THE ALDEHYDE BISULFITE COMPOUNDS. I. THE RATE OF DISSOCIATION OF BENZALDEHYDE SODIUM BISULFITE AS MEASURED BY ITS FIRST ORDER REACTION WITH IODINE

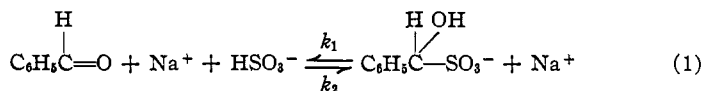BY T. D. STEWART AND L. H. DONNALLY

An excellent résumé of the work done prior to 1926 on aldehyde and ketone bisulfites is given by Raschig and Prahl,[1] who also give evidence that in the aldehyde bisulfite ion the sulfur is attached directly to the carbon, as in a sulfonic acid. They leave open, however, the question of why these compounds, as contrasted with most sulfonic acids, are very easily decomposed both in acid and alkaline solution. In spite of the enormous amount of work that has been done upon compounds of this type,[2] the questions of structure and of mechanism of formation and dissociation may be considered unsettled. For this reason a very detailed study has been undertaken.

The reaction of benzaldehyde with sodium bisulfite to form an addition product is reversible, with the equilibrium favoring the addition product.

$$\underset{H}{C_6H_5\overset{|}{C}{=}O} + Na^+ + HSO_3^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_6H_5\overset{H\ OH}{\underset{|}{C}}{-}SO_3^- + Na^+ \qquad (1)$$

This system is oxidized by iodine to form benzaldehyde and sulfate ion.

$$C_6H_5\overset{H\ OH}{\underset{|}{C}}{-}SO_3^- + H_2O + I_3^- = C_6H_5\overset{H}{\underset{|}{C}}{=}O + SO_4^- + 3H^+ + 3I^- \qquad (2$$
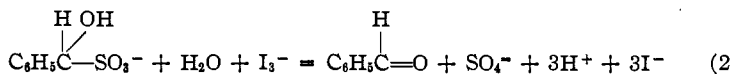
The first step in this work was to show that the rate of the reaction (2) was independent of the concentration of iodine.

Experiment.—500 cc. of benzaldehyde bisulfite solution equivalent to 51 cc. of 0.1 N iodine was put into each of two flasks. In one flask 36 cc. of iodine was added at one time; the iodine was decolorized in 378 minutes. In the other flask 36 cc. was added in 2 to 3 cc. portions, additions being made immediately after the iodine color faded. The 36 cc. of iodine was used up in 379 minutes. The approximate hydrogen-ion concentration in these two experiments was 0.01 N. In Fig. 1 the plot of the logarithm of the concentration of the unreacted benzaldehyde bisulfite against time is a straight line, for the second experiment. It will be seen later that small changes in the hydrogen-ion concentration during this experiment were unimportant.

Effect of Hydrogen Ion upon the Rate of the Reaction.—In buffered solutions it was necessary to measure the change in hydrogen-ion concentration as the reaction proceeded because of the sensitiveness of the reaction rate to change in acidity at low acid concentrations, and because of the acid produced by the reaction. The hydrogen-ion

[1] Raschig and Prahl, *Ann.*, **448**, 265–312 (1926).

[2] See Kerp, "Schweflige Säure und ihre Verbindungen mit Aldehyden und Ketonen," Verlag von J. Springer, Berlin, 1904; Schroeter, *Ber.*, 61, 1616 (1928); C. Wagner, *Ber.*, **62**, 2873 (1929).

concentrations were measured by means of a glass electrode, using a potentiometer and galvanometer, to an accuracy of 0.02 P_H.[3] In order to illustrate the method of obtaining the specific reaction rate at a specified value of P_H the runs made in the region of P_H 6.2 to 6.9 will be described in detail.
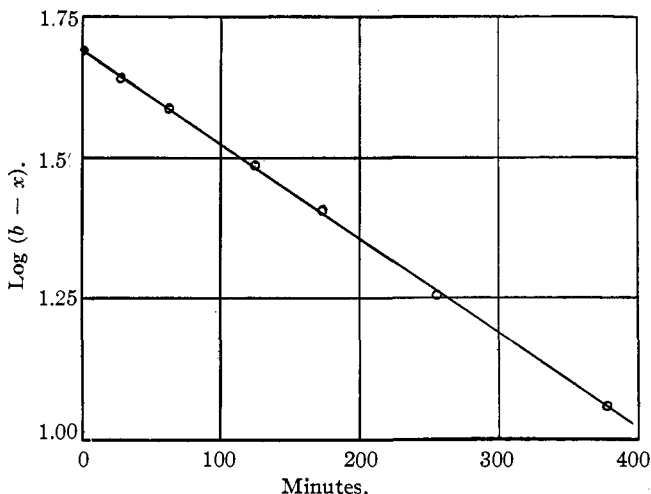

Fig. 1.—The reaction rate of sodium benzaldehyde bisulfite with iodine at about P_H 2.

Experiment.—A stock of buffer solution was made from phosphoric acid and sodium hydroxide (total phosphate, $0.111M$), to give a P_H within the range desired, as measured by the electrode.   To 500 cc. of the buffer solution was added 4.0 cc. of a sodium benzaldehyde bisulfite solution which was equivalent to about 100 cc. of 0.1 N iodine, to make the reaction mixture.   All solutions were prepared from water boiled to remove oxygen, and were stored in nitrogen.   Portions of this reaction mixture were brought to the temperature of the thermostat and 10.00-cc. portions of the standard iodine solution, which was at the same temperature, added.   The time for decolorization of the iodine was noted and another portion of iodine added immediately.   The data for a typical experiment are given in Table I and plotted in Fig. 2.

TABLE I

THE SPECIFIC REACTION RATE IN PHOSPHATE BUFFER AT P_H 6.46 TO 6.72

x, amount of iodine used; b, total amount of benzaldehyde bisulfite present expressed in cc. of iodine.   Temp., 0°C. ±0.5°

x	$b - x$	log $1/b - x$	Seconds
0.00	90.36	−1.956	0
25.00	65.36	−1.815	5
50.00	40.36	−1.606	15
70.00	20.36	−1.309	32
85.00	5.36	−0.729	74

The points do not lie on a straight line (compare Fig. 1), apparently because of changing hydrogen-ion concentration.   This assumption is made because doubling the concentration of the buffer and thereby in-

[3] Robertson, *Ind. Eng. Chem., Anal. Ed.*, **3**, 5 (1931).

creasing the ionic strength gave practically the same specific rate of reaction and decreased the above-mentioned curvature.   Also the percentage changes in hydrogen-ion concentration and in specific reaction rate during the reaction were of the same order of magnitude, each about 100%.   The specific reaction rates at selected points were therefore obtained by drawing tangents to this curve (Fig. 2).   The P_H of the solution at these same points was obtained as follows.
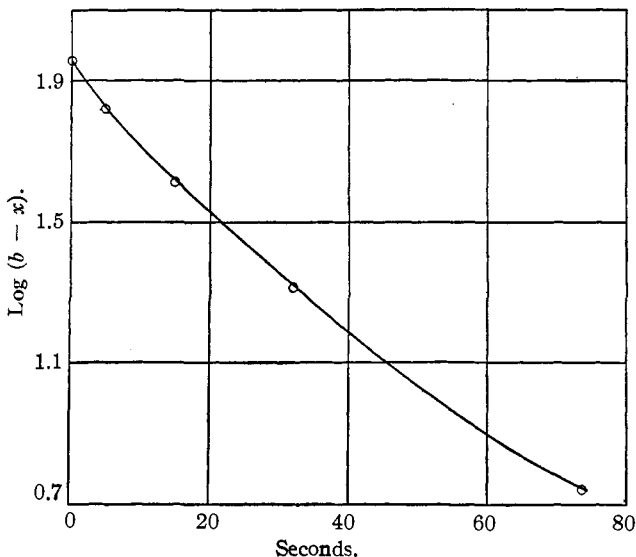

Fig. 2.—The reaction rate in the P_H range 6.45 to 6.72.

A similar portion of the reaction mixture was taken and the iodine added as before.   After each decolorization the electrode reading was taken. These readings were plotted against the corresponding calculated P_H value using Sörensen's phosphate buffer solutions of P_H 6.24, 6.81 and 7.38 to calibrate the electrode.   The electrode was calibrated both before and after each experiment and shown to be reliable.   From this plot (not given), the P_H value of the reaction mixture could be read for any selected time during the reaction.   The results of the experiments and calculations in the phosphate buffer range are presented in Table II.

TABLE II

THE SPECIFIC REACTION RATE FOR THE PHOSPHATE P_H RANGE AT VARIOUS TEMPERATURES, IN EQUIVALENTS PER SECOND

0.0°		5.5°		9.5°		21.0°	
k_1 (sec.)	P_H	k_1 (sec.)	P_H	k_1 (sec.)	P_H	k_1 (sec.)	P_H
0.0535	6.72	0.0875	6.72				
.0482	6.66	.0730	6.60				
.0437	6.60	.0596	6.50	.109	6.60		
.0316	6.46	.0538	6.46	.0945	6.50	0.372	6.50

Similar measurements for the P_H range 3.6 to 5.6 were made in exactly the same manner as in the range 6.24 to 7.38. Acetic acid–sodium acetate buffers of Walpole-Clark were used as standards. The stock buffer solution was made with a total acetate concentration of 0.111 M and 500 cc. was used as before for the preparation of the reaction mixture. Table III contains the results of the experiments and calculations in this range.

TABLE III

THE SPECIFIC REACTION RATE FOR THE ACETIC–ACETATE BUFFER RANGE, IN EQUIVALENTS PER SECOND

	9.5°		21°	
k_1 (sec.)	P_H		k_1 (sec.)	P_H
0.00292	4.91			
.00276	4.88		0.01015	4.88
.00251	4.84		.00923	4.86
.00218	4.78		.00822	4.78
.00195	4.74		.00785	4.76

Determinations were also made with chloroacetic acid–chloroacetate and phosphoric acid–monosodium phosphate buffers. Both buffer solutions were made up with the total anion concentration 0.111 M and in each of these the hydrogen-ion concentration was measured by a hydrogen electrode. The results are given in Table IV. In Table IV are also results obtained by using measured concentrations of hydrochloric acid.

TABLE IV

THE SPECIFIC REACTION RATE AT HIGHER ACID CONCENTRATIONS, AT VARIOUS TEMPERATURES, IN EQUIVALENTS PER MINUTE

Part A. Chloroacetate Buffer Range			Part B. Acid Phosphate Buffer Range		
Temp., °C.	k_1 (min.)	P_H	Temp., °C.	k_1 (min.)	P_H
20.95	0.01007	3.00	20.84	0.00392	2.30
31.58	.0335	3.00	31.77	.0146	2.30
20.99	.00923	2.96	20.90	.00378	2.27
31.59	.0307	2.96	31.78	.0140	2.27
21.06	.00849	2.92	20.92	.00364	2.23
31.59	.0282	2.92	31.81	.0137	2.23

Part B. Acid Phosphate Buffer Range			Part C. Hydrogen Chloride Solution		
20.90	0.00324	1.90	19.8	0.00450	1.00
31.74	.0122	1.90	29.0	.0154	1.00
20.90	.00313	1.85	19.8	.00904	0.55
31.78	.0120	1.85	29.1	.0317	.55
			20.5	.0286	.03
			28.8	.0903	.03

Calculations of the rates for different hydrogen-ion concentrations were made by interpolation for the single temperature of 21°. These are presented in Table V and plotted in Fig. 3.

TABLE V

SUMMARY OF DATA, CALCULATED FOR 21°, ON EFFECT OF CHANGING HYDROGEN-ION
CONCENTRATION UPON THE SPECIFIC REACTION RATE (PLOTTED IN FIG. 3) AND UPON
THE APPARENT HEAT OF ACTIVATION (FIG. 4)

P_H	k_1 (min.)	Q (calcd.)	P_H	k_1 (min.)	Q (calcd.)
6.50	22.3	$18,900 \pm 1,000$	2.23	0.00377	$21,700 \pm 300$
4.86	0.554	$19,100 \pm 500$	1.90	.00328	$22,000 \pm 300$
3.00	.0101	$20,100 \pm 300$	1.85	.00322	$22,100 \pm 300$
2.97	.00923	$20,200 \pm 300$	1.00	.00529	$23,300 \pm 300$
2.92	.00849	......	0.55	.0106	$23,800 \pm 300$
2.30	.00405	$21,300 \pm 300$	.03	.0307	$24,100 \pm 300$

Variation of Specific Reaction Rate with Temperature and the Apparent Heat of Activation.—Practically every determination of the specific reaction rate was made at two or more temperatures. Data for the neutral phosphate range are given in Table II, those for the acetic–acetate range in Table III, those for chloroacetic–chloroacetate, acid phosphate and all others are summarized in Table IV.

The data in Tables II and III were used as follows. The P_H values were plotted against log k_1 for each temperature, and a straight line of unit slope was drawn through the points. This was justified in this range of P_H by the rate of change of reaction rate with change in P_H as given in Fig. 3. In those cases where the accuracy was high the points fell well on the line. From each of these curves at an arbitrary P_H a value of k_1 was taken and in turn plotted against the corresponding value of $1/T$. From

Fig. 3.—The change in the reaction rate with changing P_H.

the slope of the best straight line was calculated (Table V) the apparent heat of activation, using the equation $Q/R = -d \ln k_1/d(1/T)$. The change in heat of activation with change in P_H is plotted in Fig. 4.

Identity of the Iodine Reaction with the Dissociation Reaction.—Since the rate of reaction (2) is independent of the concentration of iodine, there is little doubt that the rate thus measured is the rate of the reverse step
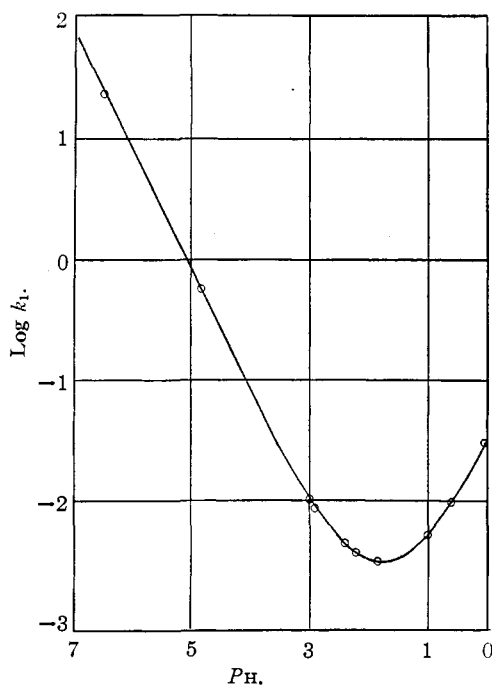
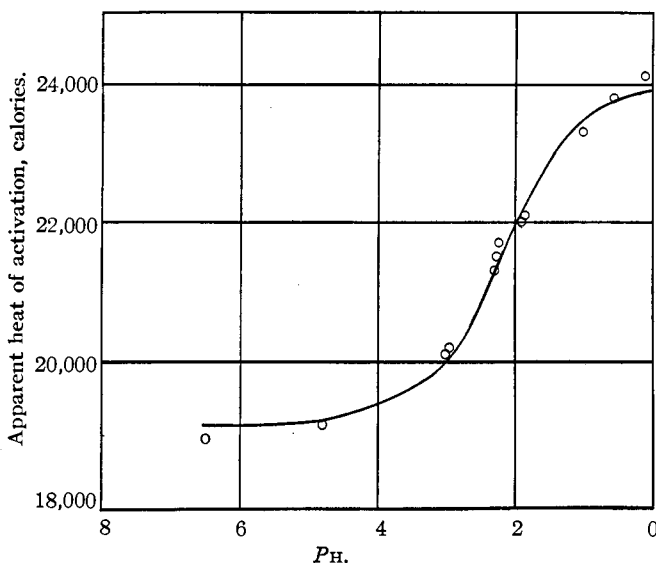of reaction (1).   In order to test this point, the rate of attainment of equilibrium of (1) was measured.

Fig. 4.—Change in the apparent heat of activation with change in P_H.

Experiment.—To 1 liter of 0.25 N hydrochloric acid was added an amount of 0.8 M sodium benzaldehyde bisulfite equivalent to 0.239 liter of 0.1180 M iodine solution; 0.029 liter of the iodine solution was added and the time when the solution became colorless was recorded as zero time.   The solution was then allowed to stand for a specified time for dissociation to take place and then iodine in slight excess of the amount of bisulfite ion formed was added and the excess back titrated.   The time that iodine was present in the solution was measured to give a correction for the amount of iodine used simultaneously according to equation (2).   Sodium bicarbonate was then added and the amount of total unused benzaldehyde bisulfite determined by titration.   The data obtained are given in Table VI.

TABLE VI

COMPARISON OF THE IODINE AND DISSOCIATION REACTIONS

cc_1 is the amount of bisulfite ion (in cc. of 0.1180 N iodine) produced after time t_1 in the absence of iodine; cc_2 the volume of iodine used up in elapsed time t_2 in the continued presence of iodine; cc_3 the reaction rate calculated by Equation 5 (Fig. 5)

cc_1	t_1	cc_2	t_2	cc_3	t_3
8.30	5.50	5.00	3.4	5.0	3.24
15.15	10.1	10.0	6.78	10.0	6.55
24.30	20.31	20.0	15.6	20.0	13.42
31.07	29.4	25.0	21.2	30.0	20.70
36.90	45.2	27.0	23.7		
39.0	60.3	30	28.7		
41.0		35	40.0		
		38	52.0		

The limiting amount of bisulfite produced in this experiment was taken to be the equilibrium amount and the equilibrium constant was calculated thereby.   Experiments were also made to determine the rate of the reaction in the constant presence of iodine for the same solution and the data are given in the third and fourth columns of Table VI.   From the rate of the reaction in the continued presence of iodine (k_1 = 0.00755) and the
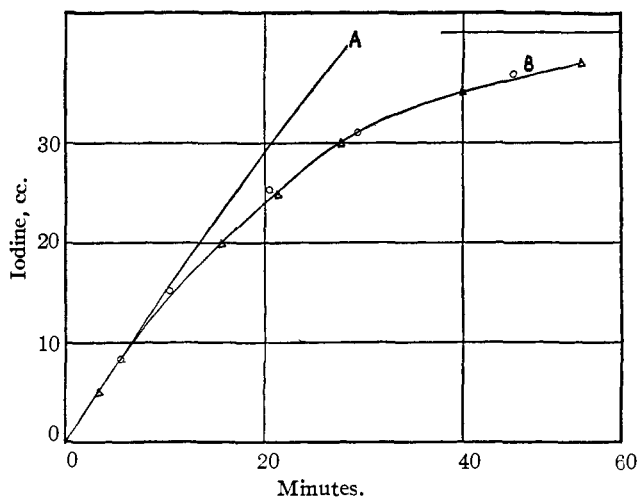

Fig. 5.—Comparison of reaction rate in the presence of (Curve A) and absence of iodine (Curve B); the approach to equilibrium ($\triangle$, calculated; $\bigcirc$, experimental, Curve B).

equilibrium constant (K_E = 0.98 $\times$ 10^3) the forward rate (k_2) was calculated as equal to 7.4 for P_H of about 1.6.   The concentration and time units for these figures are moles per liter and minutes, respectively.   The equation expressing the velocity of the net change after t minutes for this bimolecular reaction opposing the monomolecular is

$$\frac{dx}{dt} = k_1(b - x) - k_2 x(a + x) \tag{4}$$

where b and a are, respectively, the initial concentrations of addition product and of benzaldehyde.

Integrated, this gives

$$t = \frac{2.3}{k_2 \sqrt{\left(\frac{k_1 + k_2 a}{k_2}\right)^2 + \frac{4k_1 b}{k_2}}} \log \frac{\frac{k_1 + k_2 a}{2k_2} + \frac{1}{2} \sqrt{\left(\frac{k_1 + k_2 a}{k_2}\right)^2 + \frac{4k_1 b}{k_2} + x}}{\frac{k_1 + k_2 a}{2k_2} - \frac{1}{2} \sqrt{\left(\frac{k_1 + k_2 a}{k_2}\right)^2 + \frac{4k_1 b}{k_2} + x}} \tag{5}$$

By substituting the above values in the equation we may calculate the data given in Table VI, columns one and two.   These calculations are given in the last two columns of Table VI and together with points for the reaction in continual presence of iodine are plotted in Fig. 5.

The conclusion is drawn from these curves that the dissociation reaction in the absence of iodine has the same specific rate as the reaction in the presence of iodine, since in the limit, as the elapsed time becomes short, the rate of production of instantly titratable sulfite becomes the same in the presence and absence of iodine.   The multiple ionizations of sulfurous acid and of the addition compound permit several paths for the reactions of addition and of dissociation but these ionizations are presumably maintained in equilibrium.   Any extremely rapid isomerization could not be detected by these measurements.   These factors will be discussed in a later paper.

Summary and Conclusion

1.   Sodium benzaldehyde bisulfite reacts with iodine at a rate independent of its own concentration and of that of the iodine.

2.   The rate determining step is the dissociation into bisulfite or sulfite ion.   There is no evidence of the presence of isomers of the bisulfite compound.

3.   The rate changes with changing hydrogen-ion concentration, being very rapid at low hydrogen-ion concentration reaches a minimum at P_H 1.8, and increases again with higher concentrations of acid.

4.   The apparent heat of activation has been measured and found to vary with changing hydrogen-ion concentration.

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THE ROLE OF LIQUID STATIONARY FILMS IN BATCH ABSORPTION OF GASES. III.   RATES OF HYDROGEN ABSORPTION AND RELATIVE RATES OF CATALYTIC HYDROGENATION IN ALCOHOL[1]

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During hydrogenations in solutions with metallic catalysts, the reaction proper must take place at or close to the surface of the solid.   There is also good evidence that the course by which the hydrogen reaches this