199. *Studies in the Detoxication of Catalyst Poisons. Part III. The Detoxication of Cystein with Metallic Per-acids.*

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This paper gives further details of the use of metallic per-acids for the suppression of the toxicity of cystein towards a platinum catalyst in catalytic hydrogenation. Complete restoration of the activity of catalysts, previously poisoned to about 1% of their original activity, was obtained by using detoxicating solutions containing small quantities of pertungstates, permolybdates or pervanadates. Pertitanates and peruranates are less effective. These reagents do not appreciably attack the double bond of the unsaturated substance undergoing hydrogenation.

A preliminary account of the use of metallic per-acids as reagents for the conversion of various types of catalyst poisons containing sulphur into derivatives which are no longer toxic towards metallic catalysts in catalytic hydrogenation has already been given (Part I, this vol., p. 204). The efficacy of some of these per-acids for the detoxication of cystein has now been studied in greater detail.

Some of the metallic per-acids (particularly pertungstic, permolybdic and pervanadic acids or their salts), which are formed by the action of hydrogen peroxide on suitable derivatives of these metals, are highly active detoxicants; and complete detoxication of the catalyst poison can be obtained by adding moderate amounts of the reagent in one step. They do not, as a class, appreciably attack the unsaturated substance which is to be hydrogenated and in which the poison is present as an impurity; moreover, they are, unlike many of the non-metallic per-acids, readily formed even from dilute hydrogen peroxide. Further, by the operation of an effect which has already been mentioned in Part II (preceding paper), it is possible to use less than the theoretical quantity of the metallic compound in the presence of an excess of hydrogen peroxide, provided that the metal taken is of such a nature that its per-acid is not reduced—either in the course of the detoxication reaction on in other ways—to a valency state lower than that from which it can be reoxidised to the per-acid state by the excess of hydrogen peroxide present. Perchromic acid does not fall into this category, since it is easily reduced in contact with organic substances to a state from which per-compounds are not re-formed directly; *e.g.*, chromic acetate, which is produced by the interaction of perchromic acid and organic substances in acetic acid solution, does not, unlike the chromates and dichromates, re-form perchromic acid with hydrogen peroxide. Chromic and perchromic acids also attack the double bond of unsaturated substances. For both of these reasons, perchromic acid has not been included in the reagents dealt with in the present paper.

Experimental.

The detoxication procedure was mainly as has been previously described, namely, a known quantity of the detoxicating solution to be tested was added at room temperature to a standard hydrogenation system containing 0·05 g. of stock platinum catalyst, suspended in 5 c.c. of a 2N-solution of crotonic acid in acetic acid and poisoned by $0{\cdot}5 \times 10^{-5}$ g.-mol. of cystein, the hydrogenation charge being made up to 10 c.c. by the addition of a further 2 c.c. of acetic acid and 3 c.c. of water (including any water or acetic acid added with the detoxicant or with the poison). The detoxicating solutions were made by mixing dilute potassium tungstate, potassium molybdate or sodium vanadate with a solution of hydrogen peroxide prepared by the suitable dilution of A.R. " 20-volume " peroxide. The percentage of metal (tungsten, etc.) in the compounds used for making up the reagents was checked by analysis. The pertitanate and peruranate solutions were made by adding hydrogen peroxide to dilute titanous sulphate and to a solution of uranium trioxide in acetic acid, in which it is slightly but sufficiently soluble. After the addition of the detoxicating reagent to the charge containing the poisoned platinum, this charge was heated to 100° for 15 minutes to destroy the excess of peroxide and hydrogenated in a shaker at 27°, the degree of detoxication being assessed by comparing the observed hydrogenation rate with that given under similar conditions by the same amount of catalyst in an unpoisoned state. This unpoisoned rate was determined for each series by blank runs in the absence of poison and corresponded with a zero-order hydrogen absorption of slightly more than 30 c.c./min. The standard charge of poison, *i.e.*, $0{\cdot}5 \times 10^{-5}$ g.-mol. of cystein, was sufficient, in the absence of detoxicants, to reduce this rate to a negligible value (0·3 c.c./min.).

Two types of curve were determined. In the first, the amount of metal was varied, the amount of hydrogen peroxide being kept constant; in the second, the peroxide was varied, the metal content being maintained at a constant value.

The results obtained are summarised in Figs. 1 and 2, in which the ordinates represent the hydrogenation rates, after detoxication of the cystein, expressed as a percentage of the unpoisoned rate. In Fig. 1, the hydrogen peroxide was kept constant at 0·051 g. This amount corresponds with $1{\cdot}5 \times 10^{-3}$ g.-mol. and, although small, is sufficient to provide 100 times the oxygen theoretically required for the oxidation of the very small quantity of cystein present to non-toxic cysteinic acid. In Fig. 2, the quantity of the metallic salt added to form a per-acid with the peroxide corresponded in every case with $0{\cdot}75 \times 10^{-5}$ g.-atom of the metal specified.

FIG. 1.

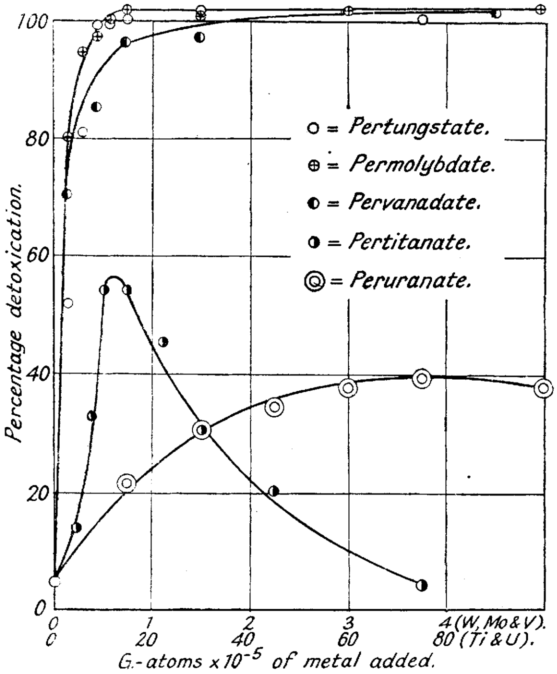
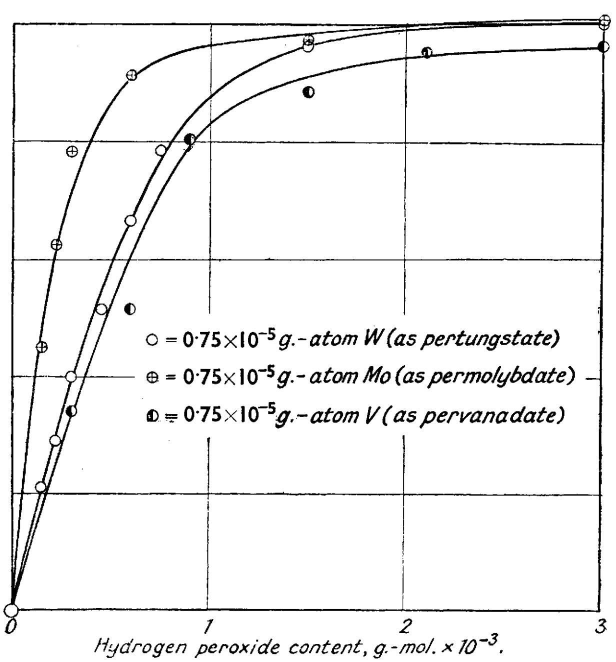


FIG. 2.



It will be seen from Fig. 1 that complete detoxication was obtained with all amounts of pertungstate or permolybdate higher than that corresponding with $0{\cdot}75 \times 10^{-5}$ g.-atom of tungsten or molybdenum and that pervanadates are only slightly less active detoxicants. Actually, the hydrogenation rates after detoxication were in some cases slightly higher than in the blank runs, this effect being probably due to the cleaning up of traces of original poisons present in the catalysts used. The extent of this small additional activation is illustrated, for the typical case of permolybdates, in the following table.

Mo content of system, g.-atoms $\times 10^{-5}$.	Hydrogenation rate, c.c./min.	Percentage of unpoisoned rate.
Blank runs	31·6—32·0	—
0·6	32·0	100
0·75	32·7	102
1·5	32·4	101
3·0	32·7	102
5·0	32·8	102

In addition to the curves given in Fig. 1, a second series of points was also determined, for both tungsten and molybdenum, in the presence of one-half (0·026 g.) of the above amount of hydrogen peroxide. This gave somewhat similar curves, with however a maximum detoxication of only about 95%.

Fig. 1 also shows the far lower detoxication obtained with pertitanates and with peruranates. This will be seen both from the curves and from the change in the scale of abscissæ to 20 times that used for tungsten, molybdenum and vanadium. Since a decrease in the effective detoxication with increasing amounts of the detoxicating agent may be due either to catalytic toxicity inherent in the detoxicant itself or to traces of toxic metals present as impurities in the specimens used, tests were carried out in order to determine whether pertitanates or peruranates are themselves appreciably poisonous. This was found not to be the case, since hydrogenation rates substantially equal to the blank rate were obtained with peruranates and with pertitanates in the absence of cystein. Actually, the rather sharp fall in the activity of the catalyst with concentrations of titanium higher than about 15×10^{-5} g.-atom was evidently due to the formation, in the dilute acetic acid solution used, of a visible precipitate (probably of free titanic or pertitanic acid), which reduced the activity of the platinum by a cloaking effect increasing with the amount of the titanium compound added.

Action of the Reagents on the Unsaturated Substance.—The degree of attack on the double bond of the unsaturated substance by the more effective metallic per-acids was tested, in the way already described in Part II, by comparing the hydrogen value of the charges before and after detoxication.

The total volumes (reduced to N.T.P.) of hydrogen absorbed, in runs carried out to completion, by the 5 c.c. of 2N-crotonic acid used in the standard charge are given in the following table. In the blank runs, no poison or per-acid was present. In the remaining runs, the usual detoxication of 0·5 × 10^{-5} g.-mol. of cystein was carried out by adding the specified amount of the metallic salt and 0·051 g. of hydrogen peroxide (together with acetic acid and water, as before), the excess of peroxide being destroyed by boiling the charge before the hydrogenation. The probable margin of error in adding the 5 c.c. of 2N-crotonic acid, from a pipette, is of the order of 0·05 c.c. (1 drop), which is equivalent to 2·3 c.c of hydrogen. This is also the order of the observed fluctuation in the hydrogen absorption values (230 ± 2 c.c.). There seems accordingly to be no indication of an appreciable attack on the double bond.

Metal (as pertungstate, etc.).	Amount of metal added, g.-atoms × 10^{-5}.	Total vol. of hydrogen absorbed, c.c.	Metal (as pertungstate, etc.).	Amount of metal added, g.-atoms × 10^{-5}.	Total vol. of hydrogen absorbed, c.c.
Blank	0	229	Tungsten	3·75	229
,,	0	232	,,	7·5	232
Molybdenum	1·5	230	Vanadium	1·5	229
,,	3·0	231	,,	4·5	231
,,	5·0	229	,,	7·5	232

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