Dalton Transactions c3dt53255k

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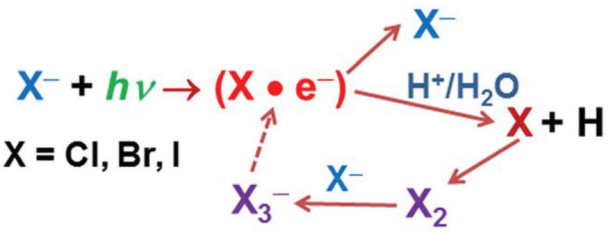
Aqueous photochemical reactions of chloride, bromide, and iodide ions in a diode-array spectrophotometer. Autoinhibition in the photolysis of iodide ions

József Kalmár, Éva Dóka, Gábor Lente* and István Fábián

The photoreactions of halide ions were studied in water using a diode array spectrophotometer. The triiodide ion has been shown to exert a strong autoinhibitory effect on the reaction.



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Dalton Transactions

PAPER

Aqueous photochemical reactions of chloride, bromide, and iodide ions in a diode-array spectrophotometer. Autoinhibition in the photolysis of iodide ions†

Cite this: DOI: 10.1039/c3dt53255k

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Received 18th November 2013,
Accepted 6th January 2014
DOI: 10.1039/c3dt53255k
www.rsc.org/dalton

The aqueous photoreactions of three halide ions (chloride, bromide and iodide) were studied using a diode array spectrophotometer to drive and detect the process at the same time. The concentration and pH dependences of the halogen formation rates were studied in detail. The experimental data were interpreted by improving earlier models where the cage complex of a halogen atom and an electron has a central role. The triiodide ion was shown to exert a strong inhibiting effect on the reaction sequence leading to its own formation. Assuming a chemical reaction between the triiodide ion and the cage complex interpreted the strong autoinhibition effect. It is shown that there is a real danger of unwanted interference from the photoreactions of halide ions when halide salts are used as supporting electrolytes in spectrophotometric experiments using a relatively high intensity UV light source.

Introduction

The photochemistry of halide ions was reasonably well characterized in the 1960s.[1–8] It was shown that excited states have very short lifetimes, and a cage complex formed between the halide atom and an electron was assumed to be an intermediate of the process. Overall, the photoreactions led to the formation of halogen and hydrogen gas.[1–8] The dependence of the quantum efficiencies on the pH was interpreted by assuming that the cage complex can react with hydrogen ions, in addition to recombination with the original halide ion. The photochemical reactions of the halides are not routinely considered as significant processes in nature or possible side reactions in non-photochemical studies. Yet experiments reported in this paper will show that photochemical changes may very well occur under normal conditions and may seriously corrupt the interpretation of experimental data. This observation is very important as halide salts, especially metal chlorides, are very frequently used as (supposedly) inert electrolytes to provide constant ionic strength in kinetic and equilibrium studies. Photochemical formation of chlorine from the chloride ion in acidic atmospheric aerosols is a process of great importance, and UV photolysis is certainly a contributing factor.[9] Similarly, the photochemical formation of bromine atoms from bromide ions on the surface of snow is understood to play a significant role in self-cleaning procedures in the atmosphere.[10,11] In addition, the photoinduced formation of carcinogenic bromate ions in seawater or simply in the presence of a lower amount of chloride ions is a major concern for the water industry.[12,13]

Diode array spectrophotometers are becoming increasingly popular for a large number of different applications. Their main advantage over traditional scanning spectrophotometers is that they can record an entire UV-vis spectrum in a very short time. However, this comes with a cost: the sample is illuminated with a light beam that is sufficiently intense to trigger photochemical reactions. There are several documented cases when neglecting this effect led to grossly erroneous conclusions, usually misidentifying a photochemical reaction as a thermal one.[14–16] In a recent case, it was shown that even the light beam in a stopped-flow instrument exerted a measurable influence on the reaction of a highly absorbing manganese(III) porphyrin complex.[17] The photochemical effect of the light of diode array spectrophotometers is usually unwanted as the instrument is intended to be used as a detector of a process without influencing it. However, a number of examples have shown that carefully planned studies can actually use this effect for a highly quantitative study of photoreactions.[16,18–26] These experiments sometimes afford mechanistic information not available from classical photochemical experiments. The limitation of the experiments is that the light source is necessarily polychromatic, although its spectral properties can be

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†Electronic supplementary information (ESI) available: Additional figures referred to in the main text. See DOI: 10.1039/c3dt53255k

changed within certain limits using suitable filters or external light sources such as LEDs.[26–28]

This work will demonstrate how the light of a commercial diode-array spectrophotometer can induce the formation of chlorine, bromine and iodine in the solutions of these halide ions. Furthermore, by improving a methodology reported in earlier literature,[18,19,25,26] we will also show how this unexpected effect can be utilized to obtain detailed information about the nature of the photochemical processes. Evidence will also be shown of a strong autoinhibitory feature in the aqueous photoreaction of the iodide ion.

Experimental

Materials

Perchloric acid (Spektrum 3D) was used as a strong acid to set the pH. The ionic strength was set with $NaClO_4$, which was prepared as described earlier.[29] All other chemicals, most importantly hydroiodic acid (Sigma-Aldrich, unstabilized, 99.99%), hydrobromic acid (Fluka, alt.) and hydrochloric acid (Scharlau, ar.), used in this study were of analytical reagent grade and purchased from commercial sources. It should be emphasized that the use of unstabilized hydroiodic acid is imperative as the most common stabilized product contains hypophosphorous acid which reacts with iodine readily. Potassium iodide (Reanal), potassium bromide (Reanal) and potassium chloride (Spektrum 3D) were also used as halide ion sources. Special problems were encountered with the purity of chlorides (see Results and discussion): the best chloride source in this respect (*i.e.* the one that showed the smallest interferences) was found to be high-purity concentrated hydrochloric acid, which was used in most of the experiments reported here. Doubly deionized and ultrafiltered water from a Millipore Q system was used to prepare the stock solutions and samples.

Instrumentation and computation

UV-vis spectra were recorded on an HP-8543 diode-array or a Perkin Elmer Lambda 2S scanning spectrophotometer. Constant temperature at 25.0 ± 0.1 °C was maintained with a built-in Hewlett-Packard 89090A Peltier thermostat or an external circulating thermal bath. In some experiments, 0.01 mm path length cuvettes were used. This posed a special problem of path length reproducibility, which was solved by developing a spectrophotometric method not requiring the exact knowledge of path length (see Results and discussion). A YSI 5100 Dissolved Oxygen Meter and a YSI Model 5239 probe with YSI 5906 membrane cap were used for measuring the concentration of dissolved oxygen. A high-power quartz lamp (Medicor, Hungary, 500 W) was used as a UV light source in the photochemical experiments using the oxygen electrode. Quantitative kinetic measurements on the photochemical reactions were performed with the HP-8543 diode-array instrument in a stoppered standard quartz cuvette (optical path length: 1.000 cm) using the method and general operating protocols described in earlier publications.[20,27] The reaction mixtures were kept homogeneous during the photochemical experiments by constant stirring with a 3 mm magnetic stirring rod using the built-in magnetic stirrer of the cell compartment of the HP-8543 instrument. The geometry of the experimental setup was carefully tested and it was made sure that the stirring rod never blocked the light beam. The light source was calibrated by ferrioxalate actinometry[30,31] as well as reproducing observations on the known photoreaction of 2,6-dichloro-1,4-benzoquinone.[18] Nanosecond flash photolysis measurements were carried out in an LKS.60 nanosecond transient absorption spectrometer manufactured by Applied Photophysics Ltd. The instrument is equipped with a Quantel Brilliant Nd:YAG laser (repetition frequency 10 Hz). The fourth harmonic generator operating at 266 nm and Q-switching were used in the present study (nominal energy: 40 mJ per pulse, pulse length: 6 ns, beam diameter: 6 mm). The analyzing light source was a 150 W ozone free xenon arc lamp (OSRAM 150W/CR OFR) and its light beam entered a 1 × 1 cm fluorescence quartz cuvette with cross-beam excitation. The analyzing light beam hit close to the front face of the cuvette, to maximize the detected concentration of transient species. A programmable f/3.4 grating monochromator with a symmetrical Czerny–Turner optical configuration was combined with a R928 photomultiplier for the transient signal detection at different wavelengths. Data points were collected by an Agilent Infiniium digital storage oscilloscope (model number DSO8064A) with a maximum sampling speed of 4 GSa s^{-1} (0.25 ns between data points), bandwidth of 600 MHz, and output impedance of 50 Ω. Transient absorption kinetic curves were registered with the control software of the LFP instrument, Pro-Data LKS (version number 1.1.0.5), and visualized using Pro-Data Viewer (version number 4.2.5). Pro-Data Viewer has a built-in curve fitting application that was used in first order fitting. Other fitting procedures were carried out using the software Scientist[32] and Matlab.[33]

Results

Basic observations

When a solution of a hydrogen halide is kept in a diode-array spectrophotometer, the formation of halogens or trihalide ions is detectable. No similar changes are observed if the same solution is kept in a scanning spectrophotometer, which clearly proves the purely photochemical origin of the chemical reactions.[16,25] A series of time-resolved spectra detected during such a process in a pure HCl solution is shown in Fig. 1. Fig. S1 in ESI† shows the corresponding kinetic trace at 230 nm. Fig. S2 and S3 in ESI† show spectral changes detected in HBr and HI solutions under similar conditions.

The photochemical nature of the observed process can be further demonstrated by the use of filters, which can be inserted into the light beam of the diode-array spectrophotometer. Fig. 2 shows such a pair of conclusive experiments in a solution of HBr. The filter in this case was a 1 mm quartz

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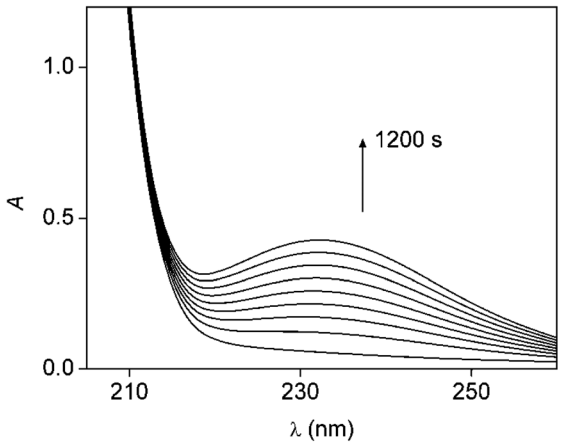

Fig. 1 Spectral changes in a HCl solution upon continuous UV illumination. [HCl] = 5.056 M, T = 25.0 °C.

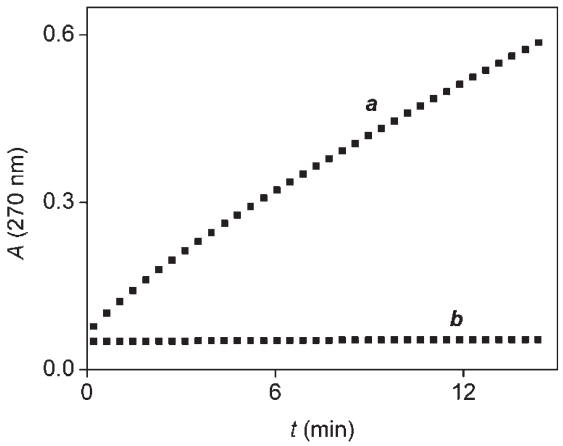

Fig. 2 Kinetic curves during the photolysis of a HBr solution with the filter after (a) or before (b) the cell. [HBr] = 0.322 M, T = 25.0 °C.

cuvette filled with pure chloroform. The absorption of this filter overlaps with the absorption of a bromide ion (both absorb significantly below 250 nm) in such a way that it almost completely shuts out light absorbed by Br^- if it is inserted before the sample (Fig. S4 in ESI†). The main absorbing product of the photochemical reaction, the tribromide ion, can be detected even with the use of the filter because Br_3^- has absorption above 250 nm. In trace **a** of Fig. 2, the filter was inserted into the light beam following the cell. Thus the intense unfiltered light went through the sample first and the filter only blocked some of the light from reaching the detector. The photochemical reaction proceeded in this case as evidenced by the absorbance change. In curve **b**, the only difference relative to experiment **a** was that the filter was placed between the light source and the sample. Therefore, light that could be absorbed by Br^- did not reach the sample in this case. As a consequence, no reaction occurred. These observations demonstrate that the light of the diode-array spectrophotometer in fact drives the photolysis of halogen ions.

Although earlier measurements clearly showed the formation of hydrogen in the aqueous photochemical reactions of halide ions,[1–8] some additional efforts were made in this work to show that dissolved oxygen does not play a significant role in the overall reaction. Decreasing the initial concentration of dissolved oxygen by bubbling with argon before experiments did not influence any of the experimental observations. Furthermore, in a few trial experiments, the concentration of dissolved oxygen was monitored during illumination. The result of such an experiment is shown in Fig. S5 in ESI.† No evidence of any loss of dissolved oxygen attributable to the photoreaction was seen.

Determination of trihalide ion stability constants. The formation equilibrium constants of trihalide ions (eqn (1)) have been reported in previous studies.[34,35]

$$X_2 + X^- = X_3^- \quad K_X = \frac{[X_3^-]}{[X^-][X_2]} \qquad (1)$$

For Br^- and I^-, we determined these constants by spectrophotometric titration in this work (Table 1); these values compare well with literature data, especially if the differences in the experimental conditions are taken into account.[34,35] For Cl^-, K_{Cl} is too low to be determined by the same method as the solubilities of chloride salts are insufficient to obtain high enough free chloride ion concentrations. This fact led us to conclude that $K_{Cl} < 1\ M^{-1}$. Consequently, a literature value ($0.194\ M^{-1}$) was used, which was obtained with a different method[34] and did not contradict our estimate for the higher estimate. The same method also yielded the molar absorption coefficients of trihalide ions needed in the calculation. The triiodide ion, however, presented a somewhat unexpected problem. To evaluate the HI photolysis data on a time scale of hours, it was necessary to determine the molar absorption coefficients of I_3^- in the entire spectral region from 200 to 500 nm. This is not a trivial problem because I_3^- can only exist at high free I^- concentrations, which makes the molar absorption coefficient determination difficult in the region where the iodide ion absorbs strongly (200–260 nm). Our solution to this problem relied on the use of cuvettes with very short path

Table 1 Equilibrium and spectral data for trihalide ions. T = 25.0 °C, I = 1.0 M

	Cl_3^-	Br_3^-	I_3^-	
K_X (M^{-1})	— 0.194[34]	9.7 ± 1.9 19[35]	(6.7 ± 0.2) × 10^2 740[35]	
λ_{max} (nm)	230	270	288	352
ε (λ_{max}) (M^{-1} cm^{-1})	(1.50 ± 0.02) × 10^4	(4.4 ± 0.4) × 10^4	(2.03 ± 0.02) × 10^4	(1.33 ± 0.02) × 10^4

lengths (0.01 mm). Unfortunately, the reproducibility of the path length between successive experiments is not satisfactory for these special cuvettes: our experiments showed that the path length may change within a factor of two. One possible reason is that small dust particles that cannot be completely washed away from the surface of the cuvette prevent the two quartz sheets from perfectly fitting onto each other every time. This problem was overcome by selecting a reference wavelength where only I_3^- absorbs and the molar absorption coefficient is measurable independently of the irreproducible path lengths. Using the absorbance measured at this wavelength, spectra can be normalized and the method can be made independent of the path length. A simple mathematical derivation based on Beer's law gives the following formula:

$$\frac{A(\lambda)}{A(\mathrm{ref})} = \frac{\varepsilon_{I^-}(\lambda)}{\varepsilon_{I_3^-}(\mathrm{ref})} \times \frac{[I^-]}{[I_3^-]} + \frac{\varepsilon_{I_3^-}(\lambda)}{\varepsilon_{I_3^-}(\mathrm{ref})} \qquad (2)$$

In this equation, every variable except $\varepsilon_{I_3^-}(\lambda)$ is known or measured directly, so the unknown value can be computed. The spectra of I^- and I_3^- are shown in Fig. S6 in ESI.† Even with this special technique, reliable molar absorption coefficients could not be obtained in a fairly narrow region from 240 to 264 nm primarily because I_3^- does not absorb significant amounts of light relative to other species present in the solution under any conditions. For Fig. S6,† values in this region were extrapolated by assuming that the overall spectrum of I_3^- was a combination of Gaussian curves. It should also be mentioned that these values do not affect the calculations for the photochemical reactions in HI solutions in any way because the absorption of the triiodide ion is insignificantly low at these wavelengths.

Quantitative observations. Quantitative information on the photochemical reactions was obtained by the initial rate method. The main advantage of this method is that the initial change in the absorbance is free from any possible effect the product might cause. The initial rate was calculated from the initial slope of absorbance (A) change measured at a wavelength where only X_3^- absorbs and using the molar absorptivities (ε) of the trihalide ions.

$$v = \frac{\mathrm{d}[X_2]}{\mathrm{d}t} = \frac{\mathrm{d}A(\lambda)}{\mathrm{d}t} \times \frac{1}{\varepsilon_{X_3^-}(\lambda)} \times \left(\frac{1}{[X^-]K_X} + 1\right) \qquad (3)$$

Continuous and interrupted illumination methods[19,25] have both been used in this study. In the latter method, periods of illumination are regularly interrupted by dark periods of various lengths by closing the shutter of the spectrophotometer. The spectrophotometer can only measure the absorbance during illuminated periods, and the initial rate measured under these circumstances is the average rate occurring during illuminated and dark periods. The dependence of the reaction rate on the illumination ratio (which is defined as the length of illumination time relative to the overall time passed) may yield information on reactions occurring in the dark period.[19] Such dependence is shown for a HBr solution in Fig. 3. The rate is directly proportional to the illumination ratio, which clearly implies that the reaction does not progress any further in the absence of light. Therefore, it is unlikely to be a chain reaction.

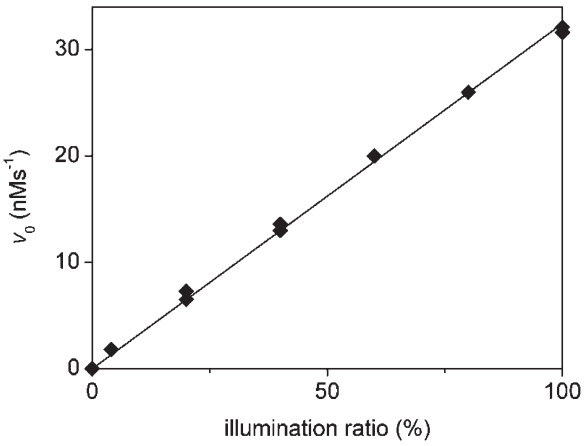

Fig. 3 Reaction rate as a function of illumination ratio for the photolysis of HBr solutions. [HBr] = 0.500 M, T = 25.0 °C.

The chloride ion presented particular problems related to purity in this study. Kinetic curves detected during the photolysis of Cl^- featured an initial region where the rate of product formation slightly accelerated (Fig. S1 in ESI† shows such an effect). This is most probably due to the fact that the starting materials contain uncontrollably low levels of organic impurities, which consume some of the Cl_2 formed at the beginning of the process. This explanation was consistent with the fact that the length of the initial, slightly accelerating phase varied depending on the source of chemicals, and could be reduced by re-crystallizing solid starting materials or decreasing the initial concentrations. The example shown in Fig. S1 in ESI† is the worst in this respect because the chloride concentration is very high there (*ca.* 5 M). In these cases, the maximum rate was used instead of the literal initial rate for quantitative purposes. Similar impurities might also be present in Br^- and I^- sources, but they understandably constitute less of a problem because the product halogens probably react with organic contaminations at a much lower rate.

The initial rate of the photochemical reaction depended on the pH. In all cases, the rate increased with decreasing pH. To display the three studied halide ions in a single graph, the rates were normalized before plotting them in Fig. 4. The experimental curves could be fitted to the following equation:

$$v = \frac{v_i[H^+] + v_f a}{[H^+] + a} \qquad (4)$$

The determined values of parameters v_i, v_f and a have been presented in Table 2 for the three studied halide ions.

Hydrogen iodide photolysis on a long time scale. The photoreaction of hydroiodic acid could be conveniently followed on somewhat longer time scales. This was not possible in the case of Cl^- and Br^- because the halogen product is much more volatile in these cases and eqn (1) is much less shifted toward the formation of the trihalide ion. The kinetic

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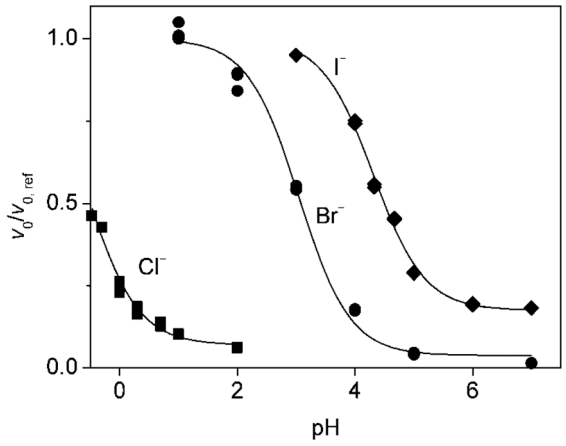

Fig. 4 Normalized reaction rate as a function of pH for the photolysis of hydrogen halide solutions [Cl^-] = 1.000 M, [Br^-] = 0.500 M, [I^-] = 1.00 mM, T = 25.0 °C.

Table 2 Kinetic parameters for the photoreactions of halide ions. T = 25.0 °C, I = 1.0 M, [Cl^-] = 1.000 M, [Br^-] = 0.500 M, [I^-] = 1.00 × 10^{-3} M

	Cl^-	Br^-	I^-
v_i (M s^{-1})	$(2.8 \pm 0.6) \times 10^{-7}$	$(1.84 \pm 0.03) \times 10^{-8}$	$(2.22 \pm 0.05) \times 10^{-4}$
v_f (M s^{-1})	$(2.0 \pm 0.3) \times 10^{-8}$	$(7 \pm 1) \times 10^{-10}$	$(3.9 \pm 0.2) \times 10^{-5}$
a (M)	4 ± 1	$(9 \pm 1) \times 10^{-4}$	$(4.9 \pm 0.4) \times 10^{-5}$

curve of a long experiment with HI is shown in Fig. 5. It is seen that the rate of I_3^- formation decreases gradually. This is not as easily interpreted as could be thought at first sight. The drop in rate does not occur because of the depletion of the reactants, as the conversion is only 2% at the end of the time scale depicted in Fig. 5 (after two hours). An alternative explanation could be the inner filter effect of the absorbing product I_3^-. In an independent series of experiments using attenuating filters inserted into the light beam, it was made sure that the initial rate is directly proportional to the photon flux[34] absorbed by iodide ions (Fig. S7 in ESI†). In the long-term

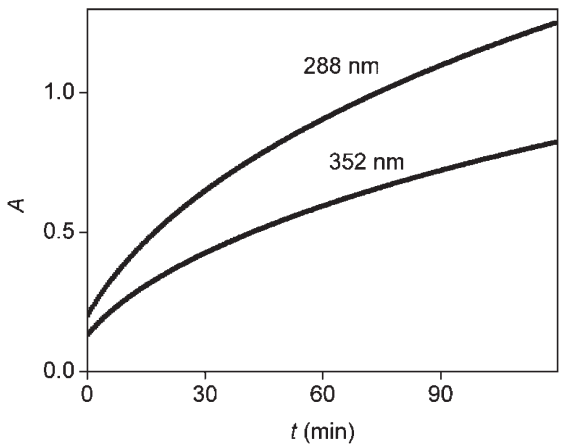

Fig. 5 Kinetic curves detected during the photolysis of a HI solution on a long time scale. [HI] = 2.00 mM, T = 25.0 °C.

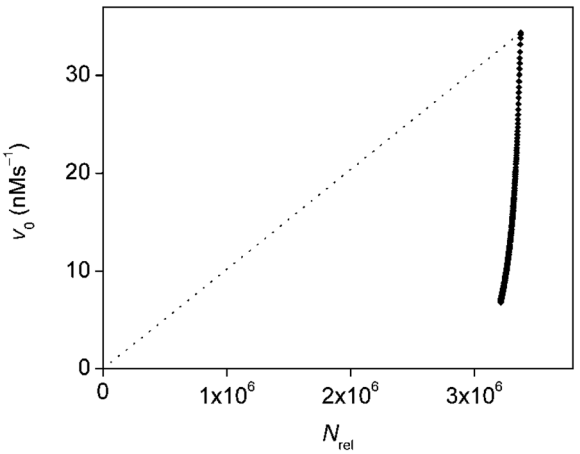

Fig. 6 Rate as a function of the (relative) number of photons absorbed by iodide ions during the photolysis of a HI solution. [HI] = 2.00 mM, T = 25.0 °C. Dotted line: expected line for the inner filter effect only.

experiments, the photon flux actually absorbed by iodide ions was calculated using the known absorption characteristics of I^- and I_3^-, and the emission properties of the light source using the following equation:

$$N_{rel} = \int_{\lambda_{min}}^{\lambda_{max}} \frac{[I^-]\varepsilon_{I^-}(\lambda)}{[I^-]\varepsilon_{I^-}(\lambda) + [I_3^-]\varepsilon_{I_3^-}(\lambda)} \times \Phi_{P\lambda} \times (1 - 10^{-A(\lambda)}) d\lambda \quad (5)$$

In this equation, $\Phi_{P\lambda}$ is the spectral photon flux. In the actual calculations, the integration in eqn (5) is replaced by summation with a base interval of 1 nm, which is set by the spectral resolution of the diode array spectrophotometer. Fig. 6 shows the detected reaction rate as a function of the number of absorbed photons by the iodide ion. Instead of the expected direct proportionality, a sharp drop is seen. Therefore, the drop in rate cannot be simply caused by the inner filter effect of the product triiodide ion. It follows that I_3^- must exert some sort of strong chemical inhibitory effect on the photoreaction.

For a more insightful analysis of the data, the normalized rate (v_{adj}) of reaction was defined during the iodide photoreaction. This normalizes the reaction rate to the photon flux absorbed by the iodide ion specifically, and therefore takes the inner filter effect into account ($v_{adj} = v/N_{rel}$). Fig. 7 displays the normalized rate as a function of triiodide ion concentration. The data collected at constant hydrogen ion concentration could be approximated by the following function:

$$v_{cor} = \frac{x}{y + [I_3^-]} \quad (6)$$

The parameters $x = (4.87 \pm 0.03) \times 10^{-13}$ M^2 s^{-1} and $y = (2.2 \pm 0.1) \times 10^{-6}$ M have been determined in this fitting procedure. Their physical meaning will be explained in the discussion.

Laser flash photolysis study of the reactions of iodine atoms in water

As the halogen atoms are very likely to play an important role during the photolysis of halide ions,[1–8] several measurements

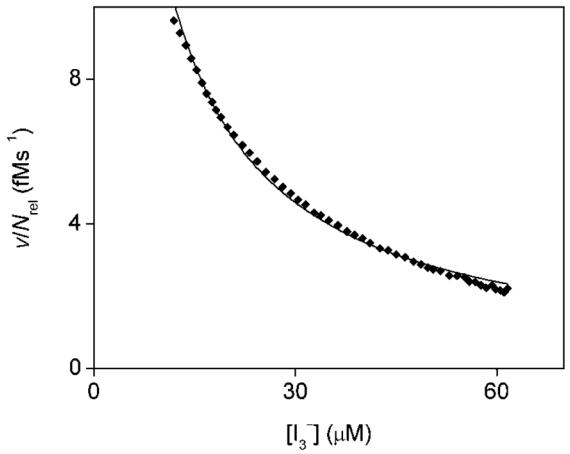

Fig. 7 Normalized reaction rate as a function of the triiodide ion concentration during the photolysis of a HI solution. [HI] = 2.00 mM, T = 25.0 °C. Straight line: best fit to eqn (7).

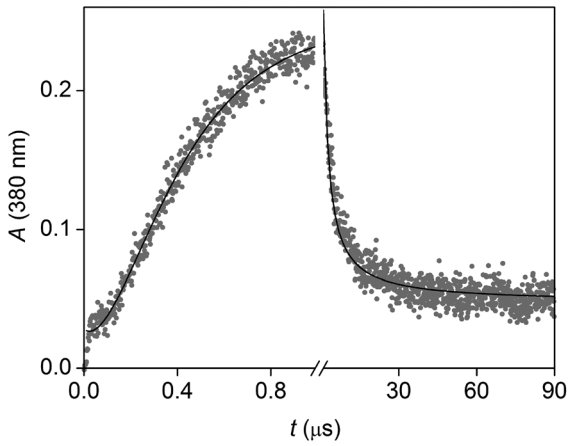

Fig. 8 Typical kinetic curve measured in a laser flash photolysis experiment on a split time base. Markers: experimental points. Lines: double exponential fit (short time scale), second-order fit (long time scale). [I^-] = 0.50 mM, [$S_2O_8^{2-}$] = 0.10 M, pH = 7 (unbuffered), T = 25.0 °C.

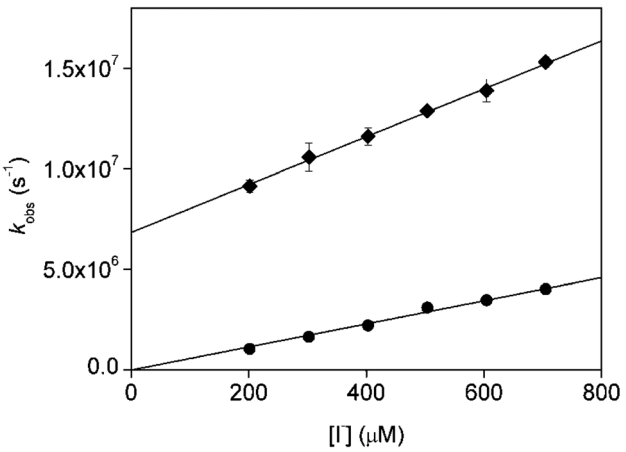

Fig. 9 Pseudo-first order rate constants determined in the double exponential fits as a function of iodide ion concentration from the laser flash photolysis experiments. [$S_2O_8^{2-}$] = 0.10 M, pH = 7 (unbuffered), T = 25.0 °C.

were carried out by laser flash photolysis to validate some assumptions about their reactions. As the results obtained during the long time scale measurements of hydrogen iodide clearly imply that the product triiodide ion seriously interferes with the photochemical reactions, a method not dependent on the direct photolysis of halide ions was considered. It was found that the reactions of iodine atoms could be favorably studied in experiments where sulfate ion radicals were used to prepare iodine atoms. A sulfate ion radical was generated through the photolysis of a peroxodisulfate ion initiated by a laser pulse at 266 nm:

$$S_2O_8^{2-} \rightarrow 2SO_4^{-} \quad (7)$$

The sulfate ion radical then reacts with an iodide ion to produce an iodine atom:

$$SO_4^{-\bullet} + I^- \rightarrow SO_4^{2-} + I^\bullet \quad (8)$$

A sample kinetic curve detected at 380 nm is shown in Fig. 8. Iodine atoms give iodine molecule ions in a subsequent reaction with excess iodide ions in a reversible process:

$$I^\bullet + I^- = I_2^{-\bullet} \quad (9)$$

The product of this reaction, the iodine molecule ion ($I_2^{-\bullet}$), is known to absorb strongly at 380 nm.[37,38] The production of $I_2^{-\bullet}$ is the reason for the increase of absorbance up to 1 ms in Fig. 8. Finally, iodine molecule ions or iodine atoms recombine to form iodine (I_2) or triiodide ions (I_3^-). This is in agreement with the observations on the longer time scale shown in Fig. 8.

As the iodide ion was used in large excess during the experiments, its concentration could be considered constant in a single experiment. The kinetic curve on the short time scale (up to 1 μs) in Fig. 8 clearly cannot be fitted to a single exponential expression, though. This is because reactions (8) and (9) have similar time scales. Experimental curves were fitted successfully with double exponential functions. The iodide ion concentration dependence of the corresponding pseudo-first order rate constants is shown in Fig. 9. It is seen that the higher pseudo-first order rate constants depend linearly on the concentration of iodide ions with a slope of $k_+ = (1.19 \pm 0.05) \times 10^{10}$ M^{-1} s^{-1} and intercept of $k_- = (6.8 \pm 0.3) \times 10^6$ s^{-1}. The lower pseudo-first order rate constants, on the other hand, are directly proportional to the concentration of iodide ions with a slope of $k_+ = (5.74 \pm 0.07) \times 10^9$ M^{-1} s^{-1}. It is well known that reaction (9) is reversible,[38] and the ratio of the slope and intercept $k_+/k_- = (1.74 \pm 0.15) \times 10^3$ M^{-1} is in agreement with earlier estimates of the equilibrium constant of the process obtained in direct photolysis studies of iodide ions.[37–43] Therefore, this double exponential curve must represent the somewhat perhaps unintuitive, but theoretically well understood, case when the larger pseudo-first order rate constant belongs to the second process in a reaction sequence.[44]

In the case of chloride and bromide ions, the reactions of sulfate ion radicals with the halide ions were too slow

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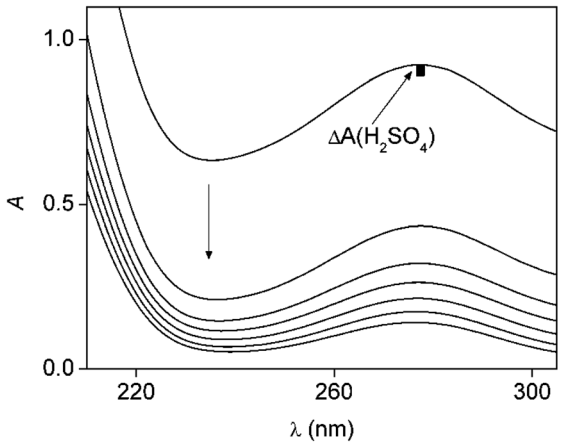

Fig. 10 Spectral changes in a sulfur(IV) solution acidified by HCl in a diode array spectrophotometer. $\Delta A(H_2SO_4)$: absorbance change in the photooxidation of sulfur(IV) measured in sulfuric acid. [HCl] = 0.0479 M, [S(IV)] = 2.02 M, [O_2] = 0.2 mM reaction time: 280 s.

compared to the formation of the halogen anions ($X_2^{-\bullet}$); therefore no information on reactions analogous to the iodide case could be obtained.

Effect of hydrochloric acid in the sulfur(IV) system

Kinetic phenomena in the uncatalyzed autoxidation of sulfur(IV) were used to demonstrate how neglecting the aqueous photochemistry of halide ions may lead to erroneous conclusions. The autoxidation of sulfur(IV) does not proceed in the absence of a catalyst and light even at high temperatures.[45–47] UV-light, however, drives the reaction.[20] In the earlier study of this process,[20] sulfuric acid and perchloric acid were used to set the acidity. Fig. 10 shows an experiment in hydrochloric acid. The loss of sulfur(IV) is much faster in hydrochloric acid than the expectations based on the results in perchloric and sulfuric acids[20] (which is shown by a small arrow in Fig. 10). The product of the photoreaction of chloride ions, chlorine, is known to oxidize sulfur(IV) quite rapidly.[48] Therefore, two parallel photochemical reactions proceed in hydrochloric acid, and both lead to the same overall reaction because of subsequent thermally activated reactions.

Discussion

Our experimental data can be interpreted by improving the scheme proposed earlier by direct photochemical measurements in aqueous solutions containing halide ions.[1–8] In the first step, a halide ion forms a halogen atom–electron solvent cage complex upon illumination:

$$\begin{aligned} &X^- + h\nu \rightarrow (Xe^-) \\ &v = q\int_{\lambda_{min}}^{\lambda_{max}} \Phi_{P\lambda} \times (1 - 10^{-A(\lambda)})d\lambda \end{aligned} \quad (10)$$

Here, q is the quantum yield of the process, whereas the remaining term gives the photon flux actually absorbed by the halide ion (see eqn (3) by substituting zero as the trihalide ion concentration). Then this cage complex can undergo either secondary recombination or chemical reaction with the solvent water or hydrogen ion to produce a halogen atom and a hydrogen atom:

$$\begin{aligned} &(Xe^-) \rightarrow X^- \\ &v = k_{rec}[(Xe^-)] \end{aligned} \quad (11)$$

$$\begin{aligned} &(Xe^-) + H_2O \rightarrow X + H + OH^- \\ &v = k_{wat}[(Xe^-)] \end{aligned} \quad (12)$$

$$\begin{aligned} &(Xe^-) + H^+ \rightarrow X + H \\ &v = k_{hyd}[(Xe^-)][H^+] \end{aligned} \quad (13)$$

Hydrogen atoms and halogen atoms can then engage in further reactions, eventually resulting in the formation of hydrogen gas and elementary halogen, the latter in equilibrium with the trihalide ion in the presence of excess halide:

$$2H \rightarrow \ldots \rightarrow H_2 \quad (14)$$

$$2X \rightarrow \ldots \rightarrow X_2 \quad (15)$$

No rate expressions are shown for reactions (14) and (15) as they are after the rate determining step. Eqn (10)–(15) essentially give the scheme that was proposed in earlier studies.[1–8] It is possible to devise more elaborate series of reactions instead of eqn (15):

$$X^\bullet + X^- \rightleftharpoons X_2^{-\bullet} \quad (16)$$

$$2X_2^{-\bullet} \rightarrow X^- + X_3^- \quad (17)$$

These assumptions are in agreement with the chemical knowledge about the properties of halogen atoms.[37–43] Although reactions (17) and (17) occur after the rate determining step in the photochemical process, their existence was confirmed and rate constants measured by a laser flash photolysis study in the case of the iodide ion.

Kinetic derivations from this scheme with a steady-state assumption for species ($X{\cdot}e^-$) show that the initial overall rate of halogen formation, as defined in eqn (3), can be given as

$$v = \frac{k_{hyd}[H^+] + k_{wat}}{k_{hyd}[H^+] + k_{wat} + k_{rec}} q\int_{\lambda_{min}}^{\lambda_{max}} \Phi_{P\lambda} \times (1 - 10^{-A(\lambda)})d\lambda \quad (18)$$

This equation is parametrically equivalent to the experimentally found expression (4) with the following connections between experimentally determined and theoretical parameters:

$$v_i = q\int_{\lambda_{min}}^{\lambda_{max}} \Phi_{P\lambda} \times (1 - 10^{-A(\lambda)})d\lambda \quad (19)$$

$$v_f = \frac{k_{wat}}{k_{wat} + k_{rec}} q\int_{\lambda_{min}}^{\lambda_{max}} \Phi_{P\lambda} \times (1 - 10^{-A(\lambda)})d\lambda \quad (20)$$

$$a = \frac{k_{wat} + k_{rec}}{k_{hyd}} \quad (21)$$

However, as already pointed out, the observations on the photolysis of hydrogen iodide solutions and the dependence of the overall rate on the concentration of the triiodide ion shown in eqn (6) strongly support some interaction between the triiodide ion and one of the reactive intermediates in the system. We found that the simplest way to interpret this effect is using the interaction of a triiodide ion with the cage complex formed as the product of reaction (10):

$$\begin{aligned} &(\mathrm{I}\cdot \mathrm{e}^-) + \mathrm{I_3}^- \rightarrow \mathrm{I_2} + 2\mathrm{I}^- \\ &v = k_{tri}[(\mathrm{X}\cdot \mathrm{e}^-)][\mathrm{I_3}^-] \end{aligned} \quad (22)$$

This additional steps and the inner filter effect of the triiodide ion give rise to a more complicated rate law:

$$v = \frac{k_{hyd}[\mathrm{H}^+] + k_{wat}}{k_{hyd}[\mathrm{H}^+] + k_{wat} + k_{rec} + k_{tri}[\mathrm{I_3}^-]} q \int_{\lambda_{min}}^{\lambda_{max}} \frac{[\mathrm{I}^-]\varepsilon_{\mathrm{I}^-}(\lambda)}{[\mathrm{I}^-]\varepsilon_{\mathrm{I}^-}(\lambda) + [\mathrm{I_3}^-]\varepsilon_{\mathrm{I_3}^-}(\lambda)} \times \Phi_{P\lambda} \times (1 - 10^{-A(\lambda)})\mathrm{d}\lambda \quad (23)$$

This theoretically derived rate expression is in full agreement with the experimental observations summarized in eqn (4) and (6).

Conclusion

The results clearly prove that the photoreactions of halide ions can be initiated by the light of a diode array spectrophotometer. The rates of halogen and trihalide ion formation can be determined and their dependence on the concentrations of reactants and light intensity can serve as a basis for postulating a mechanism. The systematic study of the photoreaction of the iodide ion has revealed that the triiodide ion has a specific (auto)inhibiting effect on the process. This inhibiting effect can be interpreted by a single reaction occurring between the triiodide ion and the aqueous cage complex of the iodine atom and an electron. It is also clear that these processes can be a source of unwanted interference in cases when halide ions are used as a background electrolyte in spectrophotometric studies using a diode array spectrophotometer, as proven by the example of the sulfur(IV)–oxygen system in this work, where using aqueous sodium chloride as a medium greatly changes the observations. It should be emphasized that the possible interference is independent of the monitoring wavelength range, and it depends on the light source of the spectrophotometer. For the chloride ion, any illumination below 235 nm could cause such an effect, whereas the same cutoff value is about 300 nm for both bromide and iodide ions. The exact details depend on the particular concentrations used in the experiments; detailed calculations or – even better – direct experiments are needed to rule out such possible interferences.

Acknowledgements

The authors thank the Hungarian Science Foundation for financial support under grant no. K77936 and NK 105156. The research was supported by the EU and co-financed by the European Social Fund under the project ENVIKUT (TÁMOP-4.2.2.A-11/1/KONV-2012-0043). The Hungarian Academy of Sciences also supported these studies through funding from Research Group on Homogeneous Catalysis and Reaction Mechanisms. Éva Dóka's participation in this research was supported by the European Union and the State of Hungary, co-financed by the European Social Fund in the framework of TÁMOP-4.2.4.A/2-11/1-2012-0001 'National Excellence Program'. Some experimental help was kindly provided by Dr Ildikó Kerezsi, whose assistance is gratefully acknowledged.

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