CEE 684 (697K)
Dichloropropanone Lab

Laboratory Project

Work in groups of three to investigate the kinetics of reaction between aqueous chlorine and 1,1-dichloropropanone (DCP). Use the paper by <u>Guthrie and Cossar</u>[1] that we discussed in class as a guide.

This project has many of the same features as the first one (bromide) such as reaction with chorine, use of the hypochlorite absorbance maximum (292 nm) to monitor pseudo-first order kinetics, as well as specific and general base catalysis. This project also includes some interesting pre-equilibria for the organic reactant, a more complex reaction scheme, multiple products, each of which can potentially react further with chlorine and an opportunity to use other lab methods to determine product yields.

I. Free Chlorine Kinetic Test Procedures

Using the HP 8452A Diode Array Spectrophotometer in room 301 (Elab II), investigate the reaction under near neutral conditions (i.e., pH 8.5) and at a temperature of 25ºC. You may use a single fixed initial DCP concentration of 1.0 mM and add an equal amount of NaOCl (1.0 mM). For this I recommend you use the maximum wavelength for hypochlorite (292 nm), but you should record other wavelengths too. You may use some of the existing solutions that were prepared by the lab captains and/or you may prepare your own.

Here's a suggested step-by-step procedure to help you get started (the beginning of this is the same as for the bromide lab):
1. Turn on Spec and computer. Please be gentle with them. The spec is 25 years old, which is about 150 in "instrument years".
2. This is an old Windows NT computer so you have to hit Ctrl-Alt-Del to get the log-in screen. There is no computer password, so leave this blank. The spec will go through a series of diagnostics and you will hear the shutter opening and closing as it checks itself out.
3. Once the two back yellow indicator lights (Power & Lamp) are illuminated in yellow on the top of the Spec, you can launch the HP UV-Vis spec software (shortcut icon on the desktop)
4. Make sure the method or task selection is for "Fixed Wavelengths". Hit the "Setup" button under the Task box. A pop-up will appear and offer you a set of 6 boxes for fixed wavelengths to follow on the tabular output. I'd suggest 254, 292, 320 and 350 nm. You can also select a range to view on the graph. For this I'd suggest something like 230 to 370 nm. No need for any background correction, and keep the Data type set for "Absorbance". Hit "OK" when done.

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[1] <u>Canadian Journal of Chemistry</u>, 64:1250-1266 (1986).

5. Fill a quartz cell (labeled 383; don't use the 181 cells – which are for visible wavelengths [>300nm] and won't work for our purposes) with DI water (you can use the squeeze bottle).
6. Place the cell in the cell holder of the sample compartment (make sure the clear windows are aligned with the light path which runs parallel with the back wall) and hit "blank" on the computer screen. This will "zero" the instrument across all wavelengths. You will see a pop-up small screen showing the noise level at various wavelengths. The numbers should be about zero ± 0.001 or smaller. If it looks OK you should not overwrite this baseline scan, which means you should not hit "Blank" again until the next time you turn on the instrument. At this point, I often run the same DI water as a "Sample" just to be sure that the baseline is very close to zero. This time it will show you the absorbance spectrum in the main screen and again the values should be about zero ± 0.001 or smaller.
7. Prepare your DCP stock solution. I'd recommend a 20.0 millimolar concentration for convenience. You can use the pre-made solution, if you'd like; at least until it runs out. If you need to make more, there is a bottle of 98% DCP in room 301, in the "flammables" cabinet under the hood closest to the MilliQ water system.
8. Prepare your NaOCl stock solution. I'd recommend a 10% dilution of the Fisher reagent hypochlorite solution (stored in refrigerator #11 in room 308; this is nominally 5.65-6 % by weight). Make sure you select a bottle that is no older than 1 year. This dilution should give you a concentration of about 0.5% or ~5,000 mg/L. Again, you can use the pre-made solution, if you'd like; at least until it runs out.
9. Prepare about 100 mL of buffer stock solution at about 1M.
10. Prepare a set of nine 50-mL buffered solutions with a DCP concentration of 1mM based on the following factorial design:
    a. Pick 3 pHs spanning the range for your assigned buffer
    b. Use three different buffer concentrations at each pH:
        i. 20 mM
        ii. 5 mM
        iii. 1 mM
11. Prepare the spec for kinetic measurements.
    a. Select the data collection frequency, wavelengths
12. Measure temperature of the pH-adjusted DCP solution after it reaches equilibrium with its surroundings
13. Remove 3 mL of the solution with the volumetric pipet (in drawer under the spec) and place in the empty cuvette
14. Return the cuvette to the holder, remember to orient it properly and hit "Sample" on the computer screen. The spec will do a full scan and show the graphical and tabular results (the table just shows absorbance at the selected wavelengths). This shows the background absorbance of the buffered DCP.
15. Next add about the requisite number of µL of your NaOCl solution to achieve a dose of 1.5 mM and have a stop watch ready
    a. You can use either a syringe (100 µL), or
    b. A properly-calibrated Eppendorf pipet
16. Quickly add the NaOCl solution directly into the cuvette and mix by placing the teflon cap on the cuvette and inverting 6 times.

17. Place the cuvette back into the holder and simultaneously hit "Start" on the computer screen in kinetics mode.
18. Continue collecting absorbance data so that you can accurately trace out the chlorine decay curve. Ideally you will collect at least a dozen measurements before the absorbance reaches 95% of its final value.
19. Run a duplicate if the reaction is fast enough to be 95% complete in 10 minutes, and a triplicate if is 95% complete in 5 minutes
20. When the kinetic runs are complete, use the remaining buffered DCP for a non-kinetic assessment:
    a. add sufficient NaOCl to dose the remaining volume at 1.5 mM.
    b. wait for a period of time equivalent to about 50-95% completion based on the kinetic runs and measure pH and temperature.

II. Combined Chlorine Test Procedures

1. Prepare monochloramine (NH_2Cl) stock solution.
    a. Prepare 50 mL of a 10 mM solution of ammonium chloride (NH_4Cl) in Milli-Q water. Adjust pH to 8.5 with a small amount of NaOH.
    b. Place this solution in to a 100-mL Erlenmeyer flask
    c. Chill to near freezing
    d. Prepare about 25 mL of neutralized solution of NaOCl at about 5000 mg/L by diluting the commercial product (as above) and adding HCl until the pH is about 8.5.
    e. Measure out the requisite volume of the neutralized sodium hypochlorite stock to produce a Cl_2/N ratio of 0.8:1 when all is added to the ammonium solution. This should be about 5.68 mL if the chlorine stock is exactly 5000 mg/L).
    f. **Slowly and with intense mixing (use a stir bar),** add the measured volume of hypochlorite stock to the ammonium chloride solution; keep on ice. This should produce a monochloramine solution of about 510 mg/L as Cl_2
    g. Dilute a 0.5mL volume to 100 mL and measure residual using the DPD ferrous titrimetric or amperometric method
2. Store this at low temperature until use. Record a full spectrum (200 nm-500 nm) of a 20% dilution of this solution. Discard when the peak absorbance at 243 nm drops by 20% from the original value.
3. Repeat Steps #11-20 above but use the NH_2Cl solution to dose instead of the NaOCl solution. Do this in the form of an orthogonal experimental design (rather than a factorial design)
    a. run the test with all 3 buffer strengths at the middle pH and
    b. all three pHs at the highest buffer strength.
4. Collect k_{obs} data and share with class.

III. Product Assessment Procedures
<p style="text-align:center">Still under development</p>

IV. Group Assignments

For this laboratory experiment, we have assigned different buffers to each group.

<u>Group #1. Borate Group (Joe, Varun & Tao)</u>
This group will use borate buffers and explore the reaction across a pH range of 7.5-9.0
- I recommend you use sodium tetraborate and adjust pH to the desired level with concentrated HCl.

<u>Group #2. Carbonate Group (Rosa, Yanjun, Soon-Mi)</u>
This group will use carbonate buffers and explore the reaction across a pH range of 6.5-8.0
- I recommend you use sodium carbonate and adjust pH to the desired level with concentrated HCl.

<u>Group #3. Phosphate Group (Cynthia, Arianne, Camilla)</u>
This group will use phosphate buffers and explore the reaction across a pH range of 7.0-8.5
- I recommend you use sodium hydrogen phosphate Na_2HPO_4 or the analogous potassium salt (K_2HPO_4) and adjust pH to the desired level with concentrated HCl.

Preparation of Pre-formed Monochloramine
1. Mix sufficient volume of the hypochlorite solution hypochlorite stock solution plus 20 mM borate pH 8.5 buffer to make 250 mL of a 1000 mg/L chlorine solution and
2. Place this solution in to a 1 L Erlenmeyer flask
3. Chill to near freezing
4. Add stir bar and mix rapidly
5. Measure out the requisite volume of 10,000 mg-N/L NH_4Cl solution to produce a Cl_2/N ratio of 1:1. This should be about 4.93 mL.
6. Slowly add the requisite volume of 10,000 mg-N/L NH_4Cl solution so that the Cl_2/N ratio is 1:1, with intense mixing; keep on ice;
7. Dilute a 0.25mL volume to 100 mL and measure residual using the DPD ferrous titrimetric or amperometric method

Part III: Kinetic Analysis & Write-up

Here you will write a short report on your experiments including a kinetic analysis (one report per group). The first step will be to tabulate and graph your absorbance data. You may choose to focus on the 292 nm data as Kumar & Margerum did. You should present at least 5 full spectra (one of a DCP solution, one of a buffer solution, one of a buffered chlorine solution, one of a buffered DCP solution and at least one of a reaction solution at completion), plotting absorbance vs wavelength (from ~200 nm to ~450 nm). Comment on why they are different and what the difference means. You should feel free to speculate as to how the possible products and reactants contribute to the spectra you show.

For each experiment, plot the absorbance data on a semi-log scale so you can determine the observed rate (k_{obs}). Tabulate and summarize these rates and share with the other groups (share only the k_{obs} values and conditions under which they were determined). . When possible, use these data to determine a rate law, employing graphical representations wherever appropriate. Comment on how your particular buffer affected the reaction.

In general, do your best to interpret your results. What do they tell you, if anything, about the nature of the reaction? Compare your rate law or results with the ones presented in Guthrie & Cossar. Do you agree with these authors? Prepare a concise report summarizing your findings. Include tables of the raw data, graphs of the linearized kinetic plots and tables of the rate constants (e.g., k_{obs}, k_2, etc), as well as the selected absorbance spectra.
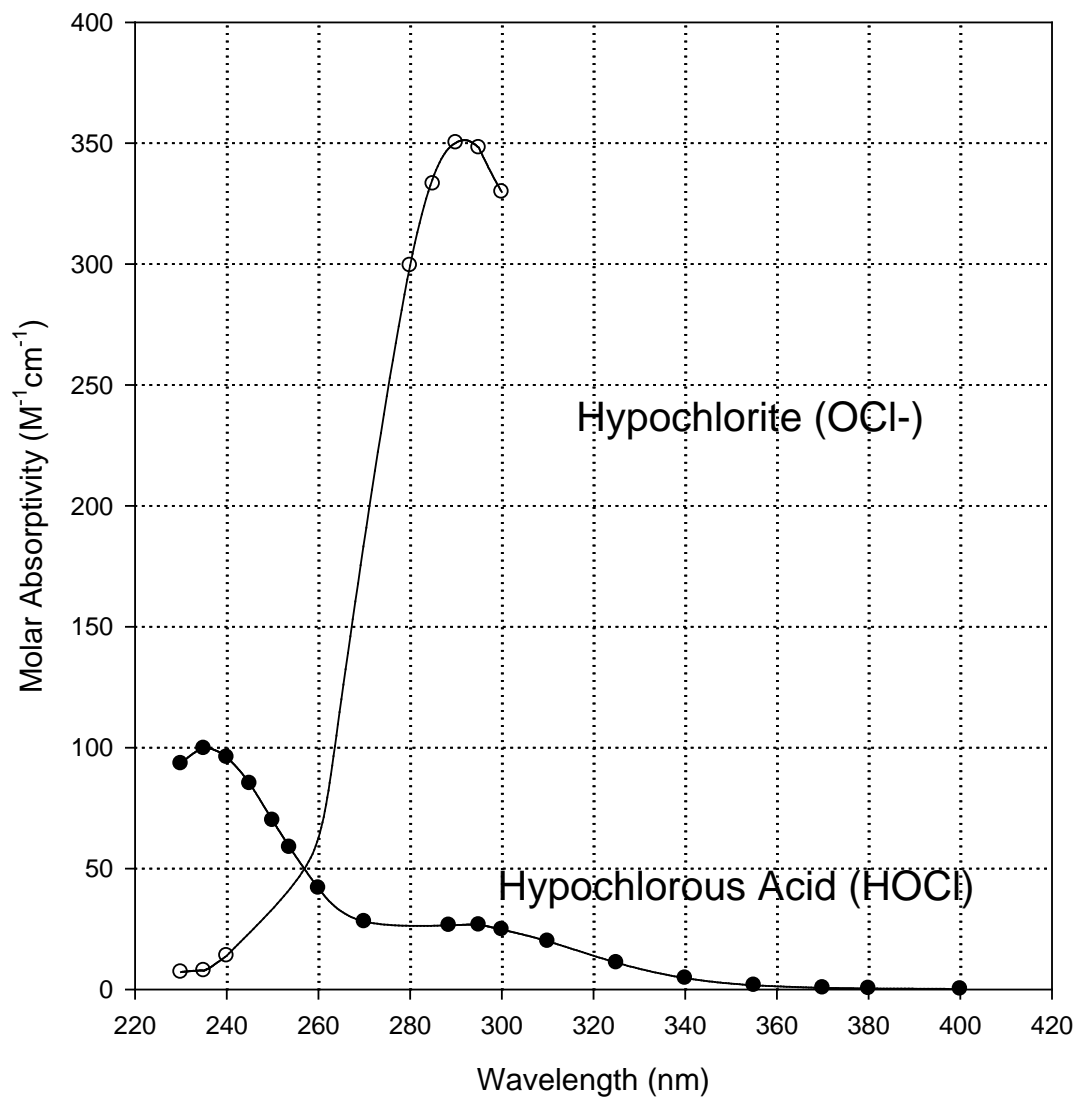
Background Information

Absorptivities:

Figure 1. Free Chlorine Absorptivity at 20 C

Table 1. Molar Absorptivities of Some Chlorine Species ($M^{-1}cm^{-1}$) at 20 C

Wavelength (nm)	HOCl	OCl⁻	NH₂Cl	NHCl₂	ClO₂
203				2120	
220			1200	67.5	
230	93.4	7.2			
235	99.7	7.8			
240	96.0	13.9			
243			445	245	
245	85.2		416 (445)[2]	(208)	
250	69.9				
253.7	58.8				
257			400	135	
260	41.9				
262			423	112	
265			414	110	
270	28.07				
278			91	182	
280	(26.0)	299.4			
285	(26.55)	333.2			
288.5	26.51				
290	(26.95)	350.2			
294			27	276	
295	26.65	348.15	(14)	(267)	
297				265	
300	24.78	329.85	25	293	
310	19.94				
325	11.06				
335				73	
340	4.68				
345				39	
355	1.71				
360					1250
370	0.64				
380	0.40				
400	0.19				

Refer to: Hand and Margerum, 1983, for more [Inorg. Chem. 22(10)1449].

You may also want to consult the absorptivity values in Table 1 of Kumar & Margerum paper.

[2] HOCl data are from Silverman & Gordon, 1980, except for values in parenthesis. Chloramine values in parentheses are from: Valentine et al., 1986