

A theoretical discussion of the vapor pressure relations of the various salts has been given.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE ALDEHYDE BISULFITE COMPOUNDS. II. THE EFFECT OF VARYING HYDROGEN ION AND OF VARYING TEMPERATURE UPON THE EQUILIBRIUM BETWEEN BENZALDEHYDE AND BISULFITE ION

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Elsewhere we have shown¹ that the specific rate of dissociation of benzaldehyde bisulfite



increases rapidly as the hydrogen-ion concentration is decreased from (H^+) 10^{-2} to 10^{-7} . Since the equilibrium at (H^+) = 10^{-7} is still in favor of the bisulfite compound, the reverse of Reaction 1 is evidently even faster. Therefore it is not possible to use an ordinary titration method for the determination of the amounts of the substances in equilibrium. The method developed is as follows.

Experiment.—Benzaldehyde which had been distilled in an atmosphere of nitrogen was added mole per mole to c. p. sodium bisulfite. Distilled water which had been boiled and saturated with nitrogen was added and the reaction allowed to go to completion. All water used was boiled and saturated with nitrogen to expel both carbon dioxide and oxygen. The salt thus obtained was washed four times with water and finally dissolved in water to make an approximately 1 *M* solution of sodium benzaldehyde bisulfite; 5 cc. of this solution was diluted for each determination to one liter, making the initial concentration of benzaldehyde bisulfite about 0.005 *M*. These solutions were allowed to stand in the thermostat to reach equilibrium.

Except for determinations at *P_H* 1 and 13 where solutions of 1 *N* hydrochloric acid and 0.1 *N* sodium hydroxide were used, buffer solutions of standard or measured *P_H* values were employed for the dilution. In the range *P_H* 1.5 to 3 and *P_H* 6 to 7.5 a phosphate buffer, and *P_H* 1.5 to 3 and *P_H* 6, acetate buffer solutions were used, the acidities of which were determined against standard buffer solutions with a glass electrode. From *P_H* 9 to 12 Sørensen standard borate buffer solutions were used. For the phosphate and acetate buffer solutions it was determined by means of a glass electrode that the bisulfite compound, benzaldehyde and bisulfite ion in equilibrium had a negligible effect on the *P_H* values of the solution. With the borate buffer a hydrogen electrode was used for this purpose. In this case because of the doubtful effect of bisulfite on the electrode benzaldehyde alone of the constituents was used. A negligible effect was found.

Analysis.—Since the dissociation reaction is slow at *P_H* 2, the determination of ionic sulfite in equilibrium in the buffer solutions was made by rapidly acidifying the solution and simultaneously adding iodine in slight excess of the ionic sulfite. For this purpose an amount of 1 *N* hydrochloric acid sufficient to acidify the particular buffer

¹ Stewart and Donnally, THIS JOURNAL, 54, 2333 (1932).

to P_H 2 was placed in a two-liter beaker. Iodine solution was added, and to the mixture with vigorous stirring the buffered equilibrium mixture was rapidly added. The excess of iodine was then back titrated with thiosulfate and the time during which the solution was in contact with excess iodine was measured. In order to make a correction for this time (which never amounted to more than 0.2 cc. out of 90), 0.2 cc. of iodine was added and the time of disappearance of this iodine was measured. Bicarbonate was then added and the amount of bisulfite addition compound was determined by further titration with iodine. The P_H value of the borate buffer solution was, when necessary, corrected for the amount of acid added as bisulfite.

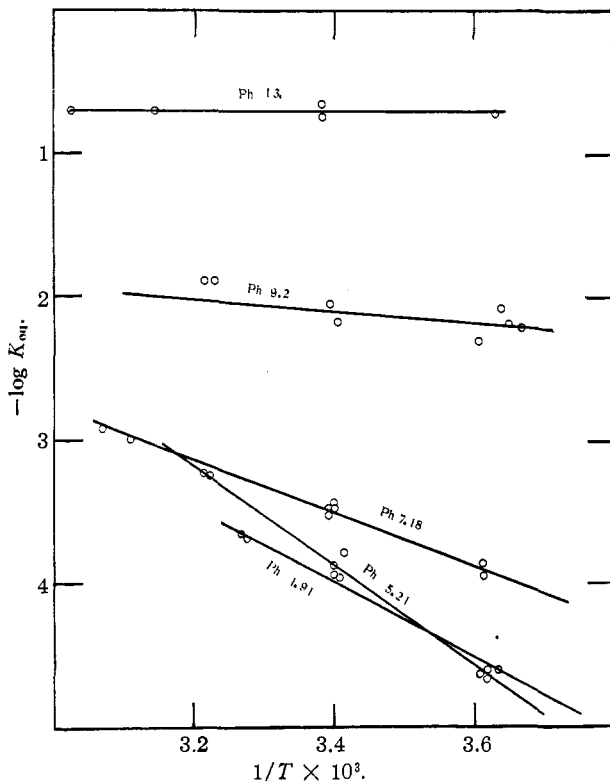


Fig. 1.—The change in equilibrium with the temperature.

It is evident that after addition to the 1 *N* acid solution the P_H can never be greater than 2, but that at the interface of the two solutions when mixed there is a time when the iodine is competing with the benzaldehyde for the sulfite ion. There is good reason to believe that the iodine-sulfite reaction is many times as fast as the benzaldehyde-sulfite reaction; nevertheless, it was decided to test the possibility of change in the equilibrium amount during this acidification. Two solutions were made up, one containing 0.0015 mole of benzaldehyde, 0.1 mole of hydrochloric acid and 0.004 mole of iodine in 300 cc., the other containing 0.0015 mole of sodium sulfite and 0.05 mole of sodium hydroxide, in 200 cc. of solution.

The second solution was added to the first and it was found that about 5×10^{-8} mole of benzaldehyde bisulfite had been formed, which is within experimental error.

Determinations were made at several values of P_H for various temperatures, the results being given in Table I, and plotted on Fig. 1. Table II gives results obtained for other values of P_H , at 21°. In Table III are average values of the equilibrium constant taken at 21° for all values of

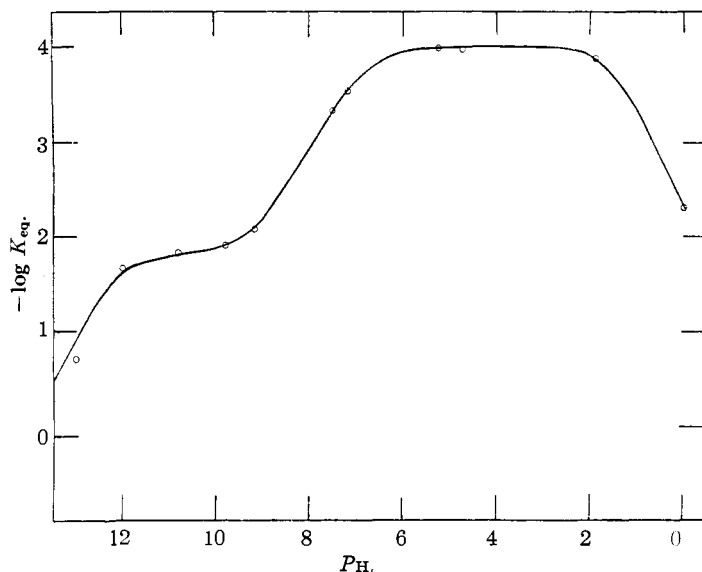


Fig. 2.—The change in the equilibrium with change in hydrogen-ion concentration at 21°.

P_H measured. On Fig. 2 we have plotted $\log K$ against P_H . The constant is defined by the equation

$$K_{eq.} = \frac{(\Sigma H_2SO_3)(\Sigma C_6H_5CHO)}{(\Sigma C_6H_5CH(OH)SO_3H)}$$

where the summation symbol implies, respectively, the total ionic sulfite, the free benzaldehyde and the total addition product in any form. The unit concentration is moles per liter.

TABLE I

EFFECT OF TEMPERATURE AND HYDROGEN-ION CONCENTRATION UPON THE EQUILIBRIUM

Phosphate buffer, P_H 1.91; phosphate buffer, P_H 7.18; acetate buffer, P_H 5.21					
Temp., °C.	$K \times 10^3$	Temp., °C.	$K \times 10^4$	Temp., °C.	$K \times 10^4$
3.2	2.20	3.4	1.12	1.7	0.244
3.4	2.48	3.5	1.37	3.5	.240
19.6	15.8	20.9	3.40	20.3	1.07
20.3	13.1	20.9	3.29	20.4	1.10
34.6	57.4	21.5	2.91	20.9	1.13
37.3	60.8	21.5	3.22	32.3	2.10
		46.2	10.2	33.0	2.21
		53.1	12.5		

TABLE I (Concluded)

0.1 N NaOH, P_H 13		Borate buffer, P_H 9.2	
Temp., °C.	K	Temp., °C.	$K \times 10^2$
2.0	0.190	0.0	0.610
22.0	.237	.9	.648
22.0	.185	4.2	.472
45.0	.193	20.4	.664
58.0	.201	21.5	.889
		35.9	1.29
		38.9	1.31

TABLE II

THE EQUILIBRIUM AT 21° AT VARYING HYDROGEN-ION CONCENTRATIONS

Borate buffer		Borate buffer		Acetate buffer	
P_H	$K \times 10^2$	P_H	$K \times 10^2$	P_H	$K \times 10^4$
12.0	1.99	9.8	1.22	4.77	1.06
12.0	2.06	9.8	1.21	4.77	1.07
12.0	2.22	9.2	0.817		
12.0	1.92	9.2	0.848		
12.0	2.05			1.0 N HCl	
10.8	1.73	Phosphate buffer		P_H	$K \times 10^3$
10.8	1.37	P_H	$K \times 10^4$	0.0	5.05
10.8	1.48	7.55	4.10	0.0	4.73
		7.55	4.15		

TABLE III

AVERAGE VALUES OF K AT TEMPERATURE 21°

P_H	K	P_H	K
0.00	4.85×10^{-3}	9.20	8.32×10^{-3}
1.91	1.26×10^{-4}	9.80	1.21×10^{-2}
4.77	1.06×10^{-4}	10.8	1.53×10^{-2}
5.21	1.00×10^{-4}	12.0	2.05×10^{-2}
7.18	2.95×10^{-4}	13.0	2.0×10^{-1}
7.55	4.15×10^{-4}		

Summary

The equilibrium in dilute solution between benzaldehyde, sodium bisulfite and sodium benzaldehyde bisulfite has been measured in the range from 1.0 N acid to 0.1 N alkali.

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