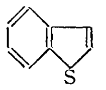
387. *Studies in the Detoxication of Catalyst Poisons. Part VIII. Thionaphthen and the Thiophthens.*

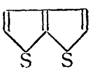
By E. B. Maxted and A. G. Walker.

The suppression of the toxicity of thionaphthen towards metallic hydrogenation catalysts, by converting the poison into a shielded and therefore non-toxic form, has been carried out by a procedure similar to that previously used for thiophen (Part V). This conversion is of interest in connection with the catalytic hydrogenation of technical naphthalene. The detoxication of two of the isomers of thiophthen has also been studied.

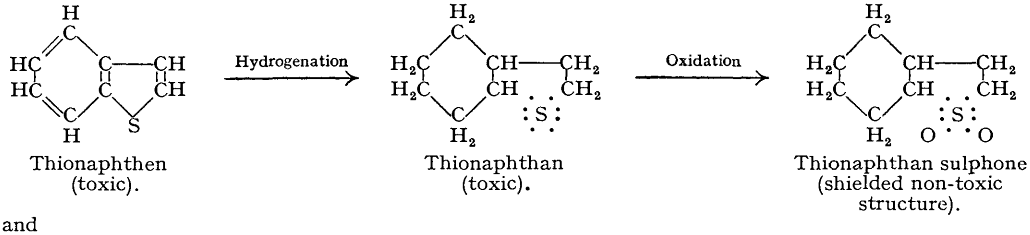
The detoxication of the catalyst poisons which occur in naphthalene is of considerable importance on account of the extent to which naphthalene is hydrogenated industrially. Coal-tar naphthalene ordinarily contains from 0·2 to 0·4% of total sulphur. Thionaphthen (I) is certainly present as a major constituent and has been isolated from naphthalene by Weissberger and Kruber (*Ber.*, 1920, **53**, 1551); and it may be noted that the relatively late actual isolation of this poison—the presence of which had long been expected from an analogy to the occurrence of thiophen in benzene—was mainly due to unusual separation difficulties and followed varying reports by earlier workers (see, *e.g.*, Boes, *Apothek. Ztg.*, 1902, **17**, 565) on the occurrence of thionaphthen in tars of various origins. In addition to thionaphthen, it is probable that thiophthens, (II) and its isomers, also occur to some extent in the sulphur poisons of naphthalene, since these condensed thiophens are known to be formed by pyrogenetic reactions similar to those which are capable of giving thionaphthen.

(I.)



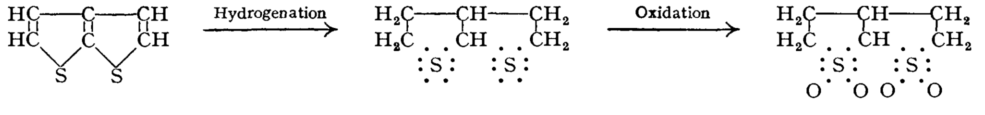


(II.)



Thionaphthen (toxic). Thionaphthan (toxic). Thionaphthan sulphone (shielded non-toxic structure).

and



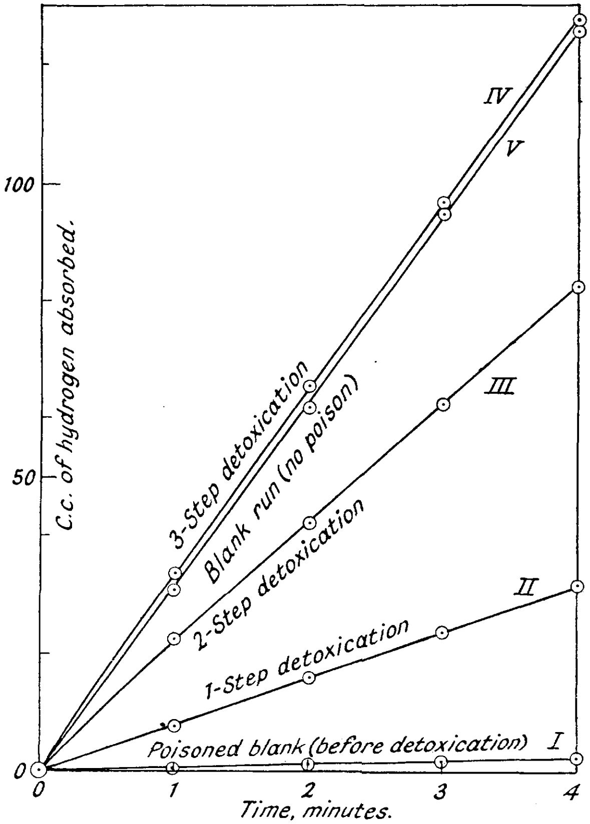
Thiophthen (toxic). Thiophthan (toxic). Thiophthan sulphone (non-toxic).

The present work, which relates to the detoxication of thionaphthen and the thiophthens added in known amounts to an artificial hydrogenation system, has been carried out in order to obtain preliminary information which can be utilised in a more detailed study of the detoxication of technical naphthalene. It has been found that all these poisons can be detoxicated by the treatment previously used for thiophen (*J.*, 1947, 624), namely, by a short preliminary hydrogenation followed by the addition of an oxidising detoxicant. As was found for thiophen, this preliminary hydrogenation stage—during which the cyclic sulphur compound, by virtue of its preferential adsorption as a poison on the catalyst, undergoes preferential hydrogenation to a product which lends itself more easily to subsequent oxidation than the original poison—is a necessary part of the detoxication procedure; and the suppression of the toxic character of the poison does not take place if the hydrogenation stage is omitted, since these cyclic thiophen derivatives, like thiophen itself, do not readily form sulphones directly. From an analogy with the corresponding case of thiophen, the course of the detoxication is probably as shown below, the electronic state of the sulphur atoms in the intermediate and in the final stages of the detoxication being indicated in the usual way.

EXPERIMENTAL.

Detoxication of Thionaphthen.—The detoxication procedure closely resembled that already described for thiophen (*q.v.*). Crotonic acid was, as before, used as a convenient unsaturated substance for following the suppression of the toxicity of the thionaphthen as a result of the detoxication treatment; and the standard hydrogenation system taken for each run consisted of 10 c.c. of a N-solution of crotonic acid in acetic acid, 5×10^{-6} g.-mol. of thionaphthen, 0·075 g. of stock platinum catalyst, and 2 c.c. of water, including water added with the detoxicant. The above amount of thionaphthen, in its original toxic state, was sufficient to reduce the hydrogenation velocity down to a small fraction (*ca.* 2%) of the rate in the absence of the poison. The main hydrogenation runs were carried out in a shaker, under standardised conditions, at 27° and at atmospheric pressure.

Detoxication of thionaphthen.



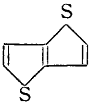
The series of runs summarised in the figure show the results obtained by using small quantities of a detoxicating reagent containing permolybdic acid, the reagent being made up, as previously described, by acting on molybdic acid with hydrogen peroxide. The poisoned charge in the hydrogenation pipette was first subjected to the usual short (2 mins.) preliminary hydrogenation, following which 0·5 c.c. of the detoxicating reagent, containing 3 × 10^{-5} g.-mol. of permolybdic acid, was added, any excess of per-acid or hydrogen peroxide being then destroyed by heating to 80° before the main hydrogenation run by means of which the extent of the detoxication was measured. In order to reach a state corresponding with a complete suppression of the toxicity of the thionaphthen it was in general necessary to repeat the above two-stage detoxication treatment several times before carrying out the main hydrogenation run. Curve I shows the hydrogenation velocity of the standard poisoned charge before detoxication. Curves II, III, and IV give the hydrogenation rates after a detoxication treatment consisting respectively of one, two, and three short hydrogenations followed, after the first hydrogenation, by the addition of 3 × 10^{-5} g.-mol. of permolybdic acid and, after each of any subsequent hydrogenations, by 0·075 g. (*ca.* 2 × 10^{-3} g.-mol.) of hydrogen peroxide. The number of detoxication treatments applied before the carrying out of the main hydrogenation run is, in conformity with previous papers, referred to in the figure as one-, two-, and three-step treatment, respectively. Curve V shows the hydrogenation velocity given by a blank charge from which the thionaphthen had been omitted. It will be seen that complete detoxication was reached after a 3-step treatment: indeed, the hydrogenation rate had then risen to a value slightly greater than that of the blank run. This effect has frequently been observed in the present type of work and is probably due to the cleaning up also of small traces of original poison contained in the platinum black.

Hydrogen peroxide, which was also tried for the oxidation phase, was found not to be a very effective detoxicant in the absence of molybdenum compounds (see also Parts II and III); but if, in a treatment involving more than one application of the hydrogenation–oxidation process, molybdenum is already present in the system from the first step, it is sufficient in the oxidation phase of any subsequent steps to add hydrogen peroxide alone, since permolybdic acid is regenerated. The oxidation phase of all steps, including the first, can on the other hand be effectively carried out by small quantities of dilute nitric acid (cf. Part II for the use of this reagent in the detoxication of cystein, which, however, requires no preliminary hydrogenation). Table I shows the effect of a 2-step and a 3-step detoxication of standard hydrogenation charges—containing the usual amount of thionaphthen—with N-aqueous nitric acid (5 × 10^{-4} g.-mol. at each step). By 100% detoxication is understood the complete re-attainment by the poisoned system of a hydrogenation rate equal to that given in an unpoisoned blank run.

TABLE I.

Number of detoxication steps.	Hydrogenation rate, in c.c. per min., after detoxication.	Detoxication obtained, %.
No detoxication	0·7	—
2	26·6	83
3	32·7	102
(Blank run omitting poison	32·0	100)

As will be seen from the table, complete detoxication was given by a 3-step treatment. The use of dilute nitric acid as a detoxicant has, however, the disadvantage that the excess of the reagent cannot be destroyed by heating and thus remains in the system; although it was shown in the previous work on cystein that the two possible complications introduced by using nitric acid—*i.e.*, the possible destruction of some of the unsaturated substance by oxidation at its double bond or, secondly, the taking up of hydrogen at an appreciable rate by the residual traces of dilute nitric acid during the hydrogenation runs—apparently do not occur to a measurable extent under the conditions employed.


(III.)

Detoxication of the Thiophthens.—Of the three known isomers, specimens of two only, namely those of the structures (II) and (III) were available and were supplied by the courtesy of Dr. E. C. Holdsworth. These will be referred to as thiophthen I and II respectively.

The detoxication of these poisons was carried out in the same way as for thionaphthen. The poisoned charge contained in each case 5 × 10^{-6} g.-mol. of thiophthen, this being sufficient to poison the hydrogenation rate down to about 0·8 c.c. per minute, the unpoisoned rate under the conditions of this series of runs being 41·3 c.c. per minute. The progress of the detoxication, measured by the movement of this very low rate towards the unpoisoned velocity given in a blank run with the omission of the poison, is summarised in Table II, the amounts of permolybdic or nitric acid used for the oxidation steps being as already given.

TABLE II.

Poison.	Detoxicant.	Number of steps.	Hydrogenation rate, c.c. of H_2 per min.	Detoxication, %.
Thiophthen I	Permolybdic acid	None	0·82	—
		1	12·8	31·0
		2	32·4	78·4
		3	40·6	98·3
		4	41·5	100·5
(Blank run without addition of thiophthen			41·3	100)
Thiophthen II	Permolybdic acid	None	0·85	—
		1	4·2	10·2
		2	25·4	61·5
		3	34·7	84·0
		4	35·6	86·2
Thiophthen I	Nitric acid	1	17·1	41·4
		2	35·1	85·0
		3	38·1	92·2
Thiophthen II	Nitric acid	1	10·9	26·4
		2	33·1	80·1
		3	37·4	90·6

It will be seen that complete detoxication of thiophthen I was obtained by a 4-step treatment with permolybdic acid. Thiophthen II is apparently more resistant, only 86% detoxication being reached by a similar treatment. The use of dilute nitric acid for the oxidation stage in the detoxication of both of these poisons was, on the whole, less successful than that of permolybdic acid.

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