307. *Studies in the Detoxication of Catalyst Poisons. Part IX.* Dimethylphenylphosphine.*

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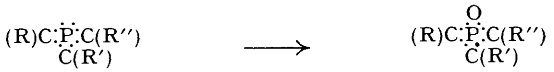
The response of this substituted phosphine to chemical detoxication by methods which have previously been used for poisons containing sulphur has been studied. The induced non-toxicity, rather surprisingly, persists in this case only if the subsequent tests for non-toxic character are made in an oxidising system. It has also been found that dimethylphenylphosphine adsorbed on platinum can be easily and completely desorbed by the washing process which forms an alternative to chemical detoxication in the revival of poisoned catalysts.

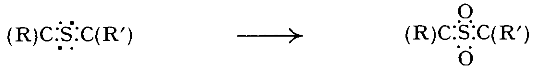
Previous papers in this series (*J.*, 1945, 204, 763, 766; 1946, 23; 1947, 624; 1948, 1091, 1093, 1916; *J. Soc. Chem. Ind.*, 1948, **67**, 93; *Chem. and Ind.*, 1951, 242) have dealt mainly with the detoxication of catalyst poisons containing sulphur by processes involving a change in the electronic configuration of the sulphur atom from an unshielded into a shielded and therefore non-toxic state. It has now been considered of interest, first, to study the effect of similar treatment on the toxicity of a poison containing phosphorus and, secondly, to examine the efficacy of the alternative desorption or washing procedure (*J.*, 1952, 4284) when this is applied to the revivification of a catalyst poisoned by a phosphorus compound.

As a suitable available poison for this work, dimethylphenylphosphine has been taken. Alkyl- or aryl-phosphines of the type PR_3 may be regarded as phosphorus analogues of the corresponding sulphides, SR_2, and it accordingly appeared probable that a change to the corresponding oxide by an oxidative process comparable with the conversion of an organic sulphide into a non-toxic sulphone, *viz.* :



$$(R)C:\overset{\cdot\cdot}{\underset{C(R')}{P}}:C(R'') \longrightarrow (R)C:\overset{O}{\underset{C(R')}{P}}:C(R'')$$

compared with :



$$(R)C:\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}:C(R') \longrightarrow (R)C:\overset{O}{\underset{O}{S}}:C(R')$$

Sulphide (unshielded, toxic type)

Sulphone (shielded, non-toxic type)

(in which the electronic configurations of the phosphorus and sulphur atoms only have been indicated) should readily lead to the required detoxication.

In order that the non-toxicity of the shielded derivative may persist under the conditions of the hydrogenation tests used to assess the degree of detoxication, it is necessary that the shielded derivative formed should not undergo reductive reversion to a toxic state under these conditions. It has been shown that this reversion does not occur with the derivatives (sulphones or sulphonic acids) formed from the common sulphur poisons, provided that the temperature used in these tests is not too high; and it seemed probable that the oxidation products of substituted phosphines also would conform to this requirement. It has, however, rather unexpectedly been found that detoxication obtained by the action of oxidants on dimethylphenylphosphine persists only if the subsequent assessment of non-toxicity is carried out in an oxidisng system instead of by catalytic hydrogenation tests.

In contrast to this anomalous behaviour of dimethylphenylphosphine with respect to chemical detoxication, the revivification of a platinum catalyst previously poisoned with dimethylphenylphospine takes place completely and without complications by desorptive

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* Part VIII, *J.*, 1948, 1916.

washing with a suitable solvent. The latter method involves no preliminary change of the chemical form of the poison into a non-toxic state; but the simple desorption is assisted by a displacement of the adsorbed poison from the catalyst surface into the free liquid phase by reason of the competitive adsorption of the unsaturated substance used in the subsequent hydrogenation tests.

EXPERIMENTAL

The platinum catalyst was taken from a stock made from chloroplatinic acid by alkaline formate reduction. This stock had previously been washed repeatedly in a shaker, and then centrifuged before each change of the washing water, until a stable activity, unaffected by further washing, had been reached. The dimethylphenylphosphine was applied in acetic acid, as a stock solution containing 10^{-5} mole of the poison per c.c. The detoxicating reagents used in the chemical detoxication tests consisted of very dilute solutions of permolybdic or perphosphoric acid, the general procedure used in applying these being similar to that already described in detail for the detoxication of sulphur compounds (see below).

Chemical Detoxication.—In the first part of this work, the effect of the detoxication treatment was followed by hydrogenation tests carried out in a hydrogenation shaker under standardised conditions at 30°. The following results were obtained in a series of three hydrogenation runs, using (i) a poison-free blank charge containing 0·025 g. of stock platinum catalyst suspended in a 15-c.c. liquid system made up of 12·5 c.c. of acetic acid, 2 c.c. of water, and, as an unsaturated substance for hydrogenation, 0·5 c.c. of *cyclo*hexene, (ii) a similar charge poisoned by the addition of 10^{-5} mole of dimethylphenylphosphine, and (iii) a similarly poisoned charge which had, before the hydrogenation test, been treated with 3×10^{-5} mole of permolybdic acid together with three additions of 0·15 g. of hydrogen peroxide and subsequent destruction of the excess of peroxide and per-acid by heating to 100°, after which the system was cooled to 30° for the hydrogenation test. The observed rates of hydrogen adsorption in the above three tests were (i) 34, (ii) 4·2, and (iii) 8·8 c.c. per min. for the blank, poisoned, and detoxicated runs, respectively. Accordingly, the degree to which the substituted phosphine has lost its toxic character as a result of treatment with permolybdic acid, under conditions which have previously been found to lead to the complete detoxication of a sulphur-containing poison, is not very great. A similar result was obtained in a further series of three runs in which perphosphoric acid was substituted for permolybdic acid as the detoxicating reagent.

Dimethylphenylphosphine is known to be oxidised easily; and it would be expected that the resulting oxide would resist subsequent reduction. However, since its failure to respond substantially to the above detoxication treatment might be due either to incomplete oxidation to a shielded derivative or to the reversion of this derivative to a toxic form during the hydrogenation process, it was of interest to try to detoxicate this poison with a per-acid as before and then to assess the degree of the response by means of a catalytic reaction carried out in an oxidising system, namely, for the decomposition of hydrogen peroxide, in place of by a hydrogenation test.

In this series, the system to be detoxicated was contained in a reaction pipette provided with a separate reservoir by means of which the charge of hydrogen peroxide required for the activity test could be added without opening the system. The detoxication preceding the test was carried out as before, namely, by adding to the poisoned system, at room temperature, a reagent containing a small quantity of perphosphoric or permolybdic acid in the presence of hydrogen peroxide and subsequently destroying the excess of per-acid and peroxide by heating to 100° until no more oxygen was evolved, the pipette being then closed by plugging in the small reservoir containing the further charge of hydrogen peroxide. This closed system was immersed in a thermostat at 20° and, after the reservoir-plug had been turned to admit the additional peroxide to the detoxicated charge, the pipette was shaken gently, by means of a mechanical shaker operating at a constant speed, in connection with a gas burette in which the rate of evolution of oxygen corresponding with the decomposition of the hydrogen peroxide during the test could be measured. It was found that, in order to obtain convenient rates of oxygen evolution, a somewhat larger charge than that used in the hydrogenation tests was preferable; and, in this series, the volume of liquid originally contained in the pipette was 58 c.c., to which was added, from the reservoir, a further charge made up of 2 c.c. of hydrogen peroxide (approx. 100-vol.) and 5 c.c. of water.

Results in the usual series of three tests, consisting of a blank run, a poisoned run, and a run after the detoxication of the poisoned system, are summarised in Fig. 1. In this, Curve II is the poisoned run obtained with a system containing 2·5 × 10^{-4} mole of dimethylphenylphosphine in 8 c.c. of acetic acid, 50 c.c. of water, and 0·025 g. of platinum catalyst, the testing charge of 7 c.c. of dilute hydrogen peroxide being added as already described. Curve III was given by a similarly poisoned system after this had been detoxicated by adding 3·5 × 10^{-5} mole of perphosphoric acid together with three additions of 0·15 g. (*ca.* 5 × 10^{-3} mole) of hydrogen peroxide and subsequent destruction of the excess of per-acid and hydrogen peroxide by heat before placing the pipette in the thermostat and adding the 7-c.c. charge of hydrogen peroxide for the activity test. In the blank run (Curve I) the poison was omitted; and, save for this omission, the system and its subsequent treatment were identical with those used for Curve III.

These results were confirmed by a further series of three tests in which permolybdic acid was used as the detoxicating reagent in place of perphosphoric acid and which gave curves approximating to those of Fig. 1. It will be seen that, although complete detoxication was not quite reached, the degree of disappearance of the toxicity of the poison as a result of the detoxication treatment is far greater when the subsequent activity test involves hydrogen peroxide decomposition than when catalytic hydrogenation is used for this assessment. As already stated, this result differs from those obtained with sulphur poisons.

FIG. 1. *Detoxication of dimethylphenylphosphine.* (Hydrogen peroxide decomposition tests.)

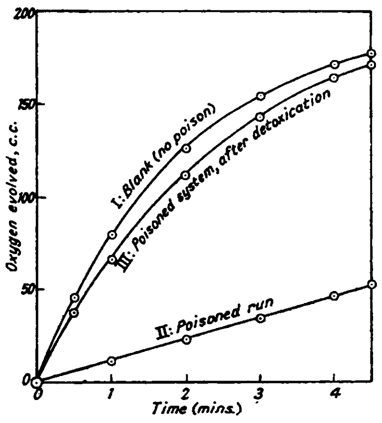
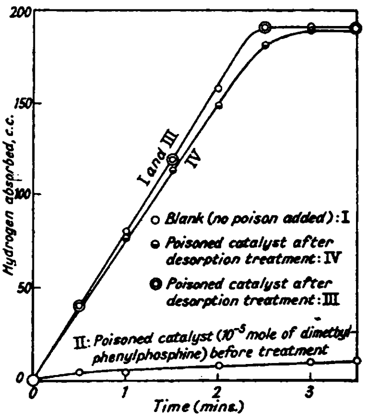


FIG. 2. *Removal of dimethylphenylphosphine from platinum.*



Removal of Dimethylphenylphosphine from Platinum Catalysts by Desorption.—It was found that dimethylphenylphosphine can be easily and completely removed by the desorptive washing method from catalysts inactivated by this poison.

In this section of the work, 0·025 g. of platinum was suspended in a hydrogenation system consisting of 9 c.c. of acetic acid and 1 c.c. of *cyclo*hexene and poisoned by the addition of 10^{-5} mole of dimethylphenylphosphine. The rate at which this poisoned catalyst induces hydrogenation was then tested in a hydrogenation shaker at 30°. Curve II of Fig. 2 gives this activity compared with the activity of a similar charge of unpoisoned catalyst in a blank run (Curve I) in which the poison was omitted. In order to examine the ease with which this poison can be removed from the platinum by desorption, the catalyst, after having been poisoned with 10^{-5} mole of dimethylphenylphosphine, was separated from the supernatant liquid by centrifuging and decantation and washed for two successive periods of 30 min. each, first with 10 c.c. of acetic acid and then (after again centrifuging and decanting off the liquid) with a normal hydrogenation charge consisting of 10 c.c. of acetic acid containing 1 c.c. of *cyclo*hexene, these washings being carried out by shaking in a closed pipette in the absence of hydrogen. Admitting hydrogen and carrying out the hydrogenation test by means of which the recovery in the activity of the platinum was assessed gave Curve III, showing a complete restoration of the activity of the previously poisoned catalyst: indeed, in a further test with a similarly poisoned catalyst, an almost complete extraction of the poison from the catalyst was reached even after one change of the supernatant liquid (Curve IV).

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