135. *Catalytic Toxicity and Chemical Structure. Part I. The Relative Toxicity of Sulphur Compounds in Catalytic Hydrogenation.*

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The variation of catalytic toxicity with the structure of the inhibitant is of considerable interest in connection with the method and degree of attachment of a poison to a catalytic surface. Unlike most adsorbed species, a poison—by virtue of its negligible rate of evaporation and, consequently, its obstructive occupation of surface—becomes attached permanently to at least one surface element by a linkage involving the poisonous element contained in its molecule. If the inhibitant in question contains, for instance, a residual non-poisonous chain of any length, although this chain may be of a structure such that in the absence of the poisonous element or group it would normally be freely adsorbed and evaporated, it may—by reason of the permanent attachment at one point—itself be in a preferential position for further attachment, in that the free evaporation of the molecule as a whole is inhibited; and, in this way, the permanent linkage at one point may cause a remaining, normally non-poisonous portion of the molecule to become toxic. This point will be discussed in the course of the following work, in which the toxicity or power of covering of a poison containing, for instance, one sulphur atom will be seen to be increased by the introduction of a normally non-poisonous chain or ring.

It has been considered of interest, as a first stage, to investigate quantitatively the relative toxicity of various types of sulphur compounds which commonly occur in substances ordinarily subjected to catalytic hydrogenation, the present work being preliminary to a more systematic investigation of the effect of structure and of chain length on toxicity, namely, on the effective power of covering of an inhibitive molecule attached to a surface by a permanently linked point. From the standpoint of practical hydrogenation, the principal types of sulphur compounds which occur in the impure substances normally employed include cyclic thio-compounds—typified by thiophen and its analogues—and, especially in products such as unsaturated glycerides, albuminoid sulphur together with albuminoid decomposition products, which may be represented by sulphur-containing amino-acids such as cysteine and, as a stage further, by hydrogen sulphide. Accordingly, in the present paper, the relative toxicity of hydrogen sulphide, carbon disulphide, thiophen, and cysteine, also of elementary sulphur, towards a platinum and a nickel catalyst, has been measured.

The sensitivity of a given catalyst to a given poison varies greatly with its degree of subdivision, a coarse-grained, relatively inactive catalyst being far more sensitive to poisoning than a finely-divided, highly active one, especially if the fineness of subdivision be increased and stabilised by the use of a carrier. For this reason, two widely differing preparations, *viz.*, a relatively coarse platinum and a far more finely-divided supported nickel catalyst, were taken, the ratio of the sensitivity towards a given poison of the former to the latter catalyst being of the order of fifty to one.

It is of interest to note that—in spite of the above wide difference in sensitivity to an individual poison—not only was the sequence of the above series of inhibitants, in order of increasing toxicity, the same for both catalysts, but also the relative toxicities of the inhibitants, *viz.*, the ratio of the toxicity of a given sulphur compound to that of another, expressed quantitatively per unit of sulphur, were found to be very similar for both metals; further, the toxicity of the poison per unit of sulphur increases in each case with the complexity of the chain or ring attached to the sulphur.

Experimental.

The platinum used was prepared by Mond, Ramsay, and Shields's method (*Phil. Trans.*, 1895, *A*, **186**, 657), *i.e.*, by the reduction of chloroplatinic acid with an alkaline formate, followed by prolonged washing. It was subsequently heated to 200° to ensure stability on storage and in use. The resulting catalyst possessed a high degree of sensitivity to poisons and could be stored, at any rate for several weeks, without measurable deterioration. The nickel was made by reduction with hydrogen of nickel carbonate on a kieselguhr support. In this

case also, for reasons of stability, the maximum possible activity was not aimed at. Accordingly, although this nickel was far less sensitive to poisoning than the platinum, it was more sensitive than an ordinary supported nickel catalyst for which permanence in activity on storing is not necessary. It was stored in stearin. Both with nickel and with platinum, the catalyst required for each measurement was taken from the same stock throughout; and each charge of catalyst was only used once.

For the measurement of the activity of each catalyst at various stages of poisoning, the general method already described (J., 1921, **119**, 225; 1935, 393, 1190) was employed, the toxicity being expressed in the form of the poisoning coefficient (J., 1934, 26, 672), *viz.*, as the coefficient, α, in an expression of the type $k_c = k_0(1 - \alpha c)$, in which k_c is the activity of the catalyst in the presence of a concentration, c, of the poison, and k_0 is the original, unpoisoned activity. It has previously been found that this expression holds for the greater part of the poisoning curve, probably up to a stage beyond which the bulk concentration of poison present begins to be too high to be substantially completely adsorbed (see J., 1925, **127**, 73) by the amount of catalyst used: indeed, in the present work, care was taken—by testing the decanted, originally poisoned supernatant liquid for freedom from poison after allowing the catalyst to settle—that the conditions were such that the poison added was completely adsorbed by the catalyst and that the adsorbed poison content was thus that represented by the bulk concentration of poison originally added. The poisons themselves were either already available in a pure condition or were carefully purified. Thus, the specimen of carbon disulphide used was sufficiently free from other sulphur compounds to possess an ethereal odour. In the case of hydrogen sulphide, which was made from magnesium hydrosulphide, it was necessary to carry out the toxicity measurements immediately after the preparation of the standard poisoning solution in order to avoid a change with time in the concentration and form of the poison in the very dilute solutions employed.

The usual precautions were taken to ensure the constancy of the rate of presentation of hydrogen and unsaturated substance at the catalytic surface. For instance, the standard conditions of agitation were maintained throughout each of the series by employing the same shaking vessel, driven at a constant, relatively high rate. Accordingly, since the same solvent and unsaturated substance were used, the conditions were identical save for the presence of the poison. This constancy of the external conditions was confirmed by duplicate tests both with the unpoisoned catalysts and with these in a known poisoned state. As a still further precaution—in view of the extremely small quantities of poison involved (of the order of 0·01—0·04 mg. in the case of platinum)—duplicate measurements involving a fresh weighing out of the poison and the preparation, by dilution, of an independent standard solution were also carried out. These agreed well in each case with those of the main series.

Relative Toxicity towards Platinum.—The series of inhibitants taken was elementary sulphur (which is slightly, but sufficiently, soluble in glacial acetic acid), hydrogen sulphide, carbon disulphide, thiophen, and cysteine. Crotonic acid was used as a standard unsaturated substance for hydrogenation; and the system contained in each case 0·05 g. of platinum, 10 c.c. of a *N*-solution of crotonic acid in glacial acetic acid, and the required quantity of the poison dissolved in a further 10 c.c. of acetic acid. The effect of various quantities of the above inhibitants on the activity of the platinum is shown in Fig. 1, the sulphur content of the system being expressed in g.-atoms of sulphur, which is equivalent to the content, in g.-mols., of the inhibitant itself, save in the case of carbon disulphide, which possesses two potentially linking sulphur atoms. Elementary sulphur also is included on the basis of the toxicity per g.-atom. The temperature employed was in each case 27°.

It will be seen that the toxicity per unit of sulphur increases with the molecular weight of the inhibitant, *i.e.*, with the complexity of the chain or ring attached to the sulphur. From the slope of the poisoning graph, the following values are obtained for α, the poisoning coefficient in respect of the catalytic surface represented by the standard amount (0·05 g.) of the platinum preparation taken, the concentration of the inhibitant being expressed as above:

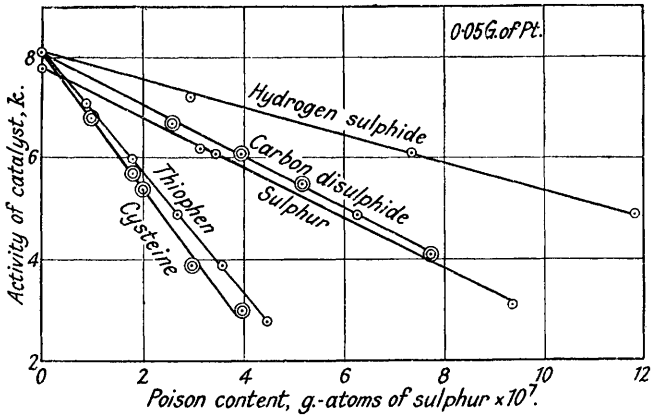
Inhibitant.	Mol. wt.	$\alpha \times 10^{-5}$.	Relative toxicity per g.-atom of S.
Hydrogen sulphide	34	3·4	1
Sulphur	$(32)_n$	6·4	1·9
Carbon disulphide	76	6·4	1·9
Thiophen	84	14·8	4·4
Cysteine	121	16·7	5·0

Relative Toxicity towards Nickel.—Since hydrogenation reactions with nickel are usually carried out at a higher temperature than with platinum, crotonic acid in acetic acid solution

cannot conveniently be used as the standard unsaturated substance for the measurement of activity. Accordingly, olive oil, previously purified by the usual fuller's earth and soda treatment, was substituted. The system taken for each measurement consisted of 0·05 g. of nickel, which was added as a suspension in stearin, and 10 c.c. of olive oil, including that added with the poison, which was in each case made up in standard olive oil solution. All materials were taken from the same stock throughout the whole of the work. The temperature employed was 160°. At this high temperature, the linear reaction path, corresponding with a process of zero order—which is normally followed in the hydrogenation of pure substances at low temperatures both in the absence and in the presence of an added poison, and which results in an approximately constant hydrogenation velocity during, at any rate, not too advanced stages of the hydrogenation—becomes curved (*J. Soc. Chem. Ind.*, 1921, **40**, 169T); and the velocity of hydrogenation decreases with the time. During early stages of the hydrogenation of an oil,

FIG. 1.

The relative toxicity of sulphur compounds in catalytic hydrogenation.



the deviation from a linear path is, however, not great; and the slight curvature may be allowed for by differentiating for zero time the equation to the absorption–time curve. The figure obtained represents the initial velocity of absorption of hydrogen, and may be conveniently employed as a measure of the activity of the nickel under conditions in which a zero-order hydrogenation path is not followed.

Save for the omission of elementary sulphur, the series of inhibitants studied was the same as for platinum. The variation of the activity of 0·05 g. of nickel with the poison content is summarised in Fig. 2. In this, the widely differing general sensitivity to poisoning between the coarse-grained platinum catalyst and this supported nickel catalyst is emphasised by the difference in the scale of the axis representing the poison content, which is 100 times as large (g.-atoms of S × 10^{-5}) as that of Fig. 1 (g.-atoms of S × 10^{-7}); but the inhibitants fall in the same sequence of toxicity as for platinum. The higher toxicity of carbon disulphide, compared with hydrogen sulphide, is in agreement with Kelber's observation (*Ber.*, 1916, **49**, 1868).

The poisoning coefficients for this preparation of nickel are given in the following table, in which the relative toxicities previously found for platinum have been included for purposes of comparison. It will be seen that, in spite of the wide difference in general sensitivity of the two

Inhibitant.	$\alpha \times 10^{-3}$.	Relative toxicity per g.-atom of S.	Relative toxicity towards Pt.
Hydrogen sulphide.....	7·5	1	1
Carbon disulphide	18·2	2·4	1·9
Thiophen.....	33·3	4·5	4·4
Cysteine	40·0	5·4	5·0

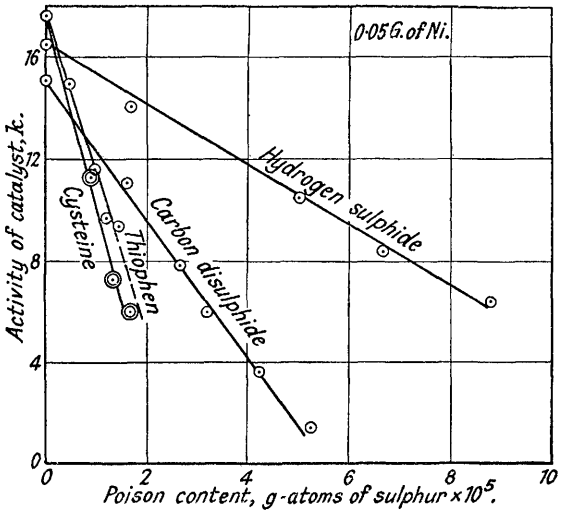
catalysts, the relative toxicity of the various poisons one to another is almost identical for nickel and for platinum.

If relative toxicity is regarded as a measure of relative obstructive covering power of a potentially catalytically active range of surface elements by a poison, this similarity in relative toxicity towards nickel and platinum might be expected on grounds of the similar-

ity in magnitude of the lattice constants of nickel and platinum (3·5 and 3·9 A., respectively). The effective lengths, in similar units, of the bonds involved in the structure of the various inhibitants is also well known on the basis of *X*-ray and other evidence; and it should thus be possible to reproduce the probable power of covering of a given structure by the superimposition of scale models of the inhibitants on to a model of the crystal lattice involved. It is hoped to deal with this point in greater detail in a later paper. It appears, further,

FIG. 2.

The relative toxicity of sulphur compounds in catalytic hydrogenation.



not impossible that relative data for power of covering may—if an inhibitant of known chain length can be used as what may be regarded as a molecular measuring scale—be made to yield evidence on the distance apart of catalytically active surface elements and on the identity or otherwise of this distance with that separating the normal lattice atoms of the catalyst. This information is of considerable interest in connection with the existence and nature of so-called active points on a catalytic surface.

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