81. *Bisulphate-ion Catalysis in the Hydrolysis of Esters.*

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IN accordance with the classical theory of acid catalysis, the accelerating effect produced by sulphuric acid in the hydrolysis of esters has been usually attributed to the action of the hydrogen ion, although the known facts are not in satisfactory agreement with this view. From experiments with monobasic acids and the corresponding buffer mixtures it has been definitely established that the catalytic effects in acid-catalysed reactions are in general to be ascribed also to the influence of the undissociated acid and the acid anion. The present experiments were undertaken to ascertain to what extent the effects observed with sulphuric acid and sulphate buffers are due to entities other than the hydrogen ion.

The catalytic properties of two dibasic acids—oxalic and tartaric—have already been subjected to detailed examination with respect to both first and second stages of ionisation (Dawson, Hoskins, and Smith, J., 1929, 1884; Dawson and Smith, J., 1930, 79; Dawson and Spivey, J., 1932, 2612) in experiments on the acetone–iodine reaction. For oxalic acid the two stages of ionisation with $K_1 = 5{\cdot}7 \times 10^{-2}$ and $K_2 = 7{\cdot}2 \times 10^{-5}$ are widely separated and the first stage corresponds with a moderately strong acid, whereas the two stages for tartaric acid with $K_1 = 8{\cdot}5 \times 10^{-4}$ and $K_2 = 3 \times 10^{-5}$ are much less widely separated and in both cases correspond with weak acids. In this respect sulphuric acid differs considerably from both the above-mentioned acids, in that the first stage probably corresponds with a very strong acid whilst the second is of the same order of strength as oxalic acid in the first stage.

As the result of a systematic examination of the relevant physicochemical data (freezing point, partition, electrical conductance, transport number, catalysis), Noyes and Stewart (*J. Amer. Chem. Soc.*, 1910, **32**, 1133) concluded that the first-stage ionisation of sulphuric acid corresponds with a very strong acid and the second stage with $K_2 = 3 \times 10^{-2}$ when the concentration falls within the range 0·025—0·10 mol. per litre. The interpretation of the data in question was, of course, based on the classical form of the ionic theory. The p_H measurements of Enklaar (*Chem. Weekblad*, 1912, **9**, 28) led to $K_2 = 1{\cdot}3 \times 10^{-2}$, and those of Kolthoff (*Rec. trav. chim.*, 1924, **43**, 207) to $K_2 = 3{\cdot}0 \times 10^{-2}$, whilst the freezing-point, conductivity, and p_H data of Drucker (*Z. physikal. Chem.*, 1920, **96**, 381) gave $K_2 = 1{\cdot}7 \times 10^{-2}$. From a reconsideration of the results of Noyes and Stewart (*loc. cit.*) in the light of the interionic force theory, Sherrill and Noyes (*J. Amer. Chem. Soc.*, 1926, **48**, 1862) gave $K_2 = 1{\cdot}15 \times 10^{-2}$ as the value of the thermodynamic constant.

In spite of the frequent use of sulphuric acid as catalyst in the hydrolysis of esters, its precise behaviour in this connexion does not appear to have been examined systematically. The experiments of Kay (*Proc. Roy. Soc. Edin.*, 1898, **22**, 493) on the hydrolysis of ethyl acetate at 35° were interpreted in terms of the simple hydrogen ion theory and are not adapted to throw much light on the nature of the effects which are involved.

The present experiments, on the other hand, show clearly that the bisulphate ion plays an important part in the catalytic action of sulphuric acid and sodium hydrogen sulphate, and further, that there is no measurable effect which can be attributed to the un-ionised acid or to the sulphate ion. In these circumstances the reaction velocity can be represented by the simple equation

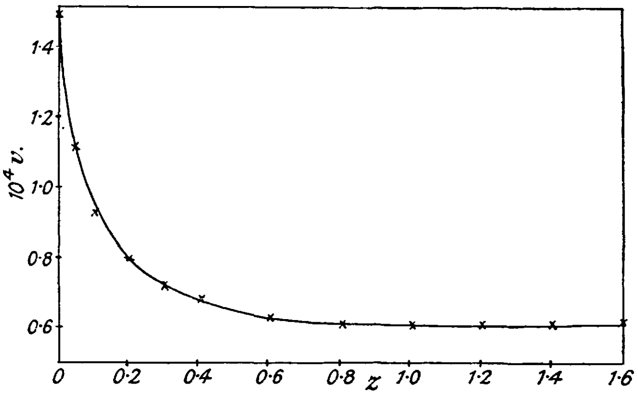
$$v = v_h + v_a = k_h[\mathrm{H}^{\cdot}] + k_a[\mathrm{HSO_4}'] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k_h and k_a are the catalytic coefficients for the hydrogen and the bisulphate ion respectively.

In reference to the absence from this equation of a term $v_m = k_m[\mathrm{H_2SO_4}]$, which would correspond with the catalytic effect of the un-ionised acid, it may be noted that for several catalysed reactions the ratio k_m/k_h has been shown to increase with the ionisation constant of the catalysing acid in accordance with the relation $k_m/k_h = aK^n$, where a and n are constants which depend on the nature of the reaction and n is a positive number less than unity. If the catalysing acid is very largely ionised, then the concentration of the un-ionised acid is given by $[\mathrm{HA}] = c^2/K$, where c is the stoicheiometric concentration. When this is combined with the empirical equation $k_m/k_h = aK^n$, we obtain $v_m = k_m[\mathrm{HA}] = ak_hK^{n-1} . c^2$, and for a fixed value of c it follows that for a series of strong acids, v_m is proportional to $1/K^{1-n}$ where $1 - n$ is a positive number less than unity. From this, it is apparent that although k_m increases with the strength of the acid, the catalytic effect produced by the un-ionised fraction decreases as the ionisation constant increases. Since the present experiments show no effect which can be attributed to un-ionised sulphuric acid, it would seem reasonable to conclude that the first-stage ionisation of sulphuric acid is practically complete in acid solutions of moderate concentration. The absence of a v_m term from the equation for the reaction velocity simplifies very appreciably the interpretation of the kinetic data which have been obtained, and the chief difficulty in this connexion would seem to be represented by the secondary effects which result from changes in the salt content of the reaction medium.

Since the hydrogen ion plays an important part in the majority of the solutions examined, the variations of K_2 and k_h with the salt content are more important sources of disturbance than is the case when the catalytic effects produced by buffer mixtures of a weak acid are in question. It has also to be recognised that these variations probably depend to some extent on the specific nature of the salt contained in the solution. Furthermore, on account of the fact that the bisulphate ion is directly responsible for a part of the observed catalytic effect, it is not possible to determine by actual experiment the variations in K_2 and k_h which are due to the inert-salt effect of sodium hydrogen sulphate. The reaction between the hydrogen and sulphate ions to form bisulphate ion precludes also the determination of the salt effects which are due to the sulphate ion.

Rate of hydrolysis of ethyl acetate at 25° in presence of sodium hydrogen sulphate (0·04 *mol. per litre*) *and sodium sulphate* (*z mols. per litre*).



The above circumstances have to be considered in any attempt to interpret the specific reaction velocities given by the expression $v = 1/t . \log_e a/(a - x)$, where a is the initial concentration of the ester and $(a - x)$ that after time t. The measurements (at 25°) were made for the most part with an ester concentration of 20·0 c.c. per litre, but salting-out effects necessitated the use of more dilute ester solutions (8·0 c.c. per litre) when large quantities of sodium sulphate were present. These variations in the ester concentration, however, made no appreciable difference to the values of the specific velocity.

The Catalytic Activity of the Bisulphate Ion.—The determination of k_a is based on the interpretation of the reaction velocities for solutions which contain sodium hydrogen sulphate in admixture with sodium sulphate. For a series of such solutions in which the concentration of the bisulphate is constant ($c = 0{\cdot}04$ mol. per litre), it has been found that the velocity is very considerably reduced by the addition of sulphate. Successive equal additions of sulphate have a gradually diminishing effect and the velocity reaches a lower limiting value which remains practically unchanged at the higher sulphate concentrations. The data are recorded in Table I and the essential features of the phenomenon are shown in the diagram.

TABLE I.

Catalyst : 0·04M-$NaHSO_4$ + zM-Na_2SO_4.

z	0	0·05	0·1	0·2	0·3	0·4	0·6	0·8	1·0	1·2	1·4	1·6
10^4v	1·50	1·12	0·93	0·80	0·725	0·68	0·635	0·615	0·61	0·61	0·61	0·615

Having regard to the order of magnitude of K_2, there can be no doubt that the fall in the velocity which occurs as the sulphate concentration increases from 0 to 0·8 is primarily due to the reduction in the concentration of the hydrogen ion. Furthermore, it would seem permissible to conclude that the limiting value of $10^4v = 0{\cdot}61$ is mainly attributable to the catalytic action of the bisulphate ion, in which case $10^4k_a = 0{\cdot}61/0{\cdot}04 = 15$. Results in close agreement with this are afforded by the velocities observed with solutions which contain a large and constant quantity of sodium sulphate and variable small quantities of sodium hydrogen sulphate. Table II gives the velocities for the series 1·0M-Na_2SO_4 + yM-$NaHSO_4$ together with the values of $k_a = v/y$.

TABLE II.

Catalyst : 1·0M-Na_2SO_4 + yM-$NaHSO_4$.

y	0·01	0·02	0·03	0·04	0·05
10^4v	0·145	0·305	0·46	0·61	0·785
10^4k_a	14·5	15·2	15·3	15·2	15·7

In assigning to k_a the value of 15×10^{-4}, it should be noted that no attempt has been made in the interpretation of the above data to apply a correction for the small residual catalytic effects of the hydrogen ion or for the inert-salt effects which the sodium sulphate may have on the bisulphate ion. For this reason, it seemed possible that a somewhat different value would be found to represent the behaviour of the bisulphate ion in much more dilute solutions, but in actual fact this value of k_a is found to provide a satisfactory account of the catalytic effects which have been observed in dilute solutions of sulphuric acid and of sodium hydrogen sulphate. Before proceeding to describe these results, it should be pointed out that the method by which k_a has been obtained does not depend on a knowledge of the value of K_2.

Sulphuric Acid as Catalyst.—In solutions of free sulphuric acid, the predominant catalyst is the hydrogen ion, but the contribution of the bisulphate ion to the total effect becomes increasingly important as the concentration of the acid increases. Since the progress of the reaction is determined by titration with alkali, the requisite accuracy can only be obtained with sulphuric acid solutions of limited concentration, and the actual measurements have reference to solutions containing 0·005—0·12 mol. per litre.

Table III affords a comparison of the measured velocities ($v_{\text{obs.}}$) with those calculated from $v = k_h[H^{\cdot}] + k_a[HSO_4']$, in which $k_h = 65{\cdot}0 \times 10^{-4}$, which is the value afforded by experiments with hydrochloric acid as catalyst at small concentrations. The concentrations of the hydrogen and bisulphate ions in these solutions are given by $[H^{\cdot}] = \sqrt{2K_2x + (x - K_2)^2/4} + (x - K_2)/2$ and $[HSO_4'] = 2x - [H^{\cdot}]$, where x is the molar concentration of the acid. The value of K_2 used in the calculation of the velocities has been derived from the kinetic data. Since $K_2 = [H^{\cdot}][SO_4'']/[HSO_4'] = [H^{\cdot}]([H^{\cdot}] - x)/(2x - [H^{\cdot}])$, it follows that the most favourable conditions for determining the value of K_2 correspond with $[H^{\cdot}] = 3x/2$, *i.e.*, when the second-stage ionisation is half completed. When the term $[HSO_4']$ in equation (1) is replaced by $2x - [H^{\cdot}]$, this equation becomes

$$v = (k_h - k_a)[H^{\cdot}] + 2k_ax$$

or $$10^4v = 50{\cdot}0[H^{\cdot}] + 30{\cdot}0x$$

whence $$[H^{\cdot}] = (10^4v - 30x)/50.$$

If this value of $[H^{\cdot}]$ is substituted in the mass-action expression for K_2, it may be shown that the optimum conditions for the evaluation of K_2 from the reaction velocities are obtained when $10^4 v = 105x$. This relation between the reaction velocity and the concentration of the sulphuric acid is found to correspond with a value of x which lies between 0·005 and 0·01 mol. per litre. For this reason the experimental data for the two most dilute solutions have been used to derive K_2. The value so obtained is $K_2 = 0{\cdot}010$, which is fairly close to the value of the thermodynamic constant given by Sherrill and Noyes (*loc. cit.*).

In order to show the relative importance of the catalytic effects which are due to the hydrogen and the bisulphate ion, the calculated partial velocities v_h and v_a are also recorded in Table III.

TABLE III.

Catalytic effects produced by sulphuric acid (x *mols. per litre*).

x	0·005	0·01	0·02	0·04	0·05	0·08	0·10	0·12
$10^4 v_h$	0·51	0·92	1·66	3·05	3·73	5·73	7·05	8·36
$10^4 v_a$	0·035	0·09	0·22	0·50	0·64	1·08	1·37	1·66
$10^4 v_{\text{calc.}}$	0·545	1·01	1·88	3·55	4·37	6·81	8·42	10·0
$10^4 v_{\text{obs.}}$	0·545	1·01	1·87	3·49	4·34	6·56	8·24	9·80

The concordance shown by the observed and calculated reaction velocities is such as to afford strong support for the conclusion that the catalytic effect of sulphuric acid is due to the simultaneous action of the hydrogen and the bisulphate ion as represented by equation (1). The observations afford no evidence of any appreciable alteration in the value of K_2 as the ionic strength of the solution increases. This apparent invariability of the classical mass-action constant is entirely in accordance with the behaviour of a number of monobasic acids (acetic, glycollic, chloroacetic, etc.) which have been previously examined with respect to their catalytic activity over a wide concentration range (Dawson, Hall, and Key, J., 1928, 2844). The constancy of the mass-action expression for the ionisation of the acid when the ionic strength of the solution is varied by increasing the concentration of the acid offers a marked contrast to the very considerable increase in the value of this expression which occurs when the ionic strength of the solution is increased by the addition of small quantities of inert salts. No explanation of this difference has yet been put forward.

Sodium Hydrogen Sulphate as Catalyst.—The contribution of the bisulphate ion to the observed catalytic effects is much greater for sodium hydrogen sulphate than for the corresponding solutions of the free acid and its relative importance increases with the concentration. The velocity–concentration curve for the bisulphate solutions is similar to those which have been previously obtained with sodium hydrogen oxalate and sodium hydrogen tartrate as catalysts for the acetone–iodine reaction.

When the velocities for the solutions are calculated from equation (1) with $10^4 k_h = 65{\cdot}0$, $10^4 k_a = 15{\cdot}0$, and $K_2 = 0{\cdot}01$, the numbers obtained are, however, in all cases less than the observed velocities and the divergence increases as the concentration of the bisulphate increases. For the most concentrated solution (0·24 mol. per litre) the observed velocity $10^4 v$ is 6·67, whilst the calculated value is only 5·81. This discrepancy is doubtless due in large measure to the variation of K_2 with the salt content of the solution. Since the effect in question is due to the inert-salt action of the bisulphate which is an important catalytically active constituent, the magnitude of the effect cannot be determined by actual experiment.

Since the maximum concentration of the sodium hydrogen sulphate solutions examined is only about 0·2 mol. per litre, it is probable that the variations of the catalytic coefficients k_h and k_a with the salt concentration can be neglected without introducing any serious error. For this range of salt solutions, the variation of K_2 is, however, very considerable and must be taken into account. Data relating to the ionisation of monobasic acids show that the influence of inert salts on the classical ionisation constant can be expressed by $\log K/K_0 = a\sqrt{x} - bx$, where K_0 refers to a salt-free solution of the acid and K to a salt solution of concentration x. Oxalic acid is the only acid for which kinetic data relating to the influence of inert salt on the second-stage mass-action constant are available, and the same formula would seem to be applicable. In this case the coefficient a is, however, twice as large as the corresponding coefficient in the formula which is applicable to the ionisation of a monobasic acid or the first-stage ionisation of a dibasic acid. This agrees with the requirements of the Debye–Hückel theory.

For oxalic acid in potassium chloride solutions, the observed variation of K_2 is given by $\log K_2/K_2^0 = 0{\cdot}81\sqrt{x} - 0{\cdot}39x$ (Dawson and Smith, J., 1929, 2530), and in the interpretation of the reaction velocity data for solutions of sodium hydrogen sulphate (Table IV) and mixtures of this with sulphuric acid (Table V) it is assumed that the inert-salt effect of sodium hydrogen sulphate on the second-stage ionisation of sulphuric acid is approximately the same. The values of K_2 have actually been calculated from the formula $\log K_2/K_2^0 = 0{\cdot}8\sqrt{x} - 0{\cdot}4x$, where $K_2^0 = 0{\cdot}01$ is the value of the mass-action constant furnished by the kinetic data for the most dilute sulphuric acid solutions. It may be noted that the variations in dilute solutions are mainly determined by the coefficient associated with the $\sqrt{x}$ term.

For a sodium hydrogen sulphate solution containing x mols. per litre, the concentrations of the hydrogen and the bisulphate ion are given by $[\mathrm{H}^{\cdot}] = \sqrt{K_2x + (K_2/2)^2} - K_2/2$ and $[\mathrm{HSO}_4'] = x - [\mathrm{H}^{\cdot}]$, where K_2 is the value of the second-stage ionisation constant for the salt concentration x. In Table IV the first four lines show the values of x, K_2, v_h, and v_a, whilst the last two afford a comparison of the calculated and observed velocities.

TABLE IV.

Catalyst : Sodium hydrogen sulphate (x mol. per litre).

x	0·008	0·02	0·04	0·06	0·08	0·10	0·15	0·20	0·24
10^2K_2	1·17	1·28	1·39	1·49	1·56	1·63	1·78	1·90	1·98
10^4v_h	0·355	0·702	1·145	1·51	1·85	2·15	2·83	3·43	3·88
10^4v_a	0·038	0·138	0·335	0·55	0·77	1·00	1·60	2·21	2·70
$10^4v_{\text{calc.}}$	0·39	0·84	1·48	2·06	2·62	3·15	4·43	5·64	6·58
$10^4v_{\text{obs.}}$	0·39	0·84	1·50	2·06	2·62	3·13	4·43	5·69	6·67

According to the figures in the foregoing table the proportion of the total catalytic effect which is attributable to the bisulphate ion increases from about 10% in the $0{\cdot}008M$-solution to about 40% in the $0{\cdot}24M$-solution. The concordance between the observed and calculated velocities is very close, and although the assumptions made in regard to the variability of K_2 and the constancy of k_h and k_a may be said to render this in some measure fortuitous, there can be no doubt that the experimental data for the catalytic activity of bisulphate solutions afford substantial support for the view that the observed effects are due to the joint action of the hydrogen and bisulphate ions.

Catalysing Effect of Mixtures of Sulphuric Acid and Sodium Hydrogen Sulphate.—The results for two series of such solutions are shown in Table V. The first of these corresponds with the general formula $0{\cdot}02M$-$\mathrm{H_2SO_4}$ + yM-$\mathrm{NaHSO_4}$, and the second with xM-$\mathrm{H_2SO_4}$ + $0{\cdot}15M$-$\mathrm{NaHSO_4}$. For both, the concentrations of the hydrogen and the bisulphate ion are given by $[\mathrm{H}^{\cdot}] = \sqrt{K_2(2x + y) + (x - K_2)^2/4} + (x - K_2)/2$ and $[\mathrm{HSO}_4'] = 2x + y - [\mathrm{H}^{\cdot}]$, where x is the molar concentration of the acid and y that of the bisulphate. The

TABLE V.

Catalyst : $0{\cdot}02M$-$\mathrm{H_2SO_4}$ + yM-$\mathrm{NaHSO_4}$.

y	0	0·008	0·02	0·04	0·06	0·08	0·10	0·15	0·20	0·24
10^2K_2	1·00	1·17	1·28	1·39	1·49	1·56	1·63	1·78	1·90	1·98
10^4v_h	1·66	1·83	2·05	2·38	2·68	2·96	3·23	3·85	4·42	4·84
10^4v_a	0·22	0·30	0·43	0·65	0·88	1·12	1·35	1·96	2·58	3·08
$10^4v_{\text{calc.}}$	1·88	2·13	2·48	3·03	3·56	4·08	4·58	5·81	7·00	7·92
$10^4v_{\text{obs.}}$	1·87	2·09	2·40	2·95	3·50	4·01	4·50	5·78	7·00	8·03

Catalyst : xM-$\mathrm{H_2SO_4}$ + $0{\cdot}15M$-$\mathrm{NaHSO_4}$.

x	0	0·01	0·02	0·03	0·04
10^4v_h	2·83	3·32	3·85	4·39	4·94
10^4v_a	1·60	1·78	1·96	2·14	2·31
$10^4v_{\text{calc.}}$	4·43	5·10	5·81	6·53	7·25
$10^4v_{\text{obs.}}$	4·43	5·12	5·78	6·51	7·16

calculated velocities for the first series are based on values of K_2 which vary with the bisulphate concentration in accordance with the formula previously given, and those for the second series (constant bisulphate concentration) are based on $K_2 = 1{\cdot}78 \times 10^{-2}$ (compare Table IV). The arrangement of the table corresponds with the previous one.

The closeness of the agreement between the observed and calculated velocities is much the same as for the solutions of the free acid and of the pure bisulphate.

The results of all these experiments show that the bisulphate ion plays a substantial part in the catalytic effects which are shown by sodium hydrogen sulphate and by sulphuric acid. The observed velocities can be satisfactorily expressed by $v = k_h[\mathrm{H}^{\cdot}] + k_a[\mathrm{HSO}_4']$ when due allowance is made for the variation of the second-stage ionisation of the acid with the salt content of the solution. There appears to be no measurable effect which can be attributed to the sulphuric acid molecule, and this is consistent with the view that the first-stage ionisation of the acid is practically complete.

The catalytic coefficient for the bisulphate ion is approximately $k_a = 15 \times 10^{-4}$ (25°) which compares with $k_h = 65 \times 10^{-4}$ for the hydrogen ion. The kinetic data lead further to the conclusion that $K_2 = 1{\cdot}0 \times 10^{-2}$ in salt-free solution; this value is only slightly less than the value $1{\cdot}15 \times 10^{-2}$ recorded for the thermodynamic constant by Sherrill and Noyes.

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