55. *Studies in the Detoxication of Catalyst Poisons. Part I. General Survey of Some Detoxicants.*

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The applicability of various per-acids for the detoxication of platinum hydrogenation catalysts poisoned by cystein, by β-thionaphthol (naphthalene-β-thiol), and by thiophen has been examined in a preliminary manner. Many of these reagents, including persulphuric, perphosphoric, perchromic, permolybdic, and pertungstic acids, have been found to be sufficiently active detoxicants to warrant further study.

THE general principles involved in the detoxication of catalyst poisons have already been discussed (J., 1940, 252; 1941, 132). Briefly, it has been found that the usual toxic character, towards metallic catalysts, of molecules containing catalytically poisonous elements such as sulphur is in general lost if the structure of the molecule is such that the normally toxic atom is associated with a completely shared electron octet. Thus, organic sulphides or thiols are toxic towards, for instance, platinum in catalytic hydrogenation, whereas sulphones or sulphonic acids are non-toxic :

Toxic.	$(R)C:\ddot{S}:C(R')$	$(R)C:\ddot{S}:H$
	Sulphide	Thiol.
Non-toxic (shielded type).	$(R)C:\overset{\overset{O}{\cdot\cdot}}{\ddot{S}}:C(R')$	$(R)C:\overset{\overset{O}{\cdot\cdot}}{\ddot{S}}:OH$
	Sulphone.	Sulphonic acid.

The conversion, *in situ*, of catalyst poisons into non-poisonous derivatives of shielded type constitutes a method of eliminating toxicity from impure systems without the necessity for actual removal of the poison by absorption or other means; and the method possesses considerable practical interest, since the removal, in the ordinary sense, of small traces of catalyst poisons from impure substances before, for instance, their hydrogenation is often difficult, particularly if the poisons are in a not easily absorbable form.

The present paper, which relates throughout to catalytic hydrogenation, contains a preliminary survey of some detoxicants for the treatment of three of the principal types of catalyst poisons containing sulphur, with the object of ascertaining what detoxicating reagents are suitable for more detailed study. Special attention has been given to the detoxication of cystein, since this has a structure similar to that of the albuminoid sulphur poisons present as impurities in the unsaturated glyceride oils, which are extensively hydrogenated in industry; but a shorter examination has also been made of the detoxication of a thiophenol and of thiophen, which are representative respectively of the sulphur poisons in industrial phenols and in technical benzene or naphthalene.

Since detoxication has, in practice, to be applied to a very small concentration of poison, contained as an impurity in an unsaturated substance, the detoxicating reagent should, as far as is possible, neither add on to the ethylenic or other unsaturated bonds of this unsaturated substance nor attack these bonds in such a way as to cause fission. In an earlier paper (*loc. cit.*) hypochlorites have been used as detoxicants. Hypochlorites and hypobromites are effective detoxicating agents for many sulphur poisons. There is, however, with these reagents, a considerable risk of halogenation of the unsaturated substance. The extent of this under favourable conditions has not yet been determined; but an apparently more valuable class of detoxicants, which can more readily be used in the presence of substances containing unsaturated bonds, has been found in various per-acids. With these, it is possible to apply detoxication either before or during hydrogenation.

In the present paper, the conversion of the poison into a shielded form has in every case been obtained by oxidation. Thus, the observed detoxication of cystein in all probability involves its passage into cysteinic acid, the sulphur atom of which has the saturated electronic configuration

$$HO:\overset{\overset{O}{\cdot\cdot}}{\ddot{S}}:CH_2\cdot CH(NH_2)\cdot CO_2H$$
$$\underset{\cdot\cdot}{O}$$

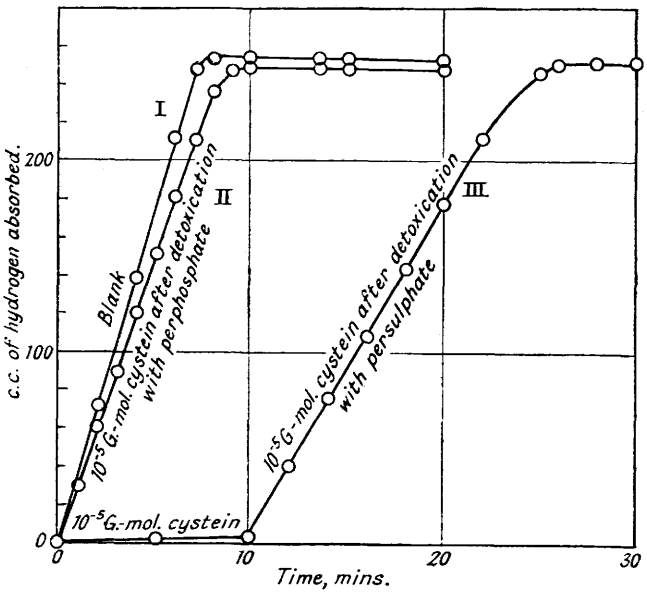
The unsaturated substance, to which the poison was added as an impurity, has consisted of crotonic acid. Platinum has, for convenience, been used throughout as the hydrogenation catalyst. The change of the poison into a non-toxic form would also apply to the hydrogenation of other unsaturated substances and to catalysis with other metals, *e.g.*, with nickel, save that, with oxidisable metallic catalysts, modifications in the actual detoxication procedure are of course necessary in order to maintain the hydrogenation catalyst in a reduced state. These will be dealt with in a later paper.

Experimental.

The standard hydrogenation charge introduced into the hydrogenation pipette consisted of 0·075 g. of stock platinum-black, 5 c.c. of a 2N-solution of crotonic acid in acetic acid, a further 3 c.c. of acetic acid and 2 c.c. of water, also the poison and the detoxicant, the water being used for extending the range of possible investigations to poisons or detoxicating reagents which are more conveniently applied in aqueous solution. The hydrogenation tests were carried out in a shaker, at 27° and under standardised conditions, the rate of absorption of hydrogen being followed in a gas burette in the usual way.

Detoxication of Cystein.—(i) *Use of persulphates.* The effect of adding a small quantity of a persulphate to the standard hydrogenation system previously poisoned with 10^{-5} g.-mol. of cystein is shown in Curve III of Fig. 1. The poisoned system was first shaken with hydrogen under standard conditions to determine the hydrogenation rate in the presence of the poison. The run was, after 10 minutes, interrupted and a small quantity of potassium persulphate (estimated at about 0·05 g.) was dropped into the hydrogenation pipette, which was removed from the thermostat and heated to 100° in a water-bath. The pipette was then re-cooled, re-attached to the hydrogenation apparatus, and, after the usual displacement of air by hydrogen, the run was continued at 27° under the same conditions as before. The detoxication effect caused by the persulphate is well seen by the abrupt change in the slope of the graph. It will also be seen that the total amount of hydrogen absorbed is approximately equal to the normal saturation value (250—260 c.c. at the prevailing temperature and pressure) of the amount of crotonic acid present, indicating little, if any, fission of the double bond of the unsaturated substance by the persulphate in addition to its detoxication of the cystein. Any excess of persulphate remaining as such after the detoxication could, even if it also undergoes hydrogenation to sulphate, only absorb a negligibly small volume of hydrogen, since the total hydrogen value of the whole of the persulphate added is only about 4 c.c.

Fig. 1.



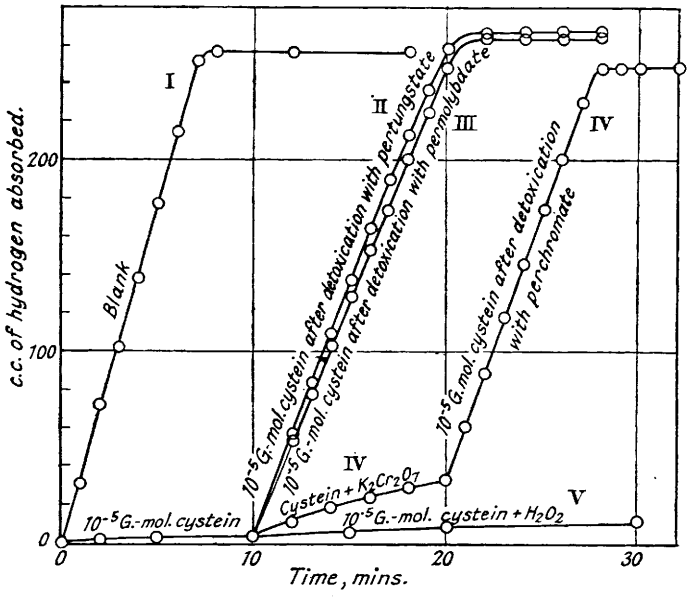
(ii) *Use of perphosphates.* The detoxicating reagent was in this case added directly as the acid. Permonophosphoric acid, H_3PO_5, is stated (Schmidlin and Massini, *Ber.*, 1910, **43**, 1162) to be formed by the interaction of phosphoric oxide with hydrogen peroxide. Accordingly, in this test, approximately 0·05 g. of phosphoric oxide was allowed to react at 0° with a few drops of hydrogen peroxide and the product was quickly mixed with a standard hydrogenation charge containing 10^{-5} g.-mol. of cystein. The mixture was heated, as before, to 100° to facilitate the oxidation of the poison and to destroy any excess of hydrogen peroxide, which quickly decomposed in the presence of the platinum catalyst with evolution of oxygen. The hydrogenation pipette containing the charge was then cooled to 27° and shaken with hydrogen. The high degree of detoxication brought about by this detoxicant is shown in Curve II of Fig. 1, the slope of which should be compared with that of the first part of Curve III (cystein without detoxication) and with Curve I, which is a blank run, without poison or detoxicant. From the figure, it would seem that perphosphoric acid is a more active detoxicating agent than a persulphate, although the conditions in these exploratory experiments—particularly from the standpoint of the amount of phosphoric oxide and hydrogen peroxide added—may not be strictly comparable with the persulphate run. It should be noted that both persulphates and perphosphates would be particularly suitable as detoxicating reagents, since they would leave as a residue only an innocuous sulphate or phosphate.

(iii) *Use of anions containing metals.* A further class of active detoxicating reagents consists of the unstable per-acids, or their salts, formed by the action of hydrogen peroxide on oxygenated anions containing metals. Most, if not all, of these metallic per-acids, especially perchromic, permolybdic, and pertungstic acids, have been shown to act as effective detoxicants. Peruranic, pervanadic, and other metallic per-acids were found to be less active; but it is not yet known whether this may have been due to toxic impurities (*e.g.*, traces of toxic foreign metals) in the specimens available. Even the per-acid formed from hydrogen peroxide and a permanganate is to some extent active, although the extent of the detoxication obtained is, at any rate in this case, almost certainly restricted by the known poisonous nature (J., 1940, 469) of the manganous salt to which the per-acid is probably reduced during the subsequent hydrogenation. Permanganates, in the absence of hydrogen peroxide, are only of about the same activity as dichromates (see later). Hydrogen peroxide, by itself, is almost inactive as a detoxicant; and this is also the case for perborates, which are not true per-acids.

Examples of detoxication by metallic per-acids are given in Fig. 2. Curve I is a blank run with the standard hydrogenation system containing no poison or detoxicant. In Curve II, 10^{-5} g.-mol. of cystein was added as the poison and hydrogenation was carried out for 10 minutes without detoxicant. At this point, the run was interrupted, and about 0·05 g. of ammonium tungstate and a few drops of hydrogen peroxide added under the same conditions as have already been given for detoxication by perphosphoric acid. The interrupted hydrogenation was then continued under standard conditions. The rise in the hydrogenation rate after the detoxication is shown by the graph after the first 10 minutes. Curve III, the first part of which (up to 10 mins.) is identical with the first part of Curve II, is a similar run with addition

of a permolybdate as the detoxicant. In Curve IV, about 0·05 g. of potassium dichromate, in the absence of hydrogen peroxide, was added after the first 10 minutes of the run, which, as in all cases in the figure, except the blank run, was with a system containing 10^{-6} g.-mol. of cystein. The extent of the detoxication with dichromate alone was not great (see the middle part, from 10 to 20 mins., of Curve IV); and, after a further 10 minutes, the usual few drops of hydrogen peroxide and a little additional potassium dichromate were added, since the chromium already present in the solution had been reduced to the green state, whereupon a sharp rise in the hydrogenation velocity occurred. The total volume of hydrogen absorbed was somewhat lower than usual, this being in agreement with the expected fission of the double bond of the crotonic acid by the dichromate, although the amount of this loss of unsaturated substance could not have been great on account of the small quantity of the chromium compound present. Curve V shows the effect of adding hydrogen peroxide alone. Little or no improvement in the hydrogenation rate occurred. The curve for the addition of sodium perborate was almost identical with Curve V and has therefore been omitted from the figure.

FIG. 2.



In place of adding these metallic per-acids during the progress of the run, they can of course be added before any hydrogenation is begun, as in Curve II of Fig. 1; and further experiments have shown that they are also effective if the metallic hydrogenation catalyst is absent during the detoxication treatment, although this catalyst assists the rapid destruction of any excess of hydrogen peroxide or of per-acid, which have otherwise to be removed by boiling. This detoxication in the absence of a hydrogenation catalyst is of importance if it is desired to use an oxidisable catalyst such as nickel for the subsequent hydrogenation.

Detoxication of β-Thionaphthol and of Thiophen.—Both of these poisons are susceptible to detoxication by the same reagents as have been used for cystein. However, whereas cystein responds directly, it was found necessary with thiophen, and helpful with thionaphthol, to apply the reagent after a period of preliminary hydrogenation, during which the poison present in the system is, by virtue of its preferential adsorption on the catalyst, preferentially hydrogenated to a derivative more easily oxidised than the original poison. This was expected from the known chemistry of thiophen, since its hydrogenated product, tetrahydrothiophen, readily forms a derivative of shielded type (a sulphone) on oxidation,

FIG. 3.

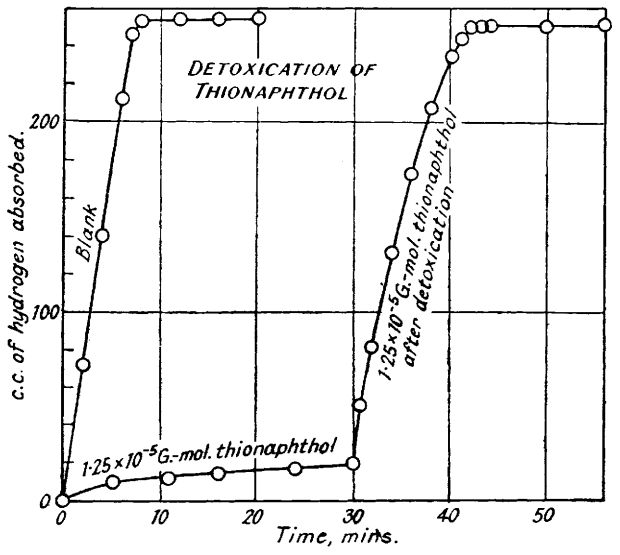
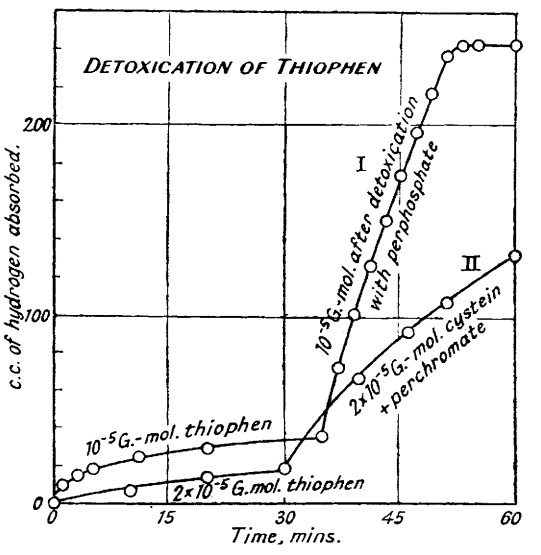


FIG. 4.



while thiophen itself is not easily attacked; but it was less expected for thionaphthol. It is not known whether the preliminary hydrogenation reduced one or both rings of the thionaphthol; but the non-toxic derivative formed by the detoxication process almost certainly consists of the corresponding sulphonic acid.

The detoxication, with perphosphoric acid, of $1·25 \times 10^{-5}$ g.-mol. of β-thionaphthol contained in the standard hydrogenation system, the catalyst being 0·075 g. of platinum, as before, is shown in Fig. 3. After hydrogenation for 30 mins., at 27°, the detoxicating reagent was added under similar conditions to those already described and the run was then continued. As with cystein, the hydrogenation velocity rose steeply after the detoxication; but, both with thio-

naphthol and with thiophen (see Fig. 4), there was visible progressive coagulation of the platinum catalyst, which led to a slightly curved reaction path. This coagulation could of course have been avoided by using a supported catalyst. In accordance with previous experience, a perchromate gave a lesser degree of detoxication than a perphosphate, and a persulphate was less active still; but, since the amounts added were only approximately comparable, their exact relative detoxicating efficiencies are still to be determined.

Fig. 4 shows the detoxication of thiophen. In the run corresponding with Curve I, 10^{-5} g.-mol. of thiophen, contained in the standard hydrogenation system, was detoxicated, after 35 minutes, with perphosphoric acid. In Curve II, 2×10^{-5} g.-mol. of thiophen was detoxicated, after 30 mins., with perchromic acid.

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