Terror in the Toilet Bowl: Problem Handouts

Terror in the Toilet Bowl

Part 1

You really had meant well. After all, how many of your friends, going home for the weekend to catch up on good food and clean laundry, would even have considered offering to take over their kid sister's job of cleaning the bathroom? (The fact that she saw you replacing the smashed taillight on your folks' car at 3am had nothing to do with it.) No, out of the goodness of your heart, you volunteered to leave no tile unscrubbed - and what do you get? Yelled at for releasing a cloud of toxic fumes that drove everyone from the house for half a freezing day, until things aired out. How were you to know that your folks had switched toilet bowl cleaners? The old stuff never did anything like that when you mixed it with the Clorox. To top it off, your folks blamed you for not knowing better: "Why am I paying tuition for you to take a chemistry course that doesn't teach you anything practical?! When you get back to campus, go ask that teacher to tell you what happened - at least you'll learn something that way!"

"Hydrazine!", announced your chem prof on Monday after you had related the whole sordid tale. "Well-known process, really - mix together some ammonia, hypochlorite, and base, and - boom! Toxic rocket fuel that reeks of dead fish! Funny thing, though - even after all this time people still aren't too sure of the actual mechanism of hydrazine formation. Listen - how would you like to try to figure this out, instead of doing the regular kinetics lab? I've actually been interested in this, and got one of last year's students to do a little work on it. You could start by looking over the data that were collected, and seeing what the rate law is. Picking up some extra credit wouldn't exactly hurt, either, given your last exam score."

Figuring that this was not the time to admit that you had no clue about any "rate law", you reported that afternoon to the prof's lab, and were handed the data below:

Table 1. Initial Rates as a Function of Initial Concentrations in the Formation of Hydrazine.

Expt.	Initial $[NH_3]$	Initial [NaOCl]	Initial $[OH^-]$	Initial rate
	M	M	M	M/min
1	0.100	0.100	0.100	7.2×10^{-5}
2	0.053	0.100	0.100	2.02×10^{-5}
3	0.025	0.100	0.100	4.5×10^{-6}
4	0.100	0.048	0.100	3.46×10^{-5}
5	0.100	0.200	0.100	1.48×10^{-4}

6	0.025	0.100	0.210	2.14×10^{-6}
7	0.025	0.100	0.051	8.82×10^{-6}
8	0.036	0.036	0.036	

"I never had the chance to work up these data - can you look them over, and figure out the rate law, including the rate constant? And please fill in the rate for that last experiment, too - I hate an unfinished table. Oh - and one more thing?..Besides these initial rate studies, Morgan also ran some concentration vs. time experiments (data given below), but as you can see, forgot to label which reactant was monitored in each case. You'll be able to figure that out, though, after you plot the data."

Table 2. Reactant A's Concentration as a Function of Time

[A]	0.250	0.232	0.202	0.162	0.131	0.105	0.0849	0.0683
t, min	0	10	30	60	90	120	150	180

Table 3. Reactant B's Concentration as a Function of Time

[B]	0.250	0.246	0.237	0.226	0.215	0.206	0.197	0.189
t, min	0	10	30	60	90	120	150	180

Can you do as the professor asks?

1. What is the rate law for the reaction forming hydrazine?
2. What rate would you expect for experiment 8?
3. How can plotting the concentration-time data let you identify which reactant goes with which data set? Which reactant is A? B?

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Part 2

Feeling pretty pleased with yourself, you showed your chemistry professor the conclusions that you had reached about the kinetics of hydrazine formation, from the data you'd been given.

"So it looks like the rate law is rate = k $[NH_3]^2$ $[OCl^-]$ $[OH^-]^{-1}$ with k being 0.0072 M^{-1} min^{-1}. I also decided that the reactant labeled A must have been hypochlorite, since it gave a linear ln[A] *vs.* t plot. Reactant B was linear with 1/[B] *vs.* t, so that had to be NH_3. (Boy, if your folks could hear you now...) Now, about that extra credit..."

"Marvelous, just marvelous! This is wonderful! Now we get to the exciting part—figuring out the mechanism! Here, let me show you some of the possibilities I've thought of. Based on the characteristics of the species involved, these mechanisms look like they might be good possibilities. Now that you have the rate law, you can decide which really looks best. I'd be glad to explain it to you, but I've really got to run off to a new brick-laying ceremony - won't do at all not to show up when the President is there, don't you know... I'm sure you can deal with it... ta-ta!"

$$\text{Hydrazine Formation: } 2\ NH_{3(aq)} + OCl^-_{(aq)} \rightarrow NH_2NH_{2(aq)} + Cl^-_{(aq)} + H_2O_{(l)}$$

Mechanism A:

(1)	NH_3	+	OCl^-	$\rightleftharpoons$	NH_2Cl	+	OH^-	fast
(2)	NH_2Cl	+	OH^-	$\rightleftharpoons$	$NHCl^-$	+	H_2O	fast
(3)	$NHCl^-$	+	NH_3	$\rightarrow$	NH_2NH_2	+	Cl^-	slow

Mechanism B:

(1)	NH_3	+	OCl^-	$\rightleftharpoons$	NH_2^-	+	$HOCl$	fast

(2)	NH_2^-	+	NH_3	$\rightarrow$	$N_2H_5^-$			slow
(3)	$N_2H_5^-$	+	$HOCl$	$\leftrightarrows$	NH_2NH_2	+	OCl^-	fast

Mechanism C:

(1)	NH_3	+	OCl^-	$\leftrightarrows$	NH_2Cl	+	OH^-	fast
(2)	NH_2Cl	+	NH_3	$\rightarrow$	$N_2H_5^+$	+	Cl^-	slow
(3)	$N_2H_5^+$	+	OH^-	$\leftrightarrows$	NH_2NH_2	+	H_2O	fast

Which would you choose, and why?