

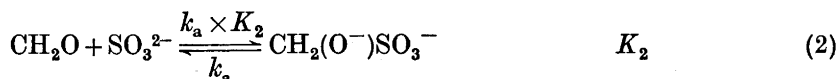
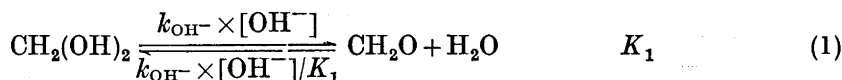
The Formaldehyde-Hydrogen Sulphite System in Alkaline Aqueous Solution. Kinetics, Mechanisms, and Equilibria

POUL ERIK SØRENSEN* and VIGGO STEN ANDERSEN

The Royal Danish School of Pharmacy, Chemical Laboratory D, Copenhagen, Denmark

Kinetic and equilibrium data for the formaldehyde-hydrogen sulphite system, at 25°C and an ionic strength of 0.1 are reported and mechanisms are discussed. The value of the acid dissociation constant of the formaldehyde bisulphite ion was found to be $10^{-11.7}$ M. Spectrophotometry in connection with a flow technique was used for the kinetic investigations. The rate of addition of sulphite to the anhydrous form of formaldehyde cannot be measured directly, as the dehydration of methylene glycol is the rate determining step of the overall reaction. The rate of decomposition of the addition product increases with increasing pH, but it has not been possible to elucidate the mechanism. Various authors have suggested a simple monomolecular process dominated by the most alkaline form of the addition product. The equilibrium experiments of the present paper seem to be in good agreement with this theory. However, a S_N2 -mechanism involving hydroxide ions seems to be in better agreement with the kinetic results.

In aqueous solution in the pH-range 9–12 the formaldehyde-hydrogen sulphite system is characterized by eqns. (1)–(3). In writing these, it has been taken into account that formaldehyde in aqueous solution exists mainly in the hydrated form (>99.9 %) and that the hydration process is catalyzed by hydroxide ions.



* Present address: Chemistry Department A, The Technical University of Denmark, Building 207, DK-2800 Lyngby, Denmark.

K and k denote equilibrium and rate constants, respectively, of the processes in question. K_A is the acid dissociation constant of the formaldehyde bisulphite ion.

Equilibrium. The equilibrium of interest in the present work is characterized by the expression

$$K_{\text{obs}} = \frac{[\sum \text{H}_2\text{SO}_3][\text{CH}_2\text{O}]_t}{[\sum \text{CH}_2(\text{OH})\text{SO}_3\text{H}]} \quad (4)$$

where \sum means all the protolytic forms of the species, *i.e.* the formal concentration and $[\text{CH}_2\text{O}]_t$ is the sum of the concentrations of hydrated and anhydrous formaldehyde. In the pH-range studied this expression can be simplified:

$$K_{\text{obs}} = \frac{[\text{SO}_3^{2-}][\text{CH}_2\text{O}]_t}{[\text{CH}_2(\text{O}^-)\text{SO}_3^-] + [\text{CH}_2(\text{OH})\text{SO}_3^-]} \quad (5)$$

As shown below, K_{obs} can be determined by iodometric titration of an equilibrium solution.

From the expressions for K_1 , K_2 , and K_3 , and from eqn. (5) it is seen that the following relationship exists between K_{obs} and $[\text{OH}^-]$:

$$\frac{1}{[\text{OH}^-]} = \frac{1}{K_1 \times K_2 \times K_3} \times \frac{1}{K_{\text{obs}}} - \frac{1}{K_3} \quad (6)$$

$K_1 \times K_2$ and K_3 , and therefore also K_A , can thus be determined by plotting $[\text{OH}^-]^{-1}$ against K_{obs}^{-1} .

Kinetics. In deriving a rate expression for the overall addition of sulphite to formaldehyde, the steady state principle is applied to free formaldehyde. The rate expression is:

$$\begin{aligned} -\frac{d[\text{CH}_2(\text{OH})_2]}{dt} &= \frac{d[\sum \text{CH}_2(\text{OH})\text{SO}_3\text{H}]}{dt} = \frac{k_{\text{OH}^-} \times [\text{OH}^-]}{1 + \frac{k_{\text{OH}^-} \times [\text{OH}^-]/K_1}{k_a \times K_2 \times [\text{SO}_3^{2-}]} [\text{CH}_2(\text{OH})_2]} \\ &- \frac{k_a}{1 + \frac{k_a \times K_2 \times [\text{SO}_3^{2-}]}{k_{\text{OH}^-} \times [\text{OH}^-]/K_1}} \times \frac{[\text{OH}^-]}{K_3 + [\text{OH}^-]} [\sum \text{CH}_2(\text{OH})\text{SO}_3\text{H}] \end{aligned} \quad (7)$$

This general rate expression can be simplified in the following two cases:

i) If $[\text{SO}_3^{2-}] \rightarrow 0$, eqn. (7) may be reduced to

$$\frac{d[\sum \text{CH}_2(\text{OH})\text{SO}_3\text{H}]}{dt} = -k_a \times \frac{[\text{OH}^-]}{K_3 + [\text{OH}^-]} \times [\sum \text{CH}_2(\text{OH})\text{SO}_3\text{H}] \quad (8)$$

Eqn. (8) is the rate expression for the decomposition of formaldehyde bisulphite. This limiting condition can be provided by adding iodine to the system.

ii) If the back reaction is neglected eqn. (7) becomes:

$$-\frac{d[\text{CH}_2(\text{OH})_2]}{dt} = \frac{k_{\text{OH}^-} \times [\text{OH}^-]}{1 + \frac{k_{\text{OH}^-} \times [\text{OH}^-]/K_1}{k_a \times K_2 \times [\text{SO}_3^{2-}]} [\text{CH}_2(\text{OH})_2]} \quad (9)$$

Conditions under which this is fulfilled are present at the initial stages of the addition reaction. The rate of dehydration of methylene glycol can easily be determined from eqn. (9) in the pH-range 9–11, since the change in pH is related to the change in $[\text{CH}_2(\text{OH})_2]$ in a simple way, the system having no buffer capacity here. By inserting the values for the involved constants and concentrations from the experiments, it can be shown that the second term of the denominator on the right hand side of eqn. (9) is small compared to 1. The equation reduces to:

$$-\frac{d[\text{OH}^-]}{dt} = k_{\text{OH}^-} \times [\text{OH}^-] \times [\text{CH}_2(\text{OH})_2] \quad (10)$$

The integrated rate expression then approximates to:

$$\text{pH} = 0.4343 \times [\text{CH}_2(\text{OH})_2]_0 \times k_{\text{OH}^-} \times t + \text{pH}_0 \quad (11)$$

From the pH vs. time plots, k_{OH^-} can be calculated when the initial concentration of methylene glycol is known.

EXPERIMENTAL

Equilibrium. For equilibrium experiments, the principle of Stewart and Donnally¹ was used. 4.00 or 5.00 ml of a 0.500 M stock solution of sodium formaldehyde bisulphite prepared and analysed according to Skrabal and Skrabal² was diluted to 500.0 ml with a buffer solution. Borate^{*} and sodium hydroxide buffers were applied for the pH-ranges 9–11 and 11–12, respectively. The ionic strength was adjusted to 0.1 by means of NaCl. $[\text{OH}^-]$ was determined by means of a thermostatted Radiometer pH-meter 26 using a glass electrode type G 200 B and a calomel electrode as reference. When equilibrium was established, iodine and hydrochloric acid to pH ≈ 2 were added rapidly (the rate of displacement of the equilibrium is at a minimum at pH = 1.8²), and the excess iodine was quickly back-titrated with thiosulphate.

Kinetics. The kinetic experiments were carried out by a spectrophotometric flow technique. The flow apparatus, which was constructed by the authors,³ was of the continuous flow type with a four jet mixing chamber and a simple Zeiss filter monochromator. The reactant solutions were forced into the mixing chamber by syringes. The apparatus had previously given data for the carbonic acid decomposition in good agreement with those of earlier workers.³

The decomposition of formaldehyde bisulphite in buffer solutions at different pH-values was followed after addition of iodine. The following two solutions were mixed in the flow apparatus:

Sol. I containing the buffer.

Sol. II containing hydrochloric acid, formaldehyde bisulphite, potassium iodide, and iodine.

The solutions had the following properties:

- i) Mixing two equal volumes gave a solution of the desired pH and ionic strength 0.1.
- ii) The mixture was a buffer and contained excess I^- and Cl^- compared to I_2 . This is a necessary condition for the spectrophotometric determination of the iodine concentration.
- iii) The pH of solution II was 1–2 in which interval the formaldehyde bisulphite decomposition is so slow that it could not be detected.

The initial concentrations of iodine and formaldehyde bisulphite were about 2.5×10^{-4} and 1.0×10^{-3} M, respectively.

* Pharmacopoea Nordica 1963, Editio Danica, Vol. I, p. 109.

The addition reaction was studied by mixing solutions of formaldehyde and sodium sulphite in the flow apparatus. The change of pH, which is a measure of the progress of the reaction, was followed by means of a protolytic indicator, alizarin yellow-R. Aqueous formaldehyde solutions of concentrations in the range 10^{-2} – 10^{-1} M were prepared by dissolving gaseous formaldehyde in distilled water, and the concentration of the solutions was determined by the sulphite method.⁴ Dilute, freshly prepared solutions of formaldehyde contain practically only monomeric formaldehyde.⁴ Aqueous solutions of sodium sulphite of concentrations about 7×10^{-3} M were made up by weight. The solutions of formaldehyde and sulphite contained 0.005 % alizarin yellow-R. Before use the pH of the sodium sulphite solution was adjusted to 9.2 with 1 N NaOH. Doubly-distilled water was used throughout, and all experiments were carried out in an atmosphere of O_2 -free nitrogen. The temperature was $25.0 \pm 0.1^\circ\text{C}$.

RESULTS AND DISCUSSION

Fig. 1 shows $[\text{OH}^-]^{-1}$ plotted against K_{obs}^{-1} according to eqn. (6). From a least square treatment K_3 is found to be $10^{-2.3}$ giving K_A (formaldehyde bisulphite) = $10^{-11.7}$ M, and K_2 is calculated to be $2.2 \times 10^5 \text{ M}^{-1}$, using the value 5×10^{-4} for K_1 .⁵

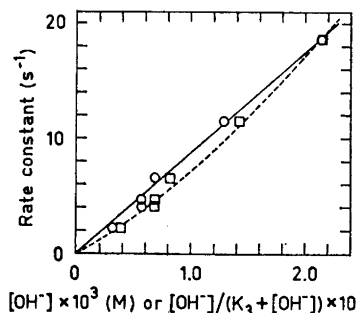
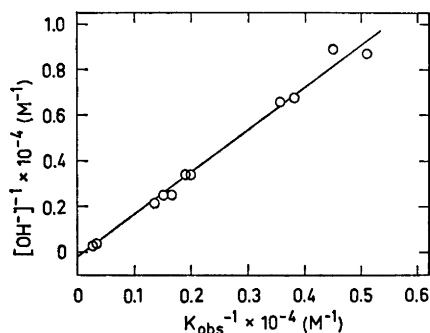


Fig. 1. $[\text{OH}^-]^{-1}$ plotted against K_{obs}^{-1} .

Fig. 2. The observed 1. order rate constant plotted against $[\text{OH}^-]$ (○) and $[\text{OH}^-]/(K_3 + [\text{OH}^-])$ (□), respectively.

At constant pH, the decomposition of formaldehyde bisulphite is first order with respect to the addition product in agreement with eqn. (8). Altering the initial concentration of iodine had no effect on the rate of decomposition. This proves the applicability of iodine as a scavenger. In Fig. 2, the first order rate constants are plotted against $[\text{OH}^-]$ and $[\text{OH}^-]/(K_3 + [\text{OH}^-])$, respectively. Theoretically both curves of Fig. 2 should pass through the origin. Experimentally, this is most satisfactorily fulfilled for the plot against $[\text{OH}^-]$. This curve corresponds to the rate expression:

$$-\frac{d[\sum\text{CH}_2(\text{OH})\text{SO}_3\text{H}]}{dt} = k \times [\text{OH}^-][\sum\text{CH}_2(\text{OH})\text{SO}_3\text{H}] \quad (12)$$

where $k \times [\text{OH}^-]$ is a pseudo first-order rate constant, and OH^- is the second reactant. The value of k was calculated from the slope of the line to be

$8.6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. The relation between k and k_a at $\text{pH} \ll \text{p}K_A$ (formaldehyde bisulphite) is

$$k = \frac{K_A (\text{formaldehyde bisulphite})}{K_{\text{H}_2\text{O}}} \times k_a \quad (13)$$

and from expression (13) k_a is found to be 43 s^{-1} .

The theoretical basis for eqn. (8) derives from Stewart and Donnally¹ 1932. These authors investigated the benzaldehyde-hydrogen sulphite system. The addition of sulphite to the carbonyl group at $\text{pH} > 3$ was supposed mainly to take place with SO_3^{2-} as the nucleophilic reagent this ion being more nucleophilic than HSO_3^- and H_2SO_3 . According to this theory the addition product is primarily decomposed in the most alkaline protolytic form. Stewart and Donnally's theory has later been applied by Blackadder and Hinshelwood⁶ and by Lamaty and Roque.⁷ Eqn. (12) derives from Skrabal and Skrabal² 1936. It is seen that the divergence between these two equations mainly originates from the fact that the equation of Skrabal and Skrabal does not consider the importance of the different kinetic behaviour of the various protolytic forms of the formaldehyde bisulphite. This has been done to a considerable extent by Stewart and Donnally.

According to Fig. 2, the equation of Skrabal and Skrabal seems to be in better agreement with our experimental data than that of Stewart and Donnally. Skrabal and Skrabal determined the value of k to be $8.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. However, Fig. 1 indicates that our equilibrium experiments are in good agreement with the theory of Stewart and Donnally. Without further experiments, a definite conclusion about the mechanism of the reaction cannot be made.

Fig. 3. pH plotted against time. (○), (□) and (△) initial concentration of formaldehyde 0.025 M. Initial concentrations of sulphite 0.029, 0.034, and 0.037 M, respectively. (●) and (■) initial concentration of sulphite 0.033 M. Initial concentrations of formaldehyde 0.020 and 0.038 M, respectively.

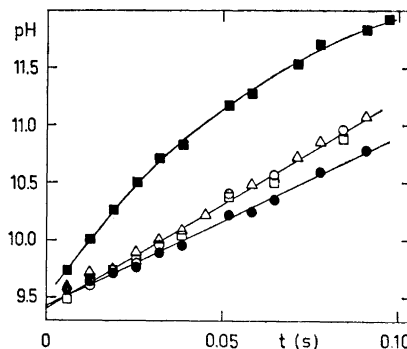


Fig. 3 shows the results of some methylene glycol dehydration experiments with varying initial concentration of methylene glycol and sodium sulphite. Plotting pH vs. time gives straight lines in the pH-range 9–11 in agreement with eqn. (11). The slopes of the various lines depend on the initial concentration of methylene glycol only, and is independent of that of sodium sulphite.

This shows the applicability of sulphite as a scavenger in these experiments. The value of k_{OH^-} was found to be $1670 \pm 20 \text{ M}^{-1} \text{ s}^{-1}$. Bell and Evans⁸

found k_{OH^-} to be $1580 \text{ M}^{-1} \text{ s}^{-1}$ by means of a similar scavenger method. However, the determination of these authors was rather inaccurate, because they worked at $\text{pH} < 8.5$. In this range it is necessary also to consider other catalysts than the hydroxide ion. The value of k_{OH^-} determined in the present work therefore seems more reliable. Brdička⁹ determined k_{OH^-} to be $1300 \text{ M}^{-1} \text{ s}^{-1}$ at 20°C by polarography, while a value determined by Le Hénaff¹⁰ disagrees with this. Using a scavenger method Le Hénaff found k_{OH^-} to be $770 \text{ M}^{-1} \text{ s}^{-1}$ at 20°C .

Acknowledgements. The authors wish to express their thanks to Dr. G. M. Nord for her kind interest in this work and for reading the manuscript.

REFERENCES

1. Stewart, T. D. and Donnally, L. H. *J. Am. Chem. Soc.* **54** (1932) 2333, 3555, 3559.
2. Skrabal, A. and Skrabal, R. *Monatsh. Chem.* **69** (1936) 11.
3. Sørensen, P. E. *Meddelelse fra kemisk laboratorium D, Danmarks farmaceutiske Højskole, Marts 1969.*
4. Walker, J. F. *Formaldehyde*, 3rd Ed., Reinhold, New York 1952.
5. Bell, R. P. *Advan. Phys. Org. Chem.* **4** (1966) 1.
6. Blackadder, D. A. and Hinshelwood, C. J. *Chem. Soc.* **1958** 2720.
7. Lamaty, G. and Roque, J. P. *Tetrahedron Letters* **52** (1967) 5293.
8. Bell, R. P. and Evans, P. G. *Proc. Roy. Soc. (London) Ser. A* **291** (1426) (1966) 297.
9. Brdička, R. *Z. Elektrochem.* **59** (1955) 787.
10. Le Hénaff, P. *Compt. Rend.* **250** (1963) 1752.

Received September 22, 1969.