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Photochemically Induced Autocatalysis in the Chlorate Ion−Iodine System

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The reactions of oxychlorine species show a number of exotic kinetic phenomena including autocatalysis,[1−4] oscillation,[5−7] and stochastic behavior.[8−9] In addition, these species are very important from a practical point of view because chlorine, hypochlorite ion, and chlorine dioxide are used for water disinfection, whitening, and industrial oxidation processes in large quantities. Chlorate and perchlorate ions are the kinetically least reactive oxychlorine species at room temperature.

In a recent Communication, Oliveira and Faria reported that chlorate ion oxidizes iodine rapidly in an autocatalytic process which the authors classified as a clock reaction.[10] Now we prove that a key factor, the initiating role of light arising from the diode-array spectrophotometer, was not recognized in that work.[10] This also requires major revision of the proposed kinetic model. In recent studies, we have already demonstrated how diode-array spectrophotometers can be used to drive and monitor photochemical reactions simultaneously.[11−13] An earlier example also showed that photochemical effects caused by the intense light source of a diode-array spectrophotometer may corrupt the experimental observations.[14]

We could not reproduce the work of Oliveira and Faria[10] in a conventional double-beam spectrophotometer (Perkin-Elmer Lambda 2S). Curve a in Figure 1 shows that no change is detectable in an acidic solution containing ClO_3^- and I_2 for 2 h (using freshly prepared $NaClO_3$ and I_2 solutions is essential). However, reproduction of the reported observations[10] was successful using a diode-array spectrophotometer provided that illumination of the sample was continuous with both the halogen and deuterium lamps switched on.

Kinetic traces in Figure 2 show experiments in a HP-8543 diode-array spectrophotometer (equipped with a built-in magnetic stirrer) using different illumination protocols. Continuous stirring was necessary to obtain reproducible results, which is characteristic of photoreactions.[11] Curve c was detected using continuous illumination with the halogen and the deuterium lamps switched on. Curve d was recorded under similar conditions, but 5-second dark periods were introduced following each measurement period. The induction period is longer in this experiment because the time-averaged light intensity is lower. Curve e was also measured with continuous illumination, but the deuterium lamp of the instrument was switched off as it is not needed for detection at 460 nm. The length of the induction period increased by about an order of magnitude in comparison with curve c. This can be rationalized by the fact that I_2 has much stronger absorption in the UV (Figure S1 in Supporting Information) and therefore the absorbed photon count[11] decreases greatly in the absence of UV light. All these observations show that light has an important role in initiating the reaction, which does not occur in conventional double-beam spectrophotometers because of the very low-intensity monochromatic light used.

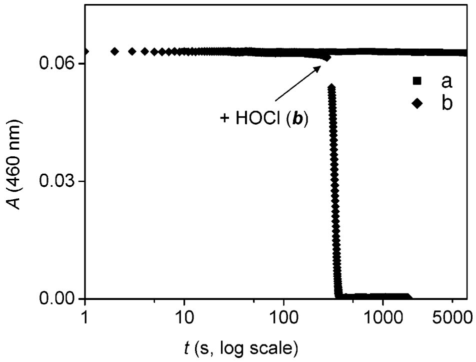

Figure 1. Kinetic curves measured in the $ClO_3^-−I_2$ system by a conventional scanning spectrophotometer without (a) and with (b) midcourse addition of HOCl (9 μM). $[ClO_3^-] = 25.1$ mM; $[I_2] = 88$ μM; $[H^+] = 0.948$ M; $T = 25.0$ °C.

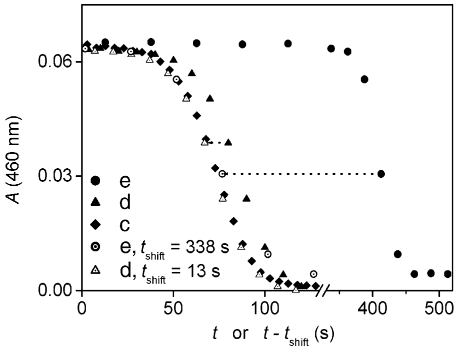

Figure 2. Kinetic curves measured during the photoinitiated reaction of I_2 with ClO_3^-; $[ClO_3^-] = 25.1$ mM; $[I_2] = 88$ μM; $[H^+] = 0.948$ M: (c) continuous illumination, (d) periodically interrupted illumination (50%), (e) continuous illumination without deuterium lamp; $T = 25.0$ °C.

The fact that the reaction is driven by the halogen lamp alone proves a significant point: I_2 is the photoactive species because no other component in the system absorbs light in the spectral region emitted by the halogen lamp. This conclusion is by no means surprising as many photochemical reactions of I_2 are known[15−17] including its non-autocatalytic oxidation by ClO_2.[17]

The autocatalytic nature of the $ClO_3^-−I_2$ reaction was demonstrated by the mid-course addition of a small amount of HOCl (Figure 1, curve b) in a kinetic experiment using the conventional double beam instrument. A rapid loss of I_2 after the addition of HOCl confirmed the autocatalysis, although did not prove that HOCl is exclusively responsible for the phenomenon. A similar feature was observed when ClO_2^- was added to the reaction. These experiments confirm that the role of light in diode-array experiments is limited to the generation of the autocatalyst(s).

This conclusion is corroborated by the analysis of the results shown in Figure 2. When curves d and e are shifted in time (13 s for curve d, 338 s for curve e), they almost perfectly superimpose on curve c (Figure S2 gives another example). This again proves that light does not have a significant role after an initial amount of autocatalyst is generated. Very similar curve-shifting can be used to show that the acidity primarily influences the length of the

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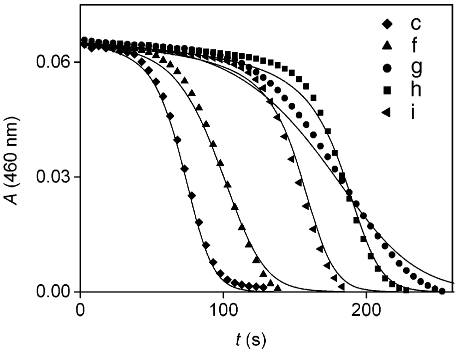

Figure 3. Measured (markers) and fitted (lines) kinetic curves in the photoinitiated reaction of I_2 with ClO_3^-. $[I_2] = 88\ \mu M$; $[ClO_3^-] = 25.1$ mM (c, h, i), 16.7 mM (f), 8.3 mM (g); $[H^+] = 0.948$ M (c, f, g), 0.237 M (h), 0.356 M (i); continuous illumination; $T = 25.0$ °C.

induction period but not the rate of the reaction after the induction period. In contrast, both the length of the induction period and the rapidly decreasing region of the kinetic curves are sensitive to a change in chlorate ion concentration (Figures S3 and S4 in SI).

Our results show that the mechanism proposed by Oliveira and Faria[10] cannot be valid as it does not involve the initiation by light. There are further weak points in that mechanism. The rate constant considered for the reaction of ClO_3^- with I^- is 4 orders of magnitude larger than the directly measured value[18] implying that I^- has a significant role in the overall process. In addition, I_3^- was proposed to contribute to the absorbance signal measured at 460 nm, which contradicts the absence of measurable absorbance at 360 nm, where I_3^- absorbs very intensely (Figures S1 and S5). Our results confirm that the reactions of I^- and I_3^- can be neglected in this system.

The results are consistent with the following stoichiometry:

$$3I_2 + 5ClO_3^- + 3H_2O \rightarrow 6IO_3^- + 5Cl^- + 6H^+$$

We postulate the following kinetic model for the interpretation of the findings (more detailed discussion is given in SI):

$$I_2 + ClO_3^- + H_2O + h\nu \rightarrow IO_3^- + H_2OI^+ + Cl^-$$

$$v_1 = \alpha_{1a}[I_2][ClO_3^-][H^+] + \alpha_{1b}[I_2][ClO_3^-] \qquad (1)$$

$$HOCl + H^+ + Cl^- \rightleftharpoons Cl_2 + H_2O$$

$$K_2 = [Cl_2]/([HOCl][Cl^-][H^+]) \qquad (2)$$

$$H_2OI^+ + ClO_3^- \rightarrow IO_3^- + HOCl + H^+$$

$$v_3 = k_3[H_2OI^+][ClO_3^-]/[H^+] \qquad (3)$$

$$H_2OI^+ + 2HOCl \rightarrow IO_3^- + 2Cl^- + 4H^+$$

$$v_4 = k_4[H_2OI^+][HOCl] \qquad (4)$$

$$I_2 + Cl_2 + 2H_2O \rightarrow 2H_2OI^+ + 2Cl^-$$

$$v_5 = k_5[I_2][Cl_2] \qquad (5)$$

H_2OI^+ is indicated in the model rather than HOI, because the protonated form dominates below pH 1.[19] Numerical integration of the proposed model showed that reactions 1−5 interpret the experimental data reasonably well. The five different curves shown in Figure 3 were simultaneously fitted using $\epsilon = 740\ M^{-1}\ cm^{-1}$ at 460 nm for I_2.[10] Literature values were fixed for $K_2 = 1000\ M^{-2}$ ($k_2 = 2.2 \times 10^4\ M^{-2}\ s^{-1}$, $k_{-2} = 22\ s^{-1}$) and $k_5 = 1.5 \times 10^5\ M^{-1}\ s^{-1}$.[4] Reaction 4 (in the form HOI + HOCl) was also often considered in previous work, but estimates for k_4 span a huge range from 0 to $10^8\ M^{-1}\ s^{-1}$.[2−6] Our calculations did not resolve k_4, only the ratio $k_3/k_4 = (1.13 \pm 0.02) \times 10^{-3}\ M^{-1}$ could be determined by least-squares fitting ($k_3 = 56.4\ s^{-1}$ and $k_4 = 5 \times 10^5\ M^{-1}\ s^{-1}$ were used in the calculations). Parameters $\alpha_{1a} = (4.5 \pm 0.1) \times 10^{-2}\ M^{-2}\ s^{-1}$, and $\alpha_{1b} = (9.0 \pm 0.2) \times 10^{-3}\ M^{-1}\ s^{-1}$ have also been calculated. It should be noted that these are instrument-specific constants as they include the emission characteristics of the lamps.[11] The goodness of the fit is shown by the measured and fitted kinetic traces in Figure 3. The model also correctly predicts the observations shown as curve b in Figure 1. (Figure S6).

In summary, the chlorate ion−iodine reaction is an autocatalytic process, in which light absorption of I_2 results in the accumulation of reactive intermediates which initiate a thermal reaction sequence. Light has no further role in the overall reaction. The variation in the induction period reflects the pH and concentration dependencies of reaction 1. The autocatalytic features are determined by the fine balance of reactions generating, step 3, and consuming, steps 4 and 5, the intermediate HOCl. We feel that this example also serves as a strong warning that it is important to test for the possible photochemical role of the intense light of a diode-array spectrophotometer.

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Supporting Information Available: Graphs and derivations of the rate equations referred to in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Grant, J. L.; De Kepper, P.; Epstein, I. R.; Kustin, K.; Orbán, M. *Inorg. Chem.* **1982**, *21*, 2192−2196.
(2) Rábai, G.; Beck, M. T. *Inorg. Chem.* **1987**, *26*, 1195−1199.
(3) Citri, O.; Epstein, I. R. *J. Phys. Chem.* **1987**, *91*, 6034−6040.
(4) Lengyel, I.; Li, J.; Kustin, K.; Epstein, I. R. *J. Am. Chem. Soc.* **1996**, *118*, 3708−3719.
(5) Epstein, I. R.; Kustin, K. *J. Phys. Chem.* **1985**, *89*, 2275−2282.
(6) Citri, O.; Epstein, I. R. *J. Phys. Chem.* **1988**, *92*, 1865−1871.
(7) Horváth, A. K.; Dolnik, M.; Zhabotinsky, A. M.; Epstein, I. R. *J. Phys. Chem. A* **2000**, *104*, 5766−5769.
(8) Nagypál, I.; Epstein, I. R. *J. Phys. Chem.* **1986**, *90*, 6285−6292.
(9) Nagypál, I.; Epstein, I. R. *J. Chem. Phys.* **1988**, *89*, 6925−6928.
(10) Oliveira, A. P.; Faria, R. B. *J. Am Chem. Soc.* **2005**, *127*, 18022−18023.
(11) Lente, G.; Espenson, J. H. *J. Photochem. Photobiol., A* **2004**, *163*, 249−258.
(12) Kerezsi, I.; Lente, G.; Fábián, I. *J. Am. Chem. Soc.* **2005**, *127*, 4785−4793.
(13) Kerezsi, I.; Lente, G.; Fábián, I. *Dalton Trans.* **2006**, 955−960.
(14) Stanbury, D. M.; Figlar, J. N. *Coord. Chem. Rev.* **1999**, *187*, 223−232.
(15) Durrant, G. G.; Griffith, R. O.; McKeown, A. *Trans. Faraday Soc.* **1938**, 389−410.
(16) Bennett, J. G.; Griffith, R. O. *Trans. Faraday Soc.* **1948**, 471−478.
(17) Rábai, G.; Kovács, K. M. *J. Phys. Chem. A* **2001**, *105*, 6167−6170.
(18) Ramette, R. W.; Harris, R. Z.; Bengali, A. A.; Noll, R. J. *Anal. Chem.* **1987**, *59*, 154−156.
(19) Lengyel, I.; Epstein, I. R.; Kustin, K. *Inorg. Chem.* **1993**, *32*, 5880−5882.

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