution at (a) 23 °C and (b) 60 °C.

Fig. 2. The disappearance of Cl_2^- as a second order process.

where β is the rate constant which is proportional to the slope of this straight line.

All the slopes obtained at 23 °C are presented in Table 1. A plot of these slopes $\beta/\epsilon L$ versus $1/[\text{Cl}^-]$ is shown in Fig. 3; the rate constant β is a function of $[\text{Cl}^-]$ with a minimum for $[\text{Cl}^-]$ equal to 0.005 M.

It is now clear that the disappearance of Cl_2^- follows a much more complicated process than the simple bimolecular reaction described by eqn. (1).

By analogy with the mechanism proposed by Grossweiner and Matheson [2] for the disappearance of I_2^- (and by Wong and Di Bartolo [7] for Br_2^-), the decay of Cl_2^- is believed to take place via the following reactions:

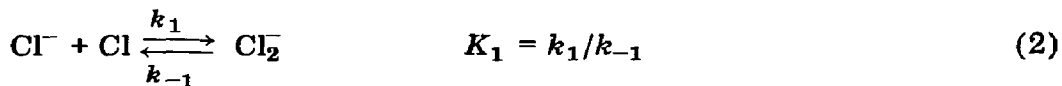
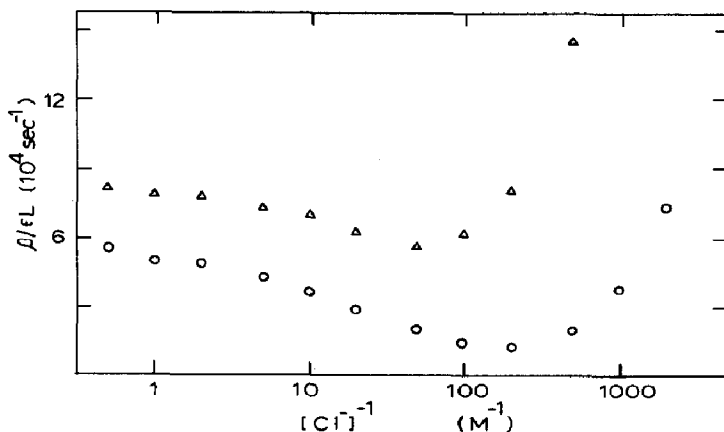


TABLE 1

Slope of the D_t^{-1} vs. t line at 23 °C

Cl^- concentration (M)	Slope $\times 10^{-4}$ (s^{-1})	
	Experimental	Calculated
2	5.42	5.37
1	5.18	5.23
0.5	4.87	4.98
0.2	4.32	4.39
0.1	3.65	3.68
0.05	2.92	2.85
0.02	1.93	1.89
0.01	1.49	1.49
0.005	1.48	1.48
0.002	2.24	2.27
0.001	3.81	3.90
0.0005	7.12	7.30

Fig. 3. Experimental values of $\beta/\epsilon L$ vs. $[Cl^-]^{-1}$ at 23 °C (O) and 60 °C (Δ).

It is then possible to derive

$$-\frac{d[Cl_2]}{dt} = \frac{2(k_2 + k_3 R + k_4 R^2)}{1 + R} [Cl_2]^2 \quad (6)$$

where

$$R = [Cl]/[Cl_2] \approx 1/K_1 [Cl^-] \quad (7)$$

Comparing eqn. (1) with eqn. (6), we obtain

$$\beta = \frac{2(k_2 + k_3 R + k_4 R^2)}{1 + R} \quad (8)$$

In order to analyze the functional dependence of β on R , we set

$$\frac{d\beta}{dR} = \frac{2(k_3 - k_2) + 4k_4R + 2k_4R^2}{(1 + R)^2} = 0 \quad (9)$$

We find that β has an extremum at

$$R_0 = -1 + \left(1 - \frac{k_3 - k_2}{k_4}\right)^{1/2} \quad (10)$$

Since R_0 is a positive number, k_2 must be larger than k_3 . The second order derivative

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

is positive at $R = R_0$; this ensures that R_0 is a point of minimum for β . From eqns. (8) and (9) we also notice that

$$\text{as } R \rightarrow 0 \quad \beta \rightarrow 2k_2 \quad (11)$$

$$\text{when } R = 0 \quad \frac{d\beta}{dR} = 2(k_3 - k_2) \quad (12)$$

$$\text{when } R \gg 1 \quad \frac{d\beta}{dR} \rightarrow 2k_4 \quad (13)$$

Using the conditions stated in eqns. (10) - (13), it is then possible to derive K_1 , k_2 , k_3 and k_4 from Fig. 3. We obtain

$$\begin{aligned} K_1 &= 1.77 \times 10^1 \quad 1 \text{ mol}^{-1} \\ k_2 &= 7.90 \times 10^9 \quad 1 \text{ mol}^{-1} \text{ s}^{-1} \\ k_3 &= 6.25 \times 10^8 \quad 1 \text{ mol}^{-1} \text{ s}^{-1} \\ k_4 &= 8.75 \times 10^7 \quad 1 \text{ mol}^{-1} \text{ s}^{-1} \end{aligned} \quad (14)$$

The slopes of the D_t^{-1} versus t lines are further calculated based on eqn. (8) using the parameters listed in eqn. (14). The results are also reported in Table 1. Excellent agreement is found between the experimental and the calculated values.

The disappearance of Cl_2^- was also studied at higher temperatures. A typical Cl_2^- decay at 60 °C is shown in Fig. 1(b). The disappearance of Cl_2^- becomes faster with increasing temperature; however, it still follows a second order process, similar to that observed at 23 °C. The slopes of the D_t^{-1} versus t plots obtained at 40 and 60 °C are tabulated in Tables 2 and 3 respectively. A plot of $\beta/\epsilon L$ against $1/[\text{Cl}^-]$ at 60 °C is also included in Fig. 3; it shows that β is dependent on $[\text{Cl}^-]$ with a minimum for $[\text{Cl}^-]$ equal to about 0.02 M.

TABLE 2

Slope of the D_t^{-1} vs. t line at 40 °C

Cl^- concentration (M)	Slope $\times 10^{-4}$ (s^{-1})	
	Experimental	Calculated
1	6.14	6.47
0.1	5.01	4.89
0.01	3.05	2.82
0.001	10.14	9.73

TABLE 3

Slope of the D_t^{-1} vs. t line at 60 °C

Cl^- concentration (M)	Slope $\times 10^{-4}$ (s^{-1})	
	Experimental	Calculated
2	8.22	8.23
1	8.07	8.12
0.5	7.84	7.92
0.2	7.32	7.41
0.1	6.98	6.81
0.05	6.20	6.12
0.02	5.66	5.61
0.01	6.15	6.10
0.005	8.15	8.05
0.002	14.53	14.96

Using the decay mechanism proposed for the disappearance of Cl_2 at 23 °C, we derived the following values for the parameters at 60 °C:

$$\begin{aligned}
 K_1 &= 2.20 \times 10^1 && 1 \text{ mol}^{-1} \\
 k_2 &= 1.20 \times 10^{10} && 1 \text{ mol}^{-1} \text{ s}^{-1} \\
 k_3 &= 4.60 \times 10^9 && 1 \text{ mol}^{-1} \text{ s}^{-1} \\
 k_4 &= 7.60 \times 10^8 && 1 \text{ mol}^{-1} \text{ s}^{-1}
 \end{aligned}
 \tag{15}$$

The slope of each D_t^{-1} versus t line was also calculated using eqns. (8) and (15) and the results are shown in Table 3. Again they are in good accord with the experimental values.

It is possible to estimate the activation energy of each individual reaction from the two sets of parameters reported in eqns. (14) and (15). Assuming an Arrhenius type of temperature dependence with temperature-independent frequency factors, the activation energies are 1.15, 2.21, 10.6

and 11.4 kcal mol⁻¹ for reactions (2), (3), (4) and (5) respectively. Based on these values a similar set of parameters can be derived for these reactions at 40 °C:

$$\begin{aligned}
 K_1 &= 1.97 \times 10^1 && \text{l mol}^{-1} \\
 k_2 &= 9.69 \times 10^9 && \text{l mol}^{-1} \text{ s}^{-1} \\
 k_3 &= 1.67 \times 10^9 && \text{l mol}^{-1} \text{ s}^{-1} \\
 k_4 &= 2.51 \times 10^8 && \text{l mol}^{-1} \text{ s}^{-1}
 \end{aligned}
 \tag{16}$$

Equations (8) and (16) allow the slopes of the D_t^{-1} versus t lines for the decay of Cl_2^- at 40 °C to be calculated. The results are shown in Table 2 together with those obtained experimentally. Fairly good agreements between the theoretical and experimental values are reached, indicating that not only does the proposed mechanism apply well at 40 °C but also the Arrhenius temperature dependence is obeyed for all three bimolecular reactions.

4. Summarizing remarks

In conclusion, the disappearance of Cl_2^- ions can be satisfactorily described by the mechanism proposed for the decay of Br_2^- and I_2^- . The rate constants for all the three simultaneous bimolecular reactions involved in the decay process have been obtained. Furthermore, all three reactions follow an Arrhenius type of temperature dependence within the range of conditions studied in this work.

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