90. *The Solvent Factor in Catalytic Hydrogenation.*

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An attempt is made to correlate velocity of hydrogenation with properties of the solvent such as viscosity or solvent power for hydrogen. Even when the partial pressure of hydrogen is corrected for that due to the solvent vapour, the specific velocity shows no simple relation to the above properties. The solvents were treated so as to secure removal of possible catalyst poisons.

The variation in the velocity of the catalytic hydrogenation of a dissolved substance with the solvent is of interest in connection with the resolution of the total hydrogenation process into its component stages, since the rate of supply of dissolved hydrogen at the catalysing surface is determined in such cases by its rate of passage from the gas phase through the solvent. On reviewing the literature, instances were observed in which the hydrogenation velocity is reported to vary widely with the nature of the solvent employed. For instance, Willstätter and Hatt (*Ber.*, 1912, **45**, 1471) found that the hydrogenation of naphthalene took place three times as rapidly in glacial acetic acid as in ether; and Kelber and Schwarz (*ibid.*, p. 1946), in order to allow hydrogenation to be carried out in acetic acid with colloidal metallic catalysts, prepared colloidal palladium in the presence of a protective colloid stable in acids.

It has accordingly been considered of interest to re-examine the solvent factor with a number of organic solvents which had previously been carefully purified from any trace of catalyst poisons, since it appeared conceivable that any observed differences might, at least to some degree, be due to the presence of small quantities of inhibitants rather than to specific solvent action. The solvents investigated included alcohol, ether, ethyl acetate, acetic acid, *cyclo*hexane, and chloroform; and the results of the work indicate that, although reaction in acetic acid takes place slightly faster than in the other media, this difference is considerably less than that given above: indeed, if a correction be made for the decreased partial pressure of hydrogen, due to the vapour pressure of the solvent, reaction takes place more quickly in ethereal solution than in acetic acid.

The system hydrogenated consisted in each case of 1 g. of crotonic acid, which was taken as a convenient unsaturated substance, together with 9 c.c. of the solvent and 0·1 g. of a standard preparation of non-colloidal platinum containing 0·0085 g. of metal. Hydrogenation was carried out in a mechanically driven shaker under standard conditions in the ordinary manner, the temperature being 20° in every case. All substances employed, including the crotonic acid, were freed from poisons by being previously allowed to remain in contact with a large excess of active platinum or nickel, from which they were subsequently separated by filtration, followed by redistillation. The relative velocities of hydrogenation in the various purified solvents are given in the table, *k* being the rate expressed in c.c. per minute. The reaction course in these poison-free solvents was very nearly of zero order up to an advanced stage of saturation.

Solvent.	*k*.	*k*, corrected for vapour pressure of solvent.	Solubility of hydrogen, $\alpha_{20°}$.	Viscosity of solvent, 100 $\eta_{20°}$.
Acetic acid	18·7	19·0	0·0563	1·24
Ethyl acetate	17·7	19·6	0·0758	0·45
Chloroform	15·2	19·3	0·0596	0·56
Ethyl alcohol	14·1	15·0	0·0766	1·72
*cyclo*Hexane	11·6	12·9	—	0·96
Ethyl ether	11·2	26·8	0·118	0·23

The concentration of the dissolved hydrogen in the solvent will be a function of the partial pressure of hydrogen in the gas phase and of the solubility coefficient; and, in addition, the rate of transport of the gas from the gas phase, through the solvent, to the catalytic surface will vary with the viscosity and with other factors which determine the rate of diffusion or mixing: accordingly, the respective values for α, the Bunsen solubility coefficient for hydrogen, at 20°, in the solvent in question, and for the viscosity of the solvent, η, in poises, have also been inserted in the table. It has been found that, for a given liquid, the hydrogenation velocity varies approximately linearly with at any rate small variations in the hydrogen pressure (*J. Soc. Chem. Ind.*, 1921, **40**, 169T), and it is consequently possible to correct for the partial pressure of the hydrogen, as has been done in col. 3 of the table; but the quantitative influence of the other factors, *i.e.*, the solubility coefficient and the viscosity, is not known sufficiently to justify the insertion of the appropriate corrections. It seems justifiable to assume, however, a saturated hydrogen–solvent layer at the gas–liquid interface, the hydrogen concentration in which is proportional to the solubility at the partial pressure in question and from which the rate of transport of dissolved gas to the catalyst—both by diffusion and by mechanical mixing—is facilitated by a decrease in the viscosity.

It will be seen that, after correction of the hydrogen pressure for the partial pressure of solvent vapour in the gas phase, there is little difference in the rate in acetic acid, ethyl acetate, or chloroform. The somewhat lower rate in ethyl alcohol may to some degree be due to the high value of the viscosity, and the higher corrected velocity in ether to the higher hydrogen solubility and lower viscosity; but any regular variation in rate on the basis of solubility and viscosity is at the best only very approximate: for instance, chloroform, with its considerably lower viscosity and approximately equal hydrogen solubility, compared with acetic acid, gives very nearly the same corrected hydrogenation velocity as that obtained in the latter solvent.

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[*Received, March 5th*, 1938.]