

628. *The Reversibility of the Adsorption of Catalyst Poisons.  
Part II.\* Derivatives of Arsenic.*

By E. B. MAXTED and G. T. BALL.

Platinum hydrogenation catalysts poisoned at room temperature by a stable arsenic derivative such as dimethylphenylarsine can be revived easily and completely by desorbing the poison by the competitive adsorption of an unsaturated compound (*cyclohexene*). At higher temperatures, complications arise owing to the decomposition of the poison on the platinum surface; and the degree of revival is incomplete. Poisons such as arsenious oxide or potassium antimonyl tartrate, which readily pass into arsine or stibine under hydrogenating conditions, resist desorptive revival even at room temperature, since the arsine or stibine readily decomposes into a non-desorbable form.

THE revival of hydrogenation catalysts which have been poisoned by arsenic or antimony compounds is of interest since this type of poison cannot be rendered permanently innocuous by chemical detoxication, in that the shielded and therefore non-toxic derivatives formed by the usual detoxication treatment are converted, under hydrogenating conditions, into toxic arsine or stibine.

In the present paper, the effectiveness of the alternative revivification method (Part I\*) involving a desorption, and especially a desorptive displacement of the adsorbed poison from the catalyst surface by the competitive adsorption of an unsaturated substance, has been examined for catalysts poisoned by derivatives of arsenic. If the poisoning of the catalyst has been carried out at room temperature with a relatively stable arsenic derivative, such as a substituted arsine (dimethylphenylarsine), it has been found that this desorptive method leads to an easy revival to a state in which the catalyst completely regains its unpoisoned activity. The degree of the possible revival is, however, diminished if the catalyst containing the adsorbed poison is heated to 100°, this effect being probably due to the decomposition of part of the poison into a non-desorbable form. This decomposition effect occurs even at room temperature if the catalyst has been poisoned by arsenic or antimony compounds which are known readily to form arsine or stibine under hydrogenating conditions. The probability that the failure to revive such catalysts by desorption is due to decomposition, rather than to an initially irreversible adsorption, is

\* Part I, *J.*, 1952, 4284.

strengthened by previous and somewhat parallel work with hydrogen sulphide. In this much earlier work (Maxted, *J.*, 1919, **115**, 1050) it was found that, if hydrogen sulphide is adsorbed on palladium and the adsorption complex evacuated at 100°, hydrogen in place of hydrogen sulphide is pumped off and the sulphur is retained as a sulphide by the metal; and it seems probable that arsine or stibine would decompose even more easily, especially by reason of the weakness of the arsenic-hydrogen or antimony-hydrogen bonds (heats of formation of  $H_2S = +5.3$ ;  $AsH_3 = -43.5$ ;  $SbH_3 = -34.8$  kcal.).

#### EXPERIMENTAL

The stock of catalyst, from which 0.025-g. portions were weighed out as required, was made from chloroplatinic acid by alkaline formate reduction, the precipitated platinum being washed exhaustively in a shaker, with separation of the black by centrifuging between the individual washes, before being dried at 100°. The poisons were applied in acetic acid solution, and the revival of the poisoned catalyst, as a result of successive displacements of the adsorbed poison by cyclohexene, was followed by means of hydrogenation runs.

*Revival of Catalysts poisoned by Dimethylphenylarsine.*—This poison was taken as a convenient arsenic derivative which is not too easily decomposed by platinum in the presence of hydrogen. In a series of revivification tests, results of which are summarised in Fig. 1, 0.025 g. of platinum catalyst was poisoned by treatment in a closed pipette at room temperature with  $2 \times 10^{-4}$  mole of dimethylphenylarsine in 9 c.c. of acetic acid, the system being allowed to remain for 16 hr., with occasional shaking in order to allow the adsorption of the poison to proceed. In order to measure the activity of the poisoned catalyst by means of a hydrogenation run, 1 c.c. of cyclohexene (which is necessary to complete the hydrogenation system but unavoidably causes some of the poison to move from the catalyst surface into the free phase) was next added. Hydrogen was then admitted to the pipette, and the system was shaken in a hydrogenation shaker under standardised conditions at 30°. This hydrogenation test with the poisoned catalyst is shown in Curve II. Curves III, IV, and V show the progressive displacement of the poison, indicated by the gradual recovery in the activity of the platinum, as the result of washing the poisoned catalyst prior to the new hydrogenation test, respectively with one, two, and three fresh charges of cyclohexene, each wash being carried out by separating the platinum from the supernatant liquid in a centrifuge, decanting this liquid, and shaking the platinum at room temperature in the absence of hydrogen with a fresh displacement charge consisting of 1 c.c. of cyclohexene and 9 c.c. of acetic acid. It will be seen that a complete recovery of the original activity, shown in Curve I which represents a blank hydrogenation run carried out with a charge from which the poison had been omitted, was obtained after three washes with the unsaturated substance: indeed, this limit was very nearly approached even after two washes.

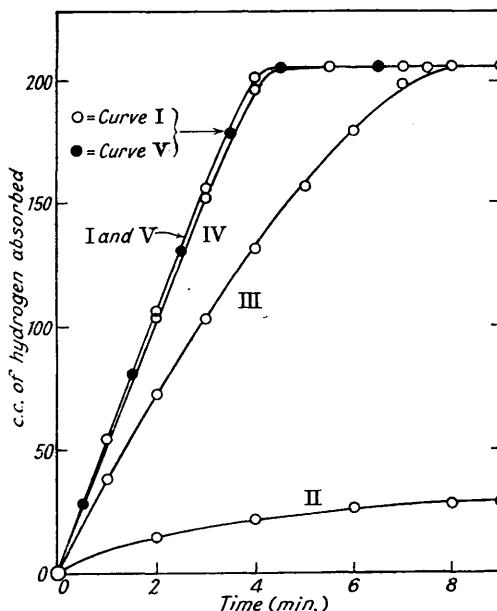
As a slight variation in the above procedure, the initial hydrogenation run with a poisoned catalyst was, in a further series, carried out with platinum which had been poisoned by allowing  $2 \times 10^{-4}$  mole of the poison, in the standard hydrogenation charge, to remain in contact with the platinum for 30 min. only, with continuous shaking, instead of for 16 hr. as before. In this case, the degree of poisoning obtained was less than for the longer time of contact; *e.g.*, the hydrogenation run with the poisoned catalyst gave an absorption of 33.4 c.c. of hydrogen after 3 minutes' hydrogenation, compared with 18.9 c.c. for the longer poisoning time under otherwise identical conditions; but the revival, on washing of the poisoned catalyst with successive charges containing cyclohexene, took place normally. Thus, after two washes of the poisoned platinum with cyclohexene, the activity was restored to a value equal to that given in a blank run with fresh unpoisoned catalyst.

*Revival of Catalysts poisoned at a Higher Temperature.*—In this series, the initial poisoning of the catalysts, prior to the revivification treatment, was carried out at 100° instead of at room temperature. In the set of hydrogenation curves contained in Fig. 2, Curve II shows the activity of 0.025 g. of catalyst poisoned by being previously shaken for 2 hr. at 100° in a closed pipette with  $2 \times 10^{-4}$  mole of dimethylphenylarsine in 9 c.c. of acetic acid. The subsequent revivification procedure—the results of which are given in Curves III, IV, and V—was similar to that used for the corresponding series of Fig. 1. With the catalyst poisoned at this higher temperature, the original activity, as shown in the blank run (Curve I), was not reached as a result of the revivification treatment, in that the exposure of the poison to a temperature of 100°, in contact with the platinum, apparently induces a partial change into a form in which it can no longer be removed by desorptive displacement with cyclohexene. The limit of its

removal seems to be reached after two successive treatments with the unsaturated substance, since Curve IV (two washes with *cyclohexene*) is identical with Curve V (three washes).

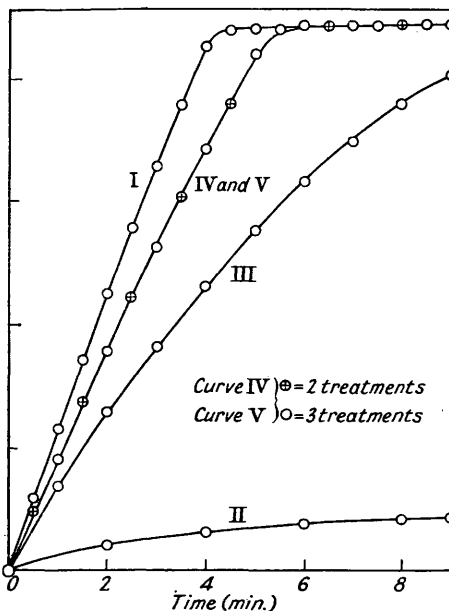
This existence of a limit to the desorptive revival of catalysts poisoned at higher temperatures was confirmed by two other series of tests. In the first of these, the poisoning time at 100° was reduced from 2 hr. to 30 min., under which conditions slightly less poison was adsorbed, and the activity of the poisoned platinum was accordingly a little greater than in Curve II of Fig. 2; but the limit of the revival by subsequent repeated washing with *cyclohexene* did not differ appreciably from that in the preceding series. Very similar results were obtained by reducing the adsorption of poison in the initial poisoning operation by adding the dimethylphenylarsine to a complete hydrogenation change (namely, in the presence of the 1 c.c. of *cyclohexene* required as an unsaturated substance, in place of in the presence of acetic acid alone, during a 2 hr.')

FIG. 1. Desorptive displacement of  $\text{AsMe}_2\text{Ph}$  from Pt. Poisoning temp. = 20°.



- I (blank) and V. (3 Treatments.)  
 II. Poisoned catalyst before treatment.  
 III. Poisoned catalyst after one treatment with *cyclohexene*.  
 IV. (2 Treatments.)

FIG. 2. Desorptive displacement of  $\text{AsMe}_2\text{Ph}$  from Pt. Poisoning temp. = 100°.



- I. Blank (no poison added).  
 II. Poisoned catalyst before treatment.  
 III. Poisoned catalyst after one treatment.

poisoning time at 100°). The subsequent revival by washing with successive charges containing *cyclohexene* did not greatly pass beyond the limiting value shown in Fig. 2.

*Attempted Desorptive Revival of Platinum poisoned with Arsine or Stibine.*—It is known that arsenious oxide, on treatment with nascent hydrogen, or with hydrogen in the presence of platinum, readily passes into arsine. In the present work, 0.025 g. of the stock platinum catalyst was first poisoned by being shaken for a few minutes in hydrogen at room temperature with a known amount of arsenious oxide dissolved in 9 c.c. of acetic acid, following which 1 c.c. of *cyclohexene* was added and the system subjected to the usual hydrogenation run at 30°. It was found that the platinum was extremely sensitive to arsenic in this form and that the use of  $10^{-5}$  g.-atom of arsenic ( $5 \times 10^{-6}$  mole of  $\text{As}_2\text{O}_3$ ) was sufficient to reduce the activity from an unpoisoned value corresponding with the absorption of about 60 c.c. of hydrogen per min. in a blank run with unpoisoned catalyst, down to an absorption of about 2 c.c. per min. in the poisoned run. The poisoned catalyst was then subjected to the usual revivification treatment; but, after three successive treatments with 1 c.c. of *cyclohexene* in 9 c.c. of acetic acid, the activity did not rise appreciably above its poisoned value.

In corresponding tests with an antimony compound which is easily converted into stibine,

similar results were obtained. Thus, on poisoning of 0.025 g. of platinum, in hydrogen at room temperature, with  $10^{-5}$  mole of potassium antimonyl tartrate, the activity of the poisoned catalyst corresponded with an absorption rate of about 2.5 c.c. of hydrogen per min. in the hydrogenation test, and with a rate of about 4 c.c. after three washings with *cyclohexene*, again compared with a blank rate of the order of 60 c.c. per min.

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THE UNIVERSITY, BRISTOL.

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