5. *The Hydrolysis of Arylsulphuric Acids. Part II. Kinetic Considerations.*

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In conjunction with the work described in Part I (preceding paper), the influence of variations in the concentration of the acid catalyst on the hydrolysis of a typical potassium arylsulphate was examined, and a method for obtaining velocity constants for these reactions developed.

Potassium *p*-tolylsulphate was used for these experiments. Different samples were prepared separately, purified, and tested according to the methods given in Part I. Apart from concentrations and temperature conditions, the procedures for the hydrolysis and measurements were also the same. The hydrolysis is represented in equation II of Part I ($R = C_6H_4Me$), and, with the symbols used therein, we have for the autocatalysed reaction

$$dx/dt = k(a + p)(b - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The values of *a* and *b* were obtained as in Part I; as before, the value 0·01 was used for the second dissociation constant of sulphuric acid, and this was applied to obtain values of *p* from the equation

$$(p + a)p/(x - p) = 0{\cdot}01 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The slopes of the curves for the graph of *x* against *t* were measured by taking tangents at various points up to 75% reaction, and the constants were obtained from equations (1) and (2).

In these experiments, 10 c.c. of hydrochloric acid of known concentration (*N*/20, *N*/10, *N*/4) were added to 50 c.c. of *N*/10-potassium *p*-tolylsulphate when both solutions had reached the temperature of the thermostat (80·5°). The constants obtained (see below) are independent of the hydrochloric acid concentration for this range and within the accuracy of these experiments. The mean value (0·00287 at 80·5°) gives 0·00237 when reduced to 78·7° by use of the activation energy (26,600 cals.) given in Part I. This is in good agreement with the value (0·00238) recorded there.

Concn. (*N*) of HCl added	0·05	0·10	0·10	0·25	0·25	0·25
k (mean) × 10^3	2·73	2·76	2·75	2·85	2·95	2·93

When the hydrolysis is half completed, the concentration of the HSO_4' ion exceeds that of the hydrogen ion except in the experiments with *N*/4-acid. From the constancy of the values of *k*, obtained at different stages of the hydrolyses, both in these experiments (see below) and by the same method in the preceding paper, it is clear that the HSO_4' ion has little or no effect on this reaction, in contrast to the hydrolysis of ethyl acetate (Dawson, Pycock, and Spivey, J., 1933, 291).

Hydrolysis, %	21·6	32·0	38·9	42·4	52·8
$k \times 10^3$	2·78	2·70	2·72	2·73	2·72

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[*Received, October* 19*th*, 1935.]