

*The Reversibility of the Adsorption of Catalyst Poisons. Part III.\*  
Adsorption and Desorption of Thionaphthen and Thionaphthol on Platinum.*

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

[Reprint Order No. 5242.]

In view of the recent application of desorptive methods to the revival of poisoned metallic catalysts, an exploratory study has been made of the adsorption and desorption of sulphur-containing catalyst poisons on to or from platinum surfaces, and of the displacement of an adsorbed poison from catalyst surfaces by the competitive adsorption of an unsaturated substance or of a second poison. The reversibility of the adsorption of such poisons at room temperature has been demonstrated. Adsorption-time and desorption-time curves show that a considerable period is required for the attainment of adsorption-desorption equilibrium.

ALTHOUGH the adsorption of strong catalyst poisons, such as toxic sulphur compounds, on metallic catalysts has been generally regarded as involving chemisorptive poison-to-catalyst bonds of sufficient strength to render this adsorption substantially irreversible at room temperature, it has been shown in Parts I and II of the present series\* (see also *J.*, 1953, 1509) that platinum or other catalysts, previously poisoned with typical catalyst poisons—including thiophen, dimethyl sulphide, dimethylphenylphosphine, dimethylphenylarsine, and toxic metallic ions such as zinc or mercury—can be revived by desorptive methods and, from this revival, a reversible type of adsorption has been inferred although the actual desorption and adsorption processes have not yet been studied. It was found that this revival of a poisoned catalyst can be facilitated by applying a second adsorbate such as an unsaturated substance, which appears to act by displacing and removing the poison by competitive occupation of the active surface: indeed, it has been shown that the washing of a poisoned catalyst with a solvent containing an unsaturated substance constitutes a very simple alternative to the chemical detoxication of the poison (*J.*, 1941, 132; 1945,

\* Part I, *J.*, 1952, 4284; Part II, *J.*, 1953, 3153.

204 and succeeding papers) and is applicable to cases of poisoning which cannot be dealt with by chemical treatment.

Little is known, however, of the rates and general kinetics of these adsorption and desorption processes with poisons, or of displacement effects in systems containing also an unsaturated component, the latter type of system being of special interest in connection with the catalytic hydrogenation of a poison-containing, unsaturated substrate. The work described in the present paper has been carried out as an exploratory survey of the above effects in liquid systems containing poisons, as a preliminary to a more detailed examination of the equilibria involved.

#### EXPERIMENTAL

The platinum black used as the adsorbent was made by alkaline formate reduction of chloroplatinic acid, followed by a stabilisation treatment of the nature to be described in detail in a forthcoming paper. The poison to be adsorbed was applied to this platinum as a solution of known concentration, the progress of the adsorption with time being followed by measuring the fall in the poison concentration of the free phase, from which the suspended platinum had been removed temporarily by centrifuging. This periodic analysis was usually carried out optically, by means of a Unicam spectrophotometer, in which case the small sample required could be quickly re-incorporated with the adsorbing system without appreciable disturbance of the adsorption course, but in some cases the estimation was made catalytically by using the sample as a component of a standard liquid-phase hydrogenation system for which a calibration curve connecting the hydrogenation velocity with the poison content had previously been made.

If the more convenient optical method of analysis is used, and if the adsorption of poison is to be determined in the presence of an unsaturated component, it is necessary to choose a poison having a strong optical absorption at a wave-length at which the unsaturated substance—which is usually present in many times the concentration of the poison—does not absorb. Similar conditions of non-interference apply also to the solvent used.

In the desorption work, the platinum was first allowed to adsorb a known amount of poison, following which the system was diluted by the addition of a known volume of fresh solvent containing no poison; or, to obtain an extreme degree of dilution, the supernatant liquid was removed as completely as possible from the poisoned platinum, by centrifuging and decantation, after which the progressive increase in the poison concentration of the free phase, as a result of desorption of poison from the platinum, was followed analytically as above.

*Adsorption and Desorption of  $\beta$ -Thionaphthol.*—The system taken consisted of 1 g. of platinum in contact with 25 c.c. of acetic acid containing  $7.5 \times 10^{-6}$  mole of  $\beta$ -thionaphthol, which was found to be an optically suitable poison, having a peak in its absorption spectrum at 2820 Å. Adsorption was allowed to proceed at 20° in a closed pipette shaken under standardised conditions for 7 hr. by means of a mechanical shaker. In order to obtain clear samples for optical analysis, the shaker was stopped periodically during the run and the adsorption process "frozen" by immediate centrifuging, it having been found by separate experiments that the rate of adsorption in the absence of shaking—namely, on to the centrifuged platinum deposit at the bottom of the reaction vessel—was negligibly small compared with the adsorption velocity on to the dispersed platinum during the vigorous shaking, and that the amount of poison thus adsorbed during the short period required for the analysis was too small to be significant. This was also confirmed by the continuous form of the curve obtained. The progressive increase in the poison adsorbed during the test is shown in curve I of Fig. 1.

In order to study the reverse process, first under conditions of extreme dilution, the run was then interrupted and the reaction vessel centrifuged to deposit the platinum, which contained  $5.64 \times 10^{-6}$  mole of the poison in the adsorbed state, after which the free phase was decanted as completely as possible and replaced by a further charge of 25 c.c. of acetic acid containing no poison. The course of the subsequent desorption of poison into the free phase under conditions similar to those used for the adsorption is shown in curve II of the Figure. These results establish clearly the reversible nature of the adsorption of the poison.

In a further test, with a system consisting of  $30 \times 10^{-6}$  mole of thionaphthol in 100 c.c. of acetic acid containing 1 g. of platinum, the adsorption was allowed to proceed for 144 hr. with periodic extraction and optical analysis of small samples. After this adsorption, instead of completely replacing the liquid phase with fresh solvent as before, 97.5 c.c. of the clear phase obtained by centrifuging at the end of the adsorption run were removed and replaced by a similar volume of poison-free acetic acid. The system, after this replacement and at the start of the

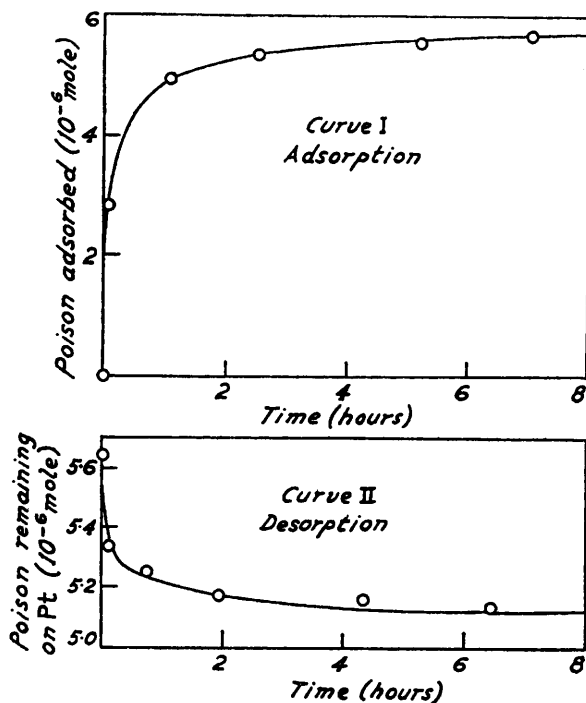
desorption measurements contained  $4.4 \times 10^{-7}$  mole of poison in the free phase; and, to obtain the amount of poison desorbed after various times, this initial poison content has, of course, to be subtracted from the amounts found analytically. The progress, first of the adsorption and subsequently of the desorption after the dilution, is shown in Table 1.

TABLE 1. Adsorption and desorption of thionaphthol.

Adsorption		Subsequent desorption		Adsorption		Subsequent desorption	
Time, hr. min.	Poison adsorbed ( $10^{-6}$ mole)	Time, hr. min.	Poison desorbed ( $10^{-6}$ mole)	Time, hr.	Poison adsorbed ( $10^{-6}$ mole)	Time, hr. min.	Poison desorbed ( $10^{-6}$ mole)
5	2.3	4	1.50	24	6.5	3 12	1.93
37	2.6	23	1.70	48	8.2	7 2	1.95
1 34	3.5	1 22	1.80	72	10.2		
4 40	4.7	2 31	1.92	144	12.4		

*Competitive Occupation of Surface by Poisons and Unsaturated Substances.*—A number of examples have been observed of the effectiveness of the competition of an unsaturated substance

FIG. 1.



for the occupation of catalyst surface in the presence of a poison under conditions similar to those operative in an ordinary catalytic hydrogenation system with a poisoned reactant, namely, in which adsorption from a relatively large concentration of a less strongly adsorbed unsaturated substrate competes effectively, by mass action, namely, by virtue of its far greater order of concentration, with the adsorption from a relatively small concentration of the more strongly bonded poison.

Fig. 2 shows the influence of the inclusion, respectively, of  $5 \times 10^{-3}$  (curve B) and  $10^{-2}$  (curve C) mole of cyclohexene on the adsorption of thionaphthol from ethyl alcohol solution on to 0.1 g. of platinum, the total volume of the liquid system being 10 c.c. and the adsorption being allowed to proceed for a fixed time of 1 hr. in each case. This series was carried out by individual adsorption tests to determine each point, the initial concentration of the poison in the free liquid phase, as shown in the abscissæ, being plotted against the amount of poison adsorbed. Curve A represents the corresponding adsorption in the absence of cyclohexene.

It will be seen from the three curves that the depression in the adsorption of the poison by the presence of *cyclohexene* is very appreciable.

Very similar results were obtained with other poisons. Thus, in a 10 c.c. system containing  $40 \times 10^{-7}$  mole of thionaphthen in acetic acid as the poison, and 0.1 g. of platinum as the adsorbent, the adsorption of poison was 3.55 and  $2.4 \times 10^{-7}$  mole in the absence and presence, respectively, of  $10^{-3}$  mole of *cyclohexene* after an adsorption time of 30 min.; or 6.6 and 4.5 units, respectively, after 24 hours' adsorption. A similar depression was also measured for the adsorption of dimethyl sulphide on platinum in alcohol, crotonic acid being used as the unsaturated displacing substance.

*Competitive Adsorption of Two Poisons.*—If the two poisons in question are reversibly adsorbed, competitive occupation of the catalyst surface takes place in a manner similar to its occupation by a poison and an unsaturated substance: further, it would be expected, on grounds of a greater parity in the adsorption bond strengths, that the displacing effect of adding a second

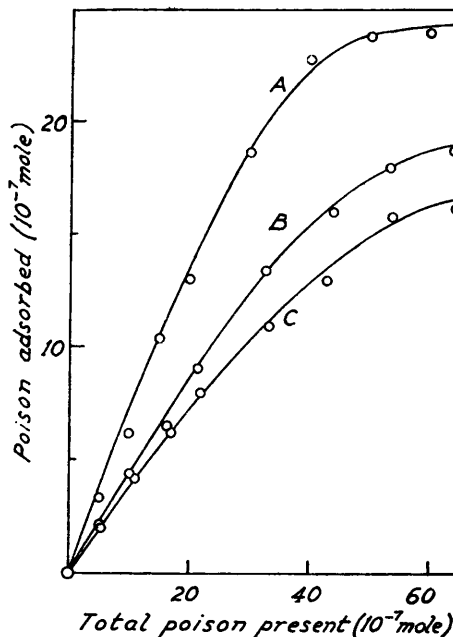


FIG. 2.

A, No *cyclohexene*.  
 B,  $5 \times 10^{-3}$  Mole of *cyclohexene*.  
 C,  $10^{-2}$  Mole of *cyclohexene*.

poison to a catalyst already poisoned by a first poison would be more intense than if an unsaturated substance is used as the displacing agent.

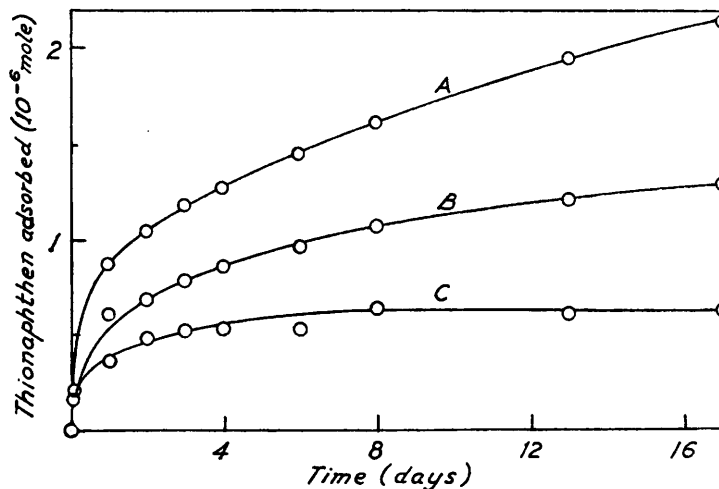
This subject has not yet been studied in detail; but, as an example of the displacement of thionaphthen by thiophen, 1 g. of platinum was allowed to adsorb  $11.9 \times 10^{-6}$  mole of thionaphthen from acetic acid solution. The poisoned platinum was then separated thoroughly from the supernatant liquid by centrifuging, and treated with  $4.5 \times 10^{-4}$  mole of thiophen in 25 c.c. of acetic acid. After 24 hr. it was found that this treatment with thiophen had displaced  $3.75 \times 10^{-6}$  mole, *i.e.*, nearly one-third, of the previously adsorbed thionaphthen from the platinum into the free phase. In this mixed adsorption work, the optical method of analysis has proved to be of great use, since it is necessary to differentiate between the two poisons in a way which cannot be done by the catalytic estimation method. The absorption peaks used were at 2870 Å for thionaphthen and at 2305 Å for thiophen.

This displacement of one poison by another—and especially the substitution, on a poisoned catalyst, of a poison which is easy to deal with by chemical detoxication, in place of one which cannot be detoxicated chemically—might constitute a practical revivification process alternative to poison desorption assisted by an unsaturated substance (Maxted and Ball, *loc. cit.*).

*Kinetics of the Adsorption and Desorption of Poisons.*—Although the rate both of adsorption and of desorption of poisons is reasonably fast during the first few hours of the process, it is evident that long periods are required for the attainment of equilibrium. This is illustrated in the series of tests shown in Fig. 3, in which the adsorption of thionaphthen from acetic acid

solutions of various initial poison concentrations was followed for 17 days with systems consisting of 0.1 g. of platinum suspended in 10 c.c. of acetic acid containing initially 1, 2, and  $8 \times 10^{-6}$  mole of poison respectively. It will be seen that an approach to a saturated state within the period of the run is obtained only in the lowest of the three runs, namely, that with  $10^{-6}$  mole of thionaphthen: indeed, in this, the adsorption has become very slow and apparently approaches equilibrium after 8 days. The systems were, however, not so vigorously shaken during these very long runs, and the results cannot therefore be directly compared with those of Fig. 1. Moreover, even in the curves of Fig. 1, the adsorption of thionaphthol, after passing through the range shown in curve I, further increased from  $5.64$  to  $6.6 \times 10^{-6}$  mole on extending

FIG. 3.



A,  $8 \times 10^{-6}$  Mole of thionaphthen. B,  $2 \times 10^{-6}$  Mole of thionaphthen. C,  $10^{-6}$  Mole of thionaphthen.

the adsorption time from 8 hours to 4 days. For this reason, the present adsorption curves cannot be used for an accurate calculation of the equilibrium constant. It is hoped to deal with this, and with the equilibria involved in the adsorption and desorption of poisons, in a later paper.

THE UNIVERSITY, BRISTOL.

[Received, March 26th, 1954.]