

Kinetics and Mechanism of the Iodine-Azide Reaction

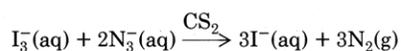
A Videotaped Experiment

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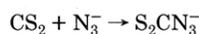
Clock reactions are a dramatic and colorful means of illustrating the determination of rate laws and the deduction of a mechanism. However, the mechanisms of most commonly used clock reactions are not simply understood and in some cases are still undetermined in detail. In addition, they are often difficult to demonstrate quantitatively in the classroom because of the lengthy set-up and clean-up time required and the unreliability of many reactions suitable for this purpose. These problems are aggravated in our classrooms, which are not well suited for demonstrations. The nonmajors introductory chemistry courses are taught to small groups of students by teaching assistants, with the aid of videotapes and comprehensive course syllabi.¹ Since one course may have as many as 1800 students divided among 70 sections, it is prohibitively expensive to set up wet chemistry demonstrations in each classroom. In addition, most of these small classrooms have no safety equipment or running water. To provide students in these surroundings with visual examples of chemical phenomena, a clock reaction with an easily determined mechanism suitable for videotaped presentation as a classroom experiment was sought.

The reaction chosen for study here is that between triiodide ion, I_3^- , and the azide ion, N_3^- , with a carbon disulfide catalyst,

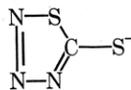


Starch is added to form the blue I_3^- -starch complex, permitting a sudden blue-black to colorless endpoint. Unlike many common clock reactions used in teaching (such as the iodide-bisulfite reaction²), this reaction, described by Niels Hofman-Bang at the Technical University of Denmark³, is not complicated by the use of a product scavenger. That is, the color change occurs when one of the reactants has been completely used up.

Carbon disulfide molecules are known to form a complex with azide ions,



The resulting product was earlier thought to be an azido-dithiocarbonate ion but is now known to be the cyclic anion, mercapto-thiotriazol,



The energy of activation for the formation of mercapto-thiotriazol is about 88 kJ/mol. Hofman-Bang and Szybalski found the rate of the carbon disulfide-catalyzed iodine-azide reaction to be directly proportional to the concentration of sodium azide (i.e., azide ions) and to the concentration of carbon disulfide, but independent of the concentra-

tion of iodine.⁴ In other words, the rate-determining step is a reaction between one azide ion and one carbon disulfide molecule, giving the rate law

$$d[I_3^-]/dt = k[CS_2][N_3^-]$$

where $k = 0.074 \text{ M}^{-1} \text{ s}^{-1}$ at 22 °C. The activation energy was found to be 84 kJ/mol, virtually the same as that for the formation of the complex in the absence of I_3^- . However, the rate constants are not the same because a chain reaction of about 17 cycles involving subsequent fast steps is initiated by the complex formed in the slow step.⁵

The kinetics are studied by students observing the experiments described below, recorded on videotape.

Experimental

Stock Solutions

- 0.25 M NaN_3 solution (16.25 g in 1 L solution).
- 0.01 M iodine solution (2.54 g iodine + 8.3 g KI in 1 L solution).
- CS_2 solution (500 mL saturated aqueous solution of carbon disulfide, diluted with water to 1 L). (The solubility of CS_2 in water is a little more than 0.027 M at 20 °C).
- Ordinary starch solution (2 g soluble starch/L solution).

Experiment 1 (Orders and Mechanism)

Since I_3^- and N_3^- do not react in the absence of CS_2 , mixtures of I_3^- and N_3^- containing starch can be prepared in advance. In one run, 50 mL 0.25 M NaN_3 , 2 mL starch solution, 5 mL 0.01 M iodine solution, and 18 mL water are mixed in a demonstration flask. Then 25 mL CS_2 solution is added. The blue I_3^- starch color disappears in about 20 s at 22.5 °C.

In other runs, the concentrations of I_3^- , N_3^- , and CS_2 are each halved or doubled, one at a time.

Experiment 2 (Activation Energy)

Four runs, using the concentrations listed above, are performed at different temperatures. The crude desk-top study of the effect of temperature on the time of reaction (solutions cooled in ice water, temperatures measured with a thermometer) allows estimation of the activation energy over the temperature range 9.5–23.0 °C.

Student Observations

The videotaped experiment has no narration, so the instructor is free to pace the experiment, calculations, and discussion to the class. For each run, when the CS_2 is added, a timer reading to the hundredth of a second is started in a

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¹ Haight, G. P. *J. Chem. Educ.* **1978**, *55*, 221.

² Lambert, J.; Fina, G. T. *J. Chem. Educ.* **1984**, *61*, 1037.

³ Hofman-Bang, N. *Acta Chem. Scand.* **1951**, *5*, 333.

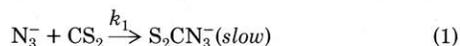
⁴ Hofman-Bang, N. Szybalski, W. *Acta Chem. Scand.* **1949**, *3*, 1418.

⁵ Hofman-Bang, N.; *Acta Chem. Scand.* **1950**, *4*, 856.

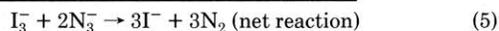
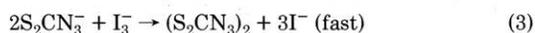
corner of the TV screen. If the cassette players have a pause button, the time of the color change can be frozen on the screen. Readings taken without stopping the action are accurate to ± 1 second as a rule. However, frozen readings can be reproduced to ± 0.2 seconds. Although the times recorded by one experimenter are printed on the screen for comparison, students take their own readings, then compute class averages. The concentrations of reactants are each varied and the cassette stopped at appropriate points so that students may deduce reaction orders and discuss the next run. As appropriate data are collected on worksheets, the rate law, rate constant, mechanism, and activation energy are determined. Results for both the rate constant and the activation energy agree reasonably well with reported values, with enough variation that students may discuss sources of experimental error. The rate constant calculated from Experiment 1 is about $0.065 \text{ M}^{-1} \text{ s}^{-1}$, a typical value for this reaction under classroom conditions.

Since the reaction is zero order in I_3^- and the concentration of I_3^- is small, the endpoint is very sharp (except for the coldest run). The concentration of CS_2 does not change during the reaction, since the catalyst is regenerated, and the concentration of N_3^- is so high that its concentration remains virtually constant during a run. Thus, for each run the rate measured is constant throughout the experiment (the same as the initial rate). The only experimental variable which is difficult to control is the CS_2 concentration since CS_2 is very volatile. In an open system the concentration of CS_2 changes rapidly, although good results can be obtained if care is taken to limit vaporization by using short reaction times. During the videotaped experiment, the stock solution of CS_2 was used up and had to be regenerated. This led to a slight variation in the results, which was called to the attention of the students.

Written materials guide the students to the formulation of the rate law and in devising a mechanism for the reaction



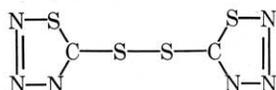
A detailed study of the reaction by other means has shown that $k_{\text{observed}} = 17k_1$ (for S_2CN_3^- formation).⁵ Step 2 thus involves a chain reaction that produces 17 net reactions (see eq 5 below) for each S_2CN_3^- complex formed.



These steps are not accessible for study by a simple kinetics experiment and are thus not included on the videotape, but they may be presented to students for classroom discussion.

As a test of the mechanism described by steps 1 and 2, it is demonstrated on the videocassette that the second step is indeed fast. A run is repeated, but this time N_3^- , CS_2 , and the starch are premixed (forming the complex), and I_3^- is added last. The brown color of I_3^- disappears instantly when the two solutions are mixed. This creates a disequilibrium in students expecting to see a dark blue color form and does indeed show that step 2 is fast.

It should be noted that the reactive intermediate, $(\text{CS}_2\text{N}_3)_2$,



should not be isolated, as it is a highly unstable explosive. Fortunately, in these solutions it is present only in low

Comparison of Results for Students Who Took the Quiz Before or After the Videotaped Experiment

	TA#	\bar{X}^a	SD	N ^b
Before Tape	1	22.22	13.75	23
	2	24.83	12.87	23
	combined	23.52	13.23	46
After Tape	1	61.85	23.00	41
	2	57.05	19.69	21
	combined	60.23	22.06	62

^a Maximum possible score was 100.

^b Total number of students was 108.

steady-state concentrations and is therefore quite safe. Both the reagents are toxic, and the catalyst is a volatile irritant; since heavy metal azides are dangerous explosives, one must dispose of waste solutions with care. Having the experiments on videotape obviates the need for expensive precautions in the lab or on the lecture table.

Despite these hazards, this reaction is particularly well suited to teach chemical kinetics. It is a straightforward reaction, two different orders are found (zero and one), the use of a catalyst is demonstrated, students see that a catalyst concentration can appear in a rate law and that a concentration of a principal reagent may not, and the reaction mechanism can be easily derived and tested. Times of reaction range from 15.4 to 104 s. The entire experiment takes 15 min on the videocassette and about 50 min in actual classroom use (if the calculations and graphs are made during the class), much less time than if it were done "live". To test this, the entire series was carried out live with a visiting high school teacher as "student". It took two hours to set up, perform the experiments, and do the calculations.

Since the videotaped experiments have no narration, the experiment number, concentration, and temperature are displayed on the screen before each run. At the end, the rate laws, plots, and mechanism are displayed for instructors to present if they wish. If there is time, the remainder of the videotape, which consists of a variety of narrated demonstrations of kinetics phenomena in other systems, is shown.

Evaluation

The videotape was tested in the spring of 1983 on 108 students in Chemistry 102P (the second semester of introductory chemistry for engineering and physical sciences majors). The teaching assistants (TA's) showed the tape and led students through the experiment in their discussion sections. The first TA (TA1) showed the tape to his three sections on Tuesday, before the principles had been presented in lecture or lab. The second TA (TA2) showed the tape to his two sections on Friday, after two lectures and a three-hour lab on kinetics. A kinetics quiz was administered to each of the five sections. One of each TA's sections took the quiz before seeing the tape; the other three sections took the quiz after seeing the tape. The results are shown in the table.

For the classes of both TA's, there was a striking difference in test scores between those who had done the videotaped experiment ("after" sections) and those who had not ("before" sections), with the biggest differences seen on questions involving analysis of data. The consistency of the results for TA1 and TA2 was unexpected, since TA2's students had had additional instruction, including a laboratory experiment involving a traditional study of the iodide-per-sulfate clock reaction. It appears that the videotaped experiment was more effective than the hands-on experiment in helping students learn to comprehend and analyze raw data. An explanation for this difference may lie in the fact that the videotaped experiment, presented with the guidance of an instructor, allows immediate feedback and reinforcement of

student observations and conclusions as the experiment is done.

In 1984, teaching assistants were surveyed about the usefulness of the videotape. Of the nine who responded, eight had found the videotape very useful. Some comments were:

These types of experiments are quite effective. They force the student to pay attention and assimilate data.

Demonstrations are very useful. They are instructive and the students enjoy them.

The TA who responded negatively reported that he had difficulty holding his student's attention. He added (about the videotaped demonstrations),

I prefer them without narration. That way I have interaction which keeps attention spans longer.

It was concluded from this study that the videotaped experiment is an effective means of introducing chemical

kinetics. It can be used with written documentation by inexperienced teachers, and it helps students learn to analyze data. The clock reaction chosen is particularly well suited to teaching reaction kinetics, and the additional series of demonstrations offer a variety of colorful examples of the concepts taught. Because of the expense, the preparation time, and the hazardous chemicals involved, videotape is the most effective and safe means for the presentation of this experiment.

Acknowledgment

The authors would like to acknowledge the assistance of producer-director Roger Inman, of the Instructional Television Division of the Office of Instructional Resources of the University of Illinois at Urbana-Champaign. The videotape was produced as part of a University Undergraduate Instructional Award. It is available for rental or purchase from the University of Illinois Film Center, 1325 South Oak Street, Champaign, IL 61820.