

7. *The Energetics of Catalysis. Part II. The Poisoning Coefficients and Energies of Activation of Hydrogenation Processes.*

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IN a previous paper (J., 1933, 502) evidence has been brought forward for the apparent energetic homogeneity of the catalysing or adsorbing points in a platinum surface from the standpoint of the activation energy of a typical heterogeneous catalytic reaction proceeding at the surface, the activation energy being apparently equal throughout the range of individual surface elements concerned in the catalysis. The result is of considerable interest in connexion with the analysis of the energy distribution within the surface of a catalyst and in relation to the broad question of the true energetic homogeneity or otherwise of such catalytic surfaces, whether or not any actual heterogeneity be regarded as inherent in peak areas (Taylor, *Proc. Roy. Soc., A*, 1925, **108**, 107) or in crystal edges or other discontinuities, as discussed by Schwab, Pietsch, and others (*Z. physikal. Chem., B*, 1928, **1**, 385; 1929, **2**, 262; **5**, 1; 1931, **12**, 427) in various papers on adlineation.

Since, however, the energy of activation is a function not only of the catalyst but also of the reaction itself, it has been considered of interest to examine the question of the effective homogeneity of a platinum surface from another standpoint, *viz.*, that of the apparent possibility of reducing the activity, by poisoning, to stages at which the surface remains active for certain more easily catalysed reactions, while it loses, by virtue of this partial poisoning, its power of catalysing other more difficult processes. Vavon and Husson (*Compt. rend.*, 1922, **175**, 277) found that platinum, on being progressively poisoned, lost in succession its power of reducing a ketone (such as acetophenone), then nitrobenzene, and finally, benzene. Heterogeneity among the potential catalysing points is therefore undoubtedly indicated.

In reviewing the series of substances examined by Vavon and Husson, it is noteworthy that benzene, the hydrogenation of which is relatively difficult, should proceed with a catalyst which would not hydrogenate the usually easily reducible nitrobenzene. It appeared, therefore, that the effect of progressive poisoning on the suppression of the activity of a catalyst for reactions of different degrees of difficulty required further study, particularly with reactants which were free from any original inhibitor; for, if the substances themselves contained traces of poisons, the amount of added poison necessary for the suppression of the activity of the catalyst for the hydrogenation of the particular reactant would not represent the true poison content of the system. Further, the absolute suppression of activity is of rather indefinite qualitative meaning: the activity of a catalyst, in the presence of an increasing concentration of an inhibitor, decreases gradually; and the final stages which correspond with complete disappearance of catalysing power cover a relatively large range of poison concentration—as far as the bulk concentration of the poison in the system is concerned—and only end at a stage of poisoning the position of which is difficult to determine experimentally.

In the work now to be described, three unsaturated compounds, of well-defined degrees of difficulty of hydrogenation, have been taken for examination from the above standpoint. These were crotonic, oleic, and benzoic acids. The lower ethylenic acids, such as acrylic or crotonic acid, are readily reduced even by nascent hydrogen, while higher acids of the same series, *e.g.*, oleic acid, are not attacked by hydrogen in this form: indeed, much of the technical significance of catalytic hydrogenation has lain in the fact that it afforded a ready means of saturation of these higher and less reducible acids. The benzene ring is

hydrogenated with still greater difficulty than ethylenic linkages, even when these are contained in a relatively long chain : for instance, many cases are known in which the ethylenic linkages in a side chain attached to an aromatic nucleus are saturated far more readily than the nucleus, or in which, if an ethylenic linkage is to be saturated with hydrogen, a less active catalyst may be employed than is required for the hydrogenation of benzenoid bonds. Each of these compounds, moreover, is readily prepared in a state of purity, free from catalyst poisons.

It was found that the amount of poison necessary to reduce the activity of a standard platinum catalyst to a given fraction of its original activity was the same for each of these substances, instead of differing from one to another, as in Vavon and Husson's work and as would be expected if the catalytic surface were heterogeneous in the sense that it consisted of elements of different effective catalytic activity. It should be pointed out, however, that all the linkages examined, although differing in difficulty of saturation, consisted of a carbon-carbon ethylenic or benzenoid bond ; and the poisoning coefficients for the hydrogenation of ketonic and other groups containing oxygen are being discussed in a separate paper.

It has been considered of interest, further, to develop the rather indefinite conception of relative ease of reduction on the basis of quantitative energetics. The activation energies required for the hydrogenation of crotonic, oleic, and benzoic acids, in the presence of the same catalyst, were found to vary in the expected sequence, *viz.*, to be least for crotonic and greatest for benzoic acid ; indeed, ease of reduction appears, at any rate in the above series, to correspond largely with the limitation of reaction velocity imposed by the value of the activation energy required, although the degree of activity of a catalyst as a whole may determine whether or not a given reaction proceeds with a measurable velocity at all.

EXPERIMENTAL.

The standard platinum catalyst employed throughout the investigation was prepared from platinum oxide, made by the fusion of chloroplatinic acid with pure sodium nitrate according to the method of Voorhees and Adams (*J. Amer. Chem. Soc.*, 1922, **44**, 1397). This oxide was suspended in pure stearic acid, from which traces of inhibitors and of unsaturated impurities had been removed by previous treatment with hydrogen in the presence of a large excess of platinum, and reduced with hydrogen at 100°. When cooled and powdered, the standard suspension of platinum in stearic acid, thus obtained, formed a convenient source of platinum of constant activity.

The specimens of crotonic, oleic, and benzoic acid were carefully purified, and were sufficiently free from impurities to give a zero-order reaction curve (Armstrong and Hilditch, *Proc. Roy. Soc., A*, 1919, **96**, 137 ; 1920, **98**, 27 ; 1921, **99**, 490). For poisoning, a standard solution of mercuric chloride in glacial acetic acid, usually corresponding to 0.025 mg. of mercury per c.c., was employed. Glacial acetic acid, taken from the same stock throughout, was used as a common solvent for the various substances treated.

The hydrogenation was carried out at atmospheric pressure, in a closed pipette immersed in a thermostat at 40° and attached to a shaker, the absorption of hydrogen being followed by a measuring system of the type previously described (*Trans. Faraday Soc.*, 1917, **13**, 36). Each charge consisted of 3 c.c. of oleic acid, or of an equivalent quantity of benzoic or crotonic acid, made up to 10 c.c. with glacial acetic acid containing the required quantity of poison. The standard weight of catalyst used was 0.1 g. of the stearic acid suspension of platinum, corresponding with 6 mg. of metal.

The effect of progressive poisoning on the activity of the same quantity of platinum for the hydrogenation of the three compounds studied is summarised in Table I. It has been shown in previous work (J., 1921, **119**, 225 ; 1922, **121**, 1760) that the effective activity of a platinum catalyst, measured by the rate of the reaction, decreases linearly with an increase in the bulk concentration of the poison up to a region of inflexion, which probably corresponds with that at which the adsorbed concentration is no longer proportional to the bulk concentration of mercury ions (J., 1925, **127**, 73). If this effect of the poison up to the point of inflexion be represented by an expression of the type $k_c = k_0(1 - \alpha c)$, in which k_0 is the zero-order velocity constant for the unpoisoned catalyst and k_c the velocity constant, also of zero order, for the catalyst in the presence of a concentration, c , of the poison, then α is a coefficient which

represents the specific effect of each unit of poison and may be termed the poisoning coefficient. This coefficient should, if a linear graph is followed, be constant for any one reactant. Further, if α should be found to possess the same value for each of the reactions studied, in spite of their widely differing activation energies (as will be discussed later), the relative decrease in the activity of the catalyst caused by a given concentration of poison will be the same for each of the reactions, instead of differing with the substance hydrogenated. In view of the above, the approximate constancy of the poisoning coefficient even with a change in the substance reduced is of considerable interest.

TABLE I.

Acid.	Poison content	h ,	α .	Acid.	Poison content	h ,	α .
	of system, mg.	c.c. H ₂			of system, mg.	c.c. H ₂	
	Hg.	per min.			Hg.	per min.	
Crotonic	0	13.5	—	Oleic	0.075	7.1	3.4
	0.05	11.4	3.1		0.10	6.3	3.5
	0.10	8.8	3.5		Benzoic	0	0.67
	0.15	6.5 *	3.4	0.025		0.61	3.6
	0.20	5.4	—	0.05		0.55	3.6
	Oleic	0.25	5.0	—	0.075	0.50 *	3.4
0		9.5	—	0.15	0.48	—	
0.05		7.8	3.6				

* The region of inflexion occurs after the points denoted thus.

If the activity of the catalyst in each of the three cases be plotted against the poison content, graphs of the type previously found are obtained; and the initial linear portions of each of these graphs prior to the point of inflexion all, when produced, intersect the poison concentration axis at approximately the same point, this concurrence being a necessary consequence of the equality of the poisoning coefficients.

Although the results indicate that the same concentration of poison has the same proportionate effect on the activity of the catalyst for each of the three reactions, yet it should be noted that any apparent homogeneity of the platinum surface elements concerned which may be suggested by this is not incompatible with Schwab and Pietsch's views on adlineation, since the adsorbing elements in crystal edges or in similar linear structures may be regarded as energetically homogeneous among themselves, although differing from adsorbing elements in non-linear portions of the crystal lattice. It is not possible by the present method to trace the effect of poisoning beyond the point of inflexion of the poisoning graph; but the concurrence of the linear poisoning graphs, for the various reactions, at the same point on the poison axis may probably be taken to indicate also that the same range of adsorbing points on the catalysing or adsorbing surface is concerned in all three processes. This, again, is not inconsistent with adlineation.

A further matter which has been investigated in connexion with the above three hydrogenation reactions consists in an attempt to correlate the not very definite conception of relative ease of reduction with the value of the activation energy. To this end, the temperature coefficients for the hydrogenation of the three acids were determined under standard conditions which were approximately the same as those used for the poisoning work. The relative velocities of the zero-order reaction, expressed, as before, in c.c. of hydrogen per minute, at 20°, 40°, and 60°, together with the mean apparent activation energies between the temperatures specified by subscripts, are given in Table II.

TABLE II.

Acid.	h_{20° .	h_{40° .	h_{60° .	Mean apparent activation energies, cals.		
				E_{20-40° .	E_{40-60° .	E_{20-60° .
Crotonic	7.8	11.3	14.8	3,400	2,800	3,100
Oleic.....	4.1	7.25	10.8	5,100	4,100	4,600
Benzoic	0.20	0.65	1.50	10,700	8,600	9,700

The values obtained for these apparent heats of activation are low for a chemical reaction and are probably composite; but it may be noted that Pease and Purdum (*J. Amer. Chem. Soc.*, 1925, 47, 1441) calculated a value of similar order, *viz.*, 10,000 cal., for the activation energy in the hydrogenation of gaseous benzene on copper. It will be seen that the activation energies increase with the degree of difficulty associated experimentally with the hydrogenation.

In view of the inability of catalysts of low activity to hydrogenate the benzene ring at all, or at any rate with measurable velocity, certain properties inherent specifically in the catalyst itself are apparently necessary for the inception of activation; but, from the standpoint of the catalytic process as a whole, rather than from that of the activating properties of the catalyst *per se*, ease of reduction is apparently synonymous with the relative reaction velocity imposed by the value of the activation energy.

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