CEE 697K
Bromide Lab

Laboratory Project

Work in groups of three to investigate the kinetics of reaction between aqueous chlorine and bromide. Use the paper by Kumar and Margerum[1] that we discussed in class as a guide. Each lab group should include at least one person with experience in lab work at UMass.

Part I: Initial Test of Reaction Kinetics under Baseline Conditions

Using the HP 8452A Diode Array Spectrophotometer in room 301 (Elab II), investigate the reaction under alkaline conditions (i.e., pH ~10.5 to pH ~13.5) and at a temperature of 25ºC. You may use a single fixed initial bromide concentration of 0.100 M and add small amounts of NaOCl (~ 0.5 mM) so that the reactions are pseudo-1st order. Use whatever wavelength or wavelengths you think appropriate. You may use the solutions that I prepared and/or you may prepare your own.

Here's a suggested step-by-step procedure to help you get started:

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.
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

[1] Inorganic Chemistry, 26:2706-2711 (1987).

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 NaBr stock solution. I’d recommend a 1.0 molar 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 1 lb bottle of the pure NaBr in room 308 near the balances.
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 50 mL of the diluted and pH-adjusted bromide solution
    a. Add 5 mL of your NaBr stock to a 50 mL volumetric flask
    b. Add the requisite amount of the 50% NaOH solution (19.07 M; stored in the “Bases” cabinet under hood # 301b) to reach the proper pH. Remember that NaOH is a strong base which completely dissociates. For example, to reach a pH of 12.70 at 25°C, you’ll need 0.050M NaOH as a final concentration in the 50 mL flask. This requires that you add 0.131 mL of the 50% NaOH solution.
    c. Fill with RO/DI water to the mark, cap and mix by inverting several times
10. Measure temperature of the pH-adjusted bromide solution after it reaches equilibrium with its surroundings (either room air, or water bath, depending on your objectives)
11. Remove 3 mL of the solution with the volumetric pipet (in drawer under the spec) and place in the empty cuvette
12. 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 alkaline sodium bromide.
13. Next add about 30 µL of your NaOCl solution and have a stop watch ready
    a. You can use either a syringe (100 µL), or
    b. A pasteur pipet (
14. Quickly add the NaOCl solution directly into the cuvette and mix by placing the teflon cap on the cuvette and inverting 6 times.
15. Place the cuvette back into the holder and simultaneously start the watch and take an initial scan (hitting “sample” on the computer) and record the time (e.g., “initial” on the “name” field in the “Sample/Results Table”).
16. 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.

Part II: Detailed Lab Investigation

We have assigned variables for each of the three groups to investigate (see below). In each case you will probably want to verify the pH and temperature. pH is especially important to verify for the group #3. You should run about a dozen experiments, and include some replicates so that you can assess uncertainty in your rate constants.

Group #1. pH Group (Joe, Varun & Tao)
This group will investigate the reaction rate under different pHs at room temperature. The four pHs we are interested are: 11.0, 11.5, 12.0, and 12.5.

Group #2. Hypochlorite Group (Rosa, Yanjun, Soon-Mi)
This group will vary the hypochlorite concentration at two pHs to either "speed-up" or "slow down" the reaction.

A. At high pH (e.g., pH=12.5, this value should match the highest pH that Group #1 will choose, so the results can be compared between groups with and without acid catalysis), increase the hypochlorite concentration to check if the reaction will go faster or not.
B. At low pH (e.g. pH=11, also this should be chosen in accordance with the pH group), reduced the hypochlorite dose and see whether the reaction will be slowed down.

Group #3. Acid Catalysis Group (Cynthia, Arianne, Camilla)
This group will catalyze the reaction with different types of acids at the highest pH (e.g. pH=12.5). Then add varying amounts of monohydrogen phosphate (e.g., Na_2HPO_4 or K_2HPO_4). Suggested concentrations in the final reaction mixture are: 0, 5, 10, 20 and 50 mM). You'll need to verify the pH of each solution, but you can do this in parallel with the actual reaction mixtures (i.e., at a convenient time, mix them in a small beaker and measure pH).

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 4 full spectra (one of an alkaline NaBr solution, one of a chlorine solution, one from the beginning of a "typical" reaction and one from the end of the same reaction), plotting absorbance vs wavelength (from ~230 nm to ~370 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. If you explored hydroxide (group #1), relate this to pH-effects, and comment on mechanistic implications. If you examined chlorine concentration (group #2),

relate this to the kinetic rate law, and again, comment on any mechanistic implications. If you looked at acid catalysis (group #3), present the 3rd order constant. Comment on how it fits the Bronsted relationship presented by Kumar and Margerum.

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 Kumar and Margerum. 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:

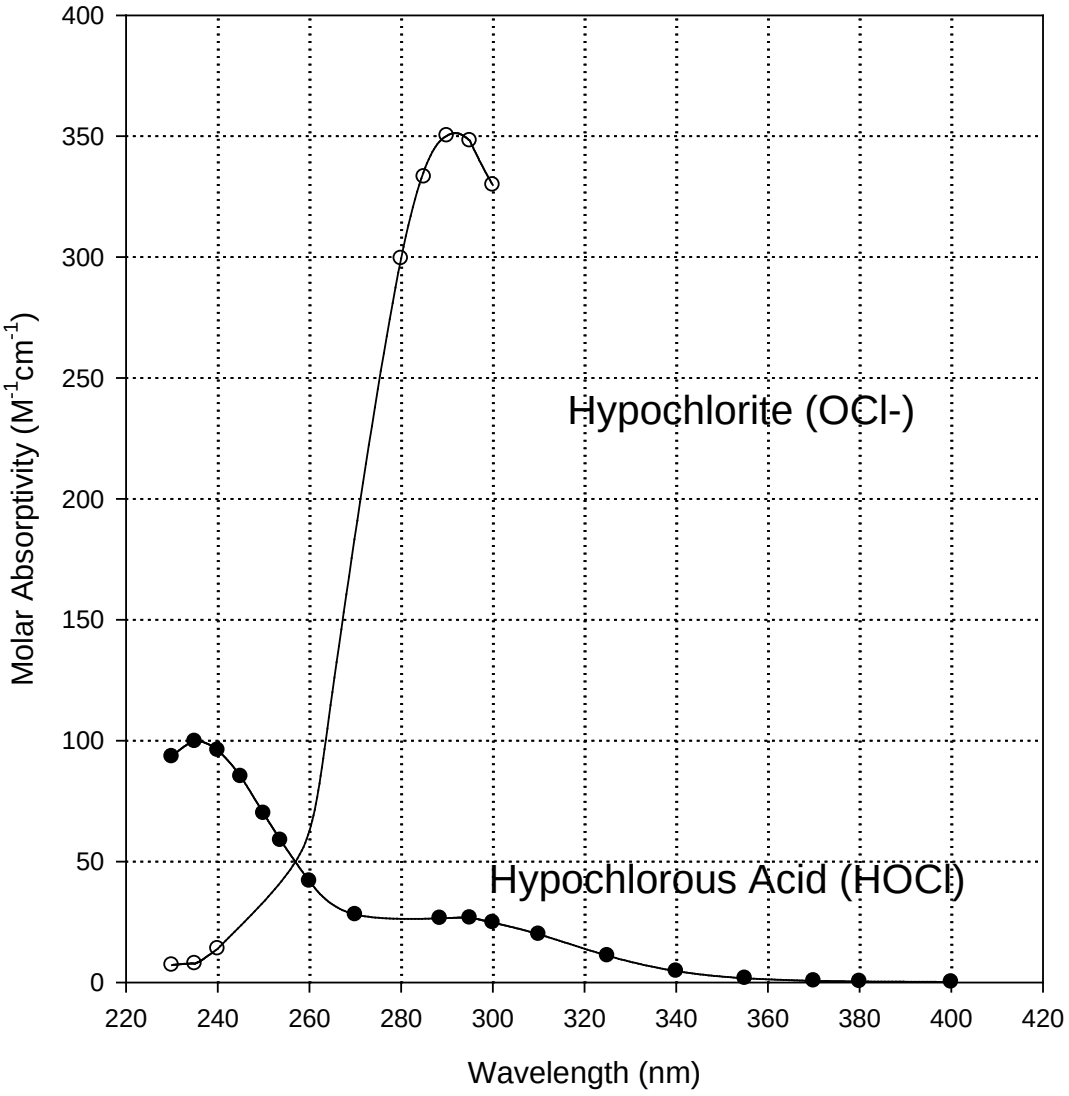

Figure 1. Free Chlorine Absorptivity at 20 C

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

Wavelength (nm)	HOCl	OCl^-	NH_2Cl	$NHCl_2$	ClO_2
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