NOTES.

The "Activated Complex" Theory and the Influence of Solvents on Reaction Velocity.

By S. Glasstone.

The " activated complex " or " transition state " theory of reaction velocity (Wynne-Jones and Eyring, *J. Chem. Physics*, 1935, **3**, 492; Evans and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 875) leads to the conclusion that for a bimolecular reaction involving A and B, the reaction velocity in solution should be $f_A f_B/f_{AB^*}$ times as great as for the dilute gas, where the f terms represent the activity coefficients of A, B, and the activated complex AB*, respectively, in the given solution, the dilute gas being taken as the standard state. Since the activity coefficients may be assumed to be inversely proportional to the saturation solubilities (s), it follows that the above factor becomes $s_{AB^*}/s_A s_B$, and the velocity of the reaction in different solvents will be determined by this quantity. According to Hildebrand's theory (" Solubility," 1924) a normal solubility is observed, provided polarity and compound formation do not interfere, when the internal pressures of solvent and solute are similar, but if they differ the solubility will be lower than the ideal value. If, in the reaction under consideration, A and B have internal pressures of the same order as that of the solvent, whereas that of the activated complex AB* is different, it is evident that $s_{AB^*}/s_A s_B$ will be small. On the other hand, if the internal pressures of AB* and of the solvent are similar, but those of A and B different, the factor will be large. If it is assumed that the activated complex is related to the reaction product, as will probably be the case in a process of the type $A + B \longrightarrow AB$, it follows that a solvent should facilitate a reaction if it has an internal pressure of the same order as that of the product but different from that of the reactants, and should retard it if the reverse is the case. This conclusion is a generalised form of the empirical rules put forward by Richardson and Soper (J., 1929, **1873**; see also Ingold and Jessop, J., 1930, **713**; Soper and Williams, J., 1932, **2297**). It may be noted that the activated-complex theory requires the entropy change of the process $A + B \longrightarrow AB^*$ to be related to the P factor in the expression $k = PZe^{-E/RT}$: Soper (J., 1935, **1393**) has found a definite parallelism between P and the entropy change of the complete reaction $A + B \longrightarrow AB$, a result which suggests, as has been assumed above, that in many instances the activated complex resembles the product rather than the reactants.

A modification of Langmuir's vapour-pressure equation (*J. Amer. Chem. Soc.*, 1932, **54**, 2798) leads to the relationship $1/s = \alpha T^{\frac{1}{2}} e^{-\Delta H/RT}$ (cf. Wynne-Jones and Eyring, *loc. cit.*), where α is a constant for non-associated substances, and ΔH is the energy required to vaporise 1 g.-mol.

of solute from the particular solution. Where the solubility in different solvents depends only on differences in internal pressure, it is evident that in the expression for the velocity constant the P factor will not change, but E, which includes the ΔH terms, will vary, for a given reaction, from one solvent to another. Since association, either chemical or physical, and compound formation influence solubility, they should have an effect on reaction velocity. If the reactant molecules are associated in a particular solvent, but those of the activated complex are not, then that solvent will tend to give a high reaction velocity; association of the complex, but not of the reactants, should result in a less rapid reaction. In these instances the values of both α and ΔH vary in the expression for $1/s$, so there should be differences in both P and E when comparing velocity constants in different media. Compound formation between one or both the reactants and the solvent will result in increase of s_A or s_B or both, and so the reaction velocity will be diminished: in such circumstances the values of ΔH will be increased, and consequently there will be a corresponding increase in the apparent activation energy of the process (cf. Moelwyn-Hughes and Sherman, this vol., p. 101).

When the solvent is itself associated, the s terms for A, B, and AB* will all be affected, mainly because of changes in ΔH, but also perhaps because the α values are affected. It is not possible, however, to predict the influence of such a solvent on reaction velocity without consideration of the nature of the substances involved.—THE UNIVERSITY, SHEFFIELD. [*Received, February 28th*, 1936.]

A Further Resinol from Matai (Podocarpus spicatus). By LINDSAY H. BRIGGS and DOUGLAS A. PEAK.

AGREEING with Haworth, Richardson, and Sheldrick (J., 1935, 1576), we have obtained a further resinol, conidendrin, m. p. 254—255°, in very small amount from the mother-liquors of matairesinol from the wood of matai (*Podocarpus spicatus*) (for the second resinol, m. p. 212·5—213°, see Briggs, Peak, and Woolloxall, *Proc. Roy. Soc. N.S. Wales*, 1935, **69**, 61). This is of interest from a phytochemical point of view, since the constitutions of matairesinol (Easterfield and Bee, J., 1910, **97**, 1028; Haworth and Richardson, J., 1935, 633; Briggs, Peak, and Woolloxall, *loc. cit.*) and conidendrin (Holmberg, *Ber.*, 1921, **54**, 2389, 2406; *Ann. Acad. Sci. Fennicae*, 1927, *A*, **29**, No. 6; Erdtman, *Annalen*, 1934, **513**, 229; Haworth, Richardson, and Sheldrick, *loc. cit.*) have been shown to be closely related. We prefer the generic name conidendrin, suggested by Erdtman (*loc. cit.*), to the synonymous names sulphite-liquors lactone and tsugaresinol.

Conidendrin was obtained from the mother-liquors of matairesinol by digestion with insufficient alcohol for complete solution, filtration of the undissolved material, and its recrystallisation from 60% acetic acid and then twice from alcohol. It, alone or mixed with authentic conidendrin, had the characteristic m. p. recorded by Holmberg (*Ber.*, 1921, **54**, 2389): slow heating, m. p. 254—255° after shrinking at *ca.* 236°; quick heating, decomp. at *ca.* 236°, m. p. 254°; rapid heating, m. p. *ca.* 232°. With alcoholic ferric chloride it gives a green coloration, and with concentrated sulphuric acid and sodium nitrite a brownish colour, becoming red and finally blue (Found: C, 67·4; H, 5·6. Calc. for $C_{20}H_{20}O_6$: C, 67·4; H, 5·7%). In acetone (0·0532 g. in 5 c.c.) it had $[\alpha]_D^{14°}$ −47°. Holmberg records $[\alpha]_D^{20°}$ −54·7° and Emde and Schartner (*Helv. Chim. Acta*, 1935, **18**, 344) $[\alpha]_D^{20°}$ −54·8°.

The dimethyl ether, prepared from 150 mg. of the resinol according to Holmberg (*Ber.*, 1921, **54**, 2406), had m. p. 178·5—179°, undepressed by authentic dimethyl conidendrin (Found: C, 68·7; H, 6·0. Calc. for $C_{22}H_{24}O_6$: C, 68·7; H, 6·3%).

The microanalyses were made by Dr. G. Weiler. We are indebted to Dr. H. Erdtman for authentic specimens of conidendrin and derivatives and one of us (D. A. P.) acknowledges the award of a Duffus Lubecki Scholarship.—UNIVERSITY COLLEGE, AUCKLAND, NEW ZEALAND. [*Received, March 5th*, 1936.]