86. *The Energetics of Catalysis. Part IV. The Influence of Deactivation by Heat Treatment on the Value of the Activation Energy.*

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In earlier papers of this series, the evidence for the energetic uniformity of the catalysing elements of a metallic surface, such as that of platinum, has been examined from various standpoints, including the influence of progressive inactivation by means of a poison (J., 1933, 502); and it has now been considered of interest to study the effect on the activation energy of partial deactivation by heat treatment. While the nature of the deactivation process involved differs essentially from inhibition of activity by the progressive and obstructive occupation by a poison of elements normally free for catalysis, the application of the present work to the question of energetic uniformity is based largely on considerations which have already been discussed in the above paper, particularly if any active points or peak areas which exist in the surface be viewed as extra-lattice projections differing among themselves in nature and in order of stability in such a way that the process of stabilisation by heat treatment might be expected to affect certain of these preferentially.

Two heterogeneous reactions, of distinct types, *viz.*, the decomposition of hydrogen peroxide and the hydrogenation of crotonic acid in the liquid phase, have, in this case, been chosen for study, the activation energies with a platinum catalyst at various stages of deactivation by heat treatment being determined in the usual way by means of the temperature coefficient of the reaction velocity.

This ratio of the reaction velocities at two given temperatures, and consequently the calculated value of the activation energy, was found in each case not to vary appreciably with the state of deactivation of the platinum, although different values were, as would be expected, obtained for the two different reactions. It may be noted that this constancy is in agreement with the observations of Pease and Harris (*J. Amer. Chem. Soc.*, 1927, **49**, 2503) for the hydrogenation of ethylene in the gas phase in the presence of a copper catalyst, supported on a ceramic base, before and after sintering.

Experimental.

The standard platinum black used was prepared by Mond, Ramsay, and Shields's method (*Phil. Trans.*, 1895, *A*, **186**, 657) by the reduction of chloroplatinic acid with an alkaline solution of sodium formate, the same preparation of platinum being employed for all measurements within a given series. From this main stock smaller portions were taken, as required, for partial deactivation by heat treatment at various temperatures, the sintering being carried out in a small Pyrex vessel contained in an electrically heated enclosure or, for lower temperatures, in an oil- or nitre-bath.

The general technique for the determination of the reaction velocity was, in the main, as previously described (J., 1921, **119**, 225; 1934, 26). For the hydrogenation of crotonic acid, a solution of this compound in glacial acetic acid, to which the platinum was added, was treated with hydrogen in a shaking pipette, under controlled conditions, in a thermostat. For the decomposition of hydrogen peroxide, a shaking method, involving the measurement of the oxygen evolved (J., 1922, **121**, 1760), was used in place of following the progress of the reaction by titration, as had been done in the work involving deactivation by poisoning (J., 1933, 502).

Decomposition of Hydrogen Peroxide.—For each measurement, 50 c.c. of a 0·16*N*-solution of hydrogen peroxide were placed in the reaction pipette and kept in the thermostat for a sufficient time to attain the required temperature. 0·025 G. of platinum, taken from a stock in a given state of inactivation and preheated to reaction temperature in 5 c.c. of water, was now added, and the shaking mechanism put into operation. The reaction follows, as is well-known, a course of the first order.

The results obtained are summarised in Table I, in which k_{10} and k_{30} are the unimolecular velocity constants, at 10° and 30°, respectively, with specimens of platinum taken from stocks previously sintered for 30 mins. at the temperatures indicated. The 20° temperature difference not only gave a convenient (approximately 3-fold) rise of reaction, but also—with the catalyst first in its highly active unsintered state and finally in the relatively inactive form produced by sintering at 400°—approximately covered the range between the limits of velocity which could conveniently be read off in the gas burettes attached to the shaker.

TABLE I.

Temp. of previous heat treatment of catalyst.	Activity, expressed as % of original activity.	k_{10}.	k_{30}.	k_{30}/k_{10}.
(Unsintered)	100	0·23	0·634	2·76
250°	23	0·052	0·142	2·73
300	7·8	0·018	0·050	2·77
350	4·4	0·0101	0·0275	2·72
400	2·6	0·00607	0·0170	2·80
			Average	2·76

It will be seen that, in the course of progressive deactivation by heat treatment involving an ultimate decrease in the activity of the platinum to less than 3% of its original activity, the value of the ratio k_{30}/k_{10} remains approximately constant, the observed deviation from the mean being of the order of 2%, which represents the degree of agreement of duplicate activity measurements. The mean value of the ratio, *viz.*, 2·76, corresponds with an activation energy of about 8,700 cals. for the temperature range 10—30°.

It was considered of interest, further, to compare the value of the activation energy given for the present, relatively dense specimens of platinum black with those which had previously been obtained for the same reaction (*loc. cit.*) with a far more finely divided form of the metal prepared by another method. Since, in the previous work, a somewhat lower temperature range had been employed, the temperature coefficient of the present platinum was determined in somewhat greater detail down to 0°. This was done with a stock which had previously been sintered at 250°, the following variation being observed:

Temp.	0°	10°	15°	20°	25°	30°
k	0·023	0·052	0·065	0·084	0·111	0·142

From this, the average activation energy, calculated in the usual way, is 10,800 cals. between 0° and 15°, compared with about 11,000 cals. found for the same temperature interval with the relatively finely divided platinum in the previous work, the agreement between 0° and 25°, although not quite so satisfactory, being within 7%. In any case, the degree of concordance between the values given by the two widely differing preparations of platinum is striking. The activation energies calculated on the basis of the simple Arrhenius equation are probably, in the case of heterogeneous catalytic reactions of the types studied in the present paper, apparent energies only; and an attempt is being made elsewhere to analyse the factors contributing to the apparent temperature coefficient, with special reference to the variation of the apparent critical energy with the temperature.

Hydrogenation of Crotonic Acid.—The standard charge taken for hydrogenation consisted of 10 c.c. of a *N*-solution of crotonic acid in acetic acid, the same stock being used throughout the whole work. This, together with the required quantity of platinum, was placed in a closed pipette, provided with a stoppered side tube to facilitate the introduction of the charge, and hydrogenated by shaking in an apparatus of the usual type (*Trans. Faraday Soc.*, **1917**, **13**, 36).

Preliminary experiments were carried out to determine the effect, under the conditions employed, of a variation in the quantity of platinum on the temperature coefficient, since it was considered necessary, first of all, to make sure that the mere diminution of the speed of hydrogenation brought in itself no change in the temperature coefficient. The results of measurements with varying amounts of platinum are summarised in Table II, in which k_{15} and k_{35} are the velocities of the hydrogenation reaction, which follows a course of approximately zero order, at 15° and 35°, respectively, the velocity being expressed in c.c. of hydrogen absorbed per minute.

TABLE II.

Pt, g.	k_{15}.	k_{35}.	k_{35}/k_{15}.	Pt, g.	k_{15}.	k_{35}.	k_{35}/k_{15}.
0·025	3·3	7·7	2·34	0·1	17·1	40·0	2·34
0·05	7·8	18·2	2·34	0·1	17·4	40·6	2·33

As was expected, this mere decrease in the amount of platinum had no effect on the temperature coefficient.

In the first series of measurements of the effect of heat treatment, a freshly prepared stock of platinum (Platinum A) was employed. In choosing a suitable temperature range, reaction temperatures below 10° were precluded by the solidification of the acetic acid solution used, but temperatures of 10° and 30° were, with 0·05 g. of this platinum, found to give hydrogenation velocities of convenient relative magnitude throughout the series. The general effect of sintering this platinum on the reaction velocities at the two temperatures in question and on the ratio of these velocities is shown in Table III.

TABLE III.

Temp. of previous heat treatment of catalyst.	Activity, expressed as % of original activity.	k_{10}.	k_{30}.	k_{30}/k_{10}.
(Unsintered)	100	4·85	12·0	2·5
200°	81	3·9	9·9	2·5
250	56	2·7	6·4	2·4
300	35	1·5	3·6	2·4
350	19	0·95	2·4	2·5

The result is similar to that observed in the decomposition of hydrogen peroxide, in that the reduction of activity by heat treatment exerts no measurable effect on the temperature coefficient. It will be noted, further, that the ratio of the velocities at 30° and 10° differs slightly from the ratio at 35° and 15° (Table II); and, on calculating the corresponding activation energies, these are again found to decrease slightly as the temperature is increased, *viz.*, from 7,600 cals. between 30° and 10° to 7,500 cals. in the somewhat higher range.

A further series of measurements was carried out with a second stock of platinum (Platinum B), which was not specially prepared but was available from other work, and had been prepared by the fusion of chloroplatinic acid with sodium nitrate, followed by the reduction with hydrogen of the platinum oxide thus produced (Voorhees and Adams, *J. Amer. Chem. Soc.*, **1922**, **44**, 1397). This platinum had, before being taken for the present purpose, been employed for a considerable time for the adsorption of ethylene and had, in the course of its use, apparently become stabilised, since it was not so sensitive to heat treatment as Platinum A; indeed, for some reason, its activity was increased by exposure to moderate sintering temperatures. As before, however, deactivation by exposure even to a relatively high temperature had, as far as could be seen, no effect on the temperature coefficient and consequently on the apparent activation energy of the hydrogenation reaction.

The results obtained with 0·05 g. of this catalyst in various states of deactivation are collected in Table IV.

Again, the ratio of the reaction velocities at the two temperatures is unaffected; moreover, the mean value of k_{35}/k_{15}, *viz.*, 2·35, corresponding with an apparent activation energy of 7,500 cals., agrees well with that calculated from Table II.

As a slight variation in the method of deactivation, the length of the sintering period was now varied, once more, however, without appreciably affecting the velocity ratio. In the

TABLE IV.

Temp. of previous heat treatment of catalyst.	k_{15}.	k_{35}.	k_{35}/k_{15}.
200°	11·4	27·0	2·4
250	12·2	28·8	2·4
300	13·4	30·8	2·3
350	13·5	31·5	2·3
400°	14·0	32·0	2·3
450	9·5	22·8	2·4
500	3·7	8·8	2·4
550	3·45	7·9	2·3

TABLE V.

Time of previous heat treatment of platinum, mins.	k_{15}.	k_{35}.	k_{35}/k_{15}.
(Unsintered)	8·8	20·8	2·4
30	9·5	21·4	2·3
60	6·8	15·3	2·3
120	6·0	13·9	2·3
180	5·1	12·0	2·4

measurements summarised in Table V, 0·05 g. of Platinum B and a uniform sintering temperature of 450° were employed.

The activation energy calculated from the above ratio is identical with that derived from Tables II and IV.

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[*Received, February* 18*th*, 1935.]