286. *Reactions of the Alkyl-sulphate Ion. Part I. Kinetics and Mechanism of the Reaction with Hydroxide Ion.*

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The bimolecular nature of the reaction between alkyl-sulphate ion and hydroxide ion has been confirmed. When N-aqueous solutions of both reactants are used no concomitant reaction of the alkyl-sulphate ion with neutral water molecules could be observed. The reaction is entirely analogous to the corresponding alkaline hydrolysis of alkyl halides except that, as it takes place between two similarly charged ions and not with an ion and a neutral molecule, its velocity increases with increasing ionic concentration.

In studying the rates of methylation of phenols with sodium methyl sulphate in aqueous alkaline solution (in the press) it was necessary to take into account the simultaneous alkaline hydrolysis of the sodium methyl sulphate which occurs as a side reaction. The kinetic equation derived for the bimolecular methylation reaction with phenol requires the knowledge of the rate constant for the bimolecular second-order hydrolytic reaction under the same experimental conditions. A study was therefore made of the latter reaction.

It is generally recognised that dialkyl sulphates react with hydroxide ions by the bimolecular process :

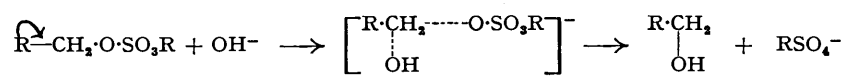
$$R_2SO_4 + OH^- \longrightarrow RSO_4^- + ROH \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

the monoalkyl sulphate formed reacting further but very much more slowly :

$$RSO_4^- + OH^- \longrightarrow SO_4^{--} + ROH \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

Reaction (1) was investigated by Kremann (*Monatsh.*, 1907, **28**, 13) who, working with diethyl sulphate in heterogeneous aqueous medium with rapid stirring (thus achieving an approximately constant diethyl sulphate concentration in the aqueous phase equal to its solubility), found an approximate proportionality between alkali concentration and speed of hydrolysis. Pollak and Baar (*ibid.*, 1917, **38**, 501) overcame the complication of two separate phases by working in alcoholic solution. However, they based their calculations on a first-order reaction and their value of *k* consequently fell as the reaction proceeded. Their results are of some value as they show that dimethyl sulphate reacts some 35 times faster than diethyl sulphate, in rough agreement with Kremann who found a ratio of 45 : 1. Klemenc (*ibid.*, p. 353) pointed out that the rate of hydrolysis of dialkyl sulphates by water cannot be neglected in comparison with the rate of hydrolysis by hydroxide ion. On this basis he recalculated Kremann's results and obtained a good constancy of the pseudo-unimolecular rate constant throughout the course of the reaction between diethyl sulphate and alkali.

There is little doubt that this reaction is entirely analogous to that between alkyl halides and hydroxide ion which has been studied in detail by, amongst others, Bateman, Cooper, Hughes, and Ingold (*J.*, 1940, 925) who confirmed the bimolecular mechanism of the reaction between a number of alkyl halides and hydroxide ion in alcoholic solution. The rate of reaction falls rapidly along the homologous series Me > Et > Pr^i owing to increasing accession of electrons on the α-carbon atom. Reaction (1) may be formulated



$$R{-}CH_2{\cdot}O{\cdot}SO_3R + OH^- \longrightarrow \left[\begin{matrix} R{\cdot}CH_2 \text{------} O{\cdot}SO_3R \\ \vdots \\ OH \end{matrix}\right]^- \longrightarrow \begin{matrix} R{\cdot}CH_2 \\ | \\ OH \end{matrix} + RSO_4^-$$

Reaction (2) has not been studied kinetically. It differs from reaction (1) and the corresponding reaction of alkyl halides in that it is between two negative ions instead of between an ion and a polar molecule. This in itself is sufficient to account for the very great difficulty of hydrolysis of the alkyl sulphate ion as compared with the neutral sulphate.

EXPERIMENTAL.

Metal Alkyl Sulphates.—The method of preparation was based essentially on that given by Cohen (" Practical Organic Chemistry," Macmillan, 1920, p. 50), AnalaR quality reagents being used. The concentrated solution of metal alkyl sulphate was evaporated until crystallisation commenced and the remainder of the water removed *in vacuo* over calcium chloride, sulphuric acid, and finally phosphoric oxide, the anhydrous salt being obtained (cf. Illingworth and Howard, *Phil. Mag.*, 1884, **18**, 123).

Analysis of Metal Alkyl Sulphates.—The metal alkyl sulphates prepared as described above were neutral to phenolphthalein and completely soluble in water to give clear solutions. Traces of carbonate and sulphate were present. These may be removed by recrystallisation from alcohol but large volumes of alcohol are required. Since the carbonate content never exceeded 0·5% it could be ignored and the total impurities allowed for by quantitative determination of the alkyl sulphate content.

Carbonate was determined by adding 5 ml. of 0·1N-hydrochloric acid to a 1-g. sample and titrating with 0·1N-sodium hydroxide to phenolphthalein.

Alkyl sulphate was determined by hydrolysing a 1·0—1·5-g. sample with 25 ml. of boiling 3N-sulphuric acid under reflux for 3 hours. Under these conditions sodium methyl sulphate is hydrolysed quantitatively, though the higher monoalkyl sulphates require less stringent conditions (Desseigne, *Mem. Serv. Chim. l'Etat*, 1944, **31**, 347). The mixture was cooled and titrated with 0·5N-sodium hydroxide to phenolphthalein. A blank determination was carried out simultaneously. A correction was applied for the acid used by the carbonate present. The analytical results are summarised below.

Preparation.	Na_2CO_3 or K_2CO_3 content, %.	Metal alkyl sulphate content, %.
Sodium methyl sulphate I	0·4	94·8
,, ,, II	0·2	94·1
Potassium methyl sulphate	0·5	91·3
Sodium ethyl sulphate	0·5	93·8

Determination of the Rate of Reaction between Alkyl-sulphate Ion and Hydroxide Ion.—Preliminary experiments showed that the reaction between sodium methyl sulphate and hydroxide ion proceeds at a measurable velocity only at temperatures of the order of 100°. This also applies to the corresponding reaction with phenoxide ion. It was, therefore, most convenient to take the b. p. of water as the temperature of reaction. Since the temperature of boiling water is dependent on atmospheric pressure, to minimise variations in temperature from one experiment to another, all reactions were conducted when the barometric pressure was between 755 and 765 mm. corresponding to a temperature of 100° ±0·2°. To facilitate calculations the experiments were conducted with equimolecular concentrations of metal alkyl sulphate and hydroxide ion:

$$\underset{(a-x)}{RSO_4M} + \underset{(a-x)}{MOH} \longrightarrow \underset{(x)}{ROH} + \underset{(x)}{M_2SO_4}$$

The velocity coefficient k' has been calculated from the usual expression for a second-order reaction, $k' = x/60ta(a-x)$, where t is the time in minutes.

The required amount of anhydrous metal alkyl sulphate was weighed rapidly into a beaker and transferred with carbon dioxide-free water to a graduated flask. The required volume of carbonate-free alkali solution (Note 1) was added by pipette or burette, and the solution made up to volume with carbon dioxide-free water. Aliquots (10 ml.) were pipetted into 6″ × 1″ test-tubes (Note 2) with widened flanges which enabled the tubes to be supported on a perforated metal sheet. The tubes were closed with rubber stoppers fitted with Bunsen valves. They were then immersed *en masse* into a vigorously boiling water-bath, the level of water in which was maintained by a constant-level device at 1½—2″ above the level of the liquid in the tubes. After 10 minutes' heating (zero time) (Note 3) and then at definite intervals tubes were withdrawn and immediately immersed in running cold water. When quite cold the contents of the tubes were titrated with standard 0·5N-hydrochloric acid to phenolphthalein (Note 4).

Note 1 : Carbonate-free sodium hydroxide was prepared according to Britton (" Hydrogen Ions," Chapman and Hall, 1932, p. 32). The carbonate-free potassium hydroxide was prepared by dissolving 64 g. of AnalaR potassium hydroxide pellets in carbon dioxide-free water and making up to 250 ml.

Note 2 : Soft-glass test-tubes were unsatisfactory as after several hours' heating the bottoms tended to drop out. No trouble was encountered with Pyrex or Monax test-tubes. The titre of N-sodium hydroxide remained unchanged in either tube (10-ml. aliquots titrated with 0·5N-hydrochloric acid to phenolphthalein) after 1 hour's heating at 100°, these conditions being more severe than encountered experimentally. Thus any dissolution of the glass by the alkali could be neglected.

Note 3 : A thermometer placed in the reaction mixture indicated that 7—8 minutes were required from the time of immersion of the reaction-tubes in the water-bath for the reaction mixture to attain the maximum temperature.

TABLE I.

Rate of reaction of sodium methyl sulphate with sodium hydroxide in aqueous solution at 100°.

Normality of NaOH = 1·000. Purity of sodium methyl sulphate = 94·8%.

Initial reaction mixture : $\left.\begin{array}{l}\text{4N-NaOH, 62·5 ml.}\\ CH_3{\cdot}SO_4Na\text{, 35·36 g.}\end{array}\right\}$ in 250 ml.

$[NaOH] = 1{\cdot}000$; $[CH_3{\cdot}SO_4Na] = 1{\cdot}000$.

Time (mins.).	Ml. of 0·5N-HCl ≡ residual NaOH.	a.*	$(a - x)$.*	x.*	$10^5k'$.
0	18·4	0·904	—	—	—
20	16·4	0·904	0·806	0·098	11·2
40	14·85	0·904	0·730	0·174	11·0
60	13·4	0·904	0·659	0·245	11·4
80	12·2	0·904	0·601	0·303	11·6
100	11·4	0·904	0·559	0·345	11·4
120	10·5	0·904	0·516	0·388	11·55
150	9·5	0·904	0·467	0·437	11·5
180	8·7	0·904	0·427	0·478	11·5
240	7·5	0·904	0·369	0·535	11·1
				Mean	11·4

* These values have been corrected for the expansion of water from room temperature (20 approx.) to 100°. The true volume of the reaction mixture is 10(1 + 0·000207 × 80) = 10·17 ml.

Note 4 : Measurements at each time interval were carried out usually in duplicate and at zero time usually in triplicate. Only the means are recorded here.

The detailed results of a typical experiment are given in Table I and a summary of the complete results in Table II.

TABLE II.

Second-order rate constants for the reaction between metal alkyl sulphates and hydroxide ion in aqueous solution at 100°.

Expt.	Metal alkyl sulphate.	Initial concn.	Alkali.	Initial concn.	Total ionic concn.*	$10^5k'$.
1A	$CH_3{\cdot}SO_4Na$	0·50	NaOH	0·50	2·00	8·3
1B	$CH_3{\cdot}SO_4Na$	1·00	NaOH	1·00	4·00	11·4
1C	$CH_3{\cdot}SO_4Na$	1·00	NaOH	1·00	4·00	11·3
1D	$CH_3{\cdot}SO_4Na$	1·50	NaOH	1·50	6·00	13·2
2	$CH_3{\cdot}SO_4K$	1·00	KOH	1·00	4·00	11·2
3	$C_2H_5{\cdot}SO_4Na$	1·00	NaOH	1·00	4·00	1·05

* Total ionic concentration $= \Sigma$ [ion] × charge. This remains constant throughout the reaction. The true ionic concentration is approximately 6% greater than given since the metal alkyl sulphates contained about 6% of impurity calculated as sodium sulphate.

DISCUSSION.

In no experiment was there observed any upward or downward trend of the rate constant. The adherence to second-order kinetics confirms the bimolecular nature of the reactions. It must be pointed out that the results presented here, by themselves, do not prove conclusively that the kinetics of the reaction are of the second order, nor does it follow that because the reaction kinetics are of the second order, the reaction is bimolecular. A satisfactory demonstration would require measurements over a wide range of different concentrations of both alkyl sulphate and hydroxide ion. As stated above, by analogy with the alkaline hydrolysis of the alkyl halides which has been proved conclusively to be bimolecular, the present reaction would be expected to be bimolecular, and the results do support this hypothesis. All reactions were carried to approximately 60% of completion except Expt. 3 (Table II) which went some 20% towards completion. The constancy of the rate constants indicates that any concomitant hydrolysis of the alkyl-sulphate ion by neutral water molecules is either non-existent or negligible. This also applies to the reaction of the corresponding alkyl iodides (Bateman, Cooper, Hughes, and Ingold, *loc. cit.*) but apparently not to the neutral alkyl sulphates (Klemenc, *loc. cit.*).

The substitution of potassium ion for sodium ion does not influence the rate of reaction. Klemenc, however, found that dimethyl sulphate was hydrolysed appreciably faster by potassium hydroxide than by sodium hydroxide which he ascribed to the catalytic influence of the undissociated alkali. The difference in rate decreased with increasing temperature. Differences between the reactivity of sodium and potassium hydroxides have been observed in other reactions, *e.g.*, the reduction of ketones by primary alcohols in the presence of strong alkali (Hargreaves and Owen, *J.*, 1947, 750).

The fall in rate on passing from methyl to ethyl is considerable, the ratio of the rates being 11 : 1. This is in very good agreement with the corresponding ratio for alkyl iodides in 80% aqueous ethanol at 35° of 12·5 : 1 (Bateman, Cooper, Hughes, and Ingold, *loc. cit.*).

There is a marked increase in rate with increasing ionic concentration as expected for a reaction between ions of like charge (Moelwyn-Hughes, " Kinetics of Reaction in Solution," Oxford Univ. Press, 1947, p. 90). It would appear that the low rate of reaction is due principally to the powerful repulsive force between the ions. The change in rate on passing from methyl to ethyl sulphate is probably due only to a change in the activation energy, since the methyl : ethyl ratio is the same as for the neutral alkyl iodides, and the velocities of reaction of the alkyl halides with hydroxide ion agree with the predictions of the simple collision theory, *i.e.*, $P \sim 1$ (Grant and Hinshelwood, *J.*, 1933, 258).

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