198. *Studies in the Detoxication of Catalyst Poisons. Part II. The Use of Various Oxidising Agents for the Detoxication of Cystein.*

By Edward B. Maxted.

The use of perphosphoric acid, potassium persulphate, hydrogen peroxide and dilute nitric acid as reagents for the detoxication of cystein in a hydrogenation system containing a platinum catalyst has been studied further. Perphosphoric acid in the presence of hydrogen peroxide is probably the most satisfactory reagent of this group. This solution, at the dilution used, does not appreciably attack the double bond of the unsaturated substance in which the cystein occurs as a poison. Except for persulphates, the detoxicating effect is greatly increased if the addition of the reagent (or of hydrogen peroxide in the case of a per-acid made from this) is made in more than one step.

The present paper should be read in connection with earlier work (J., 1941, 132; this vol., p. 204) on the conversion of small concentrations of catalyst poisons into non-toxic forms. It gives a more detailed description of the effectiveness of a number of oxidising agents (excluding metallic per-acids, which are dealt with in Part III) for the detoxication of cystein contained as an impurity in a hydrogenation system. The principles and the general technique have already been discussed.

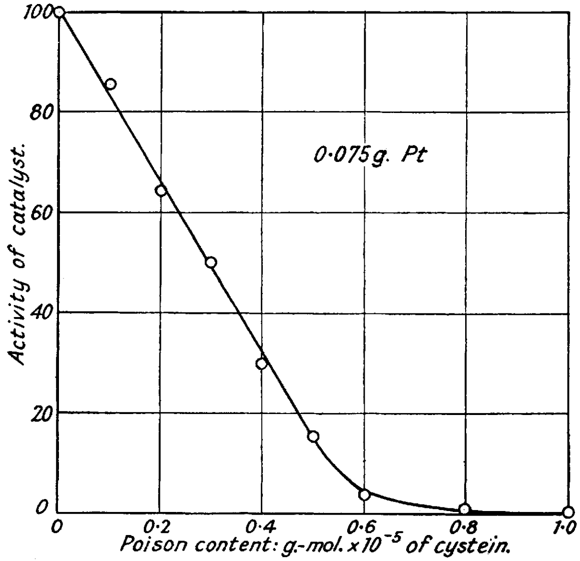
Experimental.

The hydrogenation charge taken for each run consisted of 0·075 g. of stock platinum catalyst, poisoned by 10^{-5} g.-mol. of cystein and suspended in a liquid system containing 5 c.c. of a 2N-solution of crotonic acid in acetic acid and 5 c.c. of water (including the water introduced with the cystein and with the detoxicant, both of which were added in dilute aqueous solution). Hydrogenation was, as before, carried out at 27° in a shaker. The above charge of platinum, in the absence of poison, gave a zero-order reaction rate corresponding with the absorption of 30·4 c.c. of hydrogen per minute.

Before beginning the detoxication work, the toxicity of cystein towards the standard charge of platinum catalyst was determined in the absence of detoxicants, since this curve provided data which could be used for calculating, from an observed reaction velocity, the amount of cystein still present in a toxic form in the detoxication tests. It will be seen from Fig. 1 that the amount of cystein (10^{-5} g.-mol.) adopted as the standard charge of poison in the detoxication runs was sufficient to suppress the activity of the catalyst almost completely. In this figure, the activity of the catalyst at the various stages of poisoning is expressed as a percentage of the original activity.

Detoxication by Persulphate.—The results of adding various amounts of potassium persulphate to the standard hydrogenation charge before the commencement of hydrogenation are shown in Curve I of Fig. 2, in which the vertical axis represents the activity of the catalyst, after detoxication, expressed as a percentage of its unpoisoned activity. After the addition of the detoxicating reagent, the whole charge was heated to 100° for about 10 minutes to destroy the excess of persulphate, which decomposed in the presence of the platinum. It was then cooled to 27° and hydrogenated. The close agreement of the individual hydrogenation runs with a zero-order reaction path has already been illustrated in the figures of Part I; and the slope of the linear absorption–time graphs (*i.e.*, the rate of absorption of hydrogen in c.c. per minute) was, as before, taken as a measure of the catalytic activity.

FIG. 1.

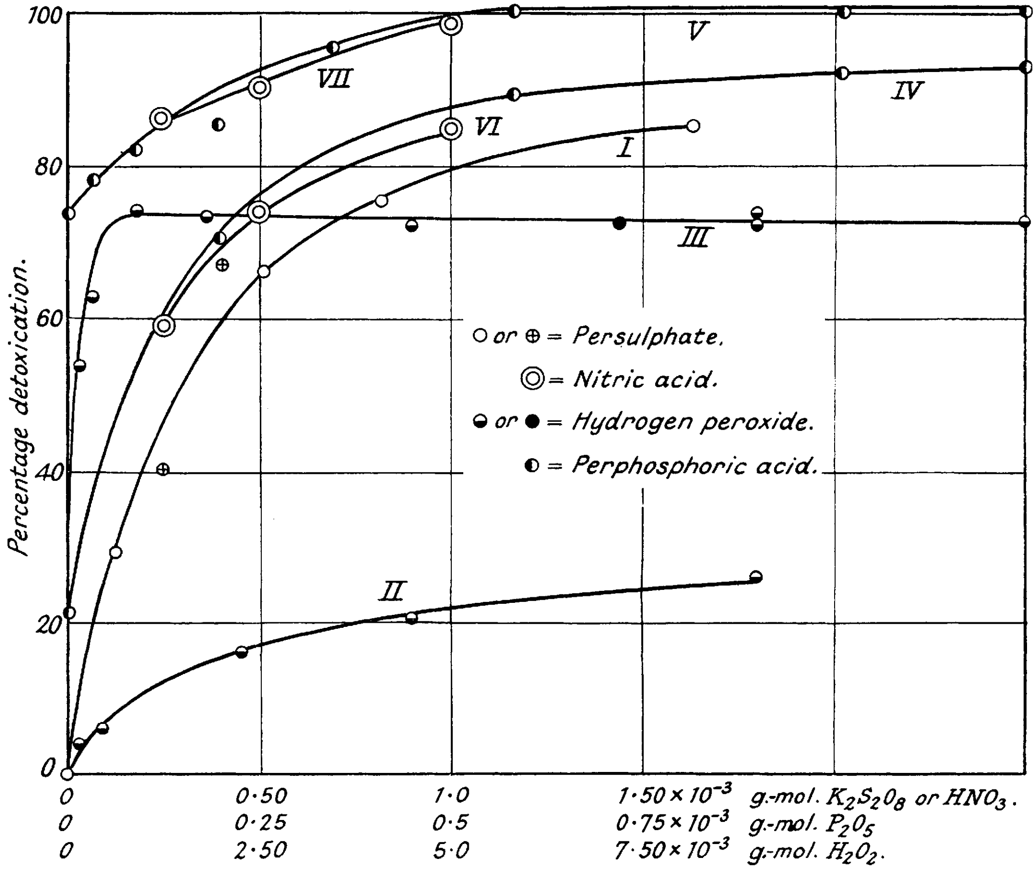


Persulphates are not very satisfactory detoxicating agents since, if they are added in quantities sufficient to cause a substantial degree of detoxication, they also attack the double bond of the unsaturated substance (see the collective table given later). For this reason, tests were not carried out with concentrations of persulphate higher than those shown in the figure. They also differ from the other detoxicants in that the addition of the reagent in more than one step, in the manner described in the next section, does not, as far as could be seen from the present tests, give an improved detoxication effect. Thus, the points denoted by crossed circles in the figure were given in runs in which the amount of persulphate indicated was added in two equal portions. It will be seen that these points fall approximately on the curve for a one-stage addition, in place of on a higher curve.

Detoxication with Hydrogen Peroxide.—The detoxicating activity of commercial specimens of hydrogen peroxide, although low for a single-stage addition, appears to be higher than was previously found: moreover, the effect obtained is greatly increased if the addition is made in stages. This also is shown in Fig. 2.

In Curve II of this figure, the hydrogen peroxide was added all at once to the charge containing the poison. In Curve III, the total amount of hydrogen peroxide indicated in the abscissæ was added in two separate equal parts. After any addition of hydrogen peroxide, the system was heated to 100° for 10 minutes to destroy the excess of peroxide. In general, the visible evolution of oxygen ceased after the first minute or so of the heating period. In many of the runs in the series involving a two-stage addition of the detoxicant, it was found convenient to measure in a single run the effect of each addition. Where this was done, hydrogenation was carried out, after the first addition of the detoxicant, for a sufficient time to determine the first reaction rate (usually until about 100 c.c. of hydrogen had been absorbed), following which the hydrogenation was interrupted,

FIG. 2.



the second part of the detoxicant added, and the hydrogenation resumed. This procedure, involving an interrupted hydrogenation run, is however not necessary, since the improved detoxication given by two-stage addition was also obtained if both portions of the detoxicant were added before beginning the hydrogenation: thus the point marked by a full black circle in Curve III resulted from the addition, before hydrogenation, of two successive charges, each of $3{\cdot}6 \times 10^{-3}$ g.-mol. of hydrogen peroxide. The form of the detoxication curve for hydrogen peroxide should be noted, in that the detoxication rose, under the conditions of Curve III, to a limiting value (about 73%) which did not increase further even if considerably greater amounts of the detoxicant were employed.

It is possible that some of the detoxication obtained with the available supplies of hydrogen peroxide may be due to its mineral acid content, since the A.R. hydrogen peroxide used for much of the work is stated to contain 10^{-6} g.-equiv. of an unspecified mineral acid per c.c. and since the efficacy of hydrogen peroxide is known to be raised by acids which react with it to form per-compounds (cf. the present results with perphosphoric acid). The effectiveness of specially purified hydrogen peroxide is being examined and will be reported later. In the meantime, the present results represent the degree of detoxication which is obtained with ordinary commercially pure peroxide.

Detoxication with Perphosphoric Acid.—Monoperphosphoric acid, H_3PO_5, is stated in the literature to result from the action of concentrated hydrogen peroxide on phosphoric oxide. In making up the solutions for detoxication, a varied small quantity of this oxide was weighed out in a stoppered tube, with precautions against access of atmospheric moisture during its transfer, and to it was added, at 0°, $4{\cdot}5 \times 10^{-3}$ g.-mol. (about 0·15 g.) of hydrogen peroxide in the form of its "100-volume" solution. The reagent was then diluted, usually with 1 c.c. of ice-cold water, and added to the hydrogenation charge containing the cystein to be detoxicated. After the usual destruction of the excess of hydrogen peroxide by heating, hydrogenation was carried out for a sufficient time to measure the detoxication. In general, in this series of tests, the effect of a second addition of $4{\cdot}5 \times 10^{-3}$ g.-mol. of hydrogen peroxide (but no further phosphoric oxide) was also measured, in a single interrupted hydrogenation run as already described in connection with detoxication by hydrogen peroxide.

It may be noted that, although no further phosphoric oxide was added with the second addition of peroxide, there is evidence that perphosphoric acid is re-formed from the additional hydrogen peroxide and the residual phosphoric acid present in the system: thus, quite small quantities of residual phosphoric acid (even of the order which remains after an imperfect washing out of a hydrogenation pipette between runs) are sufficient to raise the detoxicating activity of hydrogen peroxide to a value higher than that of hydrogen peroxide alone. It seems probable that, in this process, the hydrogen peroxide acts as an oxygen reserve for the continuous regeneration of perphosphoric acid.

The results of this series of tests are included in Fig. 2, in which Curve IV relates to a single-stage and Curve V to a two-stage addition of hydrogen peroxide to the quantity of phosphoric oxide indicated by the abscissæ. The scale for this oxide has been made one-half of that used for the persulphate, since half a molecule of P_2O_5 (as H_3PO_5) is equivalent to one molecule of $K_2S_2O_8$ from the standpoint that each gives a single atom of available oxygen. The amounts are, however, not strictly comparable on account of the action of hydrogen peroxide both as a detoxicant in itself and as a probable regenerator of perphosphoric acid.

It will be seen from the figure that far higher detoxications are obtained with this reagent than with hydrogen peroxide alone and that, in the two-stage addition curve, complete detoxication resulted with all amounts of phosphoric oxide higher than about $0{\cdot}6 \times 10^{-3}$ g.-mol. In one case, a three-stage addition of hydrogen peroxide, in increments of $4{\cdot}5 \times 10^{-3}$ g.-mol., was tried. This gave complete detoxication (absorption of hydrogen at the rate of 31·0 c.c. per minute, compared with a blank rate of 30·4 c.c.) with only 0·0045 g. ($0{\cdot}032 \times 10^{-3}$ g.-mol.) of phosphoric oxide.

Detoxication with Nitric Acid.—Since nitric acid oxidises thiols to sulphonic acids, it was considered of interest to study the effectiveness of dilute nitric acid as a detoxicant for cystein. It was added, in the form of an appropriate quantity of N- or 0·2N-solution, to the standard hydrogenation charge containing 10^{-5} g.-mol. of cystein and was of course further diluted by the water present. The system, after addition of the detoxicant, was as before heated to 100° for 10 minutes, then cooled to 27° and hydrogenated; but nitric acid, unlike hydrogen peroxide and most per-acids, has the disadvantage that any present in excess of that used in the detoxication cannot be removed by boiling. Good detoxication was however obtained, particularly for a two-stage addition. This is shown in Fig. 2, in which Curves VI and VII refer, as usual, to one-stage and two-stage addition of the detoxicant. It will be seen that substantially complete detoxication was obtained by adding two successive increments of $0{\cdot}5 \times 10^{-3}$ g.-mol. of the acid.

DISCUSSION.

In connection with all the above detoxicants, it may be noted that the percentage of cystein eliminated is, by reason of the form of the toxicity curve, considerably higher than the percentage detoxication expressed, as has been done throughout the paper, on the basis of the recovery in the hydrogen absorption rate: thus it will be seen from Fig. 1 that the destruction, by detoxication, of the first portions of cystein has little effect on the hydrogenation rate and that, for instance, a 50% detoxication (*i.e.*, a hydrogenation rate, after detoxication, of 15·2 c.c. per minute, with a blank rate of 30·4 c.c.) would correspond with a residue, in a toxic form, of only $0{\cdot}3 \times 10^{-5}$ g.-mol. out of the 1×10^{-5} g.-mol. of cystein originally present, *viz.*, with a 70% destruction of the poison.

Action of the Reagents on the Unsaturated Substance.—Detoxication has, in practice, to be carried out on small concentrations of catalyst poisons contained as impurities in a large excess of the unsaturated substance which is to be hydrogenated. For this reason it is desirable that the detoxicant should, as far as is possible, not react with the ethylenic or other unsaturated bond in this substance in such a way as to cause losses by fission. The destruction of the unsaturated substance (crotonic acid in the present work) is most readily followed by comparing the total volume of hydrogen required for saturating the standard charge, after detoxication, with the corresponding hydrogen value observed in blank runs without detoxication. Any destruction of the unsaturated substance should be more pronounced in the runs in which a relatively large amount of detoxicant has been added.

The use of the hydrogen value as an accurate measure of the amount of unsaturated substance present involves the condition that no significant amount of the reagent added for detoxication shall remain in a form in which it may itself absorb hydrogen. In the case of hydrogen peroxide and of most per-acids, the excess can, by virtue of their decomposition in the presence of the catalyst, be destroyed by boiling before the hydrogenation is begun; but, if nitric acid is used, this would probably, at the dilutions employed, largely remain as such.

The total hydrogen absorption observed with some of the higher concentrations of all the detoxicants dealt with in the present paper is contained in the following table, in which all volumes are reduced to N.T.P. In the case of perphosphoric acid, the strength is, as in Fig. 2, expressed in terms of the g.-mol. of P_2O_5 used in making up the reagent, details of which have already been given. With the exception of the persulphate, all the runs involved a two-stage application of reagent.

Detoxicant.	Amount added, g.-mol. × 10^{-3}.	Total vol. of hydrogen absorbed, c.c.
(Blank	—	223)
Persulphate	0·24	215
	0·52	214
	1·63	208
Perphosphoric acid	0·20	222
	0·58	224
	1·41	223
Hydrogen peroxide	4·5	223
	7·2	221
	9·0	225
	18·0	226
Nitric acid	0·5	226
	1·0	226

It will be seen that the persulphate is the only reagent for which there is evidence for an appreciable destruction of the unsaturated substance and that, with all the other detoxicants, the hydrogen values are within ±3 c.c. of the blank. This corresponds with the probable margin of error in adding the crotonic acid. The close agreement with nitric acid is unexpected and needs further study.

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