163. *Catalytic Toxicity and Chemical Structure. Part IV. The Relative Toxicity of Simple Phosphorus, Arsenic, Antimony, and Bismuth Compounds.*

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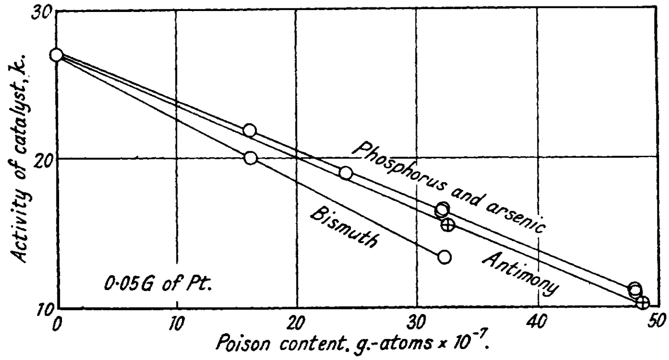
The simple hydrides of phosphorus and of arsenic—applied either as such or as compounds which, in the presence of catalytically activated hydrogen, are transformed into simple hydrides—possess the same toxicity per g.-atom of catalytically poisonous element towards a platinum catalyst in catalytic hydrogenation. The toxicity of antimony hydride is slightly, but not very appreciably, greater; and that of bismuth is definitely greater, the observed relative values of the poisoning coefficients per g.-atom being 1·0, 1·0, 1·05, and 1·29 for the series of four elements in the above order.

IN earlier papers (J., 1937, 603, 1004; this vol., p. 455), attention has been paid principally to the development of induced toxicity in complex, but normally non-toxic, molecular structures as a result of their attachment to a catalysing surface by an intrinsically poisonous constituent such as a sulphur atom. Little is known, from a quantitative standpoint, of the effect on the toxicity of variations in the atomic radius of the catalytically poisonous element itself, such as would be introduced, for instance, by changing the identity of this element within a closely related periodic group. In examining this point experimentally, it is desirable to employ the simplest possible toxic molecules in order to avoid the above complication of induced toxicity; and a suitable series of corresponding compounds for the purpose appeared to be constituted by the simple hydrides of the phosphorus group, all of which are highly toxic towards, for instance, platinum in catalytic hydrogenation.

If the adsorption of simple poisons of this type occurs stoicheiometrically, *i.e.*, if each potentially catalytically active platinum surface element binds a single poison molecule—or a given number of poison molecules—it would be expected on first principles that the toxicity per g.-atom of all the related poisonous elements would be identical, so far as considerations of overlapping coverage, due to the possession by the poison of a larger effective atomic radius than that of the adsorbing element, do not actively restrict the possibility of normal close coverage of the catalysing surface by the poison. Thus, in the simplest case, if this postulated stoicheiometric adsorption corresponds with the adsorption of a single poison atom by each platinum surface element, the toxicity of all members of the poison series should be the same up to a stage in the series at which the effective atomic radius of the poison exceeds that of the platinum.



In the course of the measurements described in the present paper, a simple relationship of the above nature among the various toxicities per g.-atom of the respective poisons has been shown experimentally to be actually followed, in that phosphorus and arsenic—which possess, respectively, effective atomic radii of 0·87 and 1·25 A., compared with an atomic radius of 1·38 in the case of platinum—have been found, in each case in the form of their trihydride, to possess the same atomic toxicity: moreover, although the atomic toxicity of antimony (atomic radius 1·45 A.), also as the hydride, differs little from that of phosphorus or arsenic, its value is apparently slightly higher than that of these elements; and, on still further increasing the atomic radius of the poison, by extending the measurements to bismuth (atomic radius 1·55 A.), the increase in atomic toxicity becomes sufficiently great to be readily measurable, although, as would be expected, the difference in toxicity is still not great.

EXPERIMENTAL.

The determination of toxicity was carried out as already described in earlier papers of the present series, *viz.*, by measuring the activity of a standard platinum catalyst, of known poison content, for the hydrogenation of crotonic acid under standardised conditions. The system taken for hydrogenation consisted in each case of 0·05 g. of platinum, 5 c.c. of a 2N-solution of crotonic acid in acetic acid, and a known quantity of the poison dissolved in a further 5 c.c. of the same solvent. The platinum was, as before, taken from the same stock throughout, and had been prepared by the reduction of chloroplatinic acid with alkaline formate. The temperature of hydrogenation was 25°.

In preparing the various poisoning solutions, known quantities of compounds either containing the hydride itself or of such a nature that the hydride was produced *in situ* were weighed out and, after suitable dilution, applied to the platinum in the usual manner. In the case of phosphorus, the hydride could be weighed directly as phosphonium iodide, but arsenic and antimony hydrides, on the other hand, are less easy to handle as such. Since soluble arsenic or antimony compounds are readily transformed into the hydride by nascent or catalytically activated hydrogen, it was, however, found sufficient to weigh out these poisons in the form, respectively, of arsenious oxide and potassium antimonyl tartrate, which, in the presence of hydrogen and platinum, pass into the required hydride. The application of bismuth as the hydride is perhaps less definite. Paneth and Winternitz (*Ber.*, 1918, **51**, 1728) have observed the formation of a hydride, for instance, by dissolving a magnesium–bismuth alloy in acids; but it was considered preferable to employ as the poisoning solution in this case a dilute solution of bismuth acetate in acetic acid, since in all probability any soluble bismuth salt, in the presence of hydrogen and of platinum sufficient for adsorption of the poison, would be reduced to hydride in an analogous manner to arsenic and antimony; and, in any case, the bismuth was present in a molecularly simple form. These strong catalyst poisons, as was found with the sulphur compounds previously investigated, are, in the proportions used, substantially completely adsorbed by the platinum present. The final poisoning solutions contained, respectively, 0·0497 mg. P, 0·1201 mg. As, 0·1951 mg. Sb, and 0·3348 mg. Bi per c.c.

The effect of various quantities of each of these poisons on the activity of 0·05 g. of platinum is summarised in the figure. From the slope of these poisoning graphs, the poisoning coefficients, α, may be calculated, as before, by means of the relationship $k_c = k_0(1 - \alpha c)$, in which k_c is the activity of the platinum in the presence of a concentration, c, of the poison in question, and k_0 is the original, unpoisoned activity. If the poison concentrations are expressed in g.-atoms per unit of effective surface represented by that exposed by the 0·05 g. of the standard platinum catalyst taken in each case, the following values are obtained.

Inhibitant.	$\alpha \times 10^{-5}$.	Relative toxicity per g.-atom of poison.	Inhibitant.	$\alpha \times 10^{-5}$.	Relative toxicity per g.-atom of poison.
Phosphorus ...	1·23	1·00	Antimony ...	1·29	1·05
Arsenic	1·23	1·00	Bismuth	1·59	1·29

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[*Received, April 20th*, 1938.]