

## THE FORMALDEHYDE-BISULFITE CLOCK REACTION: RE-EXAMINATION OF A KINETICS DEMONSTRATION

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### ABSTRACT

The objective of this investigation was to study the kinetics of the addition of bisulfite to formaldehyde in weakly acidic solution. The reaction was followed by means of an ultraviolet absorption band of sulfur dioxide, present in equilibrium with bisulfite. The rate law was found to be first order in bisulfite and first order in methanediol, the hydrated form of formaldehyde. These kinetic results were found to complement those of earlier studies which approached the system as a clock reaction. An alternative undergraduate laboratory kinetics experiment based on this reaction has been formulated.

### INTRODUCTION

Bisulfite addition to an aldehyde is a well known reaction in organic chemistry. The simplest case, using formaldehyde, forms the basis of a clock reaction which has been recommended as a demonstration (Barrett 1955, Alyea and Dutton 1965, Chen 1974). This and a flowing clock modification are also recommended for kinetic investigation in a physical chemistry laboratory text (Shoemaker et al. 1981). Some anomalous student results for the flowing clock version, together with controversy in the literature (Jones and Oldham 1963, Haggett et al. 1963), have prompted us to re-examine selected aspects of the kinetics and related chemistry in the formaldehyde-bisulfite system. Some results of this reexamination are reported here.

### MATERIAL AND METHODS

Reagent grade chemicals were used without further purification. Ion exchange water was further purified by distillation using a glass still. Buffers used include phosphoric acid/sodium dihydrogen phosphate (pH range 2-3), acetic acid/sodium acetate (pH range 4-5), and sodium dihydrogen phosphate/disodium monohydrogen phosphate (pH around 7).

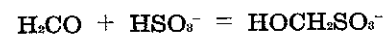
UV-visible spectrophotometry was carried out using a Varian DMS 100 spectrophotometer, a microprocessor controlled instrument. Most kinetic runs were carried out at 25.0 C, with temperature control arranged with a Polyscience circulating thermostat thermostating the cell compartment of the spectrophotometer.

Most of the kinetic runs were carried out in buffered solution, usually in the pH range 2.0-2.6 using phosphate buffer. Hand

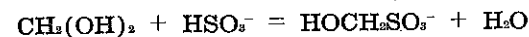
mixing was employed. A record was maintained of the time between mixing and the beginning of spectral measurements. Formaldehyde and bisulfite concentrations were in the range 0.01-0.05 M. In the phosphate buffer runs, ionic strength was 0.2-0.4 M, and 0.1-0.2 M in the acetate buffer kinetic runs.

### RESULTS AND DISCUSSION

The reaction studied may be represented as:



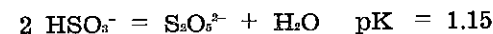
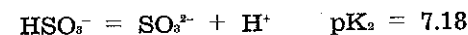
However, in aqueous solution formaldehyde exists primarily in hydrated form as methanediol (Rieche and Meister 1935). The net change thus is better represented as:



The extensive hydration of formaldehyde may be illustrated by comparing the UV spectrum of formaldehyde and acetone in dilute aqueous solution. For 0.10 M acetone we observe the n- $\pi^*$  transition at 265 nm, with molar absorptivity 16/M cm. For 1.0 M formaldehyde the molar absorptivity in this spectral region is at most 0.02/M cm. This suggests that less than 1% of the formaldehyde is in the free carbonyl form, while 99% or more is hydrated.

Despite the absence of a formaldehyde n- $\pi^*$  spectrum, a reaction mixture containing 0.050 M formaldehyde and 0.050 M sodium bisulfite ( $\text{NaHSO}_3$ ) exhibits a significant spectral band at 276 nm, with its absorbance decreasing at a convenient rate during the reaction.

It is tempting to consider this spectral band to be the spectrum of bisulfite ion. However, the apparent molar absorptivity (based on sodium bisulfite) is strongly pH-dependent, decreasing with increasing pH in the pH range 2-4, and effectively vanishing by pH 7. Thus acid-base equilibria are relevant (Moeller 1982, Sillen and Martell 1964).



It is known that  $\text{SO}_2(\text{aq})$  does not contain a significant amount of  $\text{H}_2\text{SO}_3$  (Sillen and Martell 1964).

Under the conditions of our experiments (0.005-0.05 M sodium bisulfite), the predominant sulfur species is  $\text{HSO}_3^-$  over the pH range 2-7, maximizing near pH 4.5. The observed pH dependence of the spectrum rules out bisulfite as the absorbing species at 276

nm. The spectrum in question appears instead to be that of  $\text{SO}_2$ . The electronic spectrum of  $\text{SO}_2$  gas is well known (Herzberg 1966, Atkins 1982, Ballhausen and Gray 1964). In the gas phase, sulfur dioxide has a band maximum around 290 nm, with a molar absorptivity of about (300-400)/M cm (Atkins 1982, Ballhausen and Gray 1964).

At pH 2.10 (phosphate buffer, ionic strength 0.50) we observe absorbance 0.707 at 275 nm. Assuming the pK values listed above, this leads to a molar absorptivity of 360/M cm for aqueous sulfur dioxide under these experimental conditions. This compares satisfactorily with the gas phase spectrum (Atkins 1982, Ballhausen and Gray 1964). However, given some uncertainty in the pK values as a function of ionic strength (Sillen and Martell 1964), this estimate is necessarily rather approximate.

At constant pH, the concentration of sulfur dioxide is proportional to the concentration of bisulfite, and also to the sum of the bisulfite and sulfur dioxide, as follows.

$$[\text{SO}_2] = [\text{HSO}_3^-] [\text{H}^+] / K_1$$

$$[\text{SO}_2] = (1 + [\text{H}^+] / K_1) ([\text{HSO}_3^-] + [\text{SO}_2])$$

For  $[\text{HSO}_3^-] < 0.05\text{M}$ ,  $[\text{S}_2\text{O}_5^{2-}] / [\text{HSO}_3^-] < 0.004$ , and so pyrosulfite concentrations are negligible under the conditions of this experiment. Thus the absorbance due to sulfur dioxide is proportional to the total concentration of sulfur(IV) species in the kinetic runs carried out.

Most of the kinetic runs were carried out in buffered solution, most often in the pH range 2.0-2.6. The absorbance versus time data obtained were analyzed by standard methods, based on integrated rate laws (Espenson 1981). Generally it was possible to analyze data over two half-lives or more. The data analysis was carried out on an Apple IIe microcomputer. AppleWorks software was used to enter data files into the computer. A BASIC program was written to carry out a least squares fit of kinetic data to an integrated rate law. In using an integrated rate law (Espenson 1981), the absorbance recorded at the end of the kinetic run was used as the "infinite" time value.

The repeated spectral scans of a typical kinetic run are shown in Figure 1.

In buffered solution, a second order rate law is found. Analysis according to second order kinetics leads to correlation coefficients nearly always higher than 0.99 and frequently 0.998 or higher. Some uncertainty is associated with the estimation of an absorbance at the time of mixing. However this is handled adequately

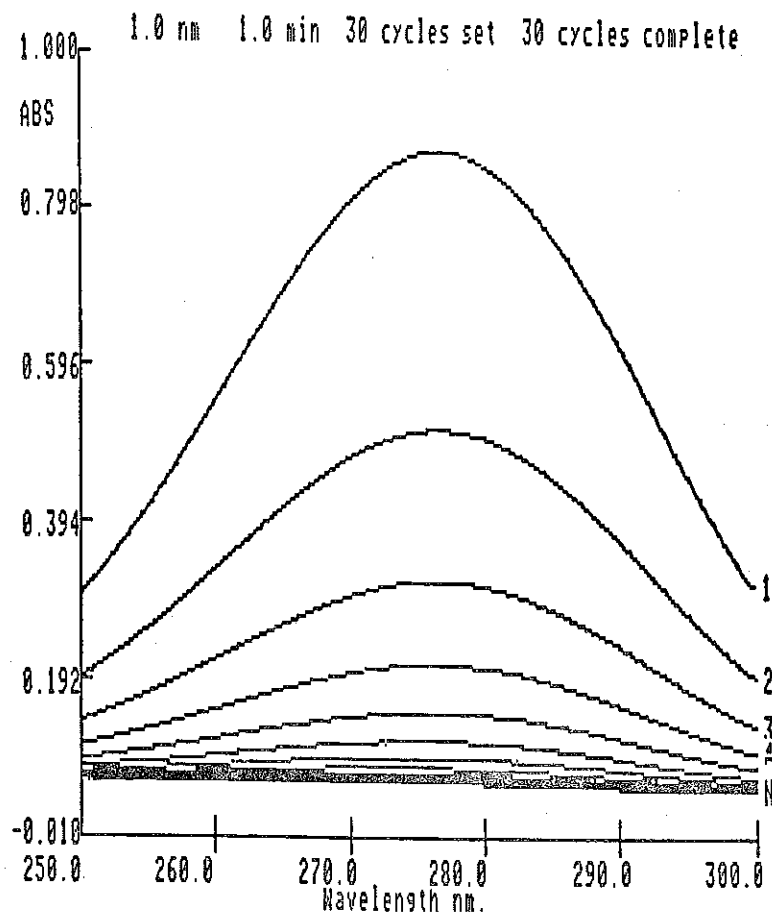


Figure 1. Repetitive spectral scans of formaldehyde/bisulfite reaction mixture. Initial concentrations: 0.043 M formaldehyde, 0.014 M sodium bisulfite, 0.14 M phosphoric acid, 0.29 M sodium dihydrogen phosphate. Temperature 25.0 C, pH 2.53.

by extrapolating the absorbance data back to the time of mixing, based on the elapsed time recorded between mixing and the beginning of spectral measurements. Even with this uncertainty, the correlation coefficients for second order rate law data analysis are significantly higher than those for a first order fit.

$$\text{Rate} = k' [\text{formaldehyde}] [\text{sulfur(IV)}]$$

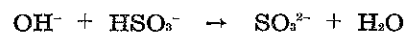
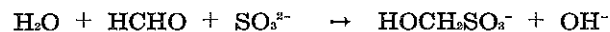
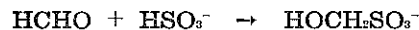
$$\text{Rate} = k [\text{CH}_2(\text{OH})_2] [\text{HSO}_3^-]$$

The data analysis yields directly a value of  $k'$ . The predominant species for formaldehyde and sulfur(IV) in this experiment are  $\text{CH}_2(\text{OH})_2$  and  $\text{HSO}_3^-$  respectively. Based on the spectral evidence, we regard formaldehyde as essentially all in hydrated form. Bisulfite and total sulfur(IV) concentrations are similar, and an equilibrium calculation based on the measured pH and the tabulated  $pK$  completes the calculation of bisulfite concentration and the determination of the rate constant. The resulting rate constant is:

$$k = 0.4 \text{ M}^{-1}$$

A curious observation arises in this system if the measurements are done using unbuffered solutions and equal formal concentrations of formaldehyde and sodium bisulfite. Under such conditions, analysis of absorbance versus time data gives a good fit to first order kinetics (and a correspondingly poor second order fit). The reason for this behavior may be traced to the rising pH during the (unbuffered) reaction as bisulfite is consumed. Because of this increasing pH, the concentration of sulfur dioxide (and thereby the absorbance) falls off more rapidly than does the bisulfite concentration during the run, a situation which thereby mimics first order kinetics with respect to variation of absorbance with time.

Jones and Oldham (1963) have discussed the clock reaction version of this formaldehyde-bisulfite reaction, which was first developed by Wagner (1929) and recommended by Barrett as a demonstration (Barrett 1955). In the demonstration the reaction mixture consists of an otherwise unbuffered solution of sodium bisulfite and sodium sulfite together with formaldehyde and a little phenolphthalein indicator, and the time from mixing until the indicator color change is measured. Wagner and Barrett consider the system to involve the following reactions:



Of these, Wagner and Barrett regard the first two as proceeding at a moderate rate and the third as rapid, with the indicator color change occurring when the bisulfite is used up (Barrett 1955, Wagner 1929). Jones and Oldham point out that the acid-base equilibrium between bisulfite and sulfite should be treated as a buffer equilibrium, rather than simply as the rapid third step, and propose that if this is done, inclusion of the second reaction is unnecessary (Jones and Oldham 1963). Jones and Oldham have reanalyzed Wagner's data (Wagner 1929) on this basis, consider the fit adequate, and report a rate constant for the first reaction as  $k = 3.9 \text{ M}^{-1} \text{ s}^{-1}$  at 20°C (Jones and Oldham 1963). This value is somewhat higher than our result reported above. The difference, if real, suggests to us that their rejection of the second reaction (reaction of sulfite ion with formaldehyde) in the higher pH range may be premature. Since formaldehyde exists in solution predominantly in hydrated form as methanediol (Rieche and Meister 1935), the reactions should also be written so as to acknowledge that the hydrated form is the predominant species.

## CONCLUSIONS

The kinetics of the addition of bisulfite to formaldehyde have been reexamined, principally in buffered solution in the pH range 2-3.

The use of the spectrum of sulfur dioxide as the basis for following the kinetics is a somewhat novel feature of interest. The system also affords a pertinent comparison between measurements in buffered and unbuffered media.

We recommend this system as a kinetics experiment appropriate for undergraduate chemistry students. This version of the kinetics investigation complements the "clock reaction" approach which has been developed by earlier workers (Barrett 1955, Jones and Oldham 1963, Haggett et al. 1963, Alyea and Dutton 1965, Chen 1974, Shoemaker et al. 1981).

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