

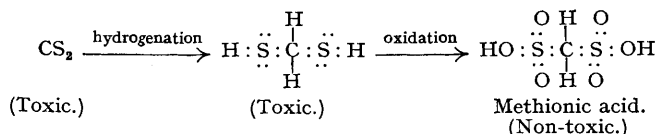
8. Studies in the Detoxication of Catalyst Poisons. Part IV. Detoxication of Carbon Disulphide.

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The suppression of the catalytic toxicity of small concentrations of carbon disulphide, contained as a poison in a hydrogenation system catalysed by platinum, has been examined. Complete detoxication of the poison was obtained by the use of reagents containing permolybdic or perphosphoric acid in the presence of an excess of hydrogen peroxide. Hydrogen peroxide alone was less effective. A further study has also been made of the greatly increased detoxication effect obtained by adding the detoxicating reagents in more than one step.

CARBON disulphide is of considerable practical interest as a poison in catalytic hydrogenation, since it accompanies thiophen in technical benzene. Its detoxication has been carried out by the general method used in Parts I, II, and III of this series (*J.*, 1945, 204, 763, 766), namely, by conversion into a "shielded" form in which the normally poisonous sulphur atom loses its toxic character by virtue of the presence of a completely shared electron octet (*J.*, 1940, 252; 1941, 132).

With carbon disulphide, as in earlier work with thiophen, the oxidising reagent was applied after a short period of preliminary hydrogenation, during which the preferentially absorbed poison apparently undergoes preferential hydrogenation to a derivative which, although still toxic and accordingly still obstructively adsorbed by the catalyst, can be more readily oxidised than carbon disulphide itself. Under these conditions, complete detoxication was easily obtained, whereas, if the initial hydrogenation stage is omitted, the detoxication fails. It is probable that the intermediate hydrogenation product formed from carbon disulphide is methylenedithiol, $\text{CH}_2(\text{SH})_2$ (Sabatier and Espil, *Bull. Soc. chim.*, 1914, 15, 228) and that the course of the detoxication is:



In the above scheme the electronic unsaturation and subsequent saturation of the sulphur atoms only are indicated.

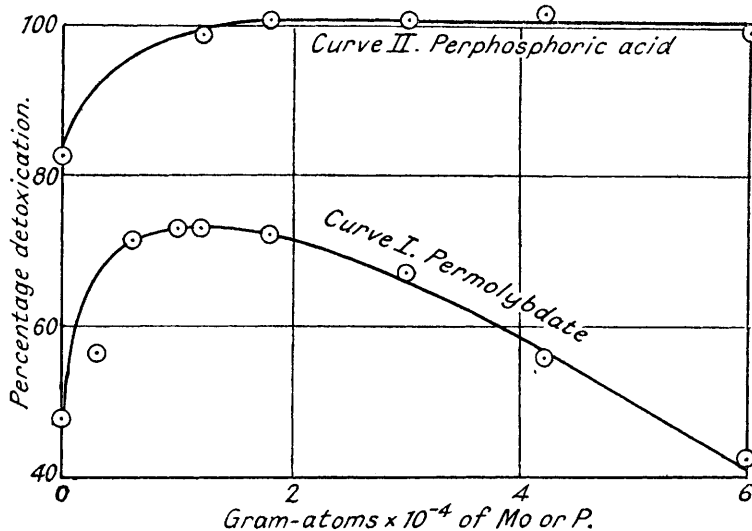
EXPERIMENTAL.

The general technique was similar to that described in earlier papers. The standard hydrogenation charge taken for each run consisted of 0.05 g. of stock platinum-black, suspended in 5 c.c. of a 2*N*-solution of crotonic acid in acetic acid and poisoned in each case by 10^{-5} g.-mol. of carbon disulphide, the system being made up to a total volume of 10 c.c. by 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 poison or with the detoxicant. This amount of carbon disulphide was sufficient, while in its normal toxic state, to poison the catalyst substantially completely.

Before addition of the detoxicants, the system was hydrogenated for 15 minutes, at 27°, for the necessary preliminary reduction of the carbon disulphide. During this initial shaking, a small volume of hydrogen, usually of the order of 2 c.c., was absorbed rapidly in the first minute or so, corresponding not only with the above reduction but also with the clean up of oxygen adsorbed on the platinum catalyst and with solution of hydrogen in the liquid and its adsorption on the catalyst; and the hydrogenation then proceeded at a steady rate of less than 0.1 c.c. per minute, which represents the poisoned rate. The system was then removed from the hydrogenation shaker and detoxicated by addition of a known amount of the detoxicating reagent under the conditions described for each series. After destruction of the excess of detoxicant (per-acid and hydrogen peroxide) by heating, the detoxicated charge was re-connected to the hydrogenation apparatus, and the rate of hydrogenation, at 27°, was measured in order to determine the extent to which the poisoned catalyst had recovered its unpoisoned activity. This original activity, which was determined in blank runs without poison, corresponded with the absorption of hydrogen at the rate of 23.6 c.c. per minute.

Detoxication with Permolybdate.—Detoxication was carried out, as before, by adding dilute, aqueous potassium molybdate followed by an excess of hydrogen peroxide to the standard hydrogenation charge containing the poisoned catalyst. Two types of detoxication curve were plotted. In the first, the amount of hydrogen peroxide added was kept constant and the amount of molybdenum salt varied; in the second, the molybdenum content was kept constant and the hydrogen peroxide varied, the detoxication observed being in each case plotted against the variable.

FIG. 1.



Curve I of Fig. 1 gives the result of a series of runs in which the hydrogen peroxide was maintained at 6×10^{-3} g.-mol. (0.2 g.), added in one step, while the molybdate was varied up to a value corresponding with 6×10^{-4} g.-atom of Mo. It will be seen that a maximum detoxication of about 75% was obtained with a little over 1×10^{-4} g.-atom of Mo, and that the detoxication then fell if the molybdenum content was further increased. Since a visible precipitate is formed on adding the larger concentrations of molybdate, this effect (which is similar to that previously observed with peruranates and pertitanates) is probably due to the cloaking of the catalyst by the precipitate. For this reason, the detoxication curves with varying hydrogen peroxide content were determined in the presence of molybdate kept constant at 1.2×10^{-4} g.-atom of Mo.

Three series of this type are summarised in Fig. 2. In Curve I of this figure, the hydrogen peroxide was added all at once. In Curve II the total amount of peroxide indicated by the abscissæ was added in two, and in Curve III in four, equal increments. The increased detoxicating effect obtained by this stepwise addition, compared with the effect of adding the same total amount all at once, has already been discussed in Part II. It may be noted that, in the runs of Curve II, the system which was being detoxicated was, after each addition of peroxide, heated to 100° and re-cooled to room temperature for the next addition, whereas in Curve III the system was, after the first addition, heated to 80–85° and maintained at this temperature, subsequent additions being made at intervals of about 15 minutes without intermediate cooling. The temperature was, of course, brought down to 27° for the hydrogenation run. It was not practicable, with the small volumes used in the present tests, to add the detoxicant in more than four steps; but the good detoxication obtained under the conditions of Curve III suggests a continuous addition, drop by drop, as an effective detoxication procedure on a larger scale.

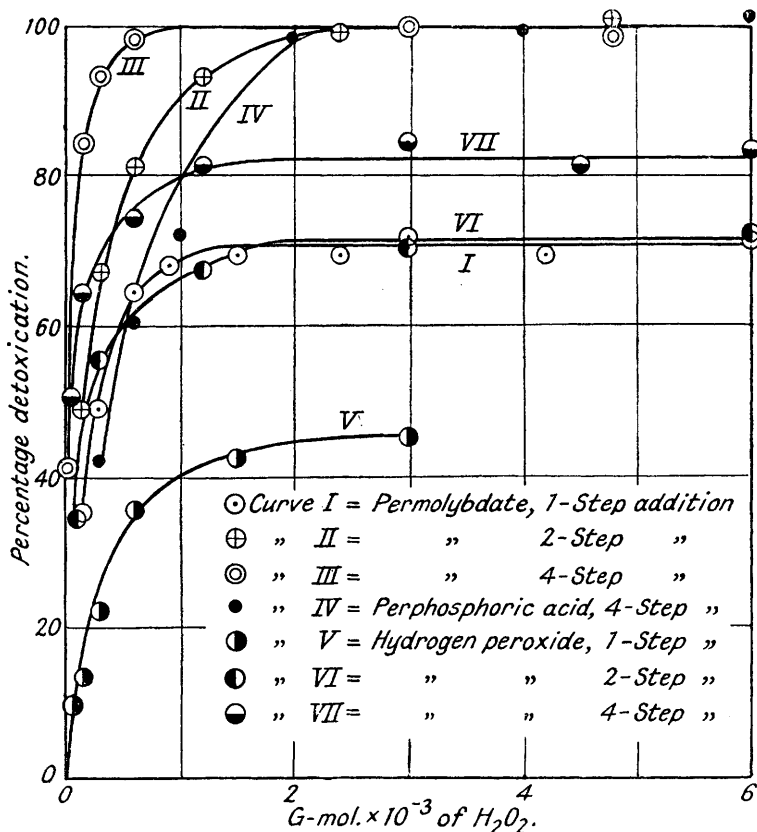
Detoxication by Perphosphoric Acid.—The reagent used (perphosphoric acid in the presence of excess of hydrogen peroxide) was made as described in Part II, namely, by acting on phosphoric oxide with an excess of 30% hydrogen peroxide at 0°, precautions being taken against access of moisture to the pentoxide during the weighing out and at all stages up to its interaction with the peroxide. The reagent could then be diluted with a convenient small quantity of ice-cold water and could be kept for about 2 days at 0° without appreciable loss in its effectiveness as a detoxicant. This allowed sufficient reagent (usually 5 c.c.) for a number of runs to be made up from one weighing of phosphoric oxide.

As before, two types of detoxication curve were plotted. In Curve II of Fig. 1, the amount of the phosphorus component (weighed as P_2O_5) was varied, the total hydrogen peroxide being kept constant at 6×10^{-3} g.-mol., which was

added in four equal increments. It will be seen that complete detoxication was reached with reagent containing about 1.8×10^{-4} g.-atom of phosphorus (0.013 g. of P_2O_5). Actually, the activity of the detoxicated catalyst was usually slightly above its unpoisoned activity, this being probably due to the cleaning up of small traces of original poison contained in the catalyst itself.

A detoxication series of the second type, in which the phosphorus component was kept constant at 0.01 g. of P_2O_5 (1.4×10^{-4} g.-atom P) and the hydrogen peroxide was varied, is summarised by Curve IV of Fig. 2. As in the previous perphosphoric acid series, the peroxide was added in four equal increments, the first addition (as reagent) being made at room temperature and the remaining additions (hydrogen peroxide alone) at $80-85^\circ$ without intermediate cooling. Complete detoxication was reached at a somewhat higher hydrogen peroxide content than in the corresponding 4-step

FIG. 2.



permolybdate curve (Curve III), namely, at slightly more than 2×10^{-3} g.-mol. of hydrogen peroxide in place of 1×10^{-3} g.-mol.

Detoxication of Carbon Disulphide by Hydrogen Peroxide Alone.—It has been shown in previous papers that hydrogen peroxide, even in the absence of a per-acid, is capable of bringing about some detoxication of cystein and that the effect, although less than that induced by using a suitable per-acid, can be increased by addition in more than one step. Similar results have been observed for the detoxication of carbon disulphide. This is shown in Curves V, VI, and VII of Fig. 2, which relate to this use of hydrogen peroxide by itself and summarise the effect of adding the total amount of peroxide indicated by the abscissæ respectively in 1, 2, and 4 equal steps. In Curve VI (2-step addition), hydrogenation at 27° under standard conditions was carried out between the addition of the two increments in order to allow a point on Curve V (1-step addition) to be determined in the same run. In Curve VII (4-step addition) the first increment was added at room temperature, and the remaining increments at $80-85^\circ$ without intermediate cooling. The reaching of a maximum detoxication value—in each case well below 100%—which is not increased by a further increase in the total hydrogen peroxide used for the detoxication should be noted, this effect being similar to that previously observed for cystein.

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