CXXXII.—*Determination of the Rate of Hydrolysis of Sparingly Soluble Esters.*

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The rate of hydrolysis of esters is most conveniently determined by estimating the amount of free acid formed at successive intervals. With sparingly soluble esters this involves the use either of large quantities of ester solutions, or of smaller quantities, giving relatively larger percentage errors. The use of strong acid (or base) for hydrolysis in order to speed up the reaction and so give increased titrations, brings in its train the difficulty of accurately determining the amount of base (*e.g.*, baryta) necessary for neutralisation of the acid. A method has been evolved which minimises the above difficulties.

In the reaction equation $dx/dt = kC$ the velocity coefficient can be interpreted as the fraction of the concentration C which is converted in the unit of time dt, and, for our purpose, it will be sufficiently accurate to define k as the fraction of the concentration C transformed in one minute. If, therefore, the solution is kept with a constant concentration C of ester, the same amount of ester will be transformed every minute. Hence it will only be necessary to keep the solution with a constant concentration of ester during a sufficiently long period to allow of a reasonable titration being obtained. The most convenient concentration is, of course, that of saturation. Hence if x c.c. of N-baryta represent the amount of ester transformed per minute in a 25 c.c. sample, the weight of ester transformed in 100 c.c. is $0{\cdot}004\ Mx$ g.

In order to test the accuracy with which k could be determined by this method, propyl acetate, ethyl propionate, and propyl butyrate (see Table I), whose velocity coefficients could also be determined in the usual way, were chosen. The results do not show such good agreement in the case of propyl acetate as of propyl butyrate, but this is ascribed to the fact that propyl acetate is more soluble, and hence diluted the aqueous layer to an abnormal extent (see below).

TABLE I.

Ester.	k (homogeneous method).	k (heterogeneous method).
Propyl acetate .	0·0063	0·0061
Ethyl propionate	0·0068	0·0071
Propyl butyrate.	0·0039	0·0039

TABLE II.

Ester.	k (by new method).	Solubility (g. per 100 c.c.).
Benzyl acetate .	0·0051	0·234
Benzyl propionate	0·0056	0·078
Phenyl acetate .	0·0046	0·588

The velocity coefficients for the homogeneous reaction were determined in the usual manner. For the heterogeneous reaction of the substances in Table I, 250 c.c. of *N*-hydrochloric acid were shaken with an excess of the ester in a 300 c.c. ground-stoppered bottle in a rotary thermostat at 25°. At intervals, 25 c.c. of solution were withdrawn, 25 c.c. of *N*-sodium hydroxide added, and the excess of acid was titrated with baryta, the amount of ester transformed per minute being calculated from the titre. In the cases of benzyl acetate, benzyl propionate, and phenyl acetate, only 25 c.c. of *N*-hydrochloric acid were placed in the bottle, an excess of ester was added, and, after a given period in the thermostat, the whole was titrated. To ensure greater accuracy, the additions of normal acid and base were checked by weighing. The solubilities of these esters were determined by basic hydrolysis of 25 c.c. of saturated solution. The results are in Table II.

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