282. *The Energetics of Catalysis. Part V. The Temperature Coefficient of Hydrogenation Processes.*

By Edward B. Maxted and Charles H. Moon.

If the activation energy of catalysed heterogeneous reactions is calculated in the ordinary way by the insertion of the observed temperature coefficient in the simple Arrhenius equation, values are obtained which probably do not represent the true activation heat of the chemical reaction involved, in that ancillary factors in the composite process, in addition to the true energy of activation, influence, and in certain circumstances even dominate, the change in the reaction rate with temperature, an extreme instance of the operation of such subsidiary factors being the production of a negative temperature coefficient.

This type of variation of rate with temperature, *viz.*, its rise to a maximum and its subsequent fall as the temperature is further increased, is known to occur, *e.g.*, in the catalytic hydrogenation of ethylene in the gas phase; for Rideal (J., 1922, **121**, 309) found a maximum velocity at about 137° in the presence of nickel, and, more recently, the reversal in the sign of the temperature coefficient of the same reaction has been investigated in greater detail by zur Strassen (*Z. physikal. Chem.*, 1934, *A*, **169**, 81), who worked at a relatively low gas pressure and observed a temperature of maximum velocity at about 60°.

The occurrence of a negative temperature coefficient is usually ascribed to a decrease in the adsorbed concentration of the reactants as the temperature is increased; but zur Strassen and also Schwab (*ibid.*, **171**, 421) consider that the exponential term in the Arrhenius equation should be modified by the insertion of the heats of adsorption of the reacting species or, in certain circumstances and as an approximation, of a dominant reactant. According to the views of these authors (see zur Strassen, *loc. cit.*, p. 89), the kinetics of the hydrogenation of ethylene are such that, below a definite temperature region, the substantial saturation, even at relatively low pressures, of the nickel surface with ethylene—and the relatively small change in this concentration with temperature—suffice to render the progress of the reaction to a large degree independent of the adsorption of this gas. On this basis, the variation of the reaction velocity with temperature is represented by a relationship of the type

$$k = ae^{-\{(E - Q_{H_2}) - Q_{C_2H_4}\}/RT}$$

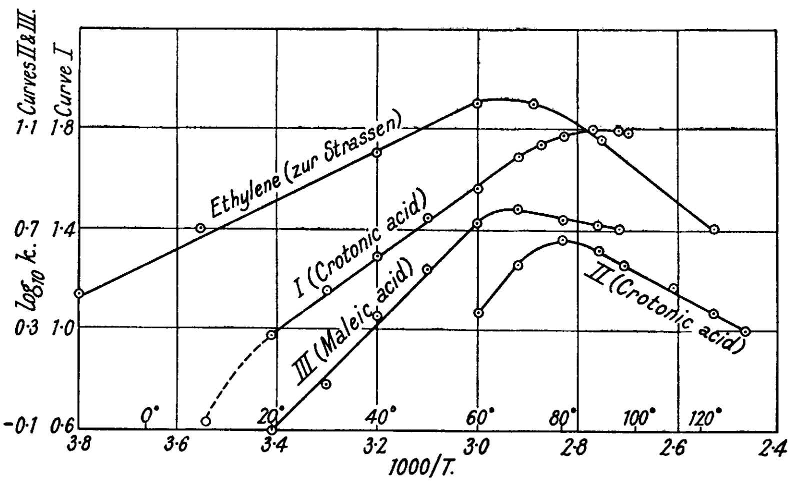
in which k is the velocity constant, E the activation energy of the hydrogenation reaction, Q_{H_2} and $Q_{C_2H_4}$ the heats of adsorption of the hydrogen and of the ethylene (exclusive of the activation heats of these adsorption processes), and a a factor involving adsorbed concentrations. In the temperature region below that corresponding with maximum velocity, the term $Q_{C_2H_4}$ becomes ineffective; and, since Q_{H_2} is less than E, the resulting temperature coefficient is positive. On the other hand, at temperatures above that at which the ethylene adsorption begins to be effectively operative, the further subtraction of the $Q_{C_2H_4}$ term leads to a negative coefficient. If this view is correct, the difference in the slope of the ascending and of the descending branch of the curve obtained by plotting log k against $1/T$ should give the heat of adsorption of ethylene; and Schwab (*loc. cit.*), using zur Strassen's curves, has calculated a value of about 17,000 cals. for $Q_{C_2H_4}$. He also quotes a value of 16,000 cals. as having been obtained calorimetrically by Schuster (*Z. physikal. Chem.*, 1931, *B*, **14**, 249) for $Q_{C_2H_4}$, in substantial agreement with the above; but this directly determined value is rather indefinite, since it was for ethylene adsorbed by a mixture of copper and iron on active charcoal and, moreover, varied considerably with the adsorbed concentration; and further work on the subject is apparently required. The figure is, however, a reasonable one for the adsorption heat in question.

Since the temperature coefficient of a hydrogenation reaction can be measured with greater accuracy in the liquid than in the gaseous phase—particularly by reason of the greater degree of temperature control possible in an exothermic process with liquid reactants—it has been considered of interest to investigate further the temperature coefficient, and particularly the occurrence of maxima, in the hydrogenation of substances in a liquid or a dissolved state. It is known in a general way (see, *e.g.*, *J. Soc. Chem. Ind.*, 1921, **40**, 169T) that an optimum temperature, which is usually about 170°, exists for the hydrogenation of liquid unsaturated glycerides in the presence of nickel; but, at such high temperatures, the possibility of a decrease in the catalytic activity of the metal by incipient sintering constitutes an additional complicating factor : indeed, zur Strassen noticed such thermal stabilising effects with nickel at or above 130°. In the present work, in which the temperature coefficient of the hydrogenation of typical ethylenic compounds in the presence of platinum has been studied, maxima have been observed at temperatures below 100°.

EXPERIMENTAL.

The apparatus and general method employed for the measurement of the velocity of hydrogenation were as already described (this vol., p. 393). The standard platinum-black was prepared, as before, by the reduction of chloroplatinic acid with an alkaline solution of sodium formate; and the same stock preparation of catalyst was used throughout each series. This stock was stabilised in bulk prior to use by being heated to 250°.

In the first series, the variation with temperature of the velocity of hydrogenation of crotonic acid in acetic acid solution was studied up to about 100°. Each charge consisted of 10 c.c. of a *N*-solution of crotonic acid in acetic acid, together with 0·05 g. of platinum, hydrogenation being carried out in a shaking pipette immersed in a thermostat and connected with a gas-measuring system, containing hydrogen, of the type previously employed. With this solvent, a correction (which becomes considerable at the higher temperatures) for the partial pressure of acetic acid is necessary. It has already been found that the velocity of hydrogenation under the above conditions is, at a given temperature and for pressures which do not differ greatly from atmospheric, approximately proportional to the hydrogen partial pressure (*J. Soc. Chem. Ind.*, 1921, **40**, 169T); but, in order to eliminate the necessity for a correction of this nature and to confirm the results obtained by applying this correction, later measurements were also carried out with a non-volatile solvent.



The results of the first series of measurements are summarised in Curve I of the fig., in which the logarithm of the velocity constant has been plotted against $10^3/T$.

It will be seen that the reaction rate increases with temperature up to about 90°, beyond which a slight decrease in rate with increasing temperature is observed. This decrease is not great; and, in view of the large correction for the vapour pressure of the solvent at and above the temperature of the velocity maximum, a further series of the nature already referred to, *viz.*, involving the use of a non-volatile solvent, was considered necessary for the more definite recognition and study of the apparent reversal.

In the second series, stearic acid, previously freed from possible traces of unsaturated impurities by treatment with hydrogen in the presence of a relatively large quantity of platinum until no further hydrogenation took place, was employed as a solvent for crotonic acid. The standard charge taken for the velocity measurements was 10 c.c. of a *N*-solution of crotonic acid in stearic acid, together with 0·05 g. of platinum, as before. Hydrogenation could not, of course, be studied below the solidification point of the solvent; and the variation of the hydrogenation velocity with temperature over the range including the previously indicated maximum is shown in Curve II. The maximum, with this solvent, occurs at a slightly lower temperature (80°, in place of 90°); and the subsequent fall in velocity is clearly indicated.

In order to study the effect of varying the compound hydrogenated, velocity measurements were carried out with maleic acid in place of crotonic acid. Each charge consisted of 0·6 g. of maleic acid, dissolved in 10 c.c. of acetic acid, together with 0·05 g. of standard platinum-black. On hydrogenating the system under the same conditions as before, the variation of velocity with temperature shown in Curve III was observed. A velocity maximum thus also occurs with maleic acid, and is probably general.

An interesting feature, which is in conformity with the above-mentioned conception of the causes underlying the reversal, is the rectilinear character, not only of the ascending, but also of the descending branch of the curve obtained by plotting log k against $10^3/T$ in each of the cases studied: for, if the reversal in sign were brought about by a mere diminution in adsorption rather than by the appearance, as an effective factor, of a further and approximately constant exponential term, this linear relationship would not persist. This characteristic is well shown in the collective graph, to which, for purposes of comparison of the general form, zur Strassen's curve for gaseous ethylene has been added, the scale of the log k axis being in the latter case reduced to one which is convenient for reproduction in the same figure as the present results with dissolved substances. The linear variation beyond the maximum is shown especially clearly in Curve II. It may be noted that the velocity of hydrogenation at 10° (Curve I) does not fit on the general curve, although its value was confirmed by duplicate measurements; and thus the apparent activation energy calculated for temperatures below 20° is somewhat greater than that derived from the normal slope. The reason for this low velocity at 10° is not apparent, and further work on the low-temperature velocity variation is needed.

On the basis of the difference in slope of the ascending and descending branches of Curves II and III, values of 15,500 and 15,000 cals., respectively, are obtained for the molecular heats of adsorption of crotonic and of maleic acid on the platinum catalyst employed, in substantial agreement with the figure of 17,000 cals. calculated by Schwab for the molecular heat of adsorption of ethylene on nickel.

Finally, an attempt at an approximate evaluation of the true activation energy of the hydrogenation of crotonic and of maleic acid can be made by means of zur Strassen's equation, by adding the heat of adsorption of hydrogen on platinum to the apparent activation energy calculated from the slope of the ascending branch of the curves. This adsorption heat, with platinum of the same type as that used in the present measurements, has been determined calorimetrically (J., 1931, 3313), and is of the order of 16,000 cals. per g.-mol. of hydrogen. In this way, the following approximate values are obtained for E.

Series.	Substance hydrogenated.	Solvent.	Apparent E, ($E - Q_{H_2}$), cals.	E, cals.
1	Crotonic acid	Acetic acid	6,800	23,000
2	Crotonic acid	Stearic acid	10,000	26,000
3	Maleic acid	Acetic acid	9,000	25,000

These figures require slight further correction for minor factors, which include the heat of solution of the reactants and of hydrogen in the solvent. They are, however, of an order of magnitude which, by analogy, appears more reasonable than the apparent values obtained by assuming the application of the unmodified Arrhenius equation. The slope of the ascending branch of the curve for crotonic acid in stearic acid, which gives a rather high value of 10,000 cals. for the apparent activation energy, is probably less accurately derivable than is the case in the other series, on account of the relatively small number of points between the temperature corresponding with the solidification point of the solvent and the temperature range in which reversal occurs.

UNIVERSITY OF BRISTOL.

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