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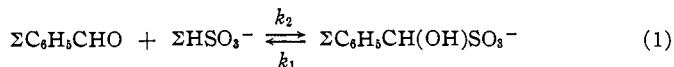
THE ALDEHYDE BISULFITES. III. THE EFFECT OF CHANGING
HYDROGEN-ION CONCENTRATION UPON THE SPECIFIC
REACTION RATE OF THE ADDITION OF SODIUM BISULFITE TO
BENZALDEHYDE. IV. DISCUSSION OF THE EQUILIBRIUM,
RATES, AND TEMPERATURE COEFFICIENTS AS AFFECTED
BY HYDROGEN-ION CONCENTRATION

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For the system benzaldehyde, sodium bisulfite and their addition product we have elsewhere¹ reported the apparent specific dissociation velocity constants from P_H 1 to 6.8 and the apparent equilibrium constants from P_H 1 to 13. From these data it is possible to calculate the apparent specific velocity constants for the addition reaction



over a range P_H 1 to 6.8 from the relation

$$\frac{k_1}{k_2} = K_{eq.} = \frac{(\Sigma C_6H_5CHO)(\Sigma HSO_3^-)}{(\Sigma C_6H_5CH(OH)SO_3^-)} \quad (2)$$

$K_{eq.}$, k_2 and k_1 are, respectively, the equilibrium constant, the specific rate of addition and the specific rate of dissociation. These calculated values, a few of which are given in Table I, have been verified by three sets of experiments made at P_H 1.91, 5.2 and 7.5. The results of these are also given in Table I.

TABLE I
CALCULATED AND OBSERVED SPECIFIC REACTION RATES OF THE ADDITION REACTION
AT 21°

| P_H | k_2 (obs.) | k_2 (calcd.) | P_H | k_2 (obs.) | k_2 (calcd.) ^a |
|-------|-------------------|-------------------|-------|-----------------|-----------------------------|
| 1.91 | 27 | 26.2 | 7.5 | 2×10^5 | 5×10^5 |
| | 26.8 | | | 4×10^5 | |
| | 28 | | | 6×10^5 | |
| | 30 | | | 4×10^5 | |
| 5.2 | 1.0×10^4 | 1.3×10^4 | | | |

^a This calculated value was obtained by a method described in Part IV which permits the calculation of k_2 from P_H 3 to 13. Only the equilibrium could be directly measured at P_H 7.5 with accuracy.

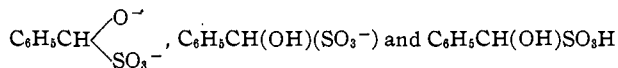
The procedure was to add benzaldehyde solution quickly to a solution of sulfite in a buffer with very vigorous mechanical stirring. The solutions were deaerated and the reaction carried out in nitrogen. At the end of a measured time the reaction was stopped by the addition of excess iodine mixed with acid precisely as described in the measurements on equilibrium.¹

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

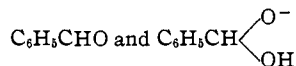
The time intervals varied from three seconds to thirty minutes. By varying concentrations of benzaldehyde and sulfite it was determined that each of these substances came into the rate law to the first power.

The calculated values are probably more accurate than the observed, because of the greater precision of the measurements of rate and equilibrium. The agreement shows complete correlation between the experimentally determined quantities and justifies the use of Equation (2).

IV. Discussion of the Equilibria, Rates and Temperature Coefficients as Affected by the Hydrogen-Ion Concentration.—By making certain assumptions with regard to rate laws it is possible to deduce the apparent specific reaction rates for both the addition and dissociation reactions in the alkaline region (P_H 7 to 13) where both reactions are too fast to measure. The change in the apparent specific rate constants, k_2 and k_1 , and in the apparent equilibrium constant, K_{eq} , with the change in P_H , may be accounted for by assuming that each of the various ionic and molecular species present in a solution of sodium bisulfite, benzaldehyde and their addition product, is concerned in a specific reaction rate characteristic of it. Only those species whose concentrations are a function of hydrogen-ion concentration are of course considered. These molecular species may be detailed as follows: (1) the three derivatives of H_2SO_3 , namely sulfite ion, bisulfite ion and sulfurous acid, which react with benzaldehyde at specific rates k_d , k_e and k_f , respectively; (2) the three derivatives of benzaldehyde bisulfite, namely



which dissociate into bisulfite or sulfite and benzaldehyde at specific rates of k_a , k_b and k_c , respectively; (3) the two species of benzaldehyde



the ion reacting with sulfite at a very slow rate and present in appreciable amount only in very alkaline solution.

The Addition Reaction.—The general rate law for the addition reaction may be written as

$$\frac{-d(\Sigma H_2SO_3)}{dt} = k_2(\Sigma H_2SO_3)(\Sigma C_6H_5CHO) = C_6H_5CHO [k_d SO_3^{2-} + k_e(HSO_3^-) + k_f(H_2SO_3)] \quad (3)$$

The constant k_2 has been evaluated in Part III of this series as a function of P_H , and $\log k_2$ has been plotted against P_H in Fig. 1. Simple rate laws corresponding to limited ranges of P_H will be established, and through them the constants k_d , k_e and k_f may be evaluated.

For the region P_H 3 to P_H 6 in Fig. 1, it is seen that within experimental error $\log k_2$ is directly proportional to P_H and that the slope of the curve is

nearly unity, which means that k_2 is directly proportional to the first power of hydroxyl ion. Since the first and second dissociation constants, $K_A'^2$ and $K_A''^3$ of sulfurous acid are, respectively, 1.7×10^{-2} and 1.1×10^{-7} , the ratio of bisulfite ion to sulfite ion in the above PH range is greater than

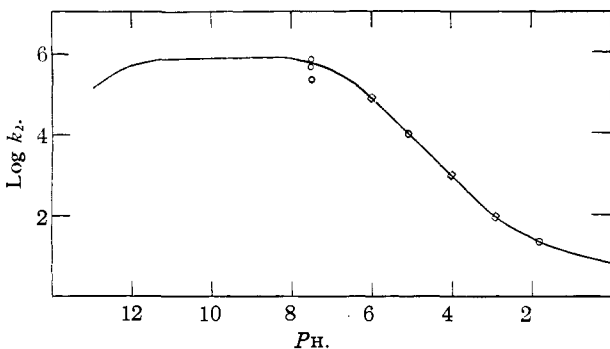


Fig. 1.—The change in the specific addition reaction rate with hydrogen-ion concentration at 21°: circles represent directly determined data; squares represent a calculation of k_2 from the ratio k_1/K_{eq} .

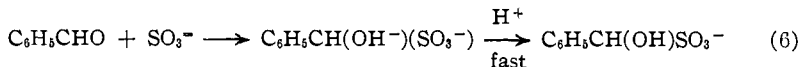
ten, and the concentration of sulfurous acid is negligible. The predominating molecular species present is therefore bisulfite ion and the empirical rate law becomes

$$\frac{-d(\text{HSO}_3^-)}{dt} = C(\text{OH}^-)(\text{HSO}_3^-)(\text{C}_6\text{H}_5\text{CHO}) = \frac{CK_W}{K_A'}(\text{SO}_3^{2-})(\text{C}_6\text{H}_5\text{CHO}) = k_d(\text{SO}_3^{2-})(\text{C}_6\text{H}_5\text{HCO}) \quad (4)$$

where C is a constant defined by the equation

$$k_2 = C(\text{OH}^-) \quad (5)$$

and K_W and K_A'' are the dissociation constants of water and bisulfite ion, respectively. It is therefore evident that in the PH region under discussion, the predominating rate-determining step may be considered as involving sulfite, not bisulfite, ion and that k_d is the specific reaction constant for that path. The equations are



The evolution of k_d from the observed k_2 is best made in the center of this PH region, since at the acid end the path involving bisulfite ion cannot be neglected, and at the alkaline end the concentration of sulfite ion deviates widely from that given by the assumption of a linear relationship to the hydroxyl-ion concentration. At PH 5.2, (H^+) is 6.3×10^{-6} and k_2 is $1.3 \times 10^4 \text{ min.}^{-1}$, from which k_d is $7.45 \times 10^5 \text{ min.}^{-1}$.

² "International Critical Tables," Vol. VI, p. 260.

³ Kolthoff, *Chem. Weekbl.*, 16, 1154 (1918).

For the region PH 6 to 11 it seems reasonable to assume that the rate-determining step involves sulfite ion also.

$$\frac{-d(\Sigma H_2SO_3)}{dt} = k_2(\Sigma H_2SO_3)(C_6H_5CHO) = k_d(SO_3^{2-})(C_6H_5CHO) \quad (7)$$

$$k_2 = k_d \frac{(SO_3^{2-})}{(\Sigma H_2SO_3)} \quad (8)$$

Using this equation it is possible to evaluate k_2 between PH 6 to 11, in which range k_d is approached as a maximum. The measured value of k_2 at PH 7.5, given in Table I, Part III, is of the correct order of magnitude, the agreement of observed and calculated values being better than the possible experimental error in k_2 .

The Dissociation Reaction.—The general rate law for the reaction of dissociation may be written as

$$\frac{-d(\Sigma C_6H_5CH(OH)SO_3H)}{dt} = k_1(\Sigma C_6H_5CH(OH)SO_3H) = k_a(C_6H_5CH(O^-)(SO_3^-) + k_b C_6H_5CH(OH)(SO_3^-) + k_c(C_6H_5CH(OH)SO_3H) \quad (9)$$

The constant k_1 has been evaluated in Part I of this series as a function of PH , and $\log k_1$ has been plotted against PH in Fig. 2.

For the region PH 3 to 6.8 (Fig. 2), covered by the observed values of k_1 , we observe the same sort of linear relationship between $\log k_1$ and PH , of unit slope, as has been discussed for the addition reaction. Since the acid, $C_6H_5CH(OH)SO_3H$, has a first dissociation constant K'_B of at least 3×10^{-2} ,⁴ the concentration of the ion $C_6H_5CH(OH)SO_3^-$ does not change appreciably in this PH range. The increase in k_1 must therefore be due either to hydroxyl-ion catalysis or a weak second dissociation of the hydroxysulfonic acid. Using the latter assumption the rate law becomes

$$\frac{-d(C_6H_5CH(OH)SO_3^-)}{dt} = k_a(C_6H_5CH(O^-)SO_3^-) \quad (10)$$

For the PH range 3 to 6, an approximate relation holds where K''_B is the second dissociation constant of the hydroxysulfonic acid.

$$k_1 = \frac{k_a K''_B}{(H^+)} \quad (11)$$

Over the PH range 3 to 11

$$k_1 = k_a \frac{(C_6H_5CH(O^-)SO_3^-)}{(\Sigma C_6H_5CH(OH)SO_3H)} \quad (12)$$

⁴ The first dissociation constant of sulfurous acid K'_A is given in the "International Critical Tables," Vol. VI, p. 260, as 1.7×10^{-2} . To compare this with the first dissociation constant of the acid $C_6H_5CH(OH)SO_3H$, 500-cc. volumes of 0.1 M solution of the salts were titrated with 6.00 N hydrochloric acid using a glass electrode. The e. m. f. measurements were

| | | | | | | |
|--|--------|--------|--------|--------|--------|--------|
| 6.0 N HCl, cc..... | 0.0 | 1.0 | 2.0 | 4.0 | 5.0 | 8.0 |
| NaHSO ₃ solution, cc..... | 0.3330 | 0.2190 | 0.0990 | 0.0790 | 0.0720 | 0.0606 |
| C ₆ H ₅ CH(OH)SO ₃ Na solution, cc. | 0.1732 | 0.0897 | 0.0772 | 0.0644 | 0.0630 | 0.0546 |

From this it appears that the first dissociation constant of the α -hydroxysulfonic acid is about 3.7×10^{-2} .

With increasing alkalinity, k_1 approaches k_a as a maximum and so the latter can be evaluated, since the equilibrium constant, K_{eq} , is known over the PH range 0-13 (see Part II) and the apparent specific addition rate constant, k_2 , can be calculated in the alkaline range by the method given in the previous section. When k_1 is thus evaluated from the product $k_1 K_{eq}$, for different values of PH , and $\log k_1$ plotted against PH , a plot similar to that of Fig. 2 is obtained, with a maximum value for k_1 reached at about PH 11 of $1.1 \times 10^4 \text{ min.}^{-1}$. Assuming this value for k_1 , and taking the observed value of k_1 at PH 5 as 7.65×10^{-1} , we find K_B'' to be 6.95×10^{-10} .

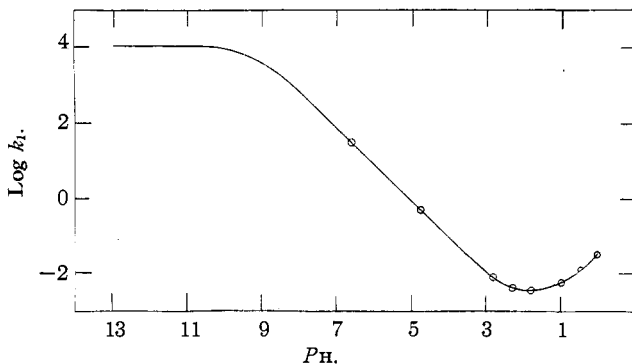


Fig. 2.—The change in the specific dissociation reaction rate with hydrogen-ion concentration at 21°.

The alternative explanation of the increased reaction rate based on catalysis by hydroxide ion seems to be unnecessary. If the calculation of the apparent specific rates of addition k_2 in the alkaline range is correct, then the calculated values of the dissociation reaction (k_1) in the alkaline range are also correct. But these indicate a marked deviation in the range PH 9 to 11 from values directly proportional to hydroxide ion (see Fig. 2), which is hardly to be expected if the increase in rate in the PH range 3 to 9 were due to catalysis by hydroxide ion.

In the region PH 1 to 3, the rate of dissociation reaches a minimum. No simple rate law is applicable, so that this region is assumed to involve all three steps postulated in equation 9.

In the region PH 1 to 0 a first order dependence of k_1 upon hydrogen ion is again observed (Fig. 2). We shall assume provisionally that this is due to the formation in small amount of the relatively reactive undissociated hydroxysulfonic acid, whose first dissociation constant K_B' we estimated above to be 3.7×10^{-2} . The first order dependence of k_1 upon hydrogen-ion concentration is obviously inconsistent, in this PH range, with this value of the dissociation constant, so we shall use the above assumption and our measurements to evaluate the constant, bearing

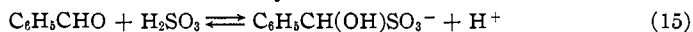
in mind that for acids of this strength the constant has little real significance. Using the same development as before we find

$$\frac{-d(\Sigma C_6H_5CH(OH)SO_3H)}{dt} = k_1(\Sigma C_6H_5CH(OH)SO_3H) = k_c(C_6H_5CH(OH)SO_3H) \quad (13)$$

and for the limited P_H range, where $\log k_1$ is proportional to P_H

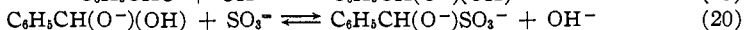
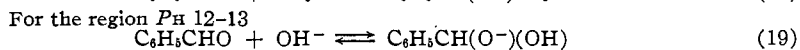
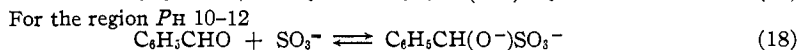
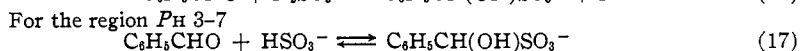
$$k_1 = \frac{k_c(H^+)}{K'_B} \quad (14)$$

Using a method to be described in the next section, the best values of k_c and K'_B are of the order $30 \times \text{min.}^{-1}$ and 1×10^3 , respectively. These values are consistent with the data involving rates and with the above assumed mechanism. The inconsistency with the measured value of K'_B may be taken as indicating the presence of a still larger number of reacting species or what amounts to the same thing, a hydrogen-ion catalysis of the reaction of the undissociated sulfonic acid. In this P_H region, then, the important rate-determining step involves hydrogen ion to the first power, and the simplest single explanation rests upon the assumption that the sulfonic acid is a very strong acid. In keeping with this, the main reaction in acid solution may be written



Measurements of the equilibrium show the proper dependence upon the hydrogen-ion concentration and suggest a difference in the strengths of the two acids of far greater magnitude than is given by the electrode measurements.⁵

The Equilibrium.—The apparent equilibrium constant is conventionally defined by Equation 2, Part III, using the dissociation as the forward reaction. The main reaction for specific P_H regions, as deduced from the foregoing and from Fig. 2, Part II are

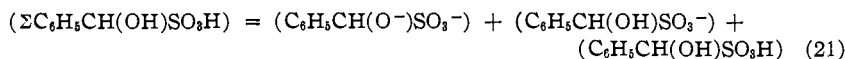


These equations describe the dependence or independence of the equilibrium with respect to P_H (Fig. 2, Part II). The intermediate regions involve a combination of these main reactions. The addition of hydroxide

⁵ An alternative explanation of the shift of equilibrium with hydrogen ion would be the removal of benzaldehyde from the equilibrium in the form of an oxonium salt. It should also be mentioned that the ionic strength of the solution in the acid range varies considerably, but that previous measurements in buffers of different concentration showed a very slight dependence of the rates and equilibrium upon the ionic strength as compared to dependence upon the hydrogen-ion concentration.

ion to benzaldehyde is assumed to explain the increase in dissociation with increase in PH in strongly alkaline solutions. There is abundant evidence of this type of reaction.

General Equations.—The apparent specific dissociation rate constant, k_1 , may be expressed in terms of the hydrogen-ion concentration, (H^+) , the two dissociation constants, K'_B and K''_B of the hydroxysulfonic acid, and the specific reaction rate constants k_a , k_b and k_c which have been previously defined. By using the relation



and substituting into Equation 9 expressions defining the above quantities we obtain

$$\frac{-d(\Sigma C_6H_5CH(OH)SO_3H)}{dt} = \left[\frac{K''_B k_a}{(H^+)} + k_b + \frac{k_c(H^+)}{K'_B} \right] \Sigma C_6H_5CH(OH)SO_3H \quad (22)$$

The first quantity in brackets on the right-hand side of the equation is the apparent specific reaction rate constant, or the constant we have designated as k_1 . We have already evaluated two of the constants in Equation 22, k_a and K''_B . The value of k_b may be found by setting up simultaneous equations, or from Fig. 2 by drawing two lines with slope plus one and minus one through the points at PH 0 and 5, respectively. The intersection of these two lines gives the moles per minute of benzaldehyde bisulfite dissociating through each of the paths $C_6H_5CH(OH)SO_3H$ and $C_6H_5CH(O^-)SO_3^-$ at the minimum point. From the curve the actual minimum is found and the difference between it and the sum of the moles per minute through the other two paths may be taken equal to k_b since the value of $(\Sigma C_6H_5CH(OH)SO_3H)$ is essentially that of $(C_6H_5CH(OH)SO_3^-)$ at PH 2. Evaluating the remaining constants simultaneously from observed values of k_1 , k_c is found to be about 30 and K'_B about 1×10^3 . A summary of the values of the constants is given in Table II.

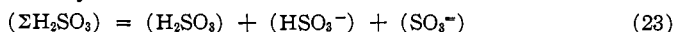
TABLE II
THE CONSTANTS OF EQUATION 22

| Constant | Numerical value | Reactant |
|----------|------------------------|---|
| k_a | 1.1×10^4 | $C_6H_5CH \begin{matrix} O^- \\ \diagdown \\ SO_3^- \end{matrix}$ |
| k_b | 2.23×10^{-3} | $C_6H_5CH(OH)(SO_3^-)$ |
| k_c | ca. 30 | $C_6H_5OH(OH)SO_3H$ |
| K''_B | 6.95×10^{-10} | $C_6H_5CH(OH)SO_3^-$ |
| K'_B | ca. 1×10^3 | $C_6H_5CH(OH)(SO_3H)$ |

Table IV gives a summary of calculated values of k_1 as calculated from Equation 22. The curve of Fig. 2 was drawn through these calculated

points; the circles on the curve are experimental points which were reported in Part I of this series.

Similarly, the apparent specific addition rate constant may be expressed in terms of the hydrogen-ion concentration, (H^+) , the two dissociation constants of sulfurous acid, K'_A and K''_B , the first dissociation constant K'_C of benzaldehyde as an acid, and the specific rate constants k_d , k_e and k_f , which have already been defined. Since



and



Equation 3 becomes

$$\frac{-d(\Sigma H_2SO_3)}{dt} = \left[\frac{k_e + \frac{k_d K'_A}{(H^+)} + \frac{k_f (H^+)}{K'_A}}{\left[\frac{(H^+)}{K'_A} + 1 + \frac{K''_A}{(H^+)} \right] \left[1 + \frac{K'_C}{(H^+)} \right]} \right] (\Sigma C_6H_5CHO)(\Sigma H_2SO_3) \quad (25)$$

It is assumed for the purpose of the calculation that the ion $C_6H_5CH(O^-)OH$ reacts at a negligible rate with sulfite ion, if at all. This leaves the same number of rate-determining steps for the addition and dissociation reactions.

The first quantity in brackets on the right-hand side of the equation is the apparent specific reaction rate constant for the addition reaction k_2 . Of the constants in this equation we have already evaluated three, namely, k_d , K'_A and K''_A . K'_C , k_e and k_f were obtained by setting up and solving simultaneous equations involving the experimental values of k_2 at different hydrogen-ion concentrations. A summary of the constants is given in Table III.

TABLE III
THE CONSTANTS OF EQUATION 25

| Constant | Numerical value | Reactant |
|----------|----------------------|------------------|
| k_d | 7.5×10^5 | SO_3^{2-} |
| k_e | 26 | HSO_3^- |
| k_f | 5.8 | H_2SO_3 |
| K'_A | 1.1×10^{-7} | HSO_3^- |
| K''_A | 1.7×10^{-2} | H_2SO_3 |
| K'_C | 5×10^{-12} | $C_6H_5CH(OH)_2$ |

In Table IV is a summary of values of k_2 as calculated from Equation 25. The curve of Fig. 1 is drawn through these calculated points; the circles represent the experimental data.

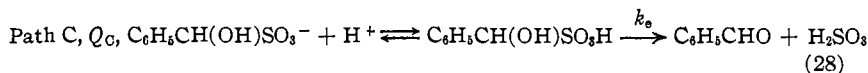
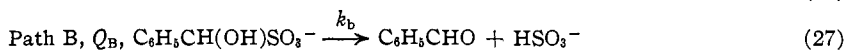
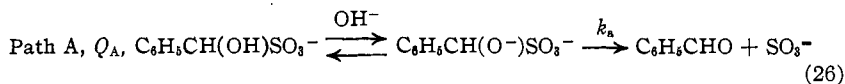
A general expression for the equilibrium constant K_{eq} in terms of the various specific reaction rates, dissociation constants and hydrogen-ion concentrations may be obtained by equating the right-hand members of Equations 22 and 25. The values of K_{eq} given in Table IV were calculated using this expression. The curve of Fig. 2, Part II is a plot of these calculated values, the circles being the experimental points.

TABLE IV

APPARENT VELOCITY CONSTANTS OF THE ADDITION AND DISSOCIATION REACTIONS, AND THE APPARENT EQUILIBRIUM CONSTANTS AT 21°

| P_H | k_2 (min. ⁻¹) | k_1 (min. ⁻¹) | $K_{eq.}$ |
|-------|-----------------------------|-----------------------------|-----------------------|
| 0.00 | 6.62 | 3.26×10^{-2} | 4.88×10^{-3} |
| 1.00 | 11.8 | 5.34×10^{-3} | 4.53×10^{-4} |
| 2.00 | 27.0 | 3.32×10^{-3} | 1.23×10^{-4} |
| 3.00 | 10.1×10 | 9.89×10^{-3} | 9.78×10^{-5} |
| 4.00 | 7.99×10^2 | 7.85×10^{-2} | 9.85×10^{-6} |
| 5.00 | 7.67×10^3 | 7.65×10^{-1} | 1.00×10^{-4} |
| 6.00 | 6.98×10^4 | 7.63 | 1.09×10^{-4} |
| 7.00 | 3.76×10^5 | 7.63×10 | 2.02×10^{-4} |
| 8.00 | 6.74×10^5 | 7.20×10^2 | 1.07×10^{-3} |
| 9.00 | 7.30×10^5 | 4.50×10^3 | 6.16×10^{-3} |
| 10.00 | 7.35×10^5 | 9.65×10^3 | 1.31×10^{-2} |
| 11.0 | 7.15×10^5 | 1.09×10^4 | 1.52×10^{-2} |
| 12.0 | 4.90×10^5 | 1.10×10^4 | 2.24×10^{-2} |
| 13.0 | 1.22×10^5 | 1.10×10^4 | 9.05×10^{-2} |

The Change in the Heat of Activation of the Dissociation Reaction with Change in P_H .—In Part I of this series we reported the measured heat of activation of the dissociation reaction as a function of the hydrogen-ion concentration. The total reaction can be represented as being composed of one or more of three steps as discussed above, each with a characteristic heat of activation. In the range covered by the measurements these three paths are



The part of the apparent heat of activation due to each path is equal to the heat of activation corresponding to that path multiplied by the fraction of molecules which react by that path. The apparent heat of activation is then the sum of three terms or

$$Q_{\text{apparent}} = \frac{k_a \left(\text{C}_6\text{H}_5\text{CH} \left\langle \begin{array}{l} \text{O}^- \\ \text{SO}_3 \end{array} \right\rangle \right) Q_A + k_b \left(\text{C}_6\text{H}_5\text{CH} \left\langle \begin{array}{l} \text{OH} \\ \text{SO}_3 \end{array} \right\rangle \right) Q_B + k_c \left(\text{C}_6\text{H}_5\text{CH} \left\langle \begin{array}{l} \text{OH} \\ \text{SO}_3\text{H} \end{array} \right\rangle \right) Q_C}{k_a \left(\text{C}_6\text{H}_5\text{CH} \left\langle \begin{array}{l} \text{O}^- \\ \text{SO}_3^- \end{array} \right\rangle \right) + k_b \left(\text{C}_6\text{H}_5\text{CH} \left\langle \begin{array}{l} \text{OH} \\ \text{SO}_3^- \end{array} \right\rangle \right) + k_c \left(\text{C}_6\text{H}_5\text{CH} \left\langle \begin{array}{l} \text{OH} \\ \text{SO}_3\text{H} \end{array} \right\rangle \right)} \quad (29)$$

Substituting in this equation the expression for the first and second dissociation constants of the hydroxysulfonic acid, we obtain

$$Q_{\text{apparent}} = \frac{\frac{k_a K_B'' Q_A}{H^+} + k_b Q_b + \frac{(H^+) k_c Q_c}{K_B'}}{\frac{k_a K_B''}{H^+} + k_b + \frac{k_c (H^+)}{K_B'}} \quad (30)$$

Using the previously calculated values of k_a , K_B' , K_B'' , k_b and k_c we are able, by setting up simultaneous equations and using our experimental data, to calculate the heat of activation corresponding to each path.

$$Q_A = 19,000 \text{ cal.} \quad Q_B = 21,500 \text{ cal.} \quad Q_C = 24,000 \text{ cal.}$$

Using these values we may now substitute values of (H^+) in Equation 30 and obtain Q apparent for any (H^+) . We have plotted in Fig. 3 the results of this calculation, drawing the curve through the calculated points. The circles represent the experimental data.

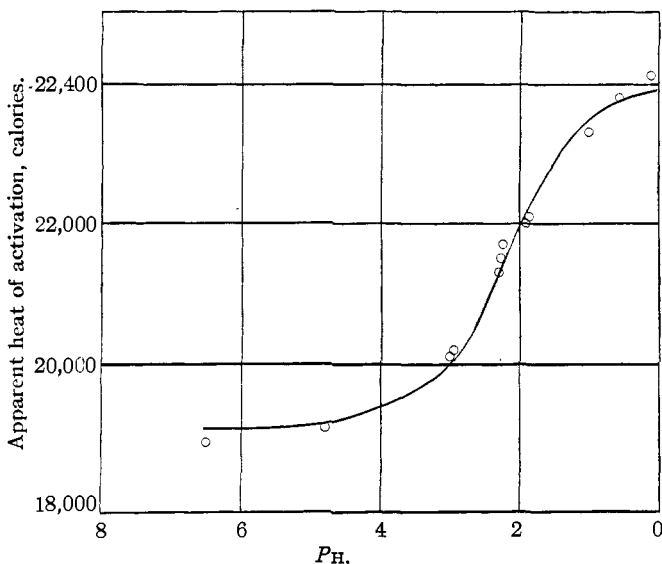


Fig. 3.—The change in activation energy with hydrogen-ion concentration at 21°.

The Heat of Dissociation of the Acid, $C_6H_5CH(OH)SO_3^-$.—The relation between heat of activation and specific reaction rate constant is expressed

$$k = S e^{-Q/RT}$$

where the symbols have their usual significance. If the factor S is the same for the rate paths A and B above, the heat of dissociation involved in path A may be calculated. S may be evaluated for path B , since Q_B is 21,500 calories and k_b is 2.23×10^{-3} at 21°. Using this value of S and the value of k_a at 21°, namely, 1.1×10^4 , Q_A is found to be 12,600 calories. The measured value of Q_A , however, is 19,000 calories, and the difference,

—6400 calories, may be taken as the energy necessary to bring about the reversible dissociation involved in path A. This may be compared with —6025 calories for the heat of dissociation of phenol.⁶ Since it is a reasonable value, the assumption of the constancy of the factor S may be considered supported for this case, which is interesting in view of the great difference (10^7 -fold) in the specific reaction rates.

A similar calculation for the heat of dissociation involved in path C above is less valid, on account of the uncertainty of the value of k_c . Using the value 30 for k_c as given above, however, the heat of activation is calculated to be 16,000 calories or 8000 calories less than the measured value. This difference is the heat of formation of the neutral molecule, $C_6H_5-CH(OH)SO_3H$, from its ions.

Summary

1. The apparent specific reaction rates of formation and dissociation of benzaldehyde bisulfite have been calculated for the P_H range 0 to 13.

2. The specific reaction rates at 21° of sulfite and bisulfite ions and of sulfurous acid, with benzaldehyde, are 7.35×10^5 , 26 and 5.8 min.^{-1} , respectively.

3. In the P_H range 3 to 13, practically all of the addition reaction involves sulfite, not bisulfite, ion.

4. The specific reaction rates of dissociation at 21° for the bivalent and monovalent ions, and of the undissociated acid, α -hydroxybenzylsulfonic acid, are 1.1×10^4 , 2.2×10^{-3} and about 30 min.^{-1} , respectively.

5. The hydroxysulfonic acid is a very strong monobasic acid; its second dissociation constant is 7.0×10^{-10} .

6. The first dissociation constant of benzaldehyde as an acid is 5×10^{-13} .

7. The heats of activation for each of the three paths involved in the dissociation have been calculated.

8. The heats of dissociation of the two acidic dissociations of α -hydroxybenzylsulfonic acid have been calculated from the activation energies.

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⁶ Landolt-Börnstein, "Physik.-Tabellen," 5 Auflage, Vol. II, p. 1577.