

**463.** *Studies on the Nature of Chemisorptive Bonds. Part II.*  
*The Catalytic Toxicity of Organometallic Compounds.*

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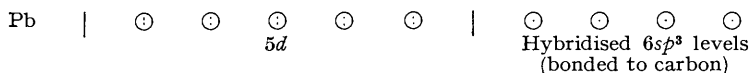
The apparent importance of *d*-shell filling in determining the capacity of a metallic derivative to form a strong chemisorptive bond to a platinum hydrogenation catalyst has been further examined by measurements of the toxicity of organometallic compounds in which *s* and *p* valency orbitals, of the next higher order to a filled *d* shell, are already occupied in covalent bonding with carbon, in place of being unoccupied as in the catalytically toxic metallic ions. The results confirm the inference that the *d* shell in toxic metals is involved in the bond to the catalyst.

It has been shown in Table I of Part I (this vol., p. 1987) that, in the case of the poisoning of a platinum hydrogenation catalyst by metallic ions, the capacity of a given ion to form a strong

chemisorptive bond—which is a characteristic of catalytic toxicity—seems to be dependent on a suitable electronic configuration in the  $d$  shell of the toxic ion immediately inside the ordinary valency orbitals, in that toxic properties are shown only by those ions which have all of the five  $d$  orbitals occupied either by electron pairs or at least by single electrons. If, on the other hand, any unoccupied  $d$  orbitals are present, or if no  $d$  orbitals are possible as in the ground states of the simpler elements, the power of forming a strong bond vanishes and the ion is accordingly non-toxic.

This apparently necessary condition for strong bonding has now been examined further with other metallic derivatives in order to obtain confirmatory evidence for the part played by  $d$  electrons in determining the observed toxicity. In the metallic ions themselves, unoccupied  $s$  and  $p$  orbitals (which have been left vacant by the loss of valency electrons and which are of the next higher order to that of the  $d$  band) also occur; and the possibility of some occupation of these vacant levels—for instance, by a relatively small excitation—by electrons, which might then take part in chemisorptive bond formation and thus obscure any inference that the strong poison bond is really due to a suitable  $d$ -shell occupation, cannot accordingly be entirely ruled out so long as these vacant  $s$  and  $p$  orbitals are present.

For this reason it has been considered of interest to carry out toxicity tests with metallic compounds in which the  $s$  and  $p$  bands, in place of being vacant as in the metallic ions, are already involved in bond formation with another element. To this end the toxicity of the series, dimethylmercury, trimethylindium, and tetramethyl-lead towards a platinum catalyst has been examined, these substances being representative organometallic compounds containing respectively a bivalent, a trivalent, and a quadrivalent metal which is known to be toxic in the form of an ion. It may be noted that the generally accepted metal-to-carbon bond structure in these organometallic compounds involves, on the part of the metal, two mutually equivalent  $sp$  hybrid orbitals for mercury, three  $sp^2$  orbitals for indium, and four hybridised tetrahedral  $sp^3$  orbitals for lead, each of these orbitals giving, by covalent bonding to carbon, a condition equivalent to electronic saturation in  $s$  and  $p$  levels of the metal. Especially in the case of tetramethyl-lead, with all four of its  $s$  and  $p$  orbitals already taken up in bond formation with carbon, *i.e.*



it will be seen that any toxicity which may be observed would seem to make quite clear the importance of the part played by the filled  $d$  band of the metal in the formation of the strong chemisorptive bond to a platinum catalyst.

As with the toxic metallic ions dealt with in Part I, it is desirable to establish the primary toxicity of the organometallic compounds as such. The evidence for strong adsorptive bonds such as would lead to the obstructive occupation of catalyst surface and consequently to catalytic toxicity follows from the degree of the observed adsorption even when the organometallic compounds are present only in extremely low concentrations; and that the seat of this strong adsorption lies in the unchanged organometallic compounds themselves can be shown by the reversibility of the adsorption indicated by the form of the adsorption isotherms, which are consistent with an adsorption-desorption equilibrium in which the organometallic compound is adsorbed and desorbed as such. Further, the limit set by this equilibrium for the degree of the removal of the compound from the free phase is not passed even on long storage in contact with platinum-black, at any rate at room temperature, as would be the case if the adsorbed compound gradually broke down into a deposit of the metal.

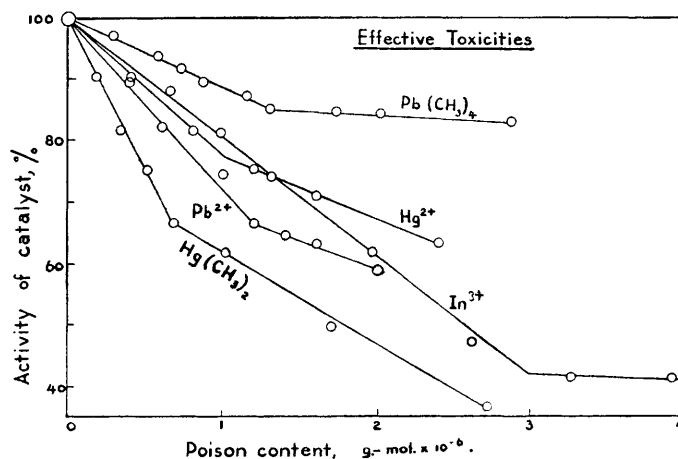
It is known that, at high temperatures and at high hydrogen pressures, organometallic compounds can be hydrogenated to the metal and a hydrocarbon in a somewhat similar way to the corresponding high-pressure reduction of metallic salt solutions. Thus Ipatiew, Rasuwajew, and Bogdanow (*Ber.*, 1930, 63, 335) have shown that, in benzene solution, the decomposition of tetramethyl-lead begins to be detectable after 24 hours at temperatures above 125° with a hydrogen pressure of 60 atm.; but it is doubtful whether this is significant under the conditions of the present tests, which were carried out at 30° at atmospheric pressure: indeed, even if it could be shown that some preferential hydrogenation of the organometallic compound took place in spite of its vanishingly small concentration (which is of the order of one ten-thousandth of the molecular concentration of the *cyclohexene*), this would in itself further emphasise the experimentally observed fact that these organometallic compounds must be very strongly adsorbed.

## EXPERIMENTAL.

The toxicity of these organometallic compounds towards platinum was measured by the technique adopted in previous work on catalyst poisoning, namely, by following the inhibitive effect of a gradually increased quantity of the poison, in *cyclohexane* solution, on the activity of a constant quantity of platinum black for the hydrogenation of *cyclohexene*, the hydrogenation being carried out in a shaker, at 30°, under standardised conditions. The charge introduced into the hydrogenation pipette consisted in each case of 0.05 g. of stock platinum-black, 2 c.c. of *cyclohexene*, and 8 c.c. of *cyclohexane* including that added with the poison. The dimethylmercury and trimethylindium were supplied by the courtesy of Mr. G. E. Coates. The tetramethyl-lead was made by a slight modification of the method described by Jones and Werner (*J. Amer. Chem. Soc.*, 1918, **40**, 1273). Standard solutions of each of these were made up by dissolving known weights of the poisons in *cyclohexane*, small quantities of these original solutions being further diluted with *cyclohexane* to the very low concentrations used. With dimethylmercury and tetramethyl-lead no special precautions were necessary, save those against loss of poison by volatility and care in preparation by reason of their physiological toxicity; but rigid precautions against the access of traces of water or water vapour are necessary with trimethylindium on account of the ease with which this is attacked even by traces of moisture.

For dimethylmercury and tetramethyl-lead both effective and true toxicity curves were plotted, the latter involving the plotting of the poisoning effect against the amount of poison actually adsorbed on the catalyst, in place of against the total poison present in the system as in the effective toxicity graphs; and the toxicity of the organometallic compound was also compared with that of the metallic ion. With trimethylindium, on the other hand, on account of the ease with which it is destroyed, it was only found possible, even by working with freshly diluted solutions of the concentration required, to show that it is strongly toxic; but this toxicity towards platinum was definitely established.

FIG. 1.



The effective poisoning graphs obtained, which are of the usual flexed linear type, are summarised in Fig. 1. In the case of the metallic ions, the hydrogenation system used, including the solvent, was somewhat different from that taken for the organometallic compounds, since the metallic chlorides used as a source of mercury, indium, and lead ions are not soluble in *cyclohexane*; and, for these, the system consisted of 0.05 g. of stock platinum-black, 5 c.c. of 2N-crotonic acid in alcohol, and 5 c.c. of water, including that added with the poison. It is known that mercuric chloride, particularly, is not easily ionised in aqueous solution; but a calculation on the basis of its dissociation constants showed that dissociation is substantially complete at the vanishingly small concentrations used in the poisoning tests.

As has already been mentioned, trimethylindium could not be stored sufficiently long in solution to enable a complete curve to be determined satisfactorily; but an indication of its high toxicity was obtained by introducing 0.005 g. of trimethylindium into a standard *cyclohexane-cyclohexene* charge taken from a stock which had been previously dried by treatment with, and distillation over, metallic sodium. Hydrogenation tests in the presence of 0.05 g. of platinum showed that this small quantity of trimethylindium was sufficient to poison the catalyst almost completely, the rate of hydrogen absorption being reduced from a value of 29.2 c.c. per minute in a blank run without the indium down to about 0.1 c.c. per minute in the presence of the indium compound.

For the determination of the true toxicity graphs for dimethylmercury and tetramethyl-lead, partition measurements in *cyclohexane* solution were carried out in the usual way (*J.*, 1938, 2071) by allowing a solution of the poison to remain in contact with a charge of catalyst under similar conditions to those in the hydrogenation tests, *i.e.*, at 30° and with 0.05 g. of the platinum-black to each 10 c.c., the unadsorbed poison in the supernatant liquid being subsequently estimated catalytically. In agreement with the general results of earlier work, the adsorption of the poison was found to be an approximately linear function of the total poison concentration throughout the poison concentration range which had been used in the effective poisoning tests. The results of these partition tests for dimethylmercury and

tetramethyl-lead are given in Fig. 2, from which it will be seen that, in the effective toxicity tests, about 61% of the total dimethylmercury present, and about 71% of the tetramethyl-lead, were adsorbed on the 0.05 g. of platinum used. Accordingly, in order to convert the effective toxicity graphs for dimethylmercury and tetramethyl-lead into true toxicity graphs, it is necessary to multiply the bulk concentrations of poison by a factor of 0.61 and 0.71, respectively. Applying this correction, the true toxicity

FIG. 2.

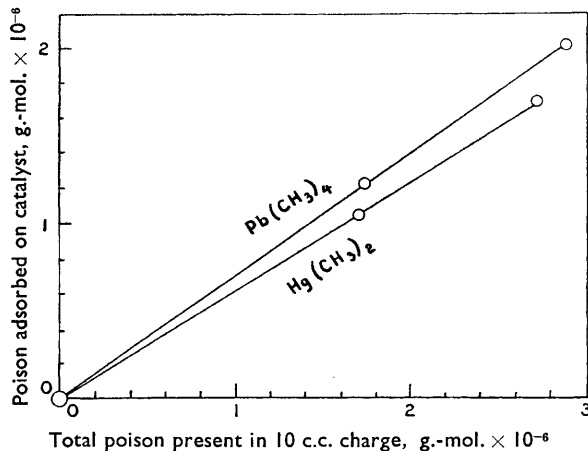
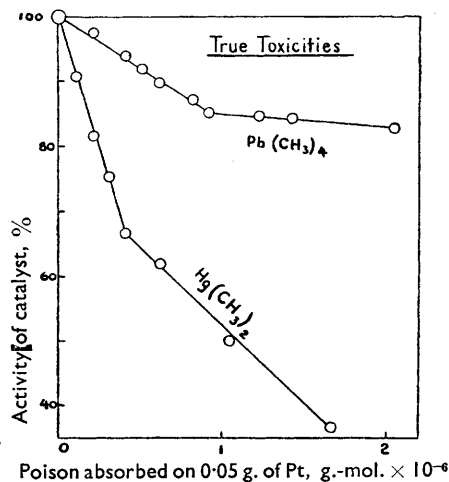


FIG. 3.



graphs are as given in Fig. 3. A point to be noticed is that tetramethyl-lead, although catalytically poisonous, is, contrary to expectations based on relative size, less toxic than dimethylmercury. This may be due to a steric factor, since the metal atom in the tetramethyl compound is probably shielded to some extent by the four methyl groups.

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