30. *Catalytic Toxicity and Chemical Structure. Part VII. Elimination of Catalyst Poisons by Conversion into Derivatives of Shielded Type.*

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The conversion of catalyst poisons into non-poisonous derivatives of shielded type—in which the inherently poisonous element, by virtue of its possession of a stable saturated electron octet (see Part V), loses its characteristic toxic properties—

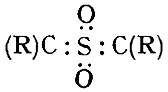
constitutes a method of eliminating catalyst poisons from impure systems which may be used as an alternative process to the often difficult actual removal of small traces of a poison by absorption or other means. The present paper contains a description of preliminary work dealing with the conversion, *in situ*, of poisons of sulphide type into non-toxic sulphones. The method has also been tried for thiophen, following preliminary hydrogenation with the object of forming tetrahydrothiophen, which, unlike the original thiophen, forms a sulphone on oxidation. A very substantial degree of detoxication was obtained in each case.

IN Part V (J., 1940, 252) it was pointed out that, in general, the catalytically poisonous character of sulphur, selenium, tellurium, and phosphorus compounds towards metallic hydrogenation catalysts is dependent on the possession by the normally toxic element of unshared electron pairs. Accordingly—save in certain phosphorus compounds, in which cases of relatively weak bond strengths between phosphorus and hydrogen occur—catalytic toxicity was found to disappear if the compound containing the inherently poisonous element has a structure in which this element is shielded by the possession of a completely shared electron octet which is stable under the conditions employed for catalysis. For instance, the hydrides of these elements, such as hydrogen sulphide or phosphine, and the sulphides, thiols, sulphites, selenites, tellurites, thiosulphates, tetrathionates, and the free elements themselves, where these are sufficiently soluble, are toxic towards platinum, whereas sulphates, sulphonates, selenates, tellurates, and phosphates are non-toxic. It should be noted, however, that, in the case of compounds of certain other characteristically poisonous elements, *e.g.*, arsenic or antimony, the necessary stability of structure of the compound during subsequent catalysis is usually absent, in that most arsenic or antimony compounds become hydrogenated to toxic arsine or stibine; and, for this reason, this shielding effect is not in general effective with arsenic or antimony, at any rate as far as their toxicity in catalytic hydrogenation is concerned.

Since the removal of small traces of catalyst poisons from impure substances prior to their hydrogenation is often difficult, particularly if the poisons are in a relatively inert or not easily absorbable form such as an organic sulphide or thiophen, it seemed possible that the above principle could be utilised as the basis of a method for eliminating poisons, the process involved being the conversion of the poison into a shielded non-toxic derivative rather than its actual removal.

In the case of organic sulphides, a convenient shielded derivative appeared to be the sulphone (II), which, unlike the original sulphide (I), possesses a saturated electronic structure. Cyclic sulphides of the thiophen type, however, cannot be oxidised directly to a sulphone; but, since tetrahydrothiophen readily forms a sulphone, a possible method of dealing with cyclic poisons of the thiophen class, including substances such as thionaphthen, which occur as poisons in commercial benzene and naphthalene, seemed to be by way of the hydrogenated derivative, followed by the conversion of this into the sulphone.

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



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

(I.) Sulphide (toxic). (II.) Sulphone (non-toxic).

Further, the conversion of a poison into a sulphone is obviously only one of many possible methods for the elimination of the unsaturated electron pairs which are apparently necessary for the formation of the relatively strong chemisorptive linkage between the poisonous atom and the catalyst which underlies the toxic action; and the effectiveness of any particular method will depend on the degree of completeness of the conversion obtainable under the experimental conditions used.

EXPERIMENTAL.

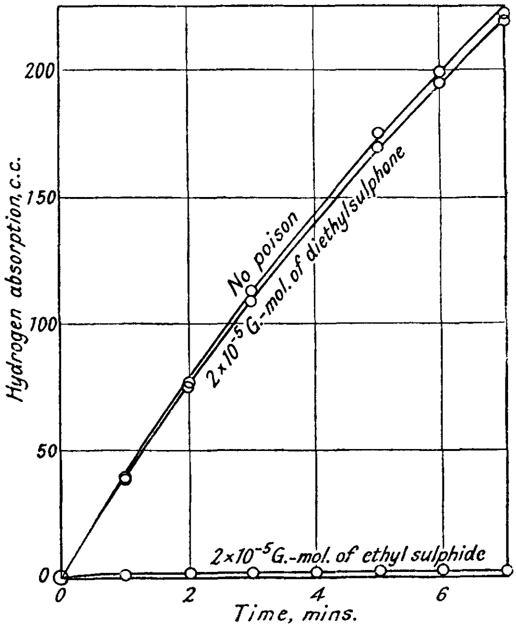
In the present work, platinum was used as the catalyst throughout, and the technique employed for measuring its activity for catalytic hydrogenation in the presence of a known quantity of the poison, or of its shielded derivative, was similar to that adopted in previous papers of this series (J., 1937, 603, 1004; 1938, 455, 839; 1940, 252, 469). Crotonic acid was, as before, employed as a convenient standard ethylenic substance for hydrogenation; and, in general, the system taken for each activity measurement consisted of 5 c.c. of a 2N-solution of crotonic acid in acetic acid, 0·05 g. of stock platinum-black, and a further 5 c.c. of acetic acid containing the poison or its derivative. In those runs in which the conversion of the poison into its shielded derivative was carried out *in situ, viz.*, in all runs after those grouped together in Fig. 1, 1 c.c. of water, containing the reagent used for the conversion, was substituted for 1 c.c. of the acetic acid, since this reagent was more conveniently added in aqueous solution; and, in all cases, the blank runs, *viz.*, the measurements of the activity of the catalyst in the absence of the poison or its derivative, were of course made in a solvent of the same composition as that used with the poison. The hydrogenation was carried out in a shaker, at 25°.

Detoxication of Ethyl Sulphide.—In order, first of all, to obtain a quantitative comparison of the toxic effect exerted by ethyl sulphide before and after complete conversion into sulphone, a specimen of this sulphide was oxidised to diethylsulphone, sodium hypochlorite being used as the oxidising agent (Wood and Travis, *J. Amer. Chem. Soc.*, 1928, **50**, 1226); and, in this case only, the sulphone was isolated as such and purified by recrystallisation from alcohol.

The general effect of approximately equal quantities (about 2×10^{-5} g.-mol.) of the sulphide and of the sulphone on the activity of 0·05 g. of the platinum catalyst is shown in Fig. 1, from which it will be seen that, whereas the activity of the catalyst is almost completely suppressed by the sulphide, the same weight of sulphur in the form of the sulphone has substantially no toxic action. In the sulphide curve, the very small hydrogen absorption, which occurred mainly in the first minute, is probably largely due to solution.

The next step consisted in examining the extent to which small quantities of ethyl sulphide, contained as a poison in a hydrogenation system, can be eliminated *in situ*, without isolating either the sulphide or the sulphone into which it is converted. In order to produce the effect of a complete removal of the poison, the conditions chosen for the oxidation should, in addition to removing the sulphide itself, also avoid the production of substantial quantities of non-shielded by-products such as the sulphoxide, which would not only, by reason of its structure, be toxic in itself but would also, unlike the sulphone, be reduced back to sulphide during subsequent hydrogenation.

FIG. 1.



The result of treating the poison *in situ* with sodium hypochlorite is shown in Fig. 2, in which Curve I represents the rate of hydrogenation of the standard quantity of crotonic acid containing $1{\cdot}85 \times 10^{-6}$ g.-mol. of ethyl sulphide, Curve II a similar charge with the addition of 1×10^{-3} g.-mol. of sodium hypochlorite, and Curve III is a blank run consisting of crotonic acid alone without any poison. It will be seen that the toxic effect of the sulphide substantially disappears.

It was considered of interest to investigate in somewhat greater detail the influence of the quantity of hypochlorite on the degree of effective elimination of the poison, particularly since the amount used in the series summarised in Fig. 2, although small in actual amount, represents a large excess (about 250 times) over that required for the oxidation of the very small quantity of poison present. To this end a series of runs was carried out in which various quantities of hypochlorite were added to a standard hydrogenation system containing, as before, $1{\cdot}85 \times 10^{-6}$ g.-mol. of ethyl sulphide, 5 c.c. of 2N-crotonic acid in acetic acid, 1 c.c. of water, and 0·05 g. of platinum, the hypochlorite being in each case added with the 1 c.c. of water. The mixture was allowed to remain for about 10 mins. in air in the hydrogenation pipette before the air was replaced by hydrogen. The reaction course followed during the subsequent hydrogenation was, as is usual, very nearly linear up to an advanced stage of hydrogenation; and the hydrogenation rates could accordingly be conveniently compared by taking the average hydrogen absorption per min. for the first 5 mins. after the initial minute—

this was excluded since uniform shaking conditions (including the uniform distribution of the finely divided catalyst throughout the liquid system) are in most cases not attained until some 15—30 secs. after starting the shaker. As an example of the degree of variation of the rate in a given run during the 5 mins. over which the average was taken, the actual hydrogen absorption per min., in a run with 1·22 × 10^{-4} g.-mol. of hypochlorite, was 13·0, 13·4, 13·6, 13·7, and 13·4 c.c., respectively, during the second, third, fourth, fifth, and sixth minutes of the run, giving an average velocity of 13·4 c.c./min. The extent of the detoxication obtained with various quantities of hypochlorite is shown in the table. The fractional activities in the last column represent the activity of the catalyst expressed as a fraction of its unpoisoned activity, and are accordingly a measure of the effective elimination of the poison. The concentration of the ethyl sulphide was 1·85 × 10^{-6} g.-mol. throughout.

FIG. 2.

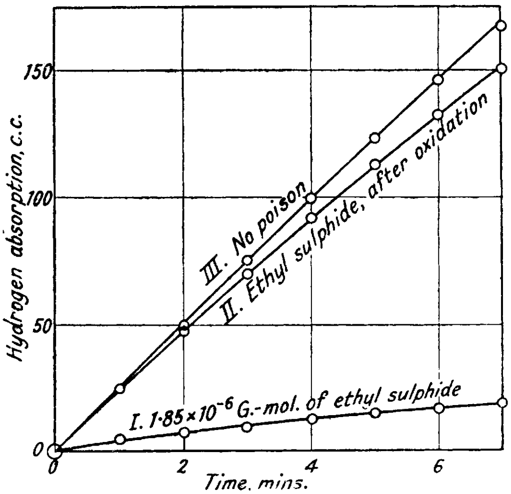
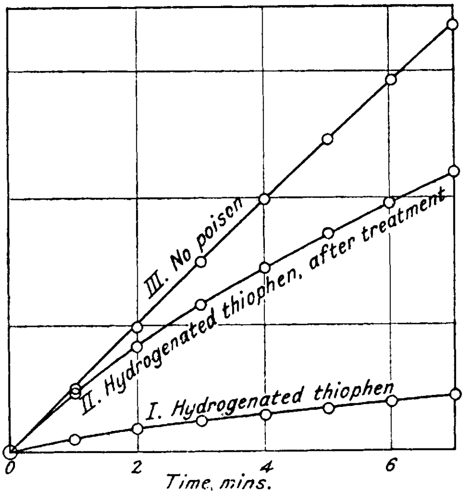


FIG. 3.



G.-mols. of NaOCl added, × 10^5.	Hydrogenation velocity, c.c./min.	Fractional activity of catalyst.
0	2·4	0·099
1·1	3·1	0·128
2·2	5·0	0·206
4·65	8·9	0·366
12·2	13·4	0·55
32·4	17·0	0·70
57·5	19·3	0·80
85·6	20·6	0·85
120	22·7	0·93
Unpoisoned velocity	24·3	1·00

It will be seen that the degree of restoration of the activity of the catalyst increases progressively with the amount of oxidising agent introduced and that, at any rate with the higher concentrations of hypochlorite, substantially complete suppression of the toxic action of the ethyl sulphide can be obtained.

For the strict assessment of the degree of detoxication, however, two possible small corrections have to be considered. First, the unchanged hypochlorite present may itself undergo catalytic hydrogenation and thus absorb hydrogen during the run, with consequent influence both on the apparent speed of hydrogenation and on the total hydrogen absorbable. Secondly, the presence of hypochlorite may affect the hydrogenation rate by changing the viscosity of the solution.

These points were investigated by blank runs with hypochlorite, crotonic acid, and platinum in the absence of the poison. The possible additional absorption of hydrogen by quantities of hypochlorite of the order used is in any case small compared with the total hydrogen absorbed during the runs. Its volume varies from 0·25 c.c. for the run with 1·1 × 10^{-5} g.-mol. to 23 c.c. for the run with 1 × 10^{-3} g.-mol. of hypochlorite, compared with an uncorrected volume of over 230 c.c. absorbed by the crotonic acid. As an example of the total absorption observed, the reaction in the run with 8·6 × 10^{-4} g.-mol. of hypochlorite came, after 10 mins., to the relatively abrupt halt characteristic of these hydrogenation processes, 239 c.c. of hydrogen being absorbed. This is almost exactly the calculated value, at the temperature and pressure of the run, for the crotonic acid present: accordingly, only a negligible additional volume was absorbed by the hypochlorite, the calculated possible absorption by this being in any case only about 20 c.c.

The effect of hypochlorite, in the absence of poison, on the velocity of hydrogenation (as distinct from its effect on the total hydrogen required for saturation) was tested similarly. In a series of six blank runs with from 1×10^{-5} to about 1×10^{-3} g.-mol. of hypochlorite, which covers the range used in the above table, the hydrogenation velocity was found to vary somewhat irregularly, the mean velocity being 24·0 c.c./min. (cf. 24·3 c.c. in table) and the maximum variation either way being about 10%. It is probable that the above relatively small variation is caused by chance differences in the hypochlorite solutions (which have to be prepared fresh for each run), but in any case the correction was too small and too irregular to justify its introduction as a correction in the table.

Detoxication of Thiophen.—The effective application of the present method to the detoxication of catalyst poisons of the cyclic sulphur type would be expected to depend largely on the degree to which these can be converted, by preliminary hydrogenation, into tetrahydrothiophen derivatives, since these reduced ring compounds, unlike the parent substances, readily pass into sulphones on oxidation; *e.g.*, Grischkevitsch-Trochimovski (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 901) readily oxidised tetrahydrothiophen to the sulphone by means of permanganate.

Although thiophen, in bulk, does not absorb hydrogen at a measurable rate when shaken with this gas in the presence of a platinum catalyst, it was thought that quantities of thiophen of the order commonly occurring in impure substances taken for hydrogenation might, by reason of the very small quantity present, undergo some measure of hydrogenation, even though the reaction velocity, measured by the actual quantity hydrogenated per unit of time, is necessarily small by virtue of the still toxic nature (and consequently long adsorbed life) of the hydrogenated product formed.

Trials showed that the poisoning effect of thiophen can be greatly decreased. A standard solution of this poison was made up by dissolving 0·0084 g. (1×10^{-4} g.-mol.) of thiophen in 10 c.c. of acetic acid. This was hydrogenated by shaking with hydrogen for 3½ hours at room temperature in the presence of 0·05 g. of platinum; and the resulting solution, after separation of the catalyst, was further diluted with acetic acid to correspond with 2×10^{-6} g.-mol. of poison per c.c. This concentration is approximate only, since some of the thiophen is undoubtedly adsorbed by the platinum used for the hydrogenation; but the hydrogenated solution was, like the original thiophen, strongly toxic : *e.g.*, 1 c.c. of the hydrogenated solution, when added to a normal hydrogenation charge containing 5 c.c. of 2N-crotonic acid and 0·05 g. of platinum (together with the usual additional acetic acid and water), reduced the hydrogenation rate to about 2·5 c.c./min. (Curve I, Fig. 3) compared with an unpoisoned rate of about 25 c.c./min. (Curve III). In order to test the degree of detoxication obtained by treating this type of poison, *in situ*, with hypochlorite, a parallel hydrogenation run was now made with a similar system containing $8{\cdot}5 \times 10^{-4}$ g.-mol. of hypochlorite in addition to the hydrogenated thiophen. The detoxication was, as with the runs with ethyl sulphide, carried out in the presence of the crotonic acid and of the platinum; and it was found advantageous to allow the oxidising agent to remain in contact with the poison for at least 20 mins., the whole system being shaken, in the presence of air, in the hydrogenation pipette before displacing the air with hydrogen and proceeding to hydrogenation. The improvement obtained is shown by the results plotted in Curve II. It will be seen that, although complete detoxication was not attained under the conditions used, the hydrogenation rate was raised from about 2·5 c.c. to about 15 c.c. per min. by the oxidising treatment; and this rise was confirmed by a duplicate run. However, with these cyclic sulphur compounds, the conversion into a sulphone depends on a two-stage process, and, with the small quantity of thiophen used in making up the standard poisoning solution, it was difficult to assess accurately the amount of hydrogenation actually obtained in the first stage (the conversion of thiophen into tetrahydrothiophen), since the total volume of hydrogen absorbable by 1×10^{-4} g.-mol. of thiophen is only of the order of 4 c.c. The effective degree of detoxication by the complete treatment corresponded with an approximately 60% restoration of the unpoisoned reaction rate, compared with an approximately 85% restoration obtained with ethyl sulphide with the same quantity of hypochlorite. Further, in view of the technical importance of thiophen as a catalyst poison, the above work—which at any rate indicates a possible method for its elimination—is necessarily only of a preliminary nature. In particular, the effectiveness of other means of oxidation, including anodic oxidation, on all these types of sulphur poisons remains to be tried.

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