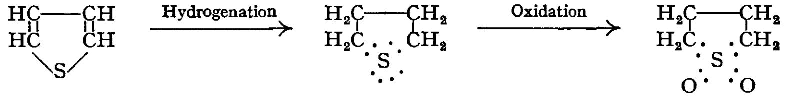
115. *Studies in the Detoxication of Catalyst Poisons. Part V. Thiophen.*

By E. B. Maxted.

The detoxication of thiophen by the general method used for other poisons in previous papers of this series has been studied (i) for thiophen added as a poison to a hydrogenation system containing crotonic acid as the unsaturated substance, (ii) for thiophen added to pure benzene, and (iii) for technical benzene containing thiophen as a natural impurity. Complete detoxication can be reached in each case; but the detoxication of systems having a relatively high thiophen content requires repeated detoxication treatment.

The detoxication of thiophen is of importance in connection with the catalytic hydrogenation of technical benzene, in which it occurs as a poison. As with carbon disulphide (see Part IV, *J.*, 1946, 23), the conversion of thiophen into a shielded derivative, by oxidation, involves the application of a preliminary hydrogenation step during which the thiophen, by virtue of its preferential adsorption on the metallic catalyst used, undergoes preferential hydrogenation to thiophan which, although still toxic, differs from thiophen in its ease of oxidation to a sulphone. The course of the detoxication is therefore :

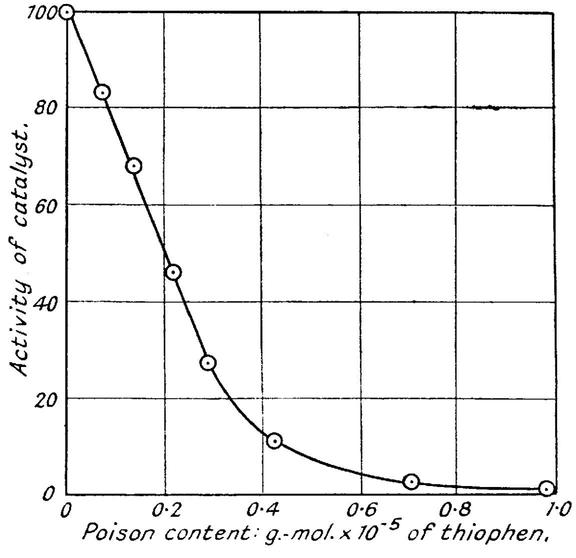


Thiophen. Thiophan. Thiophan sulphone.

the electronic configuration of the potentially toxic sulphur atom in thiophan and in the sulphone being indicated in the usual way. It will be seen that the sulphone possesses a shielded structure and is therefore non-toxic and no longer obstructively adsorbed on the catalyst, the surface of which then becomes free for the ordinary hydrogenation of the unsaturated substance in which the thiophen occurs as an impurity.

The principal difficulty in detoxication by a single hydrogenation–oxidation treatment lies in the effective limitation of the hydrogenation stage to the thiophen originally adsorbed on the catalyst. Amounts of thiophen of this order can be quickly and completely hydrogenated; and the subsequent oxidation stage leads easily to complete detoxication. If larger amounts of thiophen are present, the hydrogenation of any thiophen remaining in the free phase appears to proceed very slowly on account of the slowness of the exchange of thiophen and thiophan between the free and the adsorbed phases, since all poisons have long adsorbed lives. Concentrations of thiophen higher than that originally adsorbable by the catalyst present can, however, be completely detoxicated by repeating the alternate hydrogenation and oxidation. The second stage, involving the quantitative oxidation of thiophan to the sulphone, presents no difficulty.

FIG. 1.



EXPERIMENTAL.

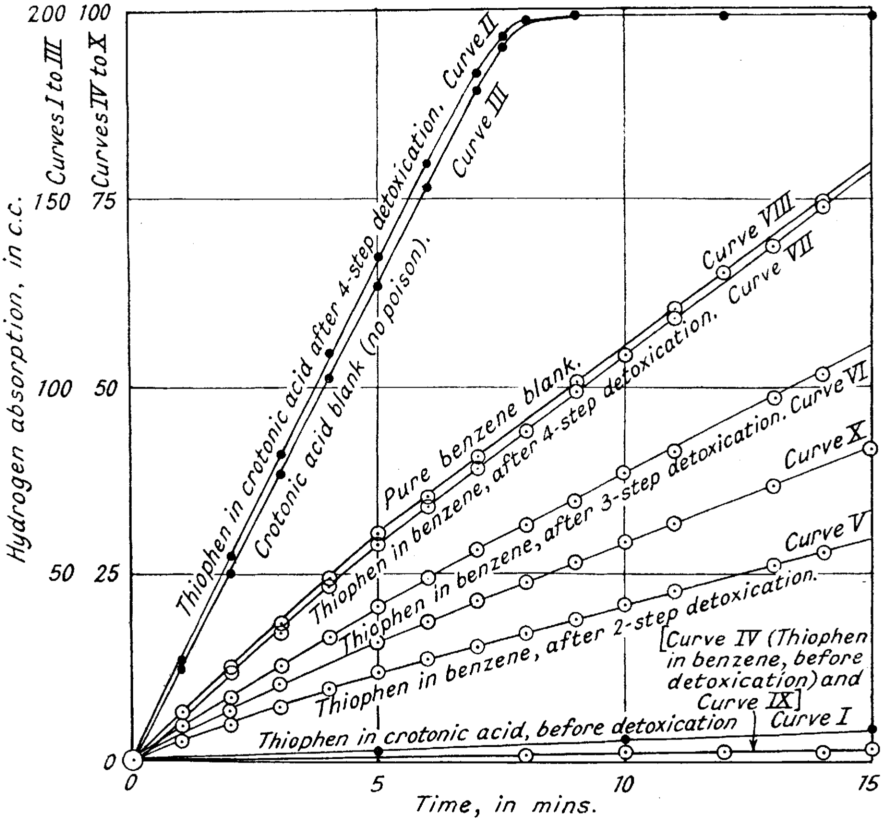
The general technique was similar to that described in previous papers of this series (*J.*, 1945, 204, 764, 766; 1946, 23). For the establishment of suitable conditions, the thiophen was, in earlier experiments, added as a poison to a hydrogenation system containing crotonic acid as a convenient unsaturated substance, since this can readily be obtained free from sulphur. Following this work, thiophen was added in known quantities to sulphur-free benzene; and, finally, the detoxication of technical benzene, in which thiophen occurs naturally, was studied. The hydrogenation catalyst used throughout was platinum black. The detoxicating reagent employed for the oxidation phase was permolybdic or perphosphoric acid, in each case in the presence of an excess of hydrogen peroxide. It has previously been shown that these reagents do not appreciably attack the double bonds of the unsaturated substances in which the thiophen is present as a poison.

Thiophen in Crotonic Acid.—The standard system taken for treatment consisted of 0·075 g. of stock platinum black, suspended in 5 c.c. of a 2N-solution of crotonic acid in acetic acid and poisoned by 10^{-5} g.-mol. of thiophen (in a further c.c. of acetic acid), the system being subsequently made up to 12 c.c. by adding 6 c.c. of water including that added with the detoxicating reagent and water used for rinsing. This amount of thiophen was sufficient to poison the catalyst down to about 2% of its original activity. The poisoning curve, on which the adoption of 10^{-5} g.-mol. of thiophen as a standard poisoning charge was based, is shown in Fig. 1. It will be seen from the form of this curve that the destruction of poison, by detoxication, will only begin to have a large effect on the hydrogenation velocity after 60—70% of the original poison has been destroyed, *i.e.*, after the original 10^{-5} g.-mol. of thiophen has been reduced to an amount below $3 - 4 \times 10^{-6}$ g.-mol.

It was found that, although complete destruction of this amount of thiophen could not be reached by a single preliminary hydrogenation followed by the addition of a detoxicant, as in the work on carbon disulphide described in Part IV, complete detoxication could nevertheless be obtained by repeating the alternate hydrogenation and oxidation. This is illustrated by the set of curves marked I, II, and III in Fig. 2. Curve I shows the rate of hydrogenation, at 27°, of the standard charge containing 10^{-5} g.-mol. of thiophen in its original state. Curve II refers to the same system after a detoxication treatment consisting of four short hydrogenations (usually of about 2 minutes each) in a shaker, followed, after the first hydrogenation, by the addition of 6 × 10^{-5} g.-mol. of permolybdic acid and, after each of the subsequent hydrogenations, of 0·075 g. (about 2 × 10^{-3} g.-mol.) of hydrogen peroxide, the excess of per-acid or peroxide being destroyed by heating, as previously described, before the subsequent hydrogenation. During this treatment, the activity of the catalyst can be observed to rise progressively with each short hydrogenation followed by an oxidation; but, under these conditions, complete detoxication was not obtained by a lesser number of hydrogenation–oxidation steps. Further, the progressive rise in the activity of the catalyst, which can be seen directly by the rate of absorption of hydrogen during the successive hydrogenation steps, is especially rapid at later stages of the detoxication, as would be expected from the form of the toxicity graph (Fig. 1). This rise through intermediate detoxication values was studied in greater detail for thiophen in benzene. Curve III is a blank run, without the addition of poison.

Detoxication of Thiophen in Benzene.—Stocks of thiophen-free benzene were prepared in two ways. In the first of these, *cyclo*hexane—which, from its method of preparation by the catalytic hydrogenation of benzene with nickel, should already be free from sulphur—was dehydrogenated over palladium at 300° (Zelinski, *Ber.*, 1911, **44**, 3121), a low pressure being used in order to push the equilibrium as far as possible towards benzene. In the second method of preparation, technical benzene, which still contained 0·09% of sulphur (as thiophen), was subjected to the exhaustive adsorption of poisons by finely divided platinum in the absence of hydrogen until no further improvement in the hydrogenation velocity of samples taken for testing occurred on further treatment. Each of these stocks was hydrogenated at about the same velocity, corresponding with the absorption of hydrogen at a steady rate of 5·2—5·3 c.c. per minute under the standard conditions used in the present series; but, since the first stock still contained, on the basis of its refractive index, a little *cyclo*hexane, and since the purity of the second stock (in the sense of its freedom from sulphur) had been confirmed by the equality of its hydrogenation rate to that of the benzene made from *cyclo*hexane, this second stock was used for the detoxication measurements.

FIG. 2.



In this series, the standard system consisted in each case of 1 c.c. of benzene, dissolved in 10 c.c. of acetic acid, 0·1 g. of stock platinum catalyst, and 2 c.c. of water including that added with the detoxicating reagent. The hydrogenation runs for testing the activity of the catalyst were carried out at 50°; but preliminary hydrogenation for the conversion of thiophen into thiophan, which appears to take place very quickly as far as the adsorbed thiophen is concerned and in any case preferentially to the hydrogenation of benzene, was carried out at room temperature in order, especially at later stages in the detoxication, not to use up too much of the benzene. However, in the preliminary or intermediate hydrogenations, which form a part of the detoxication process and which were usually carried out for three minutes each, the volume of hydrogen adsorbed was less than 3 c.c. in early stages of the detoxication and did not exceed 10 c.c. in later stages, the hydrogen value of the benzene present being a little less than 800 c.c.

The set of curves marked IV—VIII in Fig. 2 indicates the progress of the detoxication (*i.e.*, the gradual recovery by the platinum of its unpoisoned activity) obtained by repeating the detoxication treatment, each step consisting of a preliminary hydrogenation followed by the addition of a detoxicating regeant which, in this series, was perphosphoric acid. Curve IV shows the very low hydrogenation rate in the presence of 10^{-5} g.-mol. of thiophen without detoxication, and Curve VIII the unpoisoned hydrogenation rate in a blank experiment with pure benzene in the absence of thiophen.

The intermediate curves, V, VI, and VII, show the gradually increasing detoxicating effect obtained respectively by two, three, and four successive additions of detoxicant, preceded in each case by a short (2—3 mins.) hydrogenation. The detoxicant added consisted, in the first step, of $1{\cdot}25 \times 10^{-4}$ g.-mol. of perphosphoric acid and, for subsequent steps, of 2×10^{-3} g.-mol. (0·075 g.) of hydrogen peroxide. It will be seen from Curve VII that substantially complete detoxication was reached after four combined steps, each consisting of a short hydrogenation followed by an oxidation.

The lack of response of thiophen to detoxication by oxidation only, without prior hydrogenation, is shown in Curve IX, in which the charge, containing 10^{-5} g.-mol. of thiophen, was subjected to a 4-step addition of the above quantities of the oxidising reagent as in Curve VII but without preliminary or intermediate hydrogenation. The points in Curve IX fall almost exactly on those of Curve IV. Even if only a single preliminary hydrogenation was applied, followed by a 4-step oxidation, as in earlier work with carbon disulphide, the resulting detoxication was relatively poor (see Curve X, which should be compared with Curve VII).

Detoxication of Technical Benzene.—The benzene taken was the stock containing 0·09% of total sulphur, almost all of which was present in the form of thiophen. This percentage corresponds with $2{\cdot}8 \times 10^{-5}$ g.-mol. of thiophen per c.c. Accordingly, if 1 c.c. is taken in making up each experimental charge, as in the runs with pure benzene with artificially added thiophen, the poison content will be about three times that in the previous series. For this reason, it would be expected that a larger number of combined detoxication steps will be required in order to reach complete detoxication, in view of the apparent limitation of the preliminary hydrogenation phase to thiophen actually adsorbed on the catalyst. In addition to runs with 1 c.c. of the impure benzene, tests were therefore also made with charges containing smaller amounts. Save for this and for the use of permolybdic acid (in amount corresponding to $0{\cdot}6 \times 10^{-4}$ g.-atom of Mo) in the first oxidation step, in place of the $1{\cdot}25 \times 10^{-4}$ g.-mol. of perphosphoric acid used in the previous series, the standard charge and conditions of detoxication were identical with those already described in detail for artificial benzene–thiophen mixtures. Even the smallest volume (0·25 c.c.) of this impure benzene contained sufficient poison to reduce the activity of the catalyst to a negligibly low value in the absence of detoxication treatment.

Some of the results with technical benzene are summarised in the following table. As before, 100% detoxication denotes the complete recovery by the catalyst of its unpoisoned activity, *i.e.*, the attainment, in the main hydrogenation test, of a reaction velocity equal to that given in the absence of poison.

C.c. of benzene in charge.	G.-mol. of thiophen present × 10^5.	Number of detoxication steps.	Detoxication, %.	Number of detoxication steps.	Detoxication, %.
0·25	0·7	(0	3)	2	94
		1	59	3	100
0·5	1·4	(0	2)	5	100
		4	89		
1·0	2·8	(0	<2)	7	75
		5	10	8	100
		6	34		

It will be seen that about 8 treatments were required for the complete detoxication of a charge containing 1 c.c. of the impure benzene, the number being reduced to about 5 treatments for 0·5 c.c. and to about 3 for 0·25 c.c. This necessity for repeated treatment if the benzene contains a relatively large quantity of thiophen is the principal practical disadvantage in the application of the present general method to benzene. The objection does not hold for the other poisons studied in previous papers; *e.g.*, carbon disulphide (Part IV), which resembles benzene in requiring preliminary hydrogenation, could be successfully detoxicated after one preliminary hydrogenation only; and cystein (Parts II and III) responds easily to per-acid detoxication even without any preliminary hydrogenation. The possibility of introducing modifications in the detoxication procedure in order to avoid this necessity for repeated treatment in the case of thiophen is being considered separately.

It may also be mentioned that preliminary work on the detoxication of technical naphthalene has shown that the poisons (principally thionaphthen) contained in this substance can readily be detoxicated in an adsorbed state: thus, a platinum catalyst which had previously been poisoned with commercial naphthalene was found to recover its original activity after hydrogenation followed by treatment with perphosphoric acid.

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