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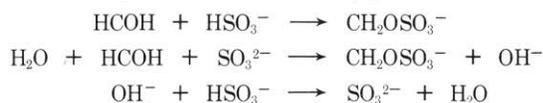University of Georgia
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# Faster Than a Speeding Bullet

## *A freshman kinetics experiment*

Clock reactions are well suited for general chemistry kinetics experiments because of the ease with which data may be obtained and because the usually dramatic endpoint stimulates interest (and even delight) among students who have not seen such reactions before. For some time we had employed a sulfurous acid-iodine clock reaction in our general chemistry laboratory, but increased enrollments in the course motivated us to explore the formaldehyde clock (*1*) reaction because the reagents are simpler to prepare. We have found that this reaction has greater pedogogical value than has heretofore been reported, in that it can be used to *simulate* the method of initial rates as applied to a bimolecular reaction (*2*). It is important to emphasize that this well-known kinetic method is only simulated in our experiment because the actual reaction is rather complex. A three-step mechanism for the formaldehyde clock reaction has been suggested in which the last step is fast compared to the first two (*3*)

$$HCOH + HSO_3^- \longrightarrow CH_2OSO_3^-$$

$$H_2O + HCOH + SO_3^{2-} \longrightarrow CH_2OSO_3^- + OH^-$$

$$OH^- + HSO_3^- \longrightarrow SO_3^{2-} + H_2O$$

Presumably, the generation of $OH^-$ in the second step provides the means for monitoring the reaction.

Two solutions are required for the experiment. A solution containing reactant "A" is prepared by dissolving 20 g of sodium bisulfite and 3 g of sodium sulfite in water to make 1 l. A solution containing reactant "B" is prepared by diluting 90 ml of formalin (37% formaldehyde solution) to 1 l with water. A phenolphthalein indicator is prepared by dissolving 1.5 g of phenolphthalein in 125 ml of ethanol and diluting to 250 ml with water. The solutions of A and B are mixed (in the presence of 10 drops of the indicator) in various proportions, as indicated in the table, and the time required for the colorless mixture to turn red is determined for each case. Such time is considered to be the "reaction time" for the system.

The reaction between "A" and "B" is assumed to be of the form

$$A + B \longrightarrow products$$

and rate of the reaction given by

$$\text{rate} = \frac{dx}{dt} k[A - x]^a[B - x]^b \qquad (1)$$

where $x$ is the concentration of reactants that have been consumed in time $t$; [A] and [B] are the initial concentrations of reactants "A" and "B", respectively; $k$ is the rate constant; and the exponents "$a$" and "$b$" are to be determined.

In the method of initial rates it is assumed that the reaction rate is measured before the reaction has proceeded to any significant extent. Under this condition, the reaction rate is proportional to the reciprocal of the reaction time, and $x$ is small compared to either A or B. Equation (1) can then be written as
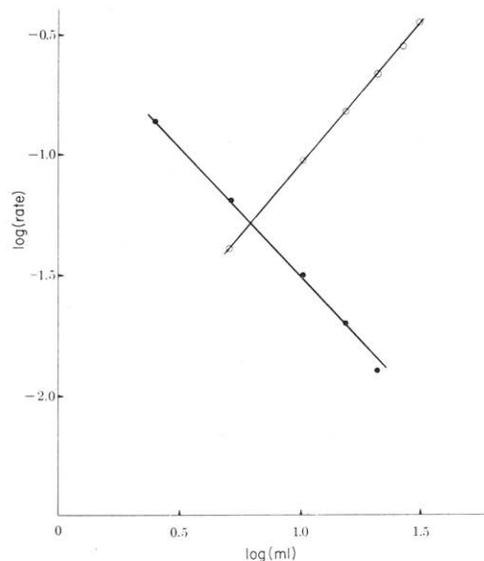
[1] Barrett, Richard L., J. CHEM. EDUC., **32,** 78 (1955).
[2] See, for example, Frost and Pearson, "Kinetics and Mechanism" 2nd Ed., John Wiley & Sons, New York, **1961.**
[3] Wagner, Carl, *Berichte*, **62,** 2873 (1929).

Figure 1. Plot of log(rate) against log(ml). Open circles correspond to mixtures in which [A] is fixed. Closed circles represent mixtures in which [B] is fixed.

$$\text{rate} = k[A]^a[B]^b \qquad (2)$$

If the [A] is fixed and the reaction time measured as a function of [B] a plot of log (rate) (i.e., log (1/time)) against log [B] should yield a straight line with slope "$b$", as is shown from the following consideration

$$\log (\text{rate}) = \log K[A]^a[B]^b \qquad (3)$$

$$\log (\text{rate}) = \log K[A]^a + b \log [B]^b \qquad (4)$$

Similarly, a plot of log (rate) against log [A] for fixed [B] will enable one to determine the value of "$a$". Typical plots are shown in Figure 1.

It is immediately apparent that exponent "$a$" has a negative value, which serves to illustrate the inhibitory effect that an increase in reactant concentration may exert upon a reaction rate. Within experimental error, the apparent order with respect to A, and B, is minus one and first-order, respectively.

The reaction may also be studied as a function of temperature. Under the assumptions of the method of initial rates the reaction rate will be directly proportional to the rate constant, $k$, for constant concentrations of A and B. Thus, $k$ in eqn. (2) may be replaced by

$$k = K(\text{rate}) \qquad (5)$$

where $K$ is a proportionality constant.

Assuming that the rate constant for the simulated reaction obeys the Arrhenius expression

$$k = Ae^{-Ea/RT} \qquad (6)$$

we may write

$$K(\text{rate}) = Ae^{-Ea/RT}$$
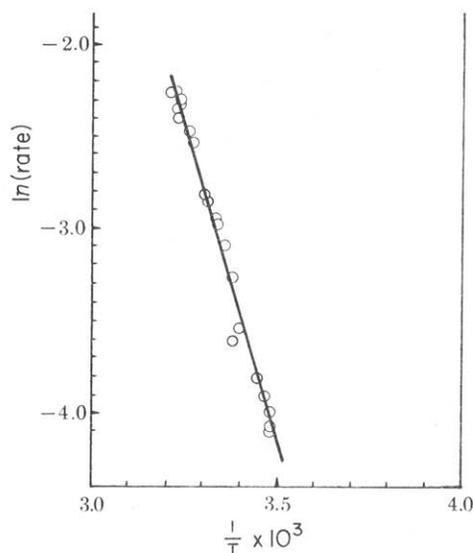
$$\text{rate} = \frac{A}{K}e^{-Ea/RT} = A'^{-Ea/RT}$$

Figure 2. Plot of ln(rate) against $1/T \times 10^3$ for the case in which 5 ml of Solution A and 5 ml of Solution B are mixed in a total volume of 425 ml. Temperature ranges from 14–38°C.

Volumes Used in the Experiment

| Variable [B] | | | Variable [A] | | |
|---|---|---|---|---|---|
| Water (ml) | "A" (ml) | "B" (ml) | Water (ml) | "A" (ml) | "B" (ml) |
| 415.0 | 5.0 | 5.0 | 417.5 | 2.5 | 5.0 |
| 410.0 | 5.0 | 10.0 | 415.0 | 5.0 | 5.0 |
| 405.0 | 5.0 | 15.0 | 410.0 | 10.0 | 5.0 |
| 400.0 | 5.0 | 20.0 | 405.0 | 15.0 | 5.0 |

whence

$$\ln(\text{rate}) = \ln(A') - Ea/RT$$

A plot of ln (rate) against $1/T$ yields a straight line from whose slope an apparent activation energy may be determined. Figure 2 shows a plot over the temperature range 14–38°C for 5-ml portions each of Solution A and Solution B.

Several points should be made concerning the manner in which the experiment is performed. Inspection of the table reveals that the total volume of the system is the same for each run. This permits one to use the number of ml of the solutions as a measure of their concentration, rather than the actual number of moles/l, in plotting the log [A] or the log [B]. The volumes in the table appear to be optimum for the concentrations employed. The reaction times range up to approximately 90 at room temperature. The use of volumes of Solution A greater than 15 ml result in data points which do not lie on a straight line, whereas volumes of Solution B much greater than 20 ml result in reaction times too fast to be conveniently measured.

It is important to stir the solutions continuously after they are mixed to ensure a sharp endpoint and thereby avoid error associated with the judgment of the endpoint. Reasonable results can be obtained using only a wristwatch with a sweep second hand, but to minimize the error in measuring the reaction time, our students work in pairs; one to do the timing and the other to observe the endpoint. The solutions are dispensed from burets, which also tends to reduce errors.

Solution A is affected by exposure to the atmosphere (solution B is apparently not affected). Evidence suggests that this is due to the uptake of carbon dioxide. If the solution is used immediately after preparation, the endpoint will be deep red. However, the intensity of the endpoint decreases the longer Solution A stands before use. If the solution is used approximately 15 hr after it is prepared the endpoint may be weakly pink, or not appear at all. Sometimes the endpoint will appear and then disappear within 1 or 2 s. These problems may be overcome by boiling and cooling Solution A immediately prior to use. On the other hand, these phenomena could serve as the basis for further independent study for interested students.

This experiment provides an introduction to one aspect of chemical kinetics at the general chemistry level and offers several points for further discussion. The ease of preparation of the reagents and the reproducibility of the results recommend this experiment for large laboratory sections.