216. *Studies in the Detoxication of Catalyst Poisons. Part VI. Use of a Revivable Filter-column.*

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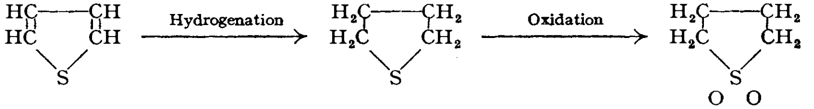
Since the detoxication of thiophen and of certain other types of catalyst poisons is greatly facilitated if the poison can be treated in an adsorbed state, a modification in procedure, involving the periodic detoxication of an adsorbent filter-column, has been developed. This avoids the necessity for a repeated detoxication treatment.

In Part V of the present series (*J.*, 1947, 624) an account has been given of the detoxication of thiophen in technical benzene and other systems by the two-stage process :



Thiophen (toxic). Thiophan (toxic). Thiophan sulphone (non-toxic).

in which the impure benzene is first subjected to a short (**2**—**3** mins.) preliminary hydrogenation before the addition of an oxidising detoxicant, the hydrogenation step being necessary for the production of a derivative more easily oxidisable than the original thiophen. It was found that the detoxication was in practice largely controlled by the degree of completeness which could be attained in the first stage; for, although thiophen in benzene tends to undergo preferential hydrogenation by virtue of its preferential adsorption on the catalyst, any very rapid hydrogenation is effectively limited to the amount of thiophen which can be initially adsorbed on the amount of catalyst used, since any subsequent interchange of thiophan for as yet unhydrogenated thiophen only takes place very slowly by reason of the toxic nature and consequently long adsorbed life of the product. The subsequent oxidation of the thiophan to its sulphone presents no difficulty; and this oxidation process, on account of the non-toxicity and short adsorbed life of the sulphone, leaves the surface of the catalyst free either for the adsorption of fresh thiophen or, if all the thiophen has undergone conversion, for the normal adsorption and hydrogenation of the benzene. Consequently, although the toxicity of very small concentrations of thiophen in benzene could be completely suppressed by a single treatment of the above nature, the detoxication of more heavily poisoned benzene, containing thiophen in excess of that which can be initially adsorbed on the small quantity of catalyst used, required a several times repeated application of this two-stage treatment before the whole of the thiophen ceased to be toxic. The following modification in procedure avoids the necessity for this repetition.

As an alternative to detoxication by the conversion of a poison into a non-toxic derivative which does not need to be removed, an impure system can obviously be freed from poisons by adsorption methods, for instance by being shaken with a suitable preliminary charge of catalyst, which is then removed; although, by reason of the partition even of strong poisons between the adsorbed and the free phase (*J.*, 1938, 2071), several successive treatments, each with a fresh charge of catalyst, would be necessary for the substantially complete removal of poison, unless a large excess of catalyst were used, even if, as with thiophen, the partition coefficient is strongly in favour of adsorption. If, however, a procedure is adopted in which the impure system is filtered through a stationary adsorbent of appreciable length, this undesirable operation of the partition effect against the complete removal of the poison in one treatment should be obviated, since the solution should become progressively weaker in poison as it passes through the adsorbent column. Further, if the column, after being used up to a stage at which it begins to allow poison to pass through, could be revivified periodically by treatment with a detoxicant, in such a way as to convert the adsorbed poison into a non-toxic form, it appeared that this use of a revivable filter might constitute a useful alternative method for freeing impure substances from poisons, since the column, when once set up, could by reason of its revivification be used indefinitely. The present short paper describes its application to benzene containing thiophen; but it should also be of interest for other poisons. Further, since the impure substance which is being prepared for hydrogenation does not, as in the general method used in previous papers, come into contact with an oxidising detoxicant—which is applied only to the spent column—this revivable filter-column method should be of particular use for the purification of substances, such as phenols, which cannot be exposed to an oxidation treatment.

EXPERIMENTAL.

Preparation of the Revivable Filter.—This preparation is given in detail, since it illustrates the method which has been adopted in this laboratory for the revival of spent catalysts. The platinum-black used for the adsorbing column did not consist of freshly prepared metal but of spent catalyst (from a platinum residue bottle) which had been previously used for miscellaneous poisoning work. About 10 g. of this were first washed with acetic acid, to remove most of the organic matter, then suspended in a further 100 c.c. of acetic acid and detoxicated by adding 30 c.c. of dilute aqueous sodium molybdate solution, containing 6×10^{-5} g.-atom of Mo per c.c., followed by 5 c.c. of 100-volume hydrogen peroxide added in 1-c.c. portions. Since all the catalyst had previously been used for hydrogenation reactions, no preliminary hydrogenation was necessary. The platinum was then washed with water and dried at 100°. A small sample (0·075 g.) was taken for testing and was found to have an activity, for the hydrogenation of crotonic acid, of the order which would be expected for fresh unpoisoned platinum. The remainder of the platinum (10·1 g., with an apparent volume of 8·1 c.c.) was used for the adsorption work.

Use of the Column for the Removal of Thiophen.—The adsorption apparatus (Fig. 1) consisted of a U-tube, approximately 70 cm. high, the length of the platinum plug being about 27 cm. The technical benzene to be purified by passage through the plug contained 0·09% of sulphur (almost all as thiophen), corresponding with $2{\cdot}8 \times 10^{-5}$ g.-mol. of thiophen per c.c. This benzene was used as a 25% solution in acetic acid.

The degree to which the thiophen was removed as a result of the passage of the benzene through the platinum column was followed by taking successive samples from the outlet tap, the hydrogenation rate of these samples being compared with that given by a stock of sulphur-free benzene which had been made, as a reference substance, by the dehydrogenation of sulphur-free *cyclo*hexane over palladium (Zelinsky, *Ber.*, 1911, **44**, 3121).

The standard system used in these hydrogenation tests consisted of 0·5 c.c. of benzene, dissolved in a total volume of 10 c.c. of acetic acid, and 0·1 g. of a stock platinum catalyst, the charge being hydrogenated under standardised conditions in a shaker at 50°. Under these conditions the sulphur-free benzene made from *cyclo*hexane absorbed hydrogen at a steady rate of 7·6 c.c. per minute, the corresponding rate with the untreated technical benzene being only 0·7 c.c. per minute. The hydrogenation rate of this benzene after passage through the adsorbing column was found also to be about 7·6 c.c. per minute, the observed rates for successive samples—expressed as a percentage of the rate given by the sulphur-free reference stock—being shown in Fig. 2. It will be seen that the hydrogenation quality of the benzene was equal to that of the reference sample up to a stage corresponding with the passage of a total of about 70 c.c. of the 25% solution through the column, after which the rate fell rather steeply to that of the original benzene owing to the saturation of the column with thiophen. The flow of benzene was then discontinued; and the platinum plug, after being washed with a little acetic acid, was revived by hydrogenation followed by treatment with a permolybdate under the general conditions already described in connection with its preparation from spent platinum. On renewing the flow of impure benzene, successive samples were again found to be free from thiophen, as is shown by the second part of the curve; and the process of periodic revivification could apparently be repeated indefinitely, in that—since the present work—it has been found possible to employ the same column as a standard apparatus for the purification of many substances, including the preparation of the sulphur-free pyridine used in the following paper.

FIG. 1.

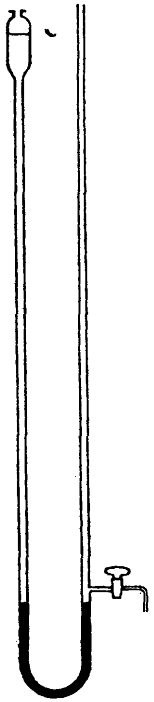
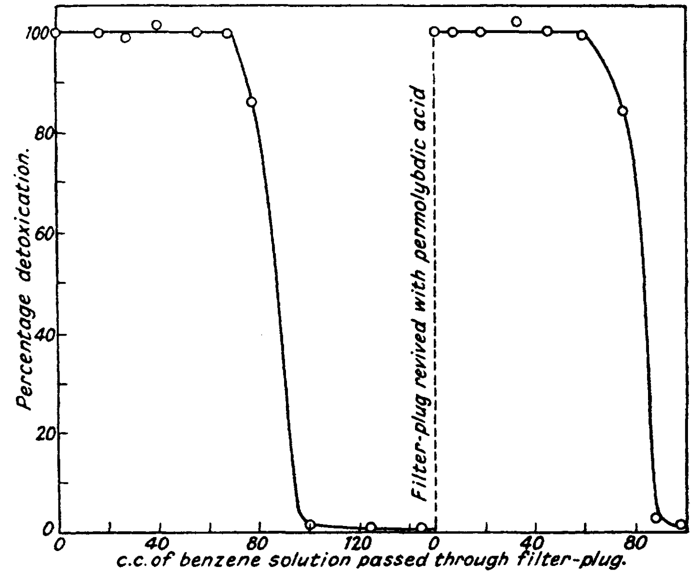


FIG. 2.



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