145. *The Energetics of Catalysis. Part VI. The Kinetics of Hydrogenation Processes in Liquid Systems.*

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In the preceding paper of this series (J., 1935, 1190), the modification of the Arrhenius equation, in heterogeneous processes involving adsorption catalysis, by the insertion of appropriate heats of adsorption has been discussed with special reference to the occurrence of velocity maxima in the hydrogenation of typical ethylenic compounds at a platinum surface.

According to the views of zur Strassen (*Z. physikal. Chem.*, 1934, *A*, **169**, 81) and of Schwab (*ibid.*, **171**, 421), the reversal in the sign of the temperature coefficient in the hydrogenation of gaseous ethylene is regarded as being due to the falling—as the temperature range corresponding with reversal is reached—of the adsorbed concentration of ethylene to a value which is insufficient to render the progress of the reaction independent of the change of adsorbed concentration of this gas. If, for instance in the catalytic hydrogenation of an ethylenic compound in a liquid system, the adsorbed concentration both of hydrogen and of the unsaturated substance is maintained throughout the reaction substantially above a critical concentration dependent on the rate of reaction, the kinetics of the process should be of zero order. If, on the other hand, the adsorbed concentration of either component sinks until a stage is reached at which the rate of available supply of this component, in addition to energetic factors, exerts an effective influence on the reaction rate, this zero order should no longer be followed. In practice, in the hydrogenation of ethylenic compounds in liquid systems, the supply of hydrogen is maintained at an approximately constant value throughout; and the normal kinetics are approximately of zero order (Armstrong and Hilditch, *Proc. Roy. Soc.*, 1919, *A*, **96**, 137; 1920, *A*, **98**, 27; 1921, *A*, **99**, 490; Maxted, J., 1921, **119**, 225), save towards the end of the reaction, where the residual concentration of the unsaturated compound is insufficient to preserve linearity.

It should be noted that other factors, in addition or as an alternative to those suggested by zur Strassen and Schwab, may conceivably give rise to a negative temperature coefficient. Some of these have recently been considered by Tucholski and Rideal (J., 1935, 1701) on the basis of the relative rates of hydrogenation of ethylene by hydrogen and by deuterium. There is, in such systems, the additional complication of deuterium–hydrogen substitution in the ethylene in addition to catalytic saturation; and the relative degree of effective incidence of the various suggested factors is difficult to apportion. However, if zur Strassen's conception of the factors underlying reversal is correct, the change in sign of the temperature coefficient should be accompanied by a corresponding change in the kinetic form of the reaction, which should deviate from its normal zero-order form at temperatures above the reversal point. This has now been investigated and found to deviate in the expected manner.

Experimental.

As a suitable ethylenic compound which could be obtained in a high degree of purity, free, above all, from traces of inhibitants and of tarry or clogging poisons, crotonic acid was taken. This was purified by repeated sublimation at a relatively low temperature (< 100°) and by treatment with a large excess of platinum-black, in order to remove, by adsorption, any traces of poison which might be present, the treatment being continued to a stage well beyond that at which further purification affected the hydrogenation velocity; and all supplies throughout the work were taken from the same standard purified stock. The standard platinum catalyst used, and the hydrogenation procedure and apparatus, were as already described in previous papers of the present series. Each charge consisted of the stated weight of crotonic acid, dissolved in 10 c.c. of pure acetic acid, together with 0·05 g. of platinum-black.

The general form of the reaction path at temperatures below the reversal point is shown in Fig. 1. The form is, as has also been found by other workers, approximately linear, the degree of curvature being only slight; and all the graphs show the relatively sudden and complete cessation of reaction which is characteristic of processes of zero order. The weight of crotonic acid hydrogenated was, in each case, 0·5906 g.

At temperatures above the reversal point (see Fig. 2), the kinetic form of the reaction apparently undergoes a fundamental change. Following a transition type during the temperature range corresponding with reversal (80—90°), the reaction path becomes evenly curved, loses its characteristic phase of sudden cessation, and, at these higher temperatures, approximates to that of a reaction of the first order. The degree of conformity to a unimolecular path is shown in the following table, in which x is the volume, in c.c., of hydrogen absorbed after t minutes; 0·574 g. of crotonic acid, corresponding with a maximum absorption of about 160 c.c. of hydrogen at 20°, was taken for each experiment of this series, in the form of a stock solution in acetic acid.

Fig. 1.

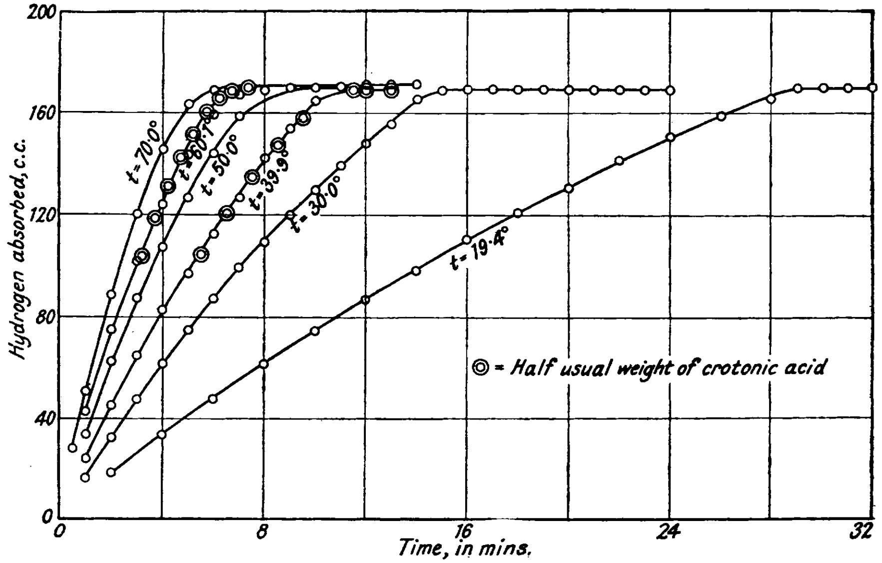
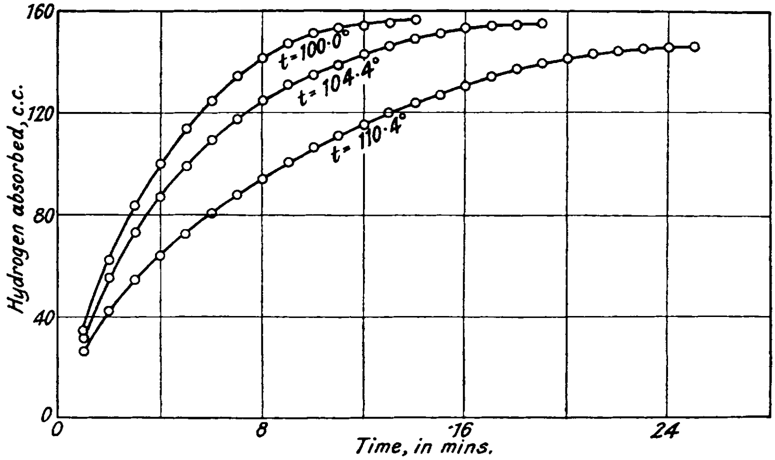


Fig. 2.



Temp. 100°.

t (mins.).	x.	k.
2	62·4	0·107
4	100·1	0·107
6	124·9	0·109

Temp. 104·4°.

t (mins.).	x.	k.
4	87·2	0·086
6	109·1	0·083
8	125·1	0·083

Temp. 110·4°.

t (mins.).	x.	k.
8	94·4	0·048
12	115·6	0·046
16	131·0	0·046

The effect of an increase in temperature beyond the reversal point has thus involved an increasing degree of incidence of a factor which, when dominant, brings about a change in the reaction order. It is possible, moreover, that this factor may be effectively present to a subordinate degree even below the temperature range corresponding with a change in sign of the temperature coefficient, and that its presence may explain the small deviation from a linear path found at these lower temperatures, at which the order of the reaction is approximately zero.

In order to test whether the slight departure from linearity was due to a gradual, if small, diminution in the activity of the platinum, which might conceivably be caused—in spite of the preliminary purification of the crotonic acid—by the deposition on the catalytic surface of small traces of tarry or other clogging poisons, such as might be formed in small quantities as secondary products, a series of measurements was next carried out with half the above quantity of crotonic acid (0·2953 g.), together with 0·05 g. of platinum as before. The reaction was in this way begun at a stage corresponding—in comparison with the previous measurements—with that at which half of the former quantity of crotonic acid had been hydrogenated, save that the catalyst was in its initial state. Thus, if no appreciable diminution in the activity of the catalyst occurs, the reaction curves during this later series should coincide with the latter half of the former curves obtained with the full amount of crotonic acid. On the other hand, if any appreciable diminution in catalytic activity had occurred (*i.e.*, if the slight curvature were due to this factor), the employment of conditions which are equivalent to the use of fresh catalyst at the stage corresponding with semi-hydrogenation should result in a more rapid rate of reaction. The alternative method of investigation, entailing the repeated use of the same catalyst for successive hydrogenations, was impracticable owing to the small quantities involved and to the danger of activity changes during the process of recovery and re-preparation for use.

The almost complete correspondence of these later measurements with the latter half of the former runs may be seen on reference to Fig. 1, in which the relative rates of absorption have been indicated. The kinetics observed are thus those of the process in the presence of a catalyst of constant activity.

Finally, while the observed change of reaction order is in conformity with zur Strassen and Schwab's conception of the causes underlying reversal, further work in confirmation of this important quantitative introduction of the heat of association into the Arrhenius equation is undoubtedly required.

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