140. *The Energetics of Catalysis. Part III. Further Studies of the Poisoning Coefficients of Hydrogenation Processes.*

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The present investigation is an extension of previous work (this vol., p. 26) on the evidence—from the standpoint of the effect of progressive poisoning—for the energetic homogeneity of such of the adsorbing points of a metallic surface as are involved in hydrogenation catalysis, and should be read in conjunction with the general discussion contained in that paper. There, it was shown that the poisoning coefficient—*viz.*, the term α in the equation : $k_c = k_0 (1 - \alpha c)$, in which k_c is the velocity constant in the presence of a concentration, c, of a poison, and k_0 that with the unpoisoned catalyst—was independent of the identity of the reaction throughout a series of hydrogenation processes of various degrees of difficulty and of widely different activation energies. The series of reactions studied, however, involved in each case the saturation of a carbon–carbon linkage only, although the nature of this was varied from an ethylenic to a benzenoid bond.

The work has now been extended to the reduction of bonds containing oxygen, with special reference to the substances which were employed by Vavon and Husson (*Compt. rend.*, 1922, **175**, 277). As before, great care was taken to free the substances used from all traces of original poison; and the poisoning coefficients for the catalytic reduction of the oxygen-containing materials now examined were also correlated with those for the hydrogenation of benzenoid and ethylenic linkages, from which the reduction processes differed in involving the formation of water in place of simple saturation with hydrogen.

It was found that the various poisoning coefficients had in all cases approximately the same value; and it would seem that this equivalence may be regarded as additional evidence for the homogeneity or mutual equivalence of the individual catalysing points and for the participation of the same range of these surface elements in all the reactions studied. This conception of uniform catalysing points is compatible with the requirements of the adlineation theory of Pietsch and Schwab (*Z. Elektrochem.*, 1929, **35**, 135; *Z. physikal. Chem.*, 1929, *B*, **5**, 1; 1931, *B*, **12**, 427) rather than with the existence of active points due to extra-lattice projections of varying types—unless such extra-lattice elements as are involved in catalysis be regarded as being uniform in nature. Further, the evidence for the existence of various types of catalysing points derived from Vavon and Husson's work would appear to be based on the employment of bulk concentrations of poison outside the range for which the adsorbed concentration is proportional to—and can thus easily be expressed, without special analysis, in terms of—the bulk concentration (J., 1925, **127**, 73), and possibly on the insufficient freeing of the substances used from traces of catalyst poison. In any case, the problem of the homogeneity or otherwise of the catalysing range of surface elements is regarded as being fundamental to the development of the energetics of processes in which such catalysts are employed.

Experimental.

The general experimental conditions were as previously described, save that the two standard preparations of platinum used, respectively, throughout the series in which mercury ions were employed as the poison and for that in which poisoning was carried out with carbon disulphide, were not identical with the catalyst previously taken, although they were prepared in a similar manner. All substances used, including the media in which the stock catalyst was suspended, were scrupulously freed from original poison, principally by the previous adsorption of any traces of these with a large excess of platinum black or of active nickel.

Series 1.—In this, a standard solution of mercuric chloride, containing usually 0·1 mg. of mercury per c.c., was used. The standard charge of unsaturated compound, platinum, and solvent (acetic acid) was as given in the previous paper, save that the platinum content was 0·038 g. throughout this series, and all hydrogenations were carried out at 40°. From previous work (J., 1925, **127**, 73) it was known that 0·04 g. of a typical platinum black should be capable of adsorbing up to about 0·3 mg. of mercury; and, although this figure necessarily varies from catalyst to catalyst, this value may be regarded as, at any rate, some indication of the order of magnitude of the range within which the adsorbed concentration of the poison can be derived directly from the bulk concentration without further investigation of the distribution relationship. The substances previously examined by Vavon and Husson included acetophenone, nitrobenzene, and benzene, in which the susceptibility to poisoning was stated to decrease in this order.

In the necessary preliminary freeing from original poison, chief interest is attached to nitrobenzene. All purchased specimens were found to be hydrogenated surprisingly slowly : indeed, this anomalous reaction velocity, in view of the generally recognised ease of hydrogenation of this compound, has been commented upon by Green (*J. Soc. Chem. Ind.*, 1933, **55**, 52T). Since, however, nitrobenzene contains much of the thiophen and other sulphur compounds present in the benzene from which it is made—possibly partly as nitro-derivatives—and may, in addition, contain traces of sulphonic acids derived from the mixture of sulphuric and nitric acids used in nitration, it appeared that this slowness might be due to the presence of original poison. Purification was accordingly carried out by agitation with dilute potassium hydroxide, followed by a large excess of catalytically active nickel in a nitrogen atmosphere, the nitrobenzene being recovered by distillation in nitrogen. By this treatment, a specimen of nitrobenzene was obtained which absorbed hydrogen under standard conditions at about 150 times the rate of absorption by the purest nitrobenzene which could be purchased, and at about 2·5 times the rate given by carefully purified oleic acid (cf. Green, *loc. cit.*). The acetophenone and benzene taken were also purified by the previous adsorption of original poison; but these compounds, as was to be expected from general experience, were only hydrogenated, even when in a poison-free state, at about one-tenth the velocity of pure nitrobenzene.

The effect of progressive poisoning, by means of mercury ions, on the hydrogenation of the three substances in question is summarised in Table I, from which it will be seen that the poisoning coefficient, α, has, within the limits of experiment, a constant value, not only as the concentration of the inhibitant is increased for any one substance up to the region of inflexion, but also from substance to substance. Moreover, the greater the relative possible accuracy of the rate measurements, the more closely do the calculated values of α correspond. For instance, with nitrobenzene, for which the original rate of hydrogen absorption amounted to over 50 c.c. per minute, the degree of agreement is closer than for the substances in which the measured differences in the reaction rates are less; but, in any case, α has, throughout the table, a mean value of about 2. In the table, k is given in terms of c.c. of hydrogen per minute.

TABLE I.

Substance hydrogenated.	Poison content of system, mg. Hg.	k.	α.
Nitrobenzene	0	54·4	—
	0·10	43·6	1·98
	0·15	38·4 *	1·96
	0·25	29·8	—
	0·50	23·2	—
Acetophenone	0	4·7	—
	0·10	3·8	1·9
	0·15	3·3 *	2·0
	0·25	3·2	—
	0·50	3·0	—
Benzene	0	5·3	—
	0·05	4·8	1·9
	0·10	4·1	2·2
	0·20	3·1	2·1
	0·25	2·6	2·0
	0·30	1·8 *	2·2
	0·50	1·3	—
	0·80	0·9	—
Oleic Acid	0	21·0	—
	0·10	16·6	2·1
	0·15	14·8 *	2·0
	0·25	13·0	—
	0·50	11·5	—

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

If the above results be plotted graphically, it will be noted that all the graphs representing the variation of the activity with the poison content, up to the region of inflexion, converge, when produced, approximately to the same point on the poison axis, indicating geometrically an identical value for α and a mutually equal susceptibility to poisoning.

It was considered of interest, further, to determine the value of α for oleic acid with the catalyst now used, in order to correlate the present data with those previously obtained for crotonic, oleic, and benzoic acids, for which α was also found to be constant; the values thus found are included in Table I. Since the poisoning coefficient for this is of similar magnitude to that for the other compounds contained in the table, it follows that all the seven widely differing substances dealt with in this and in the previous paper have identical poisoning coefficients. Hence, in contradistinction to conclusions based on the results of Vavon and Husson, there would appear to be no difference in the susceptibility of these substances to poisoning, provided that the precaution be taken to free the substances from original poison.

Series 2.—In this series, carbon disulphide was taken as the inhibitant, since it was desirable to examine the effect of the same poison as that which was employed by Vavon and Husson, although less was known of the distribution of the poison between the free and the adsorbed phase than was the case for mercury, for which this distribution had previously been investigated.

A fresh standard preparation of platinum was used throughout this series; and only the two substances which, under Vavon and Husson's conditions, showed the widest divergence in susceptibility to poisoning, *viz.*, acetophenone and benzene, were examined. The standard solution of carbon disulphide employed contained 0·01 mg. per c.c. of acetic acid, a solution of ten times this concentration being taken when more convenient; the charge used for hydrogenation, and the general conditions, were similar to those of Series 1, save that the platinum content was 0·0085 g. throughout. It will be noted that the catalyst used for Series 2 was more active, weight for weight, than that taken for Series 1, and the poisoning coefficient was correspondingly greater. The results of this series are in Table II.

TABLE II.

Substance hydrogenated.	Poison content of system, mg. CS_2.	k.	a.	Substance hydrogenated.	Poison content of system, mg. CS_2.	k.	a.
Acetophenone	0	4·2	—	Benzene	0	4·3	—
	0·02	3·5	8·3		0·01	3·9	9·3
	0·03	3·2	8·0		0·03	3·2	8·5
	0·05	2·5	8·1		0·06	2·2 *	8·2
	0·10	0·7 *	8·3		0·10	1·3	—
	0·15	0·6	—		0·15	1·2	—

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

As before, the values of α agree throughout the series, the only serious deviation from the mean value being the first point in the benzene series, for which the difference between the poisoned and the unpoisoned reaction velocity was too small to justify the accurate calculation of this ratio.

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