THE FORMALDEHYDE CLOCK REACTION

RICHARD L. BARRETT
New Mexico College of Agriculture and Mechanic Arts, State College, New Mexico

AMONG the lecture demonstrations shown by Dr. Richard E. Powell at the 1953 Workshop on General Chemistry at Pasadena was one called "The formaldehyde clock reaction." This experiment, which is due to Carl Wagner,[1] appears to have some real advantages over the familiar "Iodine clock" and deserves to be better known. Briefly, a solution of formaldehyde is quickly mixed with a solution of sodium bisulfite and sodium sulfite together with a suitable indicator. When the bisulfite ion is used up there is a sharp change in pH which is signalized by the color change of the indicator. If the proportions of the reactants are kept constant the indicated reaction time is a linear function of the dilution. A ten-degree rise in temperature approximately halves the reaction time. The reaction is equally suitable for lecture demonstration or for experiments done by the students themselves.

According to Wagner the following reactions take place:

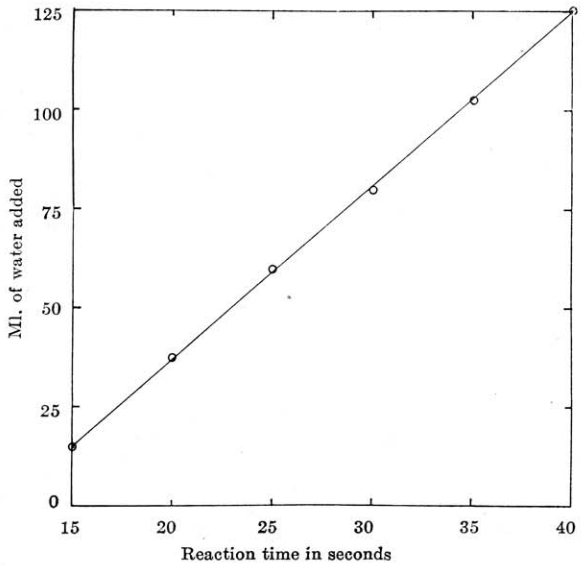
$$HCHO + HSO_3^- = CH_2OHSO_3^- \quad (1)$$

$$H_2O + HCHO + SO_3^{--} = CH_2OHSO_3^- + OH^- \quad (2)$$

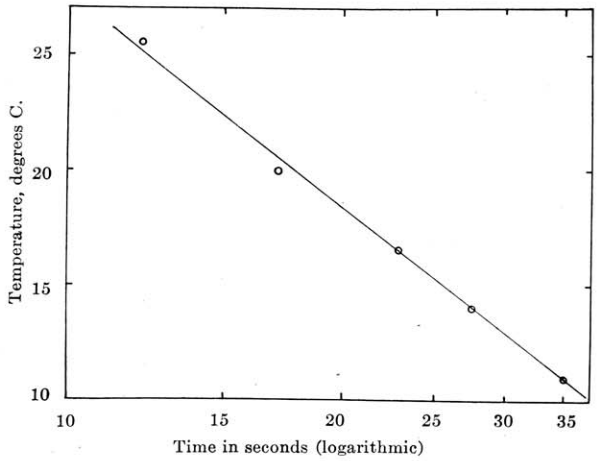
$$OH^- + HSO_3^- = SO_3^{--} + H_2O \quad (3)$$

The rate constant for (1) is given as 2.8 l./mol. sec. and for (2), 0.14 l./mol. sec. at a temperature of 20°C. Since (3) is for practical purposes instantaneous, the hydroxide ion concentration increases only when the bisulfite is used up.

[1] WAGNER, CARL, "Über die Kinetik der Reaction von Formaldehyd mit Bisulfit und Sulfit," *Berichte*, **62**, 2873–7 (1929).



Relationship Between Reaction Time and Dilution for Mixtures Containing 50 ml. of Solution *A*, 50 ml. of Solution *B*, Plus Varying Amounts of Water. Temperature 20°C.



Relationship Between Reaction Time and Temperature. Equal Volumes of Solutions *A* and *B*

In using this system as a "clock reaction" it is necessary that formaldehyde should be present in excess, and sulfite concentration should be low in comparison to bisulfite. If the ratio of the concentrations of the reactants is kept constant the system simulates a simple bimolecular reaction which is first order with respect to formaldehyde and also with respect to the sum of sulfite plus bisulfite.[2] Since reaction time is equal to the amount of bisulfite divided by the rate at which it is used, dilution affects reaction time only as it affects the concentration of formaldehyde. However, in order to preserve simplicity of treatment it is desirable to keep the concentrations of all reactants in constant ratio.

For demonstrating mass action it is convenient to make two solutions: *A*, 0.3 *M* HCHO; and *B*, 0.2 *M* with respect to $NaHSO_3$ and 0.05 *M* with respect to Na_2SO_3, plus either phenolphthalein or thymolphthalein as an indicator. Equal volumes of solutions *A* and *B* are mixed and the time required to produce the indicator color is taken. This is repeated a number of times with addition of water in increments of perhaps a fourth or fifth of the original volume, and time is plotted against total volume.

[2] See "Rate, order, and molecularity in chemical kinetics," LAIDLER KEITH, J., AND SAMUEL GLASSTONE, J. CHEM. EDUC., **25**, 382–7, (1948).

For demonstrating the effect of temperature on reaction rate the solutions are either diluted or concentrated to give convenient times at the temperatures you find convenient to employ. It is easier to control temperatures if they are kept reasonably near that of the room. The students then plot time against temperature.

The formaldehyde clock also lends itself to "chemical magic" and entertainment-type demonstrations. If the two solutions are made about 0.02 *M* in $Cd(NO_3)_2$, the completion of the end point is signalized by the formation of a white precipitate. Using three pairs of solutions, one with phenolphthalein, one with $Cd(NO_3)_2$, and one with thymolphthalein, a very pretty "Fourth-of-July" effect is produced. Probably other variations will occur to the reader.

The chief advantages of the formaldehyde clock over the well known iodine clock experiment are the greater simplicity of its kinetics, and flexibility in the use of indicators for showing the end point.

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